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A CARYOPHYLLENE DERIVATIVE FROM *FLEISCHMANNIA PYCNOCEPHALOIDES**

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Key Word Index—*Fleischmannia pycnocephaloides*; *F. multinervis*; *F. deborabellae*; *F. bohlmanniana*; *F. pycnocephala*; Compositae; Eupatorieae; new caryophyllene derivative; 15-acetoxy-5,6-dihydro-6,7-dehydrocaryophyllen-5-one.

Abstract—A new caryophyllene derivative, 15-acetoxy-5,6-dihydro-6,7-dehydrocaryophyllen-5-one, has been isolated from the roots of *Fleischmannia pycnocephaloides*. Other *Fleischmannia* sp. yielded previously known compounds.

From the large genus *Fleischmannia* [1] (Compositae, tribe Eupatorieae) only a few species have been investigated chemically [2, 3]. We have now investigated some further species. The aerial parts of *F. pycnocephaloides* (B. L. Robins.) K. et R. afforded germacrene D, lupeyl acetate and (+)-abienol (**2**), while the roots contained lupeyl acetate as well as sesamin (**4**) and the caryophyllene derivative **1**. The structure was deduced from ^{1}H NMR investigations (Table 1). All signals were assigned by systematic spin decoupling and also after addition of different amounts of Eu(fod)$_3$.

Irradiation of the olefinic triplet allowed the assignment of the signals of H-8 and H-15. As the most shifted signals were those for 3-H, the signals for 4-H could be assigned by decoupling. The presence of a caryophyllene derivative was indicated by the typical signals of H-1, H-9 and H-10, which also could be assigned by decoupling after addition of shift reagent, while in $CDCl_3$, as well as in C_6D_6, only some of these signals were detected as some of the signals were overlapped. Compound **1** thus has the structure 15-acetoxy-5,6-dihydro-6,7-dehydrocaryophyllen-5-one.

The roots of *F. multinervis* (Benth.) K. et R. only afforded germacrene D, sesamin (**4**) and the corresponding dimethoxy compound **5** [2]. The roots of *F. deborabellae* K. et R. only gave *p*-hydroxybenzoic acid, while the aerial parts contained communic acid (**3**) [4]. The roots of *F. bohlmanniana* K. et R. afforded coumarin, while the aerial parts gave germacrene D and lupeyl acetate together with further unidentified triterpenes. The aerial parts of *F. pycnocephala* (Less.) K. et R. afforded eupatoriochromene (**6**) [5] in addition to the previously isolated sesamin (**4**) [2].

The compounds now isolated show that sesamin-like compounds may be characteristic for the genus, though this type of lignan was isolated from very different groups of the Compositae.

* Part 334 in the series "Naturally Occurring Terpene Derivatives". For Part 333 see Bohlmann, F. and Gupta, R. K. (1981) *Phytochemistry* **20**, 1432.

EXPERIMENTAL

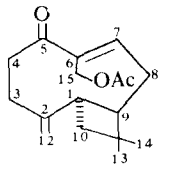
The air-dried plant material was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and by TLC (Si gel). Known compounds were identified by comparing their IR and ^{1}H NMR spectra with those of authentic material.

Table 1. ^{1}H NMR spectral data of compound **1** (TMS as internal standard, 270 MHz)

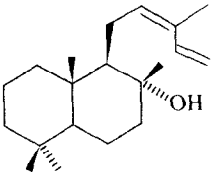
	C_6D_6	$CDCl_3$	+Eu(fod)$_3$*
H-1		2.50 *ddd*	3.30 *ddd*
H-3			4.44 *ddd*
H-3′	2.6–2.2 *m*	2.60 *m*	4.22 *dd*
H-4		2.6–2.4 *m*	3.86 *br.dd*
H-4′			3.23 *br.dd*
H-7	5.68 *br.t*	6.13 *br.t*	7.78 *br.t*
H-8	2.3 *m*	2.40 *ddd*	3.38 *ddd*
H-8′	1.73 *ddd*	2.10 *ddd*	2.73 *ddd*
H-9	1.52 *br.dd*	1.64 *ddd*	2.36 *dd*
H-10	1.65 *m*	1.80 *dd*	2.03 *dd*
H-10′		1.68 *dd*	1.96 *dd*
H-12	4.87 *br.s*	4.86 *br.s*	5.22 *br.s*
H-12′	4.74 *br.s*	4.71 *br.s*	5.00 *br.s*
H-13	0.86 *s*	1.02 *s*	1.24 *s*
H-14	0.82 *s*	0.99 *s*	1.12 *s*
H-15	4.79 *br.d*	4.82 *br.d*	9.68 *br.d*
H-15′	4.48 *d*	4.56 *d*	9.46 *br.d*
OAc	1.65 *s*	2.05 *s*	5.31 *s*

* 400 MHz.

J (Hz): 1,9 = 10; 1,10 = 8; 1,10′ = 10; 3,3′ = 13; 3,4 ~ 4; 3,4′ = 10; 3′,4 = 10; 3′,4′ ~ 4; 4,4′ = 13; 7,8 = 8; 8,8′ = 15; 8,9 = 10; 8′,9 = 2; 10,10′ = 10.5; 15,15′ = 12.5.



1



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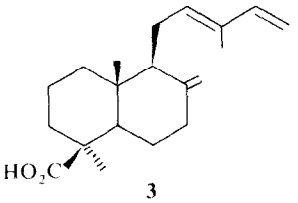

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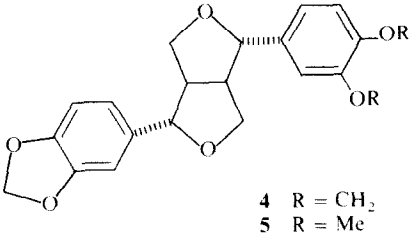
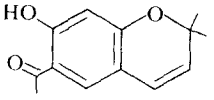


4 R = CH_2
5 R = Me



6

Fleischmannia pycnocephaloides (voucher RMK 7272). The roots (30 g) afforded 6 mg sesamin, 5 mg lupeyl acetate, and 6 mg **1** (Et_2O–petrol, 1:3), while the aerial parts (65 g) gave 60 mg germacrene D, 10 mg lupeyl acetate and 18 mg (+)-abienol (**2**).

Fleischmannia multinervis (voucher RMK 7306). The roots (60 g) afforded 15 mg germacrene D, 8 mg **4** and 12 mg **5**.

Fleischmannia deborabellae (voucher RMK 7346A). The roots (20 g) gave 5 mg *p*-hydroxybenzoic acid and the aerial parts (50 g) 30 mg **3**.

Fleischmannia bohlmanniana (voucher RMK 7190). The roots (20 g) gave 1 mg coumarin and the aerial parts (45 g) yielded 10 mg germacrene, 5 mg lupeyl acetate and 5 mg unidentified triterpenes.

Fleischmannia pycnocephala (voucher RMK 7185). The aerial parts (40 g) afforded 8 mg **4** and 3 mg **6**.

15-*Acetoxy*-5,6-*dihydro*-6,7-*dehydrocaryophyllen*-5-*one* (**1**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1230 (OAc), 1695 (C=CCO); MS *m/z* (rel. int.): 276.173 (M^+, 14) ($C_{17}H_{24}O_3$), 216 (M − HOAc, 74), 201 (216 − ·Me, 37), 173 (201 − CO, 44), 91 ($C_7H_7^+$, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-11 \quad -12 \quad -15 \quad -23} (c = 0.11, CHCl_3).$$

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