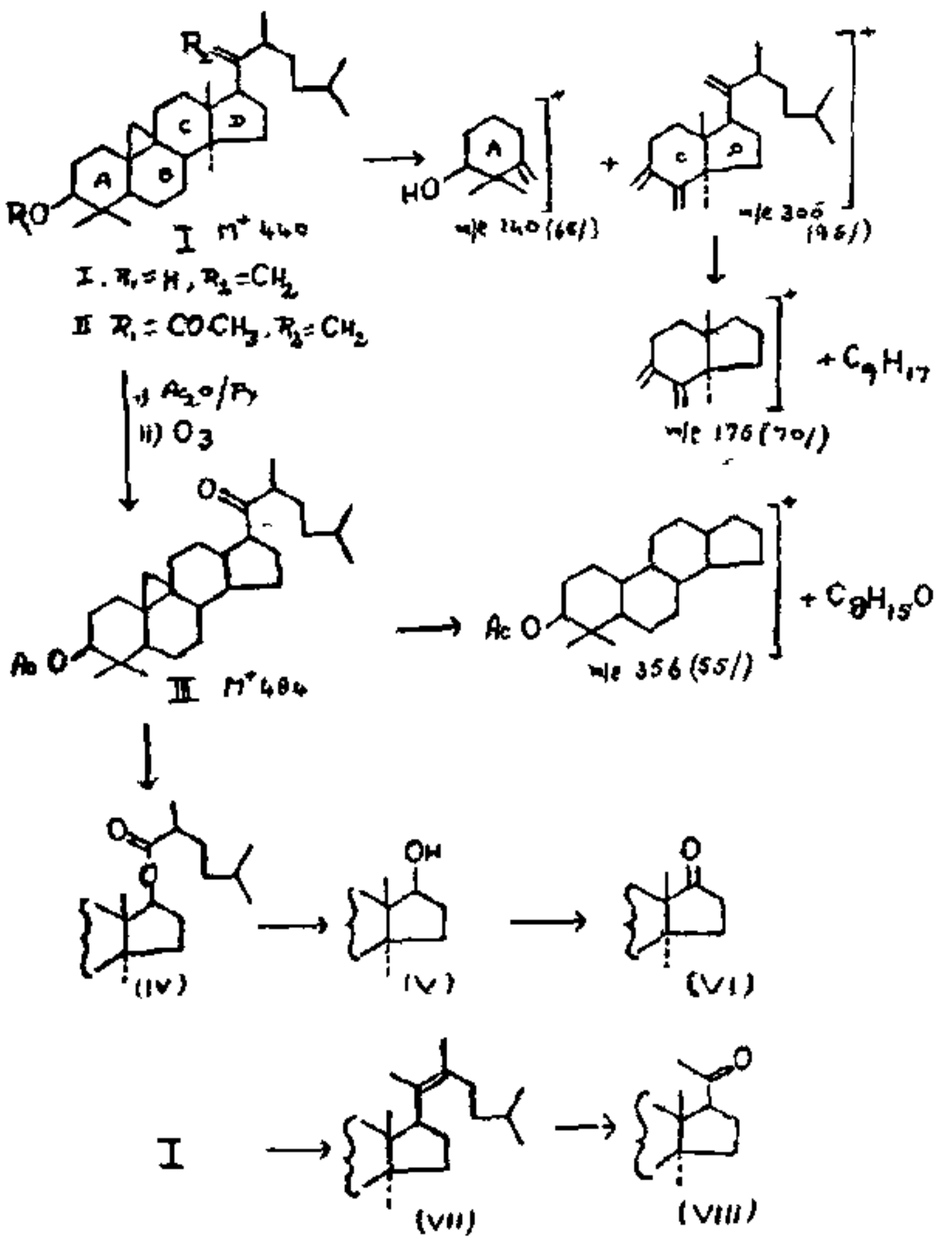
in the triterpene. The mass spectra proved unequivocally that cycloswietenol is a tetracyclic triterpene with a long side chain, C_9H_{17}, and a cyclopropane ring on C_9 and C_{10}.

Further evidence to establish the position of the side-chain and also the vinylic methylene group is sought by Baeyer-Villiger oxidation of the keto-acetate (III). Hydrolysis of the resulting product (IV, 80 mg) furnished an alcohol (V, 60 mg). It was later oxidised with Py/CrO_3 to give a ketone (VI, 15 mg) whose I.R. spectrum showed a prominent peak at 1735 cm^{-1} indicating the presence of a five-membered ring ketone. The position of the side chain at C_{17} and the ketone function at C_{20}, and consequently the vinylic methylene at C_{20} are thus confirmed.

Only the position of the extra methyl group in the side chain remains to be settled. When (I) was warmed with methanol/HCl, the vinylic double bond migrated to give the isomeric cycloswietenol (VIII) which contained a tetrasubstituted double bond. Its NMR showed two methyls on the double bond (δ 1·72, 6 H) which could be cleaved by ozonolysis. These reactions place the extra methyl at C_{22}. These reactions are taken to confirm tentatively the structure (I) for cycloswietenol. Further work is under progress.



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INFLUENCE OF PHENOLIC COMPOUNDS ON THE GROWTH AND POLYSACCHARIDE PRODUCTION OF *RHIZOBIUM LEGUMINOSARUM*

The soil polysaccharides, *senso stricto* derived from the microorganisms have been conceded to play a significant role in soil aggregation and stabilization[1]. Of the varied groups of soil bacteria, the symbiotic N_2-fixing *Rhizobia* have been known to produce enormous quantities of polysaccharides and hence play a decisive role in improving the physical properties of soils[2]. However, the growth and activity of rhizobia in soil are more often inhibited by several naturally occurring compounds like phenols, fungistatic substances, etc.[3]. The present paper examines the effect of a few phenolic compounds on the growth and polysaccharide production by *Rhizobium leguminosarum*.

The various pherolic compounds were added at 0·001 M concentration to Waksman No. 77 medium after filter sterilization and dispersed in 100 ml quantities in 250 ml Erlenmeyer flasks. One ml of the *R. leguminosarum* cells experiencing log pnase of growth (1×10^9/ml), was inoculated into the flask and incubated on a rotary shaker for 48 hr at 28 ± 1° C. The growth of the organism was measured by determining the biomass. The alkali stable polysaccharide was extracted following the methods of Hassid and Abraham[4] and quantified using anthrone reagent[5]. The constituent sugars of the polysaccharide were identified by paper chromatography using *n*-butanol: acetic acid: water :: 4:1:1 u/v solvent system and benzidine-TCA reagent served as the spray solution[6]. The spots were identified by co-chromatography of authentic sugar samples.

The results are set out in Table I. It is of interest to observe that production of polysaccharide had no bearing on cell growth. Among the different phenolic compounds, nitrophenol, rutin, and ferulic acid were more inhibitory than others towards the growth of the organism; it is also revealed that dithiazone, 1, 5-

dihydroxy anthroquinone and phthallic acid were stimulatory. This observation finds support from the work of Rao and Iswaran[7] and Purushothaman and Balaraman[8] who stated that rhizobia were inhibited by a few phenolic compounds. The polysaccharide production was strongly inhibited by *O*-phenylene-diamine and *para*-amino benzoic acid while nitrophenol, gallic acid and cinnamic acid favoured polysaccharide production.

TABLE I

Effect of certain phenolic compounds on the in vitro *growth and polysaccharide production by* Rhizobium leguminosarum

Phenolic compounds	Biomass (g)/100 ml	Quantity of polysaccharides produced (mg/g)	Qualtative differences* in polysaccharides produced
1	2	3	4
Nitrophenol	0·13	13·31	Mann, Xyl, Ara
Phloroglucinol	0·31	3·54	Rib, Raff, Xyl
Gallic acid	0·53	13·47	Mann, Xyl, Ara Fru
Quercetin	0·40	1·63	Sucrose, Glu, Rib
8-hydroxy quinoline	0·50	3·87	Fru, Rib, Raff, Ara
Cinnamic acid	0·40	11·59	Glu, Fru, Suc, Lact
Rutin	0·18	3·51	Fru, Xyl, Raff, Rib
Coumarin	0·42	3·29	Glu, Suc, Fru, Xyl
Pyrogallol	0·40	4·18	Xyl, Mann, Ara, Raff, Rib
Para-dichlorobenzene	0·40	7·80	Rib, Raff, Xyl, Mann, Ara, Fru
Hydroquinone	0·39	2·82	Xyl, Mann, Ara, Fru
o-phenylene-diamine	0·50	0·71	Rib, Raff, Xyl, Mann, Ara, Fru
Dithiazone	0·71	0·94	Glu, Rib, Raff, Fru, Xyl
1, 5-dihydroxy anthroquinone	0·68	7·44	Rib, Raff, Xyl, Mann, Ara, Glu Suc, Lact
Salicin	0·51	4·51	Lact, Glu, Suc, Rib
Ferulic acid	0·28	8·66	Rib, Raff, Glu
Benzilic acid	0·53	1·16	Fru, Xyl, Mann, Ara, Rib, Raff
Phthallic acid	0·68	1·41	Suc, Glu, Lac, Xyl
Para-aminobenzoic acid	0·48	0·94	Xyl, Mann, Ara, Fru
Anthranilic acid	0·37	5·03	Rib, Raff, Xyl, Mann, Ara
Tryptophan	0·51	5·36	Fru, Glu, Suc, Lact, Ara
Protocatechuic acid	0·38	7·73	Fru, Rib, Raff
Resorcinol	0·41	7·80	Rib, Raff, Xyl, Mann, Ara
Control	0·59	4·63	Suc, Lact, Glu

*Ara—Arabinose; Lact—Lactose; Rib—Ribose; Fru—Fructose; Mann—Mannitol; Suc—Sucrose; Glu—Glucose; Raff—Raffinose; Xyl—Xylose.

The data reveal that the presence of pherols in the medium greatly influenced the qualitative nature of the polysaccharides. When *R. leguminosarum* was grown in the presence of pherols, the polysaccharide was composed of only hexose sugar units, whereas in the absence of pherols both hexoses and pentoses were discernible. The study of Keele *e. al.*[9] on the polysaccharide composition of several strains of *Rhizobium* revealed the presence of glucose, galactose, rhamnose and mannose in all strains; however, Graham[10] indicated variations in the polysaccharide composition among different strains. No work seems to have been done on the effect of phenols on the polysaccharide composition. As many of the phenols are either reported[11] to be present in soils or released during degradation of organic materials, it is quite possible that the soil phenols affect the quantity and quality of the rhizobial polysaccharides *in vivo*. It is clear from the study that the phenolic compounds not only inhibit the growth of *R. leguminosarum* but also alter the polysaccharide composition.

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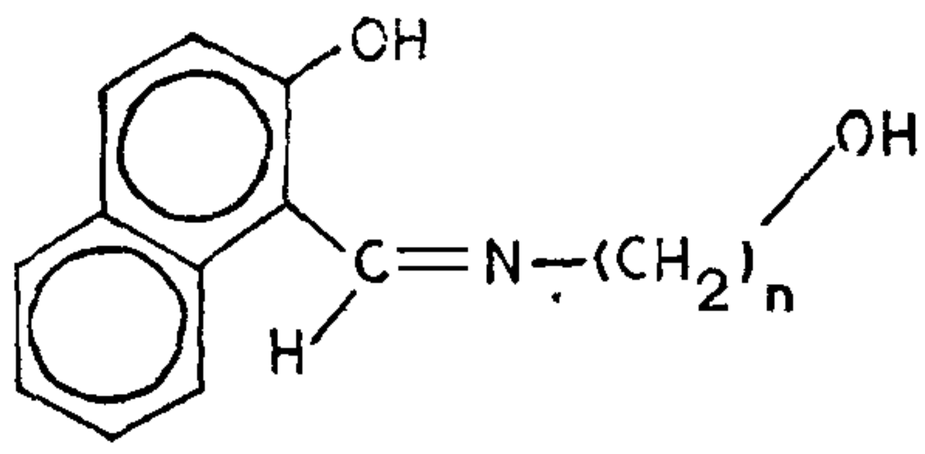
COPPER (II) COMPLEXES OF ONO DONOR TRIDENTATE LIGANDS N-(HYDROXYALKYL)-2-HYDROXYNAPHTHYLIDENEIMINES

THERE has been considerable interest in recent years on the syntheses and magnetic properties of metal (II and III) complexes with tridentate dibasic ligands[1-3]. The tridentate dibasic character of these ligands force the metal (II and III) ions to dimerise or polymerise leading to metal complexes with unusual magnetic and structural properties. We report in this communication the synthesis of copper (II) complexes of ONO donor tridentate dibasic Schiff bases (I) derived from 2-hydroxy-1-naphthaldehyde and alcoholamines, *viz.*, ethanolamine, propanolamine and isopropanolamine

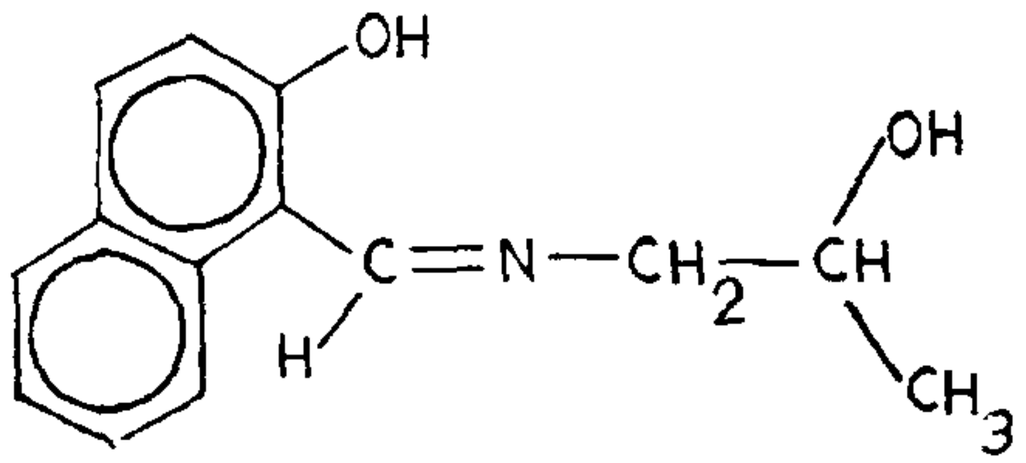
Synthesis of the Complexes

Copper (II) acetate monohydrate (0·005 mole) was dissolved in 60 ml of hot methyl alcohol. To this a methyl alcoholic solution (45 ml) of the appropriate condensed Schiff base (0·005 mole) was added and the mixture was refluxed for 2 hr. The green precipitates formed were filtered under reduced pressure, washed with methyl alcohol and dried under vacuum. The complexes are insoluble in common non-coordinating organic solvents. The analytical and characterisation data of the complexes are presented in Table I.

The data indicate 1:1 metal: ligand ratio in the complexes. The infrared spectra of the complexes do not exhibit the ν(OH) stretch and this is indicative of the dibasic behaviour of the ligands in the complexes. The magnetic moments of the complexes, copper (hydroxynaphthaldehyde-ethanolamine) and copper (hydroxynaphthaldehyde-isopropanolamine)



Ia. n=2,3.



determined by the Gouy method, increase as the temperature is lowered from 297 to 83° K. The exchange integral, J of the complexes calculated using the Bleaney-Bowers equation[4] is + 67 and + 28 cm^{-1} respectively. The positive J values and the increase of the magnetic moment with lowering of temperature are indicative of the presence of ferromagnetic exchange in these complexes[5,6]. The magnetic moment of the complex copper (hydroxynaphthaldehyde-propanolamine) is 0·46 B.M. at 297° K and the moment shows little temperature dependence. J of this complex is $-846\ cm^{-1}$. The negative J value and low magnetic moment are indicative of the presence of antiferromagnetic exchange in this complex[1]. This complex is a novel example where the spins of the interacting copper (II) ions are completely coupled having a sole population of the diamagnetic singlet state. Only few such copper (II) complexes with sole population of the singlet ground state have been reported in the literature[7]. The magnetic properties of Cu (hydroxynaphthaldehyde-propanolamine) and the other two complexes containing ethanolamine and isopropanolamine are different and it is likely that the structures of the antiferromagnetic and ferromagnetic complexes are different[1].