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SOME CONSTITUENTS OF *ULEX EUROPAEUS* L.

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Abstract—The non-saponifiable fraction of the wax of *Ulex europaeus* L. contains β-amyrin, lupeol and β-sitosterol. Soyasapogenol C is obtained from an alcoholic extract of the plant.

THE shoots, seeds and flowers of *Ulex europaeus* L. (furze, gorse whin) have been the subject of a number of investigations and alkalids,[1-5] amino acids,[6,7] glucosides[8,9] and flavonoids[5,10,11] have been isolated. The only report concerning the whole, mature plant is that of Schon[12] who obtained carotenoids, hentriacontane, sitosterol and a "sterol", $C_{30}H_{50}O$, m.p. 152–153°, from the non-saponifiable fraction of the wax. We have now re-examined this non-saponifiable material but we were unable to isolate Schon's "sterol". We have also examined the material extracted from the wax-free plant with alcohol.

Mature gorse, collected in the Glasgow area, was extracted with petroleum ether (b.p. 60–80°) and the dark green extract (2·5 per cent of the dried plant) subjected to alkaline hydrolysis. The non-saponifiable material was acetylated and the mixed acetates separated by chromatography on a column of alumina. The most easily eluted fraction was a waxy hydrocarbon, m.p. 62°, which is presumably Schon's "hentriacontane" although the sample does not depress the melting point of triacontane and its infrared spectrum is identical with that of the latter. However, the similarity in physical properties of close homologues in this series precludes a definite identification in the absence of X-ray powder photographs and the hydrocarbon may well be a mixture.

Continued elution of the column with hydrocarbon solvents gave a highly coloured carotenoid fraction, which was not further examined, and three crystalline substances identified as the acetates of β-amyrin, lupeol and β-sitosterol by comparison with authentic samples. The acetates were characterized by hydrolysis to the corresponding alcohols.

Elution with more polar solvents (ether, methanol) gave a mixture which was reacetylated and again chromatographed on alumina. The early fractions yielded the acetate of an alcohol, $C_{26}H_{54}O$, m.p. 80°, which is almost certainly ceryl alcohol although no authentic sample was available for comparison. Further fractions again yielded the acetates of β-amyrin, lupeol and β-sitosterol.

Since all of these compounds are of very wide occurrence in nature, this result is of little taxonomic interest.

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The glycosidic material, extracted from the de-waxed plant with alcohol, was hydrolyzed with mineral acid in two steps—first in aqueous solution at room temperature and then in alcoholic solution at reflux temperature. This procedure, coupled with alkali treatment to remove acidic impurities, gave a much cleaner product than that obtained by direct hydrolysis. The final product (0·4 per cent of the dry plant) was acetylated and chromatographed on alumina. Only one crystallizable fraction was obtained and this was identified as the diacetate of soyasapogenol C (olean-12,21-diene-3β,24-diol) by comparison with an authentic sample. Soyasapogenol C is of very limited occurrence, having been isolated previously from only two sources—the soya bean[13] and *Trifolium repens*.[14]

EXPERIMENTAL

Specific rotations were measured in chloroform solution. Petrol refers to petroleum ether (b.p. 60–80°).

Isolation of the non-saponifiable matter

Dry, crushed *Ulex europaeus* (4·5 kg) was extracted (12 hr) with boiling petrol. Removal of the solvent gave a dark green wax (110 g) which was refluxed (6 hr) with 5% KOH in methanol (600 ml) and water (50 ml). After working up through ether in the usual manner, the non-saponifiable fraction was obtained as a dark red wax (42 g) which was acetylated (1 hr on a steam bath) with acetic anhydride (100 ml) and pyridine (40 ml) to give a mixture of acetates (45·5 g).

Isolation of the hydrocarbon

The acetate mixture was dissolved in petrol (300 ml) and chromatographed on alumina (2 kg). Elution with petrol and petrol-benzene mixtures gave five fractions: (*a*) colourless wax (3·9 g), (*b*) crystalline solid (4·5 g), (*c*) crystalline solid (1·7 g), (*d*) crystalline solid (0·7 g), and (*e*) red gum (8 g) which was discarded. Elution with more polar solvents gave a fraction (*f*) (20 g).

Fraction (*a*) was crystallized from ethyl acetate to give waxy plates of a hydrocarbon, m.p. 62°, which did not depress the melting point of an authentic sample of triacontane and whose infrared spectrum (thin film) was identical with that of the latter. (Found: C, 84·95; H, 14·65%. M[Rast] 440. Calc. for $C_{30}H_{62}$: C, 85·2; H, 14·8%. M 422·8. Calc. for $C_{31}H_{64}$: C, 85·2; H, 14·8%. M 436·8.)

Isolation of β-amyrin, lupeol and β-sitosterol

Fraction (*b*) crystallized from chloroform–methanol in colourless rods (2·5 g), m.p. 238–240°; $[\alpha]_D$ 80°, identical (m.p. and infrared spectrum) with an authentic sample of β-amyrin acetate. (Found: C, 81·8; H, 10·9. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2 per cent). Alkaline hydrolysis of the acetate gave β-amyrin, m.p. 195–196°; $[\alpha]_D$ 85°. (Found: C, 84·5; H, 11·9. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%.)

Fractional crystallization (triangular) of fraction (*c*) from chloroform-methanol yielded more β-amyrin acetate (0·5 g) and an acetate (0·5 g), m.p. 215–217°; $[\alpha]_D$ 40°, identical (m.p. and infrared spectrum) with an authentic sample of lupenyl acetate. (Found: C,

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81·9; H, 10·9. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%.) Alkaline hydrolysis of the acetate gave lupeol, m.p. 213–214°; $[\alpha]_D$ 25°. (Found: C, 84·25; H, 11·6. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%.)

Fraction (*d*) crystallized from chloroform–methanol in plates (0·5 g), m.p. 127–128°; $[\alpha]_D$ −34°, identical (m.p. and infrared spectrum) with an authentic sample of β-sitosteryl acetate. (Found: C, 81·5; H, 11·4. Calc. for $C_{31}H_{52}O_2$: C, 81·5; H, 11·5%.) Alkaline hydrolysis of the acetate gave β-sitosterol, m.p. 134–135°; $[\alpha]_D$ −36°. (Found: C, 83·75; H, 12·0. Calc. for $C_{29}H_{50}O$: C, 84·0; H, 12·2%.) Benzoylation of the sterol gave β-sitosteryl benzoate, m.p. 150–152°; $[\alpha]_D$ −14°. (Found: C, 83·1; H, 10·2. Calc. for $C_{36}H_{54}O_2$: C, 83·3; H, 10·5%.)

Isolation of ceryl alcohol

Fraction (*f*) was reacetylated, the product (22 g) was dissolved in petrol–benzene (19 : 1, 200 ml) and chromatographed on alumina (500 g). Elution with petrol–benzene mixtures gave two fractions. The first fraction (2 g) crystallized from hexane in fine needles (1 g), m.p. 60–65°; $[\alpha]_D$ 0°, which did not give a colour in the Liebermann-Burchardt test. (Found: C, 79·2; H, 13·0%. M [Rast] 430. Calc. for $C_{28}H_{56}O_2$: C, 79·2; H, 13·3%. M 424·7.) Alkaline hydrolysis of this acetate gave the corresponding alcohol, plates from ethyl acetate, m.p. 80°; $[\alpha]_D$ 0°. (Found: C, 81·3; H, 13·9. Calc. for $C_{26}H_{54}O$: C, 81·6; H, 14·2%.) The second fraction (5 g) was fractionally crystallised to give β-sitosteryl acetate (3 g), β-amyrin acetate (0·5 g) and lupenyl acetate (150 mg).

Isolation of soyasapogenol C

De-waxed plant material (1·8 kg) was extracted with alcohol (12 l.) until no more colour was removed. The extract was concentrated to ca. 500 ml, diluted with water (2 l.) and washed with ether (3 × 600 ml) to remove the green colour. The aqueous liquor was acidified with sulphuric acid (to 5 per cent concentration) and left overnight at room temperature when a dark, resinous precipitate separated. The precipitate was refluxed (24 hr) with ethanol (430 ml) containing concentrated hydrochloric acid (70 ml), the mixture was poured into 20% aqueous KOH (400 ml) and the resulting precipitate was refluxed (1 hr) with 5% KOH in methanol (100 ml). The product (6·5 g) precipitated from the alkaline solution on addition of water and was acetylated (1 hr on a steam bath) to give 5·2 g crude acetate which was chromatographed on alumina (200 g). Elution with petrol–benzene (1 : 1) afforded a fraction which crystallized from chloroform–methanol to give soyasapogenol C diacetate, m.p. 197°; $[\alpha]_D$ 58°. (Found: C, 77·8; H, 10·3. Calc. for $C_{34}H_{52}O_4$; C, 77·8; H, 10·0%.) Alkaline hydrolysis of the diacetate gave soyasapogenol C, m.p. 240–242°; $[\alpha]_D$ 68° (Found: C, 81·6; H, 11·4. Calc. for $C_{30}H_{48}O_2$: C, 81·8; H, 11·0%), identical (m.p. and infrared spectrum) with an authentic sample.