PART VIII.

SOME ETHER-SOLUBLE CONSTITUENTS OF LAC-RESIN.

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The first systematic investigation of stick-lac was made by Tschirch and Farner [1] who extracted the material successively with light petroleum, water and alcohol. They give the following percentage results :—wax, 6 ; colouring matter (laccaic acid), 6·5 ; purified resin, 74·5, of which 65 per cent. is insoluble in ether ; residue, 9·5 and water, 3·5. The portion soluble in ether was found to contain acids, a resin, a colouring-matter, erythro-laccin, anda crystalline compound smelling strongly of shellac. The main resin after treatment with ether gave on hydrolysis a resinotannol and aleuriict acid, which has since been shown to be a trihydroxy-palmitic acid.[2]

Before the experiments described in this paper were completed a second paper on stick-lac appeared.[3] In this it is shown that laccaic acid[4] obtained from the aqueous extract is probably an anthraquinone derivative as it yields anthracene when distilled with zinc dust. The second colouring-matter, erythro-laccin, yields a tetra-acetyl derivative and is probably a tetrahydroxy-methyl-anthraquinone. The ethereal solution of the alcoholic extract is stated to contain a monohydroxy-palmitic acid (m. p. 76·5-77·0°) in addition to aleuritic acid and fatty acids.

The material used in this investigation was a sample of stick-lac produced by *Lakshadia mysorensis* grown on *Shorea talura* Roxb. As the composition of the lac probably varies with both the lac organism and the host-plant, it is advisable to give both when describing investigations on lac.

The material (5 kilos) was powdered to pass through a 60-mesh sieve and then stirred with ordinary petrol to remove wax ; after filtration the residue was washed with light petroleum (40–60°) in order

[1] *Arch. Pharm.*, 1899, 237, 35.
[2] Harries and Nage, *Chem. Umschau*. 1922, 29, 135.
[3] Tschirch and Ludy junr, *Helv. Chem. Acta*, 1923, 6, 994.
[4] Dimroth and Goldschmidt, *Annalen*, 1913, 399, 62.

to remove the higher boiling petrol. The residue, after admixture with sand, was extracted with ether by percolation, the process being continued until the extract was practically colourless. After removal of most of the ether, 4 litres of a concentrated solution were obtained and gave a solid deposit. This was removed and washed with ether, the ethereal solution and washings, after drying and removal of ether, giving 150 grams of a dark brown, viscous syrup. In order to convert free acids into esters 100 grams of the syrup was dissolved in 580 grams of methyl alcohol, the solution saturated with hydrogen chloride and boiled for five hours. Most of the alcohol was removed by distillation and the residue dissolved in ether and extracted with 2 per cent. sodium carbonate solution to remove the dyestuff. The ethereal solution was greenish yellow, and after drying and removal of ether gave a semi-solid residue which was washed with a mixture of ether and light petroleum (1–3). The solid residue (10 grams) after crystallisation from light petroleum melted at 81–82° and was found to be myricyl alcohol. The filtrate from the myricyl alcohol was hydrolysed with alcoholic potash, giving 0·1 gram of a neutral product with an odour of shellac and melting at 71–72°. The acids formed on hydrolysis were crystallised from light petroleum followed by alcohol and melted at 52–55°. On further crystallisation from alcohol three fractions were obtained melting respectively at 59·1–59·5, 55–56° and 46–47° and with mean molecular weights, 251, 248 and 234. They are probably mixtures of palmitic and myristic acids and by an additional crystallisation the first fraction gave an acid melting at 60·5° and with a molecular weight 254, thus corresponding with palmitic acid.

The remaining acids were separated into liquid and solid acids by Twitchell's method.[1] The liquid acids after solution in ether and decolorisation with animal charcoal were obtained as a viscous liquid with a mean molecular weight 270 and a refractive index 1·4635 at 60°. The analytical data agree quite well with those required for an unsaturated monohydroxy-acid,[2] $C_{15}H_{28}(OH)CO_2H$ (Found C = 71·0, H = 11·2. Theory requires 71·1 and 11·1 per cent).

The colouring-matter was recovered with some difficulty from the sodium carbonate extract and finally, after crystallisation from 95 per cent. alcohol followed by glacial acetic acid, gave Tschirsch's erythrolaccin as orange red needles which begin to decompose at 250°. The analytical values agree quite well with those required for a tetrahydroxy-methyl-anthraquinone.

[1] *J. Ind. Eng. Chem.*, 1921, 13, 806.

[2] The iodine value found by Winkler's method was 26·5, by Wijs' method 21, but by a method described by Clarke in *Hand-book of Organic Analysis* 1916, p. 225 was found to be 94. The formula, $C_{15}H_{28}(OH)CO_2H$, requires 94.

It will be noted that neither mono- nor trihydroxypalmitic acid was isolated, perhaps owing to the extraction with ether not being complete. On the other hand palmitic acid, and probably myristic acid and an unsaturated hydroxy-acid were isolated in addition to the colouring-matter erythrolaccin.

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