CHEMICAL COMPONENTS OF *SALACIA CHINENSIS* LINN.: STEMS AND LEAVES

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IN the course of studies on the Ayurvedic drug "Saptarangi", the chemistry of the stem and leaves of *Salacia chinensis* Linn. (Fam. Celastraceæ) was investigated. The powdered stem was extracted with warm petroleum ether, ether, warm acetone, cold alcohol and warm alcohol in succession and the respective solvent-free residues examined for their constituents. The petroleum ether extract yielded 0·2% of gutta (a linear isomer of natural rubber) whose identity was inferred from the following properties. The substance was a colourless crystalline powder when freshly crystallised from alcohol but acquired slight stickiness on long exposure to air and light. It melted at 57–65°; the cooled melt retained a glassy consistency for a long time. The substance analysed for $(C_5H_8)_n$. It rapidly decolourised a solution of bromine in chloroform to form a bromo compound which analysed for $(C_5H_8Br_2)$ Quantitative bromine titration and perbenzoic acid titration indicated the presence of one double bond per C_5H_8 unit. The proton signals in the NMR spectrum of the parent substance (using carbon tetrachloride as solvent and TMS as internal standard) agreed with the structure

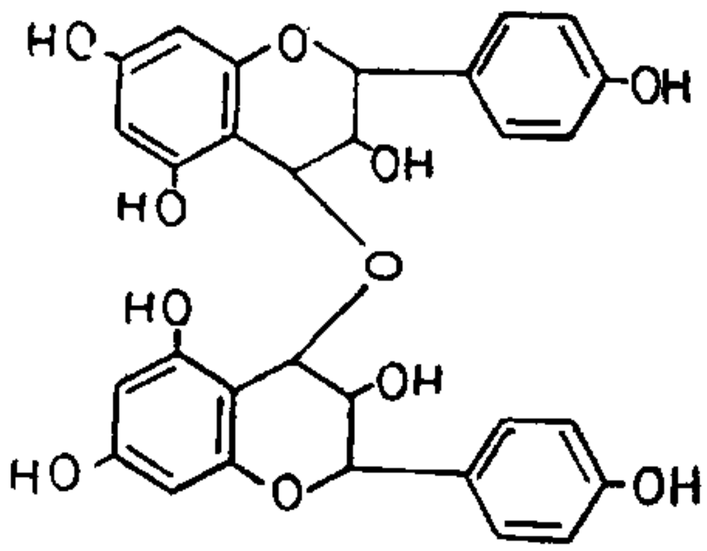
$$(H_2C - \overset{CH_3}{\overset{|}{C}} = CH - CH_2)_n$$

qualitatively and quantitatively and the spectrum compared very well with that of the isoprenoid part in ubiquinone and Kofler's quinone.[1] Molecular weight (Rast method) was *ca* 1500. Gutta has been shown to occur in several species of the family Celastraceæ.

The ether and acetone extracts of the stem did not yield any definite substance. During the concentration of the cold as well as the subsequent warm alcohol extracts, a colourless crystalline solid separated from each; they were filtered separately and crystallised from hot water. They proved to be identical (m.p. and TLC). The substance, stout colourless prisms m.p. 187–88°, formula $C_6H_{14}O_6$, formed a hexaacetate m.p. 169°, $C_{18}H_{26}O_{12}$, and a hexabenzoate m.p. 188–89°, $C_{48}H_{38}O_{12}$, all optically inactive. These properties identified the substance as dulcitol (total yield 0·06%).

After removal of dulcitol the mother liquors from the cold and warm alcohol extracts were separately encentrated under reduced pressure and the residues were macerated with cold ethyl acetate which extracted most of the material and then with cold methanol. The latter extract yielded no definite substance. The cold ethyl acetate extract in either case was concentrated to a low volume and diluted with dry petroleum ether. The solid obtained was repeatedly purified by taking in ethyl acetate and precipitating with petroleum ether. In either case the same proanthocyanidin was precipitated whose properties are described below :

The proanthocyanidin on boiling with ethanolic hydrochloric acid gave a deep red coloured flavylium salt which was obtained pure by preparative paper chromatography and identified as pelargonidin chloride by qualitative colour tests and by its absorption spectrum in 0·01% ethanolic hydrochloric acid solution (λ_{max} 535 mμ not affected by addition of aluminium chloride). No other anthocyanidin or catechin type of compound was present in the acid hydrolysate. This showed that the proanthocyanidin was made up of leucopelargonidin units only. The proanthocyanidin m.p. 180-95° (d) (yield, 0·03%) formed a methyl ether (dimethyl sulphate and potassium carbonate in acetone medium). m.p. 130-35°(d), $[\alpha]_D$ –39·3° (C, 0·29 in chloroform), $C_{36}H_{38}O_{11}$, H_2O. The methyl ether did not consume any periodate (vicinal glycol grouping absent). Its molecular weight (Rast method) was 630. Hence the proanthocyanidin should be a dimer



(I)

of leucopelargonidin having the probable structure (I) in which the linkage between the two C_{15} units is shown as C_4-O-C_4. Alternative linkages C_4-O-C_3 or C_3–O–C_3 are also conceivable.[2] The parent proanthocyanidin formed an acetate with acetic anhydride and pyridine at room temperature, m.p. 120–25° (d), $[\alpha]_D$ – 27·7° (C, 0·18 in chloroform), $C_{46}H_{42}O_{19}$.

The leaves of *Salacia chinensis* were also similarly extracted with warm petroleum ether, ether, warm acetone and warm alcohol. The petroleum ether extract yielded gutta which was identified as described under the stem. The ether extract did not yield any definite substance. The solvent-free acetone extract was macerated with petroleum ether, ether and chloroform in the cold to remove waxes and colouring matter. An almost colourless solid remained. After repeated purification by taking up in methanol and precipitating with ether the m.p. was 218–30° (d) (yield 0·1%). On boiling with ethanolic hydrochloric acid it gave rise to three flavylium salts (paper chromatography); the nature of the parent proanthocyanidin(s) is being investigated.

The warm alcoholic extract of the leaves after removal of solvents was treated in exactly the same manner as described under the acetone extract. The product, an almost colourless powder, m.p. 210-25° (d) (yield 0·5%), also gave rise to three flavylium salts. The nature of this (these) proanthocyanidin(s) is also under investigation.

ACKNOWLEDGEMENTS

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2. Lewak, S., *Roczniki Chemii, Ann. Soc. Chim. Polonorum*, 1964, **38**, 1773; *C.A.*, 1965, **62**, 14615*c*.

NMR STUDY OF MERCURIC SULFATE MONOHYDRATE

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THE X-ray structural analysis of $HgSO_4.H_2O$ was first carried out by Bonefacic.[1] In their refinement of the structure, Templeton *et al.*[2] have commented on the hydrogen bonding in the structure. In view of these comments, it was thought interesting to undertake a PMR study of the single crystal.

$HgSO_4.H_2O$ belongs to the orthorhombic space group Pmcn -D_{2h}^{16} with four molecules in the unit cell. The general positions are given by:

$$\pm [(x, y, z);\ (\tfrac{1}{2} - x,\ \tfrac{1}{2} - y,\ \tfrac{1}{2} + z);\ (\tfrac{1}{2} + x,\ \bar{y},\ \bar{z});\ (\bar{x},\ \tfrac{1}{2} + y,\ \tfrac{1}{2} - z)]$$

Crystallographically, there are two non-equivalent *p-p* vectors in any of the three crystal planes.

Large single crystals were grown in the manner described by Templeton *et al.* They were examined using a modified PKW-type of wide line NMR spectrometer constructed in our laboratory. The signals were recorded for 18 orientations of the magnetic field in the *ab*- and the *bc*-planes, at intervals of 10° each.

The Pake splitting of the signals due to dipolar interaction, Δ H (in gauss) is given by[3]:

$$\Delta H = 2\alpha\ (3 \cos^2 \delta \cos^2 \overline{\phi - \phi_0} - 1).$$

The experimental derivative curves for the rotations in the *ab*- and the *bc*-planes looked similar to the curves usually obtained for a single *p-p* vector case. From each of these curves, a small central peak had to be subtracted before further analysis. This peak is presumably due to some free water in the crystal. The curves were resolved into Pake doublet derivatives, with a proper choice of a standard derivative curve from a well-resolved spectrum. The measured Δ H-values were then fitted into the Pake equation by the method of least squares. The parameters r, ϕ_0 and δ thus obtained, specify the length and the orientation of the interproton vector with respect to the crystallographic axes.

The interproton distance, r, was found to be
1·61 ± 0·03 Å