GUM ARABIC AND CONSTITUENT SUGARS STUDIED BY ELECTRON SPIN RESONANCE

By

AHMAD BEN AHMAD SALEM MASMAS
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SUMMARY

In the present work free radicals were generated in gum arabic and its constituents D-galactose, L-arabinose, L-rhamnose and D-glucuronic acid using x-irradiation, UV irradiation, and heat treatment. Electron Spin Resonance (ESR) techniques were used, mainly, to detect and study the behavior of the generated free radicals. The study of the effects of irradiation time (dose), the decay of the ESR spectra and the effect of the microwave power helped to distinguish two spectral groups. These were labled spectral group (1) and spectral groups (2).

The ESR spectra of x-irradiated gum arabic have been measured under various microwave power at room temperature and at liquid nitrogen temperatures. Spectral group (1) showed ESR saturation at around 37.5 mW and the ESR of spectral group (2) showed a saturation at 16.2 mW.

The growth of the free radicals in gum arabic has been studied for various x-ray irradiation doses. Spectral group (1) showed a saturation after 90 minutes and spectral group (2) show a saturation after 120 minutes

The decay of the ESR spectra at room temperature of x-irradiated gum arabic shows distinctive behaviour of the two spectral groups (1) and (2). Relative spin density of spectral group (1) and spectral group (2) as a function of decay time showed exponential decay with three different zones of decay for each one.

The decay of the ESR spectra by the elevation of temperature of x-irradiated gum arabic has also been studied. Spectral group (1) showed rapid decay

between 317 to 327 K. This has been interpreted as due to the transition of gum arabic from high to low viscosity. The ESR spectra of irradiated gum arabic disappeared beyond 373 K.

ESR spectra of x-irradiated gum arabic which has also been exposed to mercury light has shown growth of spectral group (1) without affecting spectral group (2). When natural gum arabic was exposed to UV, the ESR spectra showed a singlet signal with a line-width of 13.3 gauss and g-value of 2.0046.

Free radicals in gum arabic could also be generated by heat treatment under vacuum. The ESR spectra showed a singlet signal with a line-width which varied between 8 and 5 gauss depending on the temperature and the time of heating. The g-value of this singlet is 2.0032.

Constituent sugars of gum arabic were x-irradiated individually and the ESR spectra were measured and analyzed. These were used to simulate the ESR spectra of natural gum. Proportional components of gum arabic has been irradiated and added gradually to each other. The spectral groups (1) and (2) were found to exist in the synthetic gum.

Analysis shows that the spectral group (1) consists of a singlet signal. This singlet is of the form C-O-O. and it may have been created by the reaction of the C. radical and O_2. Spectral group (2) consists of a singlet signal plus a doublet signal. The singlet signal is due to a radical of the form C-O., where the doublet signal is of the form (C.).

Line-widths of the spectral group (1) and (2) have been studied as a function of irradiation time, decay time, temperature, and UV exposure time. The

results has been interpreted by the application of the spin-spin theory and motional narrowing. Also the variation of the line-width of the singlet signal generated by heat has been discussed using the motional narrowing theory.

Ultraviolet absorption spectra have been measured for gum arabic before and after gamma irradiation. The results show an absorption peak at 276 nm before and after irradiation. The intensity of this peak increased after irradiation. The absorption at this position is known to be due to the carbonyl group or acetal group.

The results of this work may be related to studies on food irradiation and could help to asses effects of radiations and thermal treatment on gum arabic used in food manufacture and drugs.

CHAPTER ONE

GENERAL INTRODUCTION TO THE GUMS AND GUM ARABIC

1.1 GUMS

Gums in the natural form are often polysaccharides or modified polysaccharides with high molecular weights. Usually gums have colloidal properties and may produce gels when dissolved in suitable solvents. Commonly, the term gum was applied to the polysaccharide exudates from various plants, which produce viscous mixtures when dissolved in cold or hot water.

Three-quarters of the weight of the dry plants consists of polysaccharides, but the difficulties in separating the polysaccharides from the plant tissues causes us to look for plants which are rich in polysaccharides[1]. Exudate gums, seaweed gums, seed gums, starch, and cellulose derivatives are all good sources of polysaccharides. Exudate gums are exuded from most plants, but generally only in a small amounts, but there are special trees which we choose to produce commercial gums. Gums flow from incisions in the plant as a vermiform or tear shape to form thickened layers.

Starches and cellulose are available polysaccharides and are excellent materials to produce gum; starches and cellulose can be modified to gum by chemical transformation processes. Natural polysaccharides are found in linear and branch forms and some of them include carboxyl groups. Some polysaccharides contain strong acid groups while others contain basic groups[1].

1.2 GUM ARABIC

Gum arabic is an exudate natural gum. It is an important commercial polysaccharide which was used at least 4000 years ago. The term gum was applied because the material has gummy characteristics, and the name "gum arabic" because the origin of export was an Arab area, and the Arabs in early history were the important traders and vendors of this material. The name Turkey gum was also used for this material during the Turkish Empire. More than 80 names have been used for the material, depending on the local area where it was collected and on its colour and grade[2].

Gum arabic is usually produced from trees which belong to the genus acacia, subfamily mimosoidea and family leguminosea. There are more than 500 species belonging to this family, distributed over the tropical and subtropical areas of Africa, India, Australia, Central America, and South West North America.

Some authors mentioned that gum is only exuded when the tree is in an unhealthy condition and will never be produced if the tree is in a healthy condition. The gum may be obtained by making an incision in the bark of such trees, or it may exude naturally. Formation of the gum by unhealthy trees is a pathological condition resulting from a bacterial or fungal infection of the injured trees[2].

1.2.1 COUNTRIES OF PRODUCTION OF GUM ARABIC

The republic of Sudan is one of the most important countries producing gum. Senegal, Mauritania, France Sudan, Nigeria, Tanzania, Morocco, Ethiopia, and Somalia also produce significant quantities of gum. It is also produced in South Africa, India and Australia[1].

Most of the gum produced in the Sudan comes from acacia Senegal which growth to about 15-20 ft. tall and has a life of about 25-30 years. It grows in poor, sandy, reddish soil. It is found particularly in the district of Kordofan. The best quality of gum comes from acacia Senegal and is known as Hashab in the Sudan and also known as Kordofan gum[2].

90% of the gum produced in the Sudan is from these kinds of trees and about 10% of the gum comes from the Seyal variety of acacia which is known in the Sudan western part of the country and in the Nile region. The gum from Seyal trees is exuded naturally without tapping[2].

During the rainy season, no gum is formed by the trees. So, the gum is collected during the dry season between October and May or June. A suitable age for trees which can be tapped is 6-7 years. Attempts to extract gum from trees younger than this causes death of the trees. After a few weeks, the gum form in the cuts which is depending on the weather conditions is collected every 10 days during the season[1].

West Africa is the second most important area producing gum arabic. The gum produced in that area is acacia senegal which is known as gum senegal. In comparison of the Senegal gum produced in French West Africa with that from Sudan, the Senegal gum is more yellow or reddish. is not as clean as Sudan gum and it is more brittle.

1.3 PHYSICAL PROPERTIES

Gum arabic is an amber, amorphous, highly viscous material when it is in fresh form and it is solid after contact with the atmosphere, it is light in colour with shades of yellow, red or brown, depending on the sort of acacia trees, the

countries of origin and the condition of storage. It is nontoxic, odourless, tasteless, soluble in water giving a homogeneous colloidal and colourless system[1].

Molecular weight: The molecular weight of gum arabic differs from sample to sample but also depends upon the method of estimation. Anderson and co workers[3] reported the average molecular weight to lie between 260,000 and 1,160,000.

Melting point: The melting point, measured by TAFT and MALM[4], lies between 190-200°C.

Solubility: Gum arabic is completely soluble in cold or in hot water and in some oils, but it is insoluble in most of the well known organic solvents. TAFT and MALM[5] studied the solubility of gum arabic in organic solvents. The solubility of the gum was tested in aliphatic and aromatic alcohols, ketones, ethers, esters, halogen derivatives, glycols, pyridine, hydrocarbons, and liquid ammonia. It is only dissolved in ethylene glycols and glycerol with low-viscosity. Some slight solubility was observed with acetate esters and acetate alcohol mixtures and was also soluble in aqueous ethanol containing 60% of alcohol

Freezing point: TAFT and MALM[4] found that the freezing point of a gum arabic solution decreases as the concentration of gum arabic increases, as shown in figure(1.1).

Viscosity: It is important to give some details about the viscosity of a material not only because it gives information about the utilization of the material but also

it gives an idea about the molecular structure of the substance used. For this case the viscosity of gum arabic is studied carefully by varying different factors such as concentration, temperature, electrolytes, pH, solvents other than water, the time of measuring the viscosity, mechanical treatment, and the effects of ultrasonic vibrations and ultraviolet irradiation on viscosity. TAFT and MALM[4] studied the effect of concentration on the viscosity and density at 30° C (pH=7.14) the results are shown in figure (1.2).

TAFT and MALM[4] also studied the effect of temperature on gum arabic viscosity and found an inverse proportionality between the viscosity and the temperature (as the temperature increased, the viscosity of the gum decreased) a result which was confirmed by OSBORNE and LEE[6]. GABEL[7], MOORJANI and NARWANI[8] show that the viscosity of gum arabic can be increased by heating of the dry material. The results of MOORJANI and NARWANI are shown in figure (1.3). CLARRK and MANN[9] studied the effect of electrolytes on the viscosity and found that all electrolytes lowered the viscosity of gum arabic. TAFT and MALM[4] also studied the effect of the single electrolyte calcium chloride over a wide range of concentrations and they found that the addition of some calcium chloride lowered the viscosity of gum arabic. But, they observed that as the concentration of the calcium chloride increased the relative viscosity increased[1].

pH: The pH of the solution of the gum arabic has been studied by THOMAS and MURRY [10]. Figure (1.4) shows the maximum value of relative viscosity to lie between 4.58 and 6.30 after which the viscosity started to decrease gradually in between pH values of 5 to 10. TAFT and MALM[4] also found a change of viscosity with pH and found the maximum viscosity to lie between 6 and 7. Gum arabic is a suitable medium for microorganism growing. Taft and Malm[4] found that the growth of bacteria on gum arabic changed its viscosity.

The effect of mechanical stress, and of ultraviolet irradiation: TAFT and MALM[4] have studied the effect of the mechanical treatment on the viscosity of gum arabic. TRAGER[11] has been studied ultrasonic vibrations to produce colloidal dispersions. He found that the colloidal system is easily broken and irradiation of the solution by ultrasonic vibration lowers the viscosity. SZALAY[12] showed that the gum arabic solution depolymerized by ultrasonic waves and the viscosity is lowered by these vibrations. LAURENT[13] has found that the ultraviolet radiation reduced the viscosity of gum arabic. Gum arabic has maximum absorption at 2650 A.

Surface tension: The surface tension of the liquid of gum arabic was studied at different temperatures and concentrations by BANERJI[14], where he showed the decrease of the surface tension by increasing the temperature, and a decrease of the surface tension by increasing the concentration.

Electrical conductance: TAFT and MALM[4] studied the effect of the concentration on the electrical conductance of gum arabic - water solution. The graphs between logarithms of volume and equivalent conductance show that the gum arabic solutions are actually mixtures of calcium arabate and magnesium arabate.

1.4 CHEMICAL PROPERTIES

Gum arabic as a calcium, magnesium, and potassum salt of arabic acid, react with many reagents. A solution of gum arabic will give precipitates or heavy gels if it is treated with the following reagents: borax, ferric chloride, basic lead acetate, mercuric nitrate, gelatine, potassium silicate, sodium silicate, Millons reagent. In general trivalent metallic salts will cause precipitation with gum arabic[15].

A solution of gum arabic can be coagulated by ruthenium red, hexol nitrate, or desogen Geigy. Gum arabic can be hydrolized when it is treated with dilute acids to give a mixture of L-arabinose, L-rhamnose, D-galactose, and D-glucuronic acid. It also reacts with nitric acid to give mucic, saccharic and oxalic acids. OSBORN and LEE[6] studied the solubility of the acacia mucilage solution with concentrated and dilute hydrochloric acid, concentrated and dilute acetic acid, concentrated and dilute ammonium hydroxide and dilute sodium hydroxide. The acacia mucilage is solubles in all these reagents. Also it is soluble in 10% solutions of sodium chloride, mercuric chloride, bismuth chloride, and silver nitrate, but it is not soluble in a 10% solution of ferric chloride and concentrated sodium hydroxide[1].

1.5 ENZYMES

Oxidases and peroxidases are found in gum arabic and are both inactivated by the heating of the gum to 80° C for 1 hour[16]. Diastases and pectinoses are also found in the gum arabic[17].

1.6 INDUSTRIAL USES

Food Industry: A large amount of gum arabic production is used in the food industry. It is used in the food industry because of its inherent stability and because it is non-toxic, odourless, colour less, tasteless, and completely water-soluble. It does not effect the flavor, odour, or colour of the food ingredients[18].

Confectionery: Because gum arabic has an ability to prevent the crystallization of the sugars and the thickening the aqueous media. it is used as a glaze in candy products and as a component of chewing gum, cough drops, and candy

lozenges. Also, gum arabic plays a role as an emulsifier, keeping the fat uniformly distributed and preventing the floating of the fat on the surface and forming easily oxidizable, greasy film[1].

Dairy products: Gum arabic has been used as a stabilizer in frozen products, such as ice cream, ices, and sherbets, because it absorbs the water, and it prevents the growth of ice crystals. It also produces a fine texture from these products. SCHOLZ[19] has patented a method using gum arabic for the preparation of packageable milk or cream. WALDER[20] used gum arabic to protect the formation of colloids during the preparation of baby food.

Baking industry: Gum arabic is widely used in the baking industry because of its viscosity and its adhesive property. It is used in glazes and topping and it also gives a smoothness when it is used as an emulsion stabilizer. Also, when it is used in a bun glaze, gum arabic gives stability in conjunction with its free-flowing and adhesive characteristics[18].

Flavour fixative: The spray-dried technique is used to add different kinds of flavours which may be oxidized or volatile. The gum arabic forms a thin film around the flavour particle and protects them from oxidation, evaporation and from absorption of moisture from the air[1]. The tests on spray dried emulsions of aldehydes showed that the colloidal film protected them from oxidation for years, while the unprotected materials oxidized in seconds[21].

Flavour emulsifier: JOHNSTONE[22] has mixed a gum arabic with many flavour emulsions such as orange, lemon, lime, root beer, and cola. The addition of gum arabic to these materials gave them the required properties and provided a smoothness. Citrus oil emulsions consisting of citric acid, lemon oil, glycerol, water, and colouring matter, take on the most convenient properties when mixed with gum arabic-gum karaya mixtures.

Pharmaceuticals: Because the gum arabic has inherent emulsifying and demulcent and emollient characteristics, it is used in many applications in the pharmaceuticals area, from the stabilization of emulsions to the formation of tablets. Also, because the solution of gum arabic can retain its viscosity over a wide range of pH[1,18] values it is useful in this field.

In the United States Pharmacopeia[23] there is a list of preparation using gum arabic:

1. 350g of gum arabic and 2g of benzoic acid added to purified water to make 1000 ml, this mucilage solution performed to aid in the suspension of insoluble drugs and also to prevent the precipitation of heavy metals from solution.

2. Acacia syrup. Gum arabic is mixed with sodium benzoate, vanillin tincture and sucrose for use as a flavour vehicle because of its demulcent effect and its protective colloid action. A good syrup of diabetic foods is prepared from gum arabic, saccharin, methyl-p-hydroxybenzoate, and water.

3. Suspending agent. OSBORN and DEKAY[24] found that gum arabic is a convenient emulsifier and suspender for calamine suspensions, kaolin suspensions, liquid petroleum emulsions and cod liver oil emulsions. It has been found that it is an excellent medium for preparing a stable, nonsetting magnesia suspension.

Poorly soluble medicinal substances, such as steroids, fat-soluble vitamins, and barbitureates, that are suspended in gum arabic can be facilited by the incorporation of wetting agents or other emulsifiers[1,18].

4. Antiseptic preparation has been made with a mixture of colloidal silver bromide and gum arabic[25]. Silver arabate has antiseptic properties which is suitable for use as a substitute for silver nitrate and organic silver compounds in the treatment of ophthalmic infections. Silver compounds for the internal treatment of mucous membranes have been patented by VON NEERGAARD[26]. These compounds swell and liquefy in contact with moist tissues and are prepared from water-soluble silver compounds such as the nitrate.

Medicine: In 192O gum arabic was used for the treatment of low blood pressure caused by haemorrhage or surgical shock. Intravenous saline injection was not successful because the salt escaped rapidly, so the addition of 7% gum arabic solution reduced the dissipation rate of the sodium chloride[1,18]. In 1933, intravenous injections of gum arabic solution were used for the treatment of nephritic edema. In plastic surgery, a 5O% gum arabic adhesive has been used successfully in grafting destroyed peripheral nerves[1].

Cosmetics: In cosmetics gum arabic is found in a wide range of applications. In lotions and protective creams, it stabilizes the emulsion, increases the viscosity, and assists in making a homogenous mixture. It forms a protective coating and it give the skin a smooth feel. It is also used as a binder in the formulation of the compact cakes, rouges, and as an adhesive in the preparation of facial masks. Also, gum arabic is used as a foam stabilizer in the production of liquid soap[27].

Gum arabic has also entered the prescriptions which are used in hair creams and fixatives and as a binder in face powder compact. In protective creams, gum arabic can be used as a stabilizer and film-former[1].

Adhesives: Gum arabic is generally used in a wide range of the adhesives industry. It is mixed with water to form an adhesive solution, and it is sold in powder to make a safe solution for miscellaneous paper products. WOLFE[28]

employed gum arabic with sodium hydroxide as an adhesive agent for paper products. The glue of gum arabic is desirable because one finds it easy to prepare, light in colour, odourles and very stable. These glues can be improved by the addition of metal salts such as calcium nitrate and aluminum sulphate, but they have the shortcoming that they will be degraded when heated and the colourless of the glue will change to bronze and related colours. Gum arabic is also used as a glue for cellophane. Also, a good transparent cement can be made with gum arabic. Wall paper paste has been based on a mixture of gum arabic, bentonite, and starch. Sometime gum arabic is used as a binder for water cements such as gray and iron cements[1.18]

Inks: Gum arabic is an important constituent of many special purpose inks because it has an excellent protective colloid action. Gum arabic and lampblack mixed together to form a suitable ink stick which was used in the same process for over 3OOO years[1.18].

Many of the inks use gum arabic in the formula, including record ink, which is used in government writings. Soluble inks, used just to mark the cloth in the textile area. Gum arabic is a suitable binder for water colour inks because it has excellent suspending properties where this kind of ink must remain in suspension.

Gum arabic is used with ethanol as a thickener and suspension agent in fast drying inks, also it is used in fabric and laundry marking inks. In typographic ink gum arabic is used as a binder to keep the ink out of separation. the Conductive inks have a range of application in the electronic area. The most

important use of this ink is in preparing printed circuits. The most conductive inks are based on carbon black, powdered graphite. Powdered silver or copper are used and the suspension agent can be a lacquer or gum arabic[1].

Lithography: Gums are used as sensitizers for lithography plates. A solution consists of gum arabic and dichromates and can form water-insoluble substances by the effect of the light. A layer of this mixture can be formed on plastic, paper, metallic and stone surfaces and unexposed material can be removed easily by water or dilute acids. Gum arabic for this use must be of the best quality and be prepared in a special way for this purpose[1].

1.7 COMPOSITION AND STRUCTURE OF GUM ARABIC.

1.7.1 INTRODUCTION.

Gum arabic is in essence a carbohydrate. The carbohydrates or saccharides are most simply defined as polyhydroxy aldehydes or ketones and their deriatives. Carbohydrates or sugars are found in nature as monosaccharides, oligosaccharides which contain from two to ten monosaccharides, and polysaccharides which contains more than ten units of monosaccharides. Connections between the units of oligo and polysaccharides are called glycosidic linkages[29].

Polysaccharides contain many monosaccharide units joined in long linear or branched chains. It may be divided into two kinds, namely homopolysaccharides which contain only one type of monosaccharide and hetropolysaccharides which contains two or more different monomeric units.

1.7.2 COMPOSITION AND STRUCTURE.

Gum arabic is the salt of an organic acid, arabic acid, with metals such as calcium, magnesium, and potassium[30]. The hydrolysis of the gum has been shown by many authors including HAWORTH et al.[31], HOTCHKISS and GEOBEL[32,33], SCHEIBLER[34], SULLIVAN[35], BUTLER and CRETCHER[36], KIL-

IANI[37,38] and CLAESSON[39]. These authors show that gum arabic consists of D-galactose, L-arabinose, L-rhamnose, and D-glucuronic acid. ANDERSON and HIRST[40] showed that a sample of acacia Senegal gum (gum arabic) had the following approximate percentages for its various constituents. D-galactose 39%, L-arabinose 28%, L-rhamnose 14%, D-glucuronic acid 17% and 4-O-methyl-D-glucronic acid 1.5%. In addition ANDERSON and MC-DOUGALL[41,42] mentioned that gum arabic containes 2.3 to 3% of proteinaceous material.

SMITH[43] has shown that gum arabic does not only consist of different monosaccharide components, but these components are joined by no less than three different types of linkages. SMITH[43] has proved the presence of a 1,3 link between the units of gum arabic by the autohydrolysis of arabic acid, which produces degraded arabic acid and a mixture of three reducing sugars.

a) 3-galactosido-L-arabinose[43].

b) prolonged autohydrolysis of the degraded arabic acid produces the disaccharide, 3-galactosido-galactose[43].

c) 2,5-dimethyl-L-arabinose is identified as one of the hydrolysis products of methylated arabic acid[43].

From the hydrolytic product of methylated degraded and methylated arabic acid, the presence of 2,4-dimethyl galactose proved that 1,3 and 1,4 links are presented[43].

ANDERSON et. al.[40] have shown that gum arabic contains a fundamental chain of D-galactose units, exclusively involving 1,3 linkages. the presence of increased proportions of 2,4,6-tri-O-methyl-D-galactose in the methylated autohydrolysed gum suggests that some of the residues in the chains of beta 1,3 linked galactose units are 6-O substituted with acid labile arabino-furanose units[40]. The isolation of 2,3-dimethyl-glucuronic acid can suggest the presence of 1,4 links in

arabic acid[43]. The isolation and characterisation after deacetylation of 4-O-α -L-rhamnopyranoseyl-D-glucose from acetolysis of diborane-reduced acetylated gum established that some L-rhamnopyranose residues are glycosidically linked to C-4 bonds of D-glucuronic acid[44].The 1,6-type of linkage in arabic acid has been established by the following way.

a) By the isolation of the 6-β-glucuronosidogalactose from arabic acid[45].

b) By the formation of the hexamethyl 6-β-glucuronoisidogalactose by graded hydrolysis of methylated arabic acid[43].

c) By the isolation of 2,3,4-trymethyl-galactose from the methylated degraded arabic acid[43].

From the above studies and others. SMITH[43] proposed a possible structure for an arabic acid which may be shown in structure [1.1].

ANDERSON et al.[40] have degraded acacia Senegal gum through seven successive SMITH degradation processes. The study of the O-methyl derivatives of each of the polysaccharides obtained from the first five degradations and the study of the methylated polysaccharides after the fifth degradation together with the partial acid hydrolysis of the methylated polysaccharides and the degradation of the gum by autohydrolysis and the methylation of the autohydrolysed gum all lead to a modified structure of gum arabic, which is shown in structure [1.2] STREET and ANDERSON[46] provide more calculations and studies on the seventh Smith degradation which are mentioned by ANDERSON and HIRST[40]. These authors modified a model of the gum arabic molecule. This model could be shown in structure [1.3].

1.8 THE PRESENT INVESTIGATION.

Ionizing radiation has been used widely to sterilize food and medical materials by destroying the microorganisms which may grow on the materials. The application of ionizaing radiation to organic materials leads to destruction of

some centres and to change particularly the chemical structure of these materials. The presence of the damaged centres in the molecule means there are chemical active centres produced by the interaction of the ionizing radiation with the material. These centres are usually free radicals.

The study of free radicals gives information about the molecular structure of the compounds. Also, we may obtain information about the weaker bond in the compound which leads us to understand the mechanism by which the chemical reactions take place. The best technique used to observe the free radicals is the Electron Spin Resonance (ESR) technique, which can give us directly information about the free radical and the interaction of the free radical with its environment.

In this thesis a general discussion of the structure and composition of gum arabic is given. A series of investigations on the electron spin resonance (ESR) in a variety of x-irradiated samples of gum arabic and of mixtures of the main components of gum arabic, to simulate the natural material, are reported. The study of the paramagnetic centres provides further information which can be related to the structure of the material.

CHAPTER TWO

IRRADIATION STUDIES ON CARBOHYDRATES

2.1 INTRODUCTION

To our knowledge, gum arabic has not been studied by ESR spectroscopy after x-ray irradiation. The complexity of the material merits a detailed survey of the effect of the radiation on carbohydrates, from monosaccharides to disaccharides and polysaccharides. In monosaccharides we should take units other than the components of gum arabic because most of the monosaccharides have a pyranose ring which is present in monomers of gum arbic. Also, the presence of some chemical group in the monosaccharides cause some signals to be present in the ESR spectra of different sugars.

A survey of the work on the irradiation of the carbohydrates which contains a glycosidic linkage, present in gum arabic, will be presented here to provide a background on the effect of the ionizing radiation on the polysaccharides.

Starch which is composed, of 1--4 linkage α - D - glucopyranose and Cellulose which is composed of β -D- glucopyranose are selected to summarise the previous work of the ESR studies of irradiated polysaccharide materials. The selection of these two materials is due to the fact that there are similarities between these materials and gum arabic. That is the 1--4 linkage between the monomers and the chemical group $-CH_2OH$ is found in galactose which is a monomer in gum arabic and glucose which is monomer in starch and cellulose

2.2 IRRADIATION OF MONOSACCHARIEDS

COLLINS[47] has studied the ESR signals of gamma irradiated polycrystaline D-glucose, D-xylose, and D-galacturonic acid at room temperature. The ESR spectra of D-glucose structure [2.1] obtained by COLLINS showed two radicals, one of which consists of three lines and the other has one line. From the study of the chemical structure of D-glucose he postulated the formation of a stable radical at C(1) to form the singlet signal, and at C(5) to form the triplet signal, where a small amount of delocalization energy is available from the neighboring oxygen atom. The postulated locations of the radicals are as shown in structure [2.2 and 2.3].

In D-galacturonic acid structure [2.4], COLLINS[47] has detected a singlet signal in the ESR spectrum. he proposed a model for this signal as shown in structure [2.5 or 2.6] where no hyperfine interaction is to be expected.

DILLI and GARNETT[48] have gamma irradiated polycrystaline monosaccharides at room temperature. The ESR signals which has been detected for monosaccharides, (such as glucose, structure [2.1], galactose, structure [2.7] , mannose, structure [2.8], and arabinose, structure [2.9]), consist of two lines. The location of the free electron suggested by these authors to form a signal with two lines (a doublet) is at C(1) or C(6) of the pyranose ring. In lyxose structure [2.10] four line spectra were detected. They interpreted these lines by assuming the interaction of the free electron with three protons. This situation may occur if the free electron is localized at C(4) and it interacts with the three protons of C(3) and C(5).

UEDA[49] has studied two patterns of hexose monosaccharides, fructose structure [2.11] and sorbose structure [2.12]. An irradiated single crystal of these two

sugars has been studied by ESR spectroscopy at 77 K and 293 K. At 77 K The signal which has been detected for the two sugars was a doublet with 18 gauss isotropic hyperfine splitting. At 293 K fructose shows a quartet signal, but in sorbose the spectrum shows a quartet and a doublet signal. The hyperfine splitting of the quartet signal is 15 gauss. This splitting is isotropic. UEDA has proposed a model by which he interpreted the formation of these radicals in sorbose and fractose. In this model, structure [2.13], the quartet signal could be formed if the free electron at C(4) interacted equally with two protons at C(5) and a proton (H3) at C(3). This could happen if C(3), C(4), C(5) are in the same plane. The doublet signal is formed by the interaction of the electron at C(4) with an axial H5 where the P_z orbital of the unpaired electron is nearly parallel to the axial bond of H5. this could be happen if C(3), C(4), C(5) are not in the same plane. and this is the case for C(3), C(4), C(5). However, the doublet which was obsarved at 77 K in the crystals of fructose and sorbose and also in sorbose at 293 K could be explained if C(3), C(4), C(5) are not in the same plane.

BALAZS et al.[60] studied the ESR spectra of irradiated glucuronic acid structure [2.14]. In this study they found a singlet signal with g - value = 2.00124. The line width of this signal is 20 gauss. The location of the radical is proposed to be at C5 as in structure [2.15], where the radical would be stabilized by resonance interaction with the carboxylic group ($-\underset{\underset{OH}{|}}{C}=O$).

The ESR spectra of gamma irradiated polycrystaline monosaccharide such as pentoses (β-L-arabinose structure [2.9], α-D-xylose structure [2.16], β-D-ribose structure [2.17]) and hexoses (α-D-galactose structure [2.7], α-D-glucose structure [2.1], β-D-mannose structure [2.8]), were studied by NIKITIN etal[61]. These materials were irradiated at 77 K. The ESR spectra were recorded over

the range of temperature of 77 to 300 K. The signals recorded at 77 K were a doublet signal for all sugars. Triplet signal were detected for xylose, ribose, glucose and mannose and a quartet in arabinose. The triplet signals were found in monosaccharides which have a steric interaction of the hydroxyl groups at alternate carbons with the same configuration[52] . Structure [2.18] shows the interaction between the hydroxyl and the C-H bond (steric interaction). Steric interaction phenomena have been found in the sugars (xylose, ribose, glucose) where a weakened bond is located at C3. In mannose the weakened bond is located at C2. It is suggested that the doublet signal is due to cleavage of the C-H bond in C1 where this bond is weakened by the drawing of an electron by the cyclic and hydroxy oxygen atom [53,47]. The quartet signal which was found in arabinose (splitting =15 gauss) is due to interaction between a free electron at C4 with three beta protons (two protons on C5 and one proton on C3)[49]. The cleavage of the C-H bond at C4 is due to the weakening of this bond by an equatorial hydroxyl group[54]. At room temperature NIKITIN[51] found a doublet signal in all monosaccharides, a singlet was found in xylose, a triplet in mannose, and triplet - quadruplet in arabinose. The stable radicals at room temperature are determined by the presence of conjugated bonds. These bonds are produced by dehydration with the loss of one or more water molecules. Structure [2.19] illustrates the role of the loss of the water molecule in producing a stable radical.

BAUGH etal[55] studied the ESR spectra of irradiated frozen aqueous solutions of D-glucose structure [2.1]. This material was irradiated at 80 K. The ESR spectra were recorded covering the range between 80 K to 213 K. The study of the ESR spectra during the warming process, indicated different sources of ESR signals. (1) A broad anisotropic doublet (43 gauss splitting) due to a hydroxyl radical present in ice. (2) A singlet (g = 2.0014, ΔH = 14.5 gauss) which disappeared

on photobleaching with light (from 540 to 580 nm) and which due to a trapped electron, (3) A broad poorly resolved absorption signal arising from the carbohydrate. The signals due to trapped electrons and OH radicals disappear with the rise of the temperature to 140 K. The best resolved signal due to the carbohydrate has been obtained at 193 K, this is assumed to be due to increased rotation of the protons that are responsible for the hyperfine splitting. The signals which were detected at 190 K are interpreted as a superposition of two different radicals. One is a doublet with 20 gauss hyperfine splitting and g = 2.0030 and the other is a triplet with 29.5 gauss hyperfine splitting and g = 2.0025. In glucose ice, the triplet is due to the precence of the free electron at C(5) as .C(5)-C(6)H_2OH radical. The doublet is due to a free electron localized at C1.

NIKITINE etal[56]. studied monosaccharides such as pentoses (β-L-arabinose, α -D-xylose, β-D-ribose) and hexoses (α-D-galactose, α-D-glucose, β-D-mannose) while dissolved in water. The materials were irradiated at 77 K. They found that the ESR spectra which were recorded at 77 K gave a signal due to trapped electrons, and signals due to the dissolved material (monosaccharides). The latter signal was a doublet for all monosaccharides with a hyperfine splitting of 30 gauss for arabinose and from 18 gauss to 20 gauss for the other monosaccharides. The triplet signal is found in all of the studied monosaccharides except arabinose, and has a hyperfine splitting of 25 gauss. A quadruplet was found only in arabinose with hyperfine splitting of 15 gauss . A triplet of doublet signal was found only in xylose with hyperfine splitting of 30 gauss and 10 gauss. The triplet signal was interpreted by these authors as due to steric interaction of hydroxyls (1-3 or 2-4) at alternate asymmetric carbon atoms with the same configurations[52]. This interaction leads to weakened C-H bonds at C2 and C3.

So the unpaired electron is localized at C2 in mannose and at C3 in the case of xylose, ribose, and glucose. The quadruplet signal which is found in arabinose is due to location of the free electron at C4 which interacts with three equivalent beta - protons (one proton at H3 and two protons at C5). The weakening of the C-H bond at C4 in arabinose is due to the presence of the axial hydroxyl on the C(4) carbon atom[54]. This fact can be applied to interpret the triplet signal which is found in galactose, where the axial hydroxyl is located at C4, so the free electron at C(4) will interact with equivalent axial β - protons (H3 and H5). The triplet of doublet signal which was detected in xylose is due to location of free electron on C4 which interact with two axial beta - protons H3 and H5 and one equatorial beta proton H5.

The ESR and ENDOR techniques have been applied recently to study the free radicals produced in polyhydroxy compounds. More information about the free radical situation can be collected from the calculation of the g-tensor from ESR measurements, and proton hyperfine coupling from ENDOR measurements.

MADDEN and BERNHARD[57] x-irradiated a single crystal of α-D-glucopyranose structure [2.1] at 12 and 77° K. The study of the ESR and ENDOR spectra, and the comparison of the results of the g-tensor and proton coupling tensors with that of the crystallographic structure of α-D-glucopyranose indicate the presence of four radicals in this compound. They detected a primary hydroxy alkyl radical with three hyperfine couplings. This signal is localized at C6 structure [2.20]. The three hyperfine couplings arise from the interaction between the free electron at C(6) and two unequally situated protons (one alpha and one beta proton), and a small coupling due to interaction with hydroxyl proton on C6. A secondary hydroxy alkyl radical with small g anisotropy of a carbon centred radical with two

large isotropic hyperfine couplings and one small anisotropic coupling was detected. The ENDOR data explain the presence of the free electron at C3 structure [2.21] where this electron interact with beta-proton on C2 and beta proton on C4, they also suggest a weak coupling with the proton of hydroxyl group on C3. Two signals of g-factor anisotropy were identified as secondary alkoxy radicals. These two signals arise from one centre but have variable hyperfine interaction with the environment. They suggest that the location of these two radicals is C(2)-O. as in structure [2.22].

ESR spectra of gamma irradiated single crystal of rhamnose structure [2.23] were studied by SAMSKOG et al.[58,59], PANASYUK and YUDIN[60]. At 67° K a trapped electron radical was detected by SAMSKOG[59], and a signal due to alkoxy radical was found with a large g - factor. This signal was also reported at 77° K by SAMSKOG[58] and PANASYUK[60]. It consists of 4 lines arising from the location of the free electron at O4 as in structure [2.24]. A doublet of doublet signal was detected by PANASYUK[60] and SAMSKOG[59]. This radical is identified as a hydroxy alkyl radical, it arises from abstraction of hydrogen from C2, C3, or C4 , and an interaction with two beta protons one of them is the proton of OH, and the other is the beta proton. At 77 K a doublet radical was obtained by SAMSKOG[59]. This radical is assumed to be located on C1, C2, C3, or C4 and it could arise from the coupling of the free electron with one beta proton. Another radical was observed[60] with doublet - quadruplet hyperfine lines. They suggests that this radical arises from the interaction of a free electron at C5 with one beta proton at C4 and three beta protons of the methyl group as in structure [2.25]. The doublet, doublet of doublet and doublet of quartet radicals are found as stable radicals in rhamnose single crystals at room temperature[60].

2.3 IRRADIATED CARBOHYDRATES CONTAINING GLYCOSIDIC BONDS.

DILLI and GARNETT[48] have gamma irradiated polycrystaline disaccharides such as sucrose structure [2.26] and cellobiose structure [2.27]. The ESR spectra of these materials consist of two lines. They suggest C1 or C4 to localize the free electron to form a doublet. ESR spectra of lactose structure [2.28] consist of four lines. They suggest localization of the free electron at C5 to form these four lines where the free electron on this atom interacts with three protons at C4 and C6

The ESR and ENDOR spectra of an irradiated single crystal of α-methyl-glucopyranoside structure [2.29] have been studied at 77° K by MADDEN and BERRHARD[61]. Five paramagnetic centres were assigned by the study of the ESR spectra of this material. A primary alkoxy radical with anisotropic g-factor and isotropic hyperfine splitting was identified to be localized on O6 as in structure [2.30]. A secondary alkoxy radical with one hyperfine splitting is assumed to be localized at O2 as in structure [2.31]. A hydroxy alkyl radical showing hyperfine coupling is localized at C6 as in structure [2.32]. Another radical identified from ESR and ENDOR spectra may be located at C5 as in structure [2.33]. A strong ENDOR signal with an isotropic component with beta proton was observed. The possible structure of this radical is as in structure [2.34].

ESR and ENDOR spectra of irradiated single crystal of glucose-1-phosphate dipotassium salt structure [2.35] have been studied by LOCHER and BOX[62] at 4.2° K. The alkoxy radical which gives rise to a quartet of hyperfine lines was observed at a g-factor, g = 2.0254. This radical is identified as a radical centred at O6 as in structure [2.36]. It arises from an interaction of the free electron with

two beta protons. Another alkoxy radical is found at g = 2.0470. This radical arises from an interaction between the free electron and one beta proton. This radical could be localized at O2, O3, O4. The study of the g-tensors showed that another alkoxy radical could have given the resonance at g = 2.0086. This radical is located at O2, O3, O4. A hydroxy radical gives rise to a signal at g = 2.0023 structure [2.37]. This radical is attributed to the location of the free electron at C6.

2.4 IRRADIATED POLYSACCHARIDES

The study of the ESR spectra of several irradiated powder starches structure [2.38] has been carried out by ADAMIC and BLINC[63]. The spectra of irradiated starches at 77° K and at room temperature show more than one radical composed the spectra. The spectra which have been recorded at room temperature show a doublet signal with hyperfine splitting of about 15 gauss. Annealing at room temperature, gave a singlet signal after several days. The irradiation of the starches at 77° K showed a triplet signal with 18 gauss hyperfine splitting. The variation of the temperature from 77° K to room temperature varied the triplet signal to a doublet. The triplet signal was interpreted by ADAMIC as a free radical arising from the breaking of the C--O bond on C6 as in structure [2.39], so this electron is assumed to produce a triplet by interaction with two alpha protons on C6. This hypothesis interprets the transformation of the triplet signal to a doublet by migration of radiation damage from C6 to C5, which causes the separation of the $-CH_2OH$ group to localize the unpaired electron at C5 to yield a doublet signal by interaction of the free electron with H5 as in structure [2.40]. The singlet signal which is found after annealing at room

temperature has a poorly resolved hyperfine interaction, so this signal may be a doublet arising from the cleavage of the C--H bond on carbon C(1). The doublet is arises from the interaction of the free electron on C(1) with one proton at C(2).

RAFFI and AGNEL[64] have studied the kinetics of the free radicals produced from irradiated starches. The decay of the spectrum during several months caused the lineshape to change from a shape indicating several radicals immediately after irradiation to a shape consisting of single line after several months of decay. The study of the kinetics of the singlet signal shape (relation between decay time and logarithmic of relative concentration of radicals) by RAFFI shows four zones through which the radical decayed. During the first zone (several days storage after irradiation) the radicals decayed rapidly, in zone II (from several days to 2 weeks). In this zone they found the decay rate to depend on water content, in zone III it was found that the decay rate of this zone is independent of the water content. An attempt to advance a model to interpret the two species before and after annealing has been suggested by RAFFI. The model shown in structure [2.41] proposed a species consisting of a doublet signal which detected immediately after irradiation and arising from the abstraction of the hydrogen atom from C1 where the free electron on C1 will interact with beta proton on C2. The singlet signal produced after annealing is interpreted as due to the action of oxygen traces on the radicals of the glycosidic bond deriving from the break of the glycosidic link as shown in structure [2.42].

In earlier times the effect of ionizing radiation on the texture of fruits and vegetables has been studied by GLEGG and KERTESZ[65]. From the measurements of the viscosity before and after irradiation, they found a decrease of the viscosity after irradiation. They interpret this phenomena as due to a degradation

of the cellulose component of the cell wall. FLORIN and WALL[66] have studied the ESR of irradiated purified cellulose. The ESR spectra observed is asymmetric with five partially resolved peaks. The change of the microwave power and the effect of the thermal annealing shows saturation and modification of some radicals before another which means that more than one radical is present in the spectra. The addition of water and the exposure of the material to oxygen did not affect the peak location but it affected the intensity of the signals. An interpretation of the ESR spectra of the irradiated cellulose has been proposed by these authors as follows. The high intensity signal of three lines is due to a hyperfine splitting of 20 gauss. GIBSON et al.[67] has interpreted this signal as a signal due to the interaction of the free electron with 2 α or β protons. The other radical giving rise to a doublet with g - value less than the DPPH by 0.002 to 0.003 indicated more spin-orbital interaction. The small shifts in this direction are found when the free electrons are located at oxygen atoms, so the radical may be due to cleavage of a C--O or O--H bond, so the radical may be of the type shown in structure [2.44 and 2.45].

The ESR spectra of irradiated dry and wet cellulose of type I and II, which have the same unit cell but differ in the dimensions of the unit cell, have been studied by BAUGH et al[68]. Dry cellulose I and II gave an ESR signal with three lines, but the wet cellulose II gave five lines, whereas wet cellulose I still gave three lines. This change of the ESR spectrum by addition of the moisture to cellulose II may be due to the difference in the dimension of the unit cell between the two cellulose samples used. The three line signal has been interpreted by these authors as due to localization of the free electron at C5, that is because the delocalizaition energy is available from the oxygen attached to C5. Then the three lines arise from the interaction of the free electron at C5 with two β protons

on C6 as in structure [2.46]. The five line signal may be due to summation of two radicals localized at C5 and C6 with two three lines which have nearly the same g - value with different hyperfine splitting constant aC5--H and aC6--H. The singlet signal which is found in the two celluloses is due to cleavage of the glycosidic link between the monomers as in structure [2.47].

ARTHUR et al.[69] studied the effects of the different order of crystallinity of cellulose and of the water on the ESR spectra generated by free radicals due to the interaction of gamma rays and the cellulose molecule. From this work they concluded that the addition of water to the amorphous and less ordered crystallinity causes the free radical to react with water and get easily destroyed. The high order crystallinity of cellulose shows stable free radicals toward the addition of solvent or water. By the addition of water the line shape of the ESR spectra were changed, the change depending on the crystalline structure and degree of crystallinity of cellulose.

CHAPTER THREE

GENERATION OF FREE RADICALS BY IRRADIATION AND ELECTRON SPIN RESONANCE (ESR)

3.1 THE NATURE OF IONIZING RADIATION

The radiations which are of interest in our investigation are those which have sufficent energy for ionization, and can produce ions by ejecting an electron from its orbit into another state. The ionizaing radiation can be divided into two groups:

1- Particulate radiation, such as alpha particles, electrons, protons and neutrons.

2- Electromagnetic radiations such as UV, x-rays and gamma rays.

Ultraviolet radiation is electromagnetic radiation of wave length from 10 to 4000 A^0 and is an important radiation in some biological processes. The effect of ultraviolet radiation in matter is generally that of an exciting radiation, but sometimes the effect is as an ionizing radiation.

x-rays and gamma rays are electromagnetic radiations with wavelengths between 10^{-3} and 10 A^0. Gamma rays are emitted from the nucleus, but x-rays are emitted by the electronic processes. The x and gamma radiations interact with matter depending on the energy of the incident photon which is proportional to the frequency[70].

3.1.1 INTERACTION OF IONIZATION RADIATION WITH MATTER

Ionizing radiation interaction with matter depends on the photon energy of the incident radiation. The low energy ionizing radiation interacts with the electron cloud of the atom or molecule, where the high energy photons interact with the nucleus of the atoms. The interaction between the incident radiation and matter occurs via five mechanisms, which are (1) classical scattering, (2) Compton

effect, (3) photoelectric effect, (4) pair production, (5) photodisintegration[71].

When the energy of the incident photon is below 10 keV the photon will interact with matter by classical scattering in which the target atom become excited, and subsequently will release this excess energy as a secondary photon with the same wavelength of the incident photon. In the Compton effect the incident photon interacts with an outer shell electron and ejects it from the atom. The result of the Compton interaction is an ionized electron and a scattered photon. The scattered photon and the scattered electron may have sufficent energy to cause further ionizations. In the photoelectric effect the incident photon must have an energy sufficent to release an electron from an inner shell (K-shell). The result of the photoelectric effect is a photoelectron. The photoelectron will carry a kinetic energy that depends on the binding energy of the K-shell electron and the energy of the incident photon. When the incident photon have an energy more than 1.02 MeV pair production will occur; the photon will penetrate the electron cloud to interact with the nuclear field. The results will be two particles: an electron and a positron. Photodisintegration occurs when the incident photon have energy greater than 10 MeV, so the photon will penetrate the electron clouds and nuclear force field to interact directly with the nucleus and emit a nuclear fragment[71].

Ionization or excitation of the molecule can be caused directly when it receives the incident radiation and that is called a direct effect of radiation, or by transfer of energy from another molecule, which is known as the indirect effect of radiation[70].

The mechanism by which the energy of an electron may be transferred to matter is as follows.

If the energy of an electron E_e is greater than the energy of excitation $E_{exc.}$, the energy will be used to ionize or to excite the electron.

If $E_{exc.} \geq E_e \geq E_{vib.}$ where $E_{vib.}$ is the energy of the electron vibration, then the energy of the electron will be used in the vibrational excitation of molecules.

if $E_{vib.} \geq E_e \geq E_k$ where E_k is the kinetic energy of the electron. the electron energy decreases to thermal energy[72].

3.1.2 RADICAL FORMATION

When the electron is ejected from the molecule the result is a positive ion A^+ and a negative electron e^- Both the positive ion and the electron may have a great deal of energy

$$A \longrightarrow A^+ + e^- \quad (1)$$

The electron will be captured by another molecule

$$e^- + B \longrightarrow B^- \quad (2)$$

The result of these two processes is two ions one negative and the other is positive.

$$A + B \longrightarrow A^+ + B^- \quad (3)$$

Sometimes the negative and the positive ions are formed as ion pairs by radiation.

Sometimes an electron will be neutralized by the positive ion from which the electron is ejected but that is the unusual case. The molecule formed in this way A^* has more energy than that associated with normal stability.

$$A^+ + e^- \longrightarrow A^* \quad (4)$$

This molecule tends to dissociate immediately, and the result of the dissociation is a free radical.

$$A^{*} \dashrightarrow C^{0} + D^{0} \quad (5)$$

Also an ion pair EF^{-} may dissociate to form a free radical:

$$EF^{-} \dashrightarrow E^{-} + F^{0} \quad (6)$$

where E^{-} is an ion which does not contain an excess of energy, but the free radical F^{0} contains a great deal of energy[70].

3.2 ELECTRON SPIN RESONANCE THEORY

3.2.1 INTRODUCTION

Determination of the energy levels of molecules, atoms and nuclei is the fundamental object of the various forms of the spectroscopy. The energy levels can be created by the interaction between matter and radiation. The lines or the bands in a spectrum represent transitions between energy levels of molecules and hence the frequency of each line or band measures the energy separation of the two levels[73,74].

Paramagnetic resonance is a form of spectroscopy in which an oscillating magnetic field of the incident electromagnetic radiation (microwave) induces magnetic dipole transitions between the energy levels of a system of paramagnets which has a net magnetic dipole moment, assosiated with the motion of the electrons within it.

In general, any system with free radicals or any compound containing transition elements which contain unpaired electrons, can be studied by electron spin resonance spectroscopy. Naturally free radicals are found in a large number of metabolic processes of biological systems or any organic reactions, particularly in metabolic processes of cells, enzymatic reactions, oxidation - reduction reactions, intermediate of the action of the drugs and in any pathological

processes, the damage of the biological molecules by ionizaing radiation, and photosynthetic processes[75]. Electron spin resonance (ESR) spectroscopy is a physical technique designed to detect species with unpaired electrons . The systems which contain unpaired electrons can be summarized as follows:

1. Free radicals which are found in a molecules having one unpaired electron.
2. Biradicals which are found in molecules with two unpaired electrons.
3. Any system with three or more unpaired electrons.
4. Point defects in solids.
5. Most transition metal ions and rare - earth ions.

An electron has orbital and spin angular momentum due to orbital and spin motion and the result of the spin and the orbital angular momentum of the electron is a magnetic dipole moment. If the molecule which has a net magnetic moment is placed in a static magnetic field, the dipole will interact with the magnetic field component of the incident electromagnetic wave and absorption will take place.

When a molecule with a magnetic moment is situated in a magnetic field, the energy W of the magnetic dipole μ in the field H is equal to

$$W = -\mu \cdot H = -\mu \cdot H \cos(\mu,H) ------(3-1)$$

where (μ,H) is the angle between μ and H.

This expression show that the energy of the dipole W is a minimum if μ is positive and the angle (μ,H) is zero, as shown in figure (3-1)a. The energy will be a maximum $W_{max} = +\mu \cdot H$ when the angle is equal to π , which mean that the dipole is antiparallel to the direction of H as shown in figure (3-1c)[74].

3.2.2 QUANTIZATION OF ANGULAR MOMENTUM

Simple theory shows that any particle of mass m undergoing orbital motion, has an angular momentum. If the linear momentum of this particle is given by the equation p = m.v then the particle has an associated de Broglie wavelength:

$$\lambda = \frac{h}{p} \text{----------} (3-2)$$

In the propagation of the wave around the orbital, it must not interfere destructively with itself. This requires the orbital to be an integral M of the de Broglie wavelength, so, assuming a circular orbit:

$$2\pi r = M.\lambda = M\frac{\mathrm{h}}{p} \text{----------} (3-3)$$

i.e. the angular momentum p.r is given by

$$p_\phi = M\frac{h}{2\pi} = M\hbar \text{----------} (3-4)$$

where p_ϕ is the magnitude of the angular momentum of the particle. p_ϕ is required to be an integral multiple of h. For this case M will take the values 0, 1, 2, 3, ... etc. In the z - direction the angular momentum is symbolized by P_{ϕ_z}. when $M = 0$ the electron is said to be in a σ orbital, when $M = 1$ it is said to be in a π orbital. for most of free radicals, the unpaired electrons resides in π orbitals.

Quantum mechanical analysis of the motion shows that the expectation values of the z-component of the orbital angular momentum for a single electron is of the form $[l(l+1)]^{\frac{1}{2}}.\hbar$. where l takes the values 0, 1, 2, 3, ... etc. These values can represented for atomic spectra by the spectroscopic symbols

s, p, d, f, ... etc. for the total angular momentum . For the quantum number L = 0, 1, 2, 3, ...etc. is represented by S, P, D, F, ... etc. The expectation value of the z-component of the orbital angular momentum $[l(l+1)]^{\frac{1}{2}}.h$ is $M_l.\overline{h}$. For a particle in a ring. M_l can take the integral values between $-l$, *and* $+l$.

$$-l \leq M_l \leq l$$

There are $2l+1$ allowed values of M_l. The spin angular momentum expectation values are $[s(s+1)]^{\frac{1}{2}}.h$, , where s represents the spin quantum number. The components of the spin angular momentum can take $M_s \cdot \overline{h}$ values. For a single electron s can take the value $\frac{1}{2}$. For systems that have more than one electron, the M_s values are , $\frac{1}{2},1,\frac{3}{2},2,\frac{5}{2},$.....*etc*. The allowed values of M_s are $-s$ up to $+s$. there are $2s+1$ allowed values of M_s. For a free radical $s=\pm\frac{1}{2}$ the nuclear spin angular momentum is also quantized. The nuclear spin quantum number is denoted by I[74,76].

3.2.3 RELATIONS BETWEEN MAGNETIC MOMENTS AND ANGULAR MOMENTUM.

The magnetic dipole moment μ of a particle of mass m and charge q moving in a circular orbital is $\mu = i.A$. The time required for the particle to complete one orbit (one oscillation) is: $\frac{2\pi r}{v}$

Therefore the magnitude of the current i is : $i = \frac{dq}{dt} = \frac{q.v}{2\pi r}$

Thus.

$$\mu_z = i.A = q.\frac{v}{2\pi r} \cdot \pi r^2 = q.r.\frac{v}{2} \text{----------} (3-5)$$

If we multiply by the factor m up and down in equation (3 - 5) we get

$$\mu_z = \frac{q}{2m} \cdot P_\phi \text{----------} (3-6)$$

In the z-direction

$$\mu_z = \frac{q}{2mc} p_{\phi_z} = \gamma p_{\phi_z} = \gamma M_l h \text{----------} (3-7)$$

where: $\gamma = \frac{q}{2mc}$ is called the gyromagnetic ratio in general: $\gamma = -\frac{ge}{2mc}$

For an electron: $\frac{eh}{4\pi mc}$ is represented by β, which is called the Bohr magneton. The component of electron spin magnetic moment μ_z along the direction of the magnetic field H is thus

$$\mu_z = \gamma M_s \bar{h} = -g\beta M_s \text{----------} (3-8)$$

The negative sign arises because of the negative charge of the electron.

The quantization of spin angular momentum in a specified direction leads to the quantization of the energy levels of a system of magnetic dipoles μ_z in a magnetic field. If we applied the expression $W = -\mu_z . H$ to a (spin only system and substitute $\mu_z = -g\beta M_s$ we obtain a set of energies.

$$W = g\beta H M_s \text{----------} (3-9)$$

If the possible values of M_s are $+\frac{1}{2}$ and $-\frac{1}{2}$ there are two possible values of W.

$$W = \pm\frac{1}{2} g\beta H \text{----------} (3-10)$$

Equation (3 - 10) is sometimes called the electron Zeeman energy. The transition between the two Zeeman levels needs an appropriate frequency of an electromagnetic field, so, if the photon energy $h\nu$ matches the energy - level separation ΔW then:

$$\Delta W = h\nu = g\beta H_r \text{ ----------} (3-11)$$

where ν is expressed in hertz (Hz), H_r is the magnetic field at which the resonance condition is met.

Figure (3 - 2) shows the energy - levels scheme, for the ESR absorption, where W_α *and* W_β represents the energies of the $M_s=+\frac{1}{2}$ and the $M_s=-\frac{1}{2}$ states, respectivaly[74,75].

3.2.4 NUCLEAR HYPERFINE INTERACTION

Some of the nuclei exhibit a magnetic moment associated with the nuclear spin angular momentum. The interaction between an unpaired electron and a magnetic nucleus is called the hyperfine interaction. The energy of the dipole - dipole interaction $W_{dipolar}$. between an electron and a nucleus is derived clasically

$$W_{dipolar} = \frac{1-3\cos^2\theta}{r^3}\mu_{N_z}\mu_{e_z} = H_{local}\cdot\mu_{e_z} \text{ ----------} (3-12)$$

where μ_{e_z}, μ_{N_z} are the components of the electron and nuclear dipole moments respectively along a magnetic field (z-directon), r is the distance between the dipoles, θ is the angle between the magnetic field direction and a line joining the two dipoles, figure (3 - 3) shows the interaction between the two dipoles. since the electron is not localized at one position in space. The interaction energy H_{local} must be averaged over the electron probability distributions, so the average local field is obtained by inserting the value of $\cos^2\theta$ averaged over the sphere[74].

Fermi has shown that for a system with one electron the isotropic interaction energy is given approximately by :

$$W_{iso} = -\frac{8\pi}{3} |\psi(0)|^2 \mu_{e_z} \mu_{N_z} \text{----------} (3-13)$$

where $\psi(0)$ represents the wave function evaluated at the nucleus.

The energy levels of a system with one unpaired electron $s=\frac{1}{2}$ and one nucleus with $I=\frac{1}{2}$ can be derived using equation (3 - 13) by replacing the magnetic moments by their corresponding operators

$$\hat{\mu}_{e_z} = -g\beta\hat{S}_z$$
$$\hat{\mu}_{N_z} = g_n\beta_N\hat{I}_z$$

$$\hat{H} = \frac{8\pi}{3} g\beta g_N\beta_N |\psi(0)|^2 \hat{S}_z\hat{I}_z \text{-------} (3-14)a$$

$$= hA_0\hat{S}_z\hat{I}_z \text{----------} (3-14)b$$

where A_0 is called the isotropic hyperfine coupling constant

Since the eigenvalues M_s of $\hat{S}_z$ are $\pm\frac{1}{2}$ and I_z are $M_I=\pm\frac{1}{2}$, there will be four possible spin states of the system with one electron and one nucleus (hydrogen atom). The four spin states are.

$|\alpha_e,\alpha_n>$

$|\alpha_e,\beta_n>$

$|\beta_e,\alpha_n>$

$|\beta_e,\beta_n>$

Then the energies of these states are:

$$W_{\alpha_e,\alpha_n} = \frac{1}{2}g\beta H + \frac{1}{4}hA_0 \text{----------} (3-15)a$$

$$W_{\alpha_e,\beta_n} = +\frac{1}{2}g\beta H - \frac{1}{4}hA_0 \text{----------} (3-15)b$$

$$W_{\beta_e,\beta_n} = -\frac{1}{2}g\beta H + \frac{1}{4}hA_0 \text{----------} (3-15)c$$

$$W_{\beta_e,\alpha_n} = -\frac{1}{2}g\beta H - \frac{1}{4}hA_0 \text{----------} (3-15)d$$

using the selection rules for the electron spin transitions $\Delta M_s = \pm 1$ and $\Delta M_I = 0$. We can draw the states and possible transitions as shown in figure (3 - 4)[74].

3.2.5 LINE WIDTH AND THE BROADENING

The line width of the ESR spectra is affected by variouse parameters. Mainly these are:

a - Parameters due to relaxation time interaction.

1 - Spin-lattice interaction.

2 - Spin-spin interaction.

3 - Spin orbital interaction.

b - Broadening due to microwave power saturation.

c - Broadening due to exchange narrowing.

a. PARAMETERS DUE TO LIFE TIME INTERACTION

1- SPIN LATTICE INTERACTION

As a qonsequence of the Heisenberg uncertainity principle, the energy levels of the electron should have a finite width (ΔE), which can be represented by

$$\Delta E \Delta t \sim \frac{h}{2\pi} \sim \bar{h} \text{ ----------(3-16)}$$

$$\Delta E \sim \frac{\bar{h}}{\Delta t} \sim \frac{h}{2\pi} \frac{1}{\Delta t} \text{ ----------(3-17)}$$

but:

$$h \cdot \Delta \nu = g \beta \Delta H = \Delta E \text{ ----------(3-18)}$$

thus:

$$g \beta \Delta H \sim \frac{\bar{h}}{\Delta t} \text{ ----------(3-19)}$$

$$\Delta H \sim \frac{\bar{h}}{g\beta} \cdot \frac{1}{\Delta t} \sim \frac{1}{\gamma_e \Delta t} \text{ ----------(3-20)}$$

where γ_e is the electron magnetogyric ratio.

Any processes that increase the rate of transition between the two electron spin states will decrease Δt and then will increase the line width

Δt is related to time T_1 and which is called spin relaxation time. T_1 represent the coupling of the spin system with its surrounding (lattice) through the random motion of the molecules[75].

2 - SPIN - SPIN INTERACTION

Spin spin interaction is the measure of the dipole - dipole interaction between one electron magnetic moment and another electron. The dynamic effect of the dipoler interaction between spins is to cause flipping of the spin. The life time of a spin in the upper state is controlled by the spin-spin interaction. Spin - spin interaction alleviates saturation, but it contributes to the life time broadning of the line[75].

3 - SPIN - ORBITAL COUPLING

The motion of the electron about the nucleus of an atom creates a magnetic dipole. This interaction is called spin-orbital coupling and is strongly affected by the spin-lattice relaxtion time T_1. T_1 is found to be very short in transition metal ions where the spin-orbital coupling is very strong and the line width is very wide[77].

b - BROADENING DUE TO MICROWAVE POWER SATURATION

The distribution of electrons between two energy states in thermal equilibrium at a certain temperature depends on the relaxation values of the average thermal energy, $k_B T$ and the energy gap, $g\beta H$ between the two levels. This distribution follows the Boltzmann equation :

$$\frac{N^+}{N^-} = e^{-\left[\frac{E^+ - E^-}{kT}\right]} \text{----------} (3-21)$$

Where k is the Boltzmann constant and T is the absolute temperature. At room temperature.

$$\frac{N^+}{N^-} = 0.9984$$

When the microwave intensity increased the pumping of the electrons from lower state will increase the quantity $\frac{N'}{N}$ and that will affected the spin - lattice relaxation time[75].

c - EXCHANGE NARROWING

Exchange interaction occurs when the electrons are exchanged between the orbitals of different molecules. This phenomenon is a direct consequence of the Heisenberg uncertainty principle. If there are two species of radicals with two ESR lines and the electron - spin exchange rate is increased the ESR lines

broaden and finally overlap to become one line. The electron spin exchange rate is increased proportional to the free radical concentration, The broadening of the lines will lead to a single line and to narrowing of the final line. This phenomenon may occur in liquids and in solids, where the strong electron exchange in the solids arises from the overlapping of molecular wave functions. Line narrowing also occurs, due to delocalization of the unpaired electrons in a molecular orbital. In a free radical the unpaired electron moves through several atoms in its orbitals. This motion will produce an averaging of the dipolar interactions and a line narrowing.

ANDERSON and WEISS atempted to derive a detailed line shape in the case of strong exchange by using a model of random frequency modulation. This work predicted a line of LORENTZIAN shape in the centre, falling off more rapidly in the wings. The change of the line shape from GAUSSIAN to LORENTZIAN is good evidence that exchange narrowing has taken place[74].

CHAPTER FOUR

EXPERIMENTAL TECHNIQUES AND METHOD

4.1.0 EXPERIMENTAL TECHNIQUES.

4.1.1 THE ESR SPECTROMETER

In simple terms an ESR spectrometer consists as does any spectrometer, of a radiation source, sample absorption cell and a detector [73,77]. **Figure (4.1)** shows a full diagram of the ESR spectrometer. There are two main differences between the ESR spectrometer and other absorption spectrometers:

1- In ESR spectrometers the radiation source (microwave source) emits monochromatic radiation with a certain microwave frequency.

2- In an ESR spectrometer the microwave frequency is fixed and the value of the applied magnetic field is swept[77].

The main idea of the operation of the ESR spectrometer is that the absorption lines are observed in the spectrum when the separation of the two energy levels in a given magnetic field is equal to the quantum energy $h\nu$ of the incident microwave photon. The main parts of the ESR spectrometer are described in the following sections.

4.1.2 THE MICROWAVE SOURCE

The equation $h\nu = g\beta H$ suggests that any region of the electromagnetic spectrum can be used, but we want to use the best frequency that can give us a high resolution and which is practically available. For these reasons microwave radiation is used in the ESR spectrometers in the x-band range of microwaves $\nu = 9.5GHz$ and Q-band $\nu = 35GHz$ [78]. The source of the microwave radiation is the

klystron which is a vacuum tube that produce microwave oscillations with a narrow range of frequency. The klystron can be operated in several modes. The particular mode selected depends on the frequency cavity where the klystron is tuned so that the maximum absorption of the cavity occurs at the centre of the mode. For practical purposes the microwave frequency and power need to vary. The frequency of the microwaves produced from the klystron can be varied by the variation of the voltage applied to the klystron. The frequency of the radiation must be stabilized and for that purpose an automatic frequency control system is used. The amount of the microwave power is controlled by an attenuator which contains an absorptive element[74]. The frequency of the microwave oscillation may be perturbed by the reflected radiation from the system which is fed by the klystron, So the klystron is fitted with an isolator which makes the reflected microwave energy pass only in the forward direction[78].

4.1.3 THE CAVITY SYSTEM

The cavity is a box positioned in the gap between the two poles of the magnet, in which the sample is fixed. The cavity which is used in the ESR spectrometers must be tuned to the klystron frequency. The main use of the cavity is to concentrate the microwave power and to separate the two components of the microwave radiation, electric and magnetic fields since it is needed to put the sample in the magnetic region, where the interaction between the paramagnetic samples and the radiation will occur[74,78]. The cavities which are used in ESR study may be designed as rectangular or cylindrical shapes. **Figure (4.2)** shows the region where the concentration of the magnetic field component of the microwave radiation is localized. In the ESR system there are reflection and transmission cavities, The reflection cavities are often used because of their superior ability to discriminate against klystron noise.

4.1.4 MAGNETIC FIELD

The magnetic field which is used in ESR spectrometry must be very accurate and homogeneous. The high accuracy of the magnetic field require the use of very sensitive stabilizers with the power supply and highly polished and parallel magnet pole pieces[74,77].

4.1.5 MODULATION AND PHASE SENSITIVE DETECTION

When the magnetic field is scanned through the region of the resonance, the spin system will absorb a small amount of the microwave energy. The change of power can be detected by changing the detector output signal. This sensitivity can be increased by a multistage DC amplifier. Two types of modulation are employed in the detection of the microwaves. These are (1) source modulation in which the signal is amplified and detected at the modulation frequency, where the amplitude and the frequency of the microwave are modulated; (the modulation amplitude which is used must be small with respect to the line width,) (2) magnetic field modulation, is achieved by two small coils mounted inside the cavity and supplied by a 100 kHz wave. The result of the modulation is a modulated magnetic field which is superimposed on the static magnetic field (DC field). when the sample is near or at resonance, a detected signal will be modulated at 100 kHz. **Figure (4.3)** shows that as the field varies between H_a and H_b the detector current varies between i_a and i_b. The result of this process is that the first derivative of the signal is obtained as shown in **figure (4.4b)** and **(4.5c)** [73,74,75].

4.1.6 TEMPERATURE VARIATION SETUP

The system which was used to control the temperature of the sample in the ESR spectrometer is as shown in **figure (4.6)**, It consists of:

1- A liquid nitrogen evaporating circuit.

2- A controller and temperature system.

The liquid nitrogen is evaporated with an internally positioned heater. The heater is fixed at the end of a silica tube and the operation is controlled by an electric circuit and manometer.

The temperature variation system is controlled by a VARIAN variable temperature controller which uses a thermocouple to scan the temperature between 77 K and 573 K. The temperature can be controlled manually and there is a sensor to control the temperature to a fixed setting. The evaporated nitrogen gas passes through this controller, first passing through an exchange loop which is immersed in a liquid nitrogen dewar, and then passes over the sample where its temperature is controlled by the heater and the sensor.

4.1.7 RADIATION SOURCE

In this investigation we have used the following sources for sample irradiation.

a- X-ray source

b- Mercury tube 150 watt (UV and visible light). The wave length emitted is above 300 nm.

c- Mercury tube with hard ultraviolet path filter (5 watt). The filter path radiation is between 300 and 400 nm.

a- X-RAY SOURCE

In our investigation the X- ray source which is used to irradiate the samples is made by PHILIPS (no. PW 1050) and can operate with different X-ray tubes, with different excitation voltage and with different target currents. All the samples where irradiated by X-rays through a rectangular window of dimensions 10mm x 6mm without any filters. The samples were fixed as near as possible to the window, where the distance between the sample and the wall of the X-ray tube is 5mm.

b- ULTRA VIOLET SOURCES.

The ultra violet source used here is a 5watt mercury lamp using a hard ultra violet path filter. It is produced by ULTRA - VIOLET PRODUCTS, SAN GABRIEL, CALIFORNIA. The visible and UV source is a 150 watt mercury lamp connected to a power supply. The lamp is surrounded by a metal cylinder designed to absorb the heat of the lamp and hence to decrease the heat around the lamp.

4.2.0 THE EXPERIMENTAL METHOD

4.2.1.0 MATERIALS

4.2.1.1 THE ORIGIN OF THE SAMPLES

The gum arabic material was collected from HASHAB trees (acacia SENEGAL) from the KORDOFAN area of SUDAN. The basic constituent components of gum arabic: D-galactose, L-arabinose, L-rhamnose, and D-glucuronic acid have been obtained from RIEDEL DE HEAN COMPANY, HANOVER, WEST GERMANY, and WINLABE, U.K.

4.2.2 PREPARATION OF THE SAMPLES FOR THE IRRADIATION AND ESR MEASUREMENTS

The natural samples of homogeneous colour were selected and were crushed carefully by mortar and pestle to a fine powder. This powder was then dried in a vacuum desiccator for several days.

The powder of the material is prepared for X - ray irradiation in a thin transparent plastic tube of dimensions 12 mm in diameter, 25 mm in length, and 0.5 mm in thickness. The approximate weight of the irradiated material was about 0.3 grams. The material occupied about 4 mm of the tube height. The residual space of the tube was filled with paper tissue.

The tube containing the material was fixed directly in front of the window of the X - ray source. The irradiated material was stirred gently before the ESR measurements to get a homogeneous irradiated material.

4.2.3 THE ESR MEASUREMENT

The ESR measurements were carried out using an ESR spectrometer (E - line) manufactured by VARIAN ASSOCIATES. This spectrometer is controlled by a HP - 9835B computer, a HP 1350A graphics translator, and a VARIAN EPR data acquisition system. The range of the microwave frequency used was x - band. All the measurements of the ESR spectra were obtained as first derivatives of the signal using a 100 kHz modulation frequency. The modulation field used for all the measurements was 2 gauss. The ESR spectra were recorded on tape cassette. The ESR measurements were carried out on powder samples in high purity silica tubes of dimensions 20 cm in length and 3 mm in diameter. For most of our measurements the tubes were filled up to 3 cm of the tube.

4.2.4 THE VARIATION OF THE IRRADIATION TIME.

Dry powder of the gum arabic was irradiated using an X - ray cobalt tube, with 20 mA filament current and 30 kV excitation voltage. The same amount of gum was exposed to the X - ray source for different times running from two minutes to 180 minutes. The powder was gently mixed to distribute the irradiated material evenly in the powder. The irradiated powder was then transferred to the ESR sample tube which was carefully marked to locate the material at a given position in the cavity. The same amount of the powder was used every time for the ESR measurements.

4.2.5 TIME DEPENDENT DECAY.

The material which was X - irradiated for three hours was left in the cavity at room temperature, to study the decay of signal with the time. The spectra were recorded several times during 667.5 hours.

4.2.6 MICROWAVE POWER VARIATION.

Samples of gum arabic powder were irradiated with an X - ray source using a Co tube for 10 minutes with 20 mA filament current and 30 kV excitation voltage. The ESR spectra were recorded at different microwave powers that varied from 0.5 mW to 60 mW.

4.2.7 TEMPERATURE VARIATION.

The variation of the material temperature was measured in the range just above room temperature. The samples under study were irradiated for 10 minutes using an X-ray source Co tube with 20 mA filament current and 30 kV excitation voltage. The ESR spectra were recorded between room temperature and 120 C.

4.2.8 THE EFFECT OF LIGHT ON IRRADIATED GUM ARABIC.

The gum arabic material was irradiated with an x-ray source of Co target for 10 minutes using 20 mA filament current and 30 kV excitation voltage. The x-irradiated sample was studied with and without exposure to the mercury lamp. In the case of the exposed sample, the powder of gum is spread on a sheet of white paper and placed at a distance of 10 cm from a mercury lamp emit a radiation with a wave length above 300nm for a time between 0 and 355 minutes. The ESR measurements were made immediately after exposing the material to the light. The materials were always at the same position, at the same height of cavity and the same amount of material. Another sample of the gum was exposed to the mercury lamp for 24 hours with out x-irradiation to find out any effect of such light on the gum.

CHAPTER FIVE

FORMATION AND DECAY OF THE RADICALS IN GUM ARABIC

5.1 THE EFFECT OF MICROWAVE POWER VARIATION ON THE GENERAL FORM OF THE ESR SPECTRUM OF GUM ARABIC.

The microwave power causes the amplitude of a signal to increase with increase of the microwave power up to a certain level, after which the amplitude behaves in one of two ways:

1- The amplitude decreases rapidly and the resonance is said to be homogeneously broadened.

2- The amplitude is still nearly in the same level and the signal is said to be inhomogeneously broadened.

The saturation of various paramagnetic centres giving rise to ESR spectra are not necessarily the same and depend on the structure. So, the use of different microwave power levels causes some of the centres to saturate before the others. So, in this way, we could assign the signal to particular centres[75,78]. A study of the effect of variation of microwave power, during the measurements of ESR spectra of x-irradiated powder of gum arabic assists in the analysis of the spectra. The ESR spectra of gum arabic are very complex, and rather poorly resolved.

5.2 THE VARIATION OF THE MICROWAVE POWER INTENSITY AT ROOM TEMPERATURE.

5.2.1 RESULTS AND DISCUSSION

The relative spin density of the two paramagnetic centres spectral group (1) and (2), has been plotted as a function of the square root of the microwave power as shown in **figure (5.1)**. Saturation is obtained for the total spin, the spin of the spectral group (1) and the spin of spectral group (2) at microwave powers of 21.2, 37.5, 16.2 mW (see table 5.1) respectively. From these results we note that the saturation of the total spin takes place at an intermediate level to the saturation of the spectral group (1) and (2). The comparison of the saturation behaviour of the two paramagnetic centres shown for spectral group (1) and (2) with total relative spin is given in **figure (5.1)**, where the three curves are in a normalized condition. A similar behaviour is shown by the total relative spin curve and spectral group (2), but spectral group (1) does not follow the same pattern. An attempt to simulate the total spin with summation of the spectral group (1) and (2) is undertaken, to see if the spins of these two centres are the only centres responsible for the total spin or whether there are any other centres. The normalization of summation of the relative spin for the spectral group (1) and (2) and the normalization of the total relative spin have been drawn versus the square root of the microwave power as shown in **figure (5.2)**. The saturation points are 21.2 and 31.4 mW for the normalization of the total relative spin and for the normalization of the summation of the relative spins for the spectral group (1) and (2) respectively. From the saturation condition results, we could see that the two normalized curves are not the same, so, we conclude that there may be other centres which we did not to take into account.

5.2.2 THE EFFECT OF THE MICROWAVE INTENSITY VARIATION ON THE LINE WIDTH OF THE ESR SPECTRA OF GUM ARABIC.

A plot of microwave power variation and line width of the two resolved paramagnetic centres, spectral groups (1) and (2) is shown in **figure (5.3)**. The line width of spectral group (1) varied from 11.2 to 13.4 gauss. The line width of spectral group (2) shows a slight change from 22.1 to 22.8 gauss during the change of the microwave power from zero to 100 mW.

5.2.3 THE EFFECT OF THE MICROWAVE POWER VARIATION ON THE LINE HAPE OF THE ESR SPECTRUM OF GUM ARABIC.

Figure (5.4) shows various ESR spectra wich are recorded at different microwave power **figure (5.5)** shows three different ESR spectra which are recorded at different microwave powers in order to study how the spectra behave during the variation of the microwave power .During the variation of the microwave power, there is a general observation on the resolution of peaks in the spectrum, namely at low microwave power all the peaks are better resolved than at high microwave power. All the peaks still appear for all values of microwave power used and there is no absence of any peak.

5.3 THE VARIATION OF THE MICROWAVE POWER INTENSITY AT LIQUID ITROGEN TEMPERATURE.

The gum arabic material was irradiated at room temperature. The ESR spectra of the material have been recorded at liquid nitrogen temperature covering the microwave power range from 0.7 to 60 mW. **Figure (5.6)** shows the ESR spectra of gum arabic recorded at liquid nitrogen temperature. These spectra show a single broad line in all the microwave ranges studied. This line does not exhibit enough resolution to explain the presence of more than one line observed at

room temperature.

The total relative spin density versus the square root of the microwave power is as shown in **figure (5.7)**. This plot exhibits a homogeneous broadening of the signals which constitute the spectra recorded at liquide nitrogen. The microwave power intensity at which the signals saturated at liquid nitrogen is about 1.5 mW. (see table 5.1).

5.4.0 RADICAL FORMATION ON GUM ARABIC

5.4.1 POSSIBLE EVENTS ON IRRADIATION TIME VARIATION

The possible effect of ionizing radiation on gum arabic may identified from the work carried out on the component of gum arabic and from studies of the substances that have the glycosidic link between monomers. The signals which may be present in the ESR spectra of the monomers of gum arabic may be present in gum arabic spectra itself. Also, the presence of the 1-3, 1-4, and 1-6 glycosidic linkages make possible the scission of these linkages by ionizing radiation which is followed by radical formation at the scission position. Many workers have studied the ESR signals of irradiated components of gum arabic: D-galactose, L-arabinose, L-rhamnose, and D-glucuronic acid.

Dilli and GARNETT[48] studied the ESR signals of irradiated galactose at room temperature. They found a doublet signal with 18 gauss splitting and attributed this signal to the presence of a free electron at C1 or C6. CAVATORTA[79] detected two ESR signals when he irradiated a solid form of galactose at room temperature in the presence of air. One of them is a doublet which may be attributed to the presence of a free electron at C1[55], the other radical is a triplet signal, which may be interpreted by location of the free electron at C5 [55]. NIKITINE[51] has found a doublet ESR signal when he irradiated a polycrystaline

galactose at 77 K. This doublet is present when galactose is warmed to room temperature and is attributed to the presence of a free electron at C1. NIKITINE[53] has studied the ESR spectra of an irradiated aqueous solution of D-galactose at 77 K and found two signals, one a doublet and the other a triplet. The triplet signal is attributed to the presence of the free electron at C4.

DILLI and GARNETT[48] have detected an ESR signal from irradiated polycrystaline arabinose at room temperature; a doublet signal with a 17 gauss splitting. This signal is attributed to the presence of a free electron at C1 or C6 of the pyranose ring. NADZHIMIDDINOVA and SHARPATYI[60] detected a doublet ESR signal when they irradiated an aqueous solution of arabinose. They attributed this doublet to the presence of a free electron at C1. BALEY[61] detected a doublet ESR signal in irradiated polycrystaline arabinose. He attributed the doublet to the presence of the free electron at C1, C2, C3, or C4. NIKITINE[51] also found two ESR signals in irradiated polycrystaline arabinose at 77 K. One of them is a doublet and the other is a quadruplet. The doublet is attributed to the presence of the free electron on C1 and the quadruplet to the presence of the free electron at C4. The ESR signals detected in arabinose at room temperature are a doublet and a triplet of quadruplet with hyperfine splitting for the latter signal is 27, 13 gauss. The study of the ESR signals of irradiated frozen aqueous solution of arabinose at 77 k by NIKITIN[53], shows a doublet signal with hyperfine splitting equal to 31 gauss and a quadruplet with hyperfine splitting of 15 gauss.

BAILLY[61] has found a doublet signal in irradiated polycrystaline L-rhamnose at room temperature and attributes this signal to the presence of the free electron at C1, 2, 3, or 4. SAMSKOG[59] found an ESR signal consisting of four lines when he irradiated a single crystal of rhamnose at 67 K. This signal was also detected by SAMSKOG[58] and PANASYUK[60] who attributed this signal to the presence of a free electron at O4. A doublet of doublet signal has been detected by

PANASYUK[60] and SAMSKOG[59]. They interpret this signal as due to the presence of the free electron at C2, C3, or C4 and arises from the interaction of the free electron with two beta protons one of them is the proton of OH group. A doublet signal is detected by SAMSKOG[59] at 77 K and this radical is assumed to be located on C1, C2, C3, or C4 . Another radical was detected at 77 K , that is a doublet of quadruplet[60]. This radical is attributed to the presence of the free electron at C5. The doublet, doublet of doublet and doublet of quartet signals are found as stable signals in rhamnose single crystal at room temperature.
BALAZS et. AL.[50], NOZAWA et al.[82] irradiated D-glucuronic acid at room temperature. The ESR spectrum of this material shows a singlet signal. BALAZS et al.[50] attribute this signal to the presence of the free electron at C5, where the radical would be stabilize by resonance interaction with the carboxylic group.

The effect of ionizing radiation on carbohydrates which have glycosidic linkages between the monomers has been studied by many authors. PHILLIPS[84] in his study of the solid carbohydrates with a glycosidic link, has found the dominant scissions are in the glycosidic linkages. FRITSCH[85] and WAHBA[86] studied the effect of ionizing radiation on pectine powder (which consists of polygalacturonic acid) and found a scission of the glycosidic bond. LOFROTN[87] has mentioned that the major part of the radiation damage in molecules of sucrose, maltose and trehalose is in the glycosidic bonds. GLEGG[65] and DZIEDZIELA[66] found a scission of the cellulose chain when it is irradiated by ionizing radiation. BAUGH[68], ARTHUR[69], and CHIDAMBARESWARAN[89] studied the ESR spectra of irradiated cellulose with different levels of crystalline order and found a triplet in dry cellulose and a triplet and two triplets (signal with five lines) in others which contain moisture. They attribute the triplet to the abstraction of the hydrogen from C5 where the free electron will interact equally with the two

beta-protons on C6. The five line signal is attributed to the presence of the free electron at C5 and C6 at the same time where each one will interact with the two protons located on C6 to give two triplet signals with the same g-value and different hyperfine splitting. BAUGH[66] has also found a singlet signal additional to the triplet and two triplets. He attributed this singlet signal to the presence of the free electron on the oxygen atom in the cellulose chain attached either to a C1 or C4 atom.

The study of the ESR signals of the irradiated starches by ADAMIC[63] at room temperature shows a doublet signal immediately after irradiation. The annealing of the signal at room temperature gave a singlet. The doublet signal is interpreted by adamic as the location of the free electron at C5 by the cleavage of CH_2OH from C5. The singlet signal is interpreted as a signal with unknown hyperfine interaction where no stable radical is to be suggested in the starch molecule. RAFI[64] and HENDERSON[90] interpret the signal detected immediately after irradiation of starch as a doublet that arises from the interaction of the free electron on C1 with a beta proton on C2. The singlet signal which was detected after annealing is attributed to the formation of the radical presented in structure [2.42].

From the above investigation one can predict the possible ESR signals which may arise in the ESR spectrum of irradiated gum arabic.

A doublet signal is present in galactose at room temperature [48,51,79] and at 77 K[51,53] and it is present in arabinose at room temperature [81,48,51] and 77 K [51,53]. It is also present in rhamnose at room temperature[81]. At 77 K[59] a doublet signal is also detected in irradiated starch at room temperature [63,64,90]. A triplet signal was found in galactose at room temperature[79] and at 77 K[53]. The triplet signal was also detected in cellulose at room temperature [68,69,89]. A quadruplet signal was found in arabinose [48,51]. A quadruplet signal also was detected in rhamnose at 67

K and at room temperature[59,58,60]. A doublet of a doublet signal were found in rhamnose at 67 K and at room temperature[60]. A doublet of a quadruplet signal was found in rhamnose at 77 K[60]. Superimposed signals consisting of five lines were found in cellulose at room temperature [58,59,60]. A triplet of a quadruplet signal was found in arabinose at room temperature[51]. A singlet signal was found in glucuronic acid at room temperature[50,60] in cellulose[66] and in starch at room temperature[66,64].

From these investigations one can suggest the total signals which may be present in the ESR spectra of irradiated gum arabic at room temperature. A doublet signal is found in all monosaccharides at any temperature. A triplet signal is also found at room temperature. A doublet of doublet and doublet of quartet may also found at room temperature. A triplet of a quadruplet may also be present. Two triplets with different splitting may also be found. A singlet signal may also be present in the ESR spectra of gum arabic. From the above studies one can suggest a very complex ESR spectrum of gum arabic that has been irradiated at room temperature.

5.4.2 VARIATION OF IRRADIATION TIME

5.4.3 INTRODUCTION

The free radical concentration is not a linear function of dose. SNIPES[91], ROTBLANT[92], MULLER [93,94], and CONGER[95], have shown that for many organic solids, the dose response curves are often be described satisfactorily by the equation:

$$\frac{dC}{dD} = kC_{\infty} - kC \text{ -----(1)}$$

where C is the radical concentration, D is the dose, k is the rate constant of the radical formation, and C_∞ is the saturation radical concentration. The integration of equation (1) yields the expression:

$$C = C_\infty(1 - e^{-kD})$$

SNIPES[91] explained this equation in one of two ways. (1) The radicals are produced at a rate that decreases with increased concentration, (2) Radicals are produced at a constant rate and are simultaneously destroyed at a rate increasing with increased concentration, where at saturation the formation and destruction of the radicals are at the same rate. MAGE[96] and SAMUEL[97] proposed a non random distribution of radicals in irradiated water. They proposed that these radicals are formed in small increments of volume called spurs which are isolated one from another. The concentration of the radicals within a given spur decreases with time as a result of two processes, recombination and diffusion. SMITH and JACOBS[98] have proposed that the radicals which are formed in irradiated polyethylene are formed in isolated spherical spurs. They assumed that the concentration of the radicals within the spurs are decreased with time due to diffusion-like expansion of the spur. DZIEDZIELA[99] attributed the decrease of the radical concentration during the irradiation to the recombination of the radicals. PSHEZHETSKII et al.[100a] summarize the possible reasons why the trapped radical concentration decreases with time in the steady state as follows: (1) recombination of the radical, (2) capture of electrons by radicals and other charge transfer and charge recombination processes and (3) transfer of excitation energy from the environment resulting from the desiccation of radicals. WAITE[101] has stated that two particles

captured one another when they have approached a distance such that their Coulombic binding energy exceeds kT, where k is the BOLTZMANN constant and T is the temperature of the media.

5.4.4 RESULT AND DISSCUSION

The ESR spectra of x-irradiated gum arabic have been studied at various doses in relation to the irradiation time which varied between zero and 180 minutes. The spectra recorded at different doses are as shown in **figure (5.8)**. The measured total relative spin with respect to irradiation time is as shown in **figure (5.9)**. This relation shows a slight tendency to a saturation condition after 120 minutes of irradiation (see table 5.2).

A study of the behaviour of the radical formation of spectral group (1) and (2) which could be assigned from the decay studies is presented. A relation for relative spin for spectral group (1) and (2) and the irradiation time are shown in **figure (5.10)**. where spectral group (1) showed a saturation which started after approximately 90 minutes. spectral group (2) shows an obvious saturation which started after 120 minutes irradiation time (see table 5.2).

5.4.5 THE EFFECT OF THE IRRADIATION TIME ON THE LINE-WIDTH OF SPECTRAL GROUP (1) AND (2)

A relation between line width and irradiation time of the two spectral group (1) and (2) may be seen in **figure (5.11)**. This relation shows a slight increase in the line width for the two radicals. The line width of spectral group (1) has varied from 11.5 to 14 gauss and the line width of spectral group (2) has varied between 22 to 24 gauss, during the same interval, from 2 to 180 minutes (see table 5.3).

5.4.6 THE EFFECT OF IRRADIATION TIME ON THE g-VALUE OF SPECTRAL ROUP (1) AND (2)

A relation between g-value and irradiation time of the two spectral group (1) and (2) may be seen in **figure (5.12)**. This relation shows a steady g-value during the increase of irradiatin time. g-values of the spectral groups (1) and (2) are 2.0064 and 2.0054 respectively (see table 5.3).

5.4.7 THE EFFECT OF THE VARIATION OF IRRADIATION TIME ON THE LINE SHAPE OF THE ESR SPECTRA OF GUM ARABIC.

figure (5.13) shows various spectra of irradiated gum arabic, recorded at various times of irradiation. These spectra are modified in the y-direction. The formation of all the different peaks which comprise the ESR spectrum of gum arabic can be observed at low irradiation time (2 minutes). Those peaks which were observed at low doses show better resolution than the others which were observed at higher doses. During the increase of irradiation time from 2 minutes to 90 minutes **figure (5.8)**, the peaks could still be definitely assigned but after longer times of irradiation the peaks started to be overlapping.

5.5 DECAY OF THE ESR SPECTRA OF GUM ARABIC AT ROOM TEMPERATURE.

5.5.1 THE DECAY OF THE RADICALS

LOFROTH[102] and HERAK et al.[103] have mentioned that the transformation of the radicals by migration or by recombination due to diffusion of the radicals are the main processes by which the ESR signals of the radicals decay. FLORIN and WALL[66] mentioned that oxygen will react practically with any organic radical and form a non radical product and the presence of moisture usually facilitates

diffusion, which accelerates the decay of radicals. The transformation of the radicals induced by irradiation of cycloamylose has been studied by PHILLIPS[104,105]. He attributed the decay of the radical formed on the oxygen of the glycosidic linkage -C-O. to the oxidation processes, in the presence of water, to form a gluconic acid. BAUGH[106] studied the radical-radical reaction mechanisms in irradiated polycrystaline cycloamylose hydrates. The study of the end product of carbohydrates obtained after hydrolysis led them to propose that the migration of the C1, C4, C5, and C6 radicals to more stable radicals are the main processes in radical transformation. MADDEN and BERNHARD[107] studied the thermally induced free-radical reactions in alpha-D-glucopyranose single crystal. By considering the two main end products, arabinose and 2-deoxyribose they propose a radical reaction by which the C6 radical (detected at 77 K) migrates to the C1 radical at room temperature. The annealing of the material for 24 h at room temperature leads to migration of the C1 radical to C2 radical directly without scission of the pyranose ring. They proposed another mechanism by which the CO group is abstracted from the pyranose ring. The loss of H_2O lead to migration of the C2 radical to C3. MADDEN and BERNHARD[108] have studied the reaction mechanisms of free radicals formed in irradiated methyl-alpha-D-glucopyranoside single crystals after warming from 77 K to 320 K. Upon warming the material, three kind of free radical reactions have been observed. At 190 K the primary hydroxy alkyl radical located at C6, migrate to a C5 secondary oxyalkyl radical. Further warming to 230 K causes the migration of a C5 radical to a primary hydroxyalkyl radical located at C2 opening the pyranose ring. The C2 radical at 320 K, abstract a hydrogen from C5, reforming the C5 secondary oxyalkyl radical. Another possible route for the migration of the C2 radical at 320 K is to migrate to C3 by the loss of H_2 from C2 and C3. KOROTCHENKO et al.[109] and SULTANKHODZHAEVA et al.[110] have studied the conversion of the ESR

spectra of irradiated dry starch and dextrane at different temperature. They have suggested that the conversion of primary radicals at C1 may occur with either a break in the C2--C3 bond and forming the radical at C3 or by breaking the C5--O bond and forming the radical at C5. HON[111] has found that in the presence of oxygen, cellulose carbon free radicals will react with oxygen to produce peroxide radicals which are stable at 273 K. He also mentioned that the peroxide radicals have an ability to abstract hydrogen from cellulose molecules to produce polymer hydroperoxide at 273 K. HON[112] has also proposed at room temperature a migration of the radical formed by irradiation at C4 in cellulose to C1 to form a double bond at C4. HON[113] has proposed a possible radical-radical reaction of the stable radicals in irradiated cellulose as follows:

$$RO_2. + RO_2. ----\rightarrow inert\ product$$

$$RO_2. + R. ----\rightarrow inert\ product$$

$$R. + R. ----\rightarrow inert\ product$$

5.5.2 RESULTS AND DISCUSSION

The material which was irradiated as described in the latter section was fixed at the same position of the cavity of the spectrometer, throughout the decay time measurements were carried out. The spectra were recorded several time during a total period of 667.5 hours. **Figure (5.14)** shows a sequence of the ESR spectra of gum arabic recorded at different times during the decay of the spectra at room temperature.

The total number of free radicals is proportional to the area under the absorption curve. The total relative spin density has been calculated, using a software program, devloped by the VARIAN company. As proposed by RAFFI and AGNEL[64] that the decay of the radicals in irradiated starch following an exponential equation.

$$C = C_{\infty} e^{-kt}$$

$$\ln C - \ln C_{\infty} = -kt$$

where k is the decay rate constant.

t is the decay time.

Figure (5.15) shows a plot of relative spin density and decay time measured in hours. The curves show an exponential decay process. The time at which the relative spin density decreases to 1/e of its original value is 27.1 hours.

A relation between the decay time and the logarithm of the total relative spin density is shown in **figure (5.16).** This graph shows three zones of different decay rate constant. Zone (1) include the region between 0 and 25.2 hours. The decay constant rate in Zone (1) is 41.24×10^{-3} hours^{-1}. The decay constant rate in zone (11) is 5.3×10^{-3} hours^{-1}, which covers the region between 25.2 h and 158.0 h. The decay constant rate in zone (111) is 2.034×10^{-3} hours^{-1}, which covers the region between 158.6h and above.

5.5.3 THE EFFECT OF THE DECAY TIME ON THE LINE SHAPE

Figure (5.17) shows the different ESR spectra recorded at different decay times.

These spectra are modified in the y direction to show clearly how the signals behave . During the annealing of the irradiated gum arabic at room temperature and after 19 hours from the starting decay time, some of the peaks were lost from the ESR spectrum. The initial peak positions are seen in **figure (5.18).** Position (1) (2), (5) and (6) were missing from the latter spectra; positions(7) and (8) overlapped and became one peak; (9) and (10) also overlaped. If we follow the change of spectra in the decay process, we may see that positions (4) and(7) are following the same behaviour during the annealing processes; also (3) and (9) follow the same behaviour during the annealing processes. All these two groups (4), (7) and (3), (9) failed to follow the same situation during the decay processes. The positions (1), (2), (5), (6), (8) and (10) appeared to be due to other paramagnetic centres. Also we note that the peak in position (3) became wider during the annealing time, and this could be observed after 19 hours of decay time, so, it could be that position (3) overlapped with one or more than one peak.

To assign and to specify these two radicals, spectral group (2) is identified by positions (3) and (9); and spectral group (1) is identified at positions (4) and (7). Properties of the spectra such as amplitude, relative spin density , line width, and g-value, as a function of decay, have been studied.

A relation between the peak-to-peak amplitude as a function of the decay time is shown in **figure (5.19).** From the two curves shown in this **figure** we deduce that the functions for the two spectral group (1) and (2) are in the form of an exponential decay. The two amplitudes become equal after 187.4 hours decay time and then the amplitude of (1) becomes bigger than the amplitude of (2) at subsequent times.

The relative spin density as a function of decay time was studied, for spectral group (1) and (2) as shown in **figure (5.20)**. The relative spin density for the two spectral group was calculated using an approximate expression.

$$I = A(\Delta H^2)$$

where I is the approximate relative spin density, A is the peak-to-peak amplitude divided by 2 . and ΔH is the peak to peak line width.

The two relations show an exponential decay, but spectral group (2) shows a more rapid decay than spectral group (1). This could be verified from the calculation of the time at which the intensity of the two spectral group is reduced to 1/e of its initial value, where it is 37.5 and 25 hours for the spectral group (1) and (2) respectively.

Figure (5.21) show a relation between the logarithms of relative spin density as a function of decay time measured in hours, for the spectral group (1) and (2) respectively. The decay rate constants for the different zones were calculated for the two spectral group. The decay rate constant of spectral group (1) in zones (1), (2), and (3) are 51.97×10^{-3}, 8.16×10^{-3}, and 1.65×10^{-3} hours^{-1} respectively. The decay rate constants of spectral group (2) in zones (1), (2) and (3) are 40.6×10^{-3}, 7.3×10^{-3} and 2.66×10^{-3} hours^{-1} respectively (see table 5.4). Of these decay rate constants one can infer that spectral group (1) decay faster than the decay of spectral group (2) in zones (1) and (2), but in zone (3) spectral group (2) decay faster than spectral group (1).

5.5.4 THE EFFECT OF THE DECAY OF THE RADICALS ON THE LINE-WIDTH OF THE TWO SPECTRAL GROUP IN GUM ARABIC ESR SPECTRA.

During the annealing of the irradiated gum arabic at room temperature, the line width of the two spectral group was measured and a plot between line width and decay time is shown in **figure (5.22).** The graph shows a decrease of the line width for the two spectral group. The line width for spectral group (1) was decreasing from 13.5 gauss to 9 gauss during the decay interval 0 to 667.5 hours. The line width of spectral group (2) decreased from 23 gauss to 16 gauss during the same interval (see table 5.5).

5.5.5 THE EFFECT OF THE DECAY OF THE RADICALS ON THE G-VALUE OF THE TWO SPECTRAL GROUP IN GUM ARABIC ESR SPECTRA.

A relation between g-value and decay time of the spectral groups (1) and (2) may be seen in **figure (5.23).** This relation shows a decrease of the g-value of the spectral group (1) and (2) during the variation of decay time (see table 5.5).

5.6 THE DECAY OF THE RADICALS FORMED ON GUM ARABIC WITH VARIATION OF TEMPERATURE

5.6.1 INTRUDUCTION

The effect of temperature on the decay of the radicals has been studied by many authers. KURI[114] studied the effect of the temperature on the radical concentration of several materials, irradiated in powder state, such as cellulose, starch, arabinose, ribose, xylose, glucose, fructose, sorbose, galactose, sucrose, cellobose, and lactose, The radicals in all these materials were found to decay sharply near the melting point. Polyvinyl alcohol shows a rapid decay above the

glass transition temperature. For several polymers it was found that the decay region of the radicals lies around the phase transition region. KURI[115] found that the decay of the polyvinyl chloride radical occurs between 80 and 106° C. UEDA[116] has found that the acrylamide radical decays in the same region. UEDA atributeed the decay in this region to the approach of a phase transition region. TAMURA[117] showed that all radicals in irradiated polytetrafluoroethylene decayed at the melting point of the crystalline region of the polymer. In a number of amorphous polymers, such as polyisobutylene, natural rubber and synthetic isoprene rubber, polydimethylsiloxane and polypropylene, radicals disappear in the temperature region of the transition of the polymer from the glassy state to the highly lowered viscosity[100b,118].

5.6.2 RESULTS AND DISSCUSION

The ESR spectra of x-irradiated gum arabic at room temperature were measured at different temperatures. The spectra recorded at different temperatures are as shown in **figure (5.24)**. The ESR spectra of x-irradiated gum arabic recorded at various temperatures may be seen in **figure (5.25)**. The spectra in this figure are modified in y direction. A plot of temperature versus normalized relative spin for the total spin, and the spectral group (1) and (2) have been drawn in **figure (5.26)**. From this relation we can note that spectral group (1) decays rapidly between 317 and 327 K. Spectral group (2) shows a gradual decay with temperature that started at room temperature up to 323 K. After this temperature spectral group (2) decays rapidly. The relative spin density for all curves remain constant up to 331 K. Beyond this temperature the signal was unmeasurable. The decay of the total spin is similar to the decay of the radicals in spectral group (2). After allowing the sample to cool down to room temperature the ESR spectra

were recorded and it was found that the signal intensity remained at the same level observed at 331 K. On raising the temperature again to 373 K the signal was destryoed completely (see table 5.6).

5.6.3 THE EFFECT OF THE DECAY OF THE RADICALS WITH THE ELEVATION OF TEMPERATURE, ON THE LINE-WIDTH OF THE SPECTRAL GROUP (1) AND (2).

The line-widths of the spectral group (1) and (2) as a function of temperature has drown in **figure (5.27).** The line-width of spectral group (1) kept unchanged at 10 gauss after temperature of 321 K, beyong this temperature the line-width changed rapidly to 8 gauss. The line width of spectral group (2) is decreased gradually with temperature. A plot between relative spin density and the line-width of spectral group (1) and (2) may be seen in **figures (5.28), (5.29)** respectively.

5.6.4 THE EFFECT OF THE DECAY OF THE RADICALS WITH THE ELEVATION OF TEMPERATURE ON THE g-VALUE OF THE SPECTRAL GROUP (I) AND (2).

g-values of spectral group (1) and (2) as a function of temperature were drawn in **figure (5.30).** The g-value of spectral group (1) was still unchanged until 324 K beyond that temperature the g-value dropped suddenly. The g-value of spectral group (2) decreased gradually with the variation of temperature.

5.7 THE EFFECT OF MERCURY LIGHT ON X-IRRADIATED GUM ARABIC ESR SPECTRA.

Powder of x-irradiated gum arabic was exposed to the light of a (150-watt) mercury lamp, for different periods of time (doses). The ESR spectra were measured as a function of the light dose, which varied between 0 and 355 minutes of exposing . The line shape of the ESR spectra of the x-irradiated gum arabic was studied before and after exposure to mercury light.

Figure (5.31) shows the different ESR spectra of x-irradiated gum arabic recorded after different UV exposure time. **Figure (5.32)** shows three ESR spectra recorded for different UV exposure times. These spectra are modified in the y direction to assist in comparison of the signals. After 85 minutes exposure time, positions (5) and (6) in **figure (5.18)** overlapped and became very weak; positions (9) and (10) also overlapped. If we follow the spectra to the end of the exposure processes (355 minutes), we note that the positions (5) and (6) vanished completely. Positions (9) and (10) still appear but in one position, these peaks were widened.

To study the effect of the mercury light on radical components of the spectrum of gum arabic, a relation between the amplitudes of spectral group (1) which covers the positions (4) and (7) and spectral group (2) which covers the positions (3) and (9) as a function of exposure time has been drawn in **figure (5.33)**. The amplitude of the spectral group (1) is increased as the UV exposure time is increased, whereas the amplitude of the spectral group (2) is decreased as the exposure time is increased.

A plot of relative spin density as a function of exposure time has been drawn in **figure (5.34)**. This plot shows that the relative spin density of the spectral group (1) is increased as the UV exposure is increased, whereas the relative spin

density of the spectral group (2) is decreased as the UV exposure time is increased. A relation between relative spin density and the decay time at room temperature of the spectral group (1) and (2) was drawn in **figure (5.35). Figure (5.36)** and **figure (5.37)** show a relation between the relative spin density as a function of decay time and UV exposure time of spectral groups (1) and (2) respectively.

A relationship between exposure time and (A1/A2)% (where A is the amplitude), also, a relation between exposing time and (I1/I2)% (where I is the relative spin density), in **figure (5.38)** show that the amplitude and the intensity of the spectral group (1) has increased linearly, with respect to the amplitude and intensity of the spectral group (2).

The line width of the ESR spectra of spectral group (1) and (2) has been studied, as a function of the exposure to mercury light. **Figure (5.39)** shows the relation between the exposure time measured in minutes and the line width. The relation shows a steady line width for the two spectral group as the UV exposure time is increased (see table 5.7).

From the above, we could conclude that the exposure of the x-irradiated gum arabic to the mercury light could be a useful subsidary technique for distinguishing between the different radicals contributing to the ESR spectra of irradiated gum arabic since the effect of light caused more damage for ESR signals of spectral group (1) than spectral group (2).

5.8 GENERATION OF FREE RADICALS IN GUM ARABIC BY MERCURY LAMP AND ULTRAVIOLET SOURCE.

The first law of photochemistry states that. for light to be effective in promoting a photochemical reaction, it must be absorbed. The low of GROTTHUSS and DRAPER[119] states that only that part of radiation which is absorbed by the reacting medium can produce a physical or chemical effect. Thus the reactions based on the absorption of radiation by the organic molecule are of prime importance in photochemistry of the molecule. When the molecule absorb energy, the energy of the molecule is raised by a quantity equal to the absorbed photon energy. By this interaction between the radiation and the molecule, the molecule will be in the excited state and electrons from bonding and nonbonding molecular orbital changed to antibonding orbital, and free radical may formed. Bond dissocation energy of some bonds in carbohydrates are between 4.42 eV which corresponds to O-H bond and 3.59 eV which coresponds to C-C bonds. This amount of energy cover the wave length between 2800 to 3446 A°.[112]

5.8.1 RESULTS AND DISCUSSION.

Gum arabic powder samples have been irradiated at room temperature by a 5W ultraviolet source. The wave lengths emitted from this source are between 3000 and 3800 A°. The ESR measrements carried out at room temperature gave a singlet signal of 13 gauss line-width and 2.0046 g-value. **Figure (5.40)** shows an ESR spectrum of a gum arabic sample irradiated by UV irradiation for 24 hours. **Figure (5.41)** shows an ESR spectrum of gum arabic powder irradiated at room

temperature by mercury light of wave length above 3000 A°. The irradiation time was 4 hours. The ESR spectrum shows a singlet signal with a line-width of 9 gauss and g-value equal to 2.0046.

5.9.0 GENERATION OF FREE RADICALS IN GUM ARABIC BY HEAT TREATMENT

5.9.1 INTRODUCTION

It is known that when heat is applied to an organic material, decomposition of the material occurs and part of the material is converted to char, which is associated with the presence of a free radical. INGRAM and TAPLEY[120] has studied the formation of the radicals in a series of carbonized coals. BENNETT[121] has studied also the radical formation in charred carbohydrates. AUSTEN et al.[122] studied the formation of the free radicals in charred sucrose. These authors have found that the concentration of the free radical in the above materials is increased with the increase of the charring temperature up to a temperature between 793 - 823 K beyond which the free radicals decrease rapidly. They have also found that the free radical concentration increases with the increase of the carbon content. HOLA[123] has studied the ESR spectra of charred compounds of many mono - oligo - and polysaccharides. He found that the concentration of the free radicals increased with the temperature up to a temperature at which the free radical concentration dropped rapidly. The temperature at which the concentration of the free radical reached a maximum is between 773 and 793 K. All the investigations which studied the free radical formation in carbonized organic materials indicated the presence of a singlet signal with g-value near that of the free electron. This value is fixed with the variation of the free radical concentration. BENNETT[121] and HOLA[123] reported a 2.003 g-value for the charred carbohydrates. The line-width for charred carbohydrates as reported by BENNETT[122] is 8 ± 2 gauss. HOLA[123] reported a line width for mono-oligo and polysaccharides between 4 and 7.2 gauss. The line width reported by HINO-JOSA[124] for charred cellulose is between 6 and 9 gauss and depends inversely on the temperature of charring. The formation and the stablization of the free

radicals formed by heat at low temperature has been reported by many authors. INGRAM and TAPLEY[120], BENNETT et al.[121]. COLLINS et al.[125]. reported that the formation of the free radical is associated with the broken bond in the condensed carbon ring. HIRSCH[126] has shown by x-ray measurements that it is in the region where the radical concentration is growing rapidly that the carbon atoms begin to cluster in a condensed ring system. AUSTEN et al.[122] suggested that the essential mechanism in trapping and stabilization of the unpaired electrons is the existence of ring clusters containing more than a certain number of carbon atoms where the ring clusters will possess a high degree of resonance energy available for the stabilization of the electrons. Also he assumed that the radicals formed by breakage of bonds round the edge of the carbon clusters or possibly the radicals originated in the formation of defects in the ring packing.

5.9.2 PREPERATION OF THE SAMPLE AND ESR MEASURMENTS

Dry gum arabic powder in ESR silica tubes was sealed under vacuum. All the samples, measured at different temperatures, were the same in weight and volume. The microwave power which was used was 2 mW and the modulation amplitude was 2 gauss. All the samples were heated in the ESR cavity during the ESR measurements.

5.9.3 RESULTS AND DISCUSSION.

The generation of free radicals by heat in gum arabic has been carried out at different temperatures. **Figure (5.42)** shows various ESR spectra recorded at various temperatures and various times of heating. All the spectra show a singlet signal with g-value of 2.0032 close to that mentioned by Bennett[121] and Hola[123]. The relative spin density as a function of heating time at different temperatures is shown in **figure (5.43).** This shows low relative spin density at temperatures 373,

423, 473 K and a rapid increase of relative spin density at the temperatures 483, 493, 503 K. These temperatures are near the melting point of gum arabic. The free radicals which are generated at low temperatures remain fixed and steady when the temperature is returned to room temperature. At higher temperatures the materials melt for a certain time on heating.

The line width of the signal was measured for various heating times and various temperatures. A relation between heating time at a given temperature and the line width of the singlet signal generated by heat may be shown in **Figure (5.44)**. This figure shows the inverse relation proportion between the line-width and the heating time at temperatures 483, 493, 503 K, At low temperature 373, 423, 473 K it shows nearly constant line-widths. Also these curves shows that the line-width decreased as the temperature increased. The behaviour of the line-width with temperature in this case resembles the result obtained by HINOJOSA[124] who studied the effect of temperature on the line width of a signal generated in heated cellulose.

5.10.1 OPTICAL ABSORPTION OF GUM ARABIC

5.10.2 INTRODUCTION.

When an organic molecule is irradiated with electromagnetic waves, the radiations may be absorbed by the compound; depending on the energy of the incident photon and the energy separation between the ground and the excited state of the molecule. When organic molecules absorb energy in the ultraviolet and visible regions, electron in (σ),(π) or nonbonding (n) orbitals undergo promotion from the ground state to higher state, antibonding levels. The antibonding orbital related to the (σ) *and* (π) bonds are called (σ^*) *and* (π^*) respectively. There are no antibonding orbitals associated with the nonbonding electron. In general $\sigma \rightarrow \sigma^*$ transitions need high energy and shows absorption in the far ultraviolet between 100 and 200 nm. $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition absorb in the region of 200 to 700 nm wave length.

Free sugars are not normally found in the aldehydo or keto forms to any appreciable extent, but exist mainly in cyclic hemiacetal forms, which do not have (π) electrons. Free sugars are not expected to show absorption beyond 190 nm. The common chromophores encountered in carbohydrate derivatives are the C=C, C=N, N=N, C=O, C=S, S=O[127]. Reducing sugars are difficult to purify and often contain contaminants and degradation products possessing strong absorbancies. The only possible chromophore in polysaccharides like gum arabic is the hydroxy group and carboxyl group of gum arabic, or impurities of carboxyl and carbonyl group. Hydroxyl and carboxyl groups would have to be ruled out because they absorb near 200 nm or shorter wave-length[128]. The carbonyl group absorbs near 280 nm[128] so it could be responsible for the absorption in gum arabic. HON[111] mentioned that aldehyds and ketones show relatively weak absorption band with a maximum between 270 and 290 nm. BEELIK and

HAMILTON[128] mentioned that carbonyl groups which are present at C(1) in each reducing D-glucose unit, or carbonyl groups which are present in D-glucose unit as a result of oxidative damage, may initiate absorption near 280 nm. Also he postulated that the glycosidic (acetal) linkages groups at C(1) of nonreducing D-glucose units act as weak chromophores by absorbing near 265 nm. BOS[130] in his study of glucose, oligomers and polymers of glucose suggested that the acetal linkages do not contribute significantly to the absorption peak at 265 nm. He proposed that ketonic carbonyl groups are a more likely cause of this absorption. PHILLIPS[131] showed that irradiated solutions of carbohydrates have similar, characteristic ultraviolet absorption spectra. A broad absorption occurs in the region of 240 to 300 nm. The maxima, which may vary for individual carbohydrates, fall in the region of 260 to 290 nm. LAURENT and WERTHEIM[132] irradiated some polysaccharides such as dextrin, gum arabic, hyaluronic acid and pectin. An absorption maximum appeared at 265 nm. HON[111] has measured ultraviolet absorption of cellulose films before and after irradiation, with and without oxygen. Cellulose films show an ultraviolet absorption at 270 nm. Irradiated cellulose in vacuum shows the increase of the intensity at this region of absorption. After irradiation in oxygen UV absorption shows a change of absorption between 240 and 300 nm and shows an absorption peak at 260 nm. This absorption at 260 nm is attributed to the acetal groups[128] or ketonic carbonyl groups[130].

5.10.3 METHODS.

5.10.3.1 PREPARATION AND IRRADIATION OF GUM ARABIC FILMS.

A highly viscous aqueous gum solution is poured on a plastic sheet to form a spot of about 5 cm diameter. The material is left to dry in air for a few days. After the film was dry it could be easily removed from the plastic sheet. The film was

put between two stainless steel sheets and transferred on a covered hot water bath and left for a few minutes and at the same time gradual pressure was applied carefully to obtain a flat film. After that the system was transferred from the bath and left to cool. The ultraviolet spectrometer sample holder has dimensions of 50x13 mm with a window of 15x7 mm. A holder was made of thick card paper. The gum film was fixed on the window of the UV absorption holder with gum arabic glue. A knife immersed in hot water was used to cut the edges of the film since the films are brittle and very delicate.

The gum arabic films were irradiated with gamma rays emited from a Co^{60} source of 5 Ci. The samples were kept in front of the source, normal to the incident beam, for a specified time. The distance between the sample and the source was 7 cm. The irradiations were carried out at room temperature in air.

5.10.3.2 ULTRAVIOLET ABSORPTION MEASUREMENTS.

The ultraviolet spectrphotometer used for measurements on the films was a PERKIN-ELMER, (model lambda 9) UV/VIS/NIR spectrophotometer. The spectrophotometer was used to measure absorbence and in the wavelength range between 200 to 700 nm. The reference was a similar holder without a sample which had been exposed to gamma rays simultaneously with the sample.

5.10.4 RESULTS AND DISCUSSION.

Ultraviolet absorptions of gum arabic films were measured before and after gamma irradiation at room temperature. These spectra may be seen in **figure (5.45)** Both spectra show an absorption that starts below 200 nm to above 400 nm. There is an absorption peak at 276 nm. This peak shows an increase of intensity after irradiation. The centres which cause the absorption in the

unirradiated gum films could have grown in number after irradiation. It is known that the groups which may absorb near the region of 276 nm are the carbonyl groups[128,129] or the glycosidic (acetal) groups.

CHAPTER SIX

6.1 IRRADIATION OF THE COMPONENTS OF GUM ARABIC

6.1.1 RESULTS AND DISCUSSION

6.1.2 D-GALACTOSE

Figure (6.1) shows the ESR spectra of irradiated D-galactose, recorded at various microwave powers. During the recording of the spectra we got the best resolution of the spectra at low microwave power equal to 0.5 mW which may be seen in **figure (6.2)**. The higher intensity and better resolution signal shown in the spectrum show a triplet signal of intensity ratio (1:2:1). The hyperfine splitting of this signal is 21 gauss and located at a g-value equal to 2.0032.

The spectrum obtained at 10 mW microwave power as shown in **figure (6.3)** shows the higher intensity spectrum is a doublet signal. This signal shows a hyperfine splitting of 17 gauss and g-value equal to 2.0037. This spectrum obtained at 10 mW resembles the spectrum obtained by CAVATORTA et al.[79] where he analyzed the spectrum by two signals, doublet and triplet. The doublet and triplet signals have been found in many monosaccharides. It is found in glucose as obtained by BAUGH et al.[55], where the doublet has a hyperfine splitting of 20.5 gauss and g-value equal to 2.003, where the triplet has a hyperfine splitting of 29.5 gauss and g-value equal to 2.0025. NIKITIN[61] has reported that the monosaccharides which he has studied such as glucose, galactose, ribose, mannose, and rhamnose, have a doublet signal with hyperfine splitting equal to 15 gauss.

6.1.3 D-GLUCURONIC ACID

Figure (6.4) shows the spectra of irradiated D-glucuronic acid recorded at different microwave powers. These spectra show more than one radical exists in the spectrum. The best resolved and highest intensity signal can be seen in **figure (6.5)** where the spectrum recorded at 0.5 mW microwave power consists of a single line with 9 gauss line-width and g-value equal to 2.0042.

6.1.4 L-ARABINOSE

Figure (6.6) shows the ESR spectra of irradiated L-arabinose measured at different microwave power. During the variation of the microwave power the best resolved spectrum is measured at 0.5 mW microwave power as can be seen in **figure (6.7)** and is a complex spectrum. On comparison of our spectra with those studied previously we note that the closest observation to ours is that which is given by NIKITIN et al.[61] who measured ESR at room temperature. NIKITIN[61] has proposed two radicals in arabinose at room temperature, One of them is a doublet signal with 15 gauss hyperfine splitting and triplet-quadruplet has a hyperfine splitting of 26 and 13 gauss for the first and the second splitting respectively. We obtained the doublet signal with hyperfine splitting of 14.5 gauss and g-value is 2.0057. From the triplet-quadruplet signal we could distinguish the triplet splitting of 33. gauss.

6.1.5 L-RHAMNOSE

The ESR spectra of irradiated L-rhamnose at different microwave power are shown in **figure (6.8)**. The measurements showed a best resolved spectrum at microwave power 0.5 mW as may be shown in **figure (6.9)**. On comparison of our spectra with that recorded for a single crystal of irradiated rhamnose in SAMSKOG[59] and PANASYUK[60] we could distinguish three different radicals.

Two of them are well resolved and the third one is weakly resolved. Radical (1) doublet with hyperfine splitting of 11 gauss may be compared with 10.5 gauss measured by SAMSKOG[59], and 11 gauss. as is recorded by PANASYUK[60]. Radical (2) doublet with hyperfine splitting of 33.5 gauss may be compared with 35 gauss as it is recorded by SAMSKOG[59], and 38 gauss as it measured by PANASYUK[60]. The g-value for the radicals (1) and (2) equals 2.0037. The third radical which consists of doublet-quadruplet as detected by PANASYUK[60] is not measurable in our case.

6.2 SIMULATION OF THE ESR SPECTRUM OF GUM ARABIC BY MIXING THE CONSTITUENT SUGARS :

In this section we intend to simulate the ESR spectrum of natural gum by mixing of the material constituents of the natural gum.

6.2.1 CONSTRUCTION OF THE SYNTHETIC GUM ARABIC AND ESR MEASUREMENTS

A 0.35 gram powder sample of each component of gum arabic (arabinose, D-galactose, rhamnose, and D-glucuronic acid) was irradiated individually by x-ray from a Co-tube source for 10 minutes (using a 20 mA filament current and 30 kV excitation voltage). The same proportion of each material as reported in natural gum was added successively to simulate the natural gum. ESR measurements have been carried out on arabinose sugar first. After the addition of galactose to arabinose the ESR spectrum was recorded again, after that rhamnose was added to the mixture and again the ESR spectrum was recorded. In the final stage D-glucuronic acid was added to the latter mixture and ESR spectra recorded. The ESR spectra of galactose, rhamnose, and D-glucuronic acid individually have been found by subtraction of each of the two spectra of the

mixtures using computer facilities. Under the same conditions, natural gum arabic was irradiated and the ESR spectrum was recorded in order to compare with the spectrum of the mixture.

6.2.2 RESULT AND DISCUSSION

Figures (6.10), (6.11), (6.12), and **(6.13)** represent the ESR spectra of the individual components and the spectra resulting from successive mixing of the components of gum arabic. Positions 3 and 9 in the ESR spectrum of the natural gum arabic in **figure (6.13)b** show the resonance lines ascribed to spectral group (2) as has been identified in chapter five. In comparison between the two spectra (natural and synthetic) in this figure we can see that the two positions 3 and 9 are observable in the synthetic gum spectrum within the limits of errors. These two positions in the synthetic gum spectrum have originated from the doublet signal of the arabinose spectrum. The overall line-width of this signal as measured in **figure (6.13)a** is 24 gauss where it is 22.5 in the natural material and has the same g-value of spectral group (2). It is obvious that the height of position (3) in the synthetic gum spectrum is relatively lower than that in the natural one. That may be due to the absence of the singlet signal from the synthetic spectrum. Since there are no glycosidic linkages between the mixed materials in the synthetic spectrum there cannot be any free radicals resulting from the cleavage of the glycosidic linkages. Additional signal in the natural gum spectrum may be due to the rupture by irradiation of these bonds.

Positions (4) and (7) in the ESR spectra of the natural gum **figure (6.13)b** represents spectral group (1) as identified in chapter five. In comparing these two positions (4 and 7) in natural and synthetic spectra we find that the line-width is the same in both cases and is equal to 12 gauss, but the g-value of the synthetic

spectrum line is shifted to lower g-value by 0.0018. It is obvious that the addition of the irradiated D-glucuronic acid to the arabinose, galactose, and rhamnose mixture resulted in the lines at the positions 4 and 7 as can be seen in **figure (6.12).** So the signal which is represented by these positions could be ascribed to the singlet of D-glucuronic acid.

Spectral lines at positions 5 and 6 in the ESR spectrum of natural gum are very weak in the synthetic gum spectrum. By following these two positions from the beginning of the addition of the material, we may infer that the line at position 5 resulted from irradiation of arabinose and it belongs to the first line of the doublet signal of arabinose. Line position 6 belongs to the second line of the same radical. Thus positions 3, 5, 6, 9, belong to the same signal which is probably the doublet which we identified as spectral group (2).

CHAPTER SEVEN.

GENERAL DISCUSSION

7.1 INTERPRETATION OF THE ESR SPECTRA OF X-IRRADIATED GUM ARABIC.

Through the study of the rate of growth of the ESR signals versus irradiation dose and by following the decay of the ESR signals at room temperature and decay via elevation of temperature we infer the presence of two distinct centres. We have labeled these as spectral group (1) and spectral group (2). The study of the ESR signals of UV exposed x-irradiated gum arabic and the spectra of UV exposed natural gum arabic indicates that UV irradiation stimulated the growth of the signal which is labeled as spectral group (1).

Gum arabic as reported by many authors consists mainly of four major components: D-galactose, L-arabinose, L-rhamnose and D-glucuronic acid. These four major components during this study have been irradiated separately. The free radicals responsible for the ESR signals in these components have been carefully studied by us and by others[47,48,50,51,58,59,60]. Our finding are discussed in the following.

1. D-galactose: The ESR spectra of x-irradiated D-galactose powder show two signals, a triplet signal of hyperfine splitting of 21 gauss and g-value of 2.0032. The second signal is a doublet of 17 gauss hyperfine splitting and 2.0037 g-value. These two signals were observed by Covatorta et al.[79] in irradiated D-galactose. The doublet signal is attributed to the presence of a free electron at C(1) as mentioned by Baugh et al.[55] The doublet and triplet signals were found in glucose sugar by BAUGH et al.[55]. The doublet signal has a hyperfine splitting of

20.5 gauss and g-value equal to 2.003. The triplet has a hyperfine splitting of 29.5 gauss and g-value equal to 2.0025 which is attributed to the presence of the free electron on C(5) by scession of the hydrogen atom and the equal interaction of the free electron with two protons on C(6). NIKITIN[61] has reported that the monosaccharides. which he has studied (such as glucose, galactose, ribose, mannose, and rhamnose) has a doublet signal with hyperfine splitting equal to 15 gauss. He attributed a doublet signal to the presence of the free electron on C(1).

2. L-arabinose: The ESR spectra of x-irradiated L-arabinose show a doublet signal of 14.5 gauss hyperfine splitting and 2.0057 g-value. NIKITIN[61] has found the doublet signal and a triplet-quadruplet signal in irradiated L-arabinose at room temperature. The doublet signal has a hyperfine splitting of 15 gauss which he attributed to the presence of the free electron on C(1) which interacts with beta proton of C(2). The triplet of quadruplet has a hyperfine splitting of 26, and 13 gauss for the first and second splitting respectivly. In our case the triplet of quadruplet signal is unmeasurable.

3. L-rhamnose: The ESR spectra obtained by us on x-irradiated L-rhamnose powder show two well resolved signals labeled as radical (1) and radical (2). Radical (1) is a doublet of 11 gauss hyperfine splitting which may be compared with the 10.5 gauss splitting measured by SAMSKOG[59] and the 11 gauss recorded by PANASYUK[60] for the same sugar. This signal is attributed to the presence of the free electron at C(1), C(2), C(3), or C(4) and the interactin of the free electron with the beta proton. Radical (2) is also a doublet with hyperfine splitting of 33.5 gauss which may be compared with the 35 gauss obtained by SAMSKOG[59], and 38 gauss obtained by PANSYUK[60]. The g-value of the two radicals (1) and (2) is the same and equal to 2.0037.

4. D-glucuronic acid: On irradiation of D-glucuronic acid, ESR spectra showing one singlet signal of 9 gauss line-width and 2.0042 g-value are obtained. The singlet signal of the D-galacturonic acid has been interpreted by WILLEMS[134] as due to the cleavage of the C(6)-OH bond or the C(5)-H bond where no hyperfine interaction is to be expected.

The comparison of the ESR spectra of irradiated natural and synthetic gum, made of proportional components of gum arabic shows that the spectral peaks in the synthetic spectrum include lines that resemble the peaks of spectral group (2) of the natural gum spectrum. The lines attributed to spectral group (2) in natural gum spectra are similar to those of arabinose, particularly the doublet signal in arabinose which is attributed to the presence of the free electron at C(1)[48, 51]. The spectral peaks of spectral group (1) in natural gum resembles the peaks originating from glucuronic acid, particularly the singlet signal, observable in the synthetic spectrum.

The work of SMITH[43], ANDERSON et al.[46] and STEEL and ANDERSON[46] suggests that the constituent gum arabic molecules are connected together with 1-3, 1-4, and 1-6 glycosidic linkages. These linkages are distributed between the gum components as in structures frome 7.1 to 7.8.

X-ray irradiation emitted from a cobalt target has a wave length between 1.7928 to 214 A° which corresponds to 6915.3 and 58 eV respectively. This amount of energy is sufficent to break any bond in carbohydrates (see table 7.1).

From the above we conclude that spectral group (1) is a singlet signal. spectral group (2) consists of a singlet and a doublet. So, there are two singlet signals

one of them is spectral group (1) and the other is superimposed with a doublet signal to form spectral group (2). The interaction of ionizing radiation particularly x-radiation with gum arabic molecules may break any bond and lead to many possibilities for radical formation. The possible scessions of the glycosidic linkages in the gum arabic molecule which may give rise to a singlet, doublet, and triplet signal may be summarized as in reactions from 7.1 to 7.8.

From reaction (7.1) to reaction (7.8), the presence of the free electron on O. lead to the formation of a single line where no hyperfine interaction is to be expected with the neighboring atoms. Also the scession of the C(5)--H bond or the scession of the C(6)--OH in D-glucuronic acid molecule may give rise to a singlet signal where no hyperfine interaction takes place with the neighboring atoms. So, the free radical giving rise to the singlet signal may be attributed in the gum arabic molecule to a C(1)-O. of galactose, C(3)-O. of galactose as in reaction (7.1), C(1)-O. of galactose, C(6)-O. of galactose as in reaction (7.2), C(1)-O. of glucuronic acid, C(6)-O. of galactose as in reaction (7.3), C(1)-O. of rhamnose, C(4)-O. of glucuronic acid as in reaction (7.4), C(1)-O. of arabinose, C(3)-O. of galactose as in reaction (7.5), C(1)-O. of galactose , C(3)-O. of arabinose as in reaction (7.6), C(1)-O. of arabinose, C(6)-O. of galactose as in reaction (7.7) and C(1)-O., C(3)-O. of arabinose as in reaction 7.8.

Irradiation has been applied to sugars which have the glycosidic linkages such as starches, cellulose, and other oligomers. The ESR studies have been reported by many authors. ADAMIC and BLINK[63] found a singlet signal in gamma irradiated starch after a long annealing at room temperature. He assumed this signal to be a doublet with unknown hyperfine splitting. RAFFI and AGNEL[64]. RAFFI et al.[133] gamma irradiated starches and many glucose oligomers, and they found two singlet signals. One of them is obtained immediately after irradiation at room

temperature and has a line-width from 24.9 to 26.1 gauss and a g-value between 2.0044 to 2.0050. The other radical is obtained after annealing the material for a few months at room temperature and has a line-width between 8.4 and 9.3 gauss and g-value between 2.0048 and 2.0061. RAFFI and AGNEL[64] attributed the latter radical to the transformation of the C(1). radical to pyroxy radical C(1)-O-O. OGIWARA[135] has found a singlet signal when he irradiated cellulose material at 77 K and measured the ESR spectra at 77 K and room temperature. This signal has a line-width of 25 to 28 gauss and g-value of 2.003. BAUGH et al.[68] found a singlet signal after gamma irradiation and ESR measurement of the spectra of cellulose at room temperature. They attributed this signal to the scession of the glycosidic bonds between the monomers and the presence of the free electron on O atom of C(1)-O. or C(4)-O. HON[136] found a singlet signal in the UV irradiated cellulose when the ESR spectra were recorded at room temperature. This signal has a line-width of 16 gauss and is attributed to the presence of the free electron on C(1)-O. or C(4)-O. HON[137] has found a singlet signal in UV irradiated cellulose at 45 C. This signal has a line-width of 16 gauss and g-value of 2.003. DILLI[138] has gamma irradiated cellulose and measured the ESR spectra at room temperature and found a singlet signal. He attributed this signal to the broadening dipole-dipole interaction between the free electron and proton. HON[111, 113, 139] attributed the singlet signal with 16 gauss line-width to the presence of the free electron at C(1)-O. or C(4)-O. BALAZS et al.[60] and NOZAWA et al.[82] irradiated D-glucuronic acid at room temperature. They detected a singlet signal and attributed this signal to the presence of the free electron at C(5) by scession of C(5)-H bond or as suggested by WILLIAMS[134] to the presence of the free electron at C(6) by the scession of the OH group from COOH group.

The doublet and triplet signals which may be created by the scession of glycosidic linkages can be followed by the study of reactions (7.1) to (7.8). In reaction (7.1) the presence of the free electron at C(1) of galactose or C(3) of galactose leads to the formation of the doublet signal by interaction of the free electron with the proton of the H atom bonded to the same carbon atom. In reactions (7.2) and (7.3) the presence of the free electron on C(6) galactose leads to the formation of the triplet signal by interaction of the free electron with two protons located at the same carbon atom, whereas the presence of the free electron on C(1) of galactose in the reactions (7.2) and and C(1) of glucuronic acid in the reaction (7.3) lead to the formation of a doublet signal. The scession of the glycosidic linkages in reaction (7.4) leads to the formation of a doublet signal due to the presence of the free electron at C(1) of rhamnose or C(4) of glucuronic acid. In reaction (7.5) the scession of the glycosidic linkages leads to the formation of a free electron on C(1) of arabinose or C(3) of galactose which gives a doublet signal. Also in reaction (7.6) the scession of the glycosidic linkage leads to a doublet signal due to the presence of the free electron at C(1) of galactose or C(3) of arabinose. In reaction 7.7 the scession of the glycosidic linkages leads to the formation of the triplet signal due to the presence of the free electron at C(6) of galactose and doublet signal due to the presence of the free electron at C(1) of arabinose. In reaction 7.8 the C(3) and C(1) radical of arabinose lead to the formation of the doublet signal.

As a comparison between our results and the results on irradiated starches which were carried out by RAFFI[133] we note that spectral group (1) in our results has a line width of 13.5 to 9 gauss during the decay processes while for the same spectral group, as reported by RAFFI, the line width is between 9.3 to 8.4

for different starches. This spectral group is assumed by RAFFI[64] to be a radical located at C-O-O. due to the interaction between the O_2 and the C. radical as follows:

$$C. \xrightarrow{O_2} C\text{-}O\text{-}O. \text{ (peroxy radical)}$$

Our results show that the line-width of spectral group (2) has decreased from 23 to 16 gauss during the decay processes. As recorded by RAFFI[135] this spectral group has line-widths of 26.1 to 24.9 gauss and g-values between 2.0050 and 2.0044 for irradiated different starches. HENDERSON[99], and RAFFI[64] interpreted this spectral group as a doublet signal that arises from the location of the free electron at C(1) of the starch molecule due to scession of the glycosidic linkages. The comparison between the doublet of gum arabic and the doublet spectral group of arabinose during the simulation of ESR spectra of gum arabic by gradual addition indicate that this spectral group is similar to the doublet of arabinose. The decay of the ESR spectra of gum arabic at room temperature, or with the variation of temperature indecates that spectral group (2) is converted to a pure singlet. The relative intensity of spectral group (2) in the simulated ESR spectrum compared with the relative imtensity of the ESR spectra of natural gum show lower intensity of the synthetic spectra of spectral group (2) than that of the natural spectra. This may be attributed to the location of the free electron on an oxygen atom due to scessin of a glycosidic bonds. The observations that the synthetic spectra have no signals due to the glycosidic scession is due to the fact that glycosidic linkages are not found in the synthetic spectrum. This analysis supports the hypothesis that spectral group (2) is composed of two superimposed signals of a doublet and a singlet. This singlet may be attributed to the presence of a free electron at C-O. due to scsession of glycosidic linkages.

7.2 IRRADIATION OF GUM ARABIC WITH ULTRA VIOLET AND MERCURY LIGHT.

The exposure of natural gum to ultra violet radiation in the range of 3000 to 3800 A° lead to form an ESR singlet signal of 13 gauss line-width and 2.0046 g-value . The characteristics of this singlet and the singlet identified in x-irradiated natural gum arabic as spectral group (1) indicate that these two singlets belong to the same centre. The exposure of x-irradiated gum arabic to mercury light of wave length above 3000 A° showed the increase of the amplitude of spectral group (1) and slight decrease of the amplitude of the spectral group (2), with relevant increase of the spin density of spectral group (1) and decrease of the spin density of spectral group (2). This indicates that mercury light affects favourably the centre giving rise to spectral group (1) which is already created by x-irradiation. The slight decay of spectral group (2) may be attributed to a thermal process. The exposure of gum arabic to mercury light gave a signal of 9 gauss line-width and 2.0046 g-value. The exposure of natural gum to an ultra violet source (of wave length between 3000 and 3800 A°) and expos of x-irradiated gum arabic to mercury light (of wave length above 3000 A°) indicates that the radiations affected the same centre. The UV with wavelength less than 3446 A° as well as x-rays carry sufficent energy to dissociate bonds in gum arabic and create free radicals. Visible radiations in the mercury source do not carry enough energy that may break any bond in gum arabic. The maximum energy in the UV light source is about 4.14 eV which correspond to 3000 A°. This amount of energy is sufficent to break the C-C and the C-O bonds. The C-C bond in gum arabic molecule is present in the pyranose ring of all sugars. HO[N(112)] has mentioned that scession of C-C bonds in the ring of sugars is not stable, due to strong and extensive hydrogen bonding in the sugars which will hold both

radicals in close proximity, leading to rapid recombination . The C-C bond is present in galactose as -C(5)-C(6)H_2OH, in rhamnose as -C(5)-C(6)H_3 and in D-glucuronic acid as -C(5)-C(6)OOH which may give rise to free radicals located at C(5). In all these three sugars a doublet signal due to the interaction of the free electron on C(5) with one proton of C(5) may take place. The C-O bond in gum arabic is present in glycosidic linkages between the different monomers which need 4.03 eV to dissociate . This bond may give a singlet and doublet when it is broken. The highest energy of UV light source used is about 4.14 eV. Our observations show a singlet signal of 13 gauss line-width. The mercury light which is used here has a wave length above 3000 A° which corresponds to 4.14 eV. This ammount of energy can break the bond of the C-C or the C-O bonds. The detection of a singlet signal in the UV irradiated gum, and mercury light irradiated gum, lead us to suggest that the stable free radical in these cases is a singlet signal which may be attributed to the presence of the free electron on C(1)-O. of galactose, C(3)-O. of galactose as in reaction (7.1), C(1)-O. of galactose, C(6)-O. of galactose as in reaction (7.2), C(1)-O. of glucuronic acid , C(6)-O. of galactose as in reaction (7.3), C(1)-O. of rhamnose, C(4)-O. of glucuronic acid as in reaction (7.4), C(1)-O. of arabinose, C(3)-O. of galactose as in reaction (7.5), C(1)-O. of galactose, C(3)-O. of arabinose as in reaction (7.6), C(1)-O. of arabinose and C(6)-O. of galactose as in reaction 7.7 and C(1)-o., C(3)-O. in arabinose as in reaction 7.8. Also it may lead to the scission of C(5)-H or C(6)-OH in D-glucuronic acid as proposed by WILLIAMS[134]. All these possibilities lead to the formation of a singlet signal. As mentioned by HON[136] and RAFFI and AGNEL[64] the doublet signal which is formed in UV irradiated cellulose and gamma irradiated starches are converted to peroxy radical (C-O-O.). In a similar manner the doublet signal which may be formed by ultra violet irradiation is supposed to interact with an oxygen molecule to form a

peroxy radical. According to the above findings it could be assumed that the ESR singlet signal generated by UV, and mercury light irradiated gum arabic can be attributed to the presence of the free electron on the alkoxy radical (C-O.). This has been proposed by HON[111, 113, 136] for irradiated cellulose. Another possiblity is the presence of the free electron on the peroxy radical (C-O-O.). The signal can also be assigned to the presence of the free electron on C(5) of D-glucuronic acid due to the scession of the C(5)-H bond or to the scession of the C(6)-OH bond of D-glucuronic acid, where no hyperfine structure would be expected. We favour the proposal of HON [136] and RAFFi and AGNEL[64] by which they suppose that the free electron is present on peroxy radical, since exposure of x-irradiated gum arabic to UV light enhance the singlet signal labeled as spectral group (1).

7.3 THE EFFECT OF HEAT ON NATURAL GUM AS STUDIED BY ESR.

When gum arabic was heated between temperatures 373 to 503 K for various time the observed ESR spectra showed a singlet signal. This signal has a g-value of 2.0032 close to that observed by BENNETT[121] and HOLA[123] in heated charred carbohydrates. The line-width of this singlet varies between 8 and 5 gauss as shown in figure (5.44) and depends on the temperature and length of heat treatment. The value of this line width is in the range of the line widths reported by BENNET[121], HOLA([123] and HINOJOSA[124] whose results show that the line-width varies from one material to another and depends on the temperature at which the material is charried. As we have observed HINO-JOSA[124] found that the line width of the signal of heated cellulose depends inversely on the temperature of charring. When the temperature is increased or the time of heating is increased at a given temperature the carbonization of the material is increased. INGRAM and TAPLEY[120], BENNETT[121] and AUSTEN et

al.[122] have mentioned that the free radical concentration increased with the increase of carbon content. Here are two parameters that affect the line-width, the free radical concentration and the nature of the material for which the signal is recorded. Our results showed that the spin density increased slowly in the temperatures between 373 to 473 K, whereas at temperatures between 483 to 503 K the spin density increased at a fast rate. This show that above 473 K gum arabic starts to form radicals rapidly. The formation of free radicals by heat has been interpreted by INGRAM and TAPLEY[120], BENNETT et al.[121], and COLLINS et al.[125]) as being associated with the break of the bonds in the condensed carbon rings. HIRSCH[126] has shown via x-ray measrements that in the region of rapid growth of the radical concentration the carbon atoms begin to cluster in the condensed ring system. AUSTEN et al.[122] suggested that the essential mechanism in trapping and stabilization of the unpaired electrons is the existance of ring clusters containing more than a certain number of carbon atoms where the ring clusters will possess a high degree of resonance energy avaliable for the stablization of the electrons.

7.4 THE VARIATION OF THE LINE-WIDTH OF THE SIGNALS WITH THE VARIATION OF IRRADIATION TIME, DECAY TIME, EXPOSURE TO HEAT AND ULTRAVIOLET RADIATION.

On increasing the irradiation time from 2 minutes to 180 minutes the spin density of spectral group (1) increased 44 times. At the same time the line-width also increased from 11.5 to 14 gauss. The spin density of the spectral group (2) also increased to 44 times during this irradiation period and the line-width increased from 22 to 24 gauss. The intensity of spectral group (1) kept at 19.3% of the intensity of the spectral group (2) subsequent to all irradiations. On observing the

intensity of spectral group (1) and (2) during a decay period of 188 hours the intensity of spectral group (1) decreased to 1/6 of its original value and the line-width decreased from 13.5 to 10 gauss. When the intensity decreased to 1/13 of its original value the line-width decreased to 9 gauss. The intensity of the spectral group (2) decreased to 1/9.7 of its original value during the decay time of 188 hours. During this interval the line-width decreased from 23 to 17 gauss, whereas the line-width decreased to 16 gauss when the intensity of spectral group (2) decreased to 1/29 times of its original value. The percentage of the intensity of spectral group (1) to the intensity of the spectral group (2) during the decay processes was 19.4%, 33.2%, and 42% at 0, 188 and 667.5 hours respectively. The exposure of x-irradiated gum arabic to mercury light led to the increase of the intensity of spectral group (1) by 1.1 times during an exposure of 355 minutes. During this interval the line-width stayed fixed at 14 gauss. During the exposure of gum to UV for the same interval spectral group (2) decreased to 0.72 of its original value and the line-width stayed constant at 22 gauss. The relative intensity of spectral group (1) to the intensity of spectral group (2) is 20.6% and 31.5% at 0 and 355 minutes UV exposure times respectively. From the above discussion we can conclude that with the variation of irradiation time the increase of the intensity of the spectral group (1) and (2) led to a corresponding slight increase in the line-width. During the decay processes the decrease of the intensity of spectral group (1) and (2) show also a corresponding decrease of the line-width. The UV exposure of x-irradiated gum arabic did not effect the line-width when the intensity of spectral group (1) with respect to the intensity of the spectral group (2) increased. From the above it is inferred that the increase of the free radical concentration during the variation of dose gives a little change in the line-widths of the signals. On the other hand during the decay of the signals the line-widths clearly decreased, the increase of the intensity of the

spectral group (1) with respect to the intensity of the spectral group (2) during the variation of the UV exposure time did not affect the line-width. MAGE[96] and SAMUEL[97] have proposed a nonrandom distribution of radicals in irradiated ice. They proposed that these radicals are formed in small increments of volume (called spurs) which are isolated one from another. SMITH and JACOBS[98] also have proposed that the radicals which are formed in irradiated polyethylene are formed in isolated spherical spurs. The above behaviour of gum arabic under x- and UV-irradiation may be interpreted in accordance with what has been assumed by these authors and we may assume the free radicals are formed as spurs in gum arabic. These spurs are formed such that they are isolated from each other. The decay of the free radicals occurs within the spurs, so the line-width changes with the variation of the free radical concentration within the spurs.

We have three cases for change of line-widths. **Case 1:** On increasing the irradiation dose the spin density of spectral group (1) and (2) increased and the line-widths of the two spectral groups has increased slightly. **Case 2:** The decay of the two spectral group led to a decrease in the spin density and led to a decrease in the line-widths of the two spectral group . **Case 3:** On exposure of x-irradiated gum arabic to UV, the spin density of spectral group (1) is riased slightly, but the line width remained unchanged. Spectral group (2) shows a slight decrease and the line-width kept unchanged. The theory of spin-spin interaction has been treated by VAN VLECK[140] and by PRYCE and STEVENS[141]. The expresion for the mean square width of the line can be written for the electronic cases as:

$$(\Delta H)^2 = \frac{3}{4} \quad S(S+1) \quad g^2.B^2 \quad \sum\left(\frac{1-3\cos^2\theta}{r^3}\right)^2$$

For powder the only parameter in this expression to consider is the mean distance (r), So when the spin density is increased the mean distanse between the free radicals will decrease and the line-width (ΔH) will increase. So there is according to the above equation the spin density as a function of the line-width. MILLER and ADAMS[142] have studied the effect of spin density on the line-width broadening of the nitroxide radical. They found that with the increase of spin density the lines broadened and became narrower at even higher spin concentration. They explain this broadening to electron spin exchange, where at higher concentration the electron spin exchange is so fast that the time average of the hyperfine field is close to zero. In our first case when the dose has increased the line-width has also increased. This increase can be attributed to the increase of the spin density when no other parameters were involved. In the second case when the ESR signals intensity decreased at room temperature and the line-width decreased, the decrease of the line-width may be attributed to the decrease of the spin density, since there is no any other parameter change excapt spin density. In the third case when x-irradiated gum arabic was exposed to UV light the line-width kept without any change since there was no appreciable change in the spin density. In the case of the effect of temperature on the spectral group (1) and (2) the line-width of spectral group (1) is decreased rapidly at the temperature at which the spin density shows a rapid decrease. The line-width of the spectral group (2) is decreased gradually with the temperature as the spin density is decreased. The relation between relative spin density and the line-width of the spectral group (1) and (2) shows non linear relation. This means that the line-width may be affected by other parameters. These parameters are probably related to the rise of the temperature and the change of the viscosity of the material. The nature of gum arabic is a glassy material[1]. OSBORN and LEE[6] has studied the viscosity of gum arabic solutions as a

function of temperature. They found that the viscosity is inversely proportional to temperature. They observe the loss of the free radical in the region at which the glasses material changed to lower viscosity[108, 118]. From these facts one can conclude that the rise of the temperature lowers the viscosity of gum arabic and consequently affects the measruable intensity and line-width of gum arabic ESR spectra during thermal decay. In the temperature range between 317 to 327 K a rapid decrease of intensity and line width has been observed and could be accounted for by a change in viscosity which takes place rapidly at these temperature.

In the case of generation of free radicals in gum arabic by heat. The results show that at low temperatures 373, 423K the line-width stay unchanged at values of 7.7 and 7.5 respectively. At 473 the line width is about 8 gauss after 60 minutes of heating time, beyond that time the line-width starts to decrease. At these three temperaturs 373, 423, 473K the spin density shows little response to heat. At the same time the decrease of the spin density does not make the line width change by change of the viscosity of the material. At temperaturs 483, 493, 503K the line-width shows an inverse relation with heating time and the line-width decreased as the temperature increased. In the case of generation of free radicals by heat, the line-width is affected by many parameters. Three parameters changed during the measurements, the spin density, temperature, and the phase transition of the material. As mentioned above the spin-spin dipole interaction for the electron and the exchange due to higher spin density may affect the line-width and broadening may occur. In the case of temperature increase, the spin lattice relaxation time is expected to decrease as the expression of KRONIG[143] and the line-width may be broadened also:

$$\Delta H = \frac{1}{T_1} + \frac{1}{T_2}$$

From this expression and the effect of temperature and spin-spin interaction on relaxation time T1 and T2 respectively, the absorption lines expected to broaden due to higher temperature and higher spin density. The decrease of the line width with the increase of the temperature or the increase of the heating time may be then attributed to motional narrowing. Motional narrowing versus the viscosity of the material has been studied by GRIFFITH et al.[144], KNOWLES[145] and also SIMATOS et al.[146] have studied the effect of the viscosity on the ESR spectra of nitroxide radical, and they found that the powder form gave broad three lines which become narrower as the viscosity is decreased. In solids g-factors and hyperfine couplings can be orientation dependent. The powder spectrum is obtained when the spins are randomly oriented and anisotropic in nature. The principal axis of the radical assumes all possible angles relative to the magnetic field. The ESR spectrum is expected to be a superposition of all the spectra corresponding to all possible orientations. When a powder or a glassy material has changed to a lower viscosity, the motional rate or tumbling rate will increase. The rate of tumbling is measred by the correlation time (t), which can be thought of as being the average time for which the molecule moves in any one given direction. When the viscosity is lowered, the tumbling rate will increase and the correlation time will decrease and the ESR spectrum become narrwer and better resolution of the lines will be expected. We may say for our results that when the ESR spectra are recorded at higher temperatures and for longer times of heating, the viscosity of gum arabic becomes lower and narrowing due to transition of the material from high viscosity molecular orientations to faster tumbling rate at lower viscosities will be expected.

7.5 SATURATION DUE TO MICROWAVE POWER VARIATION OF THE GUM ARABIC ESR SPECTRA

The ESR spectra of x-irradiated gum arabic recorded at room temperature at different microwave powers ranging from 0.5 mW to 100 mW show that the best resolved spectra are obtainable at low microwave powers. Line-width broadening and saturation behaviour at higher microwave power can lead to broadening of the ESR lines. A relation between the square root of the microwave power and the relative spin density of the total spin density and the spectral group (1) and (2) shows different microwave power saturation responses. Spectral group (1) is saturated at 37.5 mW while spectral group (2) is saturated at 16.2 mW. The saturation of the total spin is at 20.2 mW. The shape of the curve for microwave power versus the intensity of the spectra have been compared with the theoretical ideal homogeneous and inhomogeneous curves given by SIMMONS[147] and ZIMBRICK and KEVAN[148]. Our curves show little decrease of the intensity beyomd the saturation point which indicates that the saturation curve of the total spin density and the spectral groups (1) and (2) follows the inhomogeneous broadening. The ESR spectra measured at liquid nitrogen of x-irradiated gum arabic at room temperature, show a single broad line which indicate the overlap of all peaks detected at room temperature. This convergence of the lines may due to higher immobilization of the molecules at liquid nitrogen which leads to broadening of the signals. Another possibility of the overlap of the signals is the saturation of some signals at lower microwave power measured at liquid nitrogen. The saturation at low temperature easily occurs as a result of increase of lattice relaxation time which also give rise to broader lines. The relation

between square root of microwave power ($\sqrt{P}$) and total relative spin density at liquid nitrogen indicates that the saturation occurs at 1.5 mW and the resonance line are homogeneously broadened.

7.6 OPTICAL ABSORPTION OF GUM ARABIC.

An ultraviolet and visible light absorption has been measred of gum arabic film before and after gamma irradiation. The results show an absorption at 276 nm, before and after irradiation. An increase of the intensity at 276 nm has been shown after gamma irradiatins. The groups which which absorb near the region of 278 nm are the carbonyl groups[128,129] or the glycosidic (acetal) groups.

CHAPTER EIGHT.

SUMMARY AND CONCLUSIONS.

Gum arabic is being used extensively as a constituent of drugs and food stuffs. This study outlines certain aspects of effects of irradiation and thermal treatment on such a material.

In the present work free radicals have been generated in gum arabic and its four major components D-galactose, L-arabinose, L-rhamnose and D-glucuronic acid powders using x-irradiation, UV irradiation and heat treatment. ESR techniques have been used mainly to detect and study the behaviour of the generated free radicals. Application of different radiation doses, decay of the ESR spectra, and the effect of the microwave power suggested the presence of two distinct individual spectral groups in a complex spectrum of gum arabic.

X-irradiation was used to generate free radicals at various doses up to 180 minutes of irradiation. A relation between irradiation time and spin density of the total spins for spectral group (1) and spectral group(2) showed an exponential relation which resembles what has been proposed by SNIPES[91], ROTBLANT[92], MULLER[93,94], and CONGER[95]. Irradiation time versus spin density curves for spectral group (1) and spectral group (2) showed saturation at 90 and 120 minutes of irradiation time respectively. The general shape of the ESR spectra of gum arabic show better resolved peaks at lower doses. Above 90 minutes of irradiation the peaks start to overlap. Overlap of the peaks at higher doses has been attributed to the higher spin density, where the spin-spin interaction and spin exchange may take place and may thus lead to a difference in saturation dose for different signals of the spectrum.

The decay of the ESR spectra at room temperature of x-irradiated gum arabic shows two distinct spectral group of radicals (1) and (2) and shows the transformation of the spectral group (2) to a singlet. The decay of the spectral groups (1) and (2) follow an exponential equation, which has been proposed for the decay of starches by RAFFI and AGNEL[64]. The decay of the two spectral groups (1) and (2) exhibited three different zones of different decay rate constants. The decay rate constants of spectral group (1) in zones (1), (2) and (3) are 51.97×10^{-3}, 8.16×10^{-3} and 1.65×10^{-3} $hours^{-1}$ respectively. The decay rate constants of spectral group (2) in zones (1), (2) and (3) are 40.6×10^{-3}, 7.3×10^{-3} and 2.66×10^{-3} $hours^{-1}$ respectively. Of these constant rates one can infer that spectral group (1) decay faster than the decay of the spectral group (2) in zones (1) and (2), but in zone (3) spectral group (2) decays faster than spectral group (1).

The decay of the radicals formed on x-irradiated gum arabic with the variation of temperatures shows two different behaviours of the two spectral groups (1) and (2). A plot of temperature versus relative spin density of spectral group (1) and (2) shows that spectral group (1) decays rapidly between 317 and 327 K. Spectral group (2) decay gradually between room temperature and 323 K; beyond this temperature spectral group (2) decays rapidly. The spectrum becomes very weak between 353 and 373 K and the signals are destroyed above 373 K.

Mercury light was applied to x-irradiated gum arabic. ESR spectra and dependence of the spin density on UV exposure showed that mercury light affected

spectral group (1) and increased the spin density of this spectral group, which reflects that the signal created by UV radiation is of the same nature of spectral group (1) created by x-rays.

The exposure of gum arabic to mercury light of wave lengths above 3000 A° created a singlet signal of 9 gauss line-width and g-value of 2.0046. The exposure of gum arabic to UV light of wave length above 3000 A° also created a singlat signal of line width of 13.3 gauss and g-value of 2.0046.

Natural gum was heated under vacuum at various temperatures between 373 and 503 K for various times of heating. This resulted in a singlet ESR signal with a g-vlue of 2.0032 close to that mentioned for heated charred carbohydrates. The line-width of this signal varied between 8 and 5 gauss depending on the temperature and length of heating time. The spin density at temperatures 373, 423, 473 K show little increase with the increase of heating time. At temperatures 483, 493, 503 K the spin density increased at a fast rate. The nature of this radical has been interpreted as due to carbon atoms clustering in condensed ring systems. and free radical formation when the bond in the condensed carbon ring is broken.

The ESR spectra of x-irradiated D-galactose, D-glucuronic acid, L-arabinose and L-rhamnose have been studied with the variation of the microwave power. Results obtained were as follows:

D-galactose: The ESR spectra of x-irradiated D-galactose show two signals, a triplet signal of hyperfine splitting 21 gauss and g-value of 2.0032. The triplet signal has been attributed to the presence of the free electron at C(5) which

interact equally with two protons on C(6) to form a triplet signal. The second signal is a doublet of 17 gauss hyperfine splitting and g-value of 2.0037. The doublet signal is attributed to the presence of a free electron at C(1).

L-arabinose: The ESR spectra of x-irradiated L-arabinose show an intense doublet signal of 14.5 gauss hyperfine splitting and g-value of 2.0057. This signal is attributed to the presence of the free electron at C(1) which interact with the beta proton of C(2).

L-rhamnose: The ESR spectra of x-irradiated L-rhamnose show two well resolved signals labeled as radical (1) and radical (2). Radical (1) is a doublet with 11 gauss hyperfine splitting and has been attributed to the presence of the free electron at C(1), C(2), C(3), or C(4) and the interaction of the free electron with the beta proton. Radical (2) is a doublet with hyperfine splitting of 33.5 gauss. The g-value of the two radicals is the same and equal to 2.0037.

D-glucuronic acid: X-irradiated D-glucuronic acid shows an ESR spectrum with a singlet signal. This signal has a line-width of 9 gauss and 2.0042 g-value. This signal has been attributed to the scession of C(6)-OH or C(5)-H bond where no hyperfine interaction is to be expected.

In order to simulate the natural gum, components of gum arabic of the right proportions have been irradiated and added gradually. The ESR spectra were recorded after each addition. A comparison between the ESR spectra of natural and synthetic gum showed that the lines belonging to spectral group (2) in the natural gum spectrum are similar to those of araabinose, particularly the doublet signal in arabinose. The relative intensity of the spectrum of spectral group (2) in

the ESR spectrum of synthetic gum is lower than that in the natural one. The fact that the synthetic gum has no glycosidic bonds between the monomers has led us to infer that this singlet may be due to scession of glycosidic bonds and may be of the form C-O. The spectral peaks of spectral group (1) in natural gum resemble the peaks originating from glucuronic acid, which appear as the singlet signal observable in the synthetic spectrum.

The decay of the ESR spectrum of irradiated natural gum shows that spectral group (2) is converted from a doublet immediately after irradiation to a singlet after annealing at room temperature or during the elevation of the temperature. From this result and from the comparison between the ESR spectra of synthetic and natural gum, one can infer that spectral group (2) consists of a singlet and doublet signals. The doublet signal of spectral group (2) may be converted to the singlet signal of spectral group (1) by the reaction of the C. radical with the oxygen molecule (O_2)

$$\underset{\text{doublet}}{\text{C.}} \xrightarrow{O_2} \underset{\text{singlet}}{\text{C-O-O.}}$$

The singlet signal of spectral group (2) may be attributed to the presence of the free electron on the O. atom due to scession of glycosidic linkages. The possible distribution of the free radical in gum arabic molecules to give rise to a singlet is as follows: C(1)-O., C(3)-O., C(6)-O. of galactose, C(3)-O. of arabinose, C(1)-O. of rhamnose and C(1)-O., C(4)-O. of glucuronic acid.

The doublet signal of the spectral group (2) may be attributed to the presence of the free electron on a carbon atom which may interact with the alpha proton to

form a doublet signal. The possible distribution of the free radical in gum arabic molecule that may give a doublet signal is as in C(1). C(3). of galactose, C(1)., C(3). of arabinose, C(1). of rhamnose and C(1)., C(4). of glucuronic acid.

Distribution of the free radicals in gum arabic can take the form of isolated spurs. This is suggested thrgh the study of the behaviour of the free radicals during the increase and decrease of the spin density.

The line-widths of spectral group (1) and (2) have been studied during the variation of the irradiation dose, the decay of the radicals at room temperature and with the elevation of temperature. The increase of the line-width during the increase of irradiation dose and the decrease of the line-width with the decay of the spectra at room temperature can be interpreted by the theory of spin-spin interaction of the electrons and the hypothesis of the distribution of the free radicls within the isolated spurs. The decrease of the line-width, during the elevation of the temperature can be attributed to the spin-spin interaction and motional narrowing. Decrease of th line-width of the signal generated by heat during elevated temperature or during the variation of the heating time at certain temperature can be attributed to the motional narrowing.

Ultraviolet and visible light absorption has been measured of gum arabic film. An absorption has been observed at 276 nm before and after irradiation. The intensity has increased at this region after irradiatins has been applied.

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Table (5.1): Microwave power variation.

Spectral group	Saturation condition at R.T.(mW)	Saturation condition at L.N.T.(mW)
Total spin	21.2	1.5
1	37.5	unmeasurable
2	16.2	unmeasurable

Table (5.2): Irradiation time variation.

Spectral group	Saturation condition(minutes)
Total spin	120
1	90
2	120

Table (5.3): Irradiation time variation.

Spectral group	Irradiation time (minutes)	Line-width (gauss)	g-value
1	2---180	11.5--14	2.0064
2	2---180	22----24	2.0054

Table (5.4): Decay time variation.

Spectral group	zone	Decay time interval (h)	Decay rate constant (h^{-1})
1	I II III	0------18 18------115 115-----667.5	$51.97x10^{-3}$ $8.16x10^{-3}$ $1.65x10^{-3}$
2	I II III	0------32.5 32.5---144 144----667.5	$40.6x10^{-3}$ $7.3x10^{-3}$ $2.66x10^{-3}$

Table (5.5): Decay time variation.

Spectral group	Decay time (hours)	Line-width (gauss)	g-value
1	0--667.5	13.5--9	2.0062-2.0040
2	0--667.5	23----16	2.0052-2.0030

Table (5.6): Temperature elevation.

Spectral group	Decay temperature interval (K)	Situation
1	317---327	Rapid decay
2	R.T.---323	gradual decay

Note: Spectral group (1) and (2) are destroyed completely after 373 K

Table (5.7): Exposing of x-irradiated gum arabic to mercury light

Spectral group	Exposing time to mercury light (minutes)	Line-width (guss)
1	0---355	14
2	0---355	22

Table (6.1): ESR signals of sugar component of gum arabic

Material	ESR signal	Hyperfine splitting (gauss)	g-value
D-galactose	doublet	17	2.0037
	triplet	21	2.0032
D-glucuronic acid	singlet	(line-width) 9	2.0042
L-arabinose	doublet	14.5	2.0057
	triplet of quartet	33 gauss of triplet splitting	unmeasurable
L-rhamnose	doublet	11	2.0037
	doublet	33.5	2.0037

Table (7.1): Approximate bond dissociation energy of chemical bonds in som carbohydrates

Bond dissociation	Energy (eV)	Wavelength (A°)
O--H	4.42	2800
C--H	4.29	2889
C--O	4.03	3075
C--C	3.59	3446

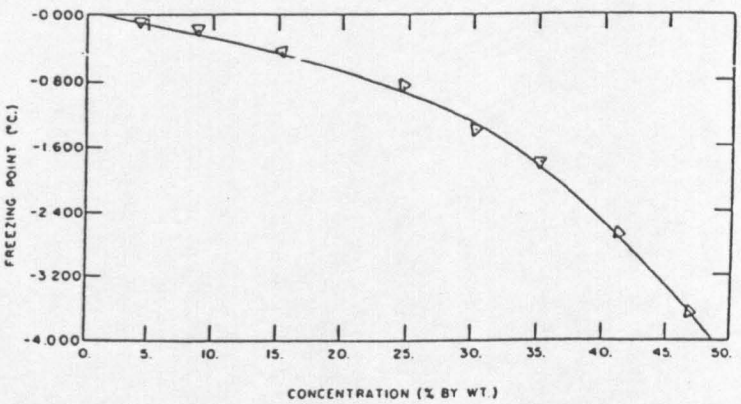


Figure (1.1) Freezing point of gum arabic solutions as a function of concentration.(TAFT and MALM).[4]

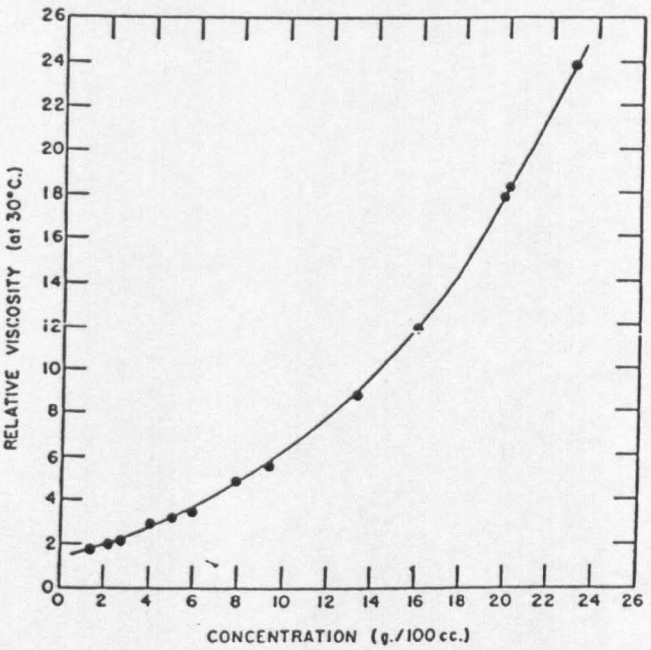


Figure (1.2) Relative viscosity as a function of concentration (TAFT and MALM).[4]

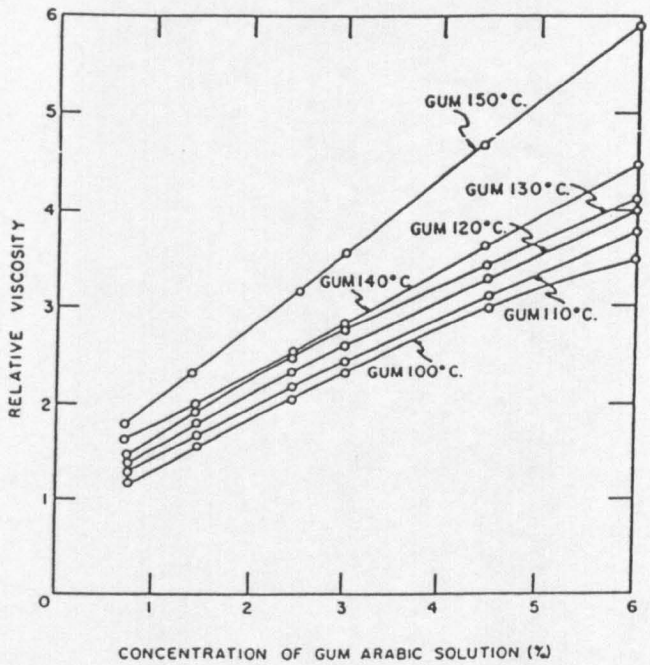


Figure (1.3) Effect of heating dry gum arabic on the relative viscosity of its solution (MOORJANI and NARWANI).[8]

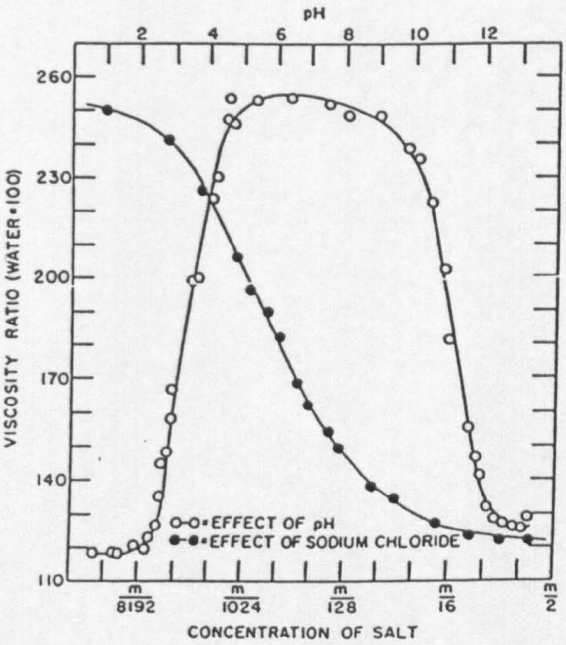
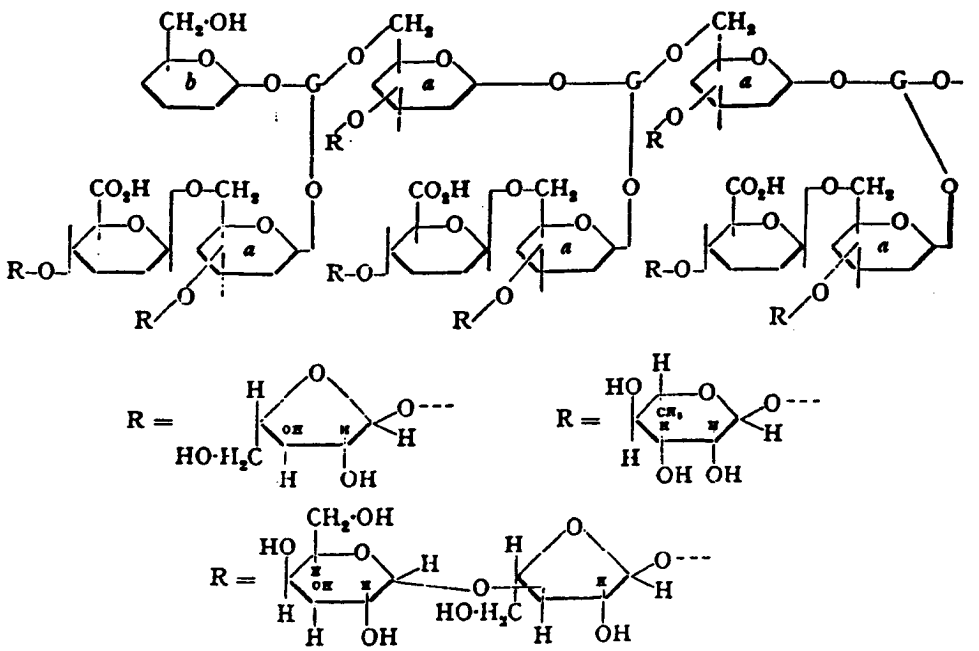
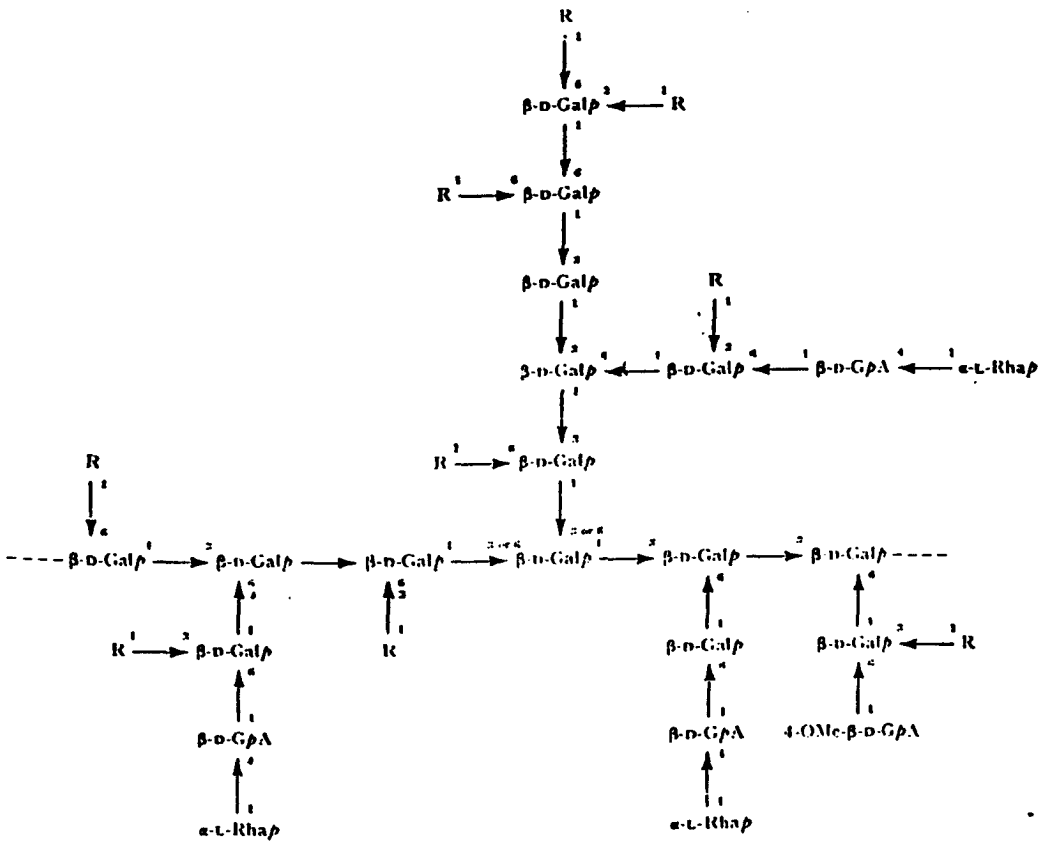


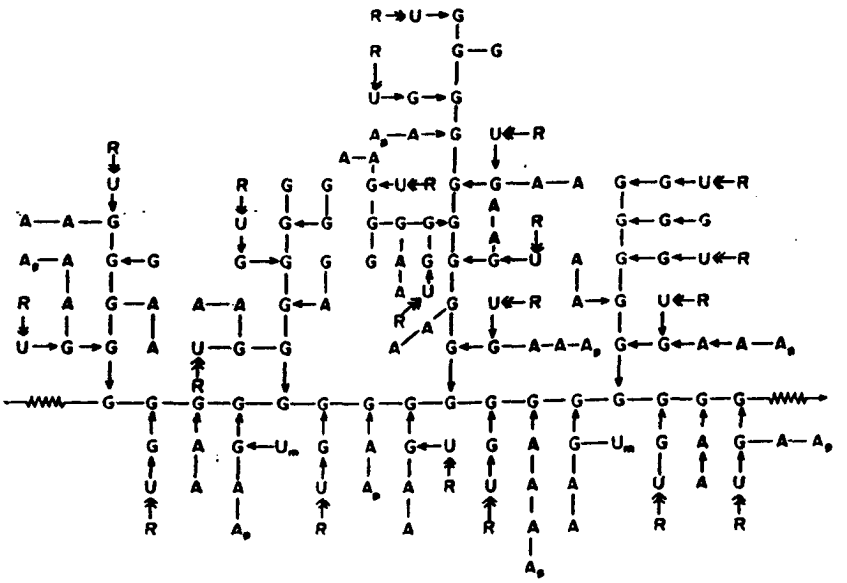
Figure (1.4) Viscosity of gum arabic solutions as a function of pH and salts (THOMAS and MURRAY).[10]



[Structure 1.1] Possible structure of a fragment of gum arabic (SMITH).[43]

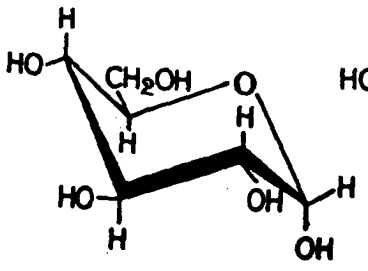


[Structure 1.2] Possible structure, fragment of gum arabic (ANDERSON).[40]

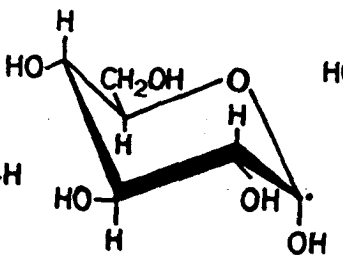


[Structure 1.3] Possible structure of gum arabic (STREET and ANDERSON).[46]

A = L-arabinose, G = D-galactose, U = D-glucuronic acid, R = L-rhamnose.
—— = beta 1,3; ——> = beta 1,6; ——>> = alpha 1,4



[structure 2.1]



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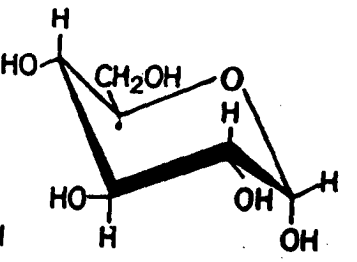
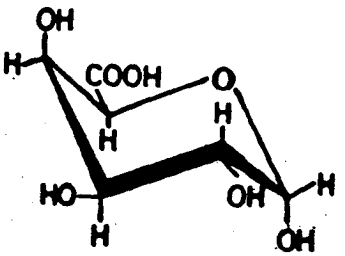


[structure 2.3]



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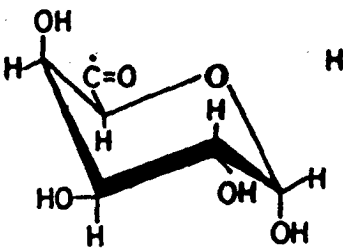

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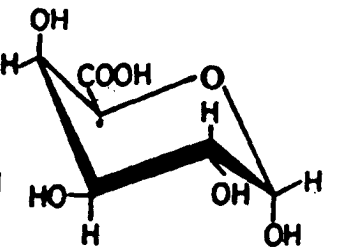

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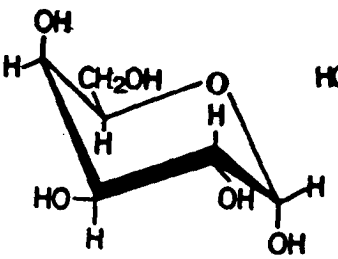

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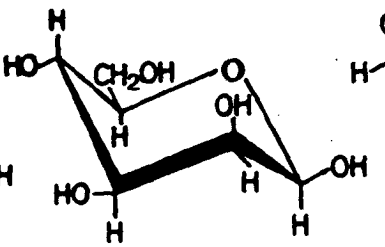

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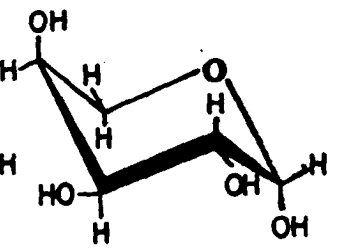

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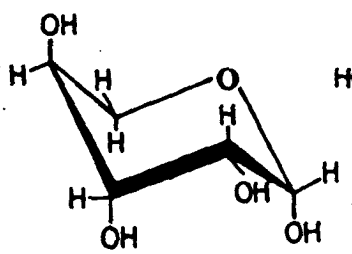
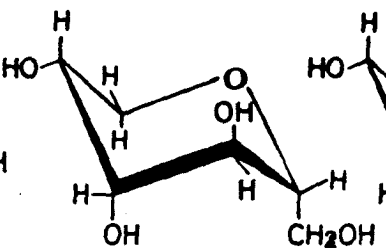


[structure 2.10]



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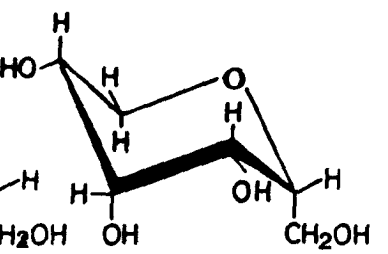
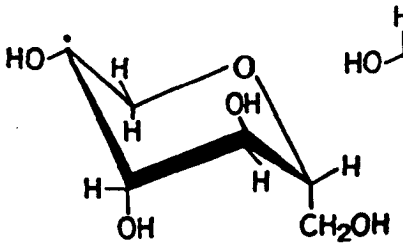
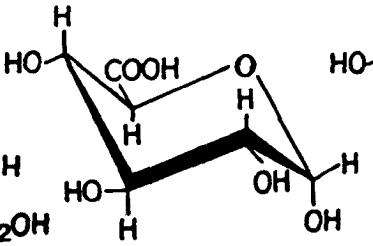


[structure 2.12]



[structure 2.13]



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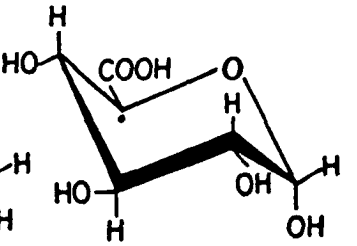

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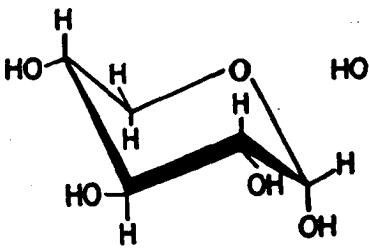

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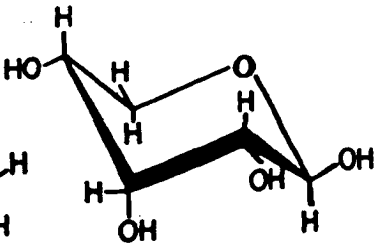

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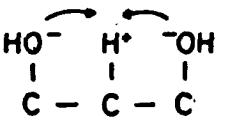

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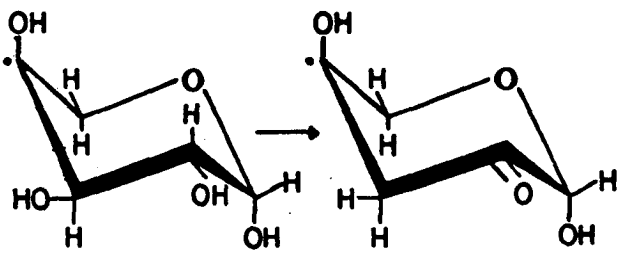

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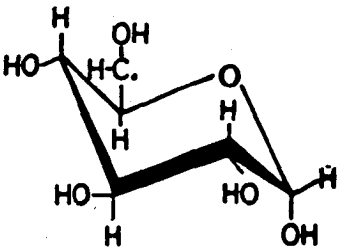

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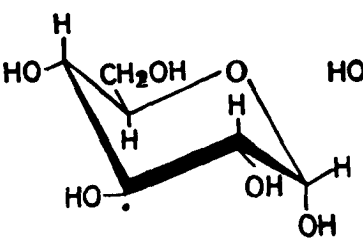

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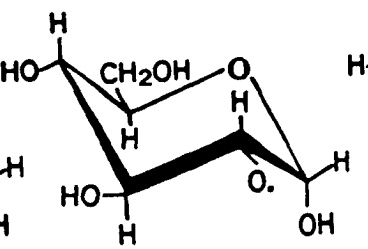

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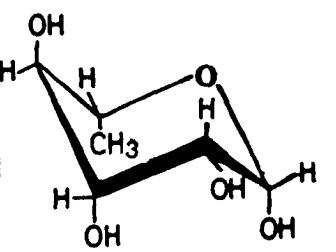

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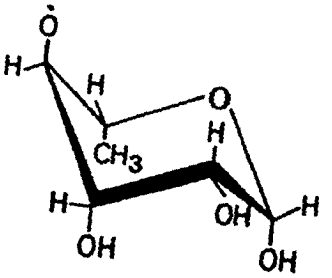

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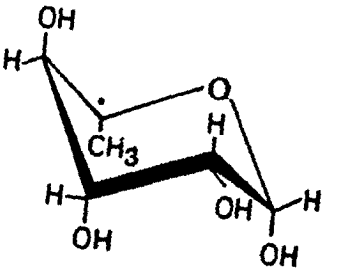

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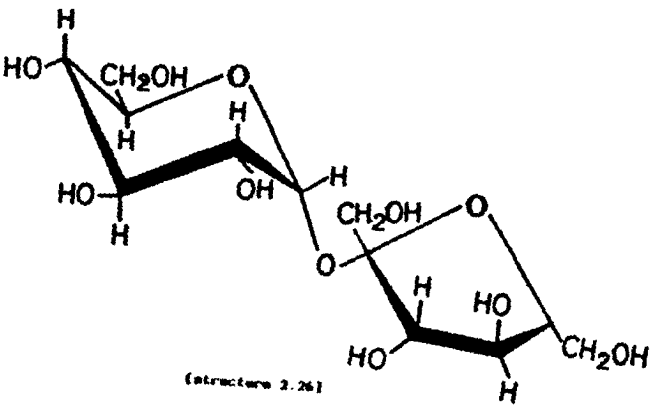

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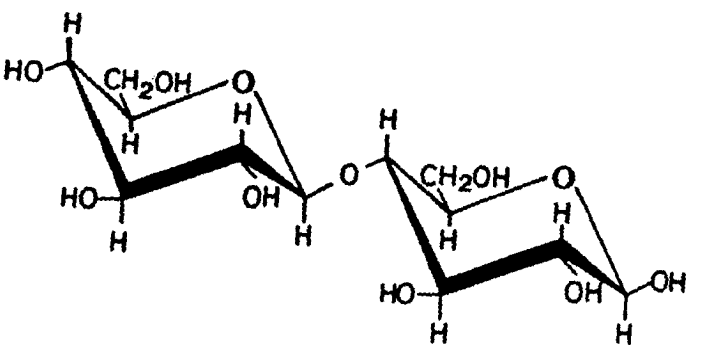

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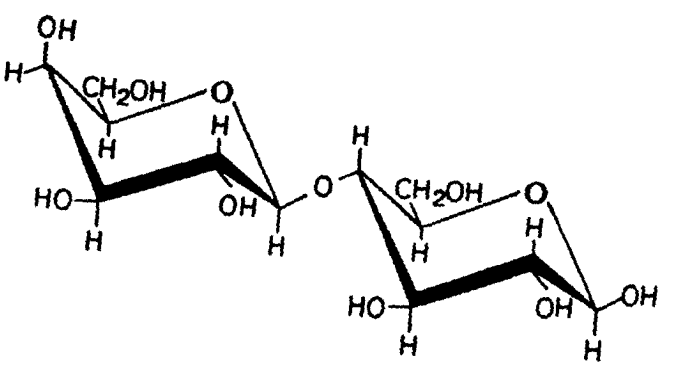

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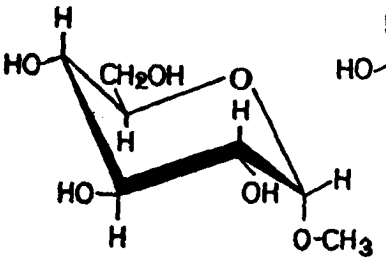

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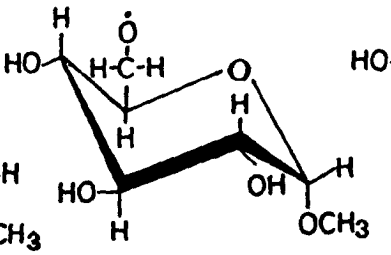

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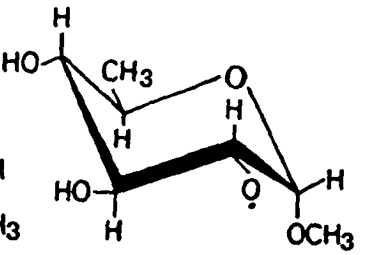

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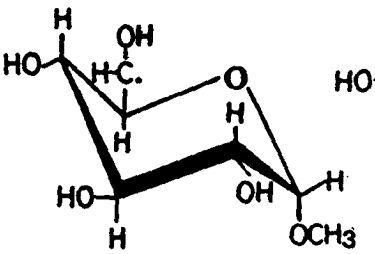

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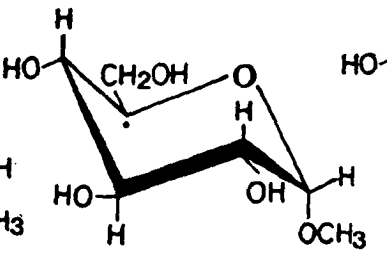

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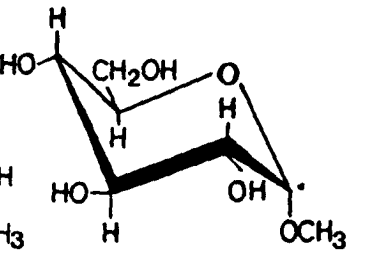
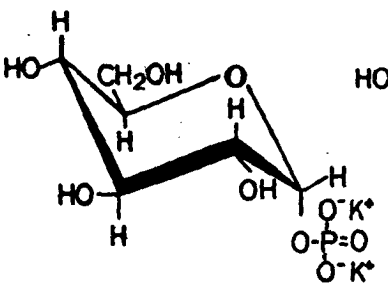
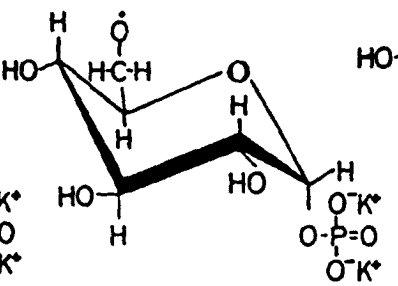


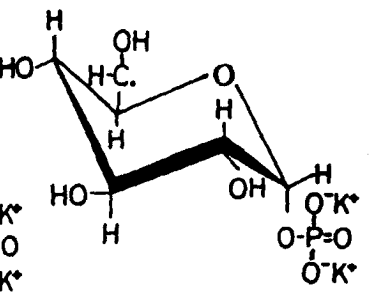
[structure 2.34]



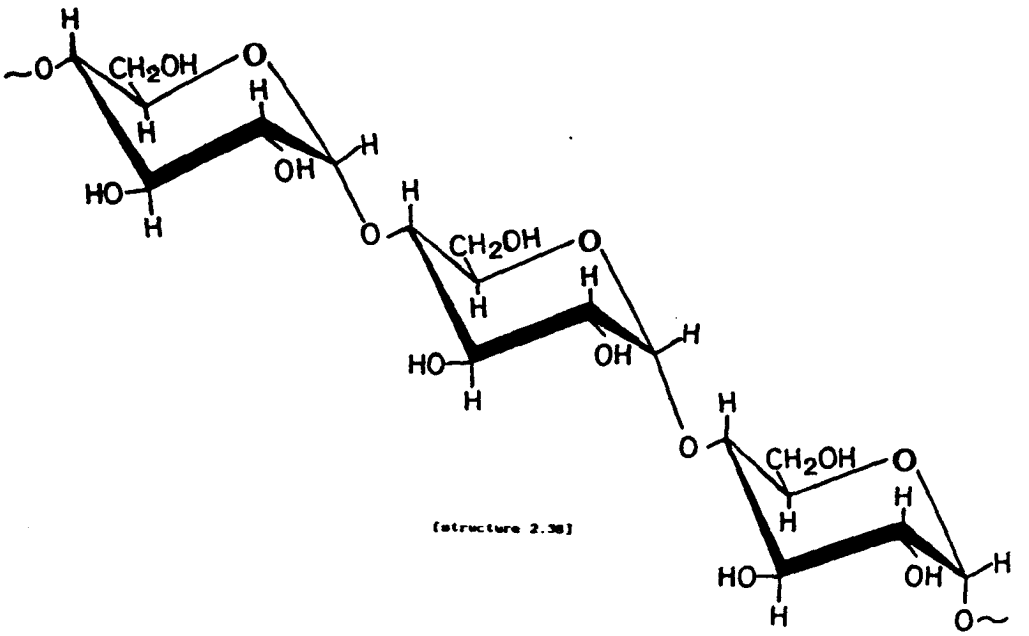
[structure 2.35]



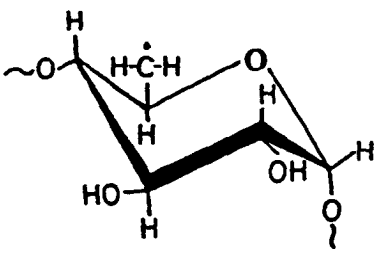
[structure 2.36]



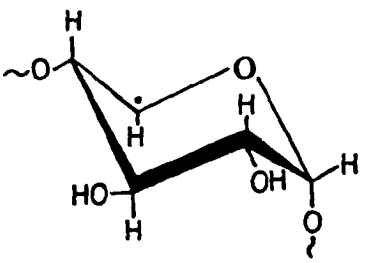
[structure 2.37]



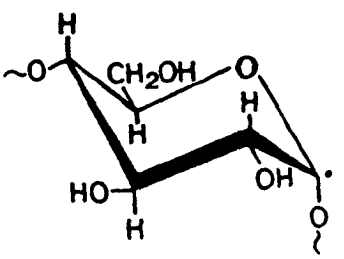
[structure 2.38]



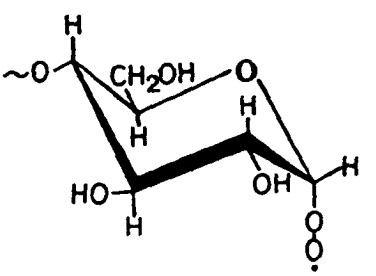
[structure 2.39]



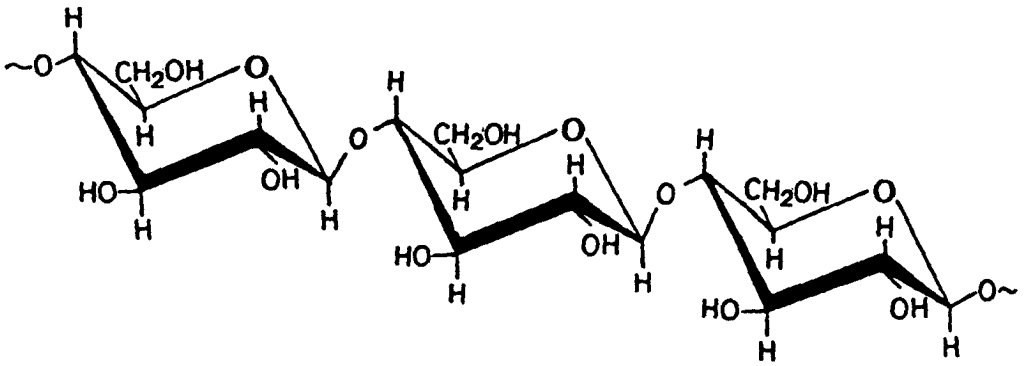
[structure 2.40]



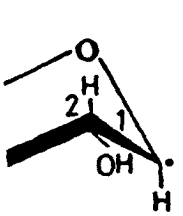
[structure 2.41]



[structure 2.42]

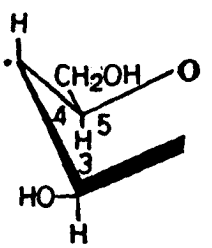


[structure 2.43]

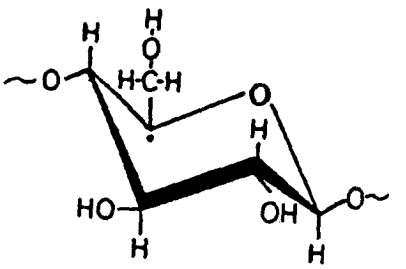


[structure 2.44]

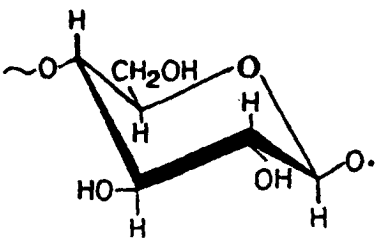
And



[structure 2.45]



[structure 2.46]



[structure 2.47]

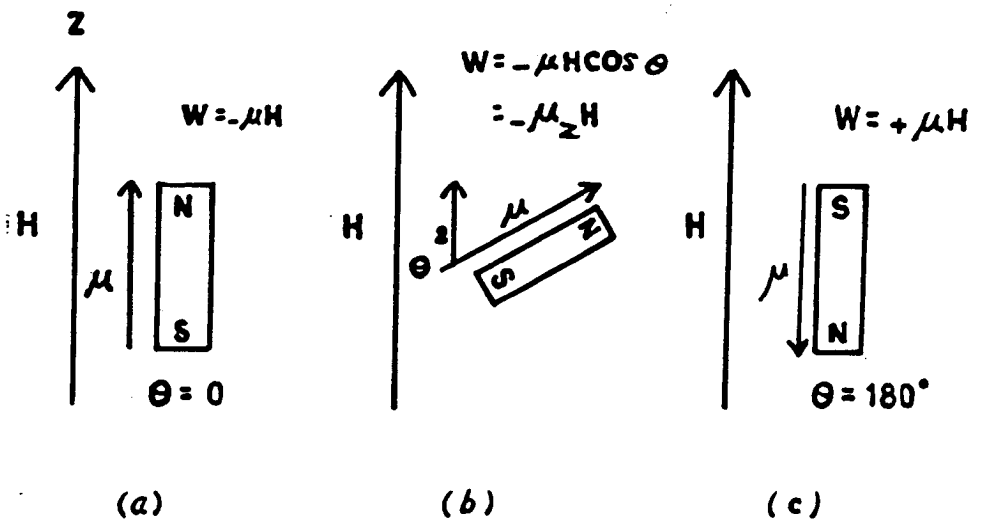


Figure (3.1) Energy of classical magnetic dipole in a magnetic field as a function of the angle θ between the magnetic field and the axice of the dipole.
(a) $\theta = 0$
(b) θ = *any angle between* 0 *and* 180
(c) $\theta = 180°$

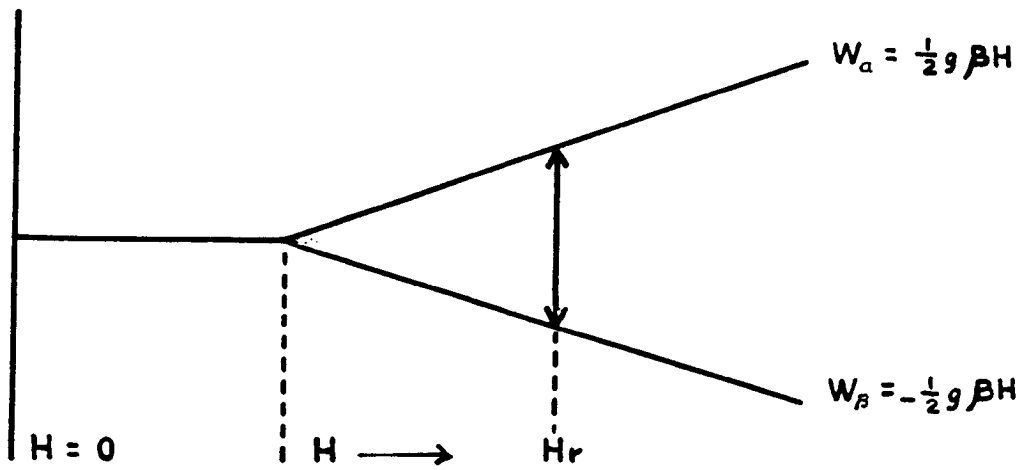


Figure (3.2) Energy level scheme for the simplest system showing ESR absorption W_α and W_β represents the energy of the $M_s = +\frac{1}{2}$ and $M_s = -\frac{1}{2}$ states respectively.

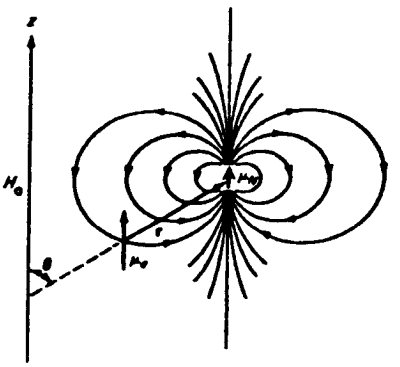


Figure (3.3) Interaction of dipoles arising from electron (μ_e) and from nuclear spin (μ_N) . where θ is the angle between the vector r and the applied field H.

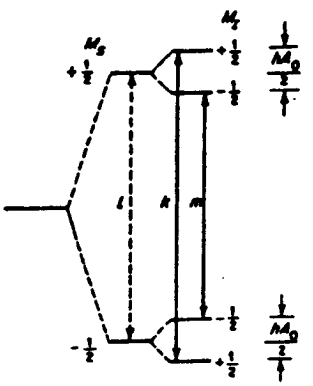


Figure (3.4) Energy levels of the hydrogen atom at constant magnetic field. The doted lines showes the transitions without hyperfine interaction, where the solid lines shows the allowed transitions corresponding to hyperfine interaction.

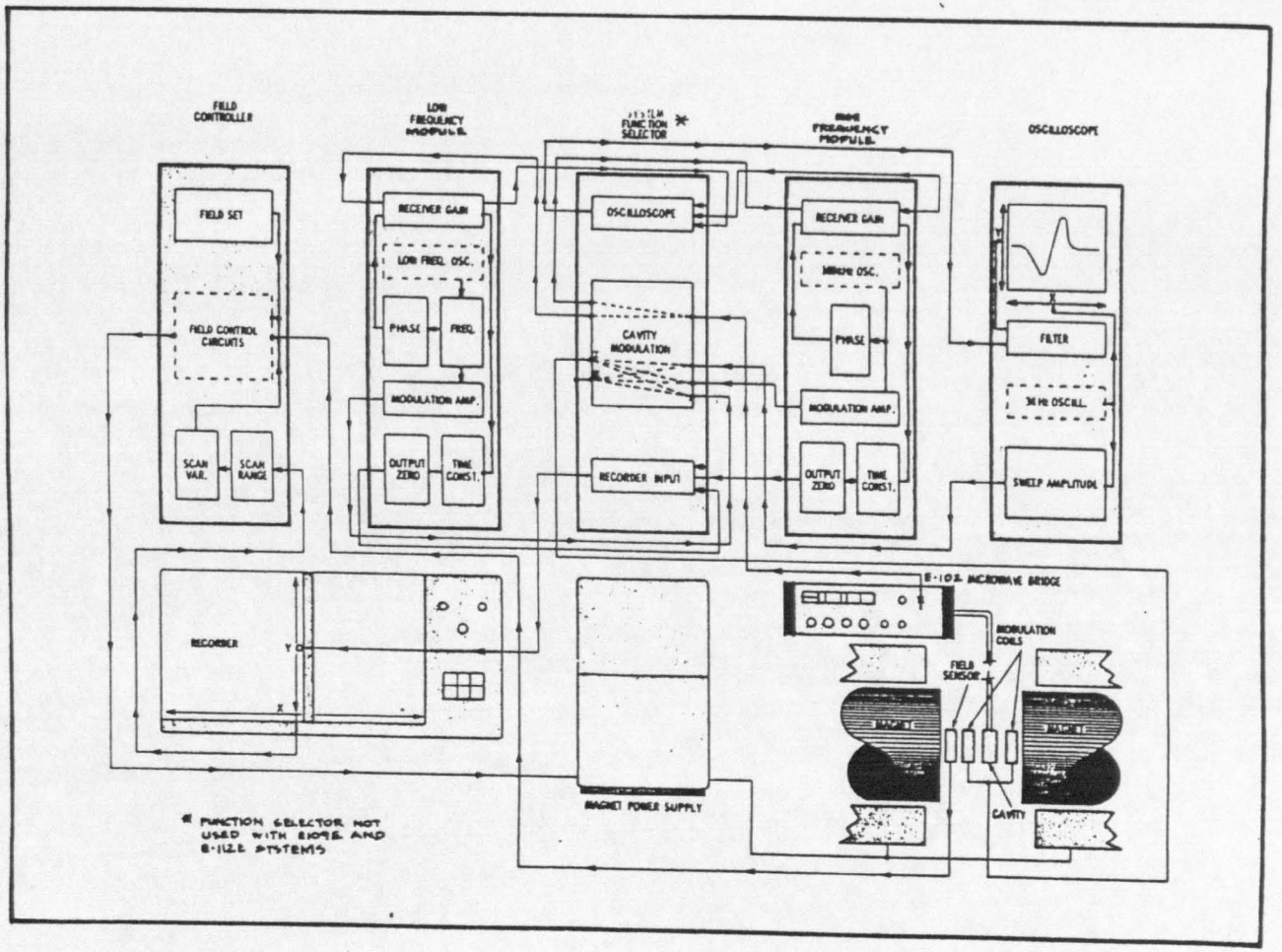


Figure 4.1 EPR System Pictorial Block Diagram

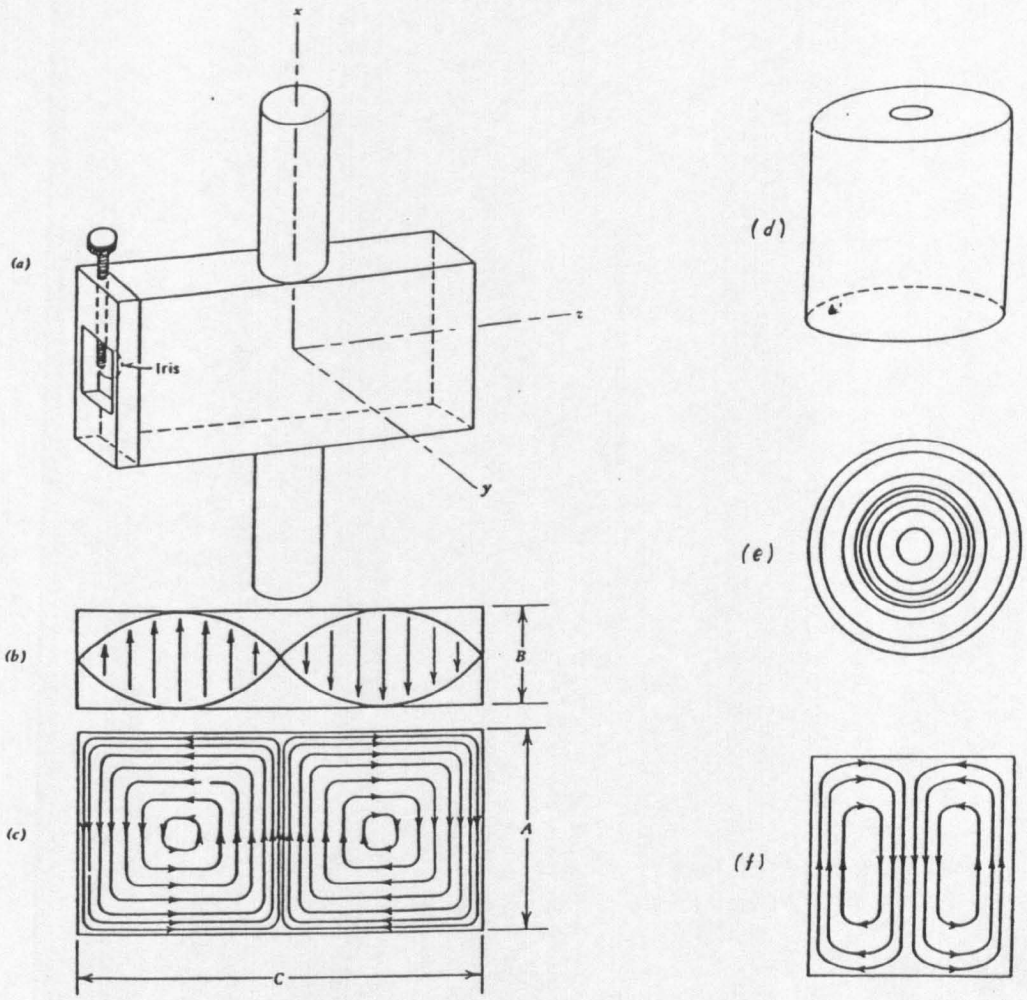


Figure (4.2)

(a) A rectangular microwave cavity.
(b) The electric field in yz plane in rectangular cavity.
(c) Magnetic field contours in the xz plane in rectangular cavity.
(d) The cylindrical cavity.
(e) Electric field contours on cylindrical cross section.
(f) Magnetic field contours along a vertical cross section.

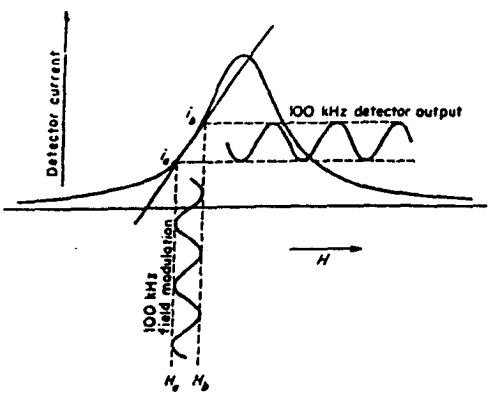


Figure (4.3) Effect of small amplitude 100 k Hz field modulation on the detector output current.

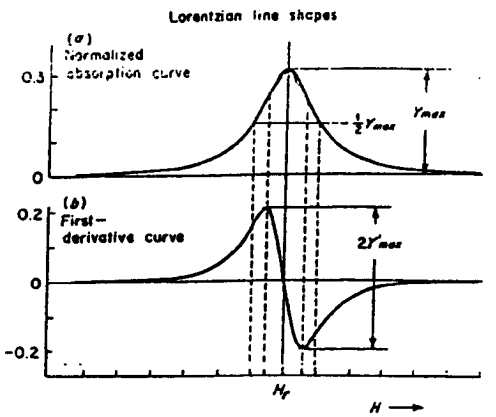


Figure (4.4) Lorentzian line shapes. (a) Absorption spectrum. (b) first derivative spectrum.

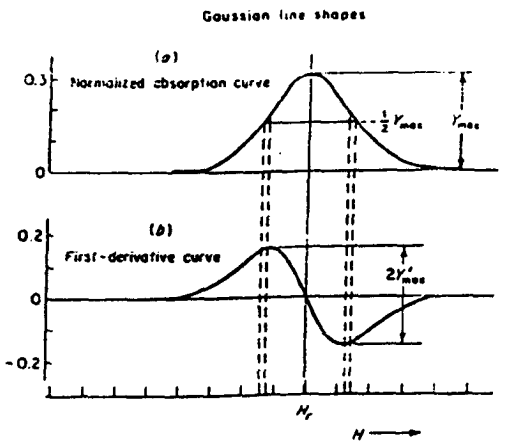


Figure (4.5) Gaussian line shapes. (a) Absorption spectrum. (b) First derivative spectrum.

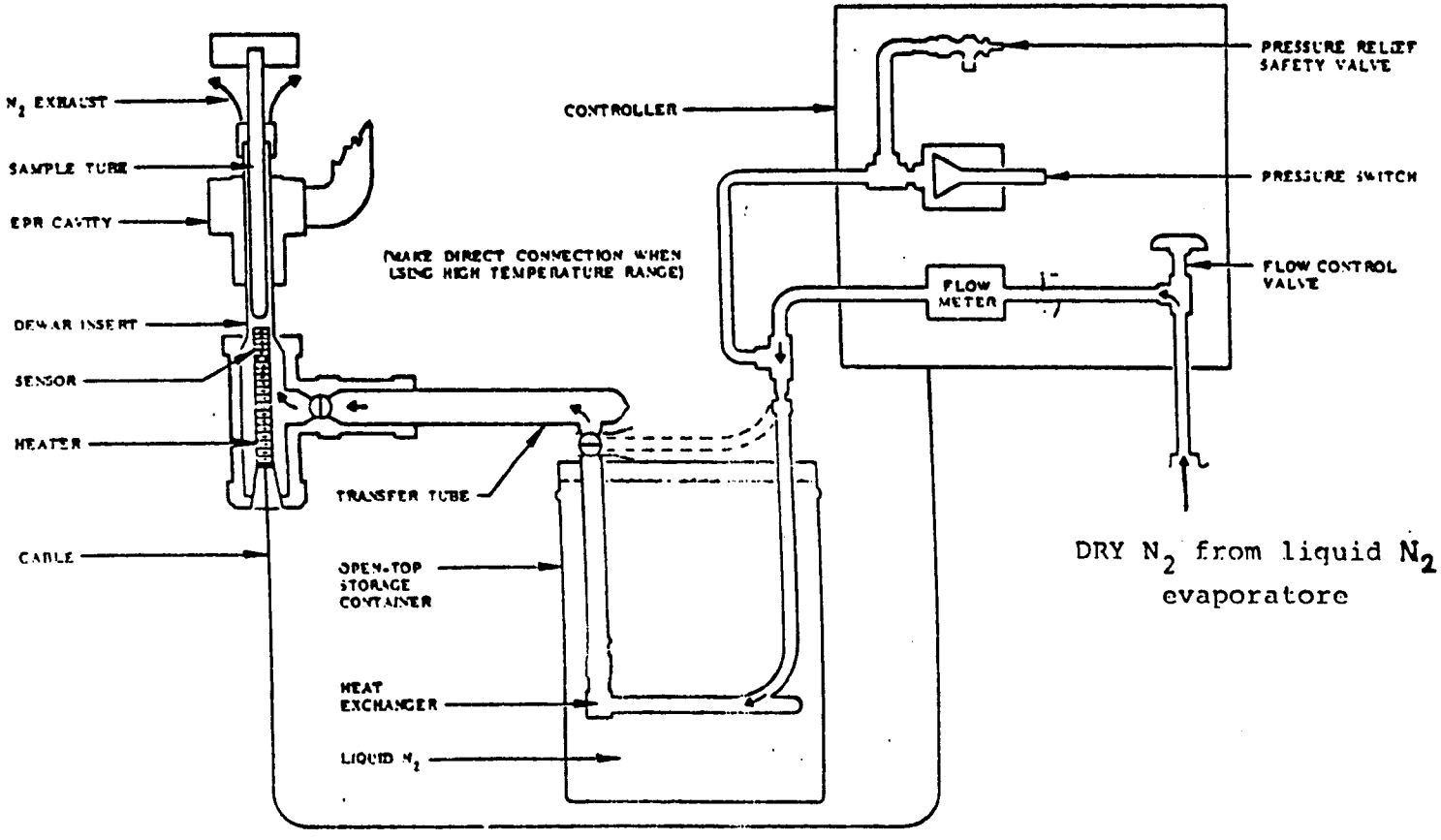


Figure (4.6) Gas flow diagram for the temperature controller.

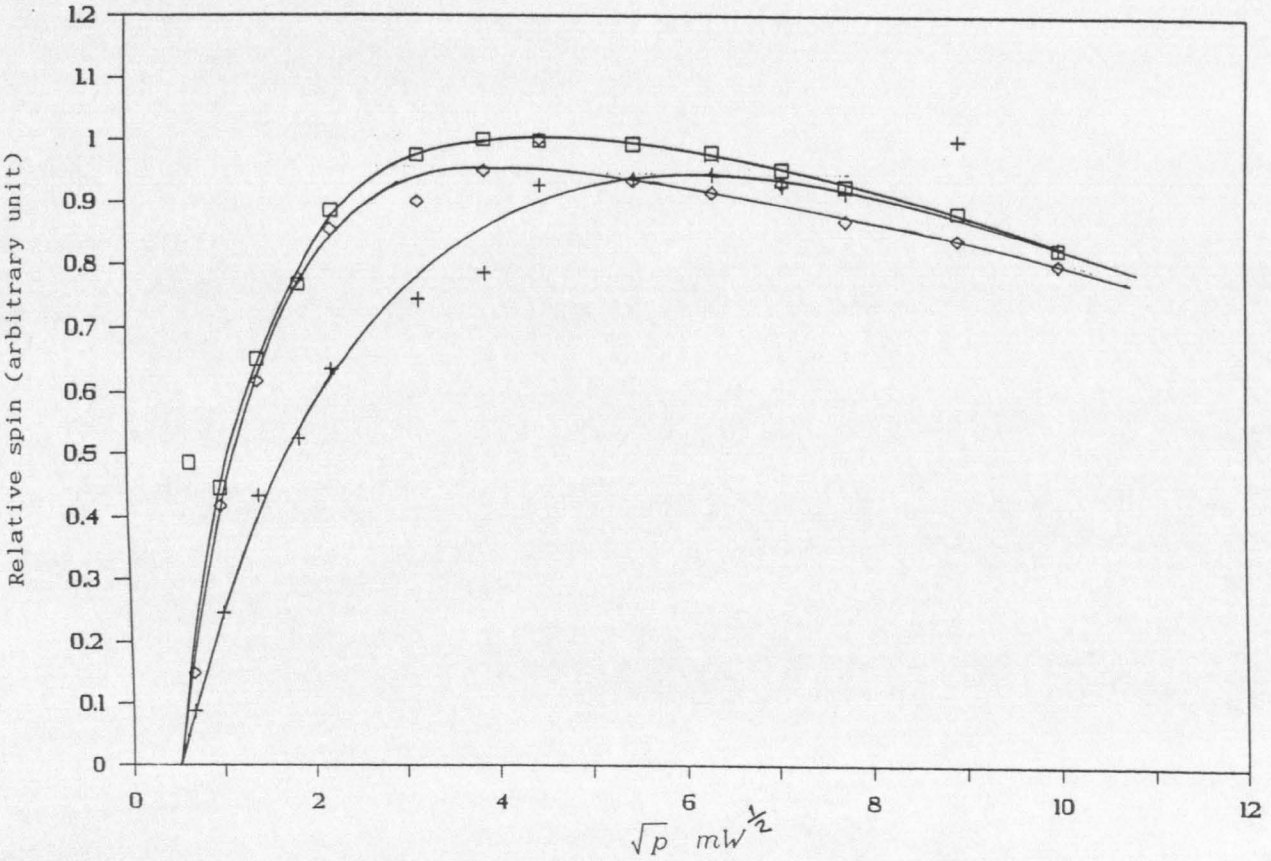


Figure (5.1) Total relative spin as a function of square root of microwave power $\sqrt{p}$ mW. The curves plotted in normalization condition.
□ Total relative spin, + spectral group (1),
◇ spectral group (2).

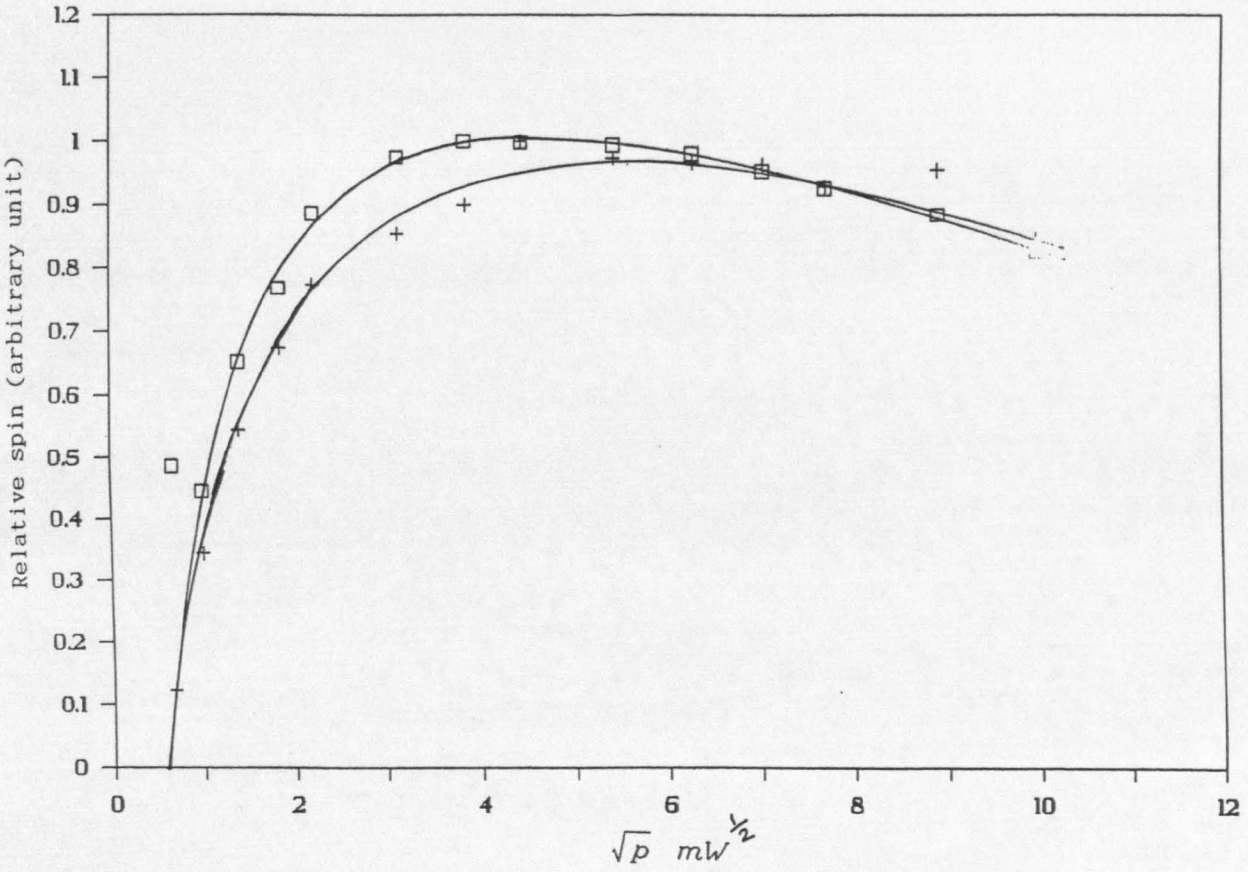


Figure (5.2) Total relative spin density as a function of the square root of microwave power. The curves were plotted in normalization condition.
□ Total relative spin density.
\+ Summation of the relative spin density of the spectral group (1) and (2).

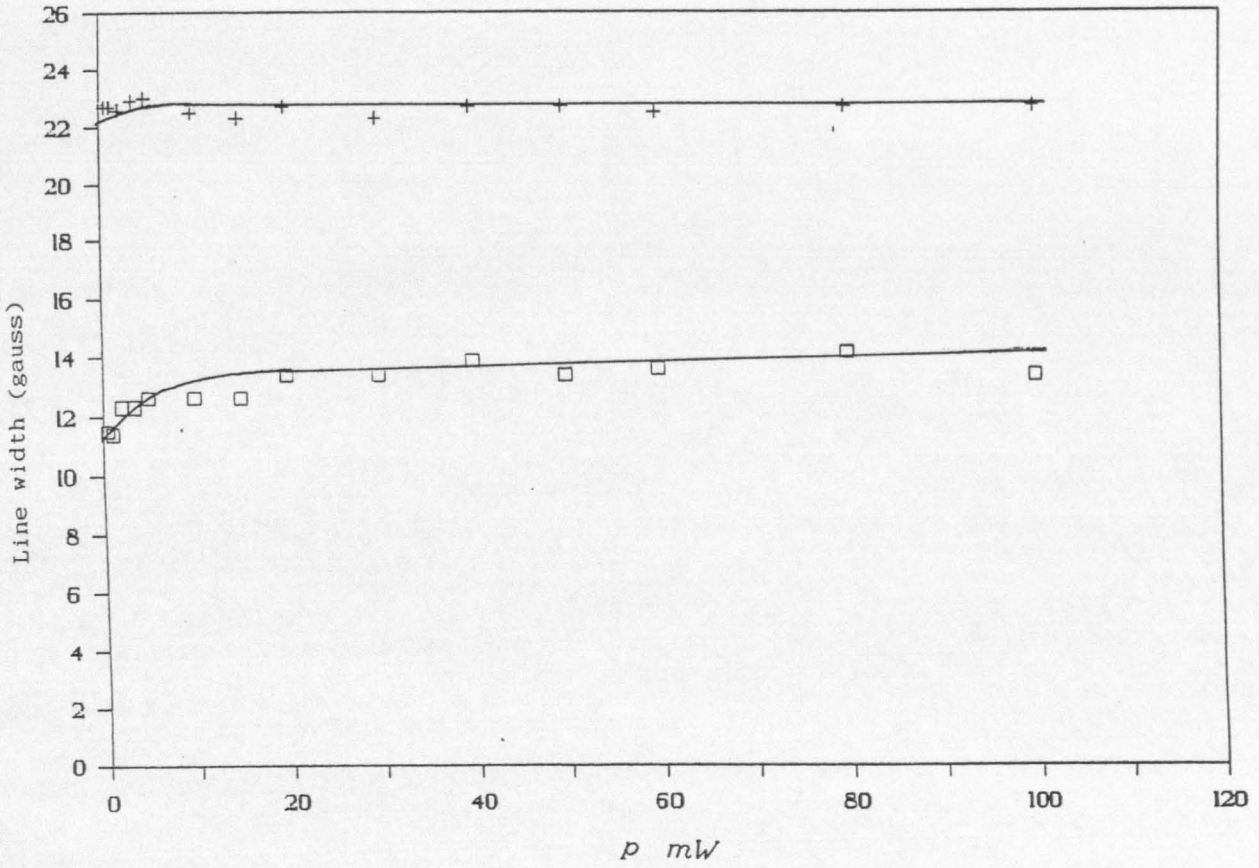


Figure (5.3) : Line width as a function of the microwave power (p).
□ spectral group (1).
+ spectral group (2).

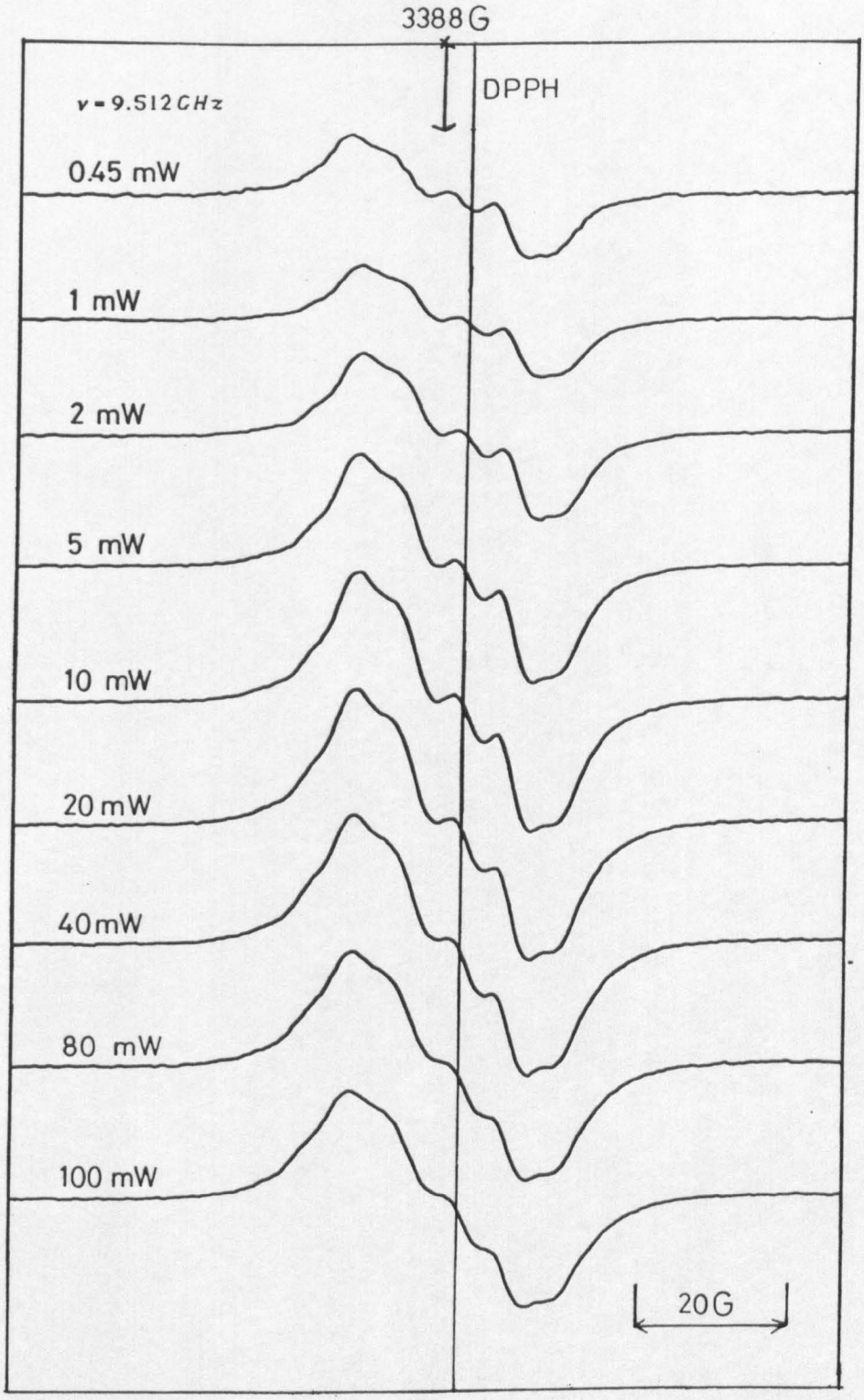


Figure (5.4) ESR spectra of x-irradiated gum arabic. The spectra were recorded at various microwave power. The irradiation and the measurements were caried out at room temperature.

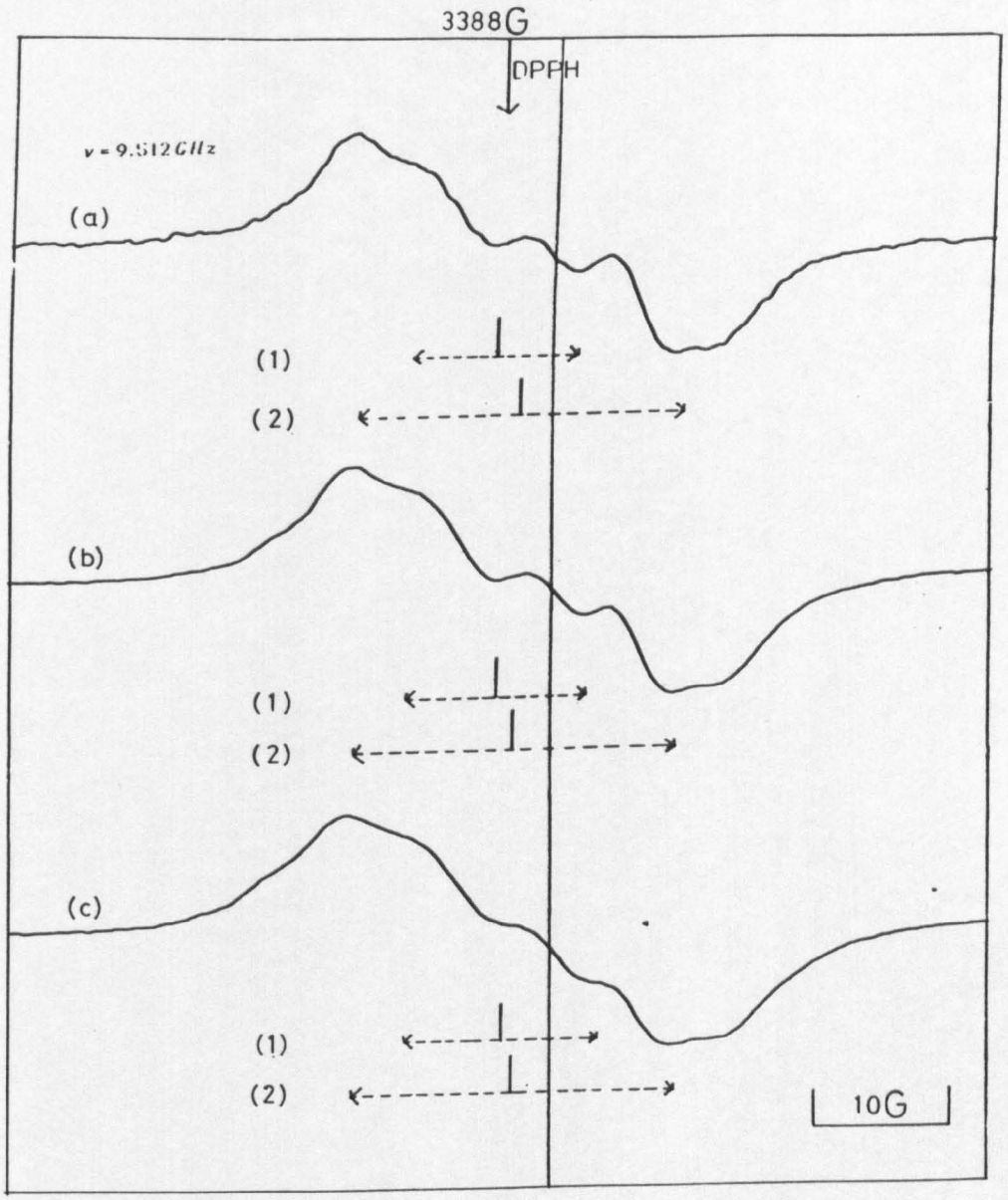


Figure (5.5) ESR spectra of x-irradiated gum arabic, recorded at different microwave power. The irradiation and the measurements were carried out at room temperature. (a) measured at 0.45 mW, (b) measured at 10 mW, (c) measured at 100 mW.

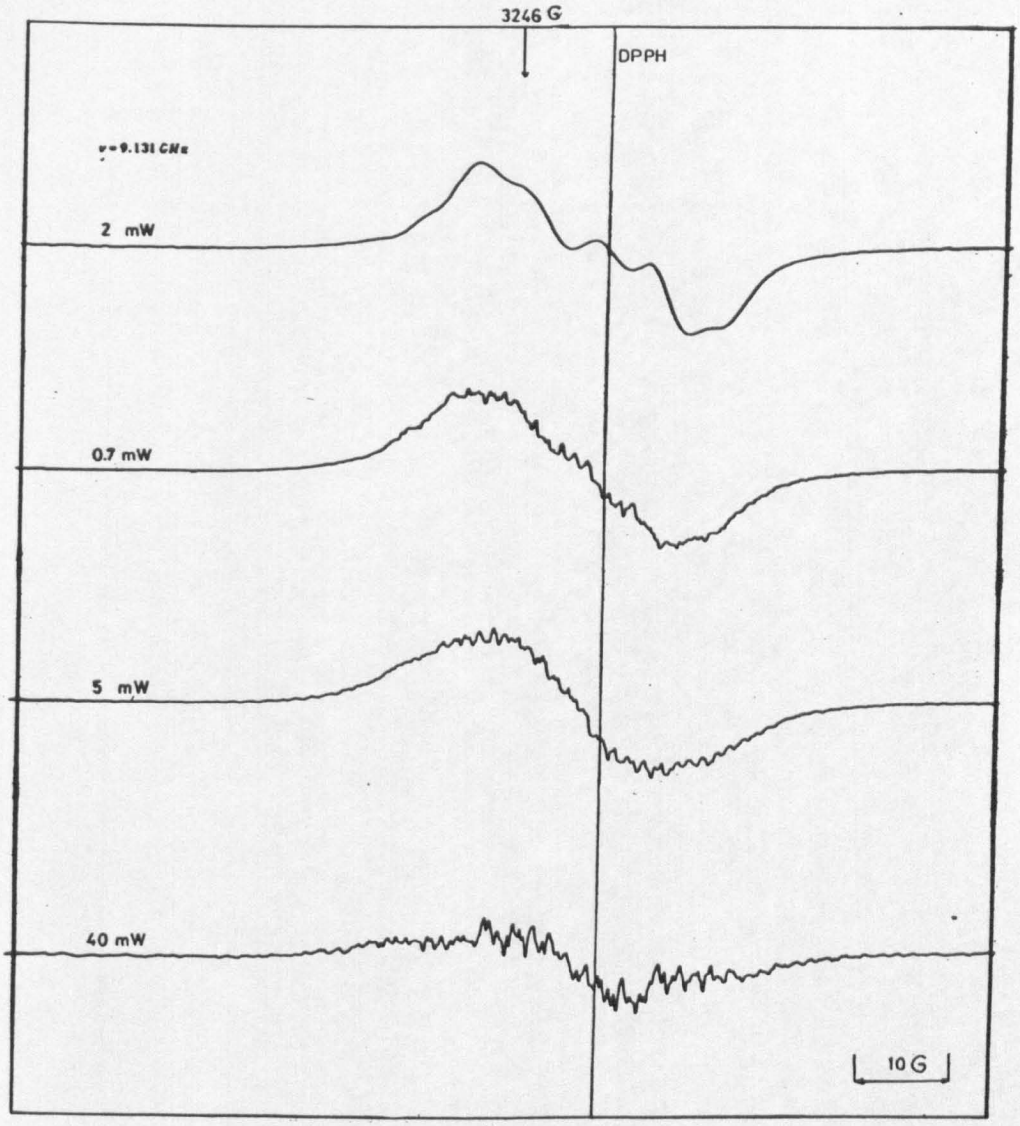


Figure (5.6) ESR spectra of x-irradiated gum arabic. The upper one irradiated and recorded at room temperature with 2 mW microwave power. The other three spectra irradiated at room temperature and recorded at liquid nitrogen temperature at different microwave power.

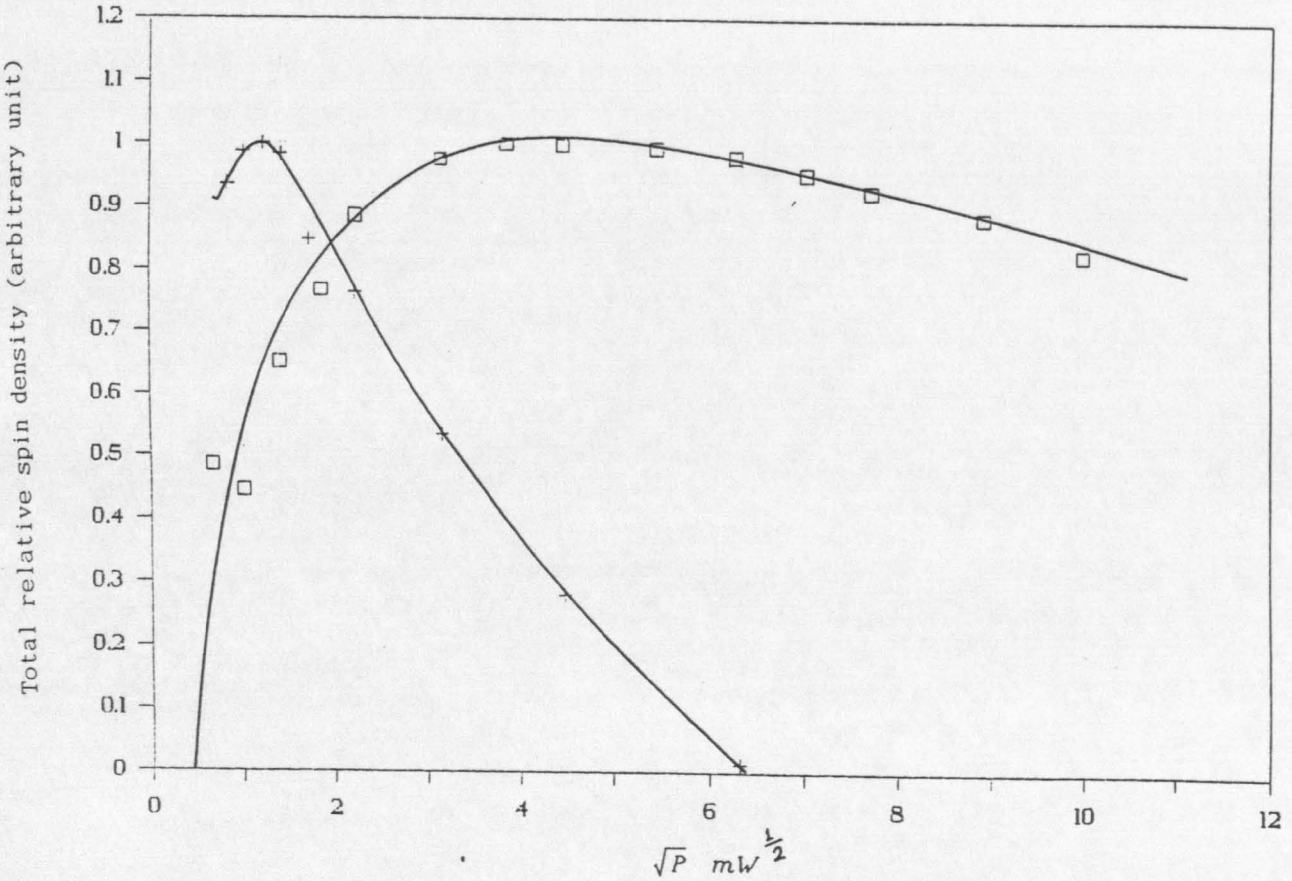


Figure (5.7) Relative spin density as a function of square root of microwave power $\sqrt{P}$.
+ measured at liquid nitrogen, □ measured at room temperature.

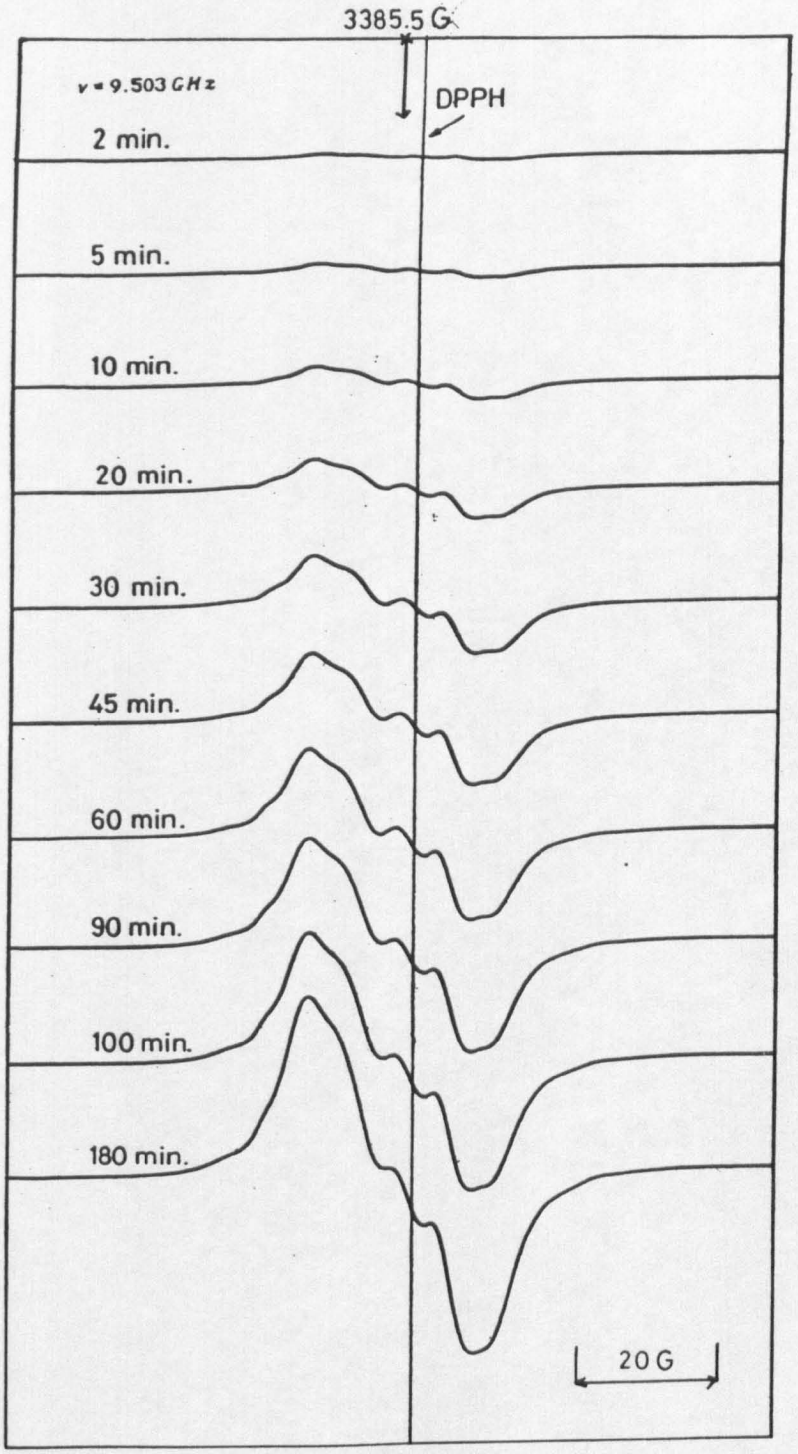


Figure (5.8) ESR spectra of x-irradiated gum arabic. The spectra were recorded at room temperature for different times.

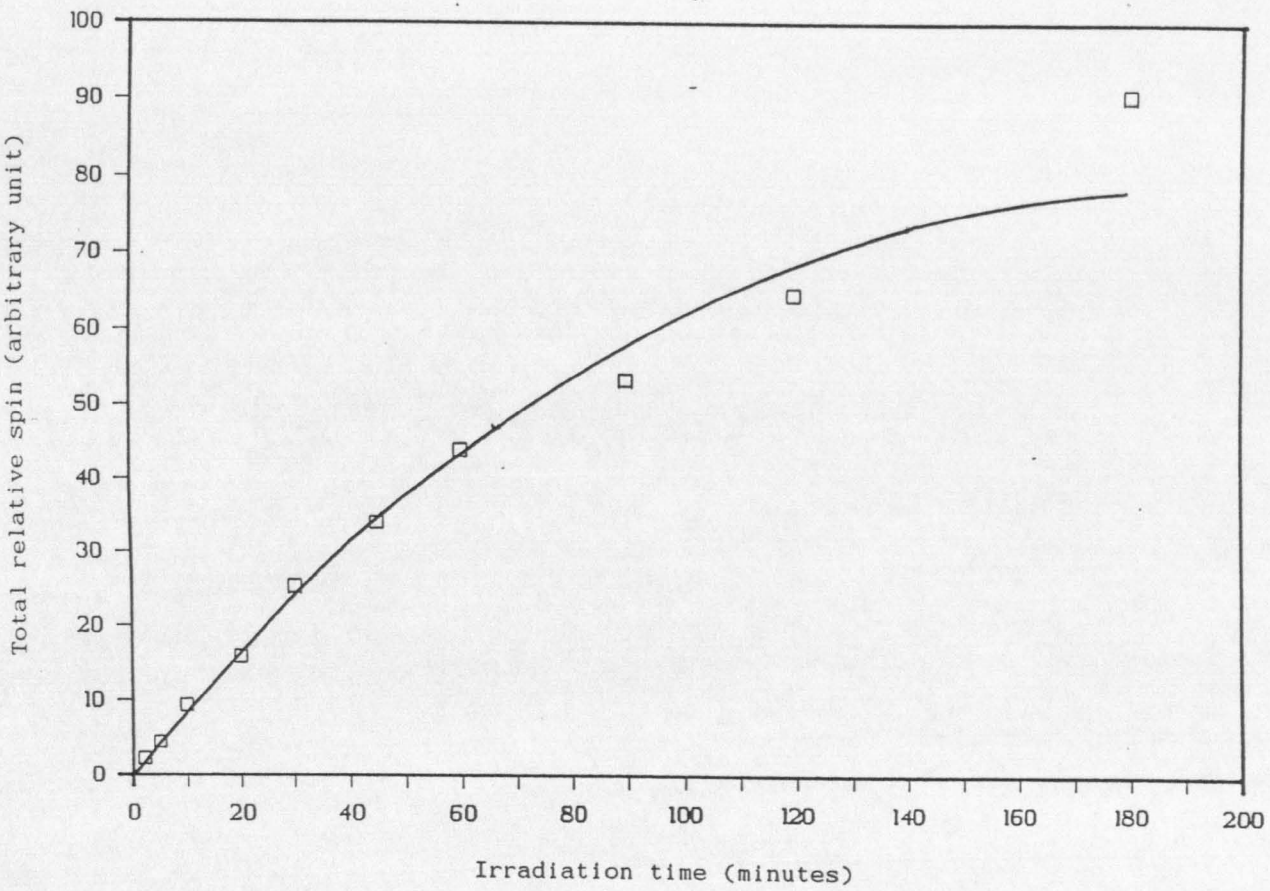


Figure (5.9). Total relative spin as a function of irradiation time for gum arabic. The irradiation were carried out at room temperature.

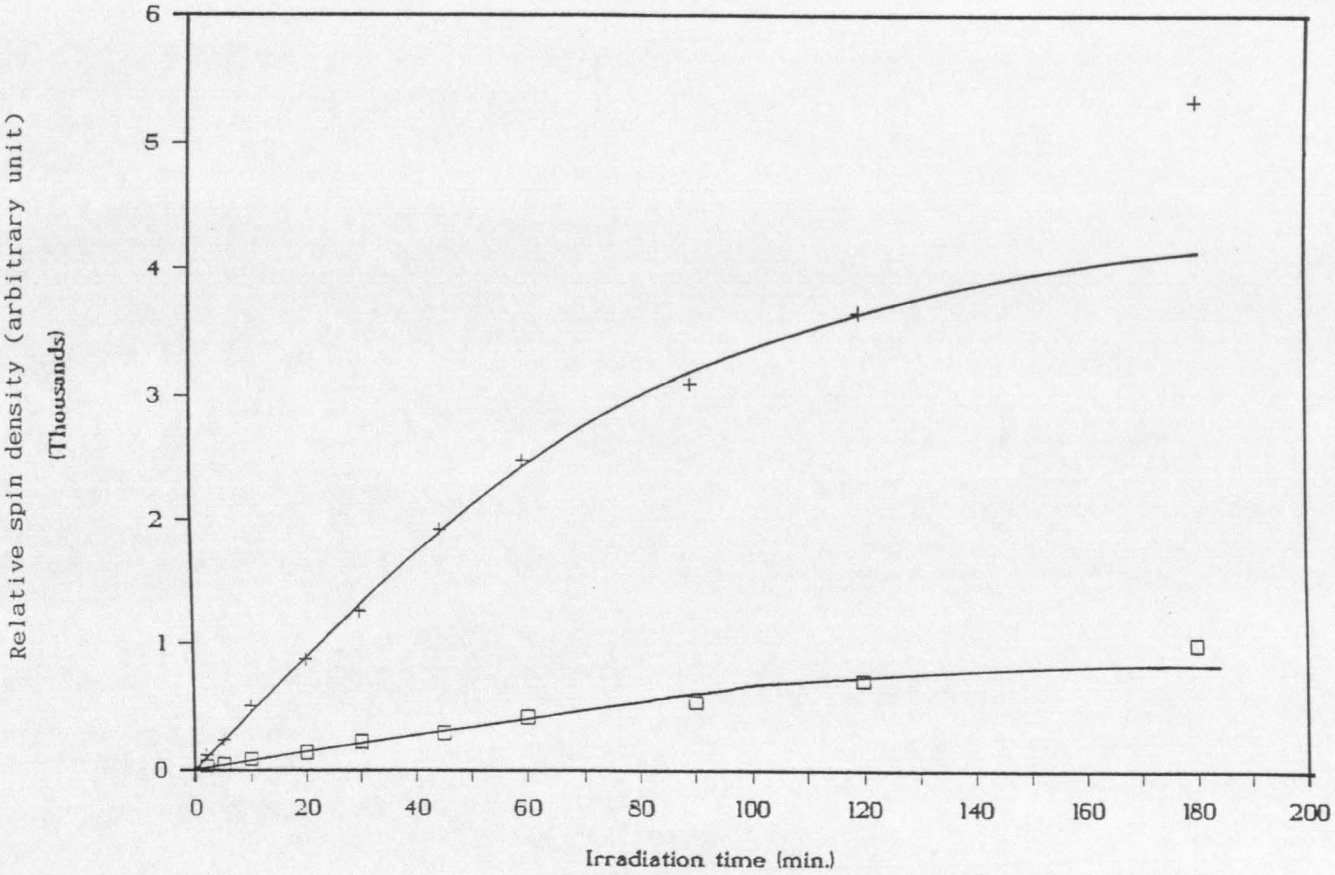


Figure (5.10) Relative spin density as a function of irradiation time.
□ spectral group (1),
+ spectral group (2).

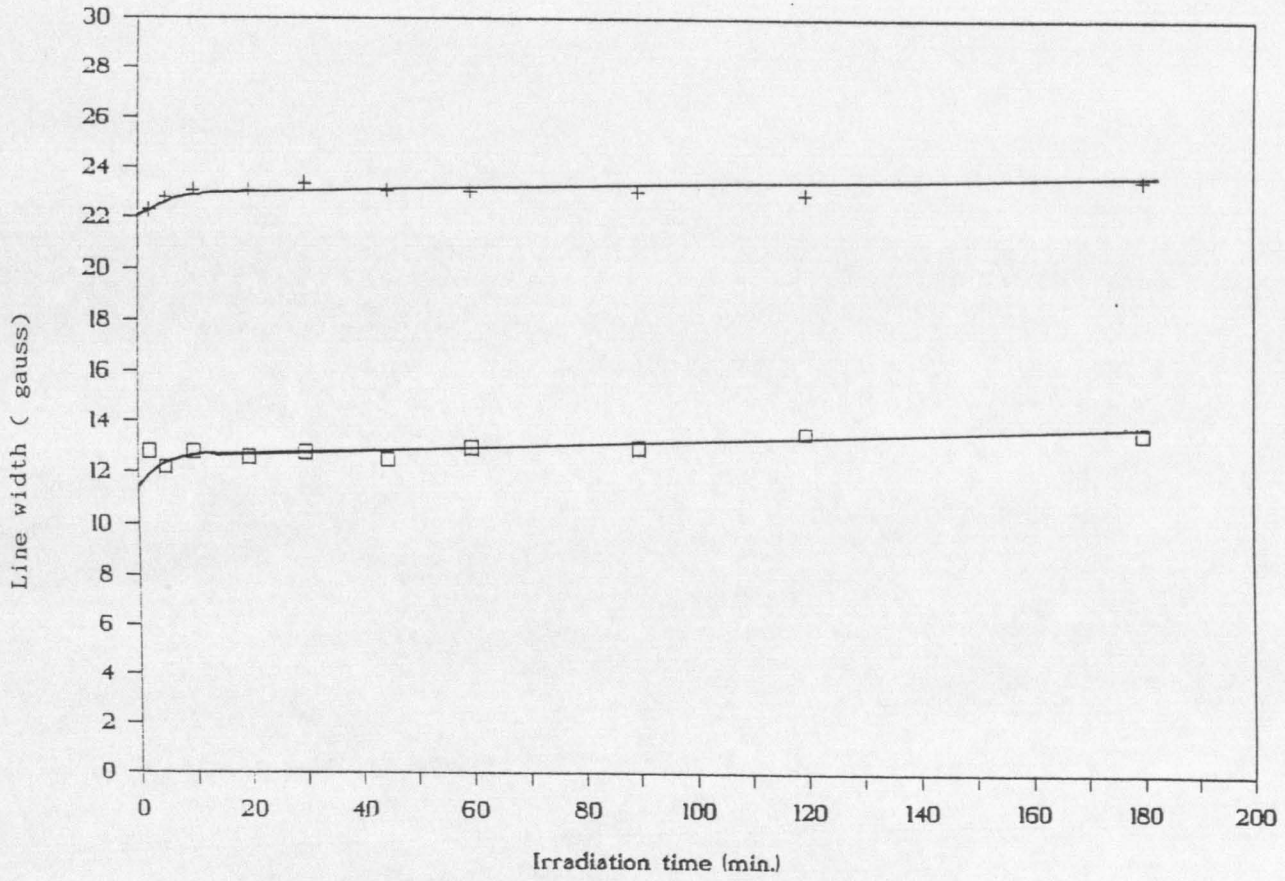


Figure (5.11) Line width as a function of irradiation time.

□ spectral group (1).

\+ spectral group (2).

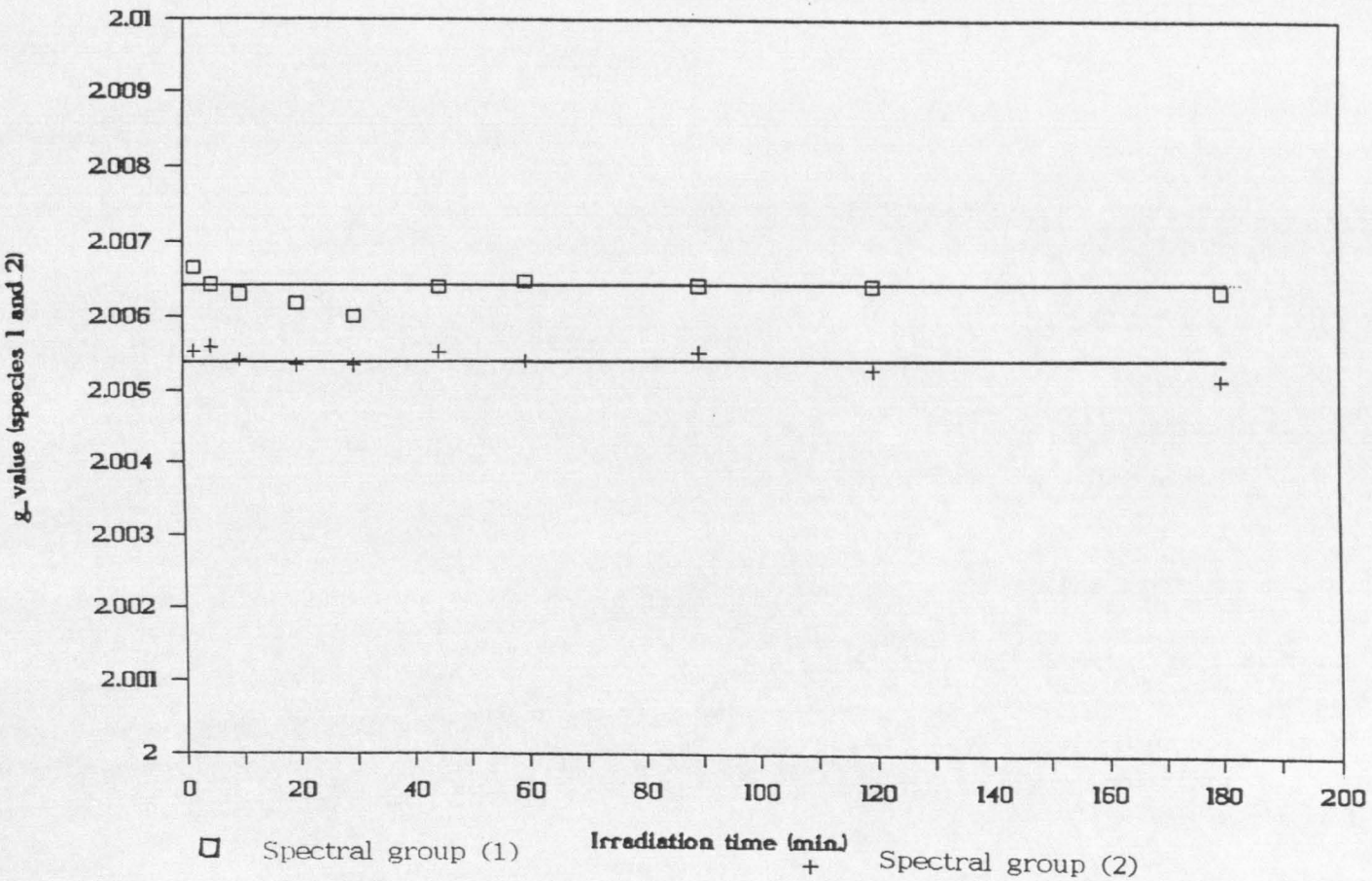


Figure (5.12) g'-value as a function of irradiation time. The irradiation and the ESR measrements were carried out at room temperature.

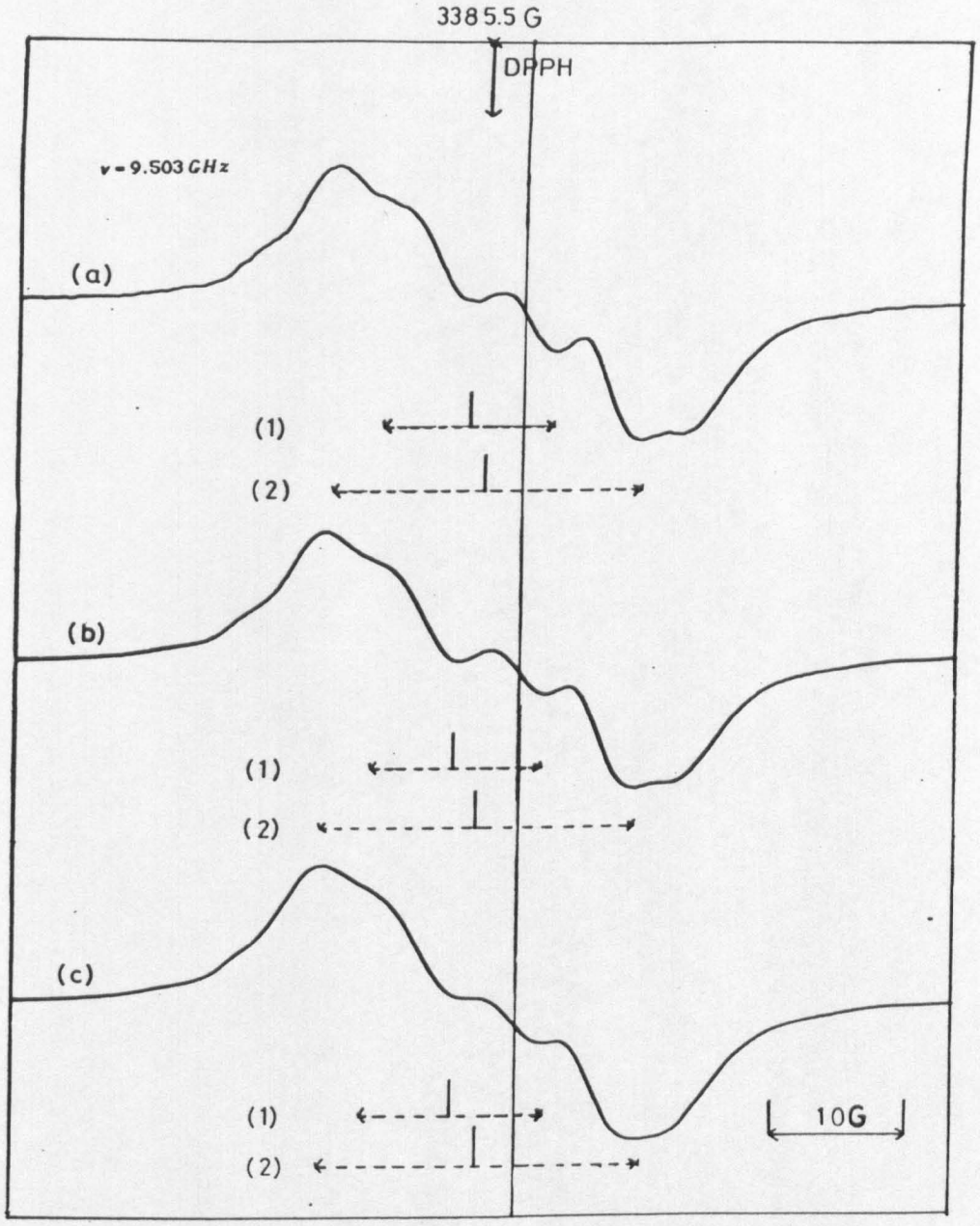


Figure (5.13) ESR spectra of x-irradiated gum, irradiated at various irradiation time. The irradiation and the measurements were carried out at room temperature. The three spectra are modified in y direction. (a) 2 min. (b) 30 min., (c) 180 min.

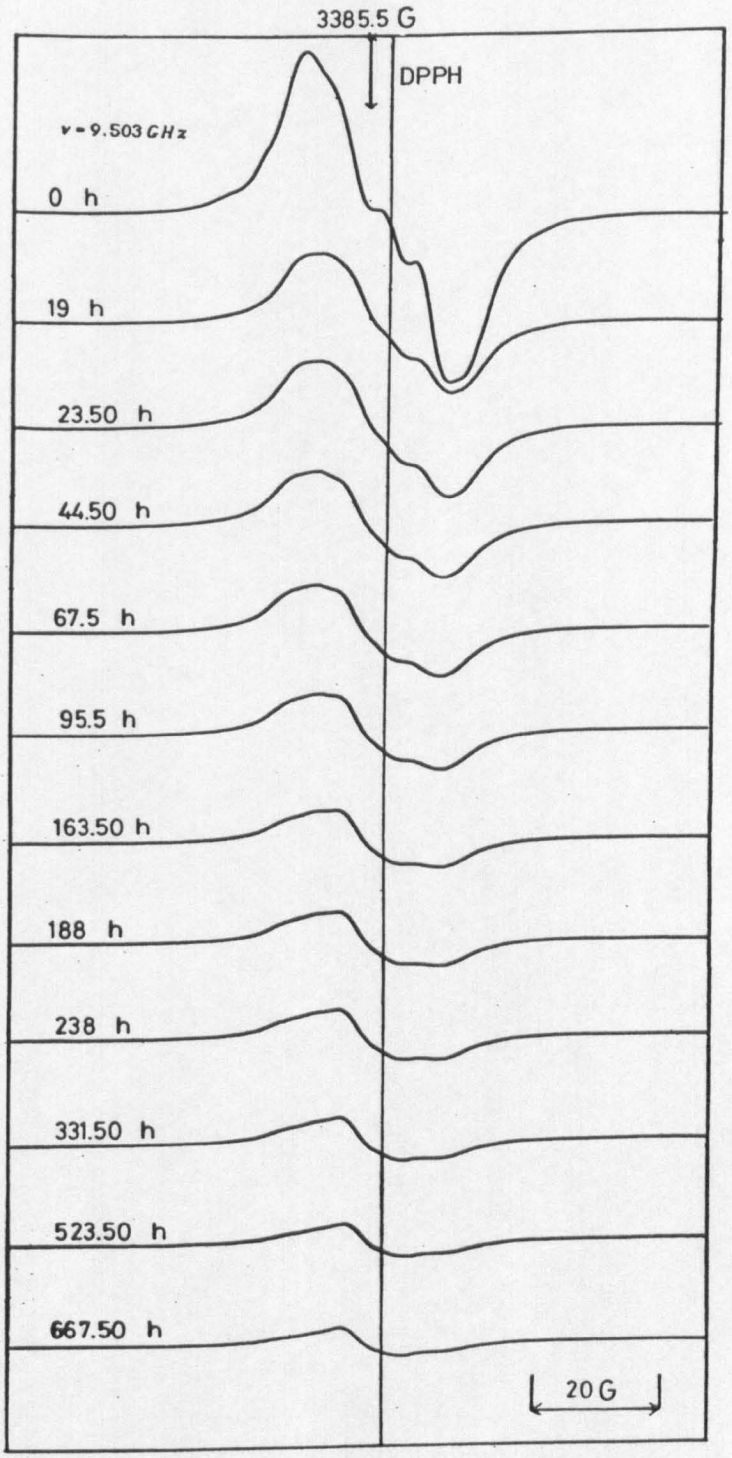


Figure (5.14) ESR spectra of irradiated gum arabic recorded at various decay timesat room temperature.

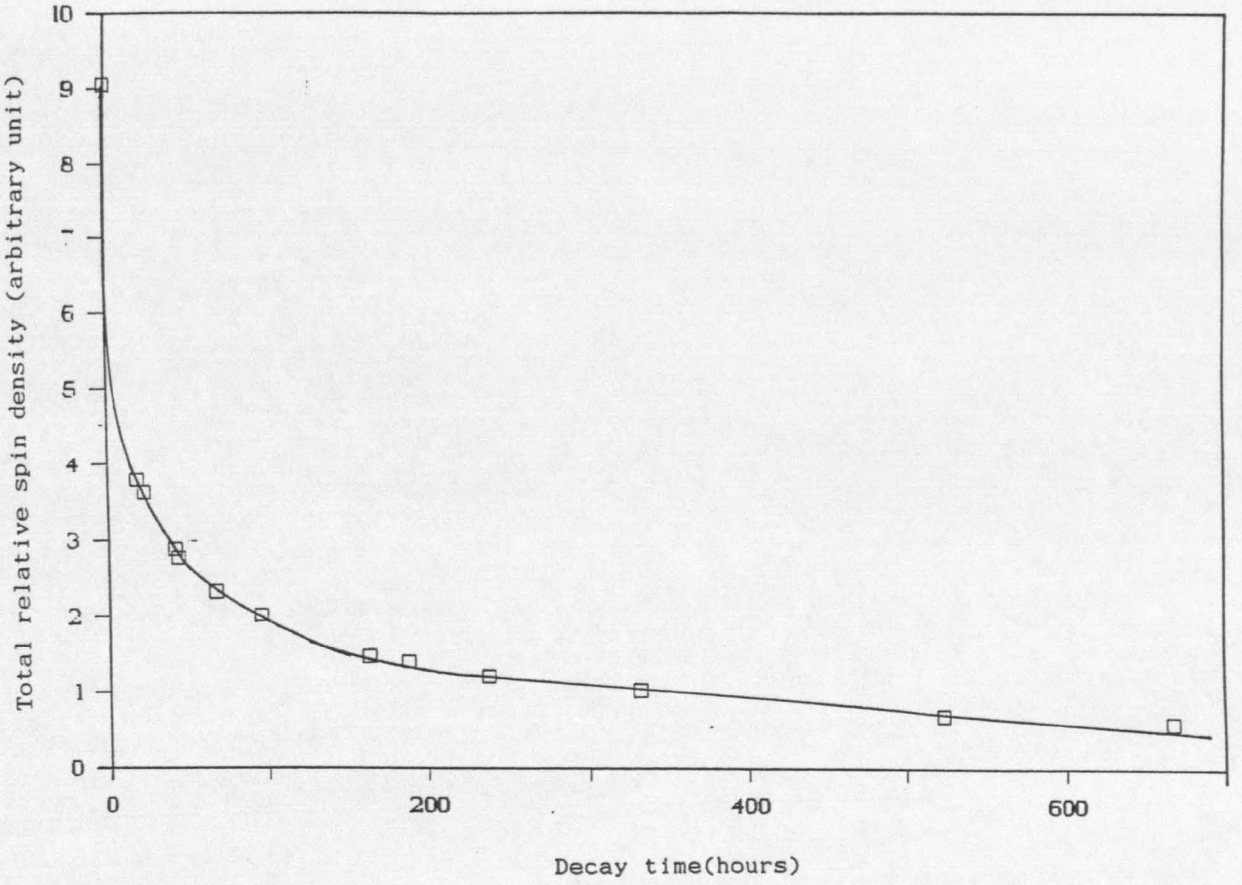


Figure (5.15) Total relative spin density as a function of decay time.

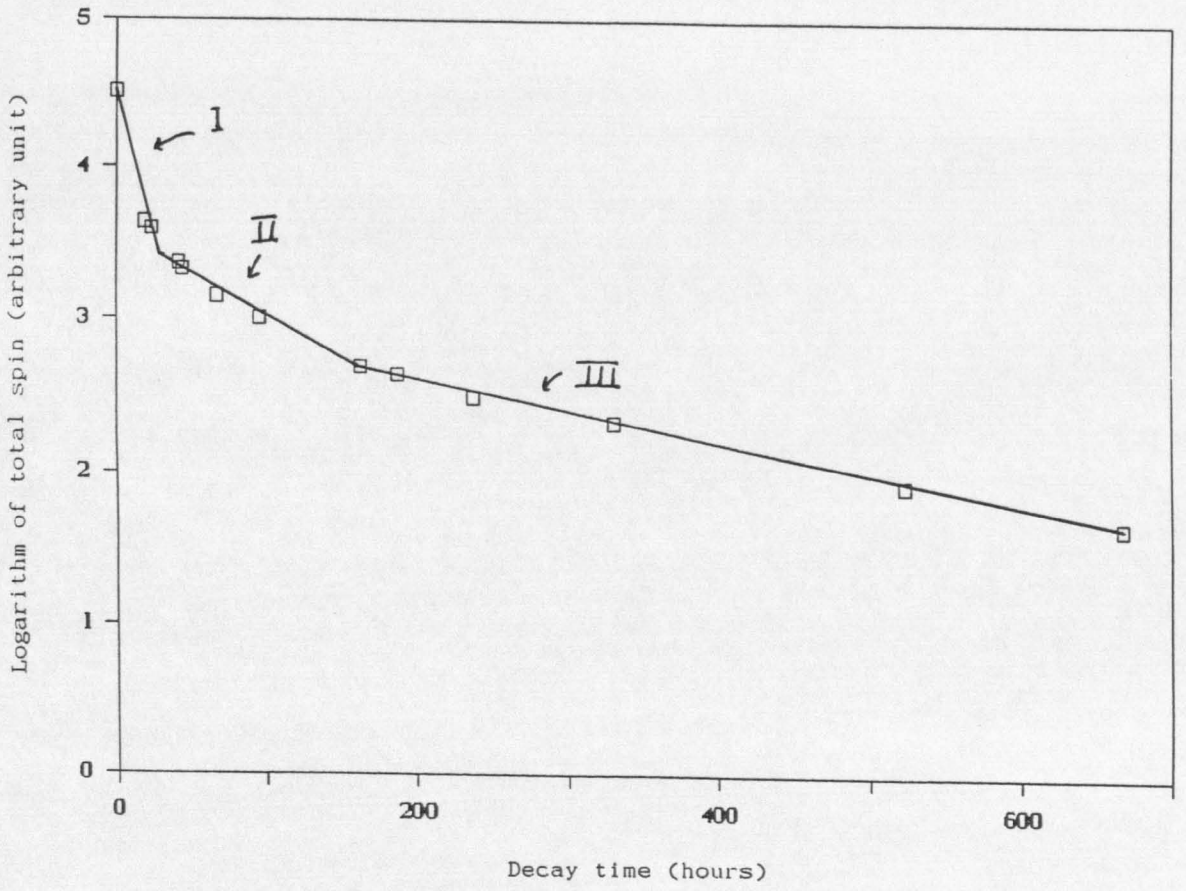


Figure (5.16) logarithm of total relative spin as a function of the decay time.

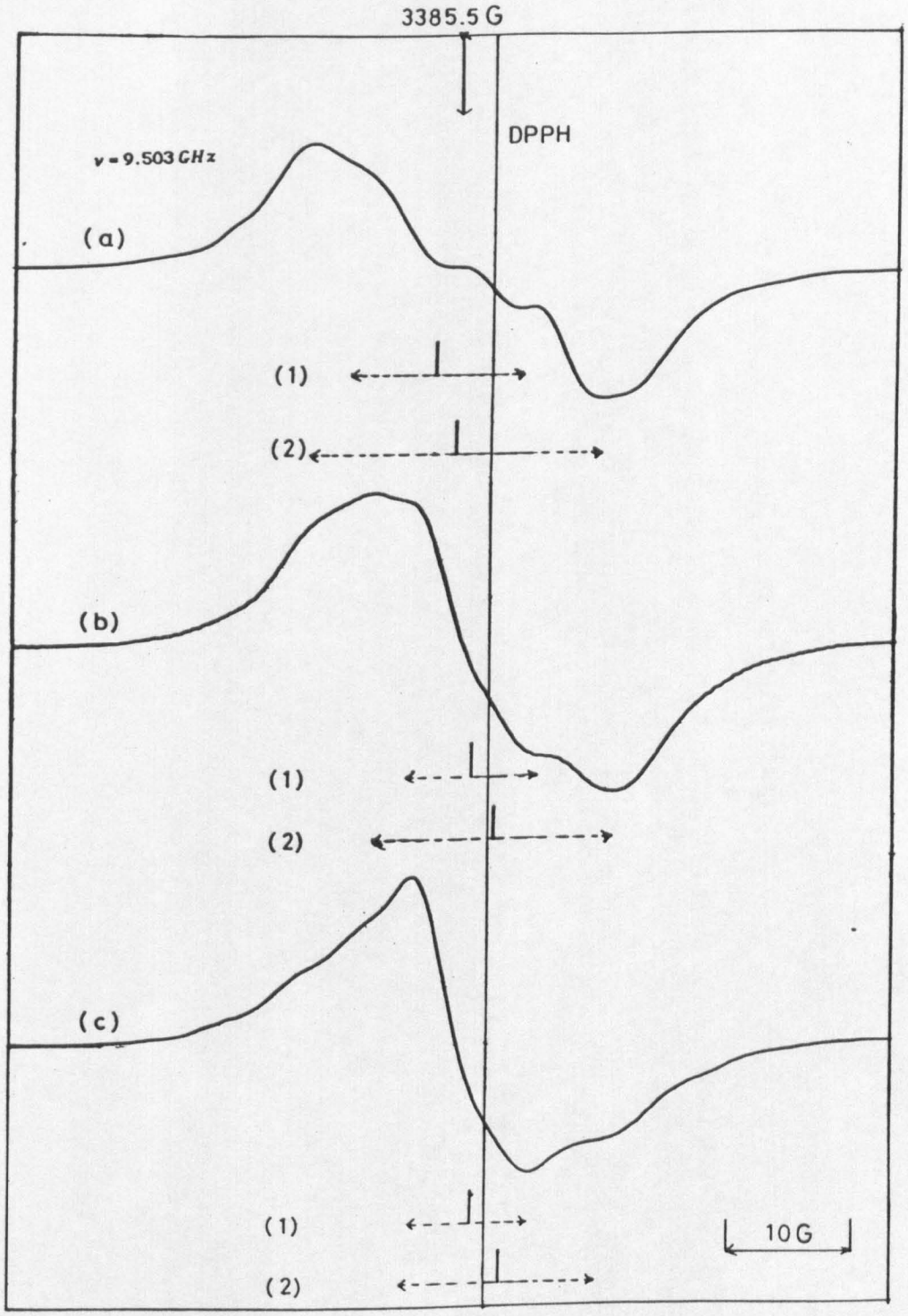


Figure (5.17) ESR spectra of x-irradiated gum arabic, recorded at various decay time at room temperature. The spectra are modified in y direction (a) recorded immediately after irradiation, (b) recorded after 95.5 hours of irradiation, (c) recorded after 667.5 hours of irradiation.

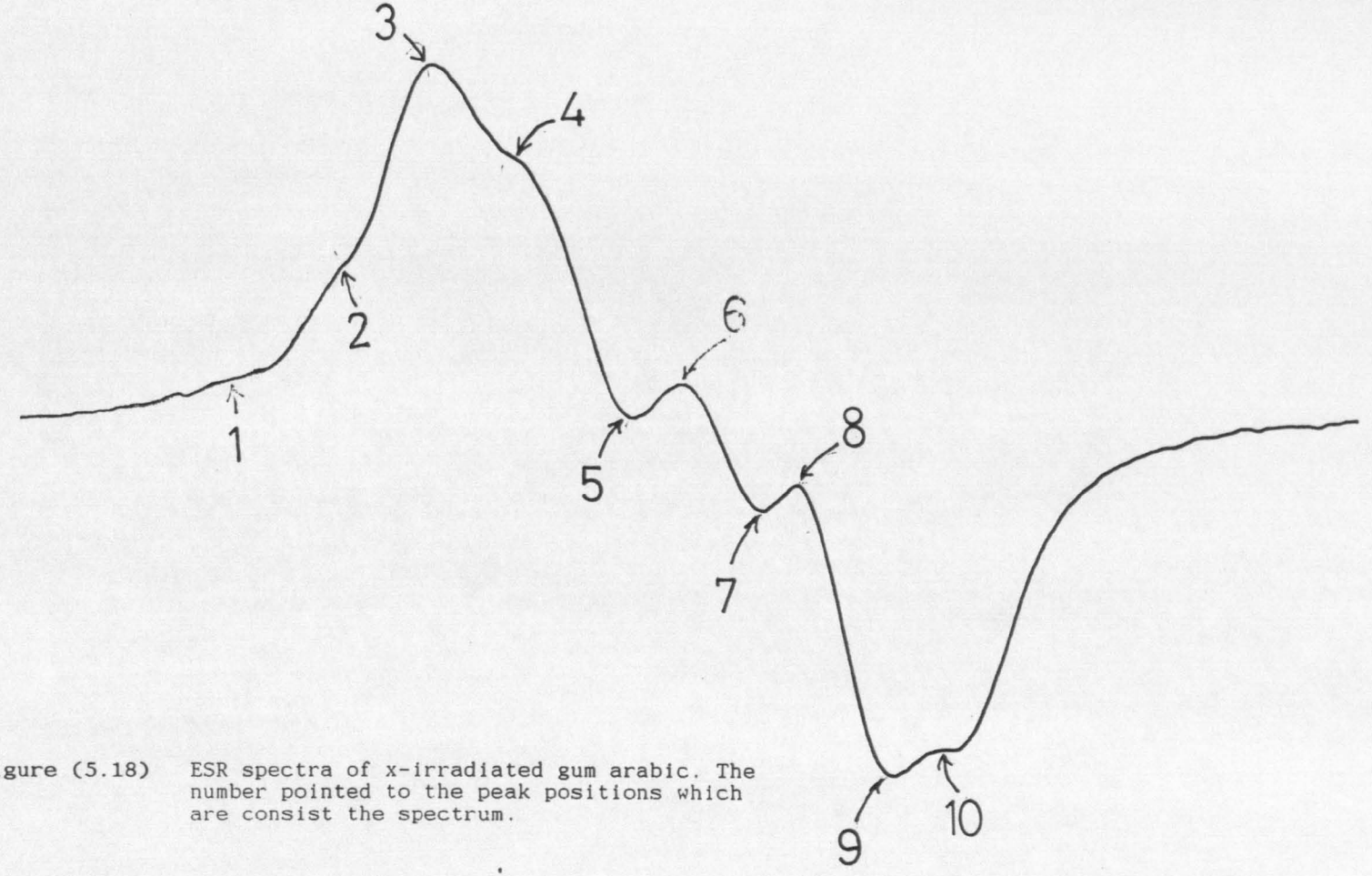


Figure (5.18) ESR spectra of x-irradiated gum arabic. The number pointed to the peak positions which are consist the spectrum.

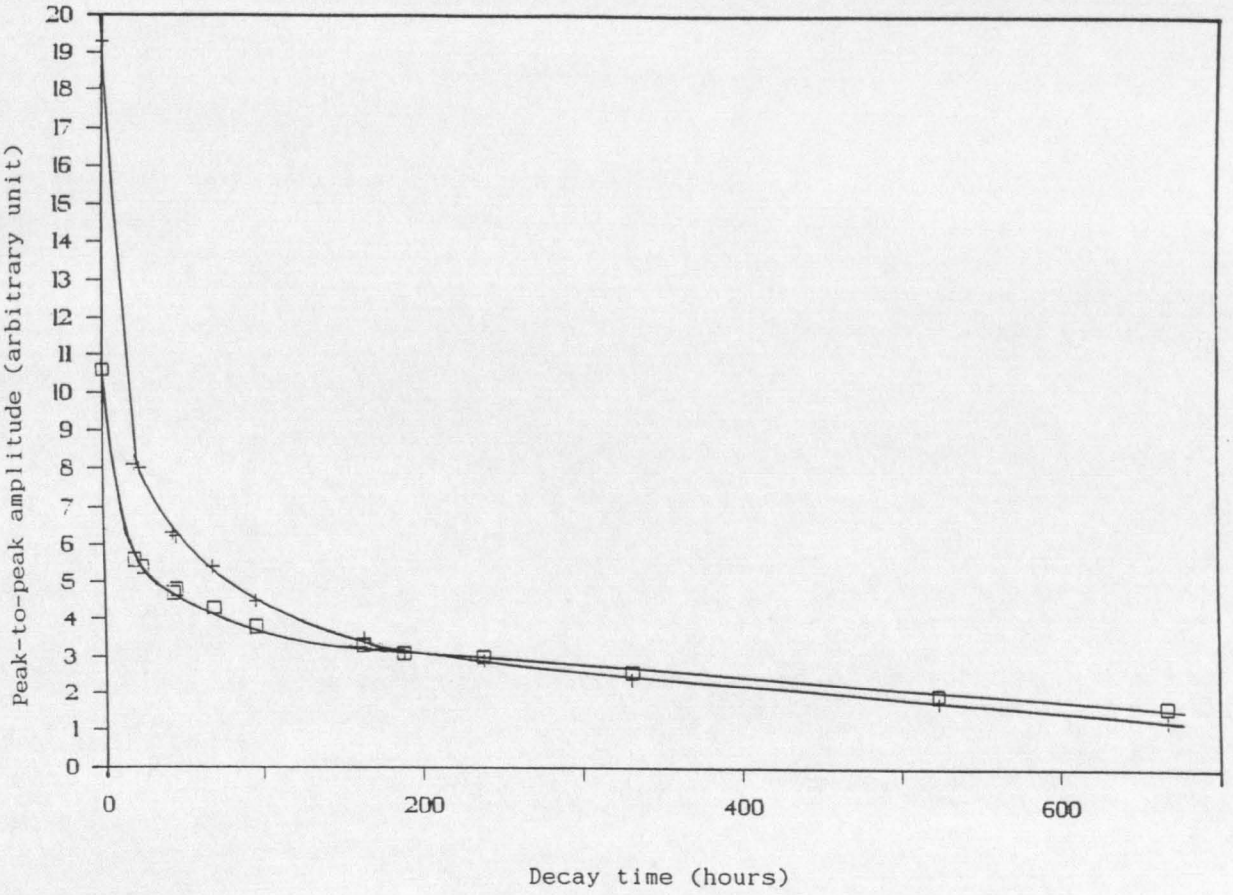


Figure (5.19) Peak-to-peak amplitude as a function of decay time.
□ spectral group (1).
\+ spectral group (2).

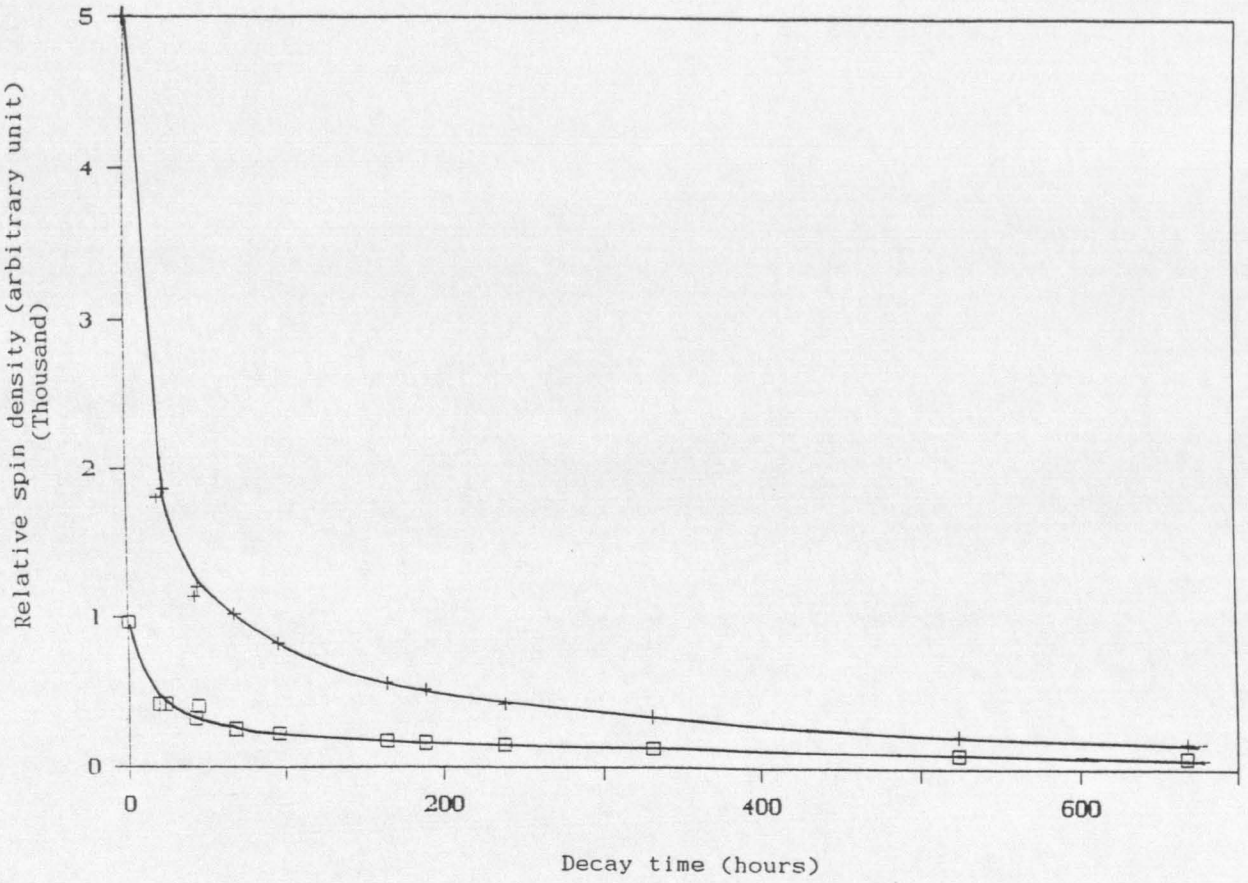


Figure (5.20) Relative spin density as a function of the decay time.
□ spectral group (1),
+ spectral group (2).

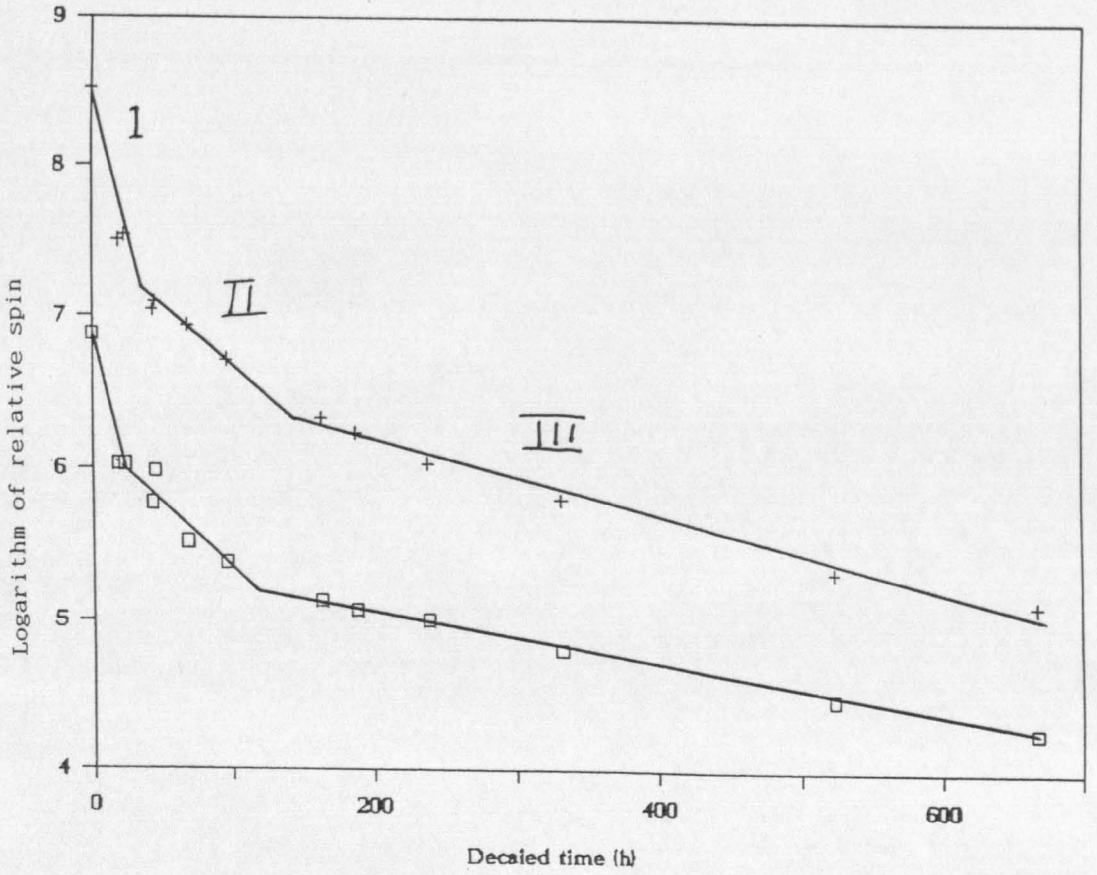


Figure (5.21) Logarithm of relative spin as a function OF decay time.
□ spectral group (1),
+ spectral group (2).

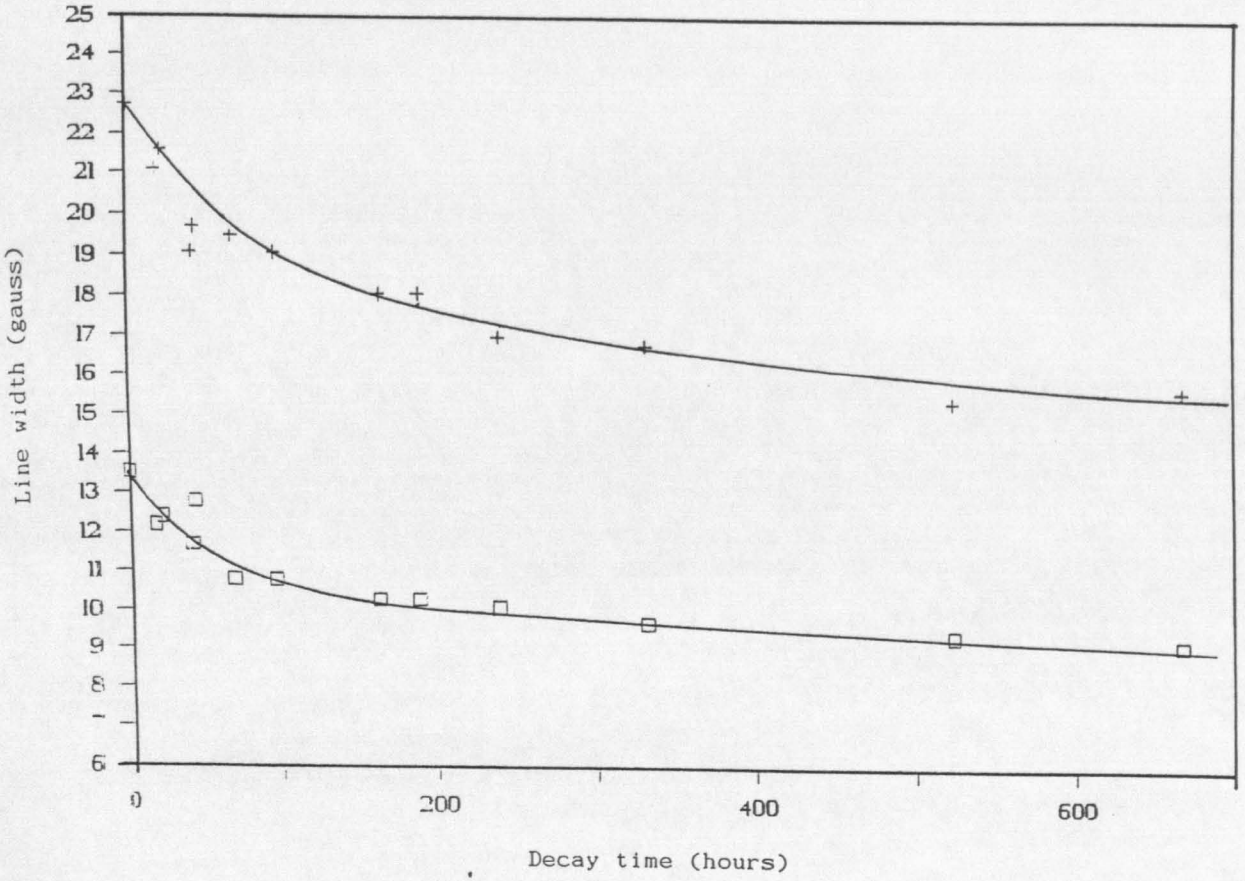


Figure (5.22) line width as a function of decay time.
□ spectral group (1),
+ spectral group (2).

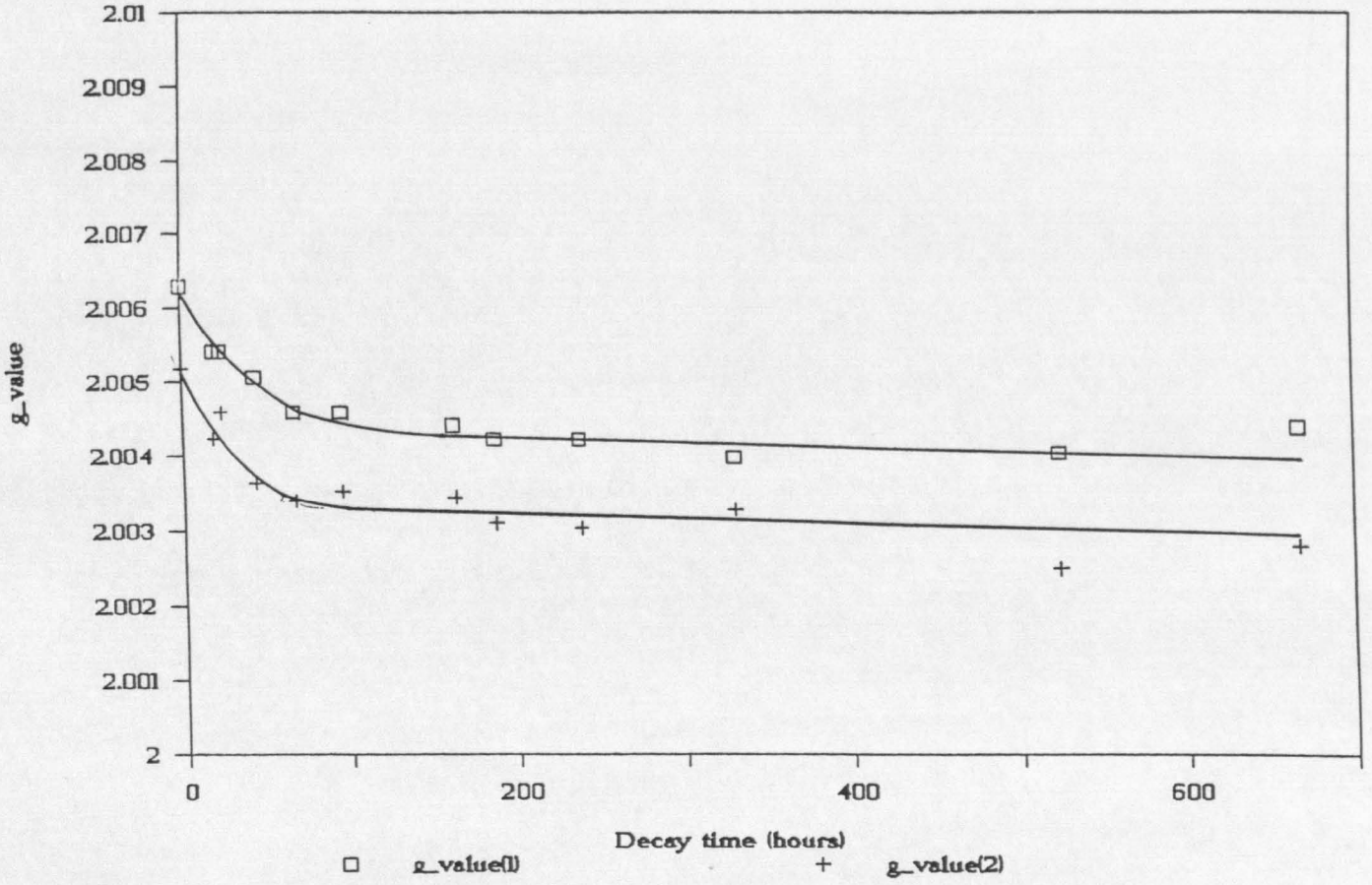


Figure (5.23) G-value as a function of decay time, of x-irradiated gum arabic at room temperature.

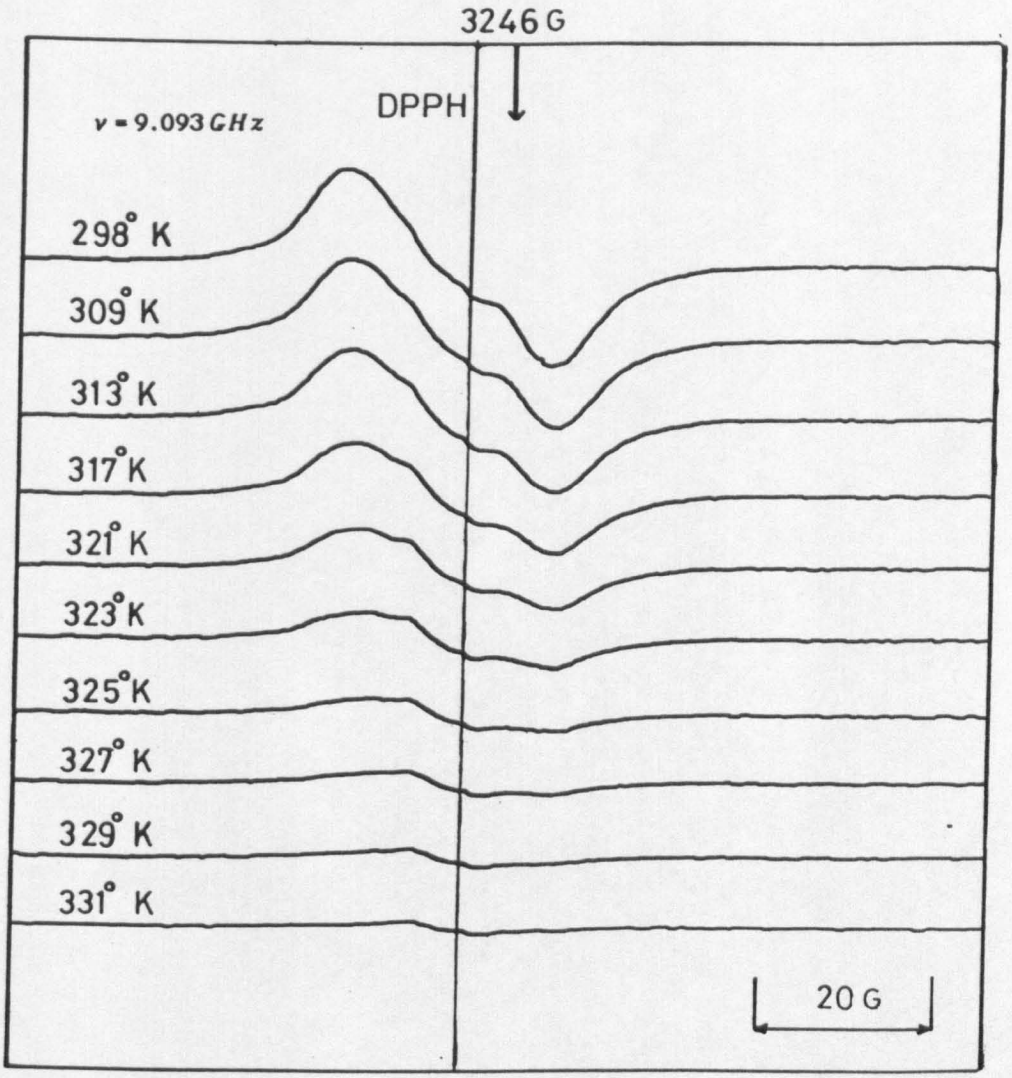


Figure (5.24) ESR spectra of x-irradiated gum arabic at room temperature. recorded at various temperature.

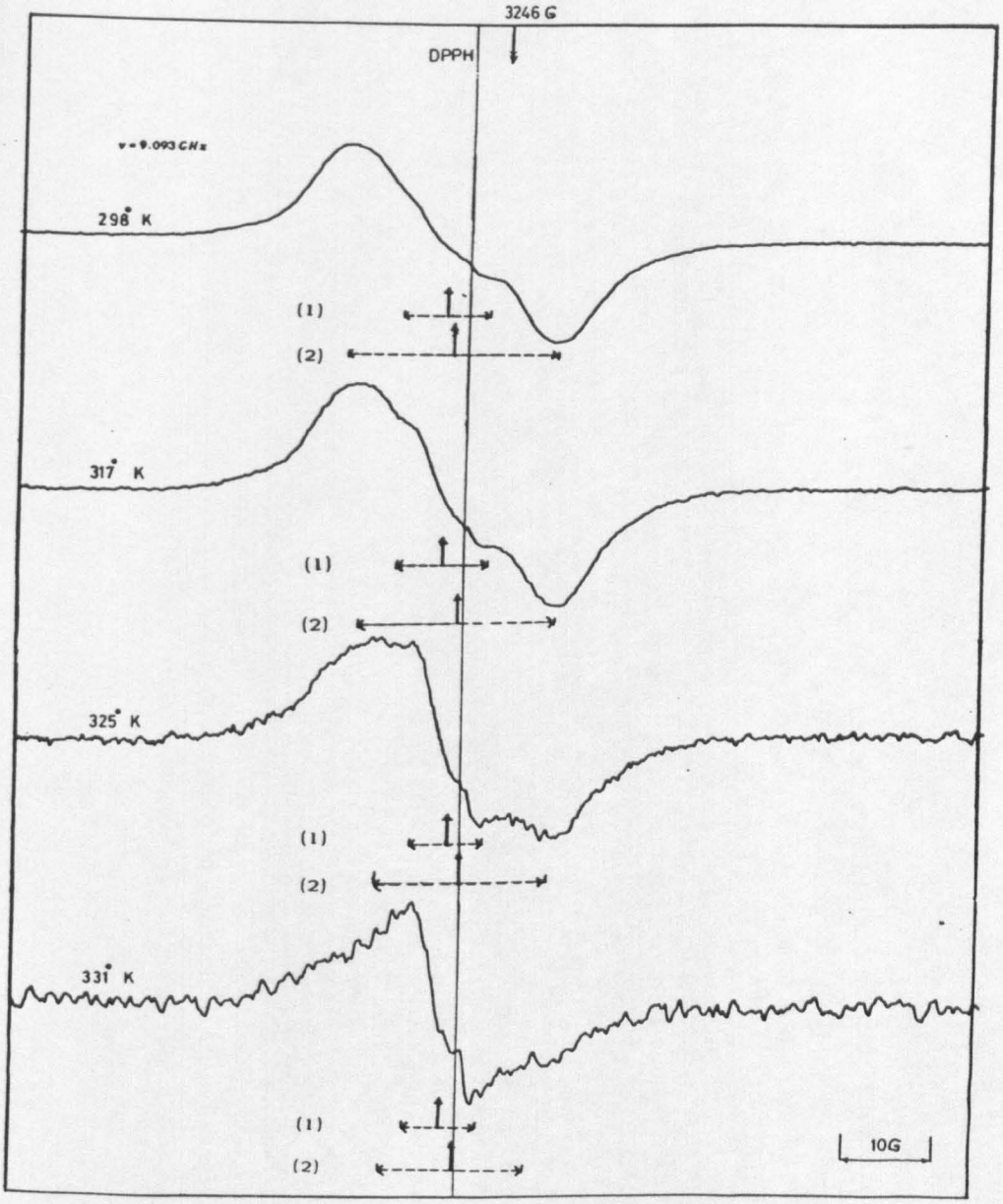


Figure (5.25) ESR spectra of x-irradiated gum arabic, recorded at variouse temperatures. The spectra are modefied in y direction.

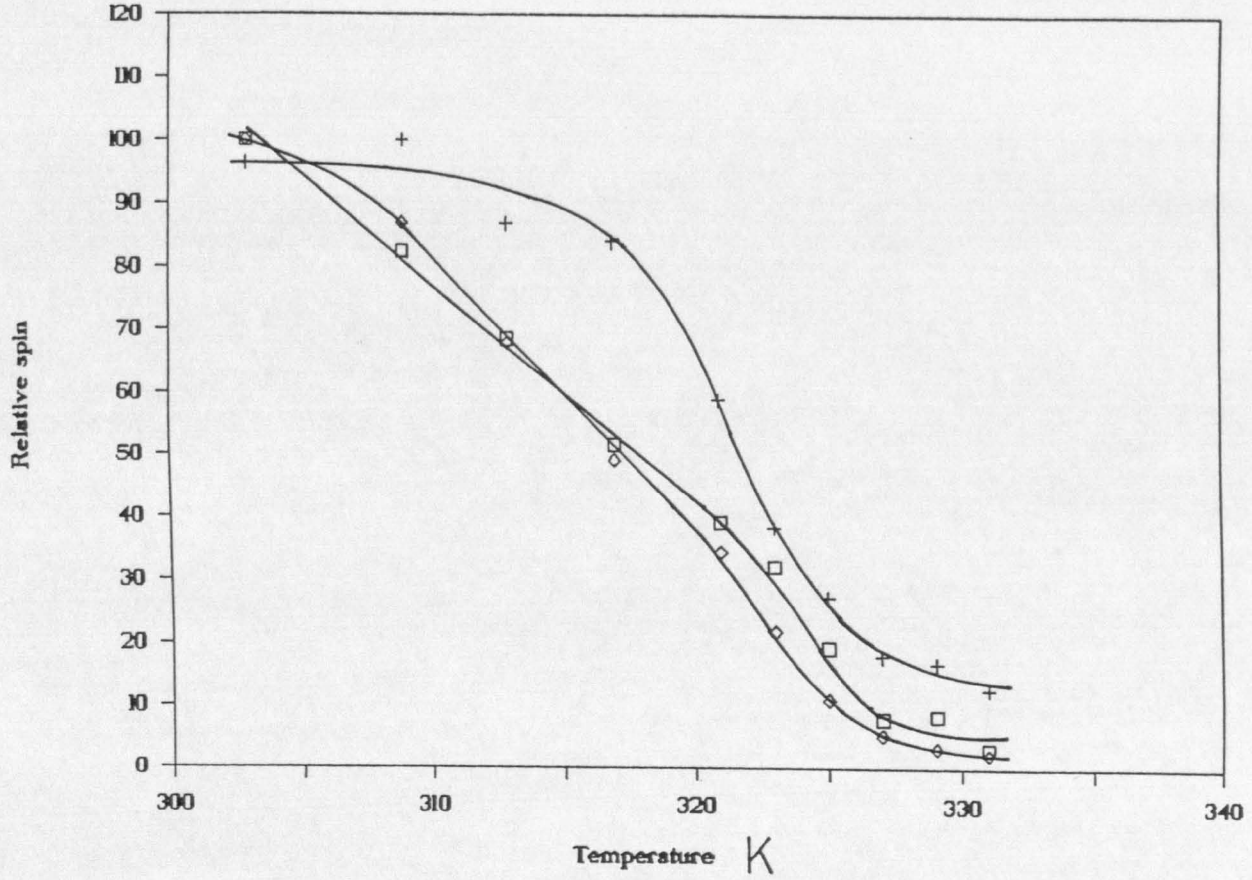


Figure (5.26) Relative spin density (in normalization condition) as a function of temperature.
□ Total spin density,
+ spectral group (1),
◇ spectral group (2).

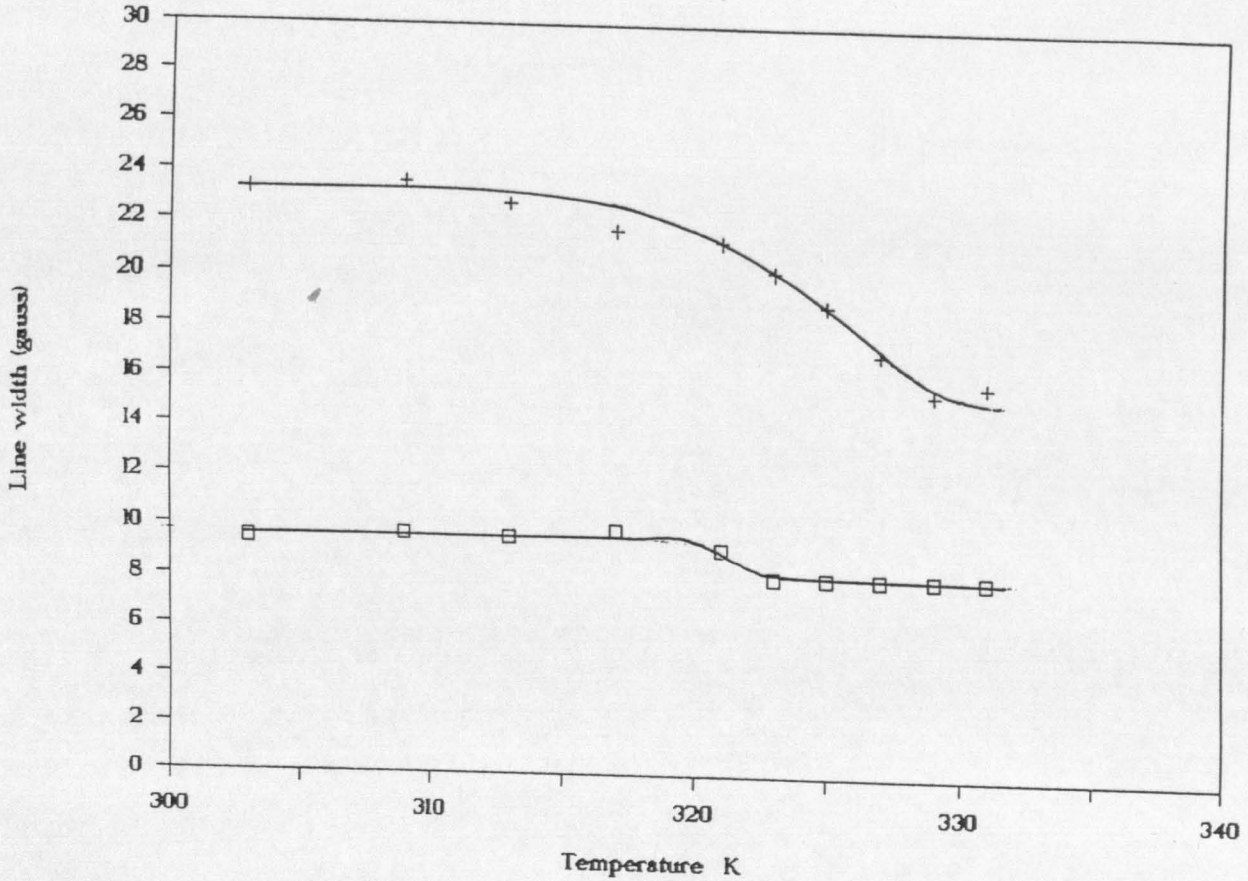


Figure (5.27) Line width as a function of temperature of x-irradiated gum arabic.
□ Spectral group (1).
+ Spectral group (2).

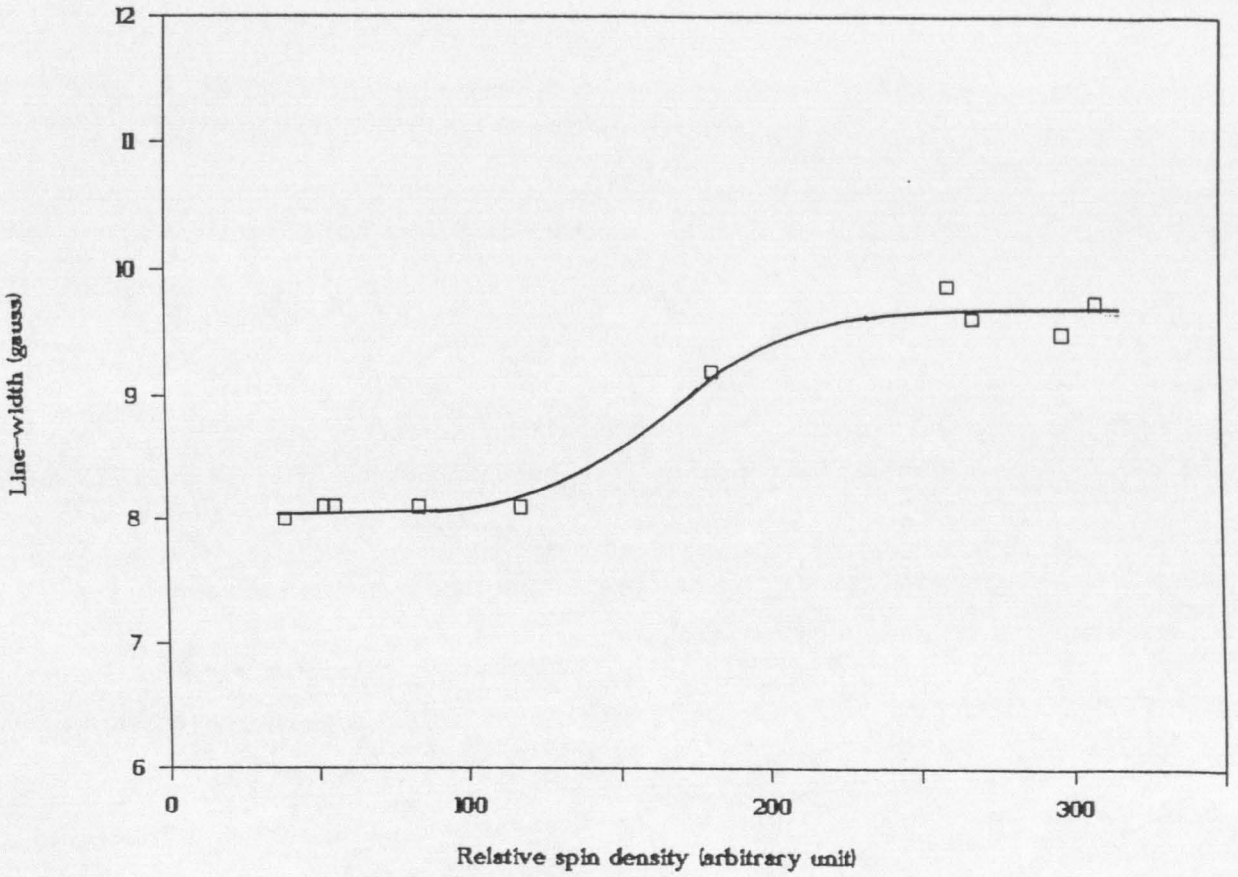


Figure (5.28) Line-width as a function of relative spin density of spectral group (1).

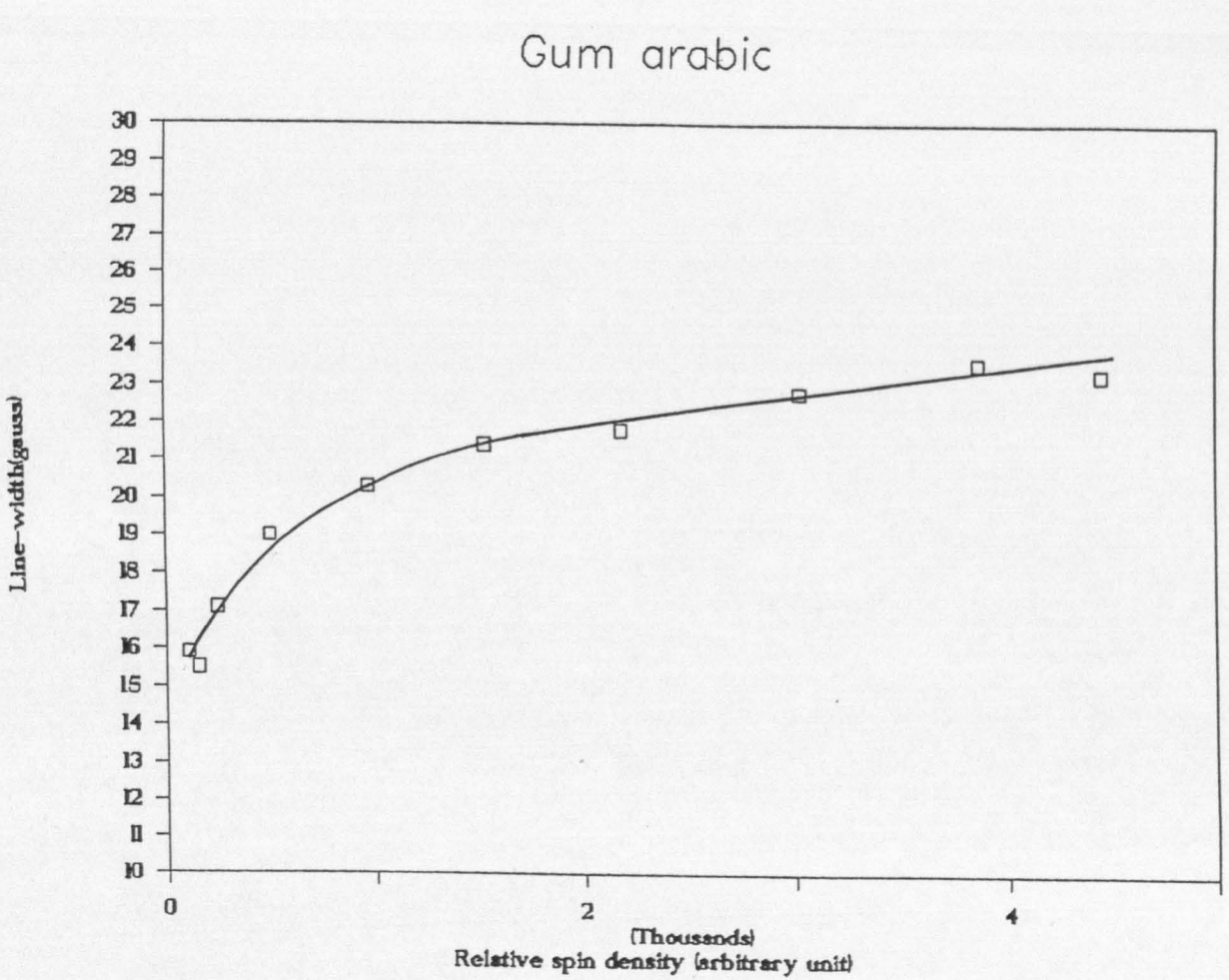


Figure (5.29) Line-width as a function of relative spin density of spectral group (2).

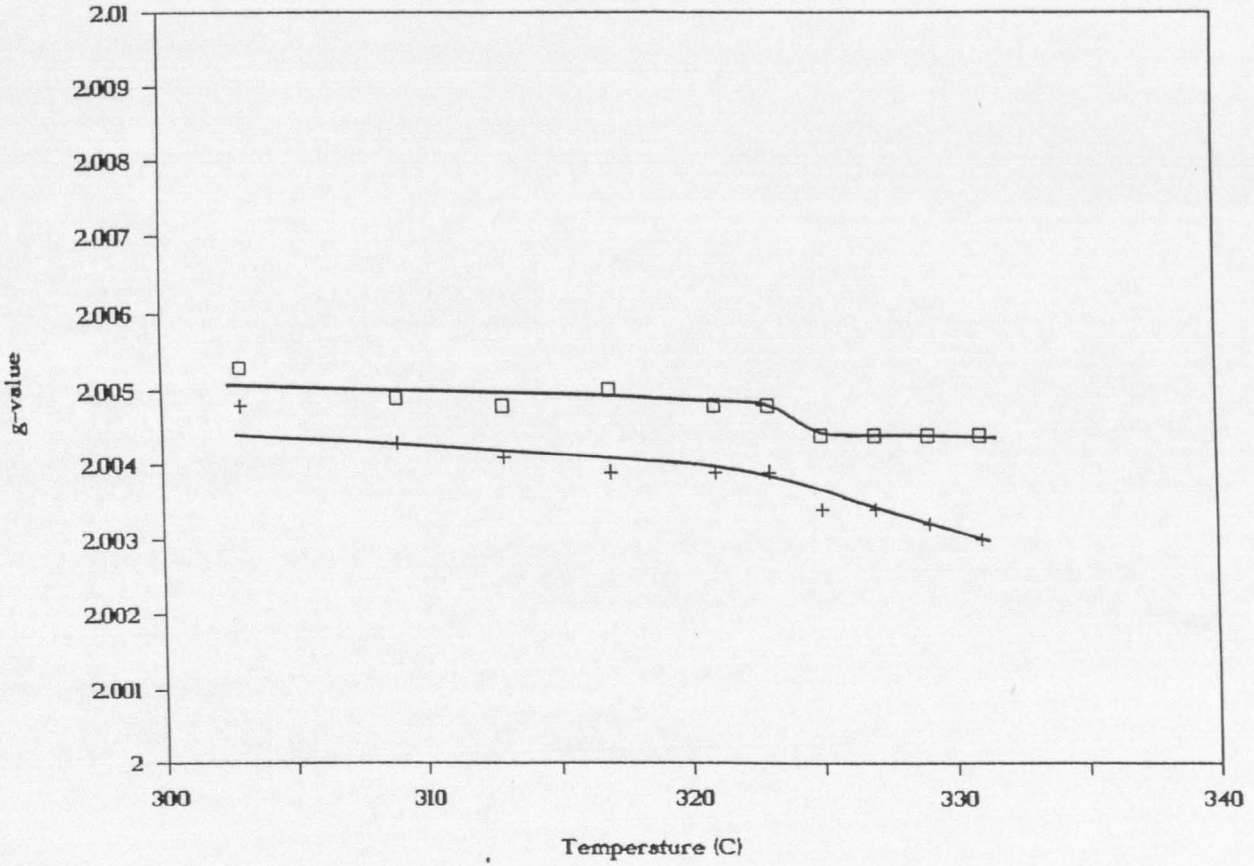


Figure (5.30) **g**-value as a function of temperature of x-irradiated gum arabic .
□ spectral group(1),
+ spectral group (2).

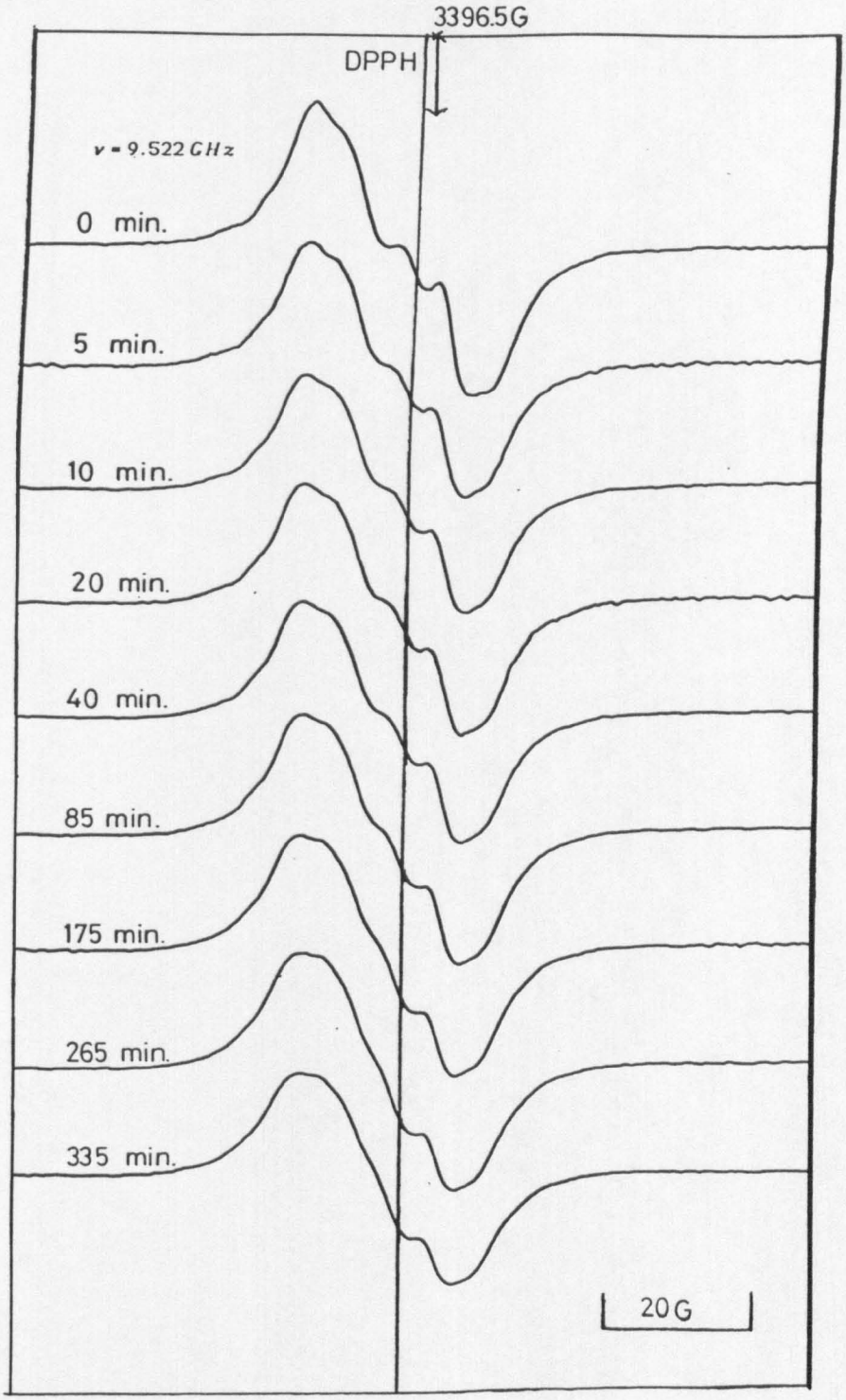


Figure (5.31) ESR spectra of x-irradiated gum arabic, exposed to mercury light with various times of irradiation.

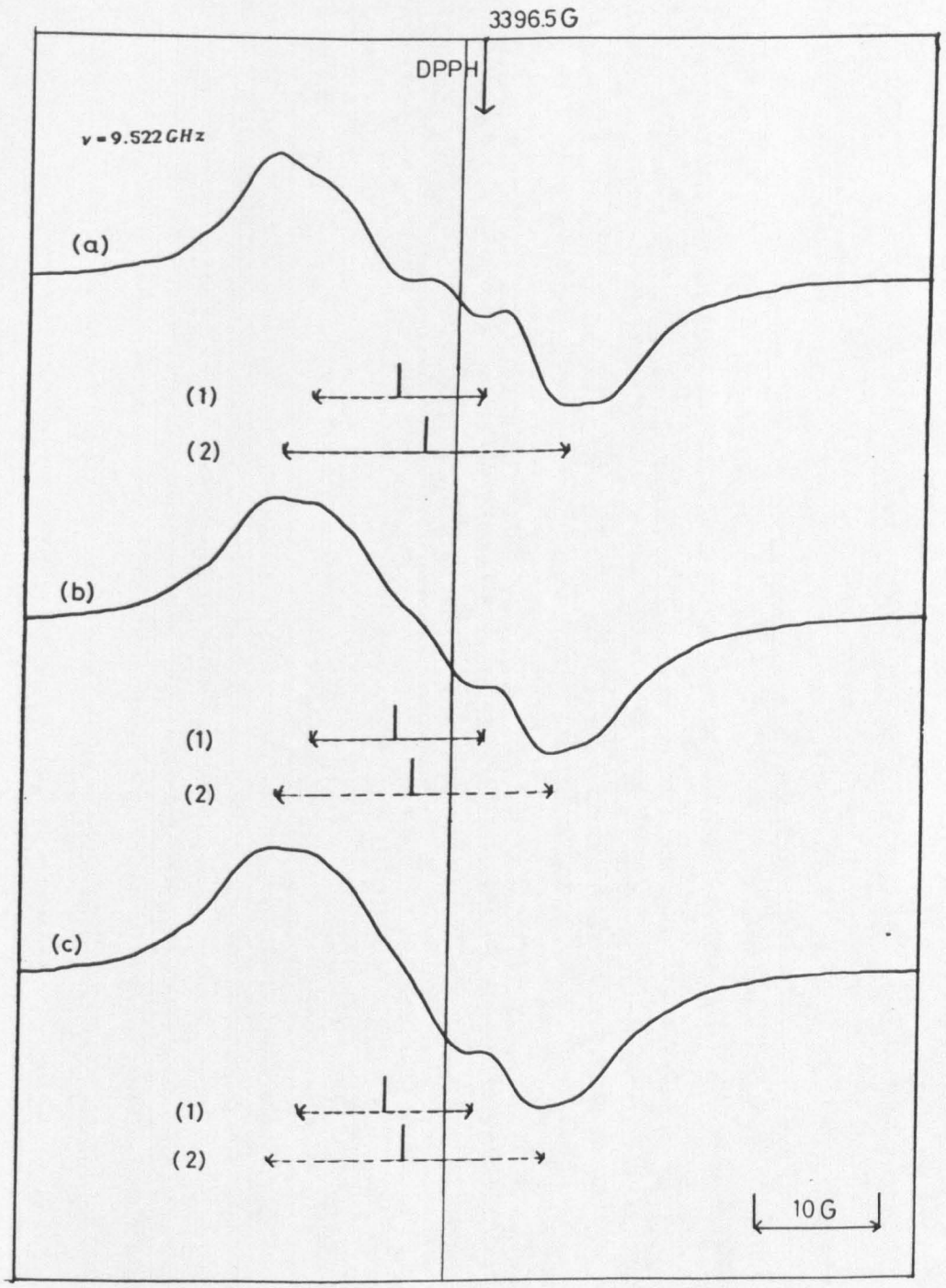


Figure (5.32) ESR spectra of x-irradiated gum arabic, recorded with various exposing time to mercury light. (a) without exposing to mercury light, (b) 175 minutes exposing to the mercury light, (c) 355 minutes exposing to the mercury light. (All the spectra are modefied in y direction.

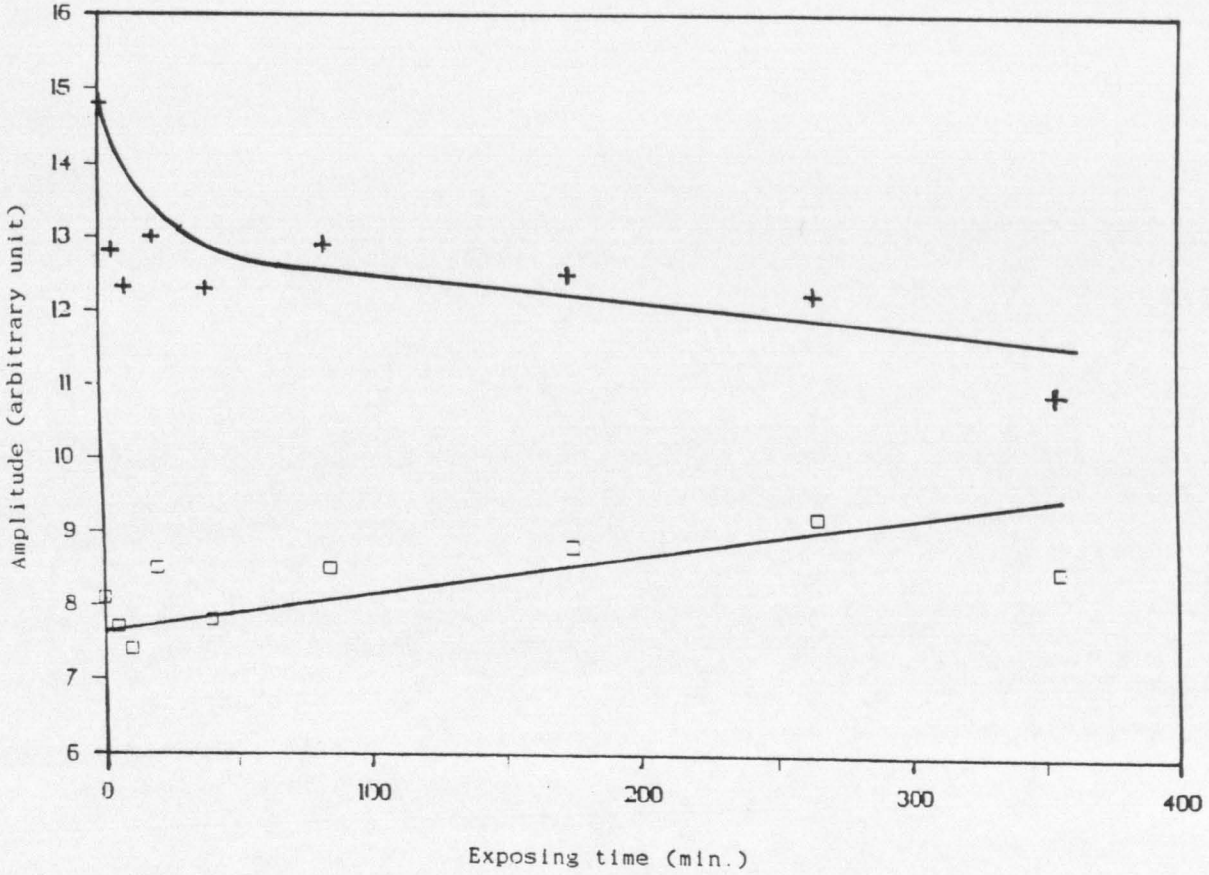


Figure (5.33) Amplitude peak-to-peak as a function of exposing time to mercury light.
□ spectral group (1),
+ spectral group (2).

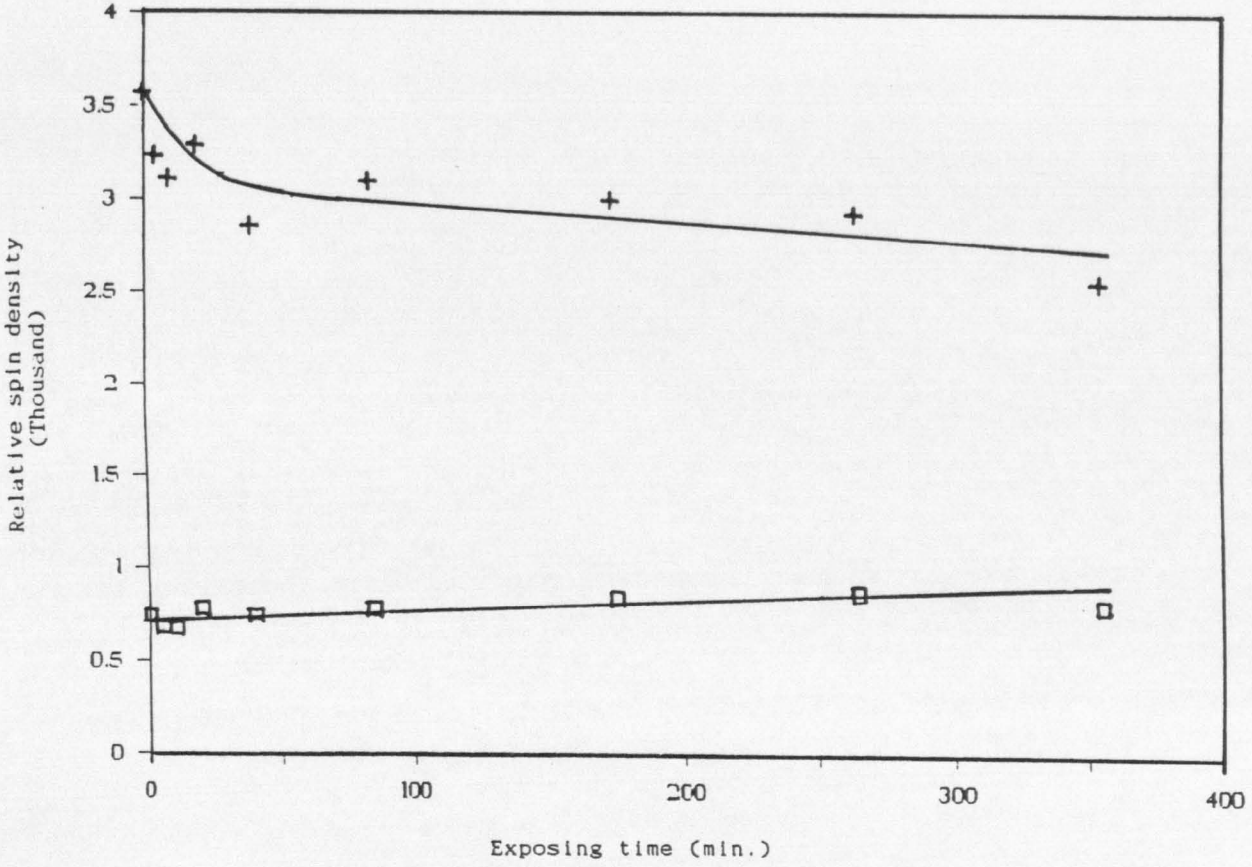


Figure (5.34) Relative spin density as a function of exposing time to mercury light.
□ spectral group (1),
+ spectral group (2).

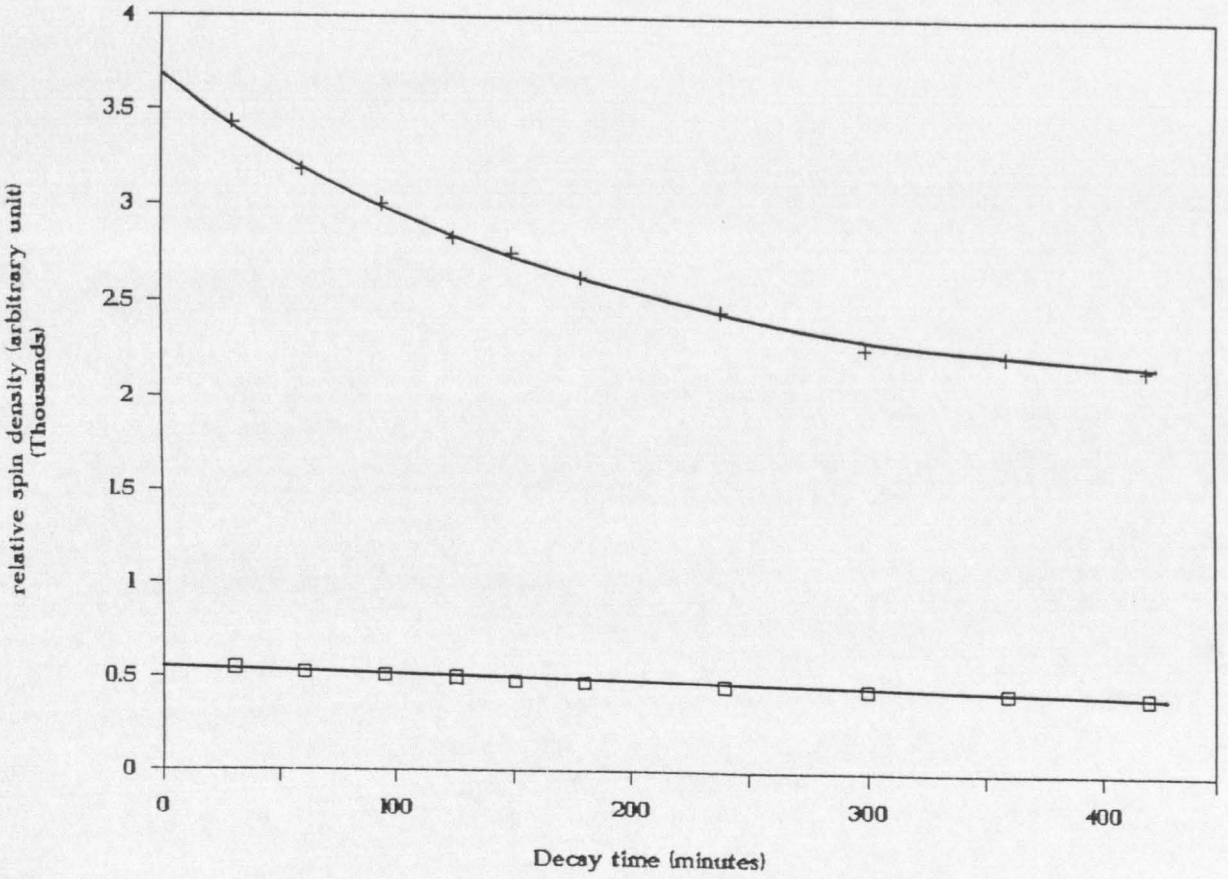


Figure (5.35) Relative spin density as a function of decay time of x-irradiated gum arabic
□ Spectral group (1),
\+ spectral group(2).

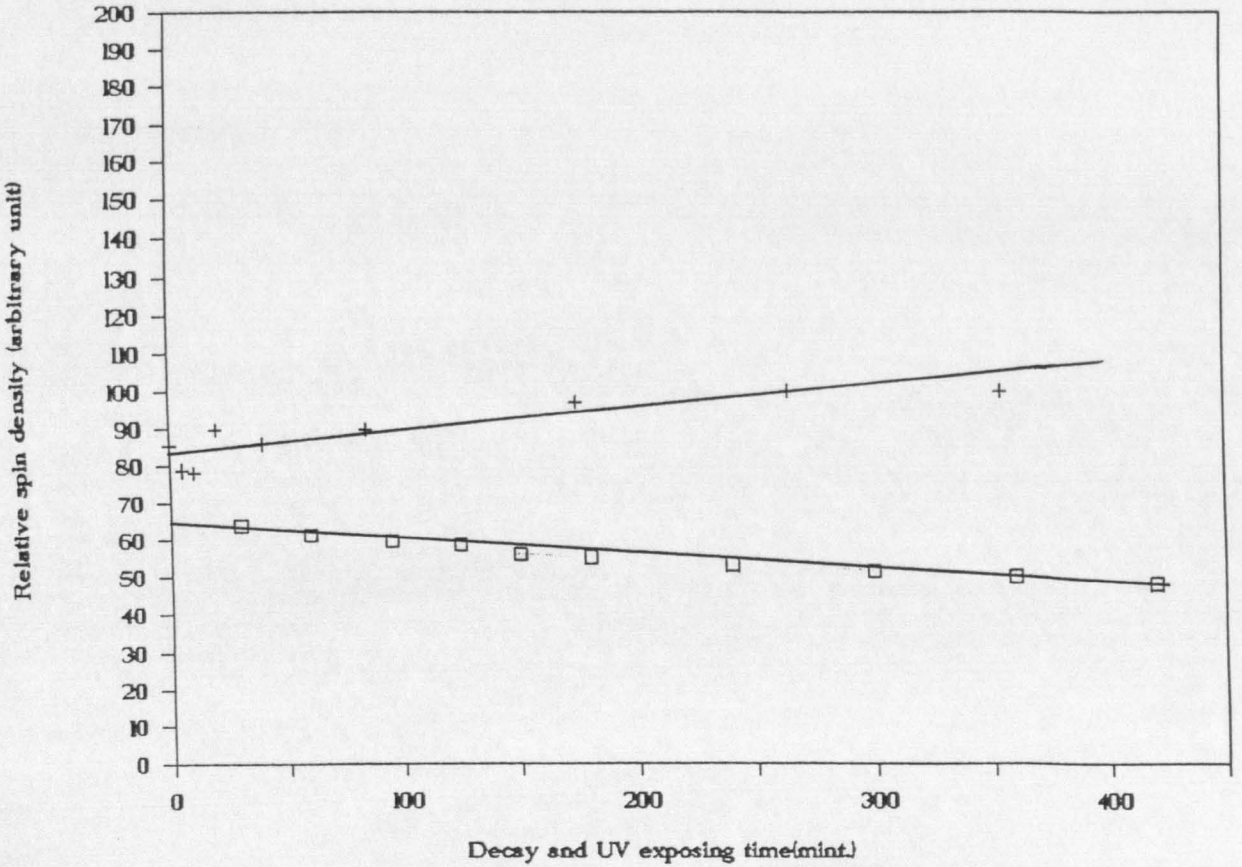


Figure (5.36) Relative spin density as a function of:
□ Decay time at room temperature,
\+ UV exposure time, of spectral group(1) of x-irradiated gum arabic.

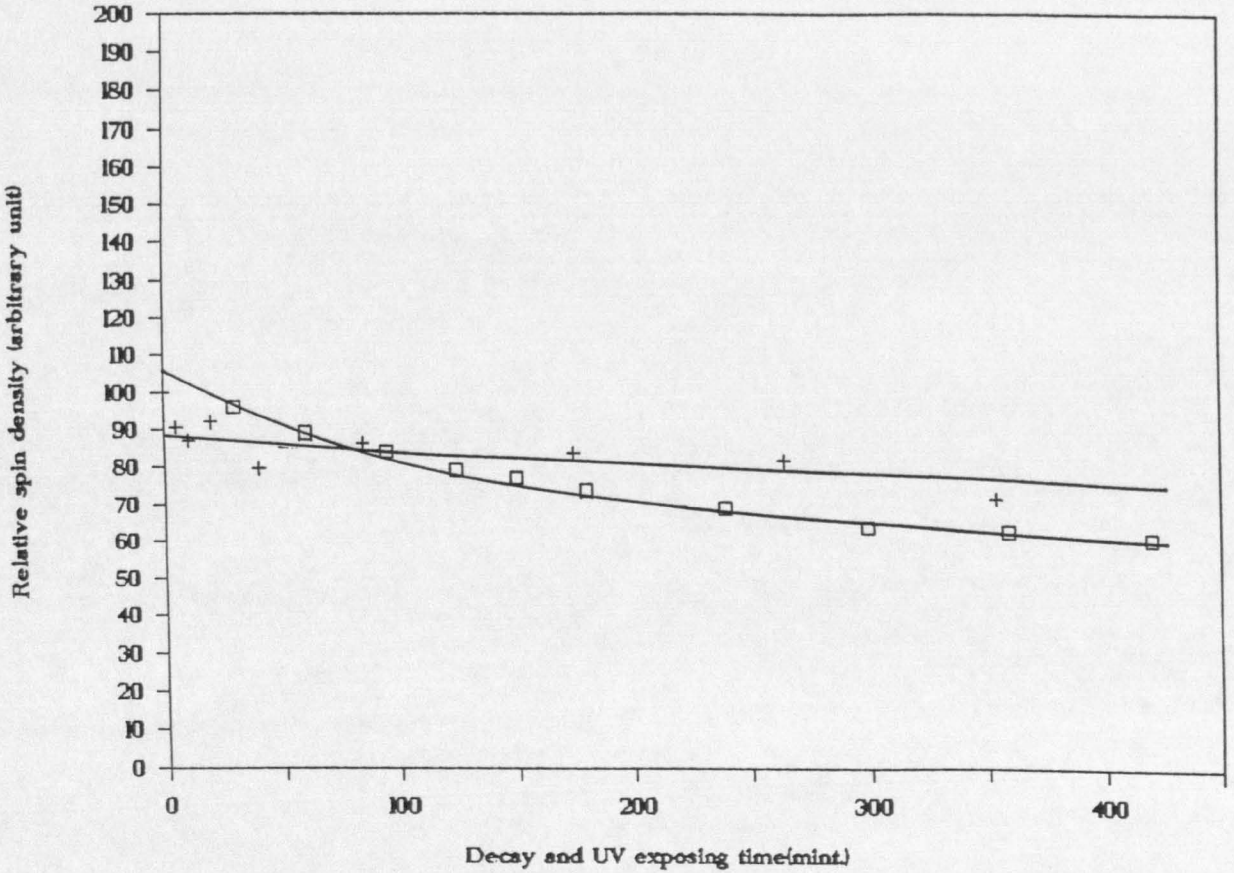


Figure (5.37) Relative spin density as a function of:
□ Decay time at room temperature,
\+ UV exposure time, of spectral group(2) of x-irradiated gum arabic.

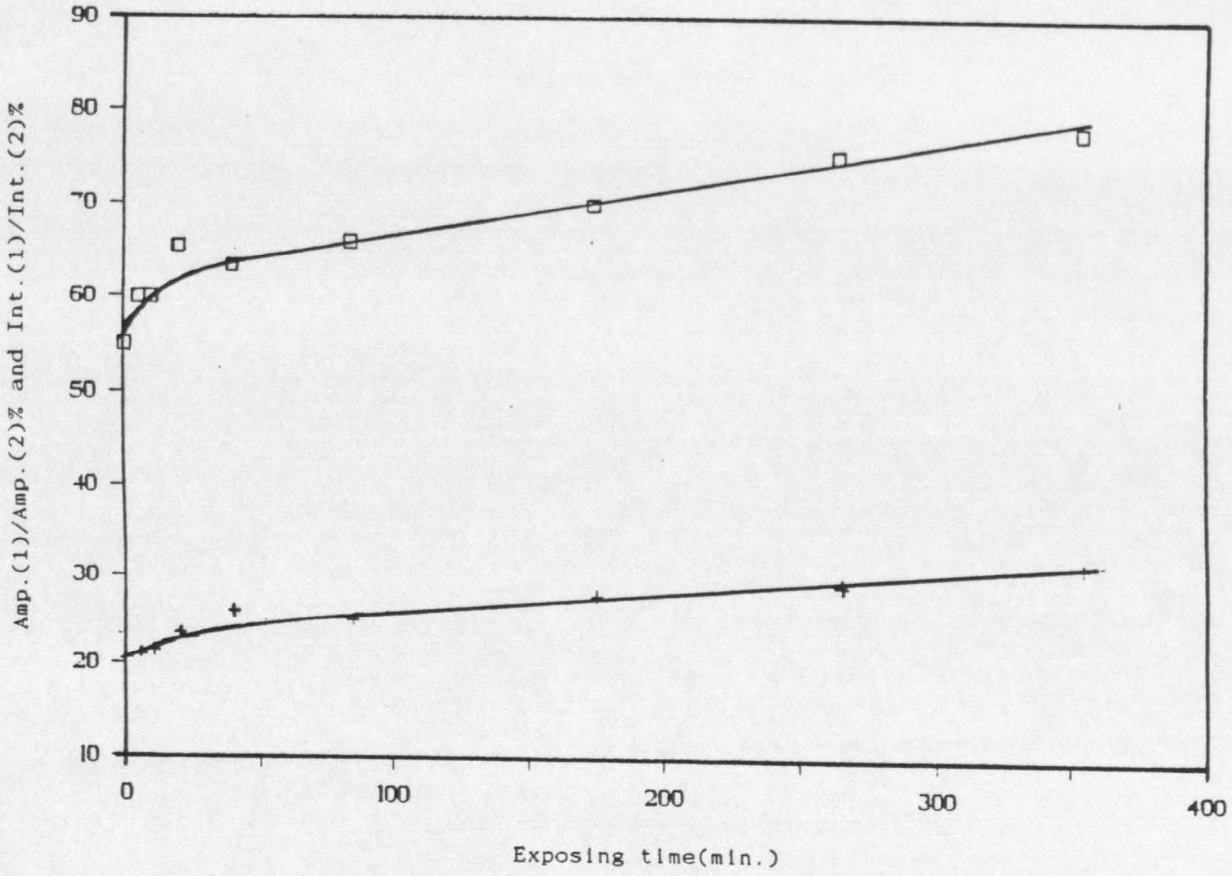


Figure (5.38) amp.(1)/amp.(2)% and int.(1)/int(2)% as a function of exposing time to the mercury light. □ Amp.(1)/Amp.(2)%, + Int.(1)/Int.(2)%.

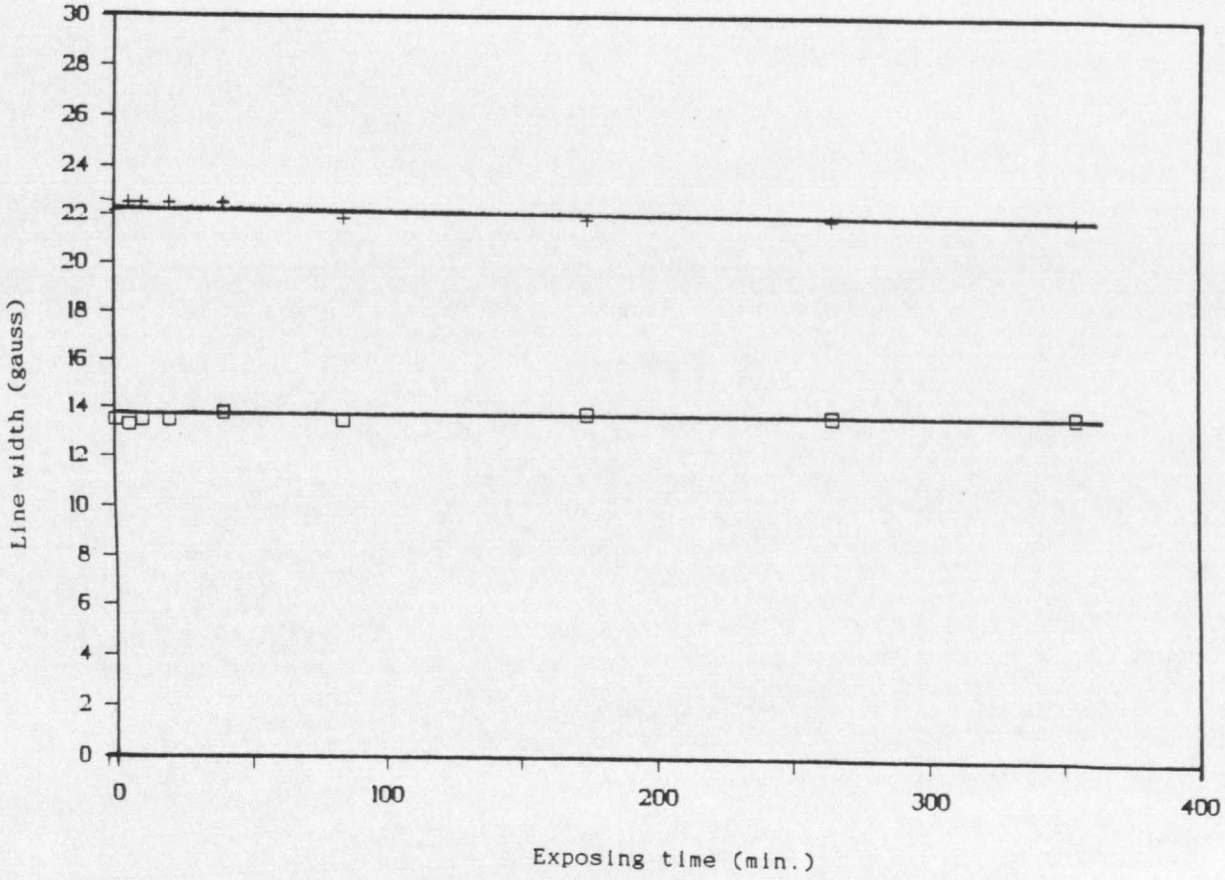


Figure (5.39) Line width as a function of exposing time to mercury light.
□ spectral group (1),
+ spectral group (2).

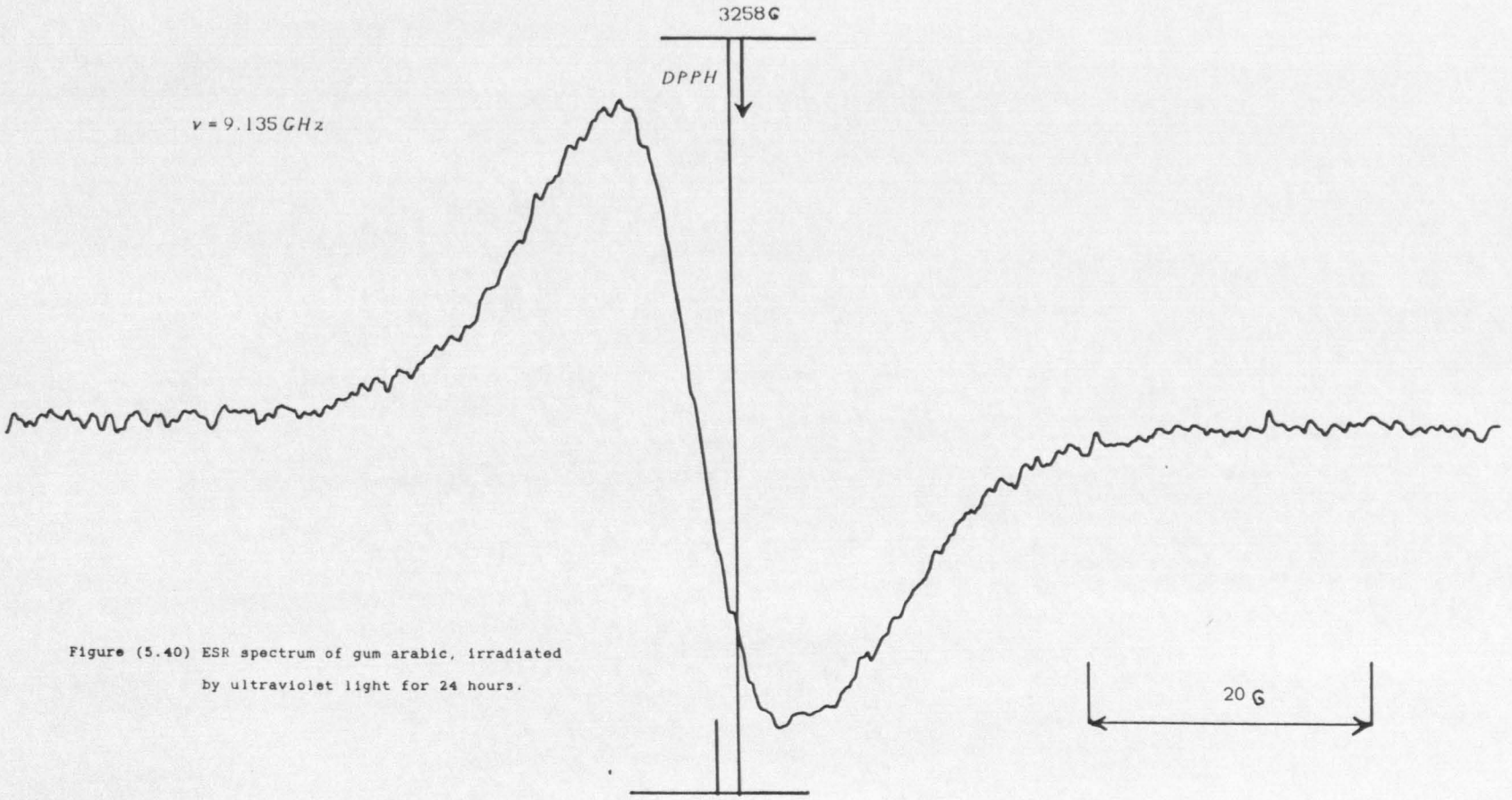


Figure (5.40) ESR spectrum of gum arabic, irradiated by ultraviolet light for 24 hours.

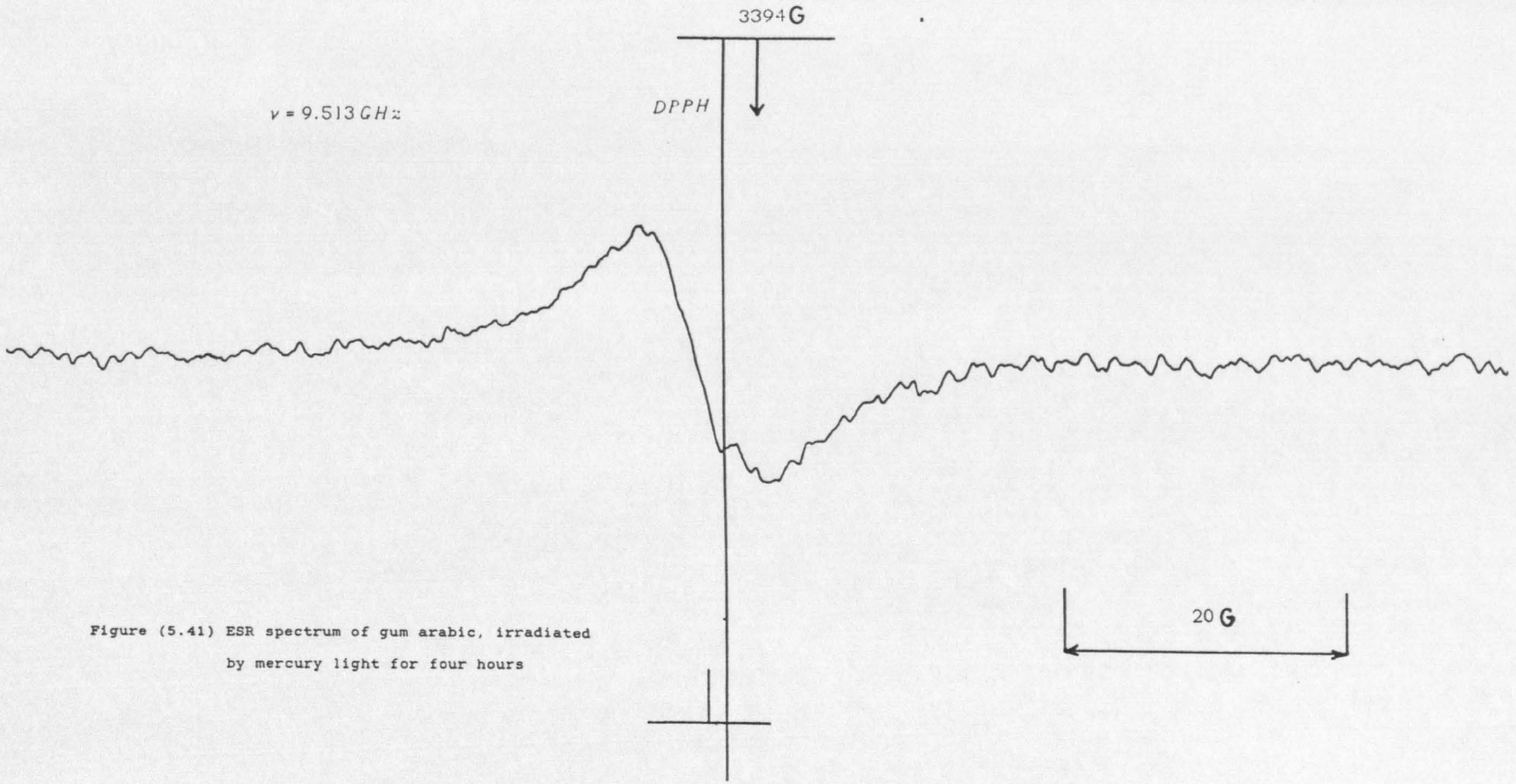


Figure (5.41) ESR spectrum of gum arabic, irradiated by mercury light for four hours

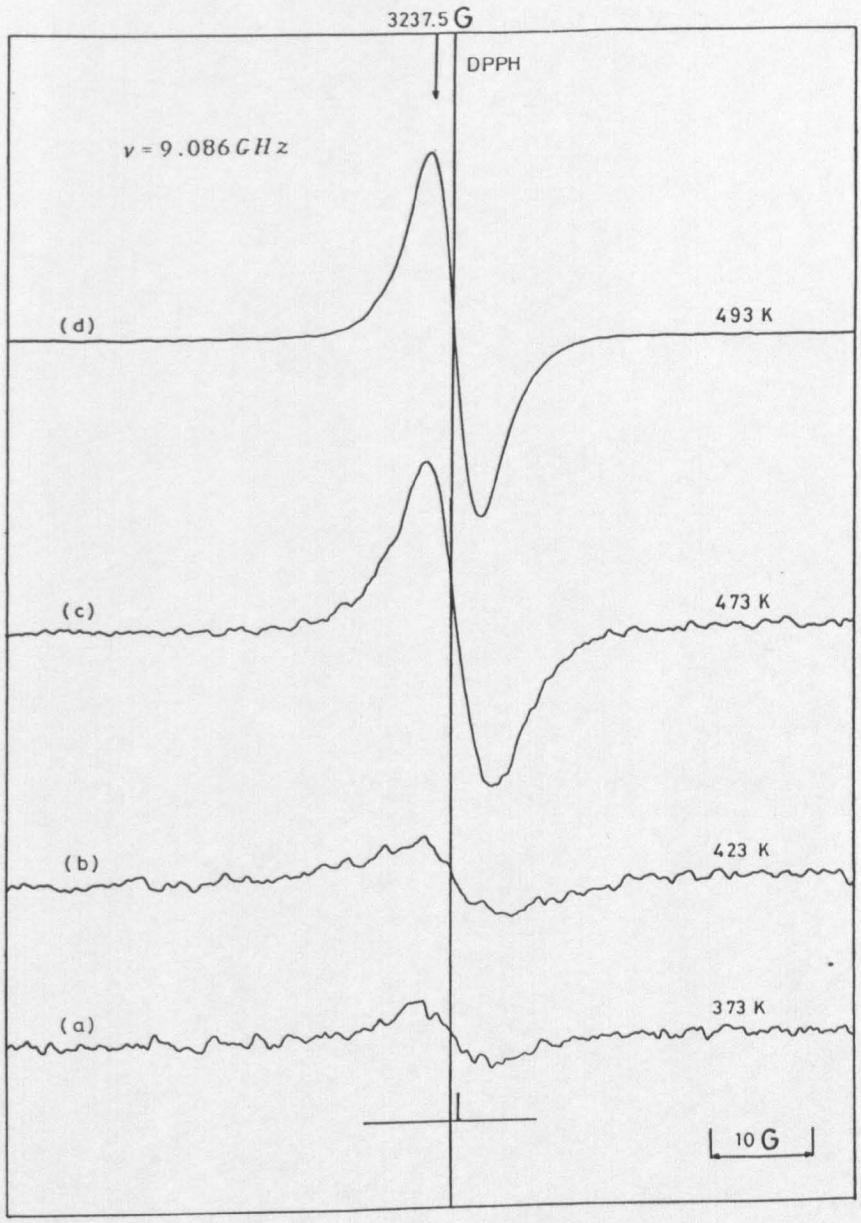


Figure (5.42) ESR spectra of heated gum. (a) recorded at 373 K for 120 minutes of heat. receiver gain $5x10^4$. (b) recorded at 423 K for 115 minutes of heat. receiver gain $4x10^4$. (c) recorded at 473 K for 110 minutes of heat. receiver gain $3.2x10^4$. (d) recorded at 493 K for 48 minutes of heat. receiver gain $4x10^3$

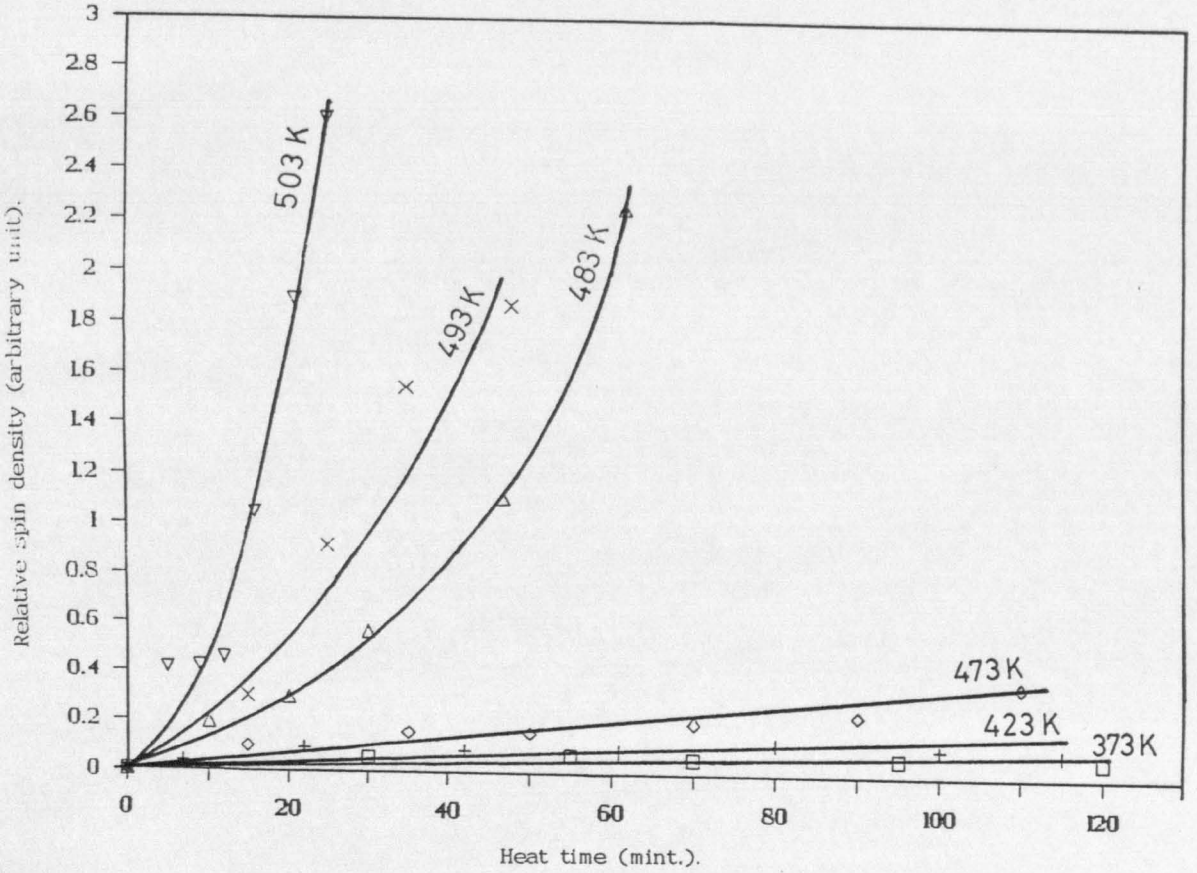


Figure (5.43) Relative spin density of heated gum as a function of heat time.

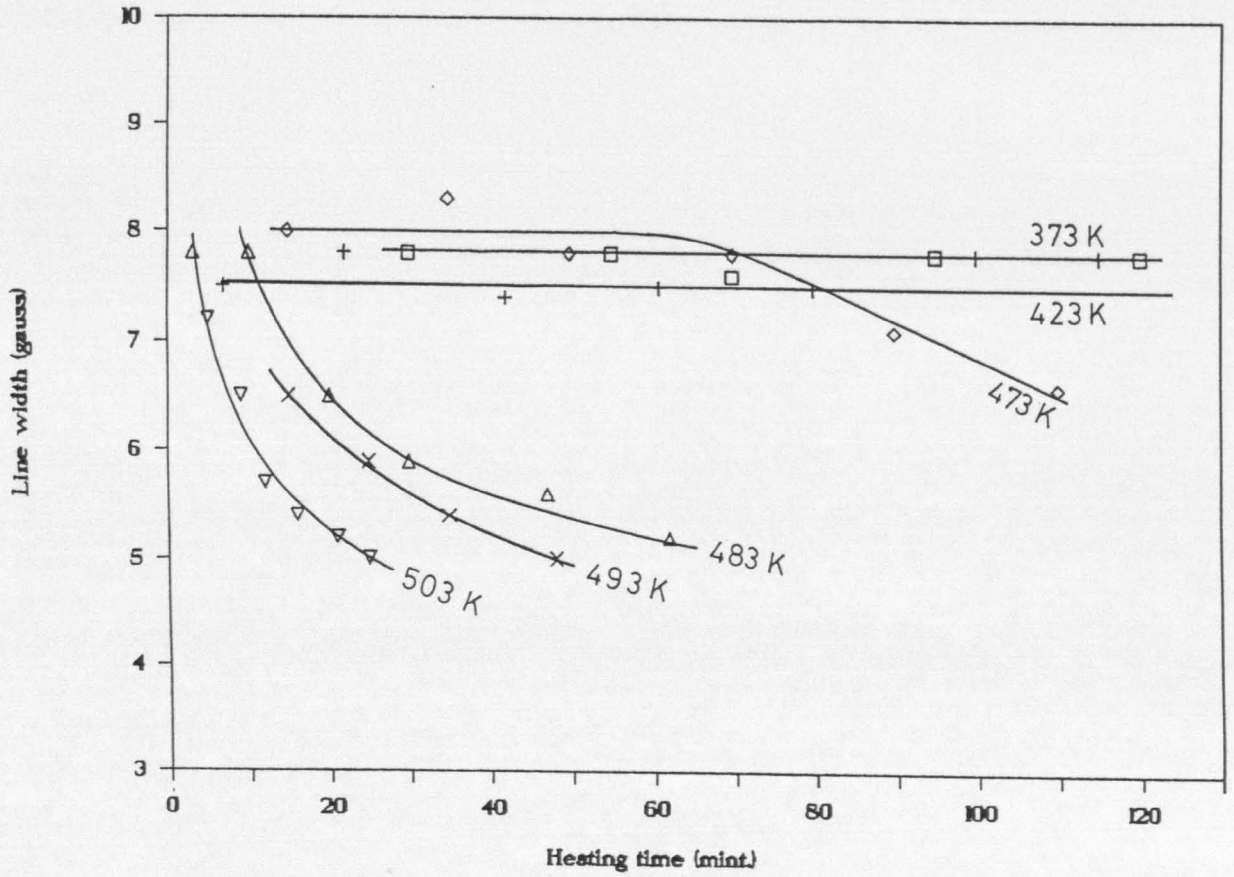


Figure (5.44) Line width of heated gum as a function of heat time.

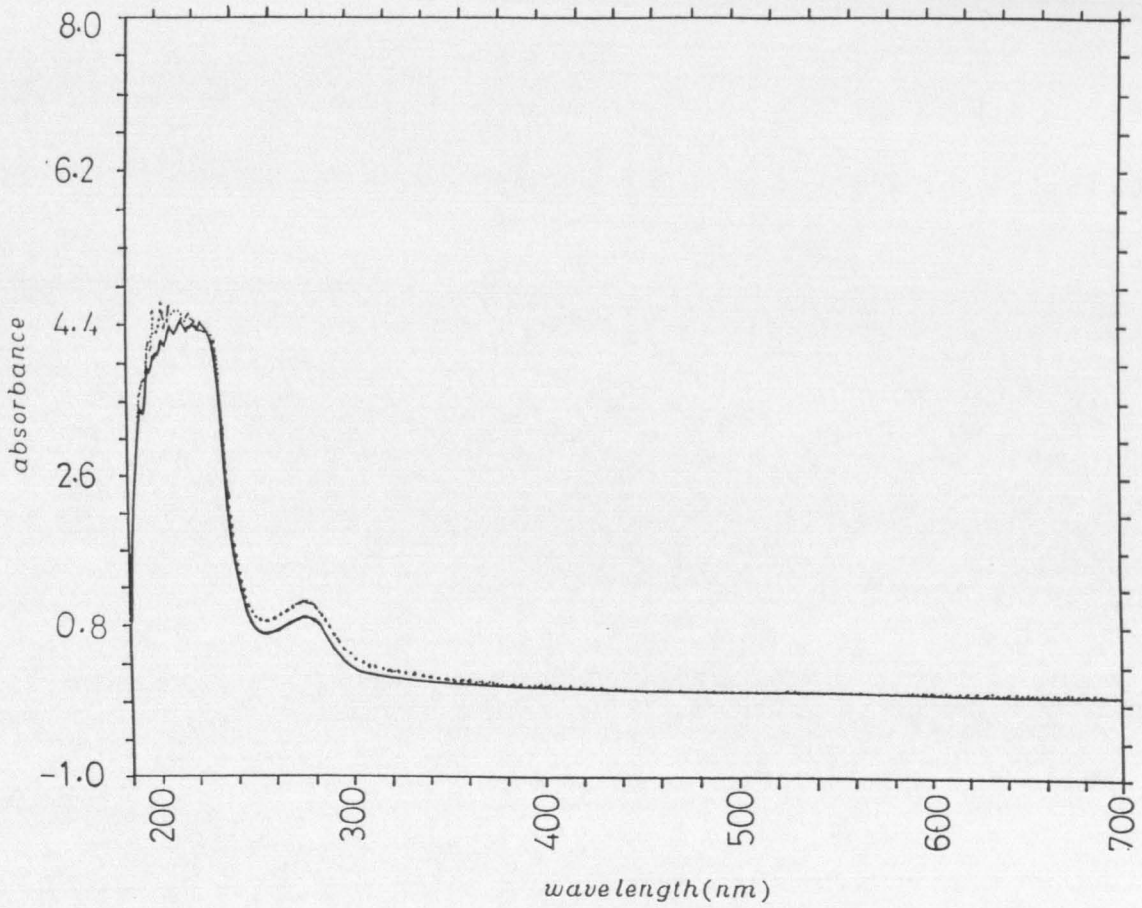


Figure (5.45') Optical absorption spectra of gum arabic.

(——) natural gum.

(.....) gamma irradiated gum.

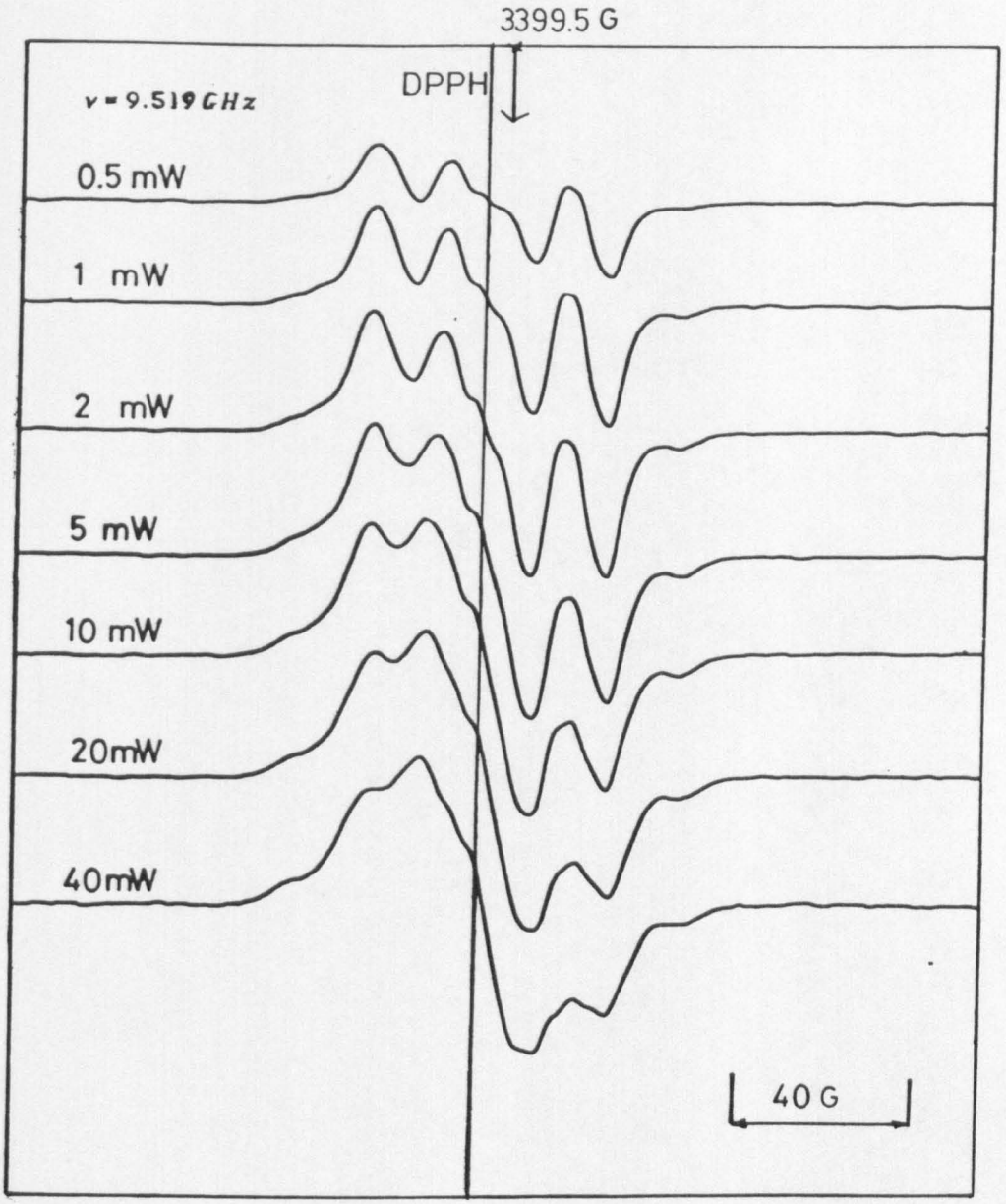


Figure (6.1) ESR spectra of x-irradiated D-galactose recorded at different microwave power at room temperature.

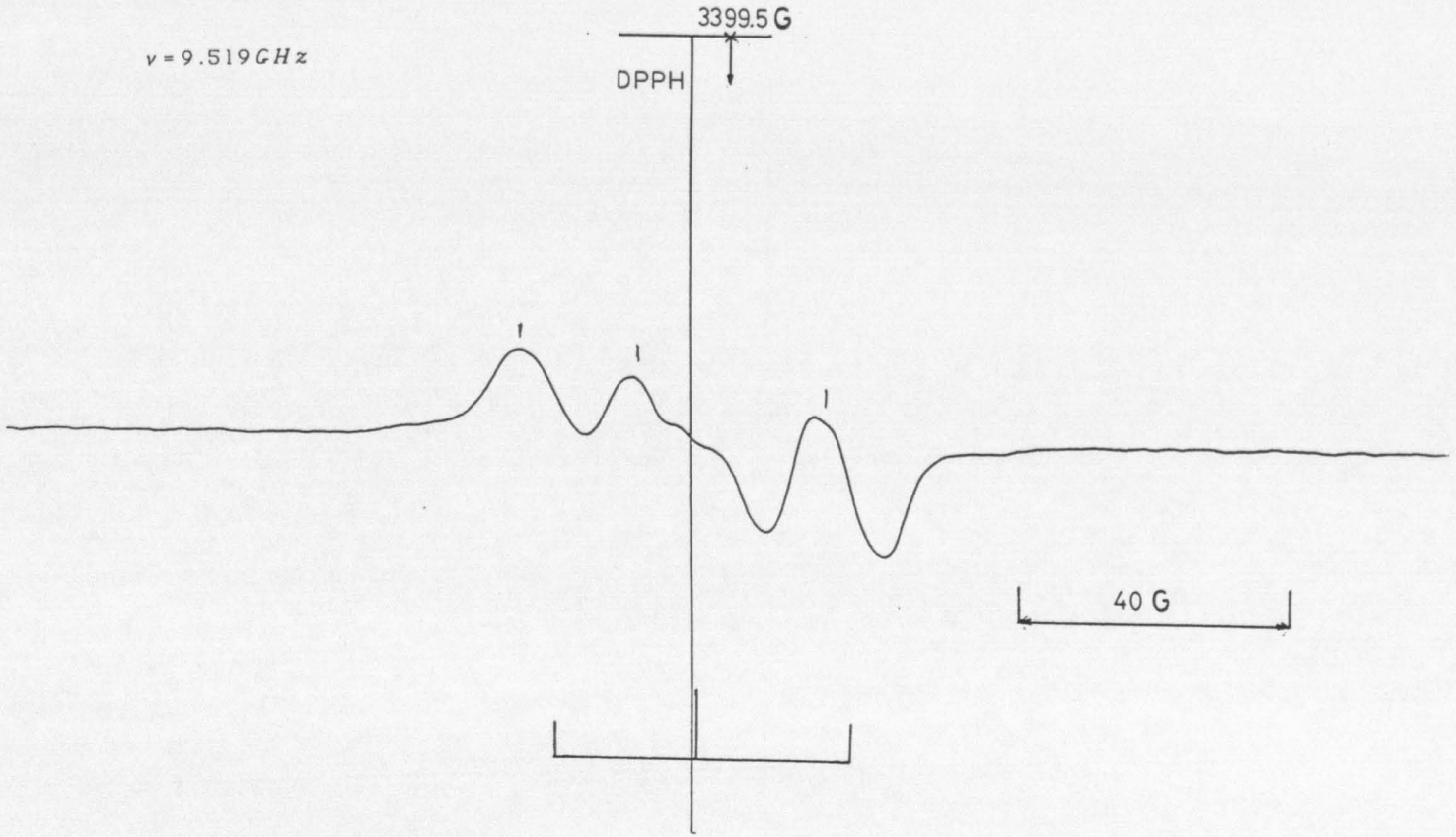


Figure (6.2) ESR spectrum of x-irradiated D-galactose recorded at 0.5 mW microwave power at room temperature.

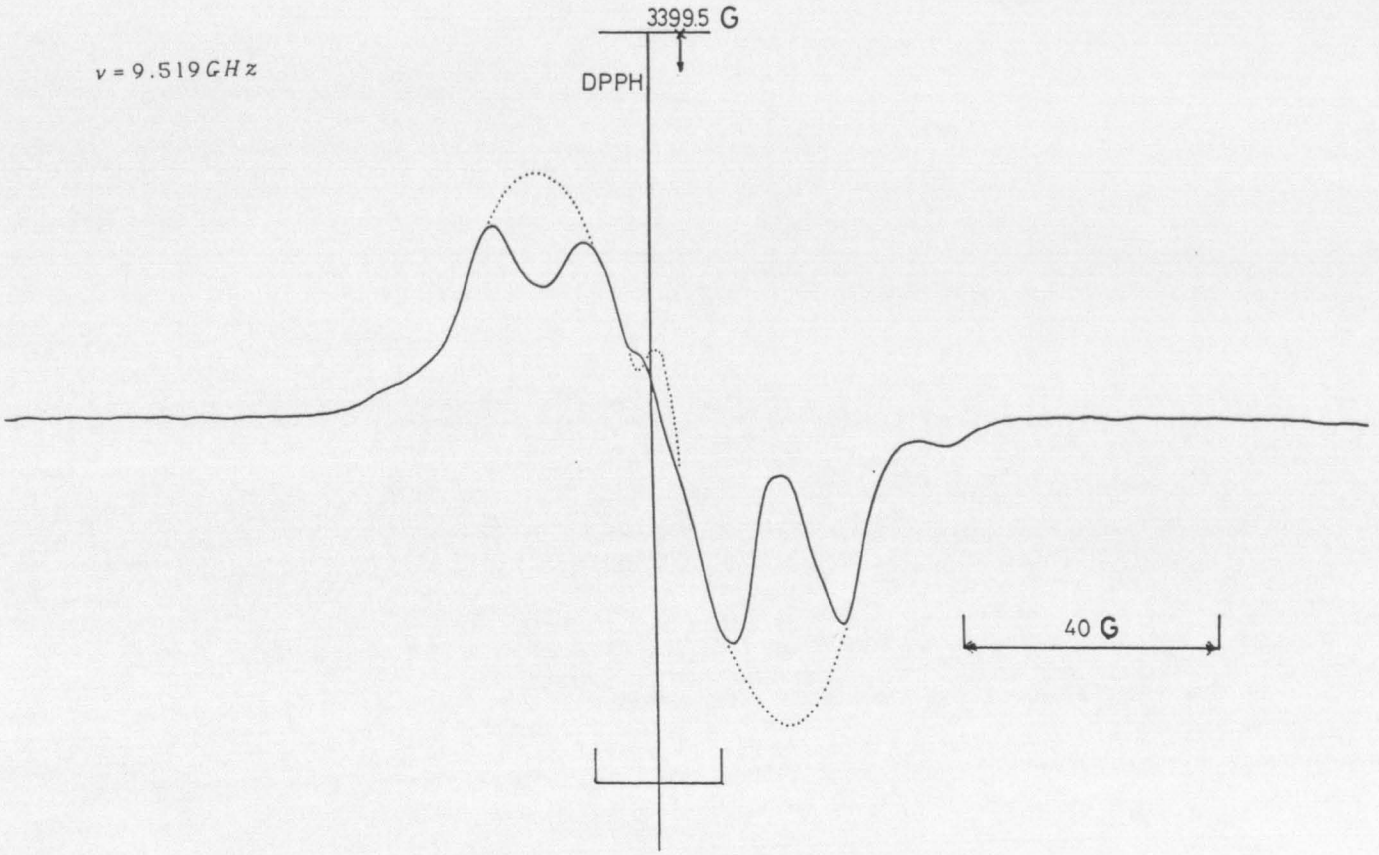


Figure (6.3) ESR spectrum of x-irradiated D-galactose recorded at 10 mW microwave power at room temperature.

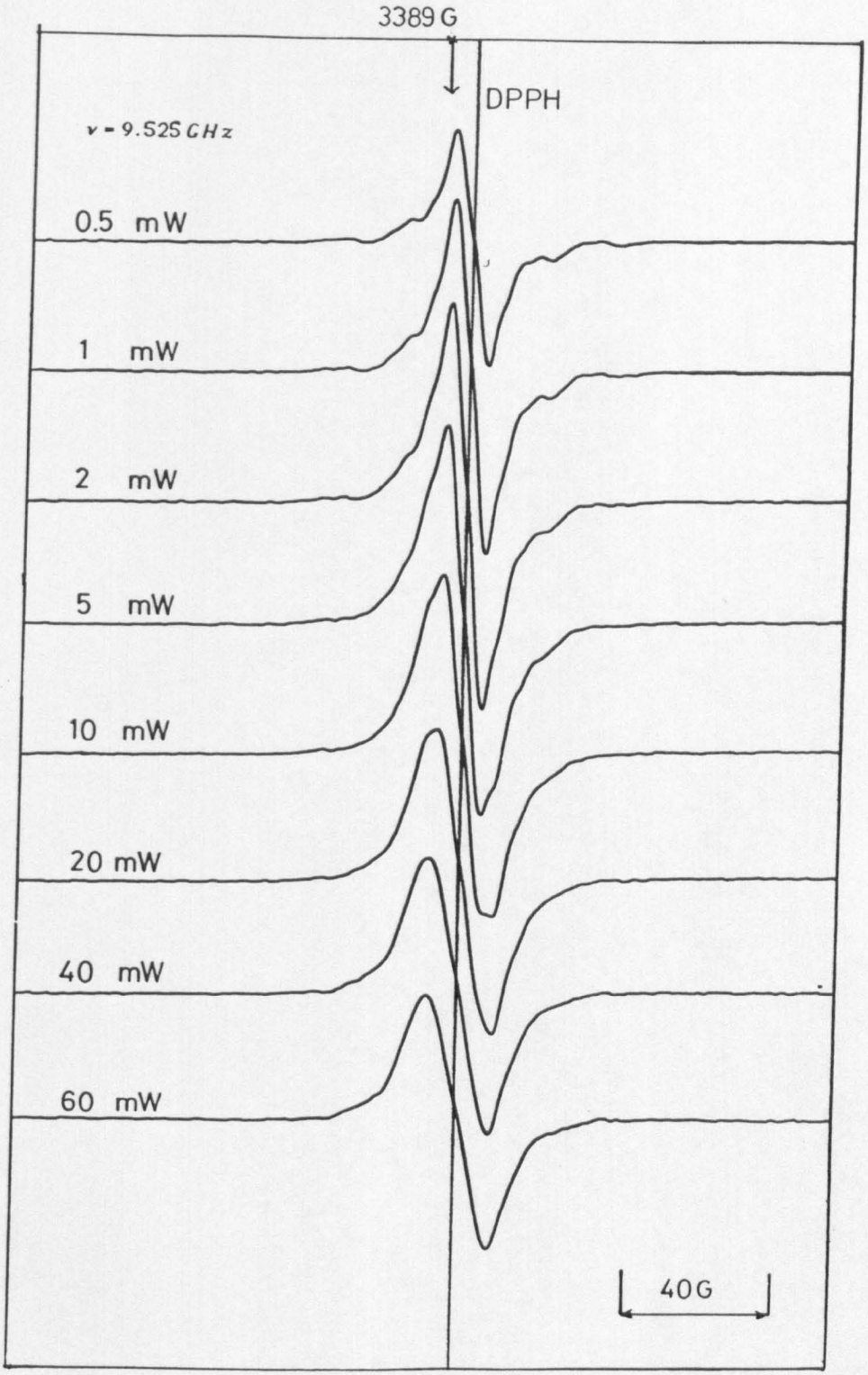


Figure (6.4) ESR spectra of x-irradiated D-glucuronic acid recorded at different microwave power at room temperature.

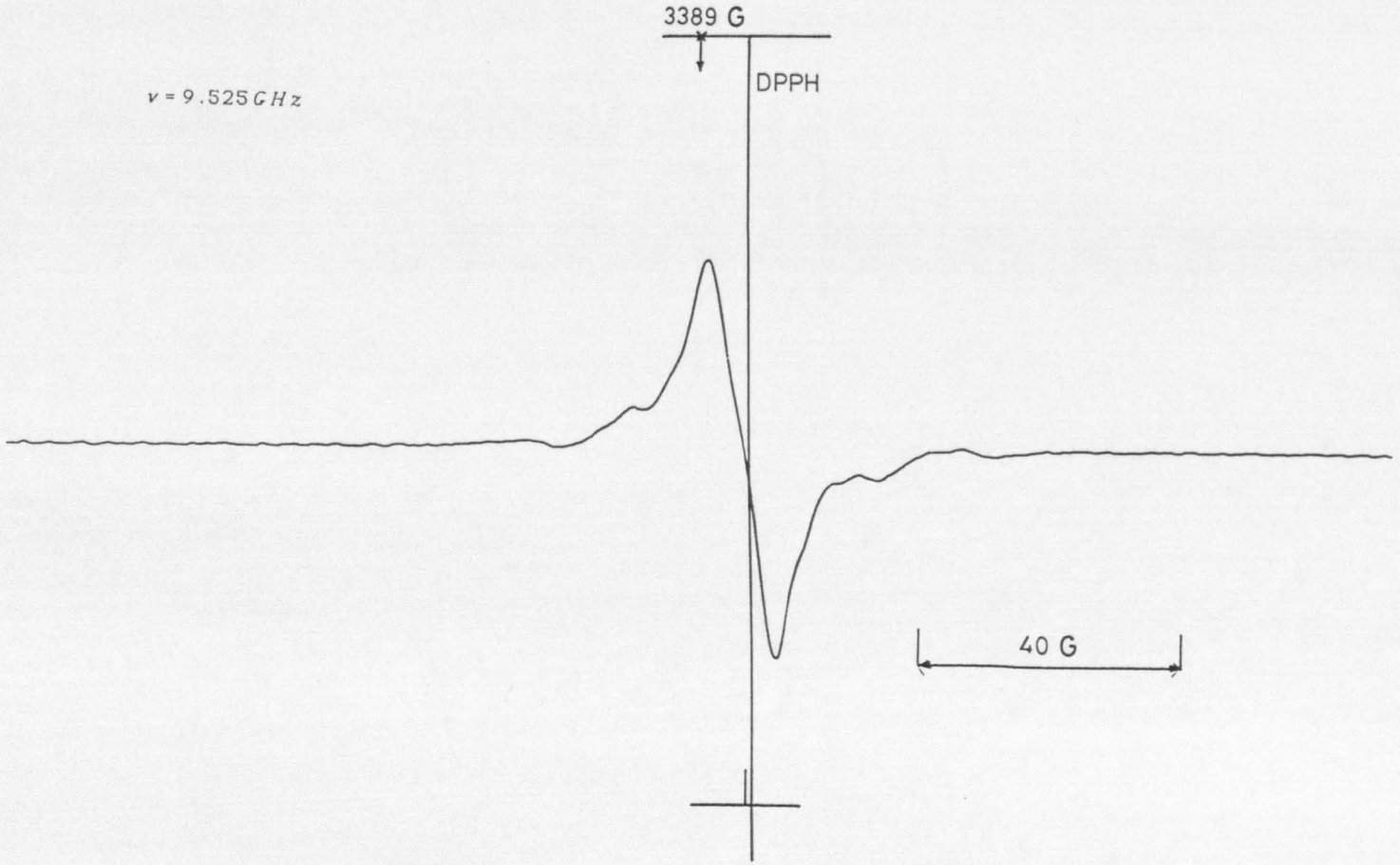


Figure (6.5) ESR spectra of x-irradiated D-glucuronic acid recorded at 0.5 mW microwave power at room temperature.

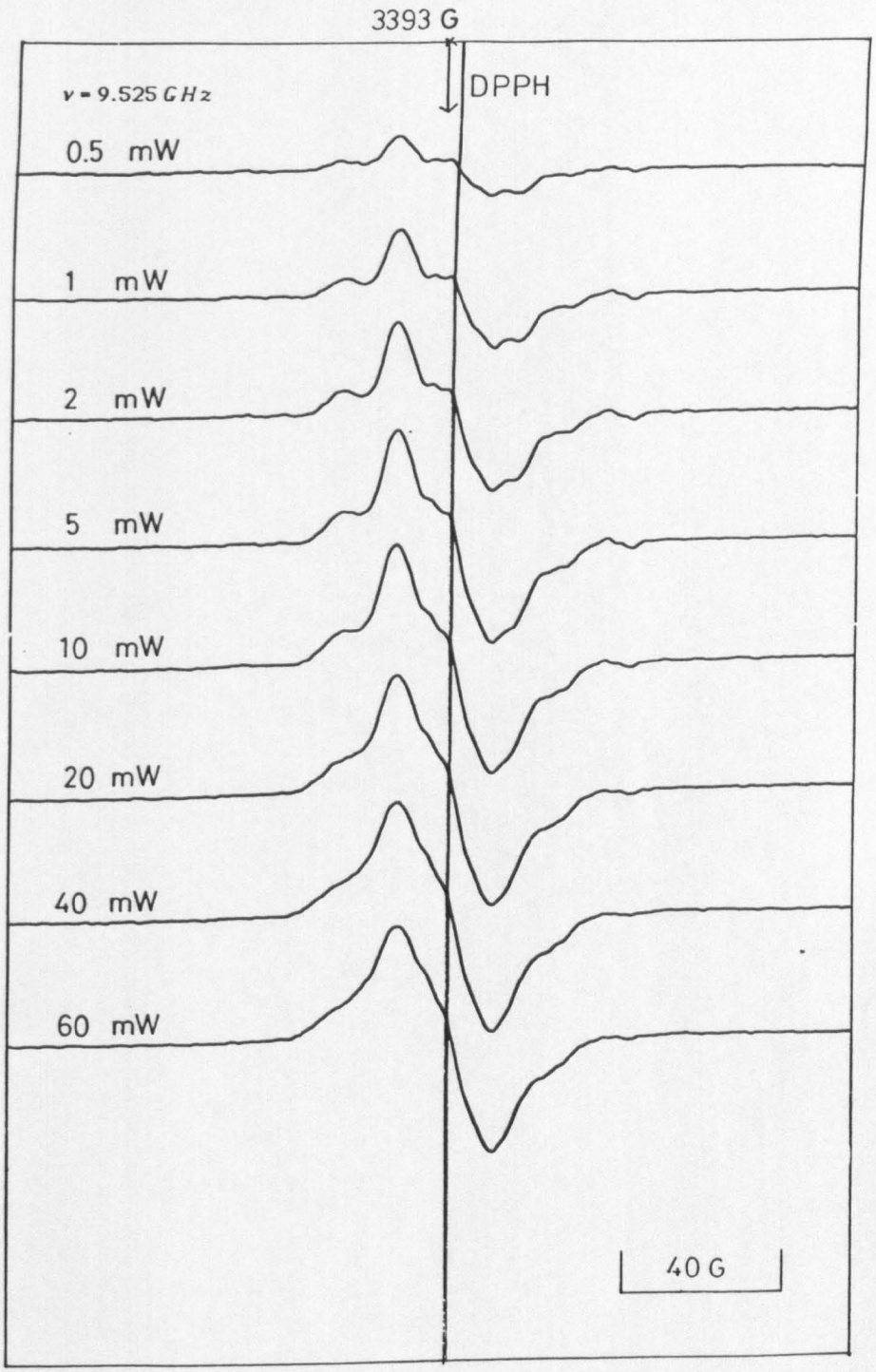


Figure (6.6) ESR spectra of x-irradiated L-arabinose recorded at different microwave power at room temperature.

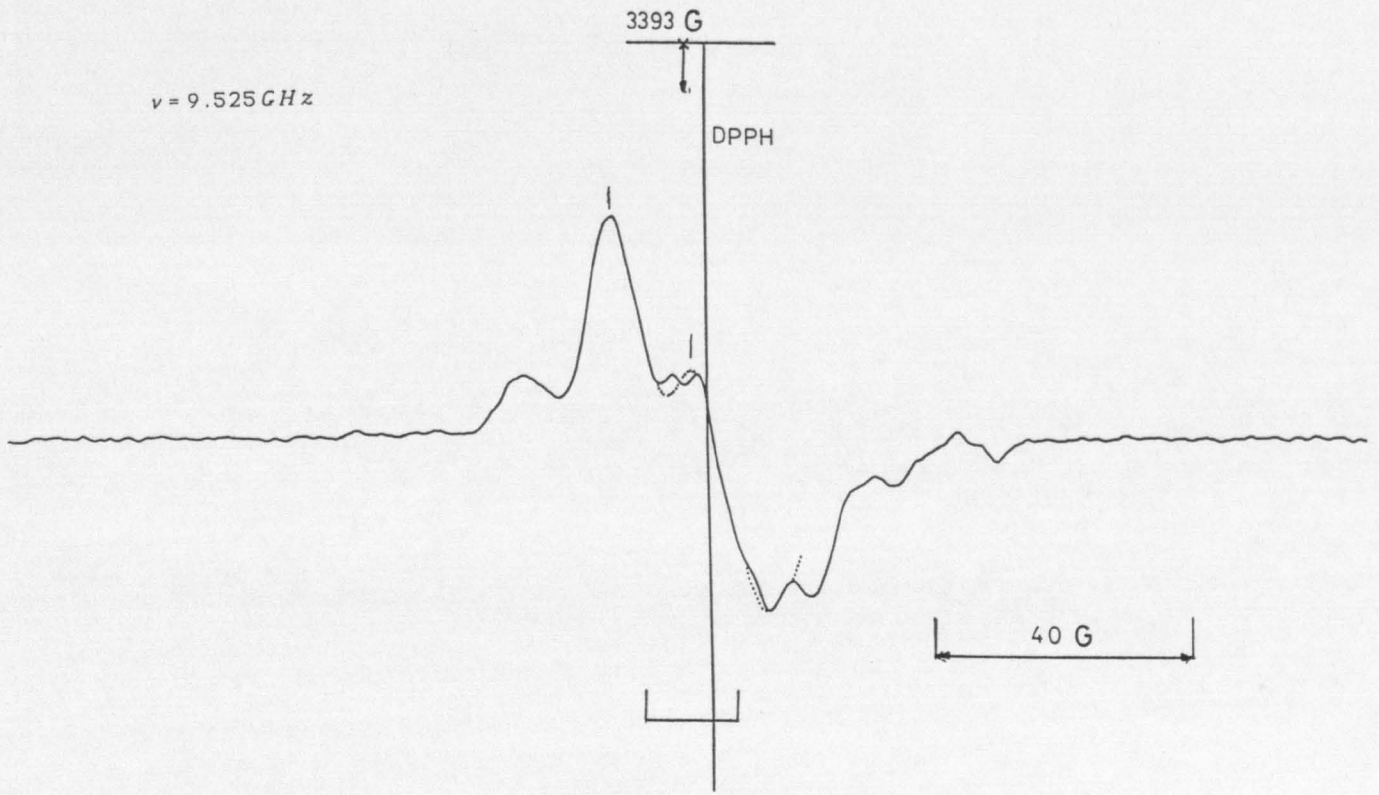


Figure (6.7) ESR spectrum of x-irradiated L-arabinose recorded at 0.5 mW microwave power at room temperature.

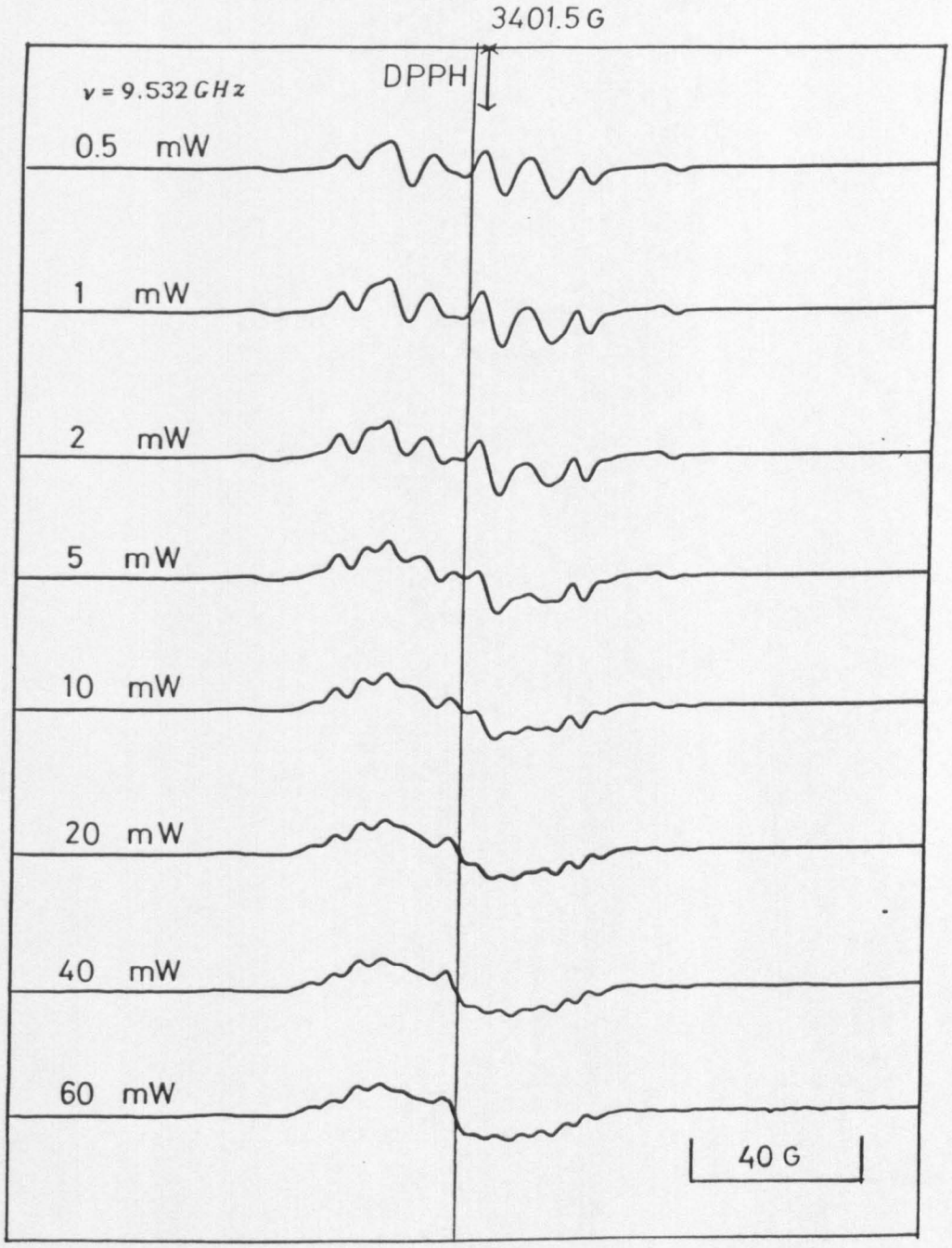


Figure (6.8) ESR spectra of x-irradiated L-rhamnose recorded at different microwave power at room temperature.

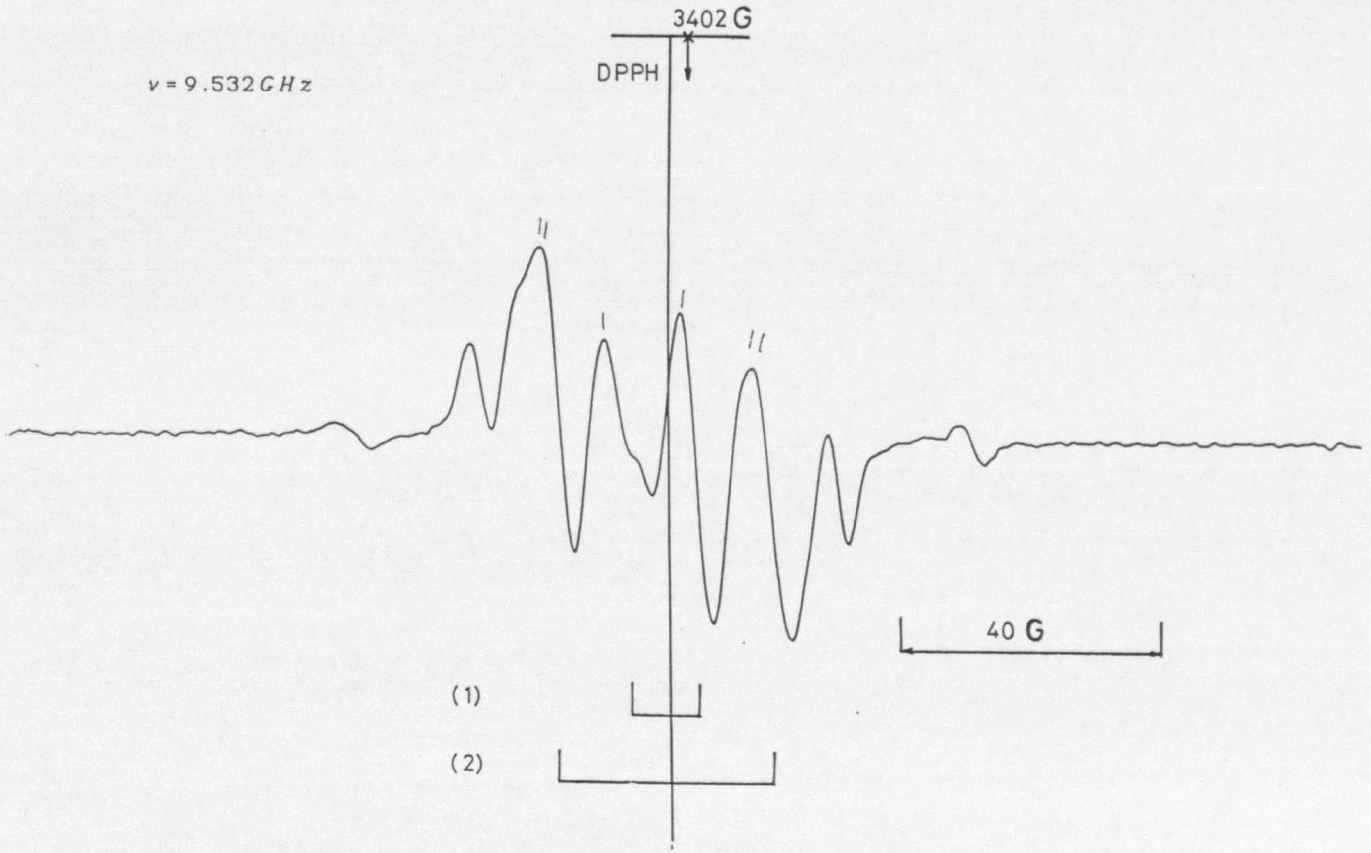


Figure (6.9) ESR spectrum of x-irradiated L-rhamnose recorded at 0.5 mW microwave power at room temperature.

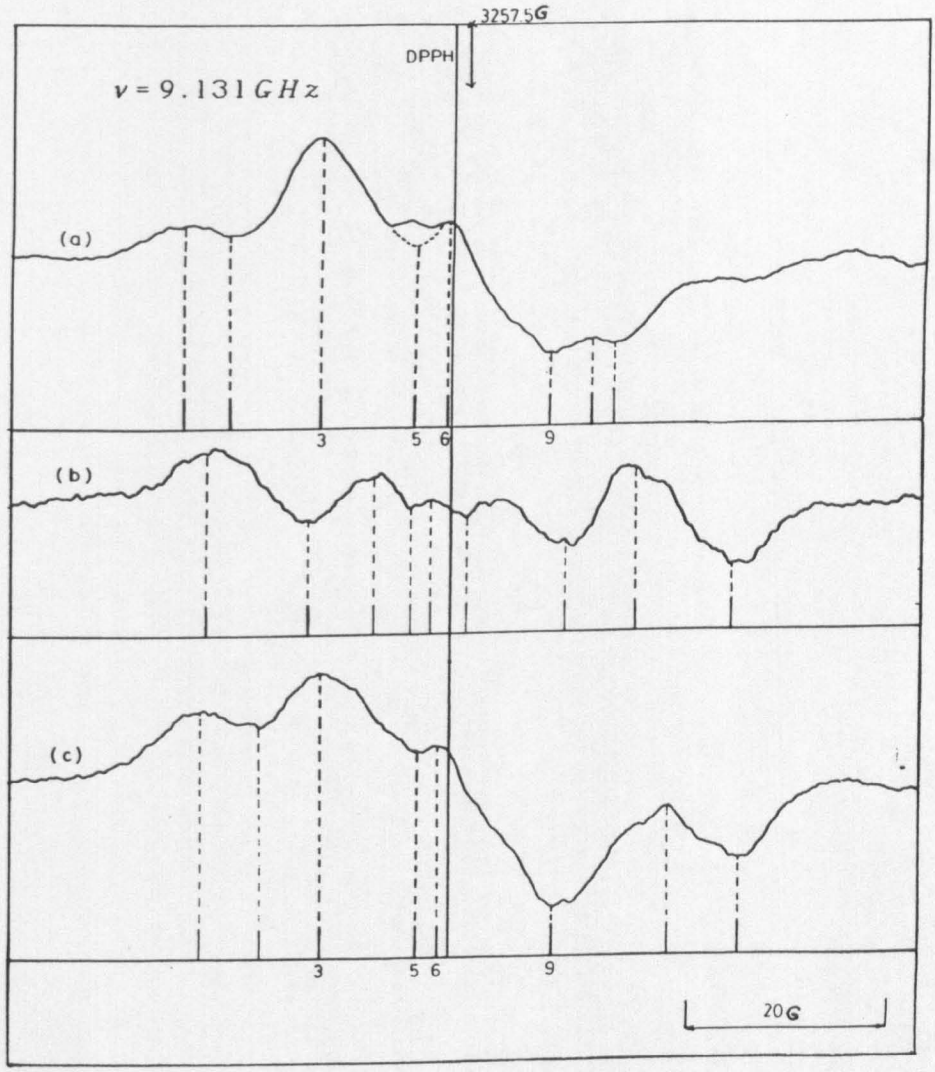


Figure (6.10) ESR spectra of x-irradiated .(a) Arabinose. (b) Galactose. (c) Arabinose + Galactose.

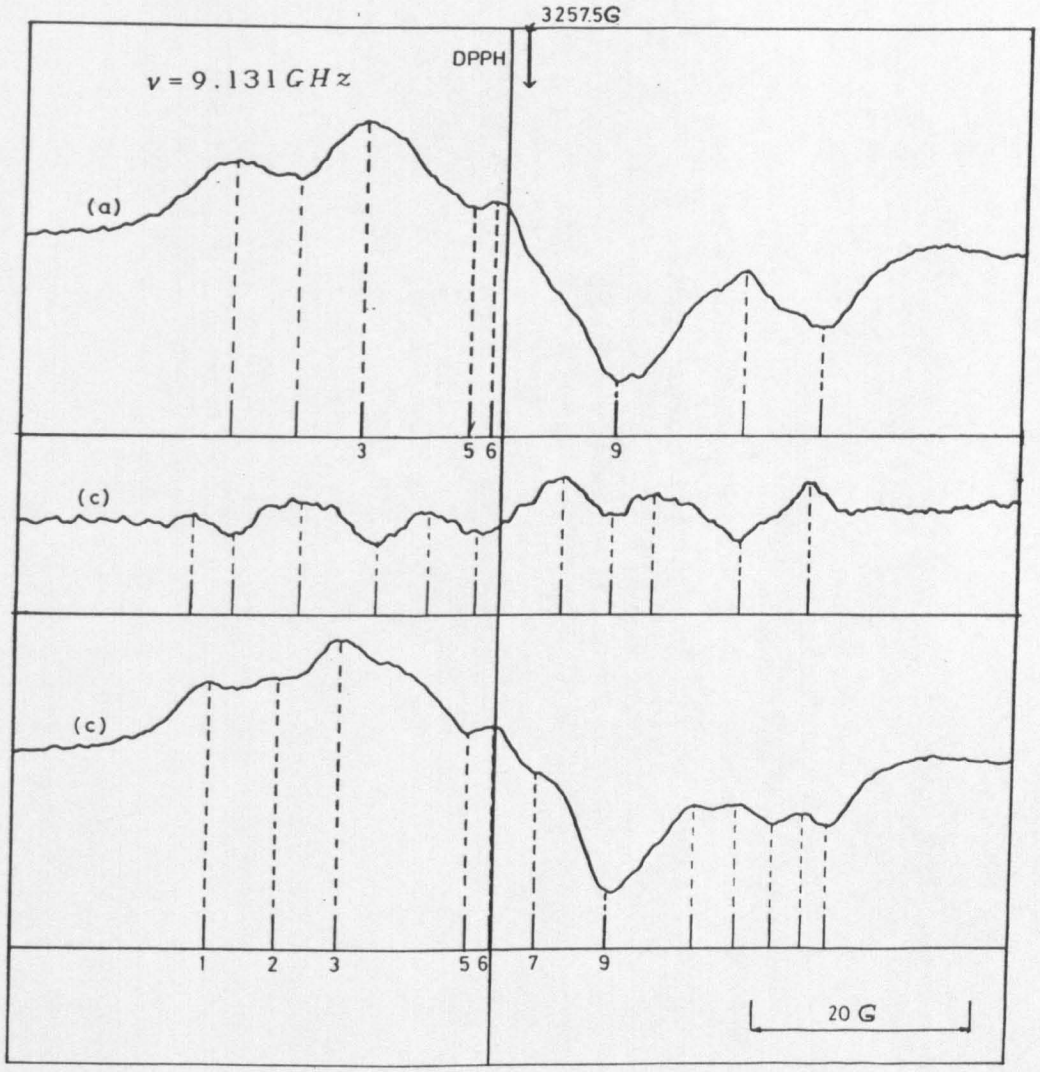


Figure (6.11) ESR spectra of x-irradiated (a) Arabinose + Galactose. (b) Rhamnose. (c) mixture of (arabinose + galactose + rhamnose).

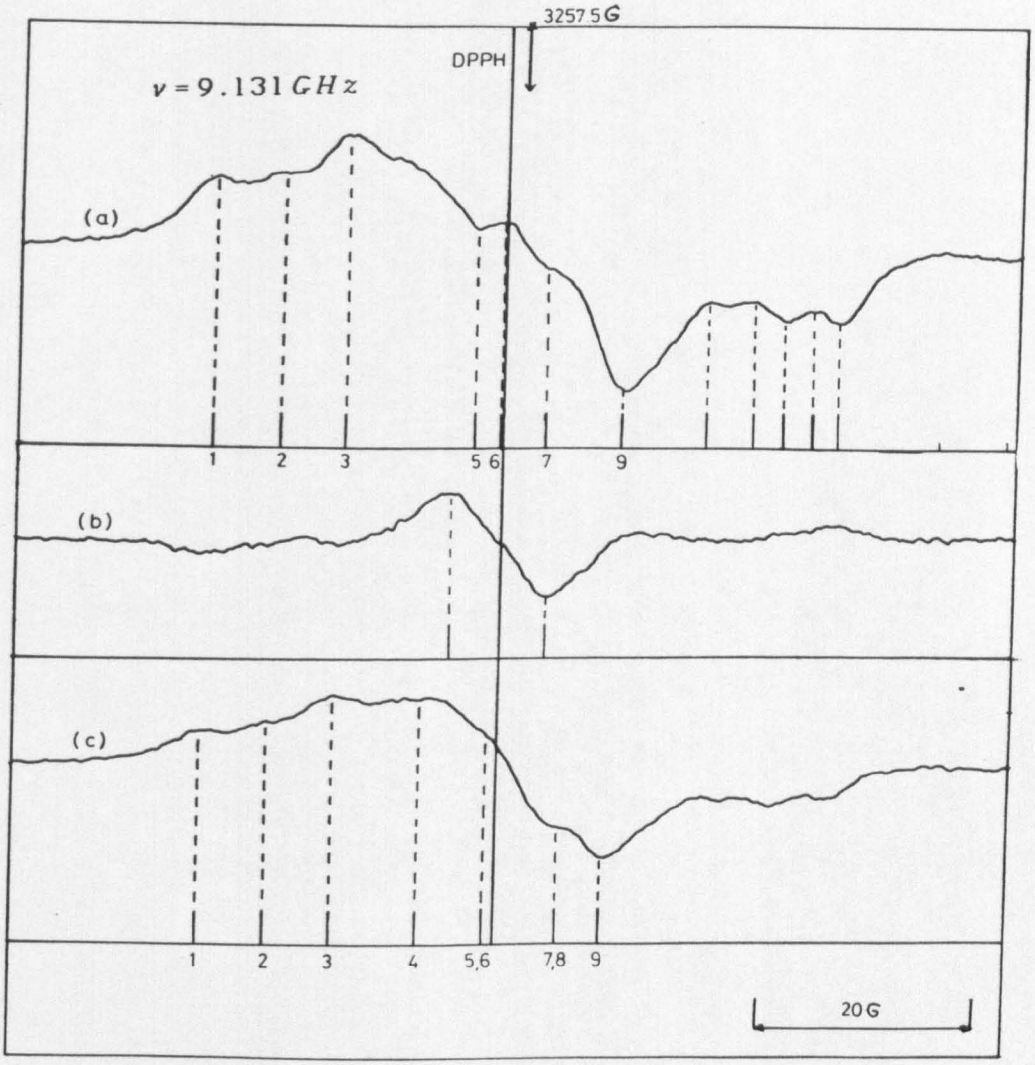


Figure (6.12) ESR spectra of x-irradiated. (a) mixture of arabinose + galactose + rhamnose. (b) D-Glucuronic acid. (c) Synthetic gum (mixture of four sugars).

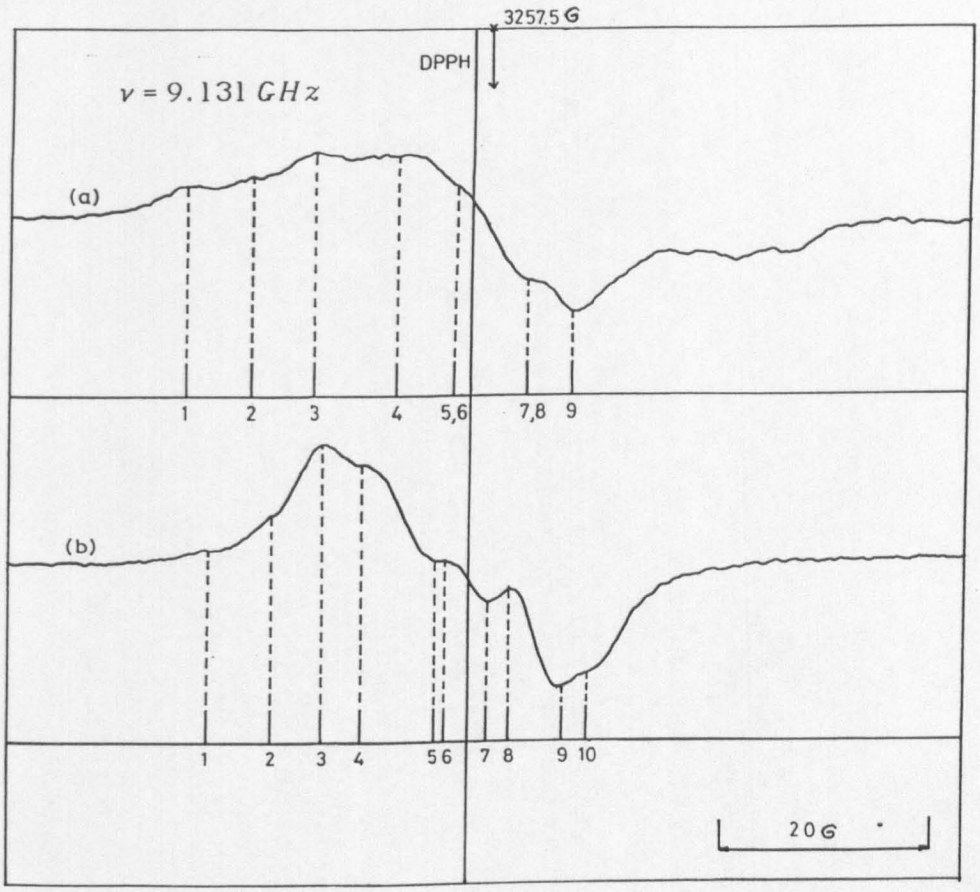
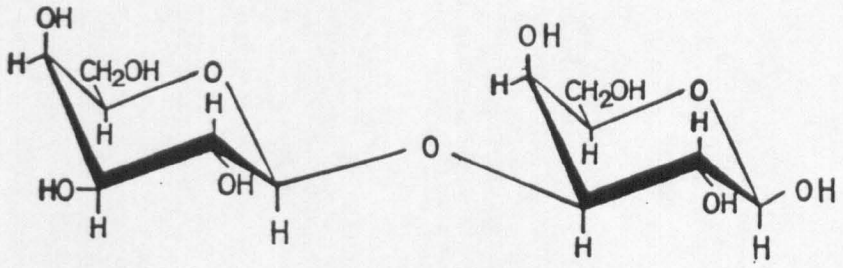
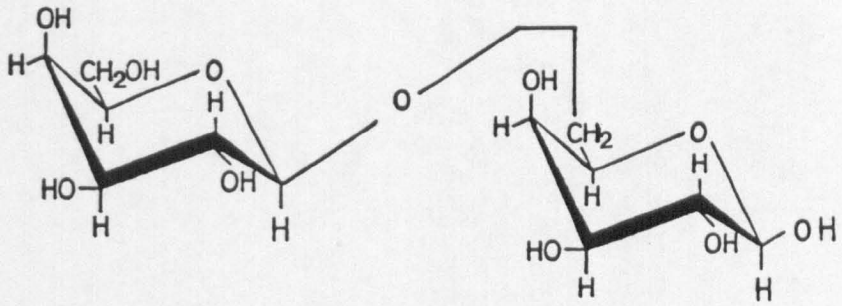


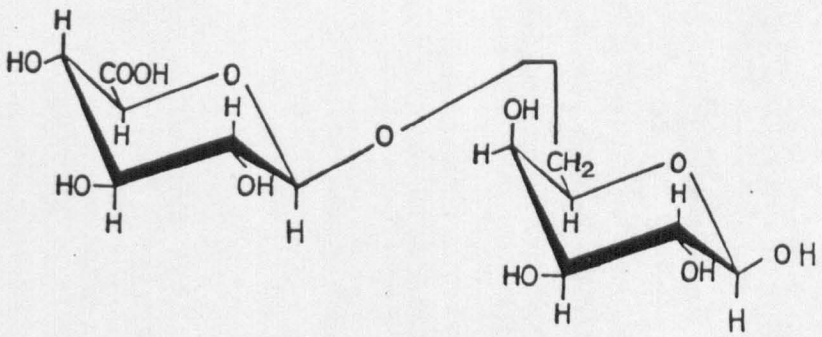
Figure (6.13) ESR spectra of. (a) Synthetic gum. (b) natural gum.



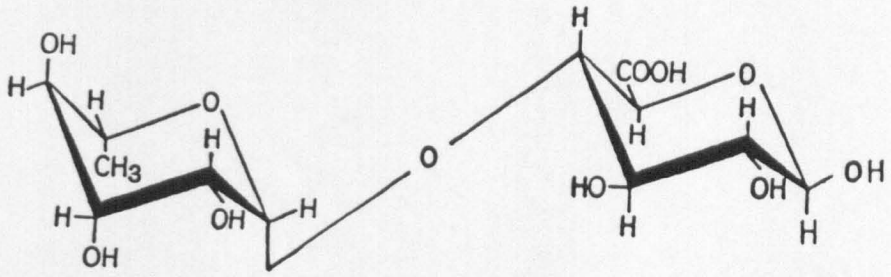
structure (7.1)



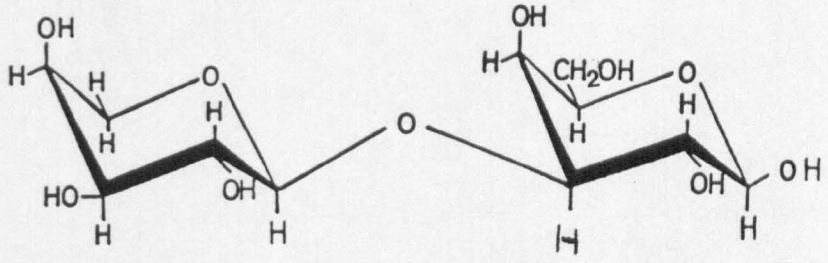
structure (7.2)



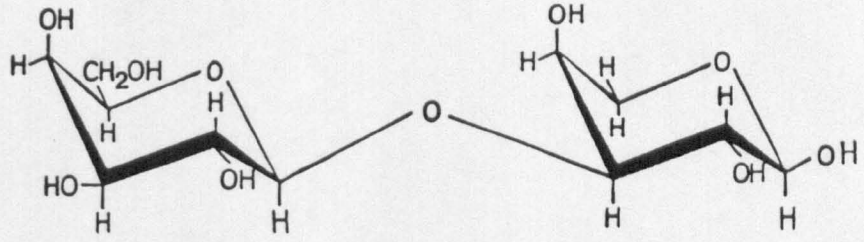
structure (7.3)



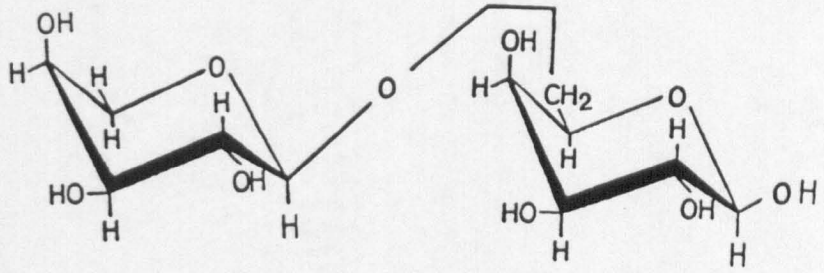
structure (7.4)



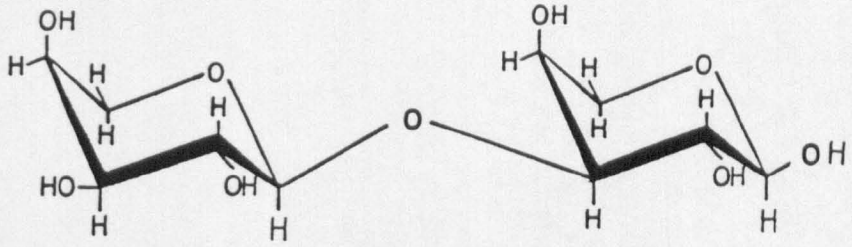
structure (7.5)



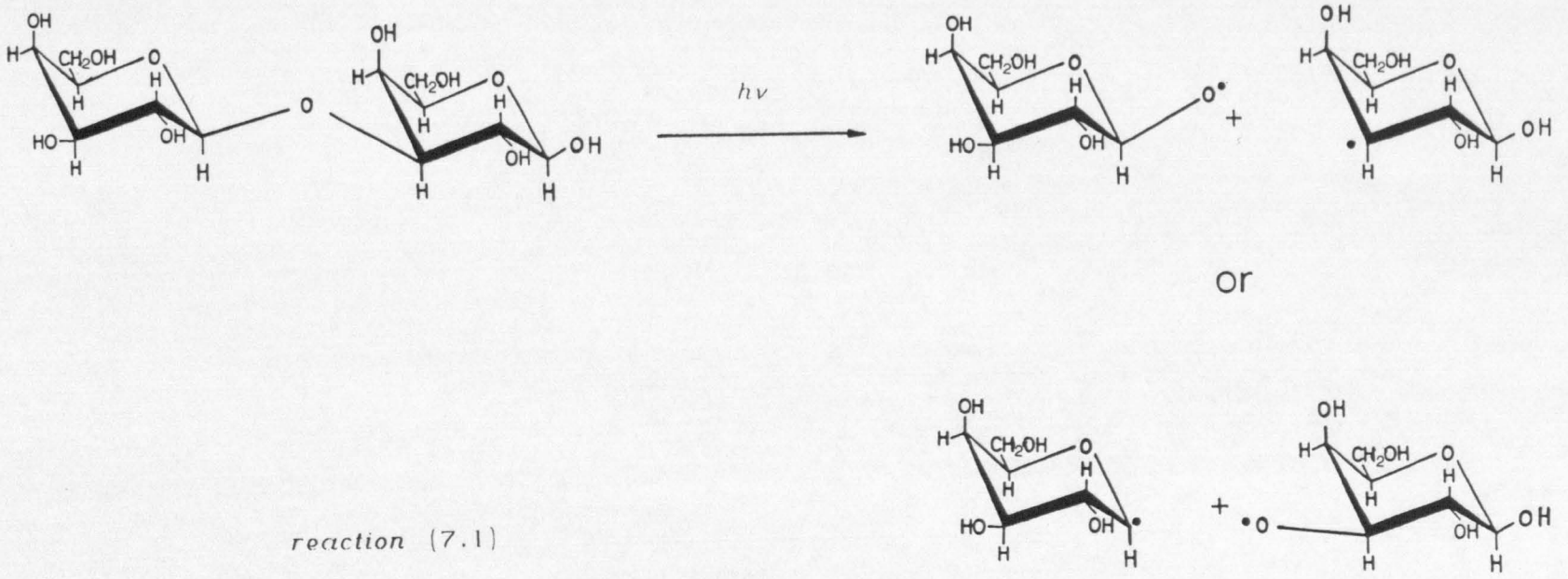
structure (7.6)



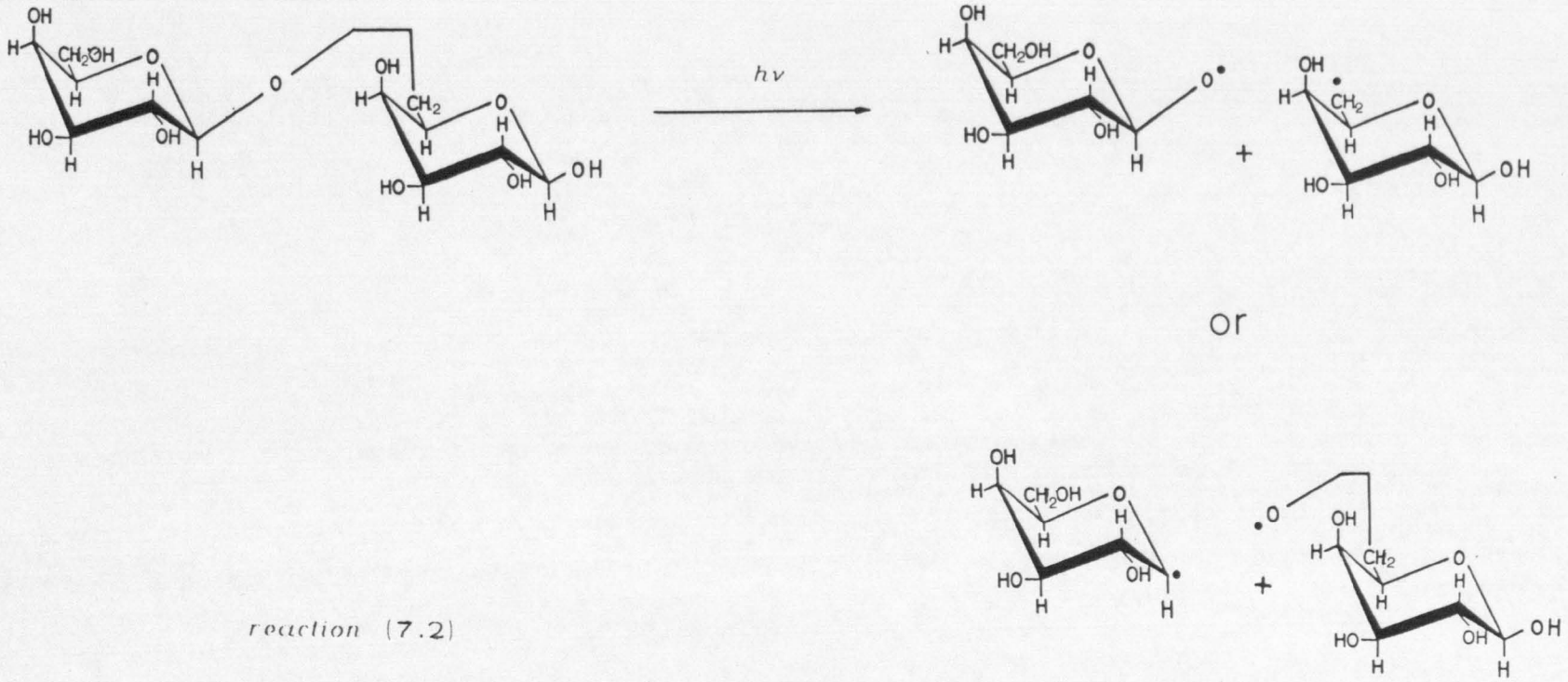
structure (7.7)



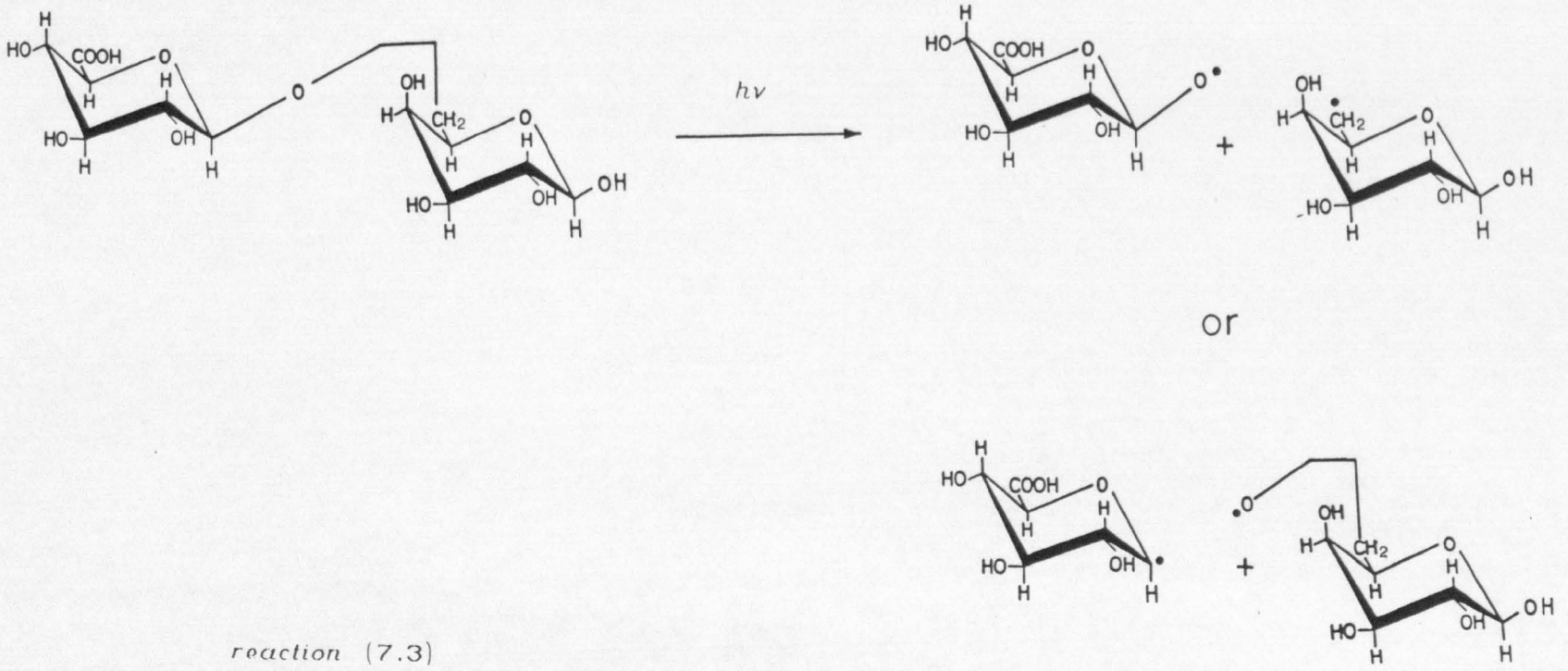
structure (7.8)



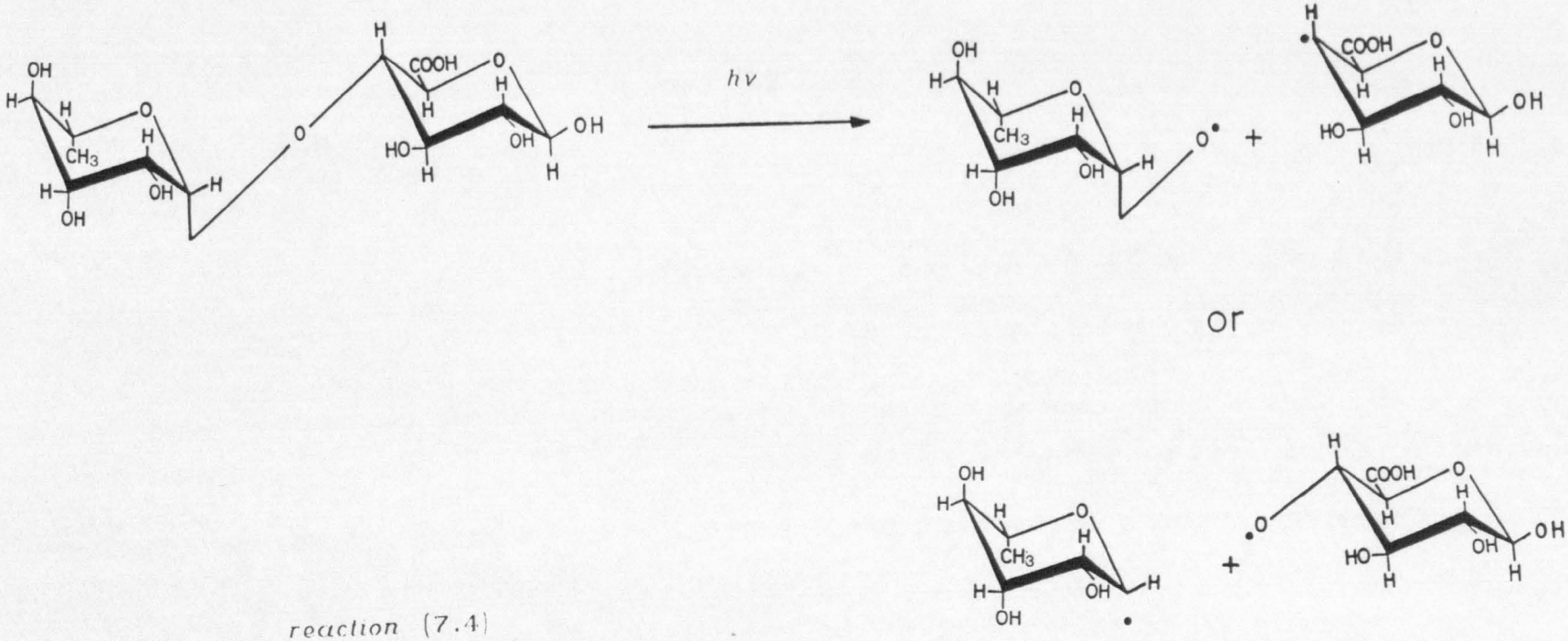
reaction (7.1)



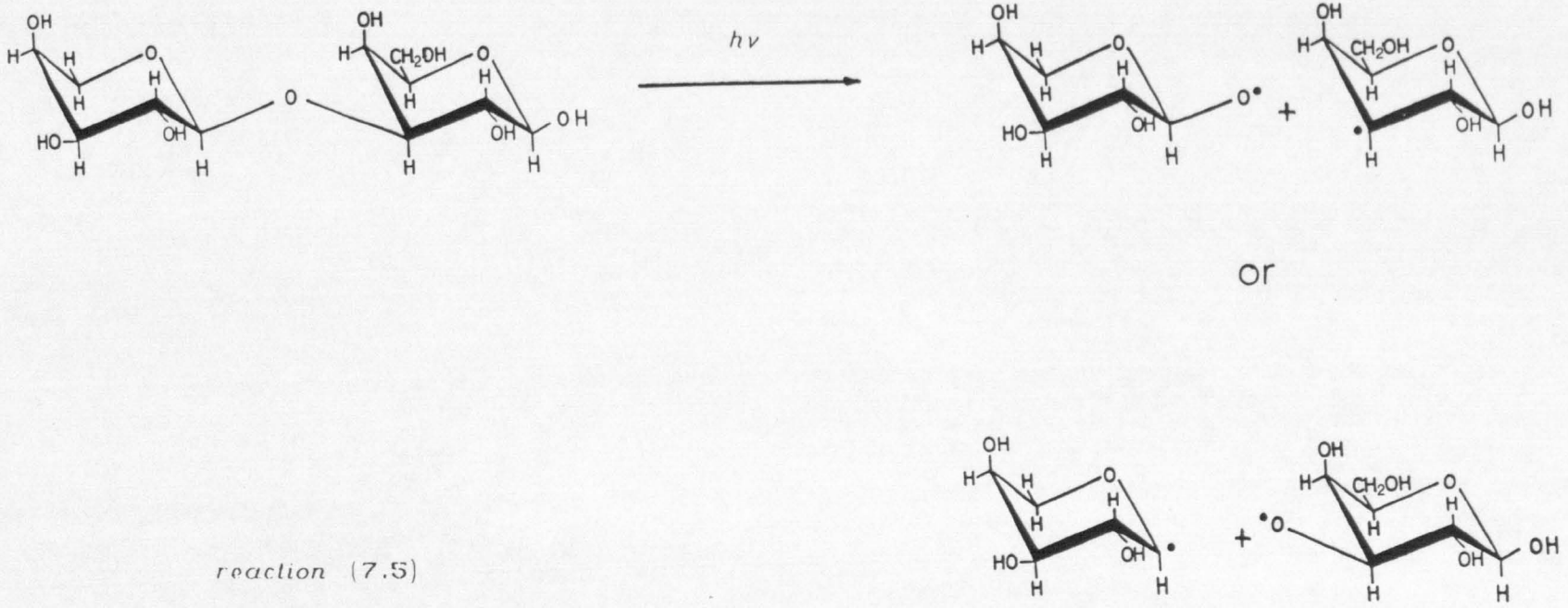
reaction (7.2)



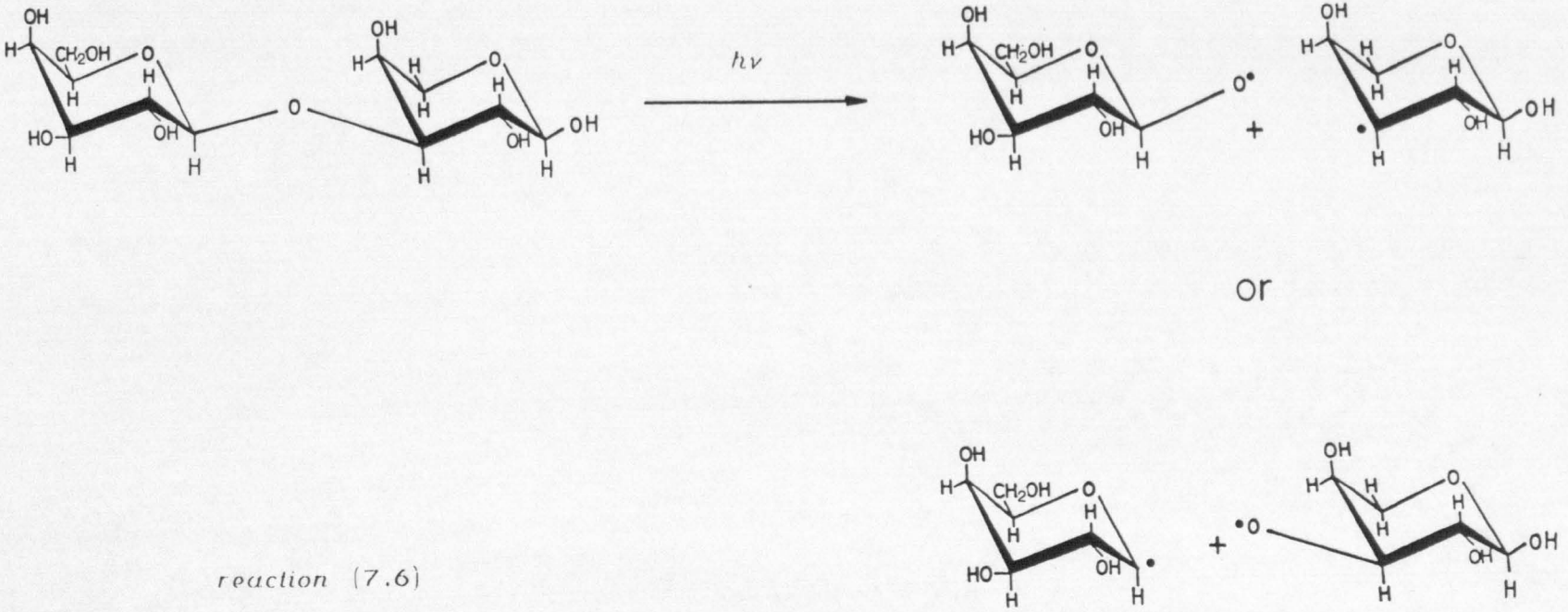
reaction (7.3)



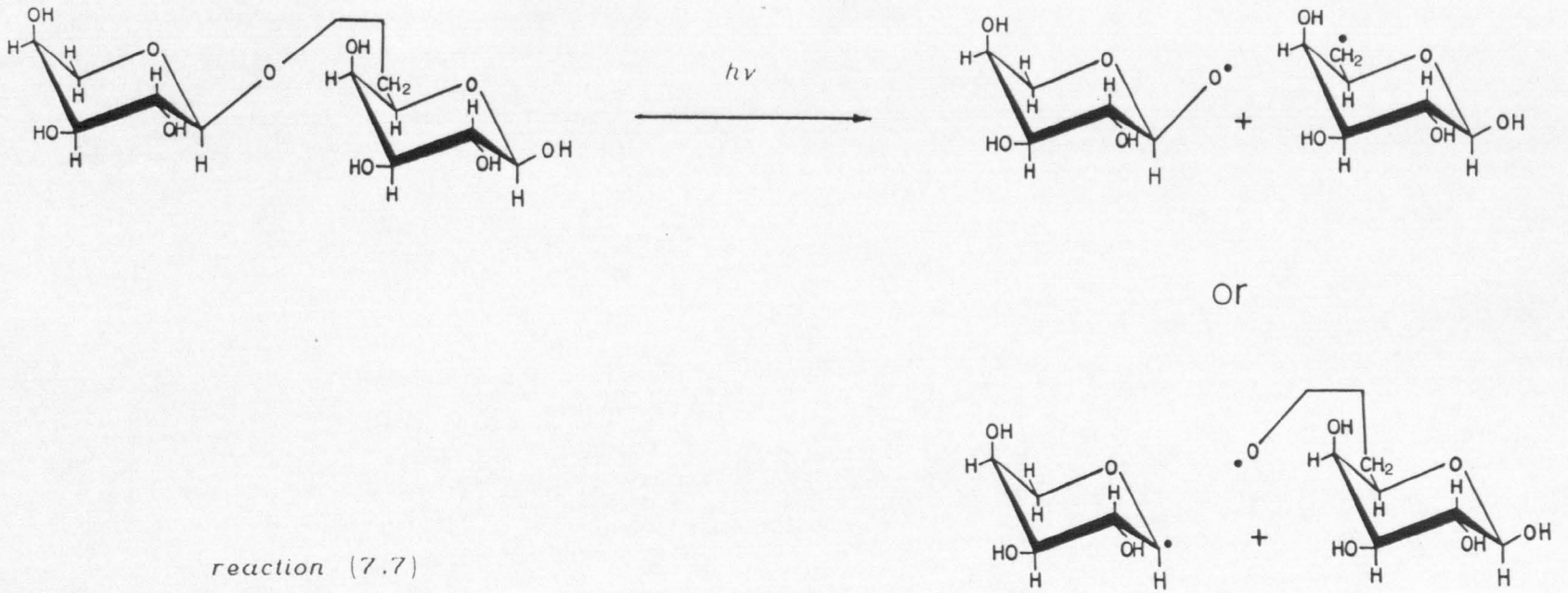
reaction (7.4)



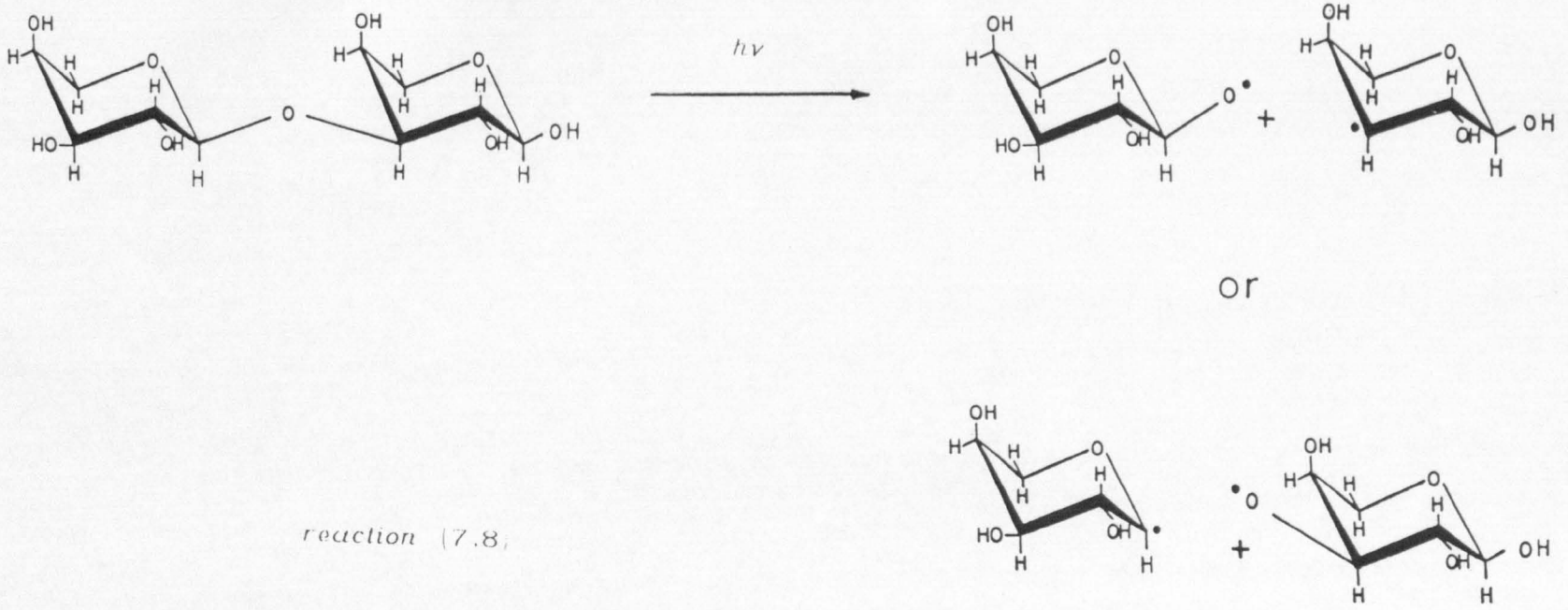
reaction (7.5)



reaction (7.6)



reaction (7.7)



reaction (7.8)