Chemical nature of extraneous components of BIJA (pterocarpus marsupium Roxb)

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SUMMARY

Extraction of locally available hardwood species-Bija (*Pterocarpus marrupium* Roxb) with ethanol-benzene (1:2 v/v) mixture (1) afforded four chemical constituents. Of these three could be characterized as phlobatannins, phlobaphenes and flavones.

Wood extractives have pronounced effect on the pulping of wood. Extraneous components of wood may reduce the pulp yield, increase chemical consumption inhibit pulping reaction proper, cause corrosion to equipment, create difficulties in recovery process and finally impair pulp and paper properties. Knowledge of extractives may help to take some corrective measures³. With the increasing use of locally available hardwoods, it is necessary to make the advances in our knowledge of the structural chemistry of wood constituents. It is with this aim that work is undertaken.

LITERATURE

King et. al ^{3,4,6} have extensively worked on the chemistry of extractives from various hardwood species in which they have reported poly nuclear and phenolic nature of these extractives. Although they have worked on the extractives of *pterocarpus* far ily in general, the species Bija (*Pterocarpus marsupium* Roxb) is not reported in early study by them.

The literature survey shows that very little attention have been given towards the study of extraneous components of Indian hardwoods in general and Bija in particular. Bose *et. al.*⁷ however, have reported the presence of kino-tannins (condensed tannins) and sterol compounds in the extraneous components of Bija while stuying this species from pytochemical study point of view. Sawhney *et. al.*⁸ reported the presence of liquiritigenin and isoliquiritigenin (compounds belonging to flavone family) and in addition to these two compounds, they also reported the presence of one neutral unidentified compound.

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In the above cases, no details of experimental work are reported. It is, therefore, proposed to study the extraneous components of Bija-wood systematically by following the scheme of Carlberg and Kurth⁹.

By applying the Carlberg and Kurth⁹ scheme and after chemical investigation, it is found that the Bija-wood contains phlobatannis, phlobaphenes-sterolester and flavones compounds. The chemical nature of these compounds is likely to be identified with the compounds reported earlier by Bose *et. al.*⁷ and Sawhney *et. al.*⁸.

For a given degree of delignification, consumption of chemicals in alkaline pulping may be more due to the presence of phlobatannis, phlobaphenes and flavones which are phenolic in nature. Oxidation of flavone may give rise to yellow green colouration in alkaline cooking conditions, thus, reducing bleachability of the pulp. Phlobaphenewood resin may give rise to foaming which may reduce the efficiency of pulp washing and subsequent concentration of black liquor. However, foamy liquor may stabilize the sulphur compounds thereby reducing atmospheric pollution.

EXPERIMENTALS

Hardwood sample was obtained from the Forest Development Corporation of Maharashtra, Nagpur. Results of proximate analysis of Bijawood on oven-dry basis carried out as per TAPPI standards (10) are tabulated in Table 1.

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TABLE 1

S. No.	Determination	Percentage
1	Ash	0.93
2	Solubility in—	
	(i) Cold water	10.55
	(ii) Hot water	7.79
	(iii) Ether	1.59
	(iv) Alcohol-Benzene	
	(1:2 v/v)	7.97
	(v) One per cent sodium hydroxide	20.52
3	Lignin (72% sulphuric acid method)	25. 99
4	Holocellulose (By Ritter and Kurth method)	82.46
5	Pentosan	24.03

PROXIMATE ANALYSIS OF BIJA Pterocarpus marsupium Roxb)

EXTRACTION WITH ETHANOL-BENZENE MIXTURE

Powdered (40 mesh) and dried Bija sample was erxtracted with ethanol-benzene (1:2 v/v)mixture for 24 hrs. with occasional stirring in a Soxhlet Apparatus. After removal of solvent, the extract was treated as per Carlberg and Kurth Scheme (1) for the separation of various compouents (9).

ISOLATION AND IDENTIFICATION OF WATER SOLUBLE COMPOUND (A)

The ethanol-benzene extract was washed with water and the solvent removed by filtration. As the filtrate was being concentrated, a reddish gummy material began to separate out. Attempts to obtain any crystalline material from this were unsuecessful as its melting point (m.p.) could not be found out being gummy in nature.

The compound (A) was precipitated from aqueous solution by lead acetate. The lead salt of (A) was soluble in acetic acid (11, 13). When (A) was treated with ferric chloride in aqueous solution, it produced a green colouration (12). The compound (A) was converted to its acetyl derivatives which crystallised from ethyl acetate, m. p. 148-155°C.

CHROMATOGRAPHY

The compound (A) was resolved over silica gel-G plate (2.5 mm thick) into pattern of zones by acetone-methanol-M-pyridine (5:4:1) solvent system. The zones were revealed by examination under ultra-violet lamp (14).

From all these properties and the similar observations made earlier, the compound (A) appears to be identical with l-acacatechin (phlobatannis). The probable general structure for compound (A) is of the type given below.



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Fig.-1 Compound (A) : Phlobatannis (1-acacatechin)

ISOLATION AND IDENTIFICATION OF ETHER INSOLUBLE COMPOUND (B)

In order to remove this as far as possible, the whole of water insoluble material left after the removal of compound (A) was shaken several times with cold ethylether. The combined ethylether solvent was filtered and preserved for the isolation of the compound (C),

EXAMINATION OF THE COMPOUND (B)

The compound (B) (0.98 g) was washed several times with light petroleum ether. The dry reddish brown compound (B) m. p. 180-181° (dec.) was crystallised by dimethyl ketone into a reddish brown microscopic crystals melting at 184-185°C. It gave an acetate m. p. 222-223°C. Elementary analysis proved the absence of nitrogen, sulphur and halogens. It felt no ash on ignition (burns with sdooty flame) indicating the presence of carbon, hydrogen and probably oxygen. Analysed and observed C, 83.03%; H, 11.42%, Calculated for C₃₀H₅₀O, C,84.21%; H,12.6%.

It is easily soluble in alcohol, glacial acetic acid, benzene and chloroform, less soluble in ethylether, sparingly soluble in petroleum ether and practically insoluble in water and sodium bicarbonate (3). It dissolves in con.sulphuric acid with the formation of a dark-brown colour. Its solution in con.nitric acid is yellow and in con hydrochloric acid, it gives a pink tinge. It produces green colouration with Liebermann-Burchard reagent (11).

QUALITATIVE ANALYSIS OF COMPOUND (B) BY DIGITONIN

The compound (B) was dissolved in 95% hot alcohol and treated with 1% hot alcoholic

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solution of digitonin. No white precipitate was obtained, indicating that the compound is "sterolester" and not the free sterol. This view is further confirmed by the fact that it was not sponified (11) and with Liebermann-Burchard, the colour developed more repidly and the intensity the colour was greater. Furthermore, it decolourised potassium permangenate solution and bromine water, indicating the unsaurated nature of the compound.

The compound (B) was heated on the water bath with 5% hydrochloric acid solution. For about an hour, the mixture was filtered. The filtrate was neutralised with sodium carbonate solution and treated with Fehling's solution. The mixture on being heated on the water bath for about 20 minutes, did not develop any cuprous oxide, thus, indicating the absence of any reducing sugar.

CHROMATOGRAPHY

The compound (B) was resolved over silica gel-G plate (2.5 mm thick) by cyclohexane-ethylacetate (99.5:05) as the developing solvent (15). The compound was detected by spraying with the phosphomolybidic acid (Rf 0.087).

The above studied properties correspond very closely with those of phlobaphenes-(phytosterols). The general skeleton assigned to compound (B) is of the type given below.



Fig. 2.

Fig.-2 Compound (B) : Phlobaphenes-unsaponifiable sterol ester (wood resins)

ISOLATION AND IDENTIFICATION OF ETHER SOLUBLE COMPOUND (C)

The excess of ether was removed from the extract by distillation. As the extract was being concentrated on water bath to about 2-3 cc, a

dark red viscous matter which had a very bitter taste began to separate out (0.67 g) m. p. $85-86^{\circ}$ C which on crystallization from petroleum etherethylacetate afforded fine needles (m. p. $86-87^{\circ}$). Analysed and observed C,71.89; H,4.62; Calculated for C₂₀H₂₄O₄, C,73.15; H,7.35.

EXAMINATION OF COMPOUND (C)

It is easily soluble in acetone and alcohol. It dissolves in aqueous solutions of sodium hydroxide and sodium carbonate with the formation of deep yellow solution with no fluorescence (16). Its solution in concentrated sulphuric acid produced violet red fluorescent (16).

Elementary analysis proved the absence of nitrogen, sulphur and halogens.

WILSON TEST FOR FLAVONES

Reagent required for this test: Solution A – absolute acetone saturated with boric acid. Solution B— absolute acetone containing 10 g of anhydrous citric acid (dried at 100° C for 2 hours) per 100 ml. Equal volumes of A and B are mixed.

The compound (C) (0.5 mg) was dissolved in about 1 ml of dry acetone and the solution was divided into two parts. To one solution of 2 ml of boricacid-citric acid-acetone solution was added, the other was diluted to an equal volume with a mixture of equal part of solution 'B' and acetone. The tube containing boric acid gave a more yellow colour in a few minutes (17 (i,ii)).

When compound (C) warmed on water bath with aqueous methanol, the whole of the compound swelled-up and formed orange yellow jelly (4). The latter when heated, lost the solvent and left very small amount of waxy residue insoluble in ethyl ether but soluble in acidulated ethyl alcohol and soluble in hot water (5). This material was not bitter but had a peculiar taste of its own. On account of its peculiar physical properties, no further work could be done for investigation of this waxy residue,

CHROMATOGRAPHY

The compound (C) was resolved over silica gel-G plate (2.5 mm) thick) using hexaneethyl acetate (3:1) as solvent system (18, 19). Three well defined bands were then visible under an u. v. lamp viz. (1) a large lower band with bright blue fluorescence, (2) a small middle band showing an intense greenish blue fluorescence, and (3) a small yellow band at top showing no fluorescence. Rf for lower band (1) 0.29, Rf for middle band (2) 0.66; Rf for top band (3) 0.82.

The above studied properties correspond very closely with those of flavone group. The general frame-work of compound (C) is given below.

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Fig.-3 Compound (C) : Flavones

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