

involved in the whole system have been tabulated in Table II. The agreement between

TABLE II
Principal excited state fundamentals of
cyanopyridines

Compound	Fundamental modes			
	ν_{6a}	ν_{12}	ν_1	ν_{13}
2-cyanopyridine	446 (462)	726 (775)	949	1154
3-cyanopyridine	415 (475)	718 (782)	981 (1010)	1163
4-cyanopyridine	445	721	958	1179

Values in brackets are corresponding ground state frequencies observed from the ultraviolet spectra.

ground state frequencies obtained from electronic spectra and infrared spectra investigated here is satisfactory. It is important to note that the order of shift observed is $2 < 3 < 4$ as expected by Mason⁵ and that our results do not corroborate the calculations of Jaffe *et al.* according to which maximum shift is expected for the 2-isomer. The detailed paper dealing with infrared and electronic spectra will be published elsewhere.

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COMPLEXES OF DIETHANOLAMINE WITH NICKEL (II) SALTS

THE hydroxylamines derived from glycols, *viz.*, mono, di, triethanolamines have been recently subjected to extensive investigations due to their ability to behave as both nitrogen- and oxygen- co-ordinating ligands. In earlier work¹⁻⁴ greater emphasis has been given to the complexes formed in solution phase and little is reported about the complexes in the solid state. Spectrophotometric studies⁵ of nickel (II) complexes with monoethanolamine show that the ligand behaves as a chelating agent.

Recently, crystalline complexes of Ni (II) salts with triethanolamine⁶⁻⁸ have been investigated in detail and significant conclusions about their structure and stereochemistry reached. In the present communication we briefly report on the synthesis and structure of several complexes of diethanolamine with Ni (II) salts. The complexes were characterized using infra-red and electronic spectroscopy, magnetic susceptibility, X-ray diffraction and electrical measurements.

Generally the complexes were prepared in the present work by the addition of diethanolamine to an alcoholic solution of the nickel (II) salt (in 2:1 molar ratio of ligand to metal) and evaporating the solution in dry atmosphere. The crystals separated were washed with alcohol and ether and preserved in dry conditions. By this method the following complexes were prepared: [Ni(DO)] Cl; [Ni(DO) (DOH)] Br; [Ni(DOH)₂] I₂; [Ni(DO) (DOH)] NO₃; [Ni(DOH)₂] SO₄; [Ni(DOH)₂] (NCS)₂; [Ni(DO) (DOH)] ClO₄; [Ni(DOH)₂] (OAc)₂, where DOH is diethanolamine and DO is its monodeprotonated form. An yet another type of thiocyanate complex, namely, [Ni(DO) (DOH)] NCS was prepared by treatment of the compound Ni(NCS)₂·4py⁹ (py = pyridine) suspended in methanol, with an excess of diethanolamine. The compositions of the complexes were arrived at by determining the nickel by dimethylglyoxime and by elemental analysis for others. All the complexes were soluble in alcohol and were readily decomposed on contact with water.

The electronic spectra and magnetic susceptibility measurements indicated unambiguously that all the complexes reported above are pseudo-octahedral. Their magnetic moments at 30° C were generally in the range 2.85–3.19 B.M. and the diffuse reflectance spectra of the powdered complexes showed the three *d-d* transitions ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P), ${}^3A_{2g} \rightarrow {}^8T_{1g}$ (F) and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F) characteristic of octahedral Ni(II) complexes. The three bands had maxima in the region 25000–27000, 15500–17500 and 9500–10500 cm⁻¹ respectively, which are again characteristic of Ni (II) pseudo-octahedral complexes containing oxygen and nitrogen mixed ligands. Thus in most of the complexes diethanolamine and the monodeprotonated form appear to be ligated to Ni(II) through the N- as well as the O- sites of coordination. Detailed information on the preparation, properties and structure of the complexes will appear elsewhere.

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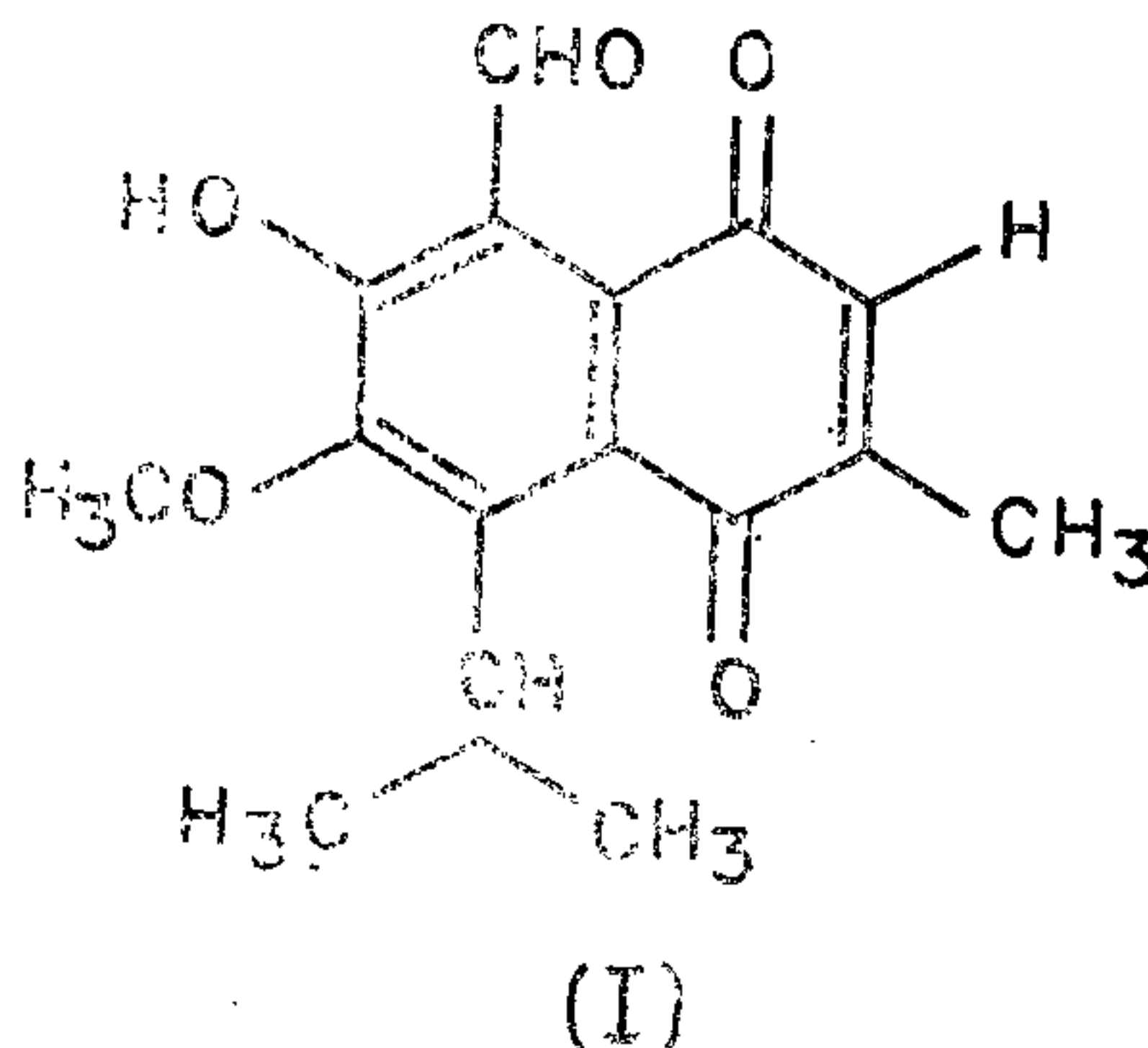
PHENOLIC COMPONENTS OF BOMBAX MALABARICUM (ROOT-BARK)

In an earlier investigation Seshadri and Rangaswami¹ isolated lupeol, β -sitosterol and β -sitosterol-D-glucoside from the stem bark of *Bombax malabaricum* DC. The root-bark has now been studied. The petroleum ether extract was fractionated into the sodium bicarbonate-, sodium carbonate- and sodium hydroxide-soluble and neutral fractions and each was examined separately. Column chromatography of the neutral portion over neutral alumina yielded lupeol and β -sitosterol.

The sodium carbonate-soluble fraction on chromatography over silica gel yielded a pure compound A which crystallised as yellow needles from petroleum ether, m.p. 87–88° (Yield, 0.01%). It analysed for $C_{16}H_{16}O_5$ (M^+ 288), gave an orange colour with $FeCl_3$, a dark-red solution with conc. H_2SO_4 and a violet colour with dilute aq. sodium hydroxide. λ_{max} nm (log ϵ): 248 (4.18), 272 (4.12) and 338 (3.6) suggestive of a naphthoquinone structure. It showed carbonyl absorption in the IR supporting this structure. The NMR spectrum of the compound in $CDCl_3$ revealed the presence of an isopropyl group [doublet centred at δ 1.26, $J = 7$ cps (6 H) and a multiplet at δ 4.35 (1 H)], a C-methyl group as a doublet at δ 2.06 coupled to the quinone proton which appeared as a quartet at δ 7.32, and an OCH_3 group (s, δ 4.07). No aromatic proton was present but peaks due to CHO proton (δ 10.6) and a chelated OH group (δ 12.46) were

observed. Methylation of the compound with CH_3I/K_2CO_3 yielded a methyl ether, the IR of which showed aldehyde absorption at 1706 cm^{-1} . Its NMR had two $-OCH_3$ peaks at δ 3.97 and δ 4.08.

The above data suggested that the compound might be a naphthoquinone containing an O-hydroxyaldehyde, an isopropyl and a methoxyl group on the aromatic ring. The compound showed a general resemblance to the dimethyl ether of gossypolone in the NMR spectrum². Based on these and on the mass spectrum of the compound, which among other things showed evidence for the presence of an isopropyl group (loss of 43) and of carbonyl (loss of 28 mass units), structure I which is also biogenetically sound is proposed for it.



The sodium bicarbonate soluble fraction yielded a small amount (0.001%) of compound B, orange needles from petroleum ether, m.p. 167–68°, $C_{15}H_{14}O_5$ (M^+ 274). It gave an orange colour with $FeCl_3$ and a red solution with conc. H_2SO_4 ; λ_{max} nm (log ϵ): 234 (4.02), 252 (3.99) and 294 (3.85); ν_{max}^{Nujol} 1639 cm^{-1} . In NMR spectrum the compound showed all the functional groups present in A, except that the peak due to $-OCH_3$ was absent. Hence it was considered to be the corresponding dihydroxy compound. This was confirmed by the methylation of B with CH_3I/K_2CO_3 when a partial methyl ether agreeing with compound A was formed initially, which, on further reaction, was converted into the complete methyl ether, identical with the methyl of A.

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