Platyconin and its hydrolysis products were identified by standard techniques.[3,10,11] R_f values are given in Table 1. In the H_2O_2 degradation of platyconin, the caffeic acid residues were destroyed and only rutinose was recovered (c.f. Ref. 2).

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COMPOSITAE

TRITERPENOIDS AND AROMATIC COMPONENTS OF DEERTONGUE LEAF

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Abstract—Lupeol and α-amyrin, together with the corresponding palmitates and acetates, and lupenone were isolated from dried deertongue leaves. A low-boiling fraction from the total extract contained 2,3-benzofuran, dihydrocoumarin, and coumarin.

INTRODUCTION

THE PLANT referred to as deertongue was initially regarded as a member of the genus *Liatris* and later as a *Trilisa* species. However, it has most recently been united to the genus *Carphephorus* and the correct name according to Hebert[1] is *C. odoratissimus* (J. F. Gmel) Hebert. The oleorosin from this plant, due to its high coumarin content, is frequently used as a fixative in perfumery. The roots were for a long time noted for their medicinal properties, and extracts from the dried leaves were used in the food flavouring industry prior to 1952 when a general ban was imposed on coumarin-containing products. The dried leaves are still however used as a flavouring additive in certain blends of tobacco and for this reason we have initially examined the volatile and low-polarity components from this source.

RESULTS

Commercially available deertongue leaf, on extraction with hexane, furnished a dark green viscous gum (3%), and further extraction with ether gave material of similar appearance (3%). Gradient chromatography (light petroleum–isopropyl ether) of the hexane soluble part of the extract yielded five fractions, the most polar of which was identified as coumarin. Thin

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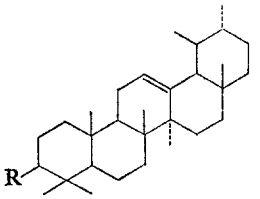
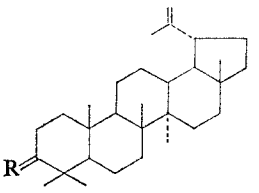
layer chromatography (TLC) of the remaining fractions on silver nitrate impregnated silica-gel revealed that, in order of increasing polarity, the first, second, and fourth each comprised two components.

The least polar fraction was separated by chromatography over silver nitrate impregnated silica-gel and the two components were isolated as waxy solids which exhibited molecular ions at *m/e* 664. Both show strong carbonyl absorptions at 1729 cm^{-1}, and the more polar compound exhibits in addition, absorptions at 3072, 1640 and 886 cm^{-1}, consistent with the presence of an unsymmetrically disubstituted terminal ethylene grouping. Both compounds, on hydridoaluminate reduction, furnished cetyl alcohol, and comparison of the complementary alcoholic residues with authentic samples enabled complete structure formulation as the palmitates Ia and IIa corresponding to α-amyrin (Ic) and lupeol (IId) respectively.

The second fraction, after separation, yielded the acetates Ib and IIb which are identical in all respects to the acetylation products of α-amyrin and lupeol.



Ia R, $-OCO(CH_2)_{14}CH_3$
Ib R, $-OCOCH_3$
Ic R, -OH



IIa R, α-H, β-$OCO(CH_2)_{14}CH_3$
IIb R, α-H, β-$OCOCH_3$
IIc R, =O
IId R, α-H, β-OH

The third fraction, a single compound, exhibits spectral properties identical to those of lupenone (IIc), though the melting point we initially recorded after crystallisation from methanol was 125–126° (lit.[2] 172°). However, recrystallisation from light petroleum furnished material m.p. 171–172·5°.

The fourth fraction, a mixture of two alcohols Ic and IId, was difficult to separate and hence it was acetylated prior to chromatography over silver nitrate impregnated silica-gel. The products were identified as α-amyrin acetate (Ib) and lupeol acetate (IIb).

It has been noted previously[3] that no essential oils are obtained from deertongue leaf. This is borne out by our studies on a low-boiling fraction from the total extract obtained by low-pressure distillation according to a recently described method.[4] Gas chromatography–mass spectrometric (GC–MS) examination of this material revealed the presence of 2,3-benzofuran, dihydrocoumarin, and coumarin in the ratio of 1:3:20 as the only significant components. The two latter compounds were isolated by preparative scale GLC and the mass spectrometric results confirmed by other physical methods.

EXPERIMENTAL

M.ps. are uncorrected and were recorded on a Kofler micro hot stage apparatus. Infrared spectra were run on a Perkin-Elmer 257 instrument in carbon tetrachloride. Nuclear magnetic resonance spectra were recorded in deuteriochloroform solution at 60 Mc/s using a Varian A60-A spectrometer. Preparative scale GLC was performed on a 2-m column (i.d. 9 mm) packed with 10% carbowax 20M on a Chromosorb G

[2] *Rodd's Chemistry of Carbon Compounds*, Vol. 2C, Elsevier, Amsterdam (1969).
[3] S. ARCTANDER, *Perfume and Flavor Materials of Natural Origin*, Arctander, Elizabeth, N. J. (1960).
[4] C. R. ENZELL, B. KIMLAND and Å. ROSENGREN, *Acta Chem. Scand.* **24**, 1462 (1970).

support. Mass spectra were recorded on a LKB 9000 spectrometer at 70eV and with an ion-source temperature of 290°. The same instrument, incorporating a 50-m stainless steel column (i.d. 0·5 mm) coated with Apiezon L and using helium carrier gas, was used for GC–MS experiments.

Commercially available deertongue leaf (351 g) was extracted for 24 hr in a Soxhlet apparatus with hexane yielding a viscous green gum (10·3 g). Further extraction with ether for 24 hr gave a product of similar appearance (10·7 g). Gradient elution (light petroleum/isopropyl ether) of the hexane-soluble part of the total extract (5·2 g) on silica-gel furnished, in order of increasing polarity, five distinct fractions, 1(1·76 g), 2(47 mg), 3(111 mg), 4(932 mg), and 5(287 mg).

Fraction 1 (800 mg) was separated into two components Ia (468 mg) and IIa (196 mg) by gradient elution (light petroleum–isopropyl ether) on a column of silver nitrate impregnated silica-gel.[5] *α-Amyrin palmitate* (*Ia*) crystallised as plates from ethanol and had m.p. 73–75°; $[\alpha]_D$ + 49° ($CHCl_3$); ν_{max} 1729 and 1174 cm^{-1}; NMR δ4·58 (q, J = 6 and 9Hz, 1H), and 5·23 (m, 1H); *m/e* (rel. %) 664 (1·5), 408 (2·3), 218 (100) 203 (22), and 189 (16); found *m/e* 664·6163, $C_{46}H_{80}O_2$ requires 664·6158. The compound was reduced with LAH to cetyl alcohol which gave identical i.r., NMR and mass spectra with authentic material, and *α-amyrin* (*Ic*) which on recrystallisation from methanol had m.p. and mixed m.p. 182–183·5° (lit.[2] 186°); ν_{max} 3628 cm^{-1}; NMR δ3·26 (q, J = 6 and 9Hz, 1H), and 5·21 (m, 1H); *m/e* (rel. %) 426 (12), 408 (2), 218 (100), 207 (11), 203 (16), and 189 (13). The above reduction products were separated by low pressure distillation of the cetyl alcohol under CO_2 and condensation at the temperature of liquid nitrogen.[4] *Lupeol palmitate* (*IIa*) crystallised as plates from ethanol and had m.p. 80–81·5°; $[\alpha]_D$ + 22° ($CHCl_3$); ν_{max} 3072, 1729, 1640, 1176, and 887 cm^{-1}; NMR δ0·81 (s, 3H), 0·87 (broad s, 9H), 0·96 (s, 3H), 1·05 (s, 3H), 1·71 (broad s, 3H), and 4·35–4·79 (m, 3H); *m/e* (rel. %) 664 (18), 408 (27), 218 (39), 205 (38), 203 (44), and 189 (100); found *m/e* 664·6157, $C_{46}H_{80}O_2$ requires 664·6158. Reduction with LAH furnished cetyl alochol and *lupeol* (*IId*) which, on recrystallisation from methanol, had m.p. and mixed m.p. 215–216° (lit.[2] 215°); ν_{max} 3626, 3074, 1640, and 886 cm^{-1}, NMR[6] δ0·77 (s, 3H), 0·80 (s, 3H), 0·85 (s, 3H), 0·99 (s, 6H), 1·05 (s, 3H), 1·70 (broad s, 3H), 3·21 (q, J = 6 and 9Hz, 1H), and 4·69 (diffuse d, 2H); *m/e* (rel. %) 426 (81), 408 (16), 218 (56), 207 (86), 203 (55), and 189 (100). The cetyl alcohol was separated from the triterpenoid and identified as described previously.

Fraction 2 (47 mg) was subjected to gradient chromatography (light petroleum–isopropyl ether) using silver nitrate impregnated silica-gel and yielded components Ib (19 mg) and IIb (23 mg). *α-Amyrin acetate* (*Ib*) on recrystallisation from methanol–isopropyl ether had m.p. and mixed m.p. 222–224° (lit[2] 226°); ν_{max} 1731 and 1246 cm^{-1}; NMR δ2·05 (s, 3H), 4·55 (q, J = 7 and 9Hz, 1H), and 5·21 (m, 1H); *m/e* (rel. %) 468 (9), 408 (7), 218 (100), 203 (18), and 189 (16). *Lupenyl acetate* (*IIb*) had, on recrystallisation from methanol–isopropyl ether m.p. 218·5–219·5° (lit.[2] 220°), mixed m.p. 218–220°; ν_{max} 3074, 1730, 1640, 1246, and 887 cm^{-1}; NMR[6] δ0·80 (s, 3H), 0·87 (s, 9H), 0·95 (s, 3H), 10·4 (s, 3H), 1·70 (broad s, 3H), 2·04 (s, 3H), and 4·35–4·80 (m, 3H); *m/e* (rel. %), 468 (45), 408 (33), 218 (36), 205 (27), 204 (36), 203 (42), and 189 (100).

Fraction 3 (111 mg) proved to be homogeneous. *Lupenone* (*IIc*) on crystallisation from methanol had m.p. 125–126°, and on recrystallisation from light petroleum 171–172·5° (lit.[2] 172°); ν_{max} 3072, 1707, 1640, and 886 cm^{-1}; NMR δ0·82 (s, 3H), 0·95 (s, 3H), 0·97 (s, 3H), 1·04 (s, 3H), 1·09 (s, 6H), 1·70 (broad s, 3H) and 4·69 (diffuse d, 2H); *m/e*[7] (rel. %), 424 (79), 218 (32), 205 (100), and 189 (40).

Fraction 4 (920 mg), a mixture of α-amyrin (Ic) and lupeol (IId), was only partially separated on Ag^+/SiO_2 TLC plates. It was hence reacted with acetic anhydride and pyridine and the resulting acetates were separated by elution (light petroleum/isopropyl ether) through a column of silver nitrate impregnated silica-gel. *α-Amyrin acetate* (*ex Ic*) (314 mg) which, on recrystallisation from methanol/isopropyl ether had m.p. 224–225°, was identical in all respects to an authentic specimen. *Lupenyl acetate* (*ex IId*) (530 mg) which, on recrystallisation from methanol–isopropyl ether had m.p. 218·5–219·5° (sealed tube), showed correct spectral properties and the melting point was undepressed on admixture with an authentic sample.

Fraction 5 comprised only *coumarin*, m.p. on crystallisation from ether 69–70°. The mixed m.p. was undepressed and the i.r., NMR and mass spectra were identical to those of an authentic sample.

Volatile Components

Deertongue leaf (42 g) was extracted for 18 hr in a Soxhlet apparatus with ether and yielded a viscous green oil (7·6 g). This was subjected to low pressure distillation at 85° using CO_2 as carrier gas,[4] and furnished a pale green crystalline distillate (822 mg). Examination of this material by GC–MS showed that the only significant peaks correspond to 2,3-benzofuran, dihydrocoumarin, and coumarin, in the ratio of 1:3:20. Dihydrocoumarin and coumarin were isolated by preparative scale GLC and they gave i.r. m.s. and NMR spectra which were indistinguishable from those of authentic samples. 2,3-benzofuran exhibited the same mass spectrum and GLC retention time as an authentic sample.

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