facilities and Professor Navarro, of this Faculty for identifying the plant material.

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TWO FURANOHELIANGOLIDES FROM *CALEA ANGUSTA**

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Key Word Index—*Calea angusta*; Compositae; sesquiterpene lactones; furanoheliangolides.

Abstract—*Calea angusta* afforded, in addition to known compounds, two new furanoheliangolides closely related to those of *Calea pilosa*.

So far chemical investigation of *Calea* species has shown that furanoheliangolides may be characteristic for this genus (see ref. [1]). This finding supports the view that most of the *Calea* genus needs to be transferred from the subtribe Galinsoginae to the subtribe Neurolaeninae [2], while the remainder, re-established as the genus *Alloisospermum*, should be retained in the Galinsoginae [3]. The results on *Calea angusta* Blake again support this conclusion.

The roots afforded zingiberene, caryophyllene, the thymol derivatives **3** [4] and **4** [5], isocomene (**5**) [6], β-isocomene (**6**) [7] and silphinene (**7**) [8], while the aerial parts gave germacrene D, α-humulene, caryophyllene, bicyclogermacrene, squalene, **1** [9], **2** [10], **3**, the furanoheliangolides **8** [1], **9** [11], **10** [1], **11** [1] and **12** [12] as well as two further ones, the epoxides **13** and **14**. In the ^{1}H NMR spectrum (Table 1) of **13** the signals of the exomethylene proton were replaced by a pair of doublets at $\delta = 3.25$ and 3.30, indicating the presence of 11, 13-epoxide, while a singlet at 5.60 together with a double quartet at 5.28 supported the presence of a furanoheliangolide. The nature of the ester residue followed from the typical signals of a methyl butyrate. Spin decoupling allowed the as-

Table 1. ^{1}H NMR spectral data of compounds **13** and **14** (400 MHz, $CDCl_3$ TMS as internal standard)

	13	**14**
H-2	5.60 *s*	5.62 *s*
H-5	6.00 *dq*	6.04 *dq*
H-6	5.28 *ddq*	5.22 *ddq*
H-7	3.28 *dd*	3.38 *dd*
H-8	5.08 *ddd*	5.01 *ddd*
H-9α	2.34 *dd*	—
H-9β	2.14 *dd*	3.95 *dd*
H-13	3.30 *d*	3.32 *d*
H-13′	3.25 *d*	3.30 *d*
H-14	1.44 *s*	1.53 *s*
H-15	2.09 *dd*	2.08 *dd*
OMeBu	2.32 *ddq*	2.35 *ddq*
	1.60 *ddq*	1.62 *ddq*
	1.40 *ddq*	1.43 *ddq*
	1.08 *d*	1.10 *d*
	0.85 *t*	0.86 *t*

J(Hz): 5, 6 = 4; 5, 15 = 6, 15 = 1.5; 6, 7 = 4; 7, 8 = 2; 8, 9α = 6; 8, 9β = 3; 9α, 9β = 15; 13, 13′ = 4.5 (**14**: 8, 9 = 5; 9, OH = 6); OMeBu: 2′,3′ = 2′,5′ = 3′,4′ = 7; $3_1'$, $3_2'$ = 14.

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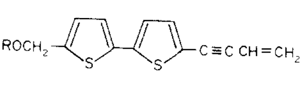
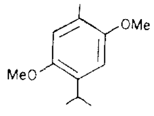
*Part 448 in the series "Naturally Occurring Terpene Derivatives". For Part 447 see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21** (in press).



1 R = H
2 R = Ac



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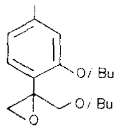

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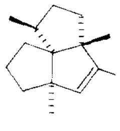

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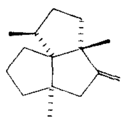

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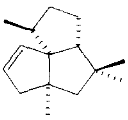

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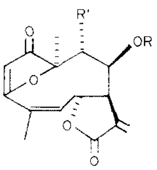
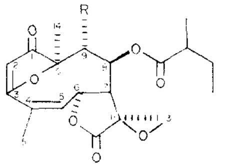


8 R = Ang, R' = OH
9 R = Tigl, R' = OH
10 R = Ang, R' = H
11 R = Tigl, R' = H
12 R = MeBu, R' = H



13 R = H
14 R = OH

signment of the remaining signals, while the stereochemistry at C-8 could be deduced from the small coupling $J_{7,8}$. The ^{1}H NMR spectral data of **14** (Table 1) were close to those of **13**. However, an additional lowfield double doublet at δ 3.95, which replaced the double doublets of H-9 clearly showed that a hydroxy group was at C-9. The stereochemistry followed from the coupling $J_{8,9}$. Compounds **13** and **14** were closely related to the corresponding angelates isolated from *Calea pilosa* [1], where an 11β, 13-epoxide was proposed. Accordingly the ^{1}H NMR spectral data were similar, only the H-8 signals being at slightly higher fields in the spectra of **13** and **14** due to the saturated ester groups. The chemistry of *C. angusta* therefore shows that it belongs to that group of species (see above), which should be placed in the subtribe Neurolaeninae.

EXPERIMENTAL

The air-dried plant material, collected in north-eastern Brazil (voucher RMK 8769, deposited in the U.S. National Herbarium, Washington) was extracted with Et_2O-petrol (1 : 2) and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material. The roots (55 g) gave 20 mg zingiberene, 5 mg caryophyllene, 500 mg **3**, 200 mg **4**, 20 mg **5**, 10 mg **6** and 10 mg **7**, while the aerial parts (200 g) afforded 200 mg germacrene D, 50 mg caryophyllene, 20 mg bicyclogermacrene, 10 mg α-humulene, 10 mg squalene, 20 mg **1**, 100 mg **2**, 50 mg **3**, 20 mg **8**, 1 mg **9**, 20 mg **10**, 5 mg **11**, 5 mg **12**, 5 mg **13** (Et_2O-petrol, 3 : 1, then C_6H_6-CH_2Cl_2-Et_2O, 5 : 5 : 1) and 1 mg **14** (Et_2O-petrol, 1 : 1, five developments).

11, 13-*Dihydro*-11, 13-*epoxyatripliciolide-2-methylbutyrate* (**13**). Colourless gum, containing small amounts of **10**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1800 (γ-lactone), 1735 (CO_2R), 1720, 1600 (RO-C=C-C=O); MS *m/z* (rel. int.): 376.152 $[M]^+$ (25), 358 $[M - H_2O]^+$ (4) ($C_{20}H_{24}O_7$), 292 $[M - O{=}C{=}C(Me)Et]^+$ (11), 274 $[M - RCO_2H]^+$ (1), 232 $[274 - C_2H_2O]^+$ (14), 85 $[C_4H_9CO]^+$ (23), 57 $[85 - CO]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589\quad 578\quad 546\quad 436\ \text{nm}}{-36\ -38\ -42\ -53}\ (CHCl_3;\ c\ 0.4).$$

9α-*Hydroxy*-11, 13-*dihydro*-11, 13-*epoxyatripliciolide*-2-*methylbutyrate* (**14**). Colourless gum, containing small amounts of **8**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1800 (γ-lactone), 1735 (CO_2R), 1710, 1600 (RO-C=C-C=O); MS *m/z* (rel. int.): 392.147 $[M]^+$ (8) ($C_{20}H_{24}O_8$), 374 $[M - H_2O]^+$ (3), 308 $[M - O{=}C{=}C(Me)Et]^+$ (5), 290 $[M - RCO_2H]^+$ (2), 85 $[C_4H_9CO]^+$ (24), 57 $[85 - CO]^+$ (100).

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