

RESINOL FROM THE NUTS OF *SEMECARPUS TRAVANCORICUS*

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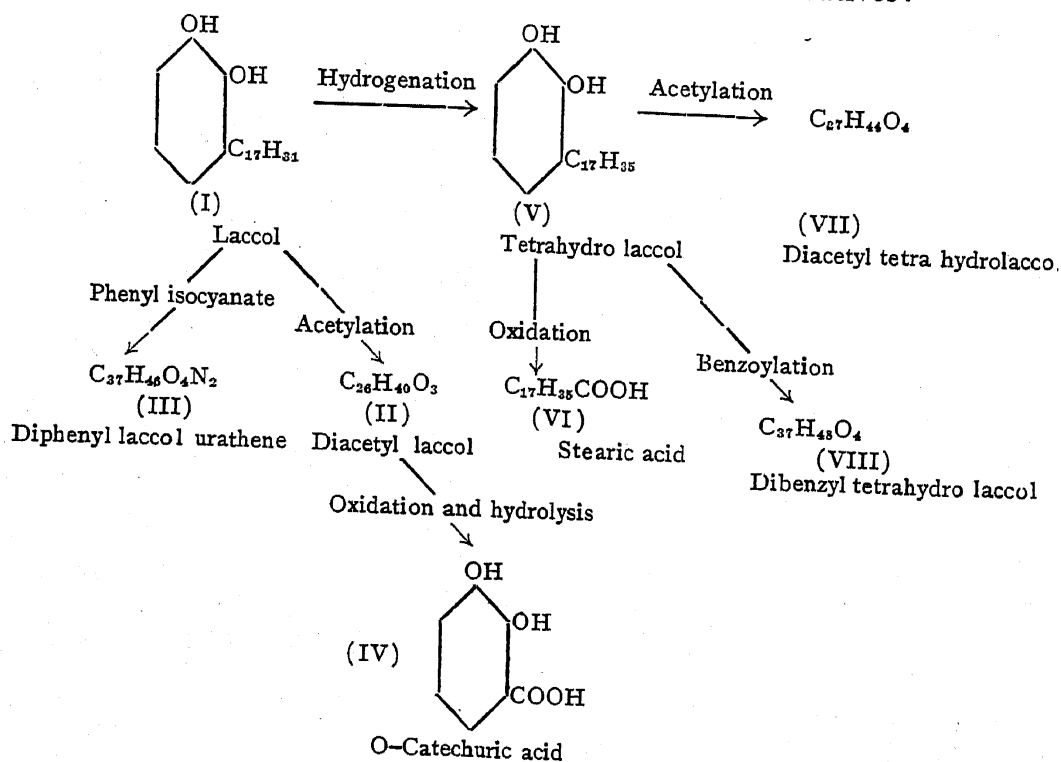
THE vesicant lattices of certain species of Anacardiaceæ to which *Semecarpus travancoricus* Bedd. belongs supply the lacquers employed in China and Japan for decorative coating of wood. A chemical examination of the active constituents of the exudations from these plants by Majima *et al.*^{1,2,3} has revealed that all of them contained catechol derivatives with unsaturated side chains of 15 or 17 carbon atoms either in the adjacent or in the vicinal position to the catechol nucleus. Pillay and Siddiqui⁴ have shown that the pericarp of the nut, marking nut or Bhilawa nut, of the allied species *S. anacardium* contains about 21 per cent. of a phenolic product named "bhilawanol" identical with urushiol,⁵ a compound having an unsaturated side chain of 15 carbon atoms in the adjacent position to the catechol nucleus, 0.1 per cent. of a monohydroxy phenol named "semecarpol" and a tarry corrosive residue. Nair *et al.*⁶ have recently reported that the bark exudation of *S. travancoricus* contains about 21 per cent. of laccol (3-heptadecadienyl catechol).³

An opportunity is now taken to present the results of work on the resinol from the pericarp of the nut (also known as marking nut and used for marking purposes in Travancore) from *S. travancoricus* Bedd., that was in progress at this Institute for the past few years.

Semecarpus travancoricus Bedd. (Tamil, *Natu shengoti* or *katha shengoti*) is a very large tree met within the forests of the Tinnevely and Travancore Hills. The pericarp of the fruit of this tree contains a resinous, black non-corrosive oil which is used for marking purposes in the same way as *bhilawa* nut oil (*Semecarpus anacardium* Linn. *f.*). The samples of the oil as obtained from the two species differ in their physical as well as chemical properties. The oil from *S. travancoricus* is not vesicating and is, therefore, easy to handle in industrial processing. Nair, G. V., *et al.*⁶ in a recent publication have mentioned that the lacquers obtained from the fruit presented difficulties when their direct utilisation as lacquer or varnish was attempted due to their non-drying and extremely vesicant properties, which is quite contrary to our findings.

The resinol has got high phenolic content, which indicates its suitability for ready conversion into solid resins with formaldehyde. On treatment with the latter, thermoplastic products,¹⁰ shining and varying in shades from reddish brown to jet black, have been obtained. Their solutions with common solvents on drying leave elastic paint films, which do not easily crack or chip off even when stoved at 150° C. for 3 to 4 hours. Like the enamels prepared from the resinol of *bhilawa* nuts they are not affected by water or dilute acid or alkalis.

Laccol⁵ (3-heptadecadienyl catechol) has been identified as the main constituent of the resinol. On hydrogenation, it formed a tetrahydro derivative, $C_{23}H_{40}O_2$, m.p. 62° C., which gave stearic acid on oxidation with potassium permanganate in aqueous acetone solution. The melting point of the tetrahydro derivative and the C_{17} side chain suggested the possibility of its identity with tetrahydrolaccol obtained by Majima³ from ivy lacquer (*Rhus toxicodendron*), Indo-Chinese lac (*Rhus succedanea*), Formosan lac (*Semecarpus vernicifera*) and *Rhus ambigua*. The identity of the two substances was further confirmed by the preparation of the derivatives of the tetrahydro compound, namely diacetyl dimethyl ether and mononitro dimethyl ether, whose m.p. agreed with the corresponding derivatives of tetrahydrolaccol obtained by Majima (*loc. cit.*). The following are some of the structural and molecular formulæ for laccol and some of its derivatives:—



From the above it would appear that the resinol from the pericarp of the marking nut of *S. travancoricus*, like the one from the marking nut of *S. anacardium* (bhilawan), would be a valuable addition to the list of natural products used for stoving enamel and lacquer purposes in industrial practices.

EXPERIMENTAL

The fruits used in our studies were received through the Conservator of Forests, Travancore, from the Game Sanctuary Range, Kunali. The dried brown to black fruits were oval shaped, $\frac{3}{4}$ " to 1" long, $\frac{1}{2}$ " wide and $\frac{1}{10}$ " thick with a portion of the hypocarp attacked. Inside there was a very thin flat kernel most of which was fungus attacked. The fruit was crushed and extracted with the following solvents and the yield of the resinol is given in Table I.

TABLE I

Solvent	Yield of Resinol
1. Alcohol (95%)	32.0 per cent.
2. Petroleum ether (40-60° C.)	35.0 per cent.
3. Ether (sulphuric)	35.5 per cent.

The chemical and physical properties of the ether extract along with those of the *bhilawa* nut are recorded in Table II.

TABLE II

Constant	Ether extract (Authors)	<i>Bhilawa</i> nut oil (Naidu) ⁷
1. Specific gravity (Westphal balance)	0.950 at 25° C. 0.891 at 40° C.	..
2. Acid value	5.6	99.3
3. Saponification value	165.7	334.2
4. Ester value	160.0	234.9
5. Iodine value	112.1	265.0
6. Acetyl value	239.7	..

This oil, in contrast with *bhilawa* nut oil, is devoid of the latter's vesicating property and is, therefore, easier to handle in industrial processing. Its saponification value is half of that of *bhilawa* nut oil pointing to its corresponding lower content of ester or saponifiable matter. Its high phenolic

content indicates its suitability for ready conversion into solid resins with formaldehyde.

Treatment with formaldehyde.—The resinol when treated with formaldehyde in the presence of alkali under reflux for varying periods yielded thermoplastic products with shining colour ranging from reddish to jet black. These are soluble in turpentine, benzene, carbon tetrachloride and drying oils. When painted on iron strips and allowed to dry, firm elastic paint films were obtained. These films did not easily crack or chip off even when stoved at 150° C. for 3 to 4 days; thus it can serve as a good stoving enamel.

Vacuum distillation of the resinol.—Distillation of the resinol under vacuum gave the following fractions:—

Resinol distilled	79.0 gm.
<i>Fraction:</i>				
1. Upto 235°/3 mm.	2.22 gm.
2. 235-40°/3 mm.	14.25 gm.
3. 230-35°/3 mm.	12.64 gm.
4. 235-40°/3 mm.	14.34 gm.
5. Residue	34.10 gm.
Loss on heating	1.45 gm.

Fractions (3) and (4) distilled with a little decomposition. After second fraction the resinol stopped distilling for a while, but on more vigorous heating it again started distilling, indicating some decomposition. All the fractions show the phenolic reactions. With alcoholic ferric chloride these gave an evanescent green colouration turning immediately to a black precipitate and a violet red on further addition of a drop of alcoholic potash indicating an orthohydroxy compound. With alcoholic lead acetate, these gave a white precipitate insoluble in water, but soluble in alcohol and ether, which darkened quickly on exposure to air due to oxidation. The other physico-chemical constants of the fractions are given below (Table III).

Fraction No. 2 has been identified as pure laccol, while other fractions contained mostly laccol together with some ester or saponifiable matter.

Fraction No. 2.—Congealed at about 20° C. to a white buttery mass [Found C, 80.2; H, 10.1; $C_{23}H_{36}O_2$ (1) requires C, 80.2; H, 10.5 per cent.]. 1.770 gm. of the substance in ice-cold chloroform absorbed 1.810 gm. of bromine; two double bonds require 1.667 gm. of bromine.

Diacetyl derivative was prepared by treatment of the substance with acetic anhydride and anhydrous sodium acetate and was obtained as a

TABLE III

	Fraction No. 1	Fraction No. 2	Fraction No. 3	Fraction No. 4
1. Density d^{30}	0.9384	0.9416	0.9228	0.9232
2. Refractive index n^{30}	1.4889	1.4931	1.4821	1.4806
3. Saponification value	36.86	7.82	75.6	80.2
4. Acetyl value	240.34	264.1	202.4	198.3
5. Iodine value	133.7	122.5	116.9	106.0
6. Solubility	Insoluble in water, but soluble in common organic solvents			

yellow liquid, b.p. 235–38°/3 mm. It has a characteristic smell and does not react with lead acetate or ferric chloride, showing the absence of hydroxy group. n^{30} , 1.4821; per cent. acetyl = 20.35 [Found: C, 75.6; H, 9.1. $C_{27}H_{40}O_4$ (II) requires C, 75.7; H, 9.3 per cent.].

Hydroxyl content (Hibbert and Sudborough's Method⁸): 0.2543 g. of the substance with magnesium methyl iodide gave 30.4 c.c. of methane at N.T.P.; 0.2543 g. of a substance of mol. wt. 344 and containing two hydroxyl groups should give 33.1 c.c. at N.T.P.

Diphenylurethane derivative was prepared by treating the substance with phenyl isocyanate and dissolving the reaction product in hot benzene, from which it comes down on cooling as colourless, rectangular rods, m.p. 228–29° [Found: N, 4.7; $C_{37}H_{46}O_4N_2$ (III) requires N, 4.8 per cent.].

Destructive Distillation.—The substance when subjected to dry distillation yielded water, a dark coloured oily distillate and inflammable gases. The oily distillate was separated by shaking in a hydrogen atmosphere with caustic soda solution into phenolic and non-phenolic components. The phenols were redistilled and the first fraction boiling between 230° and 255° C. solidified. It was recrystallised from benzene, m.p. 104° C. and identified as catechol by mixed melting point with a sample of pure catechol.

Oxidation of diacetyl derivative.—The diacetyl derivative was dissolved in a mixture of acetone (100 c.c.) and water (30 c.c.) and acetic acid (6 c.c.) and the powdered potassium permanganate in small quantities at a time was added to the solution. Worked up in the usual manner, it first yielded diacetyl *o*-catechuic acid which was hydrolysed with alcoholic potash in hydrogen atmosphere. The resulting acid was not obtained solid, but gave the colour reactions of *o*-catechuic acid (IV).

Catalytic Reduction.—To a solution of the substance (3.0 g.) in absolute alcohol (10 c.c.) was added 1 g. of platinum black, prepared according to the method of Adams,⁹ and hydrogen bubbled through for 5 hours with constant stirring. The resulting product when filtered from the platinum black and freed of the solvent on the water-bath, gave the hydroproduct as a crystalline mass. On crystallisation from xylene and low boiling petroleum ether (below 50° C.) it was obtained as white needles, m.p. 62–63° C. [Found: C, 79.1; H, 11.4. $C_{23}H_{40}O_2$ (V) requires C, 79.3; H, 11.5 per cent.] Majima³ reports the m.p. as 63–64° C.

Oxidation of Hydrogenated Product: Stearic Acid (VI).—The hydrogenated product (1.0 g.) dissolved in acetone (100 c.c.) and water (15 c.c.), was mixed with a solution of potassium permanganate (4 g.) in acetone (200 c.c.) and water (30 c.c.). The mixture was warmed until decolourised, filtered, acetone removed and the aqueous residue acidified. The acid thereby liberated, after two crystallisations out of 95 per cent. alcohol melted at 67–68° C. It was identified as stearic acid by its molecular weight (282.4) and mixed melting point with an authentic sample of the acid.

Diacetyl tetrahydro derivative was prepared by acetylation of the hydrogenated product with acetic anhydride and anhydrous sodium acetate and crystallised from alcohol, m.p. 57.5° C. [Found C, 74.8; H, 10.1; $C_{27}H_{44}O_4$ (VII) requires C, 75.0; H, 10.2 per cent.]. Nair *et al.*⁵ report the m.p. as 57.5° C.

Dibenzoyl tetrahydro derivative was prepared by treatment of the hydroproduct (0.5 g.) in dry ether (5 c.c.) with benzoyl chloride (1 g.) and working up the reaction product in the usual way. It crystallised from acetic acid as white flakes, m.p. 64–65° [Found: C, 79.7; H, 8.3. $C_{37}H_{48}O_4$ (VIII) requires C, 80.0; H, 8.6 per cent.].

Dimethyl ether of the tetrahydro derivative was prepared by treatment of the hydroproduct two times with methyl iodide and sodium ethoxide in absolute alcohol. It crystallised from alcohol in long prisms, m.p. 43–44° C. Majima³ reports the m.p. as 43–44° C.

Mononitro derivative of the above was prepared by treatment of the dimethyl ether (IX) (0.5 g.) in glacial acetic acid (3 c.c.) with a mixture of nitric acid (d. 1.48, 3 c.c.) and glacial acetic acid (5 c.c.). The mixture was warmed for half a minute on the water-bath and then kept aside to cool. The resulting yellow crystals when crystallised from alcohol gave 0.3 g. of light yellow needles, m.p. 71–72° C. Majima³ reports the m.p. as 75–76° C.

Fractions 1, 3 and 4.—These contained mostly laccol along with some ester or saponifiable matter which could not be separated and so could not

be identified. All these fractions on hydrogenation and acetylation formed the crystalline diacetyl derivatives of tetrahydrolaccol, m.p. 57.5°C ., and showed no depression in it on admixture with the corresponding compounds of fraction No. 2. The hydrogenated products in all these cases on oxidation with potassium permanganate in aqueous acetone solution gave rise to stearic acid, m.p. $67-68^{\circ}\text{C}$., confirmed by its molecular weight and mixed melting point. Their saponification values indicated the presence of some ester or saponifiable matter which, however, could not be separated.

Residue.—The tarry residue forming about 43 per cent. of the total extract could not be hydrolysed with acid or alkali. It was purified by dissolving in 80 per cent. cold alcohol (which leaves a thick dark resinous mass undissolved), treating the alcoholic solution with lead acetate and liberating the tarry phenolic product from the lead salt with hydrochloric acid. It dissolves in alcoholic potash with a fairly permanent grass green colouration. With ferric chloride it gives a very transient green colouration followed by a black precipitate. With lead acetate it forms a green precipitate. It could be acetylated but the acetylated product could not be distilled or made to solidify even when hydrogenated. On destructive distillation it gave a mixture of phenols and non-phenolic matter. All these reactions show it to be a mixture of high molecular weight phenols. It polymerised on standing to a shining friable mass, soluble in benzene, acetone and chloroform.

SUMMARY

The resinol on treatment with formaldehyde formed thermoplastic products, shining and varying in shades from reddish brown to jet black. The lacquer forming ingredient has been isolated and identified as laccol (3-heptadecadienyl catechol), confirmed by the preparation of its hydrogenated product and its derivatives.

The tarry residue, left after vacuum distillation, polymerises on standing to a shining friable mass, soluble in benzene, acetone and chloroform and appears to be a mixture of high molecular phenols.

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