TABLE 2. N-O STRETCHING FREQUENCIES OF PURE N-OXIDES AND OF THEIR MOLYBDENUM COMPLEXES

Ligands	N-O stretch	Complexes	N-O stretch (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	Ref.
PyNO	1234(s)	$MoO_2Cl_2$2PyNO	1214(s)	20	5, 6
4-NO_2PyNO	1275(s) 1286(sh)	$MoO_2Cl_2$2(4-NO_2PyNO)	1216(s)	59 —	6
QNO	1310(s) 1285(s) 1205(sh) 1230[+ρ(C-H)]	$MoO_2Cl_2$2QNO	1214(s) 1266(m) 1173(s)	—	6, 8

plexes undergo 'base solvolysis' in methanol, the detail mechanism of which would be discussed elsewhere.

The N-O stretching bands of pyridine, 4-nitropyridine and quinoline *N*-oxides undergo a considerable amount of red shift after coordination with the MoO_2^{2+} ion (Table 2). This is, obviously due to the reduction of the $O(p\pi)\rightarrow N(p\pi)$ overlap as a result of the drainage of electron density from oxygen to molybdenum (VI). There is no evidence of any characteristically well defined N-O stretching band in quinoline N-oxide in the literature and it has rather been concluded[6-8] that $\bar{\nu}$(N-O) is not a pure vibration in the above *N*-oxide but is coupled with the aromatic ring vibrations of the quinoline ring. That is why so many bands appear in the N-O stretching region even in the pure quinoline *N*-oxide and so no attempt is hereby made to tabulate the $\Delta\bar{\nu}$ in this case.

The N-O inplane bending frequency of the pyridine *N*-oxide[6] (836 cm^{-1}), 4-nitropyridine *N*-oxide (865 cm^{-1}) and of quinoline *N*-oxide (885 cm^{-1}) remains practically unaltered in the respective complexes. The constancy of this band position may be due to two opposing effects —one similar to that of coordinated water where bending vibration δ(O-H), is shifted to the higher frequency on complexation and the other, lowering in the frequency due to decrease in the π-bond character of the N-O bond.

The Mo = O stretching frequencies of the MoO_2^{2+} group are observed as strong bands at 900 and 930 cm^{-1} in the PyNO complex, at 905 and 944 cm^{-1} in the 4-NO_2PyNO complex (chloro) and at 920 and 954 cm^{-1} in the QNO complex. Since in all these cases both ν_1 and ν_3 are IR active, the MoO_2^{2+} group may have the cis(C_{2v}) configuration in the complexes. A strong band at 1346 cm^{-1} in the complex MoO_2Cl_2 2(4-NO_2PyNO) is due to the aromatic C-NO_2 stretch of the nitro group[9].

Unfortunately, the i.r spectra of $MoO_2(NO_3)_2$-2(4-NO_2PyNO) could not be recorded either in Nujol phase or by KBr disc technique. In the former method, the prepared mull reacts with NaCl cell itself and in the latter, there occurs a colour change while preparing the disc and the recorded spectrum is not well resolved and shows no band of coordinated nitrate group but shows only the characteristic band of NO_3^- ion. It might be presumed that substitution of NO_3 by Br might have occurred while making the disc. Of course, in this spectrum also, the C (aromatic) -NO_2 stretch and both ν_1 and ν_3 of MoO_2^{2+} group are observable.

The χM corr. of the MoO_2^{2+} ion in all the chloro complexes are negative (values range between −95 to -150×10^{-6} e.m.u. $mole^{-1}$) but in the nitrato complex the said value is 182×10^{-6} e.m.u. $mole^{-1}$. So, at present no comment can be made whether TIP is essentially exhibited by MoO_2^{2+} ion as presumed by some previous workers[1,10].

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Chemical Examination of the Leaves of *Murraya paniculata*

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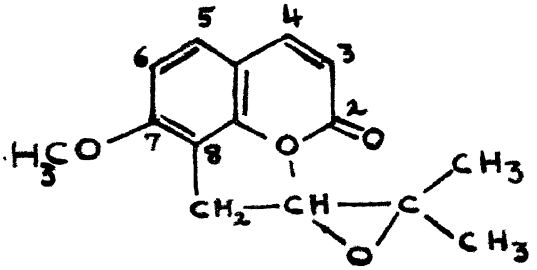
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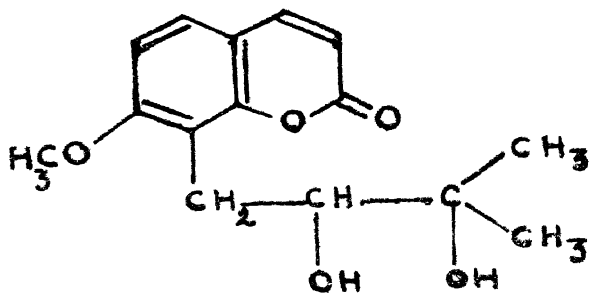
FROM the leaves of *Murraya paniculata* the isolation of phebalosin and another coumarin called compound B, $C_{15}H_{16}O_4$, m.p. 100° was reported by us earlier[1]. The isolation of mexoticin from the same plant has also been reported[2]. The present investigation was undertaken with a view to characterizing the compound B.

The IR spectrum of compound B in Nujol mull shows bands at 1255 cm^{-1} (epoxide ring) and 1725 cm^{-1} (coumarinic lactone carbonyl), 1605 cm^{-1} and

1500 cm^{-1} (benzene ring). The UV spectrum of the compound B in ethanol shows absorption maxima at 247, 257, and 322 nm which is very similar to that of citropten[3]. That compound B contains an epoxide ring is evident from the fact that it gave a diol (II), $C_{15}H_{18}O_5$, m.p. 124°, on treatment with aqueous oxalic acid (1%). The diol consumed one mole of periodic acid. The IR spectrum of the diol in Nujol mull shows bands at 3510 cm^{-1} and 3400 cm^{-1} (glycolic OH groups), 1725 cm^{-1} (lactone carbonyl), 1610 cm^{-1} and 1500 cm^{-1} (aromatic ring). The



(I)



(II)

NMR spectrum of the diol ($CDCl_3$, 60MHz) shows a pair of doublets centered at 6.22 δ(1H, *d*, J = 9.5Hz) and 7.62δ (1H, *d*, J = 9.5Hz) for the 3-H and 4-H respectively. The two aromatic protons namely 5-H and 6-H appear as another pair of doublets centered at 6.85δ (1H, *d*, J = 8.5Hz) and 7.34δ (1H, *d*, J = 8.5Hz), one of the peaks of the latter overlaps with that of $CHCl_3$. The three protons of the methoxyl group ($-OCH_3$) and the six protons of the two methyl groups attached to one of the carbinol carbon atom [$-C(OH)-(CH_3)_2$] appear ass harp singlets at 3.93δ (3H) and 1.31δ (6H) respectively. The peak at 2.62δ (2H) which disappears on D_2O treatment is due to the two protons of the alcoholic hydroxyl groups ($-C-OH$). The carbinyl proton ($-CHOH$) appears as a broad multiplet centered at 3.64δ (1H). The two benzylic protons appear as a typical multiplet centered at 3.03δ. The above data show that the diol has the structure (II). Direct comparison with an authentic sample has not been possible but there is little doubt that compound B is identical with aurapten[4] (I, Lit. record: m.p. 98°).

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*p*H metric study of complexes of some metal ions with salicylaldehyde-4-phenyl-3-thiosemicarbazone

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LIGANDS such as thiosemicarbazones are studied to a limited extent *p*H-metrically Here salicylaldehyde-4-phenyl-3-thiosemicarbazone (SPT) derivative is studied with metals like VO^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}. The formation constants for their metals were calculated by Calvin and Wilson *p*H titration technique as modified by Irving and Rossotti. The stability constants are determined in 50% aqueous dioxane medium.

Experimental

The ligand salicylaldehyde-4-phenyl-3-thiosemicarbozone was synthesized and crystallised to get analytically pure (m.p. 188°)[1]. The solution of SPT was prepared in dioxane (BDH, AnalaR grade) which was further purified by standard method of Vogel[2]. Metal nitrates used were of AnalaR grade which were estimated by standard gravimetric and volumetric methods. Phillips *p*H meter was used for *p*H measurements. *p*H meter was calibrated with buffer solutions having *p*H 4.33 and 9.1 at 25°±1°.

All titrations were carried out in a 100 ml beaker kept in water thermostat maintained at 25°±1°. Thirty five to forty five readings were taken in each case. Each titration was repeated to get reproducible results. The metal ligand ratio was maintained 1:5. The titration curves are given in Fig. 1.

Blank titrations: A mixture of 2ml of 0.1*M* HNO_3, 5 ml of 1.0*M* KNO_3, 25 ml dioxane and 18 ml of water (to make the total of 50 ml in all titrations)

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