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ADDITIONAL GERMACRANOLIDES FROM *EUPATORIUM SEROTINUM*

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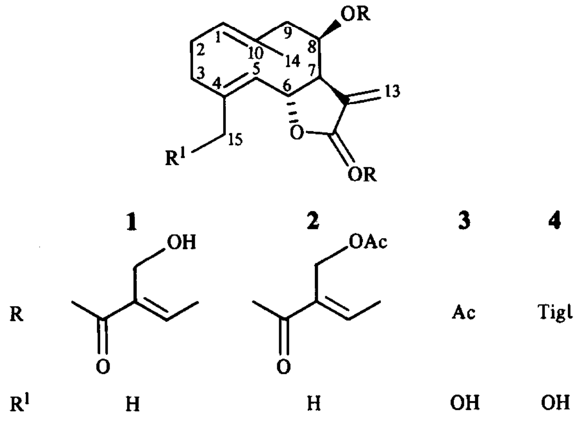
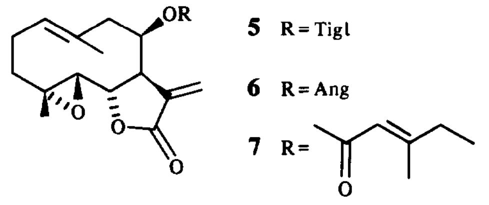
Key Word Index—*Eupatorium serotinum*; Compositae; sesquiterpene lactones; germacranolides.

Abstract—The aerial parts of *Eupatorium serotinum* afforded in addition to compounds reported previously three new germacranolides.

From *Eupatorium serotinum* Michx. several germacranolides [1] and some cubebene derivatives [2] were reported. A reinvestigation afforded in addition to the known lactones **1** [1], **2** [1], **5** [1] and **6** [3] three further germacranolides which were closely related to those isolated previously, as clearly followed from the ^{1}H NMR spectra (Table 1). The presence of the germacradienolides **3** and **4** was deduced from the characteristic signals of H-1, H-5 to H-9 and H-13 to H-15 which could be assigned by spin decoupling. The coupling of the broadened doublet of H-8 required a 8β-acyloxy group while the position of the free hydroxy group was deduced from the chemical shifts of the H-15 doublets. Inspection of models showed that all data agreed with normal conformations (methyls at C-4 and C-10 above the plane). Accordingly, the signals of H-3β and H-6 were shifted down field by the 15-hydroxy group and also the couplings of H-8 and H-9 were the expected ones.





The ^{1}H NMR spectral data of **7** were close to those of **5** [1] and **6** [3]. The nature of the changed ester group at C-8 clearly followed from the characteristic signals of a 4′-methyl senecioate. The *E*-configuration could be deduced from the chemical shifts of the olefinic methyl group at C-3′. Inspection of a model showed that the conformation of **7** resembles that of **3** and **4**. Euserotin, which has been isolated from this species previously [1], was not detected.

Table 1. ^{1}H NMR spectral data of compounds 3, 4 and 7 ($CDCl_3$, 400 MHz, TMS as internal standard)

	3	4	7
H-1	4.94 *br dd*	4.93 *br dd*	5.31 *br dd*
H-2	2.26 *m*	2.26 *m*	2.46 *m*
H-3α	2.03 *ddd*	2.05 *ddd*	2.20 *m*
H-3β	2.65 *ddd*	2.65 *ddd*	1.32 *m*
H-5	4.84 *br d*	4.87 *br d*	2.74 *d*
H-6	5.31 *dd*	5.42 *dd*	4.45 *dd*
H-7	2.86 *dddd*	2.88 *dddd*	3.14 *br ddd*
H-8	5.72 *br d*	5.80 *br d*	5.72 *br d*
H-9α	2.82 *br dd*	2.77 *br dd*	2.69 *br dd*
H-9β	2.32 *dd*	2.35 *dd*	2.36 *dd*
H-13	6.32 *d*	6.32 *d*	6.38 *d*
H-13′	5.60 *d*	5.63 *d*	5.76 *d*
H-14	1.43 *br s*	1.45 *br s*	1.76 *br s*
H-15	4.36 *br d* 4.11 *br d*	4.35 *br d* 4.14 *br d*	1.41 *s*
OCOR	—	6.83 *br q*	5.58 *tq*
		1.83 *br d*	2.19 *dq*
		1.84 *br s*	1.11 *t*
			2.17 *d*
OAc	2.06 *s*	—	—

J (Hz): Compounds **3** and **4**: 1, 2 = 11; 1, 2′ = 5; 2, 3 = 12; 2′, 3 = 6; 2, 3′ = 2; 2′, 3′ = 4; 3, 3′ = 12; 5, 6 = 10; 6, 7 = 9; 7, 8 ~ 1; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 4; 8, 9′ = 2; 9, 9′ = 15; 15, 15′ = 13; compound **7**: 1, 2 = 12; 1, 2′ = 2; 5, 6 = 6, 7 = 8.5; 7, 8 ~ 1; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 5; 8, 9′ = 1.5; 9, 9′ = 14; OTigl: 3′, 4′ = 6; OMeSen: 2′, 4′ = 2′, 6′ = 1; 4′, 5′ = 7.

EXPERIMENTAL

The air dried plant material (250 g) (collected in summer 1982 in West Virginia) was extracted for 12 hr at room temp. with 500 ml Et_2O–petrol (1:2) and the extract obtained was separated by CC (SiO_2). The fraction obtained with Et_2O and Et_2O–MeOH, 10:1, was further separated first by TLC (SiO_2 PF 254, C_6H_6–Me_2CO, 4:1) affording two bands (visible under UV light, 255 nm). The less polar band ($R_f \sim 0.7$) gave on repeated TLC (C_6H_6–Me_2CO, 3:1) a band ($R_f \sim 0.7$) containing **5**–**7**, 12 mg **2** ($R_f \sim 0.65$) and 20 mg **1** ($R_f \sim 0.60$). The mixture of **5**–**7** was separated by HPLC (RP 8, MeOH–H_2O, 7:3, detector: UV and refractometer) affording 3 mg **5** (R_t 5.5 min.), 3 mg **6** (R_t 5.7 min.) and 3 mg **7** (R_t 6.0 min.). **7**: IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1770 (γ-lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 360.194 $[M]^+$ (1) ($C_{21}H_{28}O_5$), 246 $[M - RCO_2H]^+$ (2), 228 $[246 - H_2O]^+$ (1.5), 97 $[C_5H_9CO]^+$ (100).

The more polar band of the polar CC-fraction (see above, $R_f \sim 0.6$) gave by HPLC (RP 8, MeOH–H_2O, 3:2, UV detector and refractometer) 5 mg **3** [R_t 4.5 min; IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1740 (OAc); MS *m/z* (rel. int.): 228.115 $[M - HOAc, H_2O]^+$ (10) ($C_{15}H_{16}O_2$), 55 $[C_4H_7]^+$ (100); CI (isobutane): 307 $[M + 1]^+$ (64), 247 $[307 - HOAc]^+$ (56), 203 $[247 - CO_2]^+$ (100); $[\alpha]_D \sim +30°$ ($CHCl_3$; *c* 0.3)] and 3 mg **4** [R_t 4.9 min; IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 246.126 $[M - \mathrm{TiglOH}]^+$ (3.5) ($C_{15}H_{18}O_3$), 228 $[246 - H_2O]^+$ (3), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (89)]. Compounds **3**, **4** and **7** could not be induced to crystallize though they were homogeneous by TLC in several solvent systems and by HPLC. Compounds **1**, **2**, **5** and **6** were identified by comparing the ^1H NMR spectral data with those in the lit. [1] or with those of authentic samples. Furthermore the ^1H NMR signals of **1**, **2** and **5** were fully assigned by spin decoupling.

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FIVE LABDANE DERIVATIVES FROM *KOANOPHYLLON CONGLOBATUM*

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Key Word Index—*Koanophyllon conglobatum*; Compositae; diterpenes; labdane derivatives; 7,8-*seco*-labdane derivative.

Abstract—A re-investigation of the aerial parts of *Koanophyllon conglobatum* afforded six new diterpenes, five labdanes and one *seco*-labdane, as well as two hydroperoxides which may be artefacts.

The large genus *Koanophyllon* is placed in the tribe Eupatorieae, subtribe Critoniinae [1]. So far, only two species have been studied chemically [2]. Both afforded diterpenes, some of them being characteristic. We have now re-investigated *Koanophyllon conglobatum* (DC.) K. et R.

The aerial parts afforded several widespread compounds together with koanophyllic acids B and D [2], the labdane derivatives **1**–**5**, the *seco* derivative **6**, and the epimeric hydroperoxides **7** and **8**. The ^1H NMR spectral data of **1**–**5** (Table 1) clearly showed that the presence of abienol derivatives with additional oxygen functions similar to diterpenes which had been isolated from *Austroeupatorium inulaefolium* [3]. The position and configuration of the hydroxyl groups in **1** followed from the chemical shifts of the methyl groups and from the observed couplings of the low-field double-doublet at δ 4.53, which was coupled to a pair of double-doublets at δ 2.01 and 1.68. These were obviously the signals of H-7. The downfield shifts of H-17, H-19 and H-20, when compared with the shifts in the spectrum of **2**, required axial methyl groups at C-4, C-8 and C-10, which were deshielded by the 6β-hydroxyl group. The ^1H NMR spectral data of **2** clearly showed that a 7β-acetoxy group was present.

The low-field signals in the spectrum of **3** indicated a 6β,7β-dihydroxyabienol since the couplings of H-6 and H-7 were small. Accordingly, **3** was an isomer of austrofolin [3] which differed in the stereochemistry of the 12,13-double bond and in that at C-6. In agreement with this