THE CONSTITUENTS OF SOME INDIAN ESSENTIAL OILS.

PART XVIII.

Derivatives of Abietic Acid.

By Madyar Gopal Rau and John Lionel Simonsen.

In Part XVII of this series (*Ind. For. Rec.*, 1925, xi, 207) we advanced evidence which established definitely the identity of the abietic acid separated from the rosin of *Pinus longifolia* with the well-known acid obtained from the rosin of *Pinus palustris.* Amongst other new derivatives of abietic acid we prepared a monohydroxy-abietic acid which was found on oxidation with potassium permanganate to yield crystalline products and appeared to us, therefore, likely to be a promising starting-point for experiments on the constitution of abietic acid. In view of recent publications in this field to which reference will be made below, we have decided not to pursue this investigation and we desire now to place on record the results we have obtained as they may prove of value to future workers.

Before giving an account of our experiments it appears necessary to survey briefly the present position of the chemistry of abietic acid. Aschan and Virtanen (*Annalen*, 1921, **424**, 117) and Aschan (*Ber.*, 1922, **55**, 945, 2950) gave an account of a long series of experiments on an acid which they designated pinabietic acid and which they considered to be a stereoisomeride of abietic acid. As a result of these experiments they suggest that both pinabietic acid and abietic acid most probably have the constitution represented by Formula I.

This formula has been somewhat severely criticised by Ruzicka, Schintz and Meyer (*Helv. Chim. Acta*, 1923, **6**, 1077). It is not necessary to detail here the experimental evidence upon which their criticism was based, but their objections to the formula proposed by Aschan and Virtanen appear to us on the whole to be well founded. As the result of their experiments Ruzicka and his co-workers suggest Formula II as a more correct representation of abietic acid. It will be observed that this formula differs from that of Aschan and Virtanen in three important aspects; (i) in place of one ethylene linkage and one *cyclo*propane ring it contains two ethylene linkages; (ii) the carboxyl group is changed in position and is attached to a secondary carbon atom in place of a tertiary; and (iii) the position of one of the methyl groups is changed.

Although the formula of Ruzicka and his collaborators has much to recommend it we do not consider it to be entirely satisfactory. In our opinion one weak point in the formula is the attachment of the carboxyl group to a secondary carbon atom. As is well known, abietic acid is a very weak acid and can only be esterified with difficulty, properties much more in accord with those of a carboxyl group attached to a tertiary carbon atom as in the formula of Aschan and Virtanen. In spite of this and other objections we have adopted Formula II as a working hypothesis.

In 1923 Ruzicka and his collaborators (*Helv. Chim. Acta*, 1923, **6**, 1077, 1097) described the results of systematic experiments on the oxidation of abietic acid with potassium permanganate and other oxidising agents. In their earlier experiments they were much hampered by the formation of eutectic mixtures, but they succeeded ultimately in separating and characterising a dihydroxy-abietic acid $C_{20}H_{32}O_4$, m. p. 163°, which yielded a crystalline diacetyl derivative. In a later paper Ruzicka, Meyer and Pfeiffer (*Helv. Chim. Acta*, 1925, **8**, 627) described a large number of oxidation products and although the majority of these were only obtained in an amorphous condition, they could be sufficiently characterised to enable the authors to advance Formula III as best representing the formula of their dihydroxy-abietic acid.

Prior to the experiments of Ruzicka a number of hydroxy-derivatives of abietic acid had been described as being formed by the oxidation of abietic acid with potassium permanganate. Mach (*Monatsh.*, 1894, **15**, 627) obtained an amorphous acid m. p. 123° to which he gave the formula $C_{15}H_{16}O_3$, but which Fahrion (*Zeits. ang. Chem.*, 1901, **14**, 1230) suggested should be given the formula $C_{20}H_{32}O_6$, thus representing it as a tetrahydroxy-abietic acid. A crystalline acid of this composition was described by Levy (*Ber.*, 1909, **42**, 4305). Subsequent investigators have made many, but in all cases fruitless, attempts to prepare this acid (cf. Aschan, *Ber.*, 1922, **55**, 2949; Wienhaus, *Zeits. ang. Chem.*, 1921, **34**, 254).

In our previous communication (*loc. cit.*, 213) we described the preparation of a monohydroxy-abietic acid, $C_{20}H_{32}O_3$, m. p. 230°, and we have now examined some of the products formed from it on oxidation with potassium permanganate. Under the conditions used by us the main product of the oxidation was found to be a beautifully crystalline *trihydroxy-abietic acid*, $C_{20}H_{34}O_5$, m. p. 210–212°. This acid was characterised by the preparation of the methyl ester, m.p. 172°, but attempts to prepare acetyl or benzoyl derivatives were unsuccessful.

From the mother liquor of the trihydroxy-acid a considerable quantity of liquid acids were isolated and it was proposed to attempt the separation of these acids by the fractional distillation of their methyl esters. On treatment of this mixture of acids with methyl alcohol and sulphuric acid (see p. 115) a quantity of a crystalline acid separated on cooling the solution. This acid was found to be a *dihydroxy-abietic acid*, $C_{20}H_{32}O_4$, m. p. 278°, yielding a *methyl* ester, m. p. 144° and an *acetyl* derivative, m. p. 186°. This acid is evidently isomeric with the acid obtained by Ruzicka and his collaborators. As this acid is very sparingly soluble in both ether and alcohol it cannot have been present in the original mixture of liquid acids and it appeared to be doubtful if it was a primary product of the oxidation of abietic acid. It seemed to us probable that it had been formed by the dehydration of some of the above-mentioned trihydroxy-acid which had remained dissolved in the mixture of liquid acids. This proved to be the correct explanation of its formation since if the pure trihydroxy-acid was treated with a mixture of methyl alcohol and sulphuric acid it was converted quantitatively into the dihydroxy-acid.

It now remains to consider the constitution of the three hydroxy-acids referred to in this communication. It will be recalled (*loc. cit.*, 213) that the monohydroxy-acid was obtained by treatment of the dihydrochloride of abietic acid with sodium carbonate solution. Of the possible formulæ for the dihydrochloride we consider Formula IV to be the most probable; it would lead to either Formula V or VI for the monohydrochloride, whilst the monohydroxy-acid would have either Formula VII or VIII.

Although at first sight Formula VIII would appear to be the most probable representation of the monohydroxy-acid, which is stable and shows no tendency to form a lactone, yet too much importance cannot be attached to this owing to the possibility of *cistrans*-isomerism. As the trihydroxy-acid is formed from the monohydroxy-acid it must have either Formula IX or X.

Since the trihydroxy-acid loses water readily to yield a dihydroxy-acid, we are inclined to consider Formula IX to be the correct formula containing as it does a secondary alcohol grouping which leads to Formula VII for the monohydroxy-acid and Formula XI for the dihydroxy-acid.

We suggest that the resistance of dihydroxyabietic acid to esterification by methyl alcohol and sulphuric acid under the very energetic conditions employed by us (see p. 115) supports our suggestion that the carboxyl group in abietic acid must be attached to a tertiary carbon atom. It is to be hoped that further work on these crystalline oxidation products of abietic acid, which are obtainable with comparative ease, may throw light on the difficult problem of the constitution of abietic acid.

The practice of referring to these derivatives as hydroxy- or polyhydroxy-abietic acids has grown up during the work of several investigators, and it is not proposed now to disturb it; but these compounds are actually derivatives of dihydro- or tetrahydro-abietic acid.

EXPERIMENTAL.

OXIDATION OF HYDROXY-ABIETIC ACID WITH POTASSIUM PERMANGANATE.

Finely divided hydroxy-abietic acid (100 grams) was suspended in water (500 cc.) and a solution of potassium hydroxide (17.5 grams in water 50 cc.) was gradually added, the mixture being mechanically stirred until a clear solution was obtained. To this solution, maintained at 0°, a solution of potassium permanganate (5 per cent.) was gradually added until a permanent pink colour was obtained (2,000 cc. in about six hours). After removing manganese dioxide sludge, the alkaline solution was saturated with carbon dioxide and concentrated to small bulk by evaporation on the water bath, a stream of carbon dioxide being passed through the liquid. The concentrated solution was cooled in ice and acidified with dilute sulphuric acid, when a white amorphous precipitate separated. This was collected and the filtrate reserved for later investigation. The residue, which was extremely hygroscopic becoming sticky on exposure to the air, was dissolved in the minimum quantity of ether, the ethereal extract carefully dried over magnesium sulphate and the filtered solution allowed to remain for a week in the ice-chest when a copious crystalline precipitate consisting of stout prismatic needles had separated. The acid was collected and the filtrate was kept for later examination.

The crude acid, which melted at 210–212°, was purified by crystallisation from dilute methyl alcohol, being obtained in magnificent iridescent needles decomposing at 215°. (Found: C, 67·6 and 67·4; H, 9·4 and 9·5. $C_{20}H_{34}O_5$ requires C, 67·8; H, 9·6 per cent.).

Trihydroxy-abietic Acid was found to be readily soluble in methyl alcohol, alcohol, acetic acid and ethyl acetate, more sparingly so in ether, acetone, chloroform, benzene and hexane. The *sodium* salt, which was very sparingly soluble in cold water, crystallised in rectangular plates; the *calcium* salt crystallised in rhombic plates which were somewhat soluble in water, whilst the *barium* salt crystallised in leaflets. The acid reacted vigorously with acetic anhydride and acetyl chloride, but the acetyl derivative which was probably formed could not be obtained crystalline. An alcoholic solution of the acid was optically inactive.

The *methyl* ester prepared by the action of methyl iodide on the silver salt of the acid crystallised from dilute methyl alcohol in prismatic needles m. p. 172° (Found: C, 68·2; H, 9·6. $C_{21}H_{36}O_5$ requires C, 68·5; H, 9·8 per cent.).

The original aqueous filtrate from which the crude mixture of acids had been separated was distilled in steam, when the presence of acetic acid in the distillate was established by the usual tests and by the analysis of the silver salt. (Found: Ag, 64·4. $C_2H_3O_2Ag$ requires Ag 64·4 per cent.).

Dihydroxy-abietic Acid.—The ethereal solution from which the trihydroxy-abietic acid had been separated yielded on removal of the solvent a viscid oil from which it was not found possible to separate any crystalline product either by treatment with solvents or by the preparation of salts. In the hope of separating the constituents by preparation of the methyl esters, the crude acid (100 grams) was dissolved in a mixture of methyl alcohol (400 cc.) and sulphuric acid (40 grams), while the vapour from methyl alcohol (2 litres) was passed through the boiling solution, the whole operation taking about ten hours. On allowing the reaction mixture to cool a crystalline precipitate separated. This was collected and was found to be an acid since it was readily soluble in sodium carbonate solution. This acid, dihydroxy-abietic, was purified by repeated crystallisation from acetic acid, separating in prismatic needles, m. p. 278°. (Found: C, 71·8 and 71·4; H, 9·2 and 9·3. $C_{20}H_{32}O_4$ requires C, 71·4; H, 9·5 per cent.).

Dihydroxy-abietic Acid was very sparingly soluble in ether, methyl alcohol, acetone and ethyl acetate, more readily so in acetic acid. It was readily obtained in a quantitative yield when trihydroxy-abietic acid was heated for some hours with a mixture of methyl alcohol and sulphuric acid.

The *ammonium* salt was somewhat sparingly soluble in cold water and crystallised in needles; the *calcium*, *barium* and *lead* salts were amorphous, sparingly soluble white powders. The *silver* salt prepared from a faintly alkaline solution of the ammonium salt was obtained as a caseous white precipitate. (Found: Ag, 24·8. $C_{20}H_{31}O_4Ag$ requires Ag 24·4 per cent.).

The *methyl* ester, prepared from the silver salt and methyl iodide, crystallised from methyl alcohol in needles, m. p. 144°. (Found: C, 72·4; H, 9·6. $C_{21}H_{34}O_4$ requires C, 72·0; H, 9·7 per cent.).

The *acetyl* derivative was obtained when the dihydroxy-acid was digested for some hours with acetic anhydride and anhydrous sodium acetate. It crystallised from dilute methyl alcohol in prisms, m. p. 186°.

The alcoholic solution from which the dihydroxy-acid had been separated contained a mixture of methyl esters which have not been investigated.

We are much indebted to Mr. P. H. Guest of the Turpentine Factory, Jallo, for presenting the rosin used in these experiments.

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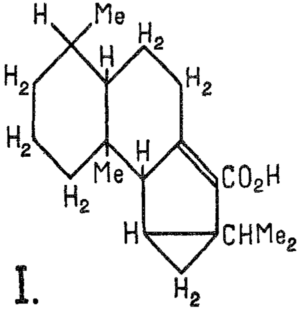
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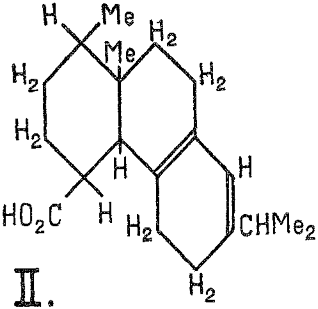
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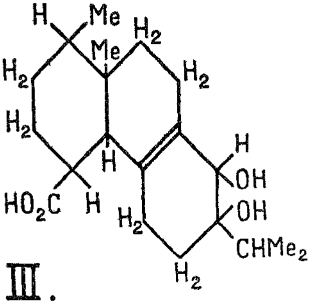
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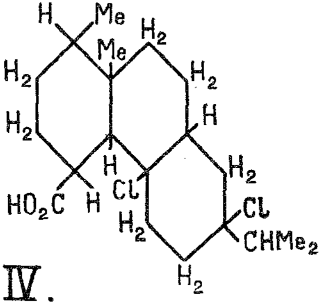
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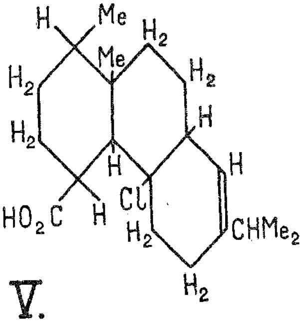

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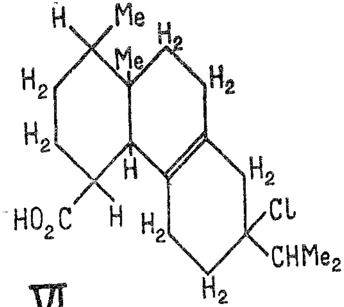

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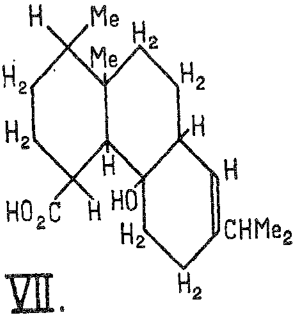

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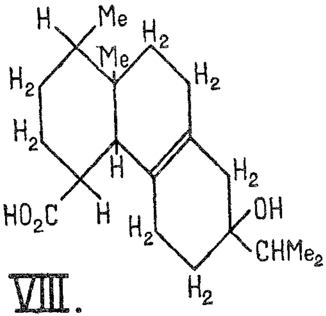

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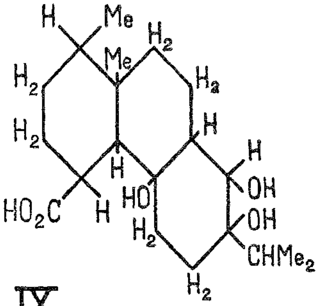
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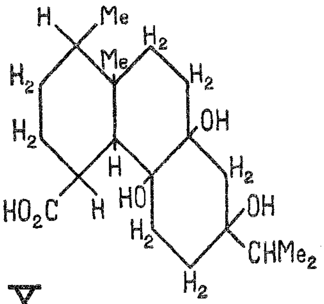
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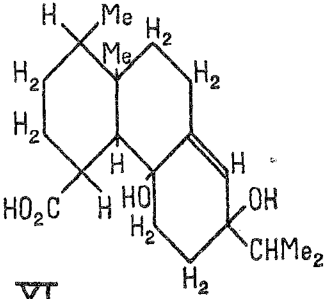
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