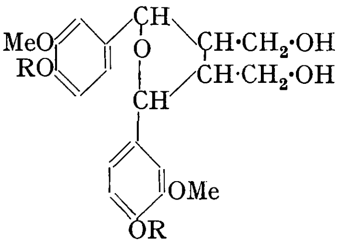
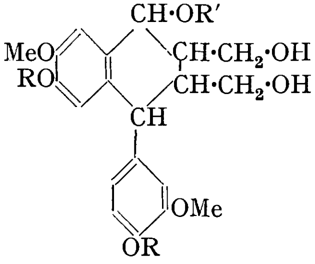
53. *The Resinol of* Olea Cunninghamii (*Maire*).

By Lindsay H. Briggs and A. G. Frieberg.

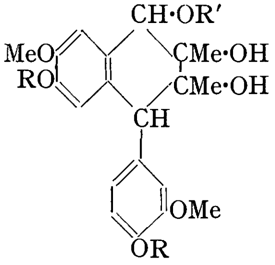
The crystalline resin occasionally found in the heart shakes of *Olea Cunninghamii* (Maori name Maire) has been identified as *iso*olivil: this is the first record of the occurrence of the substance in nature. Hitherto it has only been obtained by the action of warm dilute acetic or formic acid on olivil, from the oleo-resin of *Olea Europoea* (Körner and Vanzetti, *Atti R. Accad. Lincei*, 1903, **12**, 122). From the investigations of Vanzetti and co-workers (Körner and Vanzetti, *Mem. R. Accad. Lincei*, 1911, **8**, 749; Vanzetti, *Monatsh.*, 1929, **52**, 163; *Gazzetta*, 1929, **59**, 373; *Atti R. Accad. Lincei*, 1934, **19**, 421; Vanzetti and Dreyfuss, *Gazzetta*, 1934, **64**, 381) the formulæ (I; $R = H$) and (II; $R, R' = H$) have been proposed for olivil and *iso*olivil respectively.



(I.)



(II.)



(III.)

At the beginning of the present investigation there was no definite proof of the constitution of these resinols: the carbon skeleton was probable from chemical and phytochemical considerations, but the nature and position of the three alcoholic groups of *iso*olivil were unknown, because no derivatives of these groups had been recorded. Since the completion of this work, Dreyfuss (*Gazzetta*, 1936, **66**, 96) has oxidised *iso*olivil dimethyl ether to the lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid, identical with that synthesised by Haworth and Sheldrick (J., 1935, 636), thus confirming the carbon skeleton of *iso*olivil. The position of the alcoholic groups in (II) is supported by the present investigation.

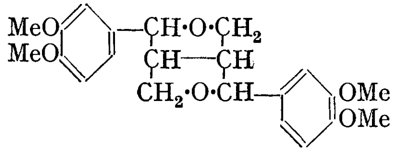
The *iso*olivil has been identified by its properties, the preparation of dimethyl and diethyl ethers, and by the oxidation of the dimethyl ether to 4 : 5-dimethoxy-2-(3′ : 4′-dimethoxyphenyl)phthalide. The diethyl ether was obtained in almost theoretical yield by the action of ethyl sulphate and alkali, but much poorer yields of the dimethyl ether were obtained by similar methods. From methylations with excess of methyl sulphate a *trimethyl* ether was obtained as a by-product, which, from the known facility of methylation of benzyl alcohol, is probably (II; $R, R' = CH_3$). It still contains two active hydrogen atoms (Zerewitinoff estimation), but was recovered mostly unchanged after attempts to benzoylate it and to form the acid phthalate under conditions usually suitable for primary alcohols. From this failure to obtain derivatives, another formula (III; $R, R' = H$) was considered for *iso*-

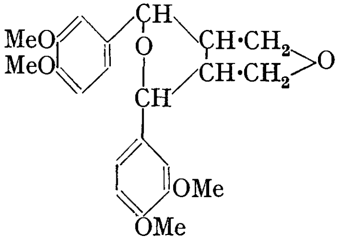
olivil, also based on the symmetrical formula of olivil but containing two tertiary instead of two primary alcoholic groups. A substance of this formula should be easily dehydrated, but, although such products were obtained with various reagents, they were amorphous in each case. The trimethyl ether, however, distils unchanged at 0·04 mm., and further evidence against (III) was provided by a *C*-alkyl determination kindly carried out by Dr. H. Roth of Heidelberg, who obtained a negative result.

An attempt was made to obtain proof of the carbon skeleton by a method used with success in the podophyllotoxin series, *viz.*, demethylation, followed by zinc dust distillation (Borsche and Niemann, *Annalen*, 1932, **484**, 126; 1933, **499**, 59), but the only product, isolated in small yield, was pyrocatechol.

Erdtmann (*Svensk Kem. Tidskr.*, 1934, **46**, 229; *Annalen*, 1935, **516**, 162), in discussing the structure of pinoresinol dimethyl ether (cf. Bamberger, *Monatsh.*, 1894, **15**, 505; 1897, **18**, 481; Bamberger and Vischner, *ibid.*, 1900, **21**, 949; Bamberger and von Kleimburg, *ibid.*, 1917, **38**, 457), enantiomorphous with eudesmin (Robinson and Smith, *J. Roy. Soc. N. S. Wales*, 1914, **48**, 449), prefers formula (IV) to the alternative one (V), suggested among others by Robinson and Smith (*loc. cit.*), which only differs from that of olivil dimethyl ether by the closing of an additional hydrofuran ring, on the ground that, unlike olivil, these resinols do not undergo ring closure to a phenylnaphthalene. Formula (V) is, however, equally consistent with the reactions of these resinols and is better supported by phytochemical considerations; failure to isomerise may be due to the stability of the two tetrahydrofuran nuclei, and additional support is given by the fact that the dimethyl and diethyl ethers of olivil are not isomerised (Körner and Vanzetti, *loc. cit.*).

(IV.)





(V.)

EXPERIMENTAL.

Olea Cunninghamii, one of four species of *Oleaceae* endemic to New Zealand, is a lofty evergreen tree restricted to the North Island.

The resin scrapings and wood chips were extracted with boiling alcohol and concentrated. On the addition of ether, the resinol crystallised in elongated rhombs; it was further purified from alcohol–ether and acetone. The pure substance is neutral in reaction, insoluble in sodium bicarbonate, but soluble in sodium hydroxide solution, freely soluble in methyl and ethyl alcohols, glacial acetic acid and pyridine and insoluble in water, ether, light petroleum, benzene and chloroform. It gives a bright green coloration with alcoholic ferric chloride, a violet coloration with concentrated sulphuric acid, and reduces Tollens' reagent. The crystals from alcohol–ether melt at *ca.* 98°, but after standing in the air for some days melt at 163—164°, $[\alpha]_D^{24°}$ + 61·8° (absolute alcohol); Vanzetti records m. p. 167°, $[\alpha]_D^{25°}$ + 61·1° (alcohol). No further loss occurs on drying in a vacuum. When recrystallised from acetone, they melt indefinitely at *ca.* 100°, but after exposure to air for a similar period contract at 144° and melt at 163—164°. In this case the air-dried crystals lose further weight on drying in a vacuum at room temperature [Found in material freshly recrystallised from alcohol–ether: *M* (ebullioscopic in acetone), 435; loss on drying in air for 1 month, 9·6%. Found in air-dried sample: C, 62·2; H, 6·3. Calc. for $C_{20}H_{24}O_7$, $C_2H_5{\cdot}OH$,$\frac{1}{2}H_2O$: *M*, 431; loss of $C_2H_5{\cdot}OH$, 10·7%. Calc. for $C_{20}H_{24}O_7$,$\frac{1}{2}H_2O$: C, 62·3; H, 6·5%. Found in sample recrystallised from acetone: loss on drying in air, 12·6%; further loss on drying in a vacuum at room temperature, 2·9%. Found in air-dried sample: C, 60·6; H, 6·5. Found in sample dried at 110°/high vacuum: C, 63·5; H, 6·5; *M* (Rast), 379. Calc. for $C_{20}H_{24}O_7$,C_3H_6O,H_2O: for loss of C_3H_6O, 12·8%. Calc. for $C_{20}H_{24}O_7$,H_2O: C, 60·9; H, 6·6; loss of H_2O, 4·7%. Calc. for $C_{20}H_{24}O_7$: C, 63·8; H, 6·4%; *M*, 376).

Methylation of iso*Olivil.*—The dimethyl ether, obtained in the usual way with methyl sulphate and alkali, crystallised from methyl alcohol in needles, m. p. 181—181·5°, $[\alpha]_D^{22°}$ + 46·6° (alcohol) (lit., m. p. 184·5°, $[\alpha]_D^{22·5°}$ + 33·58°). The yield with molecular proportions was 40%, and was increased to 60% with double quantities (Found : C, 64·8, 65·1; H, 6·9, 7·1. Calc. for $C_{22}H_{28}O_7$: C, 65·3; H, 6·9%). With 7 mols. of methyl sulphate or more, the dimethyl ether was obtained and a gummy residual product which after successive crystallisations from water and chloroform–light petroleum formed needles, m. p. 153—154°, and distilled at 0·04 mm. (temperature of bath 280°). The distilled product was a colourless glass, m. p. 55—65°, which after crystallisation from water, methyl alcohol and chloroform–light petroleum had the original m. p. 153—154°, $[\alpha]_D^{17°}$ + 26·23° (chloroform) [Found in distilled product: C, 66·0; H, 7·3; OMe, 37·5; OH (Zerewitinoff estimation in dioxan), 11·4. Found in crystalline product : C, 65·7; H, 7·3. $C_{23}H_{30}O_7$ requires C, 66·0; H, 7·2; OMe, 37·1; OH, 9·0%].

iso*Olivil trimethyl ether* (0·2 g.), dissolved in dry benzene (2 c.c.), was heated with phthalic anhydride (0·15 g.) at 100° for 1½ hours. After removal of the benzene by evaporation the product was triturated with ether. The insoluble residue (0·15 g.) crystallised from methyl alcohol in needles, m. p. 153—153·5°, undepressed by the initial material.

Oxidation of iso*Olivil Dimethyl Ether.*—To a mechanically stirred suspension of the dimethyl ether (2 g.) in 25 c.c. of 10% sodium hydroxide solution at 100° was gradually added (1½ hours) a solution of potassium permanganate (5·5 g.) in water (200 c.c.). The amorphous product obtained after passage of sulphur dioxide and standing for 2 days was dissolved in sodium hydroxide solution and reprecipitated with sulphur dioxide. After repeated crystallisations from alcohol and finally from methyl alcohol it had m. p. 186—187°. 4 : 5-Dimethoxy-2-(3′ : 4′-dimethoxyphenyl)phthalide has m. p. 188° (Vanzetti and Dreyfuss, *loc. cit.*). Other products were obtained but were not investigated.

Degradation of iso*Olivil.*—*iso*Olivil (5 g.) in glacial acetic acid solution (50 c.c.) was demethylated with hydriodic acid (20 c.c.) and the acids were removed by distillation in a vacuum. The residue was taken up in ether, washed with sodium thiosulphate solution, mixed with zinc dust, and after removal of ether distilled at 0·04 mm. The only product was a crystalline sublimate (0·1 g.), m. p. 101°, giving the characteristic colour reaction of pyrocatechol, an authentic specimen of which did not depress the melting point.

Diethyl Ether.—This, obtained in theoretical yield by means of ethyl sulphate and alkali, formed needles from alcohol, m. p. 178—178·5°, $[\alpha]_D^{19°}$ + 46·05° (alcohol) (Found : C, 66·5; H, 7·5. Calc. for $C_{24}H_{32}O_7$: C, 66·7; H, 7·4%). Vanzetti gives m. p. 179—179·5° and $[\alpha]_D^{22·5°}$ + 38·22° (alcohol).

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