finally Et_2O–MeOH (10:1). The fraction obtained with petrol was separated further by TLC (petrol) to afford 1 mg acetylenes [7] and 1 mg thymol derivatives [8–10]. The fraction obtained with 10% Et_2O was separated further by TLC (50% Et_2O) to afford 2 mg 1 and 2 mg abienol. The fraction obtained with 50% Et_2O was separated further by TLC (50% Et_2O) to give 1.5 mg of a known epoxythymol.

10-*Isovaleryloxy*-8,9-*epoxythymol*-3-*isovalerate* (**1**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1745 (CO_2R); MS *m/z* (rel. int.): 348.194 $[M]^+$ (1.2) ($C_{20}H_{28}O_5$), 246 $[M - C_4H_9COOH]^+$ (6.8), 145 [246 – isovalerate]$^+$ (23), 85 $[C_5H_9O]^+$ (57), 57 $[85 - CO]^+$ (100).

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SECO-HELENANOLIDES FROM *DUGALDIA INTEGRIFOLIA*

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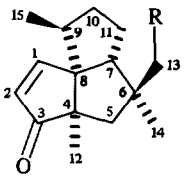
Key Word Index—*Dugaldia integrifolia*; Compositae; sesquiterpenes; *seco*-helenanolides; 13-isobutyryloxy-silphinen-3-one.

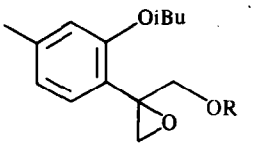
Abstract—The aerial parts of *Dugaldia integrifolia* afforded, in addition to acetylhymenograndin, floribundin, hymenoxon and isotelekin, three new *seco*-helenanolides and two derivatives of silphinene, one being isolated previously from *Dugaldia hoopesii*.

Dugaldia integrifolia (H.B.K.) Cass. [= *Helenium integrifolium* (H.B.K.) Benth. + Hook.] has been investigated previously [1]. In addition to a flavone, two pseudoguaianolides were isolated. Re-investigation of the aerial parts gave in addition to widespread compounds, acetylhymenograndin [2], isotelekin [3], floribundin [4] and hymenoxon [5, 6] isolated as its diacetate **8**, and three further sesquiterpene lactones, the *seco*-helenanolides **5**–**7**. Furthermore, the thymol derivatives **3** and **4**, 3-oxosilphinene (**1**) [7] and the isobutyryloxy derivative **2** were present. The mass spectrum of **2** gave the molecular formula $C_{19}H_{28}O_3$, and a strong fragment at *m/z* 216 agreed with the elimination of the acid part. The structure of the ester could be deduced from the ^1H NMR spectral data (see Experimental) which were close to those of **1** [7]. However, one of the methyl singlets was replaced by a pair of doublets at δ3.63 and 3.49 and, furthermore, the characteristic signals of an isobutyryloxy group were present. The observed shift differences of H-5, H-7 and H-11 in the spectra of **1** and **2** allowed the assignment of the position of the ester group. Furthermore, the *W*-coupling between H-13 and H-5α was missing, which was present in the spectrum of **1**.

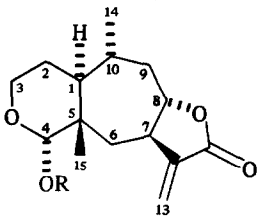
The structures of **5**–**7** also followed from the ^1H NMR spectral data (Table 1). All signals could be assigned by spin decoupling. The partial structures obtained in this way clearly showed that *seco*-helenanolides were present, differing only in the nature of the oxygen function, which



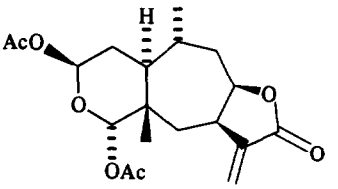
1 R = H
2 R = OiBu*



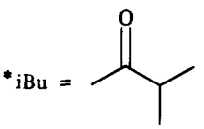
3 R = iBu*
4 R = Mebu †

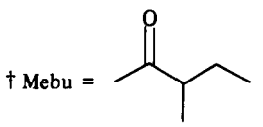


5 R = H
6 R = iBu*
7 R = Mebu †



8





was at C-4 in all cases. The molecular formula of **5** indicated that a hemiacetal was present. The corresponding ^{1}H NMR signal (H-4) was shifted downfield in the spectra of **6** and **7** where the hydroxyl group was esterified. The nature of the ester groups clearly followed from the ^{1}H NMR signals. The stereochemistry at C-4 could be deduced by comparing the chemical shifts of H-4 and H-15 with those of similar lactones with known configuration. The presence of 8α,12-lactones followed from the chemical shift of H-8, which differed typically in the spectra of **5**–**7** from those *seco*-helenanolides where *cis*-lactones were established. Also the couplings of H-8 were slightly different and the H-7 signals were shifted slightly upfield.

The isolation of **1** and *seco*-helenanolides in both *Dugalida* species may be of chemotaxonomic relevance. Furthermore, the relationship of this genus to *Hymenoxys* and its separation from *Helenium* [8] are supported again by the chemistry.

EXPERIMENTAL

The dried aerial parts (660 g, voucher *Turner* 15344*A*, TEX, collected on Cofre de Perote, Mexico) were extracted with MeOH–Et_2O–petrol (1:1:1) and worked up as usual [9]. The extract obtained was separated by CC into the following fractions: 1 (petrol and Et_2O–petrol, 1:10), 2 (Et_2O–petrol, 1:1 and Et_2O) and 3 (Et_2O–MeOH, 10:1). TLC of fraction 1 (Et_2O–petrol, 1:20) gave 220 mg **1**, 2 mg caryophyllene, 10 mg α-humulene, 5 mg **3** and 3 mg **4**. TLC of fraction 2 (CH_2Cl_2–C_6H_6–Et_2O, 4:4:1) gave 2 mg **2** (R_f 0.50) a mixture of **6** and **7**, which was separated by HPLC (RP 8, MeOH–H_2O, 13:7, flow rate 3 ml/min, *ca* 100 bar), affording 1.5 mg **6** (R_t 11.0 min) and 1 mg **7** (R_t 15.0 min), crude **5**, which was purified by TLC (C_6H_6–CH_2Cl_2–Et_2O, 3:3:1, 2 developments) to give 1 mg **5** (R_f 0.15), 15 mg acetylhymenograndin and a mixture which could not be separated by TLC (C_6H_6–CH_2Cl_2–Et_2O, 2:2:1). HPLC (RP 8, MeOH–H_2O, 13:7) gave 10 mg quercetin, 5 mg acetylhymenograndin, 8 mg 6-methoxyluteolin and 2 mg isotelekin, which was purified by TLC (Et_2O–petrol, 4:1). Fraction 3 could not be separated by TLC or HPLC. The ^{1}H NMR spectrum showed no acetate signal and the mixture was heated for 8 hr with 0.2 ml Ac_2O at 70°. HPLC (RP 8, MeOH–H_2O, 4:1) followed by TLC (Et_2O) gave 5 mg of the diacetate of hymenoxon **8** (R_f 0.42). Known compounds were identified by comparison with authentic material (400 MHz, ^{1}H NMR and co-TLC). The new compounds (**2** and **5**–**7**) were homogeneous by TLC in different solvent mixtures and showed no impurities in the ^{1}H NMR spectra.

13-*Isobutyryloxy*-3-*oxo*-*silphinene* (**2**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (CO_2R), 1710 (C=CCO); MS *m/z* (rel. int.): 304.204 $[M]^+$ (13) (calc. for $C_{19}H_{28}O_3$: 304.204), 249 $[M-COCH{=}CH_2]^+$ (32), 216 $[M-RCO_2H]^+$ (63), 201 $[216-Me]^+$ (68), 174 (42), 159 (52), 135 (56), 71 $[C_3H_7CO]^+$ (70), 57 (100); ^{1}H NMR ($CDCl_3$): δ7.59 (*d*, H-1), 6.04 (*d*, H-2), 2.25 (*d*, H-5β), 1.49 (*d*, H-5α), 2.09 (*dd*, H-7), 2.18 (*ddq*, H-9), 1.97 (*m*, H-10α), 1.42 (*m*, H-10β), 1.72 (*m*, H-11α), 1.41 (*m*, H-11β), 1.08 (*s*, H-12), 0.95 (*s*, H-14), 3.63 and 3.49 (*d*, H-13), 0.91 (*d*,

Table 1. ^{1}H NMR spectral data of **5**–**7** (400 MHz, $CDCl_3$, TMS as internal standard)

	5	6	7
H-1	2.17 *ddd*	2.10 *ddd*	2.09 *ddd*
H-2α	1.69 *dddd*	1.75 *m*	1.75 *dddd*
H-2β	1.50 *m*	1.50 *m*	1.50 *m*
H-3α	3.69 *ddd*	3.76 *ddd*	3.74 *ddd*
H-3β	3.95 *ddd*	3.81 *ddd*	3.81 *ddd*
H-4	4.71 *br d*	5.70 *s*	5.69 *s*
H-6α	2.02 *dd*	1.84 *br d*	1.84 *dd*
H-6β	1.20 *dd*	1.24 *dd*	1.22 *dd*
H-7α	3.12 *br dd*	2.92 *br ddd*	2.92 *br dd*
H-8β	3.81 *ddd*	3.83 *m*	3.82 *m*
H-9α	2.23 *ddd*	2.28 *ddd*	2.28 *ddd*
H-9β	1.52 *m*	1.51 *m*	1.50 *m*
H-10β	1.60 *m*	1.70 *m*	1.72 *m*
H-13	6.16 *d*	6.16 *d*	6.16 *d*
H-13′	5.45 *d*	5.34 *d*	5.34 *d*
H-14	0.96 *d*	1.00 *d*	1.00 *d*
H-15	1.02 *s*	1.11 *s*	1.11 *s*
OR	2.17 *br d*	1.13 *d*	0.87 *t*
		1.17 *d*	1.14 *d*
		2.54 *qq*	1.45 *ddq*
			1.67 *ddq*
			2.36 *ddq*

J (Hz): 1,2α = 4; 1,2β = 2α,2β = 2β,3α = 12.5; 1,10 = 8; 2α,3α = 3.5; 3α,3β = 12; 6α,6β = 15.5; 6α,7α = 1.5; 6β,7α = 11; 7α,8β = 10; 7α,13 = 3.5; 7α,13′ = 3; 8β,9β = 4; 9α,9β = 13; 9β,10 = 1.5; 10,14 = 7; OiBu: 2′,3′ = 2′,4′ = 7; OMeBu: 2′,3′ = 3′,4′ = 2′,5′ = 7; $3_1'$,$3_2'$ = 14.

H-15), 2.53 (*qq*, H-2′), 1.13 (*d*, H-3′), 1.14 (*d*, H-4′), [*J* (Hz): 1, 2 = 6; 5α, 5β = 14; 7, 11β = 9, 15 = 9, 10α = 7; 7, 11α = 9; 13, 13′ = 11.5; 2′, 3′ = 2′, 4′ = 7]. $[\alpha]_D^{24}$ −10° ($CHCl_3$; *c* = 0.2).

3-*Desoxy*-8-*epi*-*hymenoxon* (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 266.152 $[M]^+$ (3) (calc. for $C_{15}H_{22}O_4$: 266.152), 248 $[M-H_2O]^+$ (9), 220 $[248-CO]^+$ (10), 149 (26), 61 (84), 55 (100). $[\alpha]_D^{24}$ +45° ($CHCl_3$; *c* = 0.4).

3-*Desoxy*-8-*epi*-*hymenoxon isobutyrate* (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1740 (CO_2R); MS *m/z* (rel. int.): 336.194 $[M]^+$ (0.7) (calc. for $C_{19}H_{28}O_5$: 336.194), 249 $[M-OCOR]^+$ (37), 248 $[M-RCO_2H]^+$ (9), 220 $[248-CO]^+$ (4), 202 $[220-H_2O]^+$ (8), 122 (22), 71 $[C_3H_7CO]^+$ (100). $[\alpha]_D^{24}$ −56° ($CHCl_3$; *c* = 0.7).

3-*Desoxy*-8-*epi*-*hymenoxon*[2-*methylbutyrate*] (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1740 (CO_2R); MS *m/z* (rel. int.): 350.209 $[M]^+$ (0.5) (calc. for $C_{20}H_{30}O_5$: 350.209), 332 $[M-H_2O]^+$ (1), 266 $[M-O{=}C{=}C(Me)Et]^+$ (2.5), 249 $[M-OCOR]^+$ (35), 248 $[M-RCO_2H]^+$ (7), 85 $[C_4H_9CO]^+$ (58), 57 $[85-CO]^+$ (100). $[\alpha]_D^{24}$ −60° ($CHCl_3$; *c* = 0.5).

Hymenoxon diacetate (**8**). Colourless oil; ^{1}H NMR ($CDCl_3$): δ6.05 (*dd*, H-2), 5.74 (*s*, H-3), 3.30 (*ddddd*, H-7), 4.78 (*dd*, H-8), 6.25 (*d*, H-13), 5.42 (*d*, H-13′), 1.13 (*d*, H-14), 1.14 (*s*, H-15), 2.19 and 2.09 (*s*, OAc) [*J* (Hz): 1, 2 = 10; 1′, 2 = 3; 6, 7 = 10; 6′, 7 = 4; 7, 8 = 8; 7, 13 = 2.5; 7, 13′ = 2; 8, 9 = 12; 8, 9′ = 3.5; 10, 14 = 7]; MS *m/z* (rel. int.): 366.168 $[M]^+$ (0.1) (calc. for $C_{19}H_{26}O_7$: 366.168), 307 $[M-OAc]^+$ (12), 265 $[307-ketene]^+$ (18), 247 $[307-HOAc]^+$ (21), 192 $[247-C_3H_3O]^+$ (78), 55 (100). An authentic sample of hymenoxon afforded a diacetate which was identical with **8** (^{1}H NMR, co-TLC).

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