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Diorganotin (IV) Chelates of naturally occurring Hydroxynaphthoquinones

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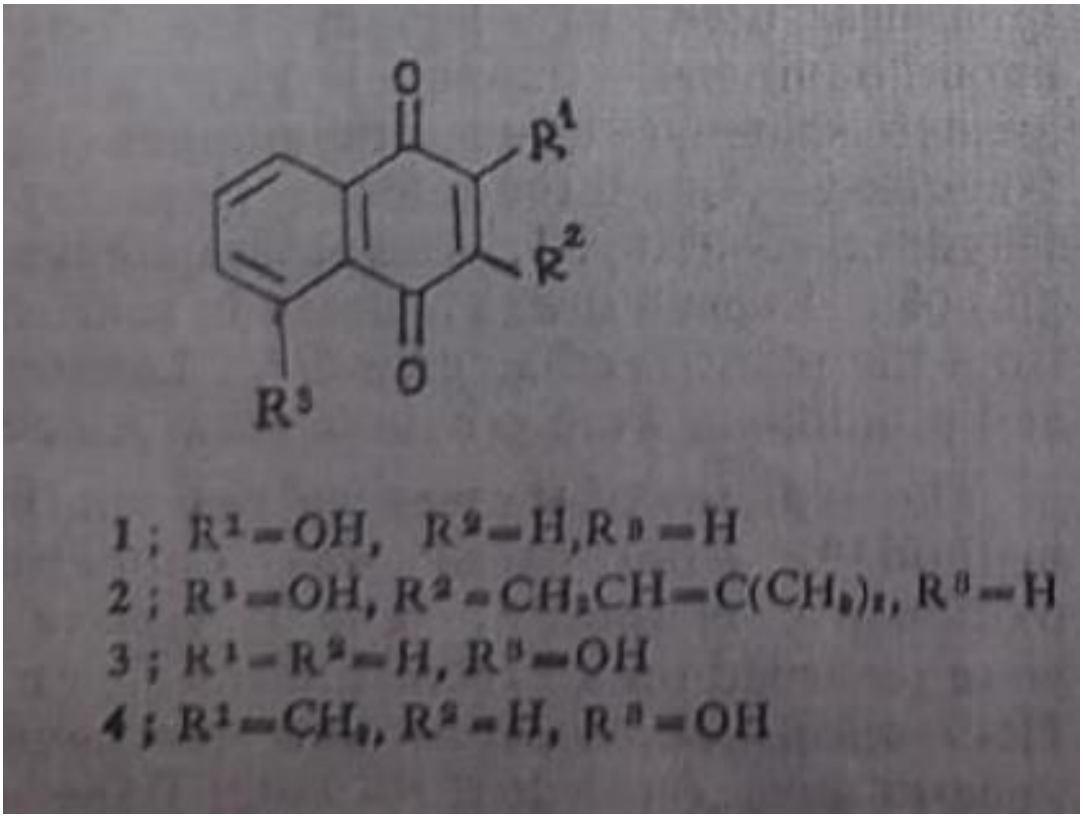
Quinones and their substituted derivatives have long been known to possess numerous chemically and biologically significant properties with many important applications in several areas [1]. Hydroxynaphthoquinones and their chelation with various metal ions increase their activity tremendously. The organotin (IV) complexes of juglone displayed more antibacterial activity then the free ligands [2]. Since in most of the applications of hydroxyquinones, their chelating ability plays an important role, the study of their metal chelates has been of great interest in understanding mechanisms of their chemical and biological activities. Consequently, during the last two decades, several papers concerning the synthesis, characterization, thermal stability, kinetic studies and biological function of some metal chelates of hydroxyquinones, hydroxynaphthoquinones have been published [3].

It seems that no study has been reported on the complexes of lawsone (1), lapachol (2), juglone (3) , plumbagin (4) and in the present communication our results concerning their chelates with tetravalent tin metal are presented.



RESULTS AND DISCUSSION

All the chelates were obtained as fine powder or microcrystalline solids (Table 1), soluble in acetone, methylene chloride and alcohol. The chelates gave satisfactory elemental analysis and their structures were determined on the basis of spectroscopic measurements.

The uv-visible spectra (EtOH) of the free ligands showed mainly three bands at $220-250, 266-278$ and $333-420$nm attributable to $\pi \rightarrow \pi^*, n \rightarrow \pi^*$ (benzenoid) and $n \rightarrow \pi^*$ (quinonoid) transitions respectively. In the spectra of the chelates, the first band remained unchanged. The second band shifted towards lower energy at $262-284$ nm. In the region $416-436$ nm, a new band appeared which was absent in the spectra of the free ligands and hence can be assigned to $M \rightarrow L$ type transitions.

Table 1-Physical Data of the Complexes

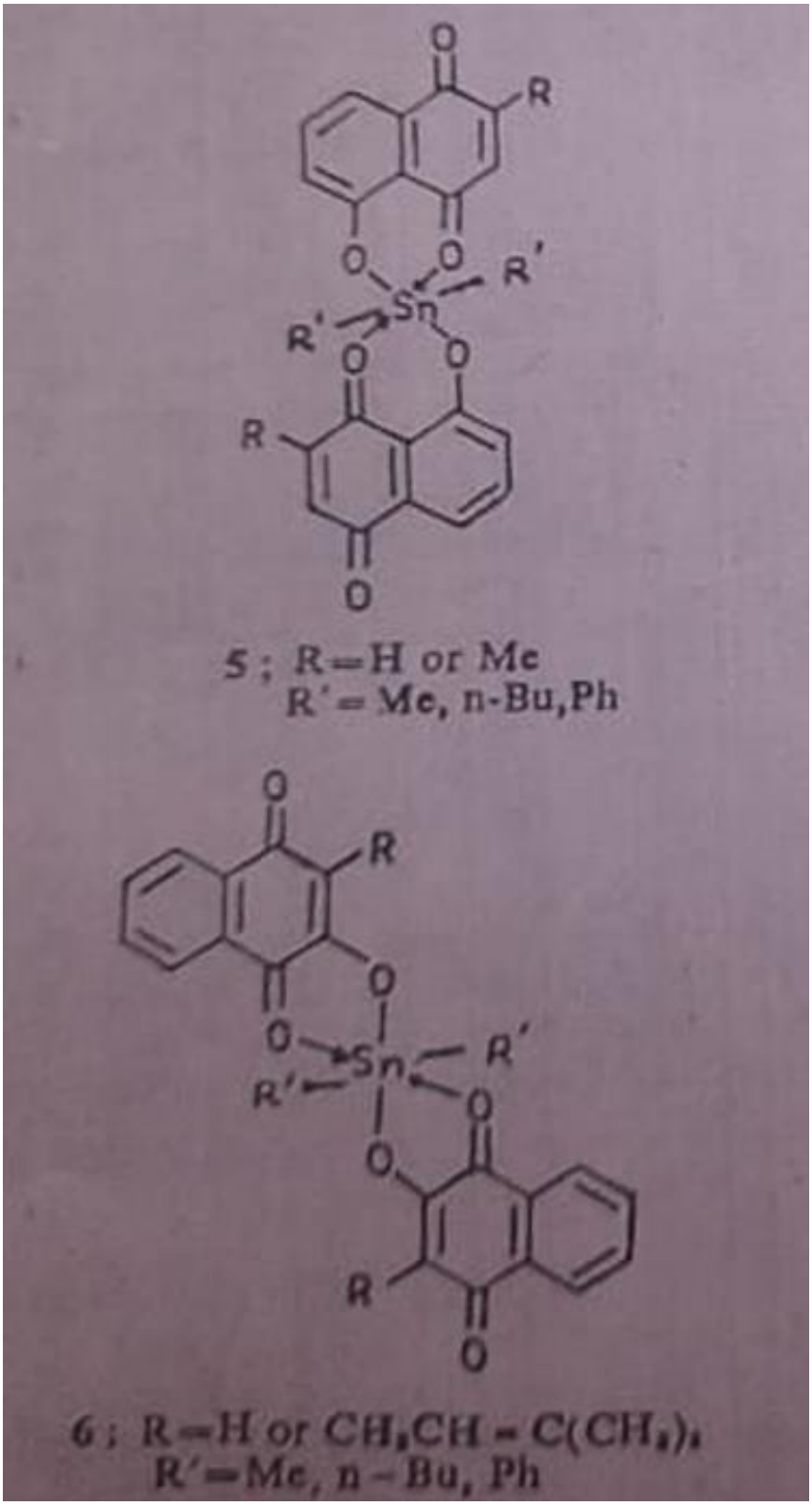
Compd.	Colour	M.p. °C	Yield %
Lawsone (1) chelates:			
Me_2SnL_2	Orange	250	72
Bu_2SnL_2	Orange	285	81
Ph_2SnL_2	Red	260	55

Lapachol (2) chelates:			
Me_2SnL_2	Brownish red	210	77
Bu_2SnL_2	Dark red	157	62
Ph_2SnL_2	Orange red	210	60
Juglone (3) chelates:			
Me_2SnL_2	Cherry red	182	78
Bu_2SnL_2	Brownish red	197	70
Plumbagin (4) chelates:			
Me_2SnL_2	Brown	190	79
Ph_2SnL_2	Dark green	172	79

The most relevant bands in the ir spectra of the chelates and their tentative assignments are shown in Table 2. The absorption around $3200\ cm^{-1}$ due to phenolic hydroxyl group in the free ligands was absent in all the chelates indicating the chelation through hydroxyl group.

The non-coordinated carbonyls ν_c ….. 0 (free) in all the complexes occurred at $1670 - 1630\ cm^{-1}$. The stretching frequency ν_c ….. 0 of the non-coordinated carbonyl group in all the chelates is similar to that of the free ligands[4]. The coordinated carbonyl groups in all the chelates appeared at lower energy at $1625 - 1610\ cm^{-1}$ as strong band. This observation can be easily explained on the basis of the structure **5** for the ligands **1** and **4** chelates and structure **6** for those of **2** and **3** chelates. In these structures, the ligand acts through its monomeric form as a chelating bidentate ligand, forming a chelated ring with the metal ion.

The absorptions in the region $1580 - 1550\ cm^{-1}$ are due to normal aromatic vibrations and the one around $1320\ cm^{-1}$ of medium intensity is due to the activating effects of the carbonyl groups on the adjacent C-C vibrations. The strong to medium absorptions at $1290 - 1230\ cm^{-1}$, found to be present in all hydroxynaphthoquinones and in their chelates, are characteristic of quinone compounds. The intense $C - O$ stretching absorption occurring in the quinones around $1220\ cm^{-1}$ appeared only as a shoulder in these chelates confirming the involvement of C-2 or C-5 hydroxyls in chelation. The olefinic C-H wagging mode appeared in all the complexes around $1000\ cm^{-1}$ and the adjacent hydrogens of aromatic ring appeared at $865 - 730 cm^{-1}$. The band at $490 - 430\ cm^{-1}$ has been assigned to $\nu_{Sn\text{-}o}$ symmetric stretching vibrations. The $\nu_{Sym}(Sn - C)$ and $\nu_{asy}\ (Sn - C)$ vibrations are assigned in the regions $510 - 530$ and $545 - 580\ cm^{-1}$ respectively, by comparison with ir spectra of the corresponding alkoxides and oxygen donor ligands, thus clearly indicating distorted octahedral structures for all these chelates.



The main feature of the pmr spectral studies of the chelates was the absence of phenolic hydroxyl protons at $\delta 7.4 - 12.5$ thereby suggesting chelation through C_2 or C_3 hydroxyl group and supplementing structures **5** and **6**. Some salient features of pmr spectra of the diorganotin-quinolates (Table 1) are the tin-methyl protons in case of dimethyltin chelates appeared in the range $\delta 0.7 - 1.0$ as singlets whereas in the case of the dibutyltin complexes, the alkyltin protons

were observed at $\delta 0.8 - 2.00$ as multiplets. A multiplet at $\delta 7.3 - 7.4$ was associated with the tin-phenyl protons of diphenyltin diquinolates. In lapachol chelates (Table 1), the sidechain alkenyl protons were observed at δ 1.62 - 1.91(s, CH_3), 3.24 − 3.50(d, J7 Hz, CH_3), 5.16 − 5.34 (t, J7 Hz, = CH). In case of dimethyltin diplumbaginate (Me_2SnL_2), the methyl protons attached to quinonoid ring appeared as singlet at 82.14 . In all the chelates, the quinonoid protons were attributed to singlets appearing at $8637 - 7.0$. The aromatic protons of the quinonoid rings appeared as two sets of multiplets at $87.3 - 7.8$ and $7.7 - 8.3$.

All these observations thus confirm the structures 5 and 6 for these chelates.

The ^{15}Cnmr spectrum ($CDCl_8$) of dimethyltin dilapacholate (Me_2SnL_2) was compared with ^{13}C nmr of the ligand. It was noticed that the coordinated carbonyl carbon at C -1 shifted from δ 181.5 ppm in ligand to δ 135.8 ppm in the chelate. Whereas the $C - 2$ hydroxyl carbon shifted from δ 155.4 to 136.3 ppm.

EXPERIMENTAL

The organotin (IV) chelates of the quinones were synthesised by the reaction of dimethyltin, di-nbutyltin and diphenyltin diisopropoxides with lawsone, lapachol, juglone and plumbagin. Owing to the highly oxidisable and extremely hydrolysable nature of organotin alkoxides, all the reactions were carried out under dry nitrogen. All the reagents were dried and purified by fractionation or distillation before use. Alkoxides of organotin were prepared and purified by the standard methods. Naturally occurring hydroxynaphthoquinones used as ligands are 2 -hydroxy-1,4-naphthoquinone (lawsone) (1), 2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone (lapachol) (2), 5-hydroxy-1,4-naphthoquinone (juglone) (3) and 5-hydroxy-2-methyl-1, 4-naphthoquinone (plumbagin) (4). Lapachol was isolated in sufficient amount from the plant Tectona grandis. Lawsone, juglone and plumbagin were procured from Aldrich.

The analysis of tin was carried out by standard method. Isopropanol was estimated by the oxidimetric method. The ir spectra (KBr/ neat) were recorded on a Perkin-Elmer 137 or Beckmann IR-9 spectrophotometers and pmr and ^{13}C nmr spectra were on a Jeol FX90 QFT spectrometer at 90 MHz and 5 KHz respectively.

Preparation of complexes: To a solution of diorganotin dialkoxide in benzene, was added a benzene solution of the appropriate ligand quinone in the stoichiometric ratio of 1:2. The reaction mixture was refluxed under a fractionating column at bath temperature, and the liberated isopropanol was fractionated azeotropically over a period of 3-5 hrs. After complete removal of isopropanol, the excess solvent was removed under reduced pressure, and the resulting solids were crystallised from benzene or benzene-hexane (1:1) mixture.

Table 2	IR SPECTRAL DATA (cm^{-1}) OF THE COMPLEXES						
Compound	C=O (free)	C=O (chelated)	C=C	C--O	as (Sn-C)	s(Sn-C)	(Sn--O)
Lawsone chelates:							
Lawsone	1655s	1620sh	1575s	1280m 1260m	---	---	---
Me_2SnL_2	1640sh	1620s	1580s 1555s	1260m 1240s	580m	508w	490m
Bu_2SnL_2	1636sh	1610m	1570s	1240m	550m	500w	425m
Ph_2SnL_2	1630sh	1620s	1580s	1260s 1235s	555w	507w	450m
Lapachol chelates:							
Lapachol	1660s	1630s	1580s	1275s	---	---	---
Me_2SnL_2	1636sh	1625s	1570s	1260s	545m	520w	490mw
Bu_2SnL_2	1630s	1610s	1560m	1270s 1230s	560m	507w	445m
Ph_2SnL_2	1630s	1625s	1575s	1260s	530w	507w	430m
Juglone chelates:							
Juglone	1670s	1647s	1550s	1220m	---	---	---
Me_2SnL_2	1645s	1625s	1585s 1575m	1235s	550w	530w	420m
Bu_2SnL_2	1665s	1640s	1600s	1240m	545w	510w	450w
Plumbagin chelates:							
Me_2SnL_2	1645s	1620s	1580s	1240s	545m	520mw	440m
Ph_2SnL_2	1655s	1625s	1590s	1280s	550w	510w	445m

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