EXTRACTIVES FROM THE BARK OF *OLEARIA PANICULATA**

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Olearia paniculata J. R. & G. Forst. (Druce) is a small evergreen tree endemic to both the North and South Islands of New Zealand. It makes an excellent hedge and is much used for this purpose. The essential oil from the leaves of this tree has already been examined,[1] and the sesquiterpene fraction was shown to contain (±)-α-curcumene, (±)-γ-curcumene, and aromadendrene.

Extraction of the finely powdered outer bark with hexane yielded a fraction (A) which was relatively insoluble in hexane, and a fraction (B) which was readily soluble in this solvent. Fraction (A) was separated by chromatography on silica gel into friedelin, epifriedelinol, and an acid fraction which was triterpenoid in nature (positive Liebermann–Burchard test). The acid fraction was shown to be a mixture of ursolic and oleanolic acids by chromatography on silica gel, followed by methylation of appropriate fractions and purification by chromatography of the methyl esters on alumina. Fraction (B) was shown to be dammaradienyl acetate.

Ether extraction of the hexane-exhausted bark yielded ursolic acid, and traces of the other triterpenoids found in the hexane extract. Finally, extraction of the residual bark with methanol gave a product which was completely soluble in water, contained no saponins (frothing test) and gave only two distinct spots, corresponding with glucose and fructose on paper chromatography in two different solvents.

This appears to be the first reported occurrence of dammaradienyl acetate in nature. The variety of the triterpenoids is also noteworthy. Representatives of the pentacyclic, oleanane, ursane, and friedelin groups and of the tetracyclic dammarane group are present in the bark.

Experimental

Melting points were taken on a Kofler block and are corrected. Infrared spectra were determined in Nujol on a Perkin–Elmer model 421 spectrometer. Alumina (standardized for chromatographic adsorption analysis according to Brockmann) supplied by Merck was used for chromatography. The silicic acid was supplied by Mallinckrodt and the silica gel by Lights.

Extraction.—The finely powdered (to pass a 30–60 mesh sieve) bark (2·08 kg) was extracted continuously (Soxhlet) with hexane for 48 hr. Concentration of the extract to 2 l. afforded a cream solid (A) (20 g), and complete removal of the solvent gave a second solid (B) (34 g). Further extraction of the bark with ether, and evaporation of the solvent, gave a light cream solid (C) (27 g). Extraction of the residual bark with methanol, gave after removal of the solvent, a brown resinous product (D) (33 g).

Hexane Extractives.—(i) *Dammaradienyl acetate.* The solid (B) (3·7 g) dissolved in hexane was run on to a column of silica gel (120 g). Elution with hexane gave dammaradienyl acetate (2·0 g), followed, on elution with hexane containing increasing amounts of ether, by a mixture composed of dammaradienyl acetate, ursolic acid, and oleanolic acid (1·7 g). This mixture was

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[1] Corbett, R. E., Jamieson, G. A., and (the late) J. Murray, *J. Sci. Fd. Agric.*, 1963, **14**, 349.

identified by infrared spectroscopy and thin layer chromatography and was not further examined. Dammaradienyl acetate crystallized from ethanol had m.p. and mixed m.p. 153°, $[\alpha]_D^{20}$ +72·5° (*c*, 0·5 in $CHCl_3$) (Found: C, 82·4; H, 11·4%. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%). Hydrolysis with 0·5N ethanolic potassium hydroxide gave a neutral fraction, dammaradienol, m.p. and mixed m.p. 133°, $[\alpha]_D^{20}$ +62·25° (*c*, 0·43 in $CHCl_3$) (Found: C, 84·1; H, 11·7%. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%). The acid fraction of the hydrolysis had R_F 0·32 (acetic acid R_F 0·32) in 95% ethanol : ammonia (100 : 1) and gave *p*-bromophenacylacetate, m.p. and mixed m.p. 84°.

(ii) *Isolation of friedelin, epifriedelinol, ursolic acid, and oleanolic acid.* Extract (A) (16·5 g) in hexane was adsorbed onto a column of silica gel (450 g of 100–200 mesh) and eluted with aliquots (500 ml) of solvent. Benzene (2000 ml) eluted dammaradienyl acetate (1·37 g), fraction 1; benzene (5 l.) eluted fraction 2 (4·9 g); benzene–ether (3·5 l. of 20 : 1) and benzene–ether (3 l. of 1 : 1) eluted fraction 3 (10·1 g).

Fraction 1, recrystallized from ethanol, gave dammaradienyl acetate, m.p. and mixed m.p. 153°.

Fraction 2 (1·2 g) in warm hexane (40°) was adsorbed onto a column of alumina (120 g). Benzene (900 ml) eluted friedelin (0·18 g), and benzene–ether (350 ml of 9 : 1) eluted epifriedelinol (1·02 g). Friedelin crystallized from benzene had m.p. and mixed m.p. 262–263°, $[\alpha]_D^{20}$ −25° (*c*, 0·595 in $CHCl_3$) (Found: C, 84·0; H, 11·5%. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%). Epifriedelinol crystallized from benzene had m.p. and mixed m.p. 290°. With pyridine–acetic anhydride it gave epifriedelinyl acetate, m.p. 299° from chloroform–ethanol (Found: C, 81·5; H, 11·5%. Calc. for $C_{32}H_{54}O_2$: C, 81·6; H, 11·6%). Oxidation of epifriedelinol with chromic oxide–sulphuric acid mixture[2] gave friedelin, m.p. and mixed m.p. 262–263°.

Fraction 3 (4·2 g) in benzene was adsorbed onto a column of silicic acid (47 by 7 cm; 720 g) made up in benzene. The column was eluted with benzene–ether (95 : 5) in aliquots (2 l.). Oleanolic acid (3·4 g) with some ursolic acid was eluted with the first ten aliquots of solvent, while ursolic acid (1·2 g) containing a small amount of oleanolic acid was eluted with a further nine aliquots of solvent. Methylation of the oleanolic acid fraction (1·3 g) with diazomethane and purification of the product by chromatography on silica gel and elution with hexane–ether (6 : 4) gave methyl oleanolate (1·0 g) which after crystallization from ethanol had m.p. and mixed m.p. 194–196°, $[\alpha]_D^{20}$ +80° (*c*, 0·959 in $CHCl_3$) (Found: C, 79·1; H, 10·7%. Calc. for $C_{31}H_{50}O_3$: C, 79·1; H, 10·7%). It formed methyl oleanolate acetate, m.p. and mixed m.p. 223°. Methylation of the ursolic acid fraction (1·0 g) with diazomethane and purification of the product by chromatography on silica gel gave, after crystallization from ethanol, methyl ursolate (0·70 g), m.p. 161° (lit.[3] 171°) $[\alpha]_D^{20}$ +55·5° (*c*, 0·55 in $CHCl_3$). Methyl ursolate acetate prepared with acetic anhydride–pyridine had m.p. and mixed m.p. 244–246°.

Ether Extractives.—Solid (C) (12 g) in ether (3 l.) was fractionated with 2N sodium hydroxide solution (3 × 200 ml), and the insoluble sodium salts collected and washed with ether and with water. These sodium salts, dissolved in ethanol (400 ml) and acidified with concentrated hydrochloric acid, gave an amorphous precipitate (7 g). The infrared spectrum of this product showed that it was ursolic acid, with a small amount of oleanolic acid. Methylation of the acid (1 g) with diazomethane and chromatography of the methyl ester on alumina (Woelm grade II) gave methyl ursolate, m.p. and mixed m.p. 160–161°. Acidification of the aqueous alkaline layer gave a product (3 g), which from its infrared spectrum was largely ursolic acid, and this was confirmed by thin layer chromatography on silica gel (hexane–ether–methanol 50 : 44 : 6). Evaporation of the ether from the above fractionation gave a neutral product (1 g), which was shown by thin layer chromatography to be a very complex mixture, and was not investigated further.

Methanol Extractives.—A portion of the brown resinous compound (D) was dissolved in water and the solution, clarified with charcoal, was examined for sugars by descending paper chromatography with the solvent systems, butan-1-ol–acetic acid–water 4 : 1 : 5, and butan-1-ol–

[2] Bowers, A., Halsall, T. G., Jones, E. R. H., and Lemin, A. J., *J. Chem. Soc.*, 1953, 2548.
[3] White, D. E., *Rev. Pure Appl. Chem.*, 1956, **6**, 231.

ethanol–water 5 : 1 : 4. In each case two well-defined spots only could be discerned, corresponding to glucose and fructose. Tests on the solution for polyols and cyclitols were negative.

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