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GERMACRANE AND EUDESMANE DERIVATIVES FROM *CALEA RETICULATA**

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Key Word Index—*Calea recticulata*; Compositae; sesquiterpenes; germacra-4(15),5,10(14)-trien-1-one; eudesmane derivative; 6-epi-β-verbesinol coumarate.

Abstract—*Calea reticulata* afforded in addition to known compounds two new sesquiterpenes. These were germacrane and eudesmane derivatives, identified as germacra-4(15), 5, 10(14)-trien-1-one and 6-epi-β-verbesinol coumarate, respectively.

The aerial parts of *Calea reticulata* Gardn. afforded germacrene D, the triynenepoxides **1** and **2** [1] and ichthyotherol (**3**) [2]. Furthermore, a sesquiterpene ketone was present, molecular formula $C_{15}H_{22}O$. The ^{1}H NMR spectrum (Table 1) showed that it was probably a derivative of germacrene D as the typical signals of H-5, H-6, H-12, H-13 and H-15 were nearly identical with those of germacrene D. A pair of downfield shifted narrowly split signals at δ 5.51 and 5.71 indicated a methylene ketone which was supported by the IR band at 1680 cm^{-1}. Spin decoupling allowed the assignment of all signals, which led to the structure **4**. The roots gave germacrene D and γ-humulene as well as a sesquiterpene coumarate, its ^{1}H NMR spectral data led to the structure **5**. (Table 2). The nature of the ester residue followed from the typical pairs of doublets, while the presence of an eudesmane derivative was indicated by comparing the ^{1}H NMR spectral data with those of β-verbesinol coumarate [3, 4]. However, the large couplings $J_{5,6}$ and $J_{6,7}$ clearly showed that the ester group was α-orien-

Table 1. ^{1}H NMR spectral data of compound **4** (400 MHz, $CDCl_3$, TMS as int. standard)

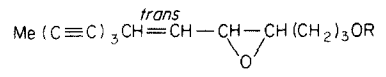
H-2	3.03 *m*	H-9	2.32 *m*
H-2′	2.50 *ddd*	H-9′	2.38 *dd br*
H-3	2.77 *ddd*	H-11	1.48 *dq*
H-3′	2.32 *mm*	H-12	0.88 *d*
H-5	5.75 *d*	H-13	0.81 *d*
H-6	5.25 *dd*	H-14	4.82 *s br*
H-7	1.78 *dddd*	H-14′	4.73 *s br*
H-8	1.96 *dddd*	H-15	5.71 *s br*
H-8′	1.55 *m*	H-15′	5.51 *d*

J (Hz): 2, 2′ = 12.5; 2, 3 = 10; 2′, 3 = 4; 2′, 3′ = 7; 3, 3′ = 13; 5, 6 = 15.5; 6, 7 = 10; 7, 8 = 10; 7, 8′ = 3.5; 7, 11 = 11, 12 = 11, 13 = 7; 8, 8′ = 15; 8, 9 = 4; 8, 9′ = 12; 8′, 9 = 5; 8′, 9′ ~ 1.5; 9, 9′ = 12.5; 9, 14 = 1.5.

Table 2. ^{1}H NMR spectral data of compound **5** (400 MHz, $CDCl_3$, TMS as int. standard)

HA5	2.11 *d*	H-2′,6′	6.84 *d br*
H-6	5.18 *dd*	H-3′,5′	7.39 *d br*
H-7	2.29 *m*	H-7′	7.59 *d br*
H-12, H-13	0.92 *d*	H-8′	6.29 *d*
H-14	0.80 *s*		
H-15	4.76 *s br*		
H-15′	4.36 *s br*		

*Part 431 in the series "Naturally Occurring Terpene Derivatives". For Part 430 see Bohlmann, F., Ahmed, M. and Jakupovic, J. (1982) *Phytochemistry* **21**, 1793.



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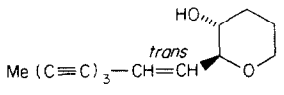

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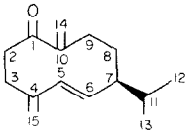

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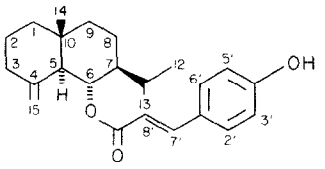

5

tated. Therefore the ester **5** was 6-epi-β-verbesinol coumarate. Sesquiterpene lactones, which are frequently found in *Calea* species, were not detected.

Ichthyotherol is known from four genera of the Heliantheae, *Ichthyothere*, *Clibadium*, *Dahlia*, *Calea* and from the tribe Anthemideae. The presence of this fish-killing compound in the first two genera has long been a factor in suggestions of their close relationship. Now, structural features of the two genera, and the occurrence of the same compound in other remotely related genera such as *Dahlia* and *Calea* raise serious doubts about the relationship.

EXPERIMENTAL

The air-dried plant material collected in N.E. Brazil, voucher RMK 8880, deposited in the U.S. National Herbarium, Washington, was extracted with Et_2O–petrol (1:2) and the extracts obtained were separated by CC (Si gel) and repeated TLC (Si gel). Known compounds were identified by comparing the spectral data with those of authentic material. The roots (10 g) gave 20 mg germacrene D, 10 mg γ-humulene and 40 mg **5** (Et_2O–petrol, 1:1), while the aerial parts (300 g) afforded 300 mg germacrene D, 50 mg **1**, 10 mg **2**, 40 mg **3**, and 5 mg **4** (Et_2O–CH_2Cl_2, 1:4).

Germacra-4(15), 5, 10(14)-*trien*-1-*one* (**4**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1680 (C=CC=O), 3090, 910 ($C=CH_2$); MS *m/z* (rel. int.): 218.167 $[M]^+$ (11) ($C_{15}H_{22}O$), 203 $[M-Me]^+$ (10), 189 (13), 175 (25), 147 (27), 133 (30), 119 (30), 105 (55), 91 (58), 69 (60), 57 (100); $[\alpha]_D = +30°$ ($c = 0.1$, $CHCl_3$).

6-*Epi*-β-*verbesinol coumarate* (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3610 (OH), 1712 (CO_2R), 1640 (C=C), 1610, 1595, 1520 (aromate), 850 ($C=CH_2$); MS *m/z* (rel. int.): 368.235 $[M]^+$ (8) ($C_{24}H_{32}O_3$), 204 $[M-RCO_2H]^+$ (91), 189 $[204-Me]^+$ (13), 161 $[204-C_3H_7]^+$ (100), 147 $[HOC_6H_4CH{=}CHCO]^+$ (65), 119 $[147-CO]^+$ (18);

$$[\alpha]_{24°}^{\lambda} = \frac{578 \quad 546 \quad 436\,nm}{-57 \quad -57 \quad -156} \quad (c = 0.4,\ CHCl_3).$$

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