TABLE II

Temp. °C		Resorcinol	Hydroquinone	Pyrogallol	Phloroglucinol	Catechol
30	ΔF_1 Kcal. per mole	—13·64	—14·16	—13·18	—11·77	—14·20
	ΔF_2 Kcal. per mole	—11·93	—12·99	—11·46	—11·10	—12·10
40	ΔF_1 Kcal. per mole	—13·30	—13·93	—13·01	—11·83	—13·75
	ΔF_2 Kcal. per mole	—11·86	—12·84	—11·34	—10·83	—11·83
30	ΔS_1 e.u.	—31·12	—20·46	—14·13	—02·44	—52·74
	ΔS_2 e.u.	—45·87	—11·06	—15·25	—21·72	—24·36
40	ΔS_1 e.u.	—31·22	—20·54	—14·22	—0·217	—49·29
	ΔS_2 e.u.	—46·66	—11·19	—15·46	—21·89	—24·44
	ΔH_1 Kcal. per mole	—23·07	—20·36	—17·46	—12·51	—29·18
	ΔH_2 Kcal. per mole	—13·32	—16·34	—16·18	—17·68	—19·48

The values of free energy ΔF, enthalpy ΔH and entropy ΔS have been determined applying the standard equations[3]. The average values of ΔH, ΔS and ΔF are recorded in Table II.

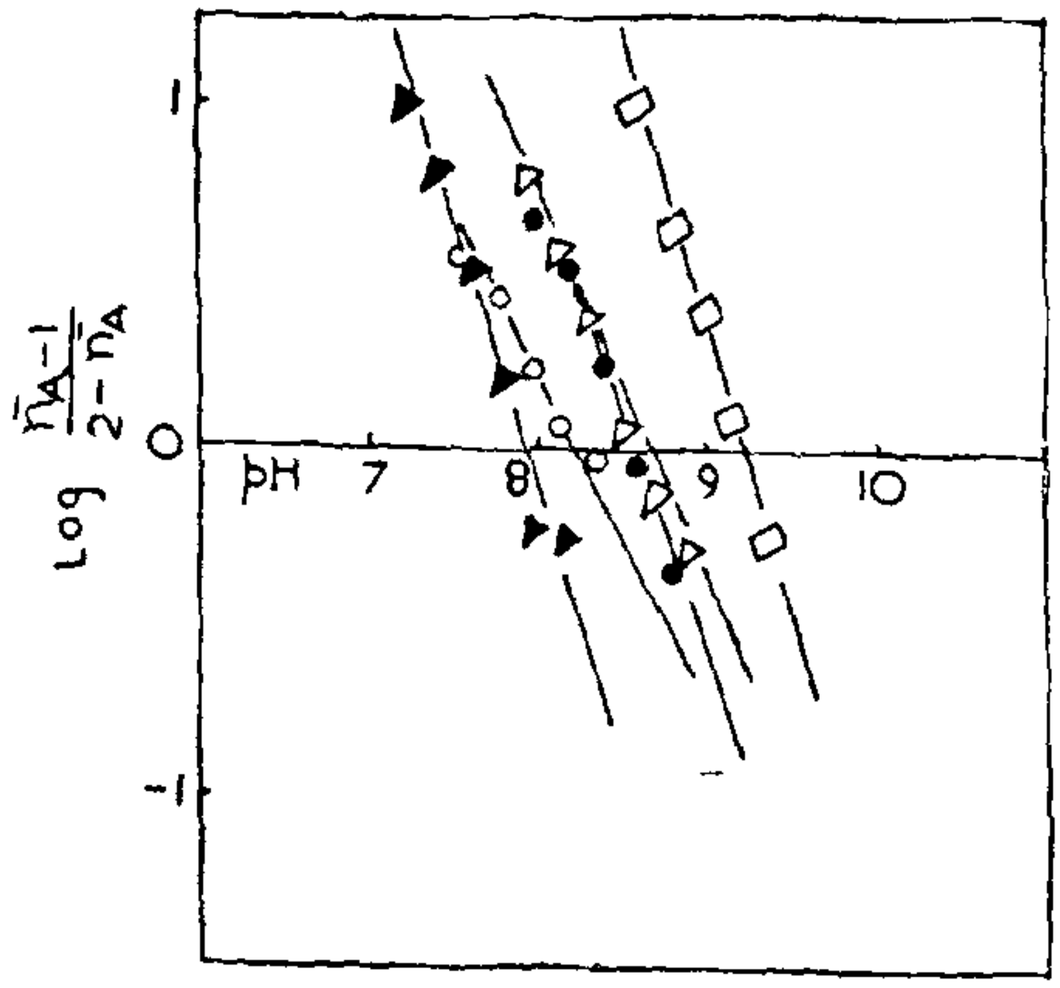

FIG. 3. Linear Plot Method for log K_2^H. ○—Pyrogallol; ▲—Phloroglucinol; ●—Resorcinol; △—Catechol; □—Hydroquinone.

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POLAROGRAPHIC STUDY OF PALLADIUM/ AMINO-ACID COMPLEXES

Introduction

THE electrochemistry of the halocomplexes of palladium[1,2], its ammine[3] and pyridine[4] complexes have been well investigated. The present paper deals with the study of the palladium complexes of three amino acids, namely glycine, valine and glutamic acid. The effects of pH, concentration of the ligand, reversibility, etc., have been examined critically. The number of electrons involved in the reduction of the complexes has been fixed by coulometry as 2·1 and the polarographic curves (though irreversible) have been found to be of analytical use in the pH range of 4·5–7 for estimating Pd upto 250 ppm.

Reagents

The ligand stock solutions of glycine, valine and glutamic acid were prepared in 0·1 M concentration from Analar chemicals. Other solutions were prepared by standard methods employing A.R. chemicals. Britton Robinson buffers[5] were employed for pH control. A pen recording polarograph (PO3) was used in this work. Capillary characteristics were $m = 2·71$ mg/sec., and $t = 3·74$ sec.

For the polarographic estimations, the final concentration of metal was about 10^{-4} M and the ligand concentration was always kept about 100 times that of metal to ensure complete complexation. The

concentration of maximum suppressor was 0·01% while that of the supporting electrolyte (KCl) was 0·1 M.

Behaviour of Uncomplexed Palladium-chloride

Previous workers[6] have reported that the polarographic behaviour of palladium group metals is vitiated by chemical reactions. Salts of this group are spontaneously reduced to the black metal in contact with mercury (d.m.e.)[7] and the resultant mercurous ions give a polarographic wave with $E_{\frac{1}{2}} = +0{\cdot}06$ V. That this wave was due only to mercurous, was confirmed by us by running a polarogram with a solution of mercurous chloride (10^{-5} M), which gave an analogous wave with the same $E_{\frac{1}{2}}$.

Polarographic Behaviour of the Palladium-Amino acid Complexes

When palladium is complexed with amino acid, the $E_{\frac{1}{2}}$ shifts to a negative potential, and if the complexation is complete, the interference due to chemical reaction does not occur.

An exploratory work was done to ascertain the concentration at which complete complexation occurred. Polarograms were recorded keeping the metal ion concentration constant ($0{\cdot}4 \times 10^{-4}$ M), while ligand concentration was varied from 2 to 150 times that of metal at a constant pH = 3·5. At lower concentration of ligand, two waves were observed, the first due to mercurous and the second due to complex reduction. The latter gradually grows at the expense of the former, which completely disappears at a ligand concentration of about one hundred times that of metal.

Reversibility

Figure 1 shows the effect of variation of mercury reservoir height[8] on the palladium-glycine wave at pH 5·5. It is seen, that the current at the bottom of the wave is almost independent of the mercury head, whereas, at the limiting region ($\gamma = 1$), it is practically directly proportional to $\sqrt{h}$. Despite the reaction being irreversible, the i_d was proportional to the concentrations, making the polarograms analytically useful.

Influence of pH

Below pH 2, no complexation occurred, as there was only the mercurous wave with $E_{\frac{1}{2}} = +0{\cdot}06$ V. At pH 3·5 the polarographic wave due to the palladium–glycine complex appeared at an $E_{\frac{1}{2}} = -0{\cdot}265$ V. As the pH was increased, the wave shifted to more negative potentials. Thus at pH 4·5, 5·5 and 6·5 the $E_{\frac{1}{2}}$ is $-0{\cdot}300$ V, $-0{\cdot}360$ V, $-0{\cdot}40$ V, respectively. Above pH 7·5 no polarographic reduction of the complex is observed.

Results

In comparison with nickel, palladium is expected to have three species in solution depending on pH

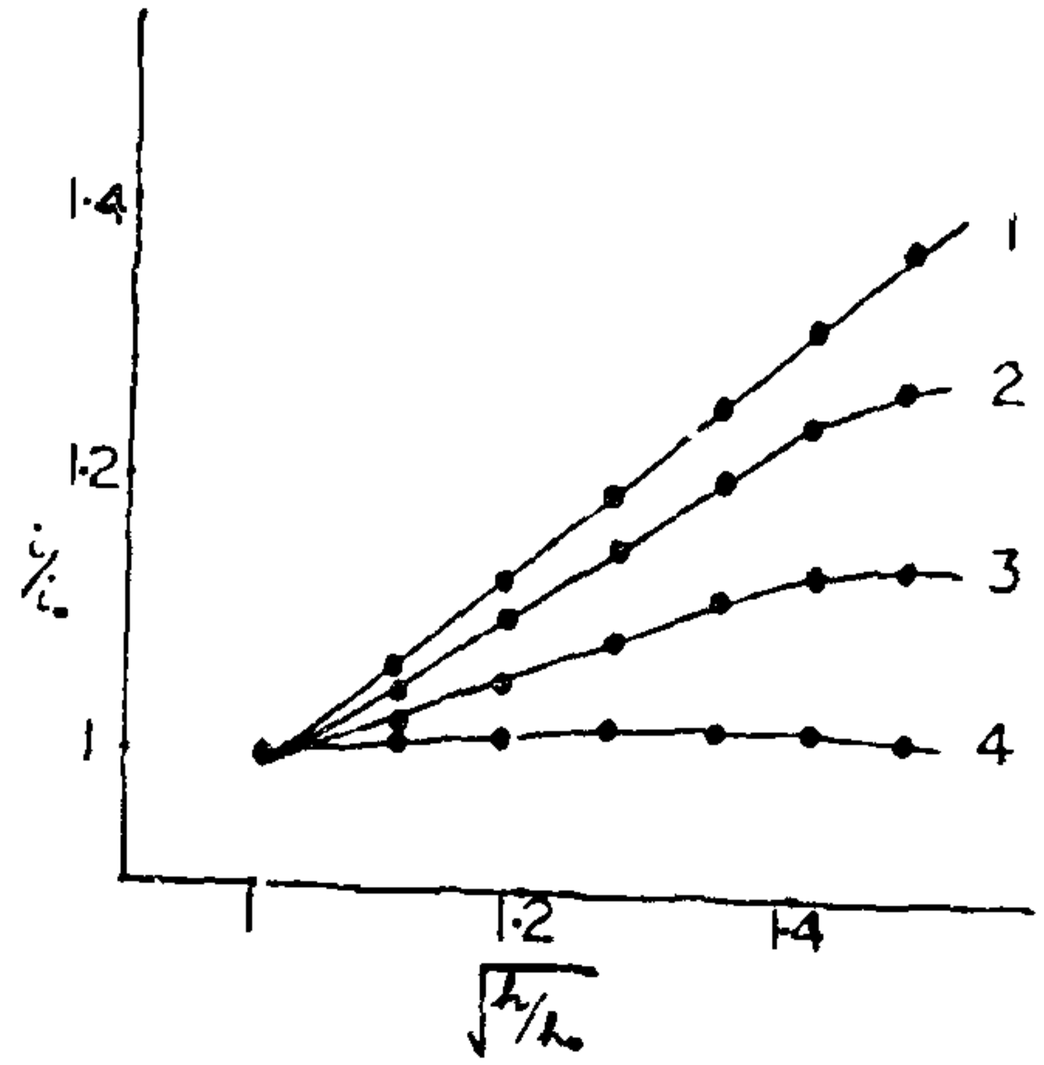

FIG. 1. Effect of variation of mercury reservoir height on the maximum current at various points on the reduction wave of the palladium–glycine complex at pH 5·5. Concentration of complex = 1×10^{-4} M. Height of reservoir varied between 25–55 cm.

Curve	(i/i_0)
1	1
2	0·65
3	0·32
4	0·16

(*a*) $[Pd(Gl)_1]^+$ ($E_{\frac{1}{2}} = -0{\cdot}265$ V, between pH 3·5 and 4·5), (*b*). $[Pd(Gl)_2]^\circ$ ($E_{\frac{1}{2}} = -0{\cdot}300$ V, between pH 4·5 and 7·5), and (*c*) $[Pd(Gl)_3]^-$ above pH 7·5. The absence of polarographic wave above pH 7·5 is due to the polarographically non-reducible anionic complex.

Analytical Applications

The curve obtained between pH 4·5 and 7 is well-defined and is found to be of analytical use. A number of polarograms of known concentrations of palladium gave a linear graph when their i_d's were plotted against the corresponding concentrations of the complex.

Polarographic estimation of palladium through its amino acid complex can be considered a truly micro or semi-micro technique, the quantities handled being below 50 mg. This technique is suitable for the estimation of Pd present in hydrogenation catalysts and in dental and ornamental alloys. In alloys, it is generally found in association with gold, platinum, silver and sometimes with base metals like copper and zinc. Palladium has to be isolated from its associates by any suitable method[9–12]. The precipitation of Pd with O-Hydroxyacetophenoxime[13] was adopted in this lab. This method was picked for its simplicity,

not involving extraction and also due to the minimum interferences of other ions.

TABLE I

The results of estimations of palladium

	Constituent metals Dental alloy (simulated)	Concentration ppm	Palladium found polarographically after isolation ppm	Error ppm
1.	Platinum	21·3	21·1	−0 20
	Palladium	21·3		
	Gold	10·65		
	Copper	42·6		
	Zinc	10·65		
2.	Platinum	42·6	10·55	−0·10
	Palladium	10·65		
	Gold	21·3		
	Copper	10·65		
	Zinc	21·3		
3.	Platinum	10·65	85·50	+0·3
	Palladium	85·2		
	Gold	42·6		
	Copper	42·6		
	Zinc	42·6		
4.	Platinum	85·2	42·80	+0·20
	Palladium	42·6		
	Gold	21·3		
	Copper	21·3		
	Zinc	10·65		
5.	Platinum	10·65		
	Palladium	10·65	10·80	+0·15
	Gold	10·65		
	Copper	42·6		
	Zinc	42·6		
7.	Platinum	85·2		
	Palladium	170·4	169·8	−0·6
	Gold	42·6		
	Copper	10·65		
	Zinc	10·65		
7.	Platinum	10·65		
	Palladium	181·05	179·55	−1·50
	Gold	85·2		
	Copper	85·2		
	Zinc	42·6		

Synthetic solutions were made of a mixture of platinum, palladium, gold, copper and zinc, simulating the composition of a dental alloy. The palladium was isolated from the mixture as the oxime, filtered through a No 3 sintered crucible and washed with hot water. The precipitate in the sinter was dissolved in the minimum amount of aqua-regia and the solution heated on a water-bath for half an hour to decompose the organic ligand. The solution thus prepared was mixed with the complexing amino acid, supporting electrolyte, maximum suppressor, and the pH adjusted to 5·5. The results of several estimations are given in Table I.

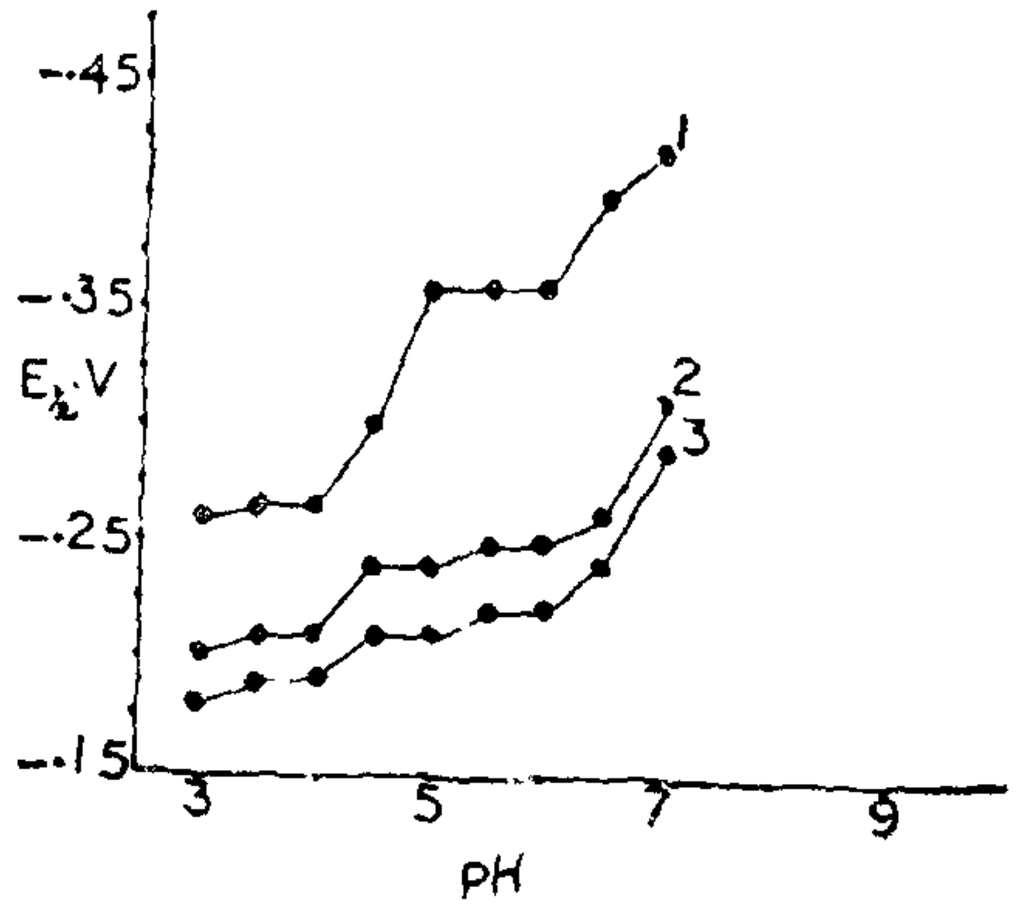

FIG. 2. Variation of $E_{\frac{1}{2}}$ of the palladium-amino acid complexes with pH. 1 = palladium-glycine complex. 2 = palladium-valine complex. 3 = palladium-glutamic acid complex.

Polarographic Conditions:

Concentration of metal = $1 \times 10^{-4} M$
Concentration of ligand = 1×10^{-2} M
Concentration of supporting electrolyte (KCl) = 0·1 M.
Concentration of maxima suppressor (gelatin) = 0·01%.

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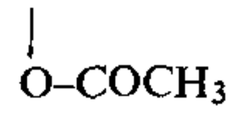
SELENIUM DIOXIDE OXIDATION OF SAUSSUREALACTONE

IN continuation of our studies on the selenium dioxide oxidation of sesquiterpenic lactones[1, 2, 6] we now report our results on the selenium dioxide oxidation of saussurealactone.

Saussurealactone (I), obtainable from dihydrocostunolide (II) by thermal (Cope's) rearrangement[3] possesses two double bonds of which, only the one at C_3–C_4, has methyl and methine groups in the allylic positions. The other double bond, however, does not have any such oxidisable groups in the allylic positions. When (I) is subjected to selenium dioxide oxidation (refluxing benzene, 20 h), a mixture containing five compounds (TLC) was obtained. Of these, three compounds have been isolated pure (TLC), by chromatography, followed by crystallisation.

The least polar of these, the major product of the reaction (30%) has been identified as the conjugated aldehydolactone (III), $C_{15}H_{20}O_3$, M^+ 248, m.p. 150–2° (benzene + 10% hexane); $(\alpha)_D$ + 40° (c, 0·5; $CHCl_3$) IR* 1770 (γ-lactone), 1681, 2778 ($_H\!>\!C\!=\!O$) 1639, 1621, 900 (conj. and non-conj. $>C=CH_2$); NMR ($CDCl_3$): 8·97 (3H, s, C_{10}–CH_3); 8·8 (3H, d, J = 6 Hz, C_{11}–CH_3); 7·0 (1H, d, J = 12 Hz, C_5–allylic proton); 5·2 (2H, m, C_2 olefinic protons); 5·74 (1H, t, J = 12 Hz, C proton); 4·44 (1H, m, C_1-olefinic proton); 3·75 (2H, s, conj. C_3-olefinic protons) and 0·52 (1H, s, aldehydo proton). UV λ_{max} 218 $m\mu$, ϵ_{max}, 8000; 2:4 DNP $C_{21}H_{24}O_6N_4$, m.p. 190–2°.

Sodium borohydride reduction of (III) gave the corresponding hydroxylactone (IV), $C_{15}H_{22}O_3$ (low melting solid m.p. < (40°); $(\alpha)_D$ + 44° (c, 2·2; $CHCl_3$); $n_D^{31.5}$ 1·5037; IR, 3650 (OH), 1776 (γ-lactone), 1639, 892 ($>C=CH_2$); NMR (CCl_4): 8·92 (3H, s, C_{10}–CH_3); 6·14 (2H, s, –CH_2OH at C_4); 5·93 (1H, t, J = 10 Hz, C_6-proton); 6·67 (1H, d, J = 10 Hz, C_5-olefinic proton); 5·14 (4H, m, olefinic protons at C_2 and C_3); 4·27 (1H, m, C_1-olefinic proton) and at 7·4 exchangable with D_2O (1H, hydroxyl proton). On acetylation, lactone (IV) gave a liquid acetate lactone (V), $C_{17}H_{24}O_4$ with the following spectral properties. IR, 1770 (γ-lactone), 1739, 1235 (acetate) 1639, 895 ($>C=CH_2$); NMR (CCl_4): 8·78, 8·92 (6H, C_{10}- and C_{11}–CH_3); 7·97 (3H, s, acetate methyl at C_4); 6·44 (1H, d, J = 15 Hz, C_5-olefinic proton); 6·0 (1H, t, J = 12 Hz, C_6 proton); 5·58 (2H, s, –CH_2 at C_4); 5·0 (4H,



m, C_2 and C_3 olefinic protons), 4·24 (1H, m, C_1-olefinic proton).

The lactone (IV) could also be isolated from the tail fractions of chromatography (identified by IR NMR, TLC and $(\alpha)_D$ + 42° (c, 1·2; $CHCl_3$); $n_D^{31.5}$ + 1·5034). The identity was further confirmed by converting it into acetate (V) and comparing the spectral properties.

From the middle fractions of chromatography a crystalline dialdehydo lactone, $C_{15}H_{18}O_4$, M^+ 262, m.p. 200–2° (benzene + 30% hexane) has been isolated though in very low yields (<1%), which has been assigned structure (VI) on the basis of spectral data; IR 1776 (γ-lactone), 1681, 2786 (aldehyde), 1621 (conj. $>C=C<$); NMR ($CDCl_3$): 8·81 (3H, d, J = 7·2 Hz, C_{11}–CH_3); 4·73 (1H, t, J = 10·8 C_6-proton); 3·47 (1H, t, J = 7·8 Hz, C_1-olefinic poton); 3·87 (1H, d, J = 10 Hz, C_5-olefinic proton) and at 0·53–0·17 (2H, aldehydo protons); UV λ_{max} 225 $m\mu$, ϵ_{max} 20,000; 2: 4DNP $C_{27}H_{26}O_{10}N_8$, m.p. 207°. The above spectral data indicated that compound (VI) contains two aldehydo groups, probably both of which are conjugated. The possibility of any conjugation between the double bonds was eliminated, from the fact, that the dihydroxylactone (VII), obtained by sodium-borohydride reduction of (VI) shows in its UV spectrum only the end absorption for isolated trisubstituted double bonds (ϵ_{205}, 3000). The NMR spectrum of (VI) indicated the presence of only one secondary methyl, *viz.*, one at C_{11}. It therefore appeared that the two CH_3 groups (C_4 and C_{10}) of I are involved in allylic oxidation and must have been converted into the aldehydo groups. This, however, is not possible for a compound like (I), as such, without undergoing rearrangement. The appearance of the triplet for the C_6-proton in the NMR spectrum of VI, clearly suggested that there must be one proton on each side of C_6-which is available for coupling, *viz.*, at C_5 and C_7. The C_6-proton in the spectra of compounds like I, III, IV appeared as triplets at 5·9, 5·74 and 6·0 respectively and even in compounds such as VIII and IX[4] where the C_6-proton is allylic to the double bond at C_4–C_5, it is observed at 5·55 and 5·52 respectively. The significant down field shift of the C_6-proton from the normal value of 5·8 to 6·0τ to 4·73τ, suggests that it is in a different environment and such a downfield shift is possible only when it is allylic to a conjugated double bond as in (VI). Structure (VI) satis-