4α,15-Dihydroencelin (**3**). Colourless crystals, mp 175° (Et_2O); IR $\nu^{CCl_4}_{max}$ cm^{-1}: 1760 (γ-lactone), 1670 (C=CC=O); MS *m/z* (rel. int.): 246.126 $[M]^+$ (21) ($C_{15}H_{18}O_3$), 231 $[M-Me]^+$ (3), 218 $[M-CO]^+$ (3), 97 (71), 95 (79), 69 (100), 55 (98).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+14 \quad +14 \quad +20 \quad +53}\,\text{CHCl}_3;\ c\ 0.1$$

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2-ACETOXY-3α,4α-EPOXY-3,4-DIHYDROKAUNIOLIDE FROM *GROSVENORIA COELOCAULIS*

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Key Word Index—*Grosvenoria coelocaulis*; Compositae; sesquiterpene lactones; guaianolides.

Abstract—The aerial parts of *Grosvenoria coelocaulis* gave the known guaianolides dehydroleucodin, desacetoxymatricarin, kauniolide and a new one, 2β-acetoxy-3α,4α-epoxy-3,4-dihydrokauniolide.

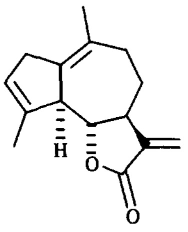
Grosvenoria (Compositae, tribe Eupatorieae) is a small genus [1] ranging from central Ecuador into northern Peru, which is placed in the subtribe Critoniinae [2]. So far nothing is known on the chemistry of this genus. We have now investigated *Grosvenoria coelocaulis* (B. L. Robins.) K. et R. from northern Peru. The aerial parts afforded α-curcumene and α-zingiberene as well as the known guaianolides kauniolide (**1**) [3], dehydroleucodin [4], desacetoxymatricarin [5] together with a new one, $C_{17}H_{20}O_5$. The IR spectrum of the latter indicated the presence of a γ-lactone and an acetate group (1770, 1738, 1245 cm^{-1}). From the ^{1}H NMR spectrum (Table 1) the presence of 6α,12-methylene lactone could be deduced. A typical fourfold doublet at δ2.80 was due to the H-7 signal. Accordingly, its irradiation collapsed the H-13 doublets to singlets, the double doublet at δ3.63 to a doublet and changed the overlapped multiplet around 2.10 while a quartet at 1.33 collapsed to a triplet. Addition of deuteriobenzene allowed the assignment of all signals by spin decoupling. As H-2 showed a *W*-coupling with H-5 and an allylic coupling with H-14 the whole sequence leading to the structure **2** could be assigned. The chemical shifts of H-2 and H-3 in combination with the other data indicated a 2-acetoxy derivative of kauniolide where the 3,4-double bond was transformed to an epoxide. Inspection of a model showed that the small coupling $J_{2,3}$ required a *trans*-orientation of H-2 and H-3, while the chemical shift of H-15 obviously was influenced by the deshielding effect of the lactone oxygen at C-6. This, however, required a 4β-methyl group as the stereochemistry at C-5–C-7 clearly followed from the *trans*-diaxial couplings of H-5–H-7. Also the observed couplings of H-8 and H-9 nicely agreed with the angles which could be deduced from a model. Thus the new compound is 2β-

Table 1. ^{1}H NMR spectral data of **2** (400 MHz, TMS as int. standard)

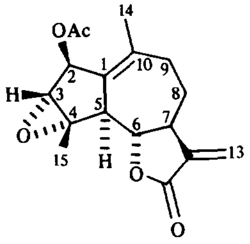
	$CDCl_3$	$CDCl_3$–C_6D_6 (2:1)
H-2	5.73 *br s*	5.54 *ddq*
H-3	3.65 *br s*	3.45 *br d*
H-5	3.33 *br d*	3.05 *br d*
H-6	3.63 *dd*	3.16 *dd*
H-7	2.80 *dddd*	2.34 *dddd*
H-8α	2.10 *m*	1.68 *dddd*
H-8β	1.33 *dddd*	0.96 *dddd*
H-9α	2.29 *br dd*	1.94 *br dd*
H-9β	2.16 *m*	1.82 *ddd*
H-13	6.15 *d*	5.97 *d*
H-13′	5.40 *d*	5.08 *d*
H-14	1.70 *s*	1.50 *br s*
H-15	1.65 *s*	
OAc	2.12 *s*	1.90 *s*

J (Hz): 2, 3 = 2; 2, 5 = 2, 14 ~ 1; 5, 6 = 6, 7 = 10; 5, 14 ~ 1; 7, 8α = 3; 7, 8β = 11; 7, 13 = 3.5; 7, 13′ = 3; 8α, 8β = 13; 8α, 9α ~ 1; 8α, 9β = 6; 8β, 9α = 12; 8β, 9β = 1.5; 9α, 9β = 14.

acetoxy-3α,4α-epoxy-3,4-dihydrokauniolide (**2**). The chemotaxonomic relevance of such guaianolides may be shown by further investigations of *Grosvenoria* species as well as of species of other genera placed in the subtribe Critoniinae. So far sesquiterpene lactones only are reported from *Critonia* species [6, 7]. Guaianolides closely related to those isolated now were isolated from *Kaunia* species [3], a genus of the related subtribe Oxylobinae.



1



2

EXPERIMENTAL

The air dried plant material (110 g, voucher RMK 9258, collected in January 1983 in northern Peru) was extracted with Et_2O–petrol–MeOH (1:1:1). The extract obtained was separated first by CC (silica gel) after methanol insoluble parts were removed. The petrol fractions gave by TLC (silica gel, $AgNO_3$ coated, petrol: detection always by UV-light and spraying with $KMnO_4$) 10 mg α-curcumene (R_f 0.45) and 50 mg α-zingiberene (R_f 0.40). The combined fractions with Et_2O–petrol (1:1, Et_2O and Et_2O–MeOH, 10:1) were further purified by TLC (silica gel PF 254, Et_2O–petrol, 3:1) leading to a crude fraction containing a methylene lactone (^{1}H NMR). HPLC (RP 8, MeOH–H_2O, 3:2) gave 5 mg **1** (R_t 5.4 min), its ^{1}H NMR spectrum being identical with that of authentic kauniolide. A more polar fraction from the TLC contained a mixture which was not separated by HPLC (RP 8, MeOH–H_2O, 3:2: R_t 4.1 min). TLC (silica gel, $CHCl_3$–C_6H_6–Et_2O, 2:2:1) gave 15 mg dehydroleucodin (R_f 0.65, identical by ^{1}H NMR and mp with authentic material), 5 mg desacetoxy matricarin (R_f 0.60) (identical with authentic material by ^{1}H NMR and mp) and 5 mg **2** (R_f 0.52). Quantities were determined by weight.

2β-Acetoxy-3α,4α-epoxy-3,4-dihydrokauniolide (**2**). Colourless crystals, mp 191° (Et_2O). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone), 1738, 1245 (OAc); MS *m/z* (rel. int.): 304.131 $[M]^+$ (4) (calc. for $C_{17}H_{20}O_5$: 304.131), 289 $[M-Me]^+$ (3), 262 $[M-\text{ketene}]^+$ (33), 261 $[289-CO]^+$ (100), 247 $[262-Me]^+$ (50), 244 $[M-HOAc]^+$ (56), 216 $[244-CO]^+$ (61), 135 (95).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+92 \quad +96 \quad +107 \quad +173}\ CHCl_3;\ c\ 0.17$$

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