

THE CONSTITUTION OF MATAIRESINOL.

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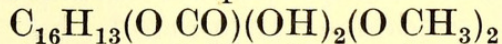
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In the heart shakes or cracks of the wood of *Podocarpus spicatus* (Maori name—matai) a resinous but often crystalline substance occurs which has been isolated and characterised by Easterfield and Bee (*Trans. N.Z. Inst.*, 1910, 43, 54; *J.C.S.*, 1910, 97, 1028). The pure substance, to which the name of matairesinol was given, has a m.p. of 119° and was shown to have the molecular formula $C_{19}H_{20}O_6$.

Of the six oxygen atoms two were shown to be present as hydroxyl groups by the formation of a monoacetyl derivative, m.p. 110°, and a dibenzoyl derivative, m.p. 133°. A Zeisel determination indicated two methoxyl groups. The remaining two oxygen atoms were present in a lactone ring which underwent fission on solution in dilute sodium hydroxide from which the free hydroxy acid, matairesinolic acid, $C_{19}H_{22}O_7$, was precipitated by acidification with dilute acetic acid. A disulphonic acid derivative was also prepared. From their investigations matairesinol possessed the partial formula



and was assumed to be of the phenanthrene type.

With Professor Easterfield's kind permission we have continued the investigation of this resin, and we are now able to present a full formula.

Further analyses of matairesinol supported by analyses of derivatives have shown it to possess the formula $C_{20}H_{22}O_6$.† It is thus isomeric with pinoresinol which

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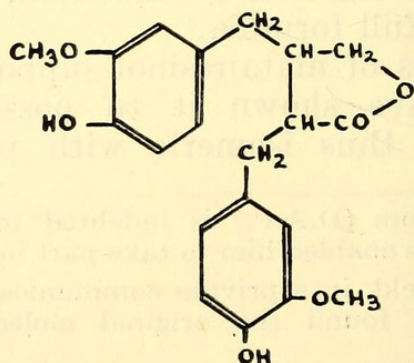
† Professor Easterfield, in a private communication, intimated that Mr. McClelland had found the original molecular formula to be incorrect.

also has now been shown to have the formula $C_{20}H_{22}O_6$, and not $C_{19}H_{20}O_6$ as previously supposed (Erdtman: *Svensk. Kem. Tidskr.*, 1934, 46, 229). The analysis of the acetyl compound agrees for a diacetyl derivative on the new formulation instead of a monoacetyl derivative.

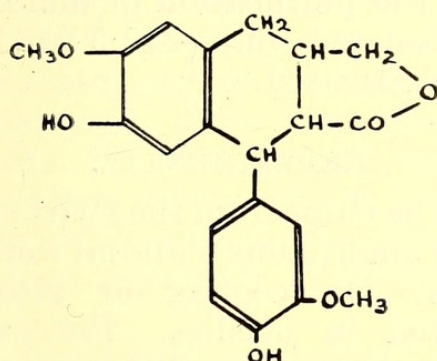
The benzoyl compound also gives an analysis still in agreement with a dibenzoyl derivative. Strange to say, it is precipitated from the alkaline solution with the lactone group still intact. Methylation with dimethyl sulphate and alkali yields a dimethyl ether, m.p. $126.5-127^\circ$, which still retains a lactone group since dimethyl matairesinolic acid may be obtained similarly to the free resinolic acid. The two free hydroxyl groups must therefore be phenolic and the lactonic hydroxyl aliphatic.

Matairesinol contains no aliphatic double bonds and is recovered unchanged from attempts to hydrogenate it with Pd-norite and hydrogen.

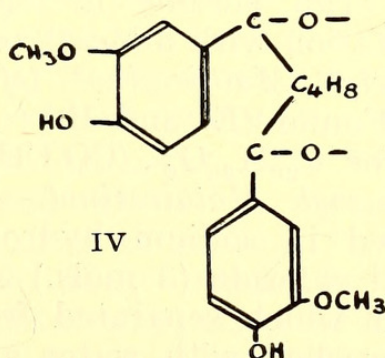
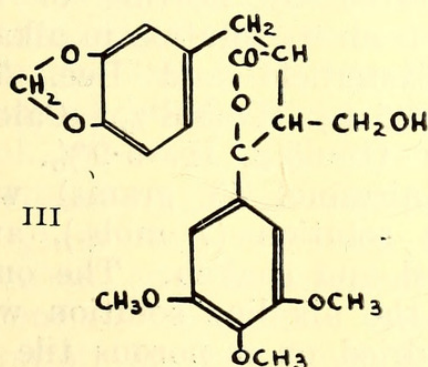
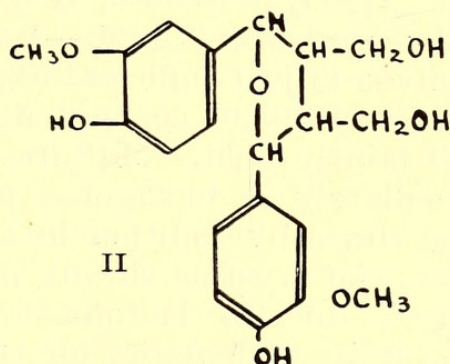
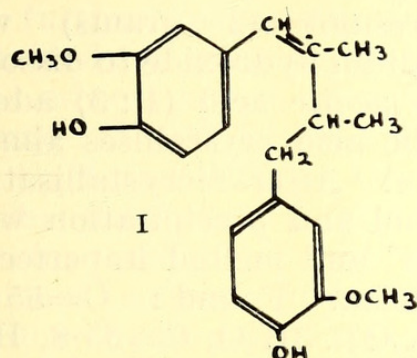
Dimethylmatairesinol on oxidation with alkaline permanganate yields veratric acid in over 50% yield. Since a compound containing one veratryl residue could only give a theoretical yield of 47% of veratric acid, it is apparent that two veratryl residues are present in the methylated resin. No trace of the stable veratroyl formic acid could be obtained from the oxidation mixture or in other oxidation experiments using smaller quantities of oxidising agent. It is clear therefore that the groups adjoining the veratryl residues are methylene groups and not attached to the lactonic oxygen. Compounds like olivil give good yields of veratroyl formic acid on similar oxidation (Vanzetti: *Monats.*, 1929, 52, 163). The substance shows all the properties of a γ lactone, so that on the above evidence supported by phytochemical considerations matairesinol may be formulated as :



A similar formulation has been given by Emde and Schartner (*Naturwiss.*, 1934, 22, 743) to sulphite liquor lactone which is identical with tsugaresinol (Kawamura : *Bull. Imp. Forestry Exp. Stat. Tokyo*, 1932, No. 31, 73), but this substance has since been shown to possess the molecular formula $C_{20}H_{20}O_6$ and the following structural formula (Erdtman : *Ann.*, 1934, 513, 229) :



The carbon skeleton of matairesinol is also the same as that of guairetic acid (I) (Schroeter, Lichenstadt and Irineu : *Ber.*, 1918, 51, 1587 ; cf. Haworth, Mavin and Sheldrick : *J.C.S.*, 1934, 1423), olivil (II) (Vanzetti and Dreyfuss : *Gazzetta*, 1934, 64, 381), podophyllotoxin (III)



(cf. Borsche and Niemann: *Ann.*, 1933, 499, 59; Spath, Wessely and Nadler: *Ber.*, 1932, 65, 1773; Robertson and Waters: *J.C.S.*, 1933, 83), and probably pinoresinol (IV) (Erdtman, *loc. cit.*).

Some of the above substances are active physiologically, due probably in the main to the lactonic grouping. The physiological activity of matairesinol is being investigated while further degradative work is in progress. From the mother liquors of the purification of matairesinol a second resinol has been isolated, m.p. 212.5-213°, but it has not yet been fully investigated.

EXPERIMENTAL.

Matairesinol—The chips from the heart shakes containing the crystalline and amorphous material were twice extracted with hot alcohol. On cooling or after concentration the resin separated in needles. Recrystallisation from alcohol gave a product, m.p. 78°, containing alcohol of crystallisation which is lost on warming *in vacuo*. From 60% acetic acid it crystallised in large anhydrous rhombic crystals, m.p. 119°. For analysis a sample was recrystallised three times from alcohol and three times from 60% acetic acid. Found: C=66.7, 66.7; H=6.0, 6.0%. Calculated for $C_{20}H_{22}O_6$: C=67.0, H=6.1%; calculated for $C_{19}H_{20}O_6$: C=66.3, H=5.8%.

Matairesinolic Acid.—Matairesinol (2 grams) was dissolved in just sufficient 5% sodium hydroxide to dissolve it, diluted to 50 cc. and dilute acetic acid (1:3) added until faintly acid. Matairesinolic acid crystallises almost immediately in hexagonal plates. After recrystallisation three times by solution in alcohol and precipitation with water, the crystals shrank at 78° and melted imperfectly at 81°, due to lactone formation. Found: C=55.9; H=6.9%. Calculated for $C_{20}H_{24}O_7 \cdot 3H_2O$, C=55.8, H=6.9%; calculated for $C_{19}H_{22}O_7 \cdot 3H_2O$, C=54.8, H=6.7%. The lactone is regenerated by heating or by precipitation with mineral acids from its solution in alkali.

Diacetyl Matairesinol (cf. Easterfield and Bee, *loc. cit.*).—Found (E. and B.): C=65.4; H=5.8%. Calculated for $C_{20}H_{20}O_6 \cdot (COCH_3)_2$: C=65.2, H=5.9%.

Dibenzoyl Matairesinol.—Matairesinol (5 grams) was dissolved in sodium hydroxide solution (7 mols.), and benzoyl chloride (5 mols.) added and shaken. The only product which separated from the alkaline solution was twice washed with water and dried on a porous tile *in*

vacuo. After two crystallisations from alcohol the needles shrank at 133° and melted at 134.5° , unchanged on further recrystallisation (Easterfield and Bee, *loc. cit.*, m.p. 133°). Found in dried material : C=71.4 ; H=5.3%. Calculated for $C_{20}H_{20}O_6(COC_6H_5)_2$: C=72.1 ; H=5.3%. (E. and B. : C=71.6, 71.8 ; H=5.1, 5.0%.)

It is remarkable that the benzoyl derivative is precipitated from the alkaline solution, a fact which would appear to be due to the opening of the lactone ring and the formation of a benzoic acid anhydride by the action of benzoyl chloride on the sodium salt of the resinolic acid. Such is not the case, however, since the dibenzoyl derivative, although insoluble in cold dilute aqueous potassium hydroxide, is soluble in cold alcoholic or aqueous alcoholic potassium hydroxide (compare the similar properties of dimethylmatairesinol especially in attempted ester formation).

Dimethylmatairesinol.—Matairesinol (1 gram) was dissolved in sodium hydroxide solution (25 cc. of 10%, 21 mols.), shaken in the cold with dimethyl sulphate (5.3 grams, 15 mols.) and finally heated for five minutes at 100° . The cooled solution was acidified with hydrochloric acid and the sticky precipitate crystallised from alcohol in double wedged crystals. After three recrystallisations from alcohol it had m.p. $126.5-127^{\circ}$, not raised by further recrystallisation. A less pure product was obtained by using smaller quantities of dimethylsulphate. The substance lost no weight on drying *in vacuo* at 100° . Found : C=67.8 ; H=6.8 ; $OCH_3=32.8\%$. Calculated for $C_{18}H_{14}O_2(OCH_3)_4$: C=68.4 ; H=6.8 ; $OCH_3=32.1\%$.

The substance is still a lactone, being insoluble in sodium carbonate, but slowly soluble on boiling with aqueous sodium hydroxide, easily soluble in alcoholic sodium hydroxide. Its alcoholic solution is neutral to litmus, and no coloration is given with ferric chloride or concentrated sulphuric acid. The molecular weight was estimated by solution in excess standard sodium hydroxide solution and back titration with standard hydrochloric acid, phenolphthalein being used as indicator. Found : mol. wt.=383. Calculated for $C_{22}H_{26}O_6$: mol. wt.=386.

Dimethyl Matairesinolic Acid.—Dimethyl matairesinol (1 gram) was dissolved in excess of sodium hydroxide solution and neutralised with dilute acetic acid. The colourless crystalline precipitate was recrystallised by solution in cold alcohol and precipitation with water,

yielding needles, m.p. 80-84°, indefinite due to lactone formation. The m.p. rises on standing. When the alkaline solution was made acid with hydrochloric acid the lactone was regenerated. The free acid dissolves easily in sodium hydroxide and slowly in sodium carbonate solution, while its alcoholic solution is acid to litmus.

Attempts to form the methyl ester of dimethyl matairesinolic acid by solution in a minimum amount of sodium hydroxide or sodium carbonate solution and treatment with excess of dimethyl sulphate gave only the lactone, even in the presence of a large excess of sodium carbonate.

Oxidation of Dimethylmatairesinol with Permanganate.—Dimethylmatairesinol (1 gram) was dissolved in sodium hydroxide solution (20 cc. of 1%), heated to 100°, and potassium permanganate solution (120 cc. of 3%, i.e., slight excess over 12 atoms of oxygen) run in slowly. The cooled solution was saturated with sulphur dioxide, when a clear yellow solution was obtained which gradually deposited clusters of needles homogeneous under the microscope (0.51 g.), m.p. 173-178°. After several recrystallisations from benzene it had m.p. 178.5-179.5° (veratric acid m.p. 179.5°). Found: no loss of weight on drying at 100° *in vacuo*. Found: C=59.2; H=5.5%. Calculated for $C_6H_3(OCH_3)_2COOH$: C=59.3; H=5.6%.

Attempt to Hydrogenate Matairesinol.—Matairesinol (1 gram) dissolved in glacial acetic acid (10 cc.) was shaken in an atmosphere of purified hydrogen in the presence of Pd-norite. Only a small amount of hydrogen was absorbed, probably by the norite. The catalyst was filtered off and the filtrate concentrated and diluted with water, when the unchanged resin crystallised out, giving no depression of m.p. of the pure resin.

Tetrabromo Matairesinol.—Matairesinol (2 grams) was dissolved in chloroform (20 cc.) in a stoppered bottle and bromine (1.77 grams, 8 atoms) in chloroform (35 cc.) gradually added. The reaction was complete after standing for thirty-six hours. The chloroform solution was washed with dilute sodium carbonate solution, again with water, and dried over calcium chloride. After removal of the solvent the gummy mass was recrystallised from alcohol and then from chloroform to give colourless needles, m.p. 169.0-169.5° (yield nearly theoretical). The bromo-derivative was recovered unchanged after treatment with alcoholic potash. The recovered product after recrystal-

lisation from alcohol had m.p. 171° , but a m.p. $169-169.5^{\circ}$ after a further crystallisation from chloroform, unchanged on mixture with the untreated material. Found on material dried at 70° *in vacuo*: C=35.7; H=2.8%; Br (Robertson's method)=48.1, 46.7%. Calculated for $C_{20}H_{18}O_6Br_4$: C=35.6; H=2.7; Br=47.5%.



Peak, D A, Briggs, Lindsay H, and Woolloxall, J L D. 1935. "The constitution of matairesinol." *Journal and proceedings of the Royal Society of New South Wales* 69(1), 61–67. <https://doi.org/10.5962/p.360124>.

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