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SESQUITERPENES FROM *LIABUM FLORIBUNDUM*

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Key Word Index—*Liabum floribundum*; *L. solidagineum*; *L. bourgeaui*; Compositae-Liabeae; sesquiterpenes; eudesmane derivatives; germacrane derivatives.

Abstract—The aerial parts of *Liabum floribundum* afforded in addition to widespread triterpenes two new eudesmane derivatives and a keto acetate derived from germacra-1(10),4-diene.

A collection of *Liabum floribundum* Less. from Ecuador has been studied previously. In addition to a heliangolide an unusual tricyclic sesquiterpene was isolated [1]. We now have studied a further sample from Peru. The polar fractions of the extract from aerial parts afforded the sesquiterpenes 3, 5 and 6.

The structure of 5, molecular formula $C_{15}H_{24}O_2$, followed from the ^{1}H NMR spectrum (Table 1) which clearly showed that an eudesmane derivative was present with a keto group at C-8 and a conjugated 6,7-double bond with an isopropyl group at C-7. Accordingly, the H-11 signal was at low fields and one of the H-9 signals showed a w-coupling with the 10-methyl group. The presence of an 4α-hydroxy group followed from the down field shift of the H-1α signal which together with the other signals, could be assigned by spin decoupling. This further showed that a transfused decalin system was present. The only remaining stereochemical question was the configuration at C-4. The couplings observed indicated a β-orientated methyl group.

The presence of an eudesmane diepoxide followed from the ^{1}H NMR signals (Table 1) at δ3.00 (*br s*) and 2.86 (*br dd*) in the spectrum of 3. The only possible position of these groups was deduced from the fact that the H-11 signal only showed coupling with H-12 and H-13. NOE difference spectra gave effects between H-14, H-6 and H-8. Though the signals of H-1–H-4 were overlapped multiplets, the only plausible structure for the diepoxide was 3. A w-coupling between the epoxide protons further supported the proposed stereochemistry and biogenetic considerations also agreed with this assumption. If the diene 1 is transformed to the endo peroxide 2, formation of 3 and 5 could easily occur (see Scheme 1).

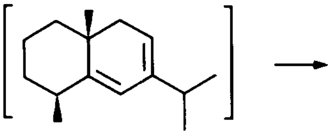
The structure of 6 followed from the molecular formula and the ^{1}H NMR spectrum (Table 1). The presence of a conjugated keto acetate already could be deduced from the characteristic IR bands while the relative position of the oxygen functions followed from the chemical shifts of H-14 and from spin decoupling. The stereochemistry was deduced from the NOE difference spectra. Irradiation of H-15 gave effects with H-2α, H-3α, H-6 and H-14, H-3β with H-5, H-2α with H-14 and H-15, H-5 with H-3β and H-9β and H-6 with H-15. This required the proposed stereochemistry and a conformation with both C-14 and C-15 below the plane leading to a situation with an axial isopropyl group. Accordingly, now large couplings of H-7 were visible. Surely 6 is derived from germacra-1(10), 4-diene.

The aerial parts of *L. solidagineum* (HBK) Less. gave in addition to widespread triterpenes small amounts of santamarin [3], while the roots of *L. bourgeaui* Hieron. afforded costunolide and dehydrocostus lactone as well as

Table 1. ^{1}H NMR spectral data of 3, 5 and 6 (400 MHz, $CDCl_3$, TMS as int. standard)

	3	**5**	**6**
H-1α	1.3–1.8 *m*	1.88 *ddd*	—
H-1β		1.16 *br d*	—
H-2α		1.47 *br d*	3.23 *ddd*
H-2β		1.74 *ddddd*	2.15 *m*
H-3α		2.09 *dddd*	2.47 *ddd*
H-3β		1.55 *m*	2.15 *m*
H-4	1.47 *m*	1.99 *ddq*	—
H-5	—	—	5.01 *br d*
H-6	3.00 *br s*	6.42 *s*	5.44 *br dd*
H-7	—	—	0.84 *m*
H-8α	2.86 *dd*	—	1.89 *dddd*
H-8β		—	1.29 *dddd*
H-9α	1.55 *ddq*	2.91 *dq*	2.92 *br d*
H-9β	1.40 *dd*	1.95 *d*	1.81 *ddd*
H-11	1.85 *qq*	2.91 *br qq*	1.55 *m*
H-12	1.02 *d*	1.03 *d*	0.92 *d*
H-13	1.12 *d*		0.87 *d*
H-14	1.11 *d*	1.08 *br s*	5.75 *s*
H-14′			5.54 *br s*
H-15	1.14 *d*	1.07 *br s*	1.61 *s*
OAc	—	—	1.96 *s*

J (Hz): Compound 3: 6, 8 ~ 0.5; 8, 9α = 3; 8, 9β = 7; 9α, 9β = 14; 9α, 14 = 1; 4, 15 = 11, 12 = 11, 13 = 7; compound 5: 1α, 1β = 1α, 2β = 13; 1α, 2α = 3.5; 2α, 3α = 5; 2β, 3α = 10; 3α, 3β = 13; 3α, 4α = 5; 4, 15 = 7; 9α, 9β = 16.5; 9α, 14 = 1; 11, 12 = 11, 13 = 7; compound 6: 2α, 2β = 2α, 3β = 13; 2α, 3α = 6; 2β, 3α = 13; 3α, 3β = 13; 5, 6 = 7; 6, 7 = 2.5; 7.8α = 3; 7, 8β = 4; 8α, 8β = 8α, 9β = 14; 11, 12 = 11, 13 = 7.



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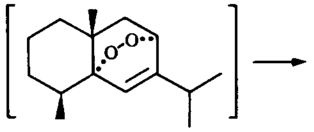

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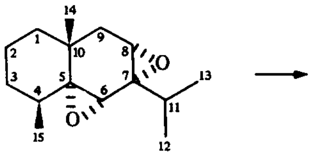

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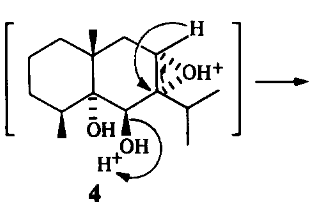

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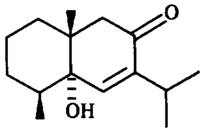

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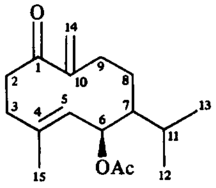

6

trideca-pentaynene and trideca-1,11-dien-3,5,7,9-tetrayne [1, 3]. The aerial parts only gave triterpenes and traces of sesquiterpene lactones.

The chemotaxonomy of the genus *Liabum* is still far from clear. The roots always appear to contain polyacetylenic hydrocarbons but the constituents of the aerial parts show no clear systematic distribution. However the isolation of sesquiterpene lactones from the genus allows its clear separation from the Senecioneae where it was placed previously [4].

EXPERIMENTAL

The air dried plant material was worked up in the usual fashion [5]. The extract of the aerial parts (70 g) of *Liabum floribundum* Less. (voucher RMK 9119, collected in January 1983 in Peru) gave by CC a polar fraction (Et_2O–petrol, 1:3 and 1:1) (250 mg) which was further separated by TLC (C_6H_6–CH_2Cl_2–Et_2O, 4:4:1) affording three zones (R_f 0.44, 0.75 and 0.83). TLC of the polar zone (Et_2O–petrol, 3:2) gave 2.0 mg **5** (R_f 0.61), of the second zone (C_6H_6–CH_2Cl_2–Et_2O, 6:6:1) 2.2 mg **6** (R_f 0.64) and of the least polar zone (Et_2O–petrol, 1:1) 5.1 mg **3** (R_f 0.71). The purity of **3**, **5** and **6** was checked by TLC in different solvent mixtures and by 400 MHz ^1H NMR spectroscopy and no impurities could be detected. The CC fraction with Et_2O–petrol (1:10) gave lupeol, stigmasterol, sitosterol and phytol (identified by comparison with authentic material).

The extract of 220 g aerial parts of *L. solidagineum* (voucher RMK 9236, collected in Peru) gave by CC and TLC 2.4 mg santamarin (identical with an authentic sample by TLC and ^1H NMR) and the triterpenes lupeol, its acetate, sitosterol, stigmasterol, taraxasterol and squalene, all identified by comparison with authentic standards (TLC and 400 MHz ^1H NMR spectra). The extract of 120 g of roots from *L. bourgeaui* (voucher RMK 7114, collected in Guatemala) gave by CC and TLC 0.5 mg tridecapentaynene, 0.5 mg trideca-1,11-dien-3,5,7,9-tetrayne, 10 mg costunolide and 4 mg dehydrocostus lactone. Again all compounds were identified by comparing with authentic material (TLC and 400 MHz ^1H NMR spectra).

5α,6α,7α,8α-Bisepoxy-4αH-eudesmane (**3**). Colourless oil, IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 2975, 2940, 2880, 1480, 965, 920; MS *m/z* (rel. int.): 236.178 $[M]^+$ (11) (calc. for $C_{15}H_{24}O_2$: 236.178), 218 $[M-H_2O]^+$ (13), 203 $[218-Me]^+$ (10), 193 $[M-C_3H_7]^+$ (26), 175 (27), 121 $[C_9H_{13}]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-21 \quad -22 \quad -24 \quad -38} (CHCl_3;\ c\ 0.41)$$

5α-Hydroxy-4αH-eudesm-6-en-8-one (**5**). Colourless oil, IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1680, 1615 (C=CCO); MS *m/z* (rel. int.): 236.178 $[M]^+$ (28) (calc. for $C_{15}H_{24}O_2$: 236.178), 221 $[M-Me]^+$ (8), 218 $[M-H_2O]^+$ (9), 208 $[M-CO]^+$ (24), 193 $[208-Me]^+$ (54), 165 $[193-CO]^+$ (37), 152 $[C_{10}H_{16}O + C_9H_{12}O_2]^+$ (64), 55 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+9 \quad +10 \quad +10 \quad +16} (CHCl_3,\ c\ 0.15)$$

6β-Acetoxy-germacra-4E,10(14)-dien-1-one (**6**). Colourless crystals, mp 100°, IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1735 (OAc), 1684, 1640 (C=CCO); MS *m/z* (rel. int.): 278.188 $[M]^+$ (5) (calc. for $C_{17}H_{26}O_3$: 278.188), 236 $[M-\text{ketene}]^+$ (12), 218 $[M-HOAc]^+$ (38), 190 $[218-CO]^+$ (21), 175 $[218-C_3H_7]^+$ (69), 109 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-113 \quad -118 \quad -138 \quad -258} (CHCl_3;\ c\ 0.18)$$

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FURTHER EUDESMANOLIDES FROM *DIMEROSTEMMA* SPECIES

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Key Word Index—*Dimerostemma asperatum*; *D. bishopii*; Compositae; sesquiterpene lactones; eudesmanolides; degraded syringenin.

Abstract—The aerial parts of a new *Dimerostemma* species afforded four eudesmanolides which are all derivatives of arbusculin B and an aldehyde, obviously a degradation product of syringenin. A reinvestigation of *Dimerostemma asperatum* gave a further dimerostemmolide.

From the small Brazilian genus *Dimerostemma* (Compositae, tribe Heliantheae) placed in the subtribe Ecliptinae [1], so far three species have been investigated chemically [2–4]. In addition to more widespread compounds, eudesmanolides with a special substitution pattern were isolated.

The aerial parts of *Dimerostemma bishopii* K. et R. afforded in addition to known compounds minute amounts of the aldehyde **6** and four eudesmanolides (**1–4**), all being derivatives of arbusculin B. The structure of **6** followed from the ^{1}H NMR spectrum (see Experimental). The presence of a symmetrical tetrasubstituted aromatic aldehyde was indicated by the two aromatic protons and the two methoxy groups which displayed sharp singlets. The nature of the oxygen function at C-4 easily could be deduced from the characteristic ^{1}H NMR signals. Though no molecular ion was observed in the mass spectrum the structure could be assigned clearly.

The ^{1}H NMR spectral data of **1–4** (Table 1) showed that these compounds only differed in the nature of the ester group at C-1 and the substitution at C-15. The signals in the spectrum of the main constituent **2** could be assigned by spin decoupling. Since the broadened double triplet at $\delta 4.59$ was partly decoupled by irradiation of the signals at $\delta 2.37$ and 2.26 respectively the whole sequence could be established. The nature of the ester groups also followed from the typical ^{1}H NMR signals. The relative position of the acetate group in the lactone **3** could be deduced from the mass spectrum which showed elimination of 4-hydroxymethacrylic acid and acetic acid. A 4′-*O*-acetate of **2** was absent. Also the ^{1}H NMR signal agreed much better with structure **3**. Accordingly, spin decoupling by irradiation of the H-6 signal showed allylic coupling with down field shifted H-15 signals.

A reinvestigation of the aerial parts of *D. asperatum* Blacke afforded in addition to the compounds isolated previously [3], a further dimerostemmolide (**5**). The ^{1}H NMR spectral data (Table 1) showed that the 8-*O*-isobutyrate of the known 1-*O*-[5-hydroxyangelate] of dimerostemmolide was present. The relative position of the ester group was deduced from the chemical shift of H-1 which was identical with that of corresponding lactones with an unsaturated ester group at C-1.

EXPERIMENTAL

The air dried aerial parts (150 g) of *Dimerostemma bishopii* (voucher RMK 8803, collected in the province Bahia, Brazil) was extracted with Et_2O–petrol, 1:2, and worked-up in the usual fashion [5]. The CC fractions (100 ml) of the extract were as follows: 1 (petrol), 2 (Et_2O–petrol, 1:4), 3 (Et_2O–petrol, 1:1) and 4 (Et_2O and Et_2O–MeOH, 10:1). TLC (SiO_2, PF 254, detection by UV light) of fraction 1 and 3 gave only widespread compounds. TLC (Et_2O–petrol, 1:4) of fraction 2 afforded 0.5 mg **6** (R_f 0.52), while repeated TLC of fraction 4 (Et_2O–petrol–Me_2CO, 17:2:1) gave 30 mg **2** (R_f 0.52), 24 mg **3** (R_f 0.67) and a mixture of **1** and **4** (R_f 0.72) which after TLC (CH_2Cl_2–C_6H_6–Et_2O, 1:1:1) gave 4 mg **1** (R_f 0.60) and 0.5 mg **4** (R_f 0.55) (quantities calculated from the ^{1}H NMR spectrum of the original mixture of **1–4**, separation caused considerable losses).