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CONSTITUENTS OF THE GENUS *OXYLOBUS*

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Key Word Index—*Oxylobus adscendens*, *O arbutifolius*, Compositae, labdane derivative, euparin derivative

Abstract—The aerial parts of *Oxylobus arbutifolius* and *O adscendens* gave eudesmanolides and labdane derivatives as well as two new euparin derivatives

The small genus *Oxylobus* (Compositae, tribe Eupatorieae) is placed in the subtribe Ageratinae [1] So far, two species have been studied chemically While *O glanduliferus* gave labdane derivatives [2], *O oaxacanus* afforded sesquiterpene lactones [3] We have now studied two more species The aerial parts of *O arbutifolius* (HBK) A Gray gave costunolide, β-cyclocostunolide [4], arbusculin B [5], 11α,13-dihydrocostunolide [6], 8,15-dihydroxylabdane, also present in *O glanduliferus* [2], isolated as its 15-*O*-acetate, the corresponding 15-acid [7] and the thymol derivatives **2** and **3** [8]

The aerial parts of *O adscendens* gave α- and β-cyclocostunolide [9], arbusculin B, costunolide, the acetate of the thymol **2**, 2-oxo-labd-8(17)-en-15-oic acid as well as the acetate **1**, which has already been prepared from the corresponding alcohol [7]. The configuration at C-13 was not determined Furthermore, the hydroperoxide **4** and the euparin derivatives **5** and **6** were present

The structure of **6** could be deduced from the ^{1}H NMR spectrum (see Experimental), which was similar to that of the corresponding angelate [10] In the ^{1}H NMR spectrum of **5**, the H-8 quartet was shifted upfield, indicating that the corresponding alcohol was present (see Experimental) The structure of **4** also followed from the ^{1}H NMR spectrum (see Experimental) The presence of a hydroperoxide was deduced from the broadened singlet at δ7 84 Most signals were similar to those of arbusculin B The configuration at C-3 was deduced from the small couplings, which agreed only with the presence of an axial oxygen function on inspection of a model Biogenetic considerations also agreed with this assumption

The chemistry of *Oxylobus* seems to be very uniform The occurrence of labdanes, thymol and euparin derivatives indicates a close relationship with *Ageratina* while the sesquiterpene lactones may be useful in separating these two genera

EXPERIMENTAL

The air-dried plant material (800 g) of *Oxylobus arbutifolius* (voucher Turner 15357, TEX) was worked up in the usual way [11] The CC (SiO_2) fraction obtained with Et_2O–petrol (1 9) on TLC (SiO_2, same solvent) gave 800 mg **2** and 30 mg **3** The CC fraction with Et_2O–petrol (1 3) afforded 200 mg costunolide The CC fraction with Et_2O–petrol (1 1) on standing in Et_2O at −20° gave 7 g crystals, mp 107°, which were identical with costunolide TLC (Et_2O–petrol, 1 1) of the mother liquor gave 60 mg β-cyclocostunolide (mp 67–68°, lit 68–69° [4]), 300 mg arbusculin B (mp 85°, lit 86–88° [5]), 300 mg 11α,13-dihydrocostunolide (mp 76°, lit 77° [6]) and 500 mg costunolide The CC fraction with Et_2O and Et_2O–MeOH (9 1) (^{1}H NMR no acetate methyl) was heated for 1 hr with Ac_2O TLC (Et_2O–petrol, 1 1) gave 500 mg of the monoacetate of 8,15-dihydroxylabdane and 300 mg of the corresponding acid

The air-dried plant material (320 g) of *Oxylobus adscendens* (voucher Turner 15399, TEX) was worked up as usual [11] The CC (SiO_2) fractions were as follows 1 (Et_2O–petrol, 1 9), 2 (Et_2O–petrol, 1 1) and 3 (Et_2O and Et_2O–MeOH, 9 1) TLC of fraction 1 (Et_2O–petrol, 1 9) gave 6 mg of the acetate of **2** TLC of 10% of fraction 2 (Et_2O–petrol, 1 2) afforded 16 mg **6** (R_f 0 65), 80 mg **1** (R_f 0 55) and 45 mg **5** (R_f 0 47) Repeated TLC of fraction 3 (Et_2O–petrol, 1 1 and Et_2O–CH_2Cl_2–C_6H_6, 1 1 1) gave 250 mg α-cyclocostunolide, 80 mg β-cyclocostunolide, 150 mg arbusculin B, 20 mg **4** (R_f 0 55), 75 mg costunolide and 80 mg 11α,13-dihydrocostunolide Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material, amounts being determined by wt All compounds were homogeneous by TLC in different solvent mixtures

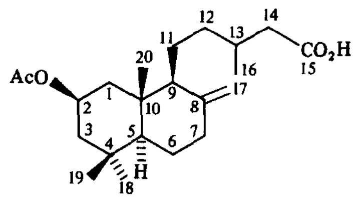
2β-Acetoxylabd-8(17)-en-15-oic acid (**1**) Colourless oil, which was purified as its methyl ester (CH_2N_2, TLC, Et_2O–petrol, 1 3, R_f 0 62), IR $\nu_{max}^{CCl_4}$ cm^{-1} 1735 (CO_2R, OAc), MS m/z (rel int) 378 160 $[M]^+$ (3) ($C_{23}H_{38}O_4$ 378 160), 347 $[M-OMe]^+$ (0 5), 318 $[M-HOAc]^+$ (84), 303 $[318-Me]^+$ (19), 189 $[C_{14}H_{21}]^+$ (11), 135 $[C_{10}H_{15}]^+$ (100), ^{1}H NMR (400 MHz, $CDCl_3$) δ5 14 *dddd* (H-2, J = 4, 4, 4, 4 Hz), 1 98 *m* (H-7α), 2 39 *br d* (H-7β, J = 13 Hz), 2 27 *dd* (H-14, J = 15, 6 Hz), 2 11 *dd* (H-14′, J = 15, 8 Hz), 0 91 *d* (H-16, J = 7 Hz), 4 85 and 4 49 *br s* (H-17), 0 95 *s* (H-18), 0 89 *s* (H-19), 0 84 *s* (H-20), 2 01 *s* (OAc), 3 65 *s* (OMe)

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{-28 \quad -34 \quad -41 \quad -71} \; (\mathrm{CHCl_3},\, c\ 1\ 0)$$

This compound was identical with the acetate of the corresponding alcohol from *Fleischmannia principes* [7]

3α-Hydroperoxyarbusculin B (**4**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1775 (γ-lactone), MS (CI, isobutane) m/z (rel int) 265 $[M+1]^+$ (7), 247 $[265-H_2O]^+$ (100), 231 $[265-H_2O_2]^+$ (20), ^{1}H NMR (400 MHz, $CDCl_3$) δ1 10 *s* (H-14), 2 04 *d* (H-15, J = 1 5 Hz), 6 16 *d* and 5 46 *d* (H-13, J = 3 Hz), 4 52 *ddq* (H-6, J = 11, 1 5, 1 5 Hz), 2 65 *ddddd* (H-7, J = 11, 10, 3, 3, 3 Hz), 4 20 *br s* (H-3), 7 84 *br s* (OOH)

8-O-Dihydroeuparin 6-O-methyl ether (**5**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3520 (OH), 1630, 920 (C=CH_2), MS m/z (rel int)



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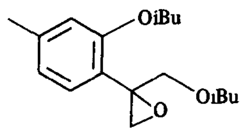

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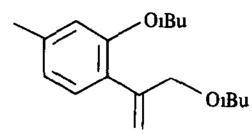

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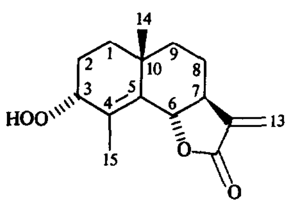

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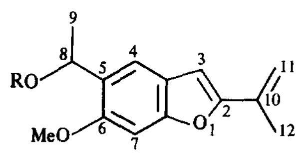

5 R = H
6 R = Ac

232 110 $[M]^+$ (8) (calc for $C_{14}H_{16}O_3$ 232 110), 214 $[M - H_2O]^+$ (100), 199 $[214 - Me]^+$ (8), 171 $[199 - CO]^+$ (17), ^1H NMR ($CDCl_3$). δ6 54 *s* (H-3), 7 46 *s* (H-4), 6 99 *s* (H-7), 5 15 *q* (H-8, $J = 7$ Hz), 1 53 *d* (H-9, $J = 7$ Hz), 5 69 and 5 09 *br s* (H-11), 2 10 *br s* (H-12), 3 91 *s* (OMe).

6-O-*Methyl*-8-O-*dihydroeuparin*-8-O-*acetate* (**6**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1740, 1235 (OAc), 1620 (aromate), MS *m/z* (rel int): 214 $[M - HOAc]^+$ (100), 199 $[214 - Me]^+$ (4), 171 $[199 - CO]^+$ (31), ^1H NMR ($CDCl_3$): δ6 53 *br s* (H-3), 7 48 *s* (H-4), 6 96 *s* (H-7), 6 26 *q* (H-8, $J = 7$ Hz), 1 50 *d* (H-9, $J = 7$ Hz), 5 69 and 5 09 *br s* (H-11), 2 09 *br s* (H-12), 2 10 *s* (OAc), 3 87 *s* (OMe)

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