CHEMICAL EXAMINATION OF THE HEARTWOOD OF VARIOUS WEST PAKISTANI TREES

Part 1.—The Heartwood of Prosopis specigera (Jandi)

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Ethanol extraction of the heartwood of *Prosopis specigera* yields 0.5% material which contains 26% sugars consisting of sucrose, glucose, fructose, arabinose and mannose. The extract also contains 0.4% n-decanol, 0.5% β-sitosterol and 7.7% of the esters of lauric, myristic, palmitic, stearic, oleic and linoleic acids. The presence of 5 flavanones in the acetone-soluble fraction of the extract was also indicated. The major portion of the extract was tannins.

Introduction

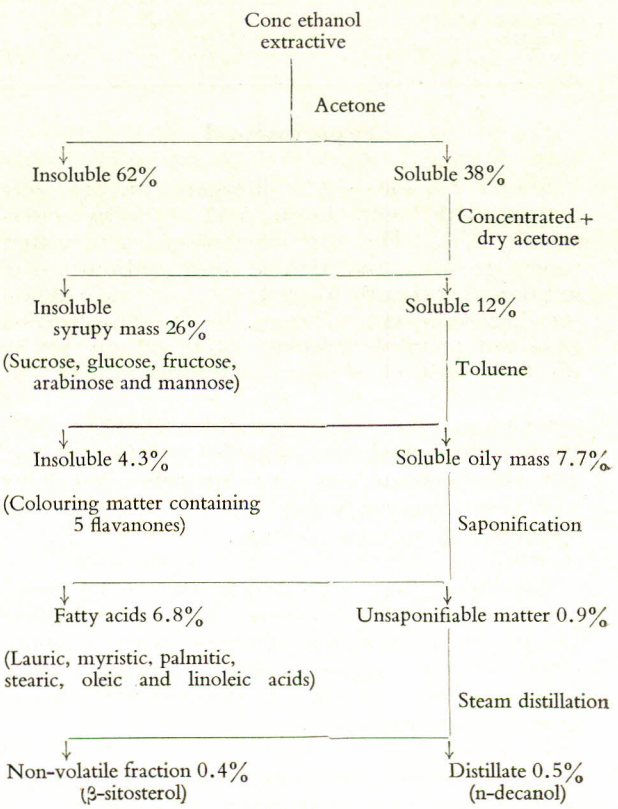
Of the heartwood of many trees in commercial use in West Pakistan, some are resistant to decay and insect attack, whereas others are perishable. In general, this durability is restricted to the so-called heartwoods. Some heartwoods have been, and still are, highly esteemed for building purposes. For example, the heartwood of *Dalbergia sisso* locally known as "Sheesham" is highly valued for its resistance to rot and termite.

It was recognised early that the durability might be dependent, besides other factors, upon the occurrence of some specific substances in the heartwood. In recent years, a large number of heartwoods,[1,2] which grow in various parts of the world have been examined chemically. The most common classes of compounds which occur in these woods include resins, terpenes, flavanoids, fatty acids, glycosides, alkaloids and alkanes. However, heartwood of only a few trees growing in Pakistan have so far been investigated for their chemical constituents. A research project has, therefore, been initiated for such investigations.

The present paper deals with the chemical examination of the heartwood of *Prosopis specigera* locally known as "Jandi". It is a small or medium-sized evergreen tree. It is found throughout the plains of the former Punjab where the rainfall is less than 30 in. It is the chief tree of "rakhs" where it grows to 20 ft in height and 2-3 ft in girth. Its heartwood is rather scanty, purplish-brown but very hard. As firewood, it is preferred to many other woods. Botanical sources[3] neither mention any particular resistance to decay of this wood, nor has it found any commercial use.

Exhaustive ethanolic extraction of the heartwood of a mature tree, cut in December, yielded 0.5% of a soluble material. The fractionation scheme of this material and the yields of various compounds isolated from it are shown in Chart 1.

CHART—1. FRACTIONATION SCHEME AND YIELDS OF VARIOUS COMPOUNDS ISOLATED FROM THE HEARTWOOD OF *Prosopis specigera*.



Experimental

M. ps were determined by Fischer-John apparatus. IR spectra were recorded on Leitz Wetzlar N 105 Infrared spectrograph, using KBr disc or

film technique. GLC was obtained with radium ionisation detector.[4]

Extraction of the Wood.—4.6 kg of shade-dried wood sawdust (moisture content 6.2%, ash content 2.52%) was exhaustively extracted with 95% ethanol. The cherry-red extract was filtered and the filtrate concentrated on a water bath under reduced pressure. The concentrate (about 1.5 l) was treated with (250 ml) dry acetone. The resulting brown mass (14.25 g) was filtered off. The filtrate was again concentrated and dry acetone (200 ml) was added to the concentrate. The process was repeated, till water was almost totally removed and, instead of a brown mass, a white precipitate formed. This precipitate on standing for sometime assumed the consistency of a thick, colourless syrupy mass. The acetone solution was decanted and the syrupy mass was again triturated and washed with dry acetone when white solid mass A (6 g) was obtained. The acetone washings were combined with the acetone solution. Acetone was distilled under reduced pressure to give dark brown mass B (3.2 g, 12%). In all 63.5 kg of the wood sawdust was processed as above to yield 45 g of the dark brown mass B.

Examination of White Solid A.—The white solid mass A gave positive Molisch test. Tests with Fehling's solution and Tollen's reagent were also positive. When burnt the solid smelt of burning sugar. All these tests confirmed the presence of sugars.

A 5% solution of the solid in 10% aqueous isopropanol was subjected to paper chromatography, using n-butanol: acetic acid: water= 40:10:22 v/v (upper layer) as solvent.[5] The descending chromatogram was sprayed with *p*-anisidine reagent.[6] Spots corresponding to glucose, fructose, sucrose, arabinose and mannose were obtained which were confirmed by comparison with the chromatogram of a known mixture of the above-mentioned sugars.

Separation of the Constituents of Acetone-soluble Fraction B.—Fraction B (30 g) was triturated with hot toluene (250 ml) and filtered. The insoluble solid mass (10.6 g, 4.3%) was reddish-brown in colour. This solid when subjected to Gripenberg's chromatographic technique[7] on paper using chloroform: ethanol: water=8:2:1 v/v solvent with the addition of 2% acetic acid showed the presence of five flavanones, detailed study of which is being carried out and will be communicated later.

Identification of the Fatty Acids.—The toluene-soluble fraction when freed from the solvent under reduced pressure gave 19.2 g (7.7%) thick oily liquid (iodine value 65.8).

The liquid was saponified[8] with 0.5 N alcoholic potassium hydroxide under reflux in an atmosphere of nitrogen for 6 hr. The soap was extracted with diethyl ether to remove the unsaponifiable matter. The residual soap solution was acidified with 4N sulphuric acid. The liberated acids were extracted in ethyl ether and dried (Na_2SO_4). The solvent was removed by a stream of carbon dioxide. The fatty acids were esterified with diazomethane. The esters were then analysed for their fatty acids by GLC on a SEG column (20% diethylene-glycol succinate on chrom P at 190°). Argon was used as the carrier gas at a flow rate of 20 ml/hr.

The fatty acids were identified from their retention times which were correlated with the retention times of a known mixture of fatty acids. The percentages of the acids were determined from the areas under the peaks by the triangulation method. The results are presented in Table 1.

TABLE 1.—GLC OF THE FATTY ACIDS OF THE HEARTWOOD OF *Prosopis specigera*.

Component fatty acid	*Rf* value	Peak area	Fatty acid in mixture %
C_{12}:0	0.14	0.056	0.30
C_{14}:0	0.28	0.035	0.19
C_{16}:0	0.53	6.300	33.66
C_{18}:0	1.00	2.800	14.90
C_{18}:1	1.16	5.130	27.34
C_{18}:2	1.48	4.440	23.66

Unsaponifiable Matter.–The unsaponifiable matter was 0.9% of the total extractable matter in the wood. 2.25 g of it was steam-distilled so that about 2 l. distillate collected. The distillate, after saturating with sodium chloride was extracted with diethyl ether. The ether extract was dried (Na_2SO_4) and the solvent distilled on a water bath to give 1.25 g of a sweet-smelling, colourless liquid, b.p. 231°C, d_4^{20} 0.829. The IR spectrograph was found to be similar to that of n-decanol. This was confirmed from its *p*-nitro-benzoate derivative, m.p. 30-31°C.

β-*Sitosterol.*—The non-volatile residue in the distillation flask was extracted with diethyl ether and the extract freed from the solvent to give a solid mass. This was subjected to column chromatography using neutral alumina. The column was eluted first with petroleum ether

(40-60°): ether=1:1 v/v for removing traces of unsaponified fatty acid esters, and then with ethanol: ether=1:1 v/v when a white solid, giving positive Liebermann Burchard reaction, m.p. 135.5-137°, was obtained. This was crystallized from ethanol to give β-sitosterol, m.p. 136-137°C. On acetylation of the compound (0.58 g) with acetic anhydride (2 ml) and pyridine (2 ml), and recrystallization from acetone, β-sitosterol acetate (0.12 g), m.p. 128°C, was obtained.

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References

1. J.W. Cook, *Progress in Organic Chemistry*, (Butterworth Scientific Publisher, 1952), vol. I, p. 22.
2. T. Swain, *Chemical Plant Taxonomy* (Academic Press, London and New York, 1963), p. 89.
3. R.N. Parker, *A Forest Flora for the Punjab with Hazara and Delhi* (Government Printing Press, West Pakistan, 1956), p. 200.
4. D. Glick, *Methods of Biochemical Analysis* (Inter Science Publishers, N.Y., London, 1963), vol. II, pp. 79-80.
5. Block, Durrum and Zwerg, *Paper Chromatography and Electrophoresis* (Academic Press Inc. Publishers, N.Y., 1958), second edition, p. 172.
6. S. Mukerjee and H.C. Srivastava, Nature, **169,** 330 (1952).
7. Gripenberg, Acta. Chem. Scand., **6,** 1153 (1952).
8. K.A. Williams, *Oils, Fats and Fatty Foods* (J. & A. Churchill Ltd., London), third edition, p. 100.