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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).

Table 1. ^{1}H NMR spectral data of compounds **1–5** (400 MHz, $CDCl_3$, TMS as int. standard)

	1	**2**	**3**	**4**	**5***
H-1	4.89 *dd*	4.91 *dd*	4.9 *t*	4.86 *dd*	4.95 *br dd*
H-2	1.95 *m*	1.95 *m*	1.95 *m*	1.92 *m*	
H-3α	2.34 *m*	2.37 *br dd*	2.25 *br dd*	2.33 *m*	
H-3β		2.26 *br d*	2.16 *br d*		
H-6	4.60 *br dt*	4.59 *br dt*	4.58 *br dt*	4.60 *br dt*	3.89 *dd*
H-7	2.60 *ddddd*	2.60 *ddddd*	2.64 *ddddd*	2.59 *ddddd*	2.76 *dddd*
H-8α	2.17 *br d*	2.15 *br d*	2.20 *br d*	2.21 *br d*	5.21 *ddd*
H-8β	1.70 *dddd*	1.76 *dddd*	1.67 *dddd*	1.70 *m*	
H-9α	1.83 *ddd*	1.83 *ddd*	1.84 *ddd*	1.85 *m*	1.67 *br dd*
H-9β	1.51 *ddd*	1.51 *ddd*	1.53 *ddd*	1.54 *m*	1.82 *dd*
H-13	6.19 *d*	6.19 *d*	6.18 *d*	6.21 *d*	6.11 *d*
H-13′	5.53 *d*	5.55 *d*	5.50 *d*	5.55 *d*	5.70 *d*
H-14	1.26 *s*	1.27 *s*	1.25 *s*	1.25 *s*	1.26 *s*
H-15	4.45 *br d*	4.37 *br d*	5.09 *br d*	4.46 *br d*	3.42 *d*
H-15′	4.17 *br d*	4.24 *br d*	4.84 *br d*	4.17 *br d*	2.44 *d*
OCOR	6.08 *dq*	6.24 *br s*	6.24 *br s*	3.10 *d*	2.41 *qq*
	5.59 *dq*	5.84 *dq*	5.86 *dq*	2.78 *d*	1.22 *d*
	1.95 *dd*	4.32 *br s*	4.32 *br s*	1.59 *s*	1.13 *d*
OAc	—	—	2.04 *s*	— OCOR	6.40 *br q*,
					2.11 *br d*
					4.32 *br d*

*H-5, 2.59 *d*.

J (Hz): 1, 2α = 2.5; 1, 2β = 4; 3, 6 = 2; 6, 7 = 11; 7, 8α = 3; 7, 8β = 12; 7, 13 = 3.2; 7, 13′ = 2.6; 8α, 8β = 13; 8α, 9α = 4; 8α, 9β = 3; 8β, 9α = 12; 8β, 9β = 3; 9α, 9β = 13; 15, 15′ = 11.5; OMeacr: 3′, 3′ = 3′, 4′ ~ 1; $OCOC(CH_2OH)=CH_2$: 3′, 3′ = 3′, 4′ ~ 1; OEpoxyiBu; 3′, 3′ = 6; compound **5**: 1, 2 = 2.5; 5, 6 = 6, 7 = 7, 8 = 11; 7, 13 = 3.5; 7, 13′ = 3; 8, 9α = 11; 8, 9β = 4; 15, 15′ = 4.3; OiBu: 2, 3 = 2, 4 = 7; 5-hydroxy ang: 3, 4 = 7; 5, OH ~ 5.

A reinvestigation of the polar fractions of the aerial parts (170 g) of *Dimerostemma asperatum* (voucher RMK 8951) gave in addition to dimeroperatic acid and the eudesmanolides isolated previously [3] by HPLC (RP 8, MeOH–H_2O, 7:3) of the TLC fraction containing the eudesmanolides [3] (Et_2O) 1 mg of the dimerostemmolide **5** (R_t 3.5 min). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material. Due to the very small amounts compounds **1–6** could not be induced to crystallize.

15-*Hydroxy*-1α-*methacryloyloxy-arbusculin B* (**1**). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1765 (γ-lactone), 1705 ($C=CCO_2R$); MS *m/z* (rel. int.): 246.126 $[M-RCO_2H]^+$ (17) ($C_{15}H_{18}O_3$), 228 $[246-H_2O]^+$ (48), 213 $[228-Me]^+$ (20), 69 $[C_3H_5CO]^+$ (100); CI (isobutane): 333 $[M+1]^+$ (28), 315 $(333-H_2O]^+$ (78), 229 $[315-RCO_2H]^+$ (100).

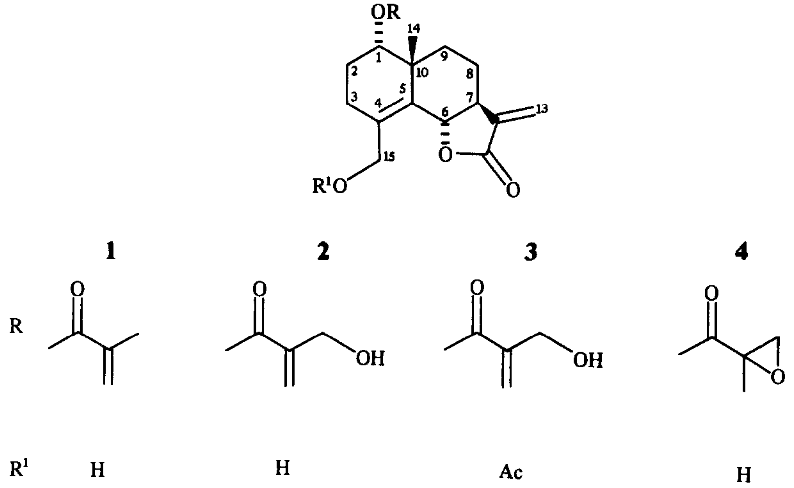
15-*Hydroxy*-1α-[4-*hydroxymethacryloyloxy*]-*arbusculin B* (**2**). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 3595 (OH), 1770 (γ-lactone), 1710 ($C=CCO_2R$); MS *m/z* (rel. int.): 348.157 $[M]^+$ (0.3) ($C_{19}H_{24}O_6$), 330 $[M-H_2O]^+$ (4), 246 $[M-RCO_2H]^+$ (38), 228 $[330-RCO_2H]^+$ (100), 213 $[228-Me]^+$ (32), 85 $[RCO]^+$ (82).

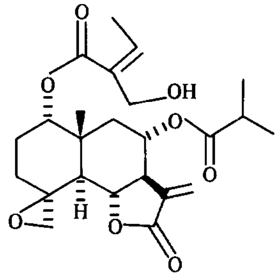
15-*Acetoxy*-1α-[4-*hydroxymethacryloyloxy*]-*arbusculin B* (**3**). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1730 (OAc), 1710 ($C=CCO_2R$); MS *m/z* (rel. int.): 330.147 $[M-HOAc]^+$ (3.5) ($C_{19}H_{22}O_5$), 288 $[M-RCO_2H]^+$ (2), 246 $[288-\text{ketene}]^+$ (22), 228 $[288-HOAc]^+$ (100), 213 $[228-Me]^+$ (27), 85 $[RCO]^+$ (37); CI (isobutane): 391 $[M+1]^+$ (3), 331 $[391-HOAc]^+$ (100), 229 $[331-RCO_2H]^+$ (34); $[\alpha]_{578} = +16$ (*c* 1.0, $CHCl_3$).

15-*Hydroxy*-1α-[2,3-*epoxyisobutyryloxy*]-*arbusculin B* (**4**). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}, 3600 (OH), 1770 (γ-lactone), 1730 (CO_2R); MS *m/z* (rel. int.): 246.126 $[M-RCO_2H]^+$ (4) ($C_{15}H_{18}O_3$), 228 $[246-H_2O]^+$ (10), 85 $[RCO]^+$ (38), 57 $[85-CO]^+$ (100); CI (isobutane): 349 $[M+1]^+$ (7), 331 $[349-H_2O]^+$ (100).

8-*O*-*Isobutyryl-dimerostemmolide*-1-*O*-[5-*hydroxyangelate*] (**5**). IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3595 (OH), 1770 (γ-lactone), 1720 ($C=CCO_2R$); MS *m/z* (rel. int.): 378 $[M-O=C=C(Me)_2]^+$ (1), 360, 157 $[M-C_3H_7CO_2H]^+$ (3) ($C_{20}H_{24}O_6$), 332 $[M-C_4H_6(OH)CO_2H]^+$ (1.5), 244 $[332-C_3H_7CO_2H]^+$ (32), 99 $[C_4H_6(OH)CO]^+$ (100), 71 $[C_3H_7CO]^+$ (18).

3,5-*Dimethoxy-4-hydroxybenzaldehyde* 3′,3′-*dimethylallyl ether* (**6**). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 2720, 1685 (CHO); MS *m/z* (rel. int.): 182 $[M-\text{isoprene}]^+$ (66), 69 $[Me_2C=CHCH_2]^+$ (100); ^{1}H NMR ($CDCl_3$): 9.87 *s* (CHO), 5.55 *br t* (H-9, *J* = 7 Hz), 4.68 *br d* (H-8, *J* = 7 Hz), 1.68 *br s* and 1.59 *br s* (H-11, H-12), 3.93 *s* (6H, OMe), 7.12 *s* (2H, H-2, H-6).





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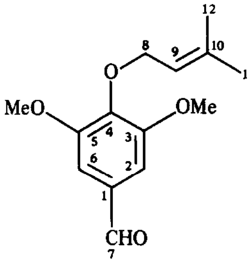

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