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ABSTRACT

The electron paramagnetic resonance of X-irradiated (~ 10 krad.) tyrosine, thyronine and their iodine-derivatives in the form of compressed pellets in vacuum-sealed quartz tubes have been measured between 100°K and 300°K at ~ 9 G Hz. The EPR spectra of tyrosine, 3-5 diiodo thyronine and thyronine, in the order of decreasing line-width, are spectrally similar and hence indicate that the electron spin density, g = 2.004 or 2.005, is trapped mainly in the ring from which the hydroxyl proton is lost. The samples having iodine on the same ring as the OH group show a rather large anisotropy in g≈2.04 presumably due to the presence of small spin density on the iodine[5]

The Gr value, i.e. the number of paramagnetic centers produced by 100 ev as deduced from the temperature dependence of the magnetic absorption, of the irradiated iodine-derivatives increases with the number of iodines on the molecule. The G_r values of tyrosine and thyronine, however, can not be estimated from the magnetic absorptions, since their absorption increases with the temperature indicating the antiferromagnetic exchange between spin densities on the neighboring molecules.

I. INTRODUCTION

The effects of X and γ radiation on tyrosine, thyronine and their iodine-derivatives have been measured by Van de Vorst et al[1] with electron paramagnetic resonance, EPR, on powder samples at room temperature. They also reported[1] the yeld of free radicals, i.e. G_r = number of free radicals produced by absorbing 100 ev, based on the room temperature EPR spectra in the region, where this signal is linearly proportional to the radiation dose.

In order to resolve the EPR spectra and hence to reveal the origin of the free radicals produced by the γ-irradiation, Gordy et al[2] used crystal of L-tyrosine-HCl and found that the free radical was formed by loss of a proton, H, from the hydroxyl group attached to the ring.

We have recently repeated the work of Van de Vorst et al[1], except with following two modifications:

(1) Low radiation dose, i.e ~ 10krad, instead of Mrad.[1] or more.

By applying low dose of radiation we may expect to reduce the number of types of free radicals produced and hence to facilitate the qualitative interpretation of the EPR spectra of iodine-derivatives even in the powder samples, since single crystals of iodine-derivatives are not easily available.

(2) EPR measurements from 300°k to 100°k.

By running EPR spectra to lower temperatures we obtain the temperature-dependence of the paramagnetic free radicals. The temperature-dependence of the doubly-integrated EPR

signal will reveal the interactions between the paramagnetic free radicals in the solids and will also provide a more reliable determination[3] of the yields of free radicals through the Curie-Weiss formula.

II. EXPERIMENTAL AND DISCUSSION

The EPR of X-irradiated, ~ 10 krad., tyrosine, thyronine and their iodine-derivatives were measured between 100°k and 300°k at about 9.3 G Hz. The samples were in the form of compressed powder pellets vacuum-sealed in the EPR quartz tubes. We shall first discuss the EPR spectra in A and discuss their temperature dependence in B.

A. EPR spectra

The room-temperature EPR are summarized in Fig. 1, which shows many regularities among various samples and are more consistent than that obtained with higher radiation dose[1]. The curves in Fig. 1 exhibit following two general features:

1. All spectra show the same free radical which is produced by the loss of the hydroxyl proton[2], with $g_A = 2.005$. The linewidths, however, are different among various samples.

2. All the spectra whose sample have iodines on the ring having OH group show a rather larger anisotropy in g, which must arise from some small spin density[3] on the iodine.

2'. Those which have two iodines on the OH-bearing ring show a greater anisotropy than do those with only one iodine on this ring.

Further comparative details between the spectra are:

α) Tyrosine, thyronine and 3,5 - diiodo-thyronine have similar spectra of $g = 2.006$ with their linewidths $\Delta H = 12.2, 9.9$ and 11.8 Oe., respectively. The resonance of the latter two compounds are sharper than that of tyrosine because the electron spin density is further removed from CH_2 group which in tyrosine gives to some unresolved proton coupling[2,3]. Evidently the electron spin density is trapped mainly in the ring from which the hydroxyl proton is lost.

β) 3-iodo-L-tyrosine and 3,3', 5-triiodo-thyronine both have one iodine on the OH-bearing ring and both have similar EPR spectra in Fig. 1. However, the EPR spectrum of the former at $g = 2.006$ is stronger and broader, $\Delta H = 22.9$ Oe, than that of the latter, $\Delta H = 13.6$ Oe.. We speculate that the broadening of resonance at $g_A = 2.006$ in the 3-iodo-L-tyrosine is due to the fluctuation of interactions between spins on the neighboring molecules, since the temperature dependence of the magnetic susceptibility of this compound, in Fig. 2, suggests the interactions being intermediate between antiferromagnetic and paramagnetic.

γ) 3,5-diiodo-L-tyrosine and thyroxine both have two iodines on the OH-bearing ring and show similar spectra. The former, however, show more prominent and symmetric structure around $g_c = 2.04$ presumably due to equivalent iodine atoms at 3,5

positions of the tyrosine ring, while the iodines at 3',5' positions in thyroxine are not equivalent with respect to the inner ring of the thyronine[6].

B. Temperature dependence of magnetic susceptibility and the yiesl of paramagnetic free radicals, G_r.

The temperature dependence of EPR signals are plotted as 1/A versus temperature T in Fig. 2, where A is the doubly integrated area of the EPR spectra and hence is proportional to the paramagnetic susceptibility χ of the free radical spins in the sample. The data in Fig. 2, which covers from 100°k to 300°k, show that the interactions between spins ranges from(1) antiferromagnetic in tyrosine and thyronine, through(2) the intermediate case in 3-iodo-tyrosine and finally to(3) paramagnetic in 3,5-diiodo-thyronine and the rest of iodine-derivatives. Correspondingly, the Weiss constants in the Curie-Weiss Law (1) cannot be determined from the data of tyrosine and thyronine, (2) may be estimated from the high temperature, i.e. near 300°k, data of 3-iodo-tyroxine and(3) are obtained from the data through the entire temperature range, 100°k to 300°k, of 3,5-diiodo-thironine etc., respectively. The Weiss constants determined in this manner, the G_r (correct) values evaluated[5] with the corresponding Weiss constants and the G_r values of Van de Vorst et al[1] ignoring the Weiss constants are summarized in Table 1 along with the structural data of EPR spectra in Fig. 1.

As expected, the G_r (correct) values increase with the number of iodines in the molecule, since the iodine being heavy atom nas large photoelectric crossection to absorb the X-ray.

There are two possible reasons, both are due to the heaviness of the iodine, to explain the observation that the temperature dependence of tyrosine and thyronine is antiferromagnetic on one hand while that of their iodine-derivatives is paramagnetic. Firstly, the large static diamagnetic susceptibility of iodine may supress the antiferromagnetic interactions between neighboring paramagnetic free radicals. Secondly, the number of free radicals in an average cluster produced by X-irradiation is presumably much fewer in iodine-derivatives due to the large photoelectric crossection of iodine. Antiferromagnetic interactions being cooperative phenomena are ineffective in a small cluster.

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RÉSUMÉ

On a mesuré, la résonance paramagnétique électronique (EPR) de tyrosine, thyronine et ses dérivés iodés, irradiés avec rayons-x (~ 10 krad) sous la forme de pelotes comprimées, placés à l'intérieur d'un tube de quartz evacué, à températures entre 100°K et 300°K et ~ 9 GHz. Les spectres de tyrosine, 3,5 diiode thyrosine et thyronine, en ordre décroissante de la largeur de ligne, sont spectralement similaires, donc, ils indiquent que la densité du spin électronique g d'ordre de 2,004 ou 2,005 est concentrée principalement dans l'anneau duquel le proton hidroxyl est écarté. Les échantillons contenant l'iode dans le même anneau, comme le groupe OH, montrent une anisotropie relativement grande, g ≈ 2,04, qui est probablement causée à la présence de basse densité du spin d'iode.

La valeur de G_r, i.e., le nombre des centres paramagnétiques produits par 100 eV, déduit de la dépendance, avec la température, d'absorption magnétique des dérivés iodés irradiés, augmente avec le

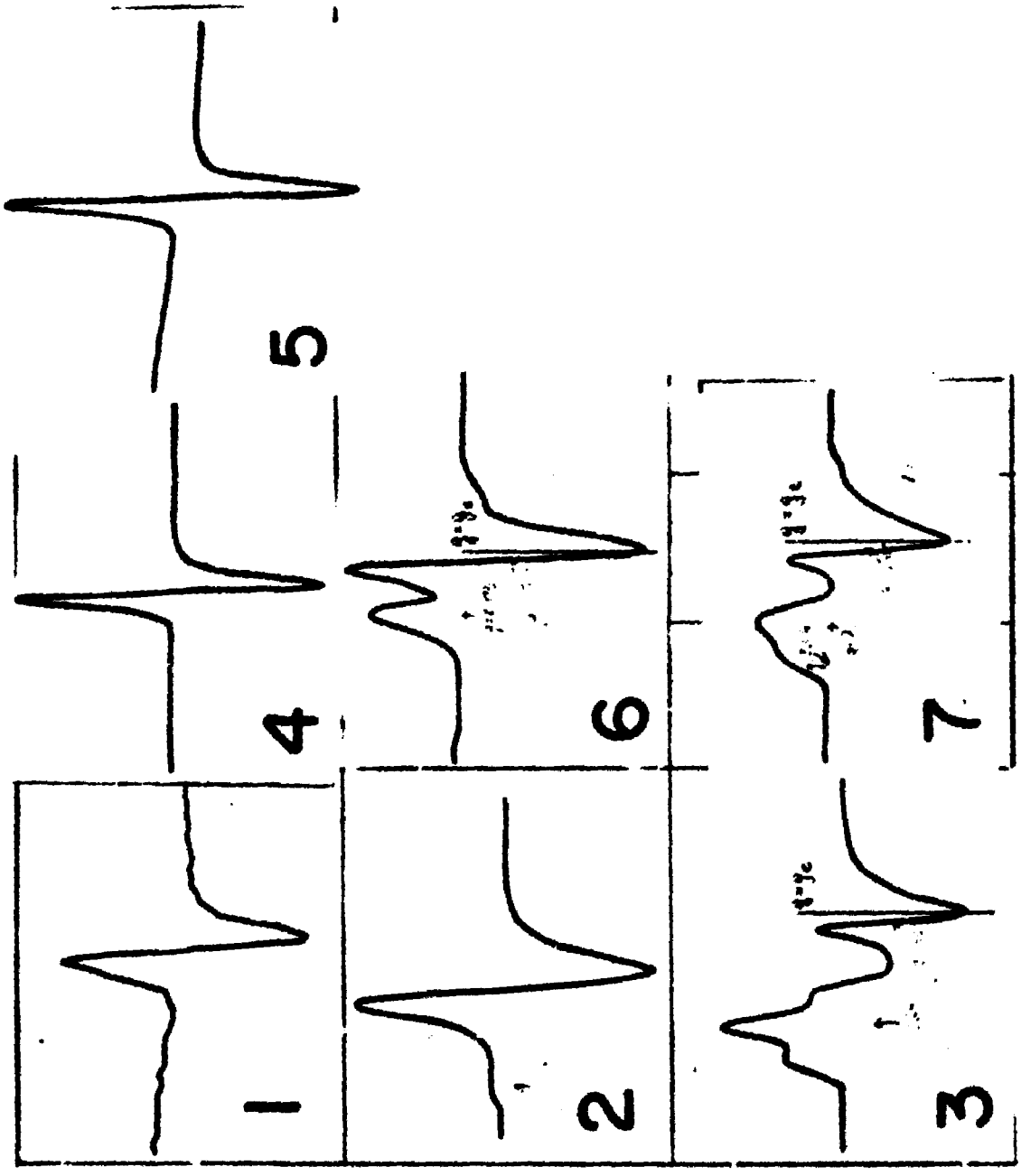
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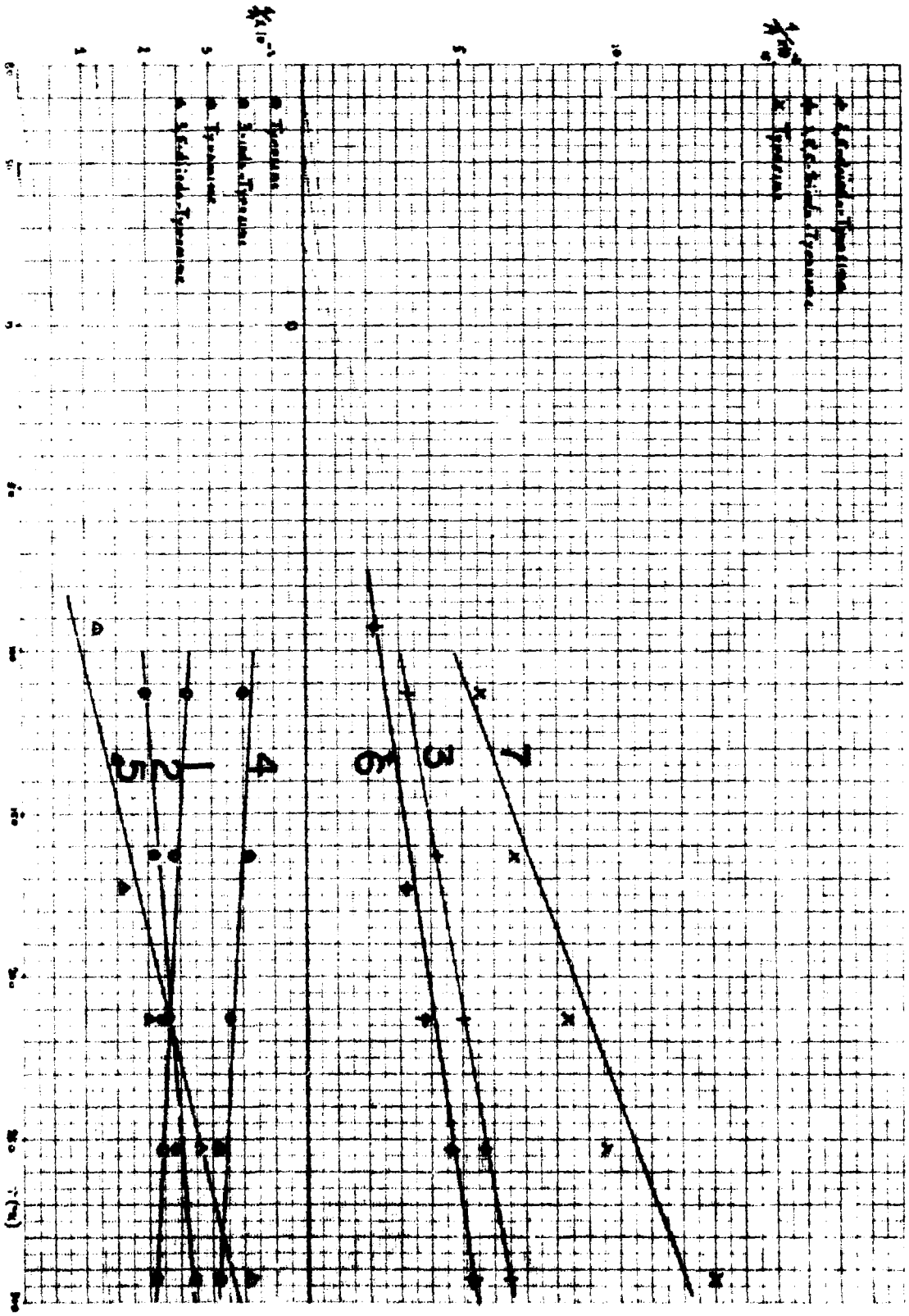
TABLE I

Summary of Paramagnetic free Radicals Produced in Tyrosine, Tyronine and their Iodine-derivatives by 10 krad. X-irradiation

samples (pressed powder pellets in vacuum sealed quartz tubes)	Structures in EPR spectra at room temperature					Temperature-dependence of paramagnetic resonance absorption between 100°K and 300°K		G_r (Van de Vorst[1])
	g_A	H_A (Oe)	g_B	g_C	g_D	Weiss Constant θ °K	G_r (correct)	
tyrosine	2.004	12				Antiferromagnetic	?	0.4
3-iodo-tyrosine	2.005	23		2.04		- 75°	0.12°	0.06
3,5-diiodo-tyrosine	2.005	10.4	2.03	2.04	2.05	- 70	0.16	0.08
tyronine	2.005	9.9				Antiferromagnetic	?	0.1
3,5-diiodo thyronine	2.005	11.8				+ 25	0.22	0.15
3,3',5-triiodo-thyronine	2.005	13.6	2.03			- 54	0.35	0.19
tyroxine	2.005	11.2	2.03	2.04		- 24	0.73	0.43

° Weiss constant obtained by expolating from only two experimental points near 300°K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nombre des iodes dans la molecule. Les valeurs de G_r de la tyrosine et de la thyronine ne peuvent pas être évalués des absorptions magnétiques, dés que son absorption augmente avec la température, ce qu'indique une échange antiferromagnétique entre les densités du spin dans les molécules voisines.

RESUMO

Foi medida a ressônancia paramagnética eletrônica (EPR) de tirosina, tironina e seus derivados iodados, irradiados com raios-x (cerca de 10 krad), na forma de pelotas compressas, colocados em tubos de quartzo a vácuo a temperaturas entre 100°K e 300°K e cerca de 9 GHz. Os espectros de tirosina, 3,5 di-iodo tironina e tironina, na ordem decrescente de largura de linha, são espectralmente similares e, portanto, indicam que a densidade de spin eletrônico g de ordem de 2,004 ou 2,005 é concentrada principalmente no anel do qual o próton hidroxila foi expelido. As amostras tendo iodo no mesmo anel, como o grupo OH, mostram uma anisotropia relativamente grande, $g \approx 2{,}04$, possivelmente devido à presença de baixa densidade de spin no iodo.

O valor de G_r, i.e., o número de centros paramagnéticos produzidos por eV, valor deduzido da dependência com a temperatura de absorção magnética, dos derivados iodados irradiados, aumenta com o número de iodos na molécula. Os valores de G_r de tirosina e tironina não podem, porém, ser calculado das absorções magnéticas, uma vez que, a sua aborção aumenta com a temperatura, indicando a troca antiferromagnética netre a densidade de spin nas moléculas vizinhas.

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