ALKALOIDAL CONSTITUENTS OF *SENECIO SCANDENS*

Senecio scandens is a glabrous, climbing, slightly pubescent plant. Its flowers were examined earlier[1] and found to contain epoxycaroterexs and xanthophyll in large amount. Lutein was present in leaves along with β-carotene. But the plant was not examined earlier for the alkaloidal corstituents.

The whole plant collected from Darjeeling was extracted with hot ethanol and the extract concentrated to a small bulk after making it acidic with aqueous citric acid. The non alkaloidal constituents were removed by extracting successively with petroleum ether and ether. The aqueous solution was made strongly basic with ammonia and extracted with chloroform. The chloroform extract on evaporation gave a gum which showed positive test for alkaloids but did not show the presence of N-oxides. Further, aqueous solution left after extraction with chloroform contained no N-oxide since on reduction with zinc dust and hydrochloric acid followed by extraction with chloroform did not yield any tertiary amine.

The alkaloidal residue was shown to be a mixture of three by paper and thin layer chromatography. Crystallisation of the residue from ethanol gave a mixture, consisting of two components as shown by paper chromatography using butanol-acetic acid as solvent. It was separated into two constituents (A and B) using cellulose column.

Constituent A showed a spot (R_f 0·56) on paper chromatography, m.p. 236–38° (d), yield 1·5 g, $[\alpha]_D$ − 55·8° (c_2 1·0 mg/ml in chloroform). It gave a picrate m.p. 193–94°. On alkaline hydrolysis[2], it yielded senecic acid lactone m.p. 153–55° and retronecine hydrochloride. These data suggest the alkaloid to be senecionine and it was confirmed by direct comparison with an authentic sample (m.m.p., paper chromatography and infra-red absorption).

The other constituent B had R_f 0·50 (paper chromatography). m.p. 216–18°, yield, 0·7 g. $[\alpha]_D$ − 138° (*c*, 1·27 mg/ml in chloroform). On alkaline hydrolysis it gave seneciphyllic acid (R_f 0·87, m.p. 115–16°) and retronecine hydrochloride (m.p. 161°). It was identified as seneciphyllin by comparison with an authentic sample (m.m.p., paper chromatography and Infra-red absorption).

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1. Valden and Mummery, *Phytochemistry*, 1967, 6 (7), 983.
2. Adams and Govindachari, *J. Am. Chem. Soc.*, 1949, **71**, 1953.

A NEW TRITERPENE FROM *SWIETENIA MAHOGANII* JACQ.

The leaves of *Swietenia macrophylla*[1,2,3] are known to contain two interesting terpenoid lactones swietenine, and swietenolide of unusual structure. This encouraged us to study the chemical constituents of the heartwood and leaves of *S. mahoganii* as a part of our general scheme on Indian heartwoods.

From the leaves, swietenine and stigmasterol glucoside were isolated and identified from their physical and chemical properties. The hexane extract of the heartwood, after extensive chromatography on silica gel, could be separated into six triterpenes, of which β-sitosterol, lupeol benzoate, hederagenin and cycloartenol were identified by comparison with authentic specimens. Of the remaining two triterpenes, one was secured as a major component, (yield : 0·1%), colourless needles from methanol, $C_{31}H_{52}O$, M+ 440, m.p. 145°, $(\alpha)_D$ + 55°, (C; 1·0 in $CHCl_3$). L.B. test positive. I.R. 3300 (for hydroxyl), 3040 (for cyclopropane ring) and 890 cm^{-1} (for $=CH_2$). It is characterised by its acetate, colourless plates from $CHCl_3$-MeOH, $C_{33}H_{54}O_2$, m.p. 123°, $(\alpha)_D$ + 79° (C, 1·0 in alcohol). Its physical constants suggested that it could be new and therefore, it is named cycloswietenol (I).

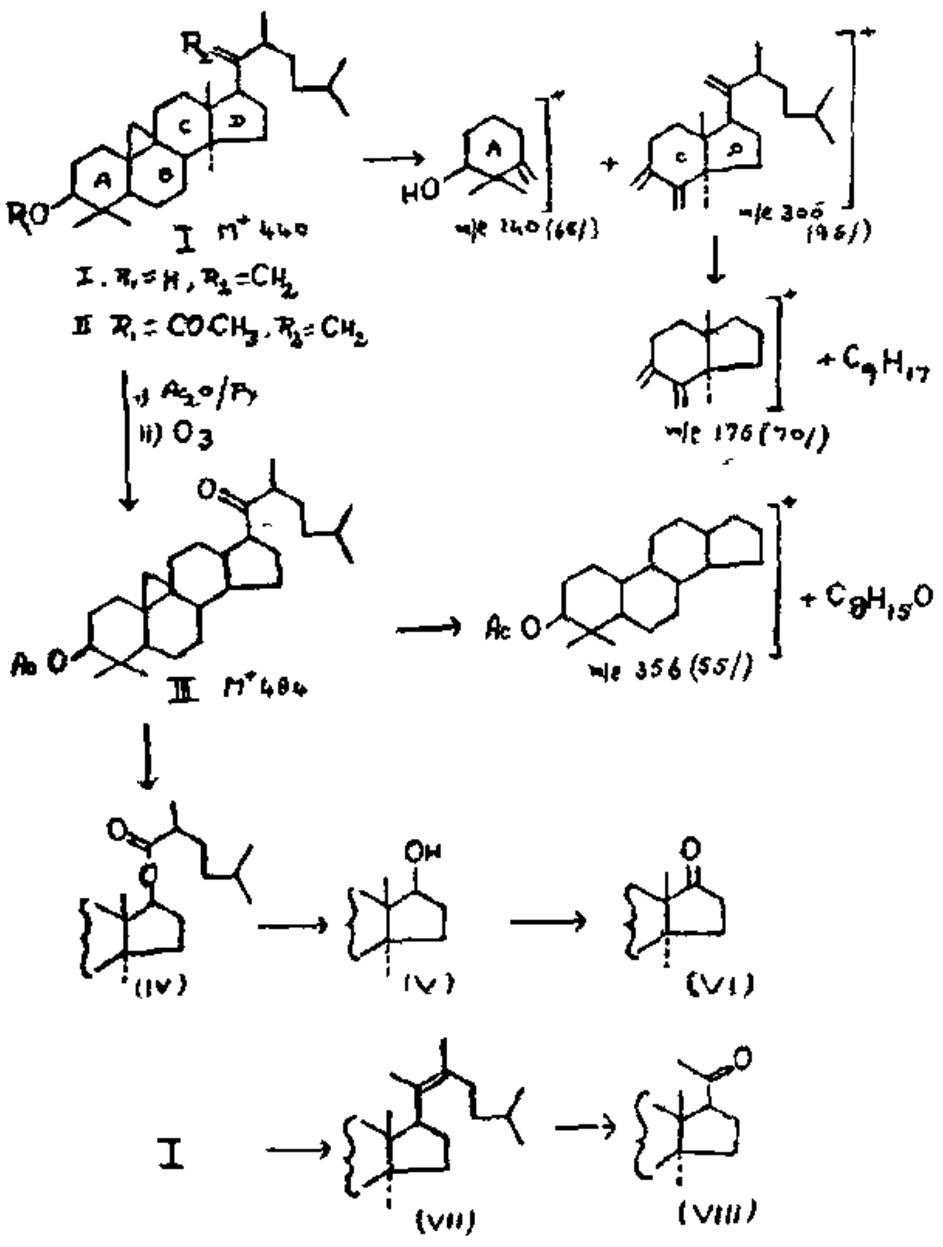
The ^1H NMR spectrum of cycloswietenol (I) as well as its acetate (II) revealed the cyclopropane ring system ($>CH_2$ δ 0·31 *d/d*), and a vinyl methylene at δ 4·72 (*m*) There were 7 methyls between δ 0·92 to 1·1 suggesting that there is an extra methyl in the molecule as in 24-methylene cycloartanol. Hydrogenation of (I) with Pd/charcoal at 30° furnished a dihydro derivative, m.p. 117°, $(\alpha)_D$ + 21·5° (C, 1·0 in $CHCl_3$) in which the multiplet resonance at δ 4·72 (for $=CH_2$) disappeared and methyl protons increased by one more methyl. Ozonolysis of II afforded formaldehyde, detected by its dimedone derivative and also by its colouration with chromotropic acid. The corresponding ketocycloswietenol acetate (III) m.p. 98°, $(\alpha)_D$ + 16° (C, 1·0 in alcohol) contained cyclopropane ring system ($>CH_2$, δ 0·31).

The mass spectra of cycloswietenol (I) and its ketone acetate (III) exhibited the characteristic cleavage at ring B to given two fragments m/e 140 (65%) and m/e 300 (95%) indicating the position of the cyclopropane ring system at C_8 and C_{10} as in cycloartanol[4]. The ketoacetate (III) suffered a prominent α-cleavage to give a major fragment, m/e 356 (55%) with loss of $C_8H_{15}O$ (127). Similar loss of the side chain C_9H_{17} (125) was also noticed in cycloswietenol (I) suggesting that the side chain is attached to the C_{17} position

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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1. Chakraborty, D. P., Basak, S. P., Das, B. C and Beugelmans, R., *Phytochemistry*, 1971, 10, 1367.
2. —, Das, B. C. and Basak, S. P., *J. Ind. Chem. Soc.*, 1969, 46 (3), 273.
3. Chakrabartty, T., Connolly, J. D., McCrindle, R., Overton, K. H. and Schwarz, J. C. P., *Tetrahedron*, 1968, 24, 1503.
4. Audier, H. E., Beugelmans, R. and Das, B. C.; *Tetrahedron Letters*, 1966, p. 4341.

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-