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A HYDROXYGERMACRENE AND OTHER CONSTITUENTS FROM *PSEUDOBRICKELLIA BRASILIENSIS**

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Key Word Index—*Pseudobrickellia brasiliensis*; Compositae; sesquiterpene; 4β-hydroxygermacra-1(10),5-diene; triterpenes; 11α-hydroxy-α-amyrin.

Abstract—*Pseudobrickellia brasiliensis* afforded, in addition to known compounds, a new germacradiene derivative and a hydroxy-α-amyrin.

The small genus *Pseudobrickellia* is placed in the subtribe Alomiinae (tribe Eupatorieae) [1]. So far nothing is known on the chemistry of this genus. The aerial parts of *P. brasiliensis* (Spreng.) K. et R. afforded lupeol and its Δ^{12} isomer, β-amyrin acetate, spathulenol, cadinene, cadinol, oplopanone (**1**) [2] and a further sesquiterpene alcohol. The structure of the latter followed from the ^{1}H NMR spectrum (Table 1) which was very close to that of **2** [3]. However, the chemical shifts of H-5 and H-6 had changed, the double doublet of H-6 now being at higher field. Nuclear Overhauser experiments showed by irradiation of the signal of H-15 a clear effect on the signals of H-3β and H-5. Inspection of models showed that obviously the preferred conformations were the same for both **2** and **3**, a chair-chair conformation with the 10-methyl and the 4-methyl (in **2**) or 4-hydroxyl group (in **3**) quasi-axial above the plane. This clearly followed from the couplings observed. Accordingly, the new sesquiterpene alcohol is the 4-epimer of **2** with a quasi-axial hydroxyl at C-4. Furthermore two isomeric triterpene diols were present

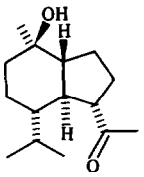
Table 1. ^{1}H NMR spectral data of compounds **2** and **3** (400 MHz, $CDCl_3$, TMS as internal standard)

	3	**2**	**2** (C_6D_6)
H-1	4.95 *d br*	4.95 *d br*	4.97 *d br*
H-2α	1.95 *d br*	1.96 *d br*	1.96 *m*
H-2β	2.50 *dddd*	2.51 *dddd*	2.67 *dddd*
H-3α	1.54 *m**	1.52 *m*	1.35 *m*
H-3β	1.64 *ddd*	1.65 *ddd*	1.50 *ddd*
H-5	5.25 *d*	5.17 *d*	5.06 *d*
H-6	5.17 *dd*	5.25 *dd*	5.30 *dd*
H-7	2.02 *m*	2.02 *m*	1.96 *m*
H-8	1.39 *m*	1.41 *m*	1.35 *m*
H-9	2.25 *m*	2.26 *m*	2.21 *m*
H-11	1.39 *m*	1.41 *m*	1.35 *m*
H-12	0.82 *d*	0.84 *d*	0.95 *d*
H-13	0.78 *d*	0.80 *d*	0.91 *d*
H-14	1.54 *s br*	1.55 *s br*	1.59 *dd*
H-15	1.19 *s*	1.21 *s*	1.12 *s*

*$CDCl_3$–C_6D_6, 2:1, H-3α 1.40 *ddd*.

J (Hz): 1, 2α ~ 2.5; 1, 2β = 11.5; 2α, 2β = 14; 2α, 3α ~ 3; 2α, 3β = 3.5; 2β, 3α = 11; 2β, 3β = 3.5; 3α, 3β = 14; 5, 6 = 16; 6, 7 = 9.3; 11, 12 = 11, 13 = 7.

*Part 461 in the series "Naturally Occurring Terpene Derivatives". For part 460 see Greger, H., Zdero, C. and Bohlmann, F. (1983) *Phytochemistry* **21**, 2085.



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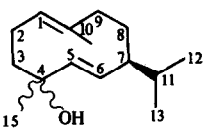
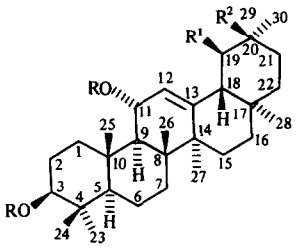


2 αOH
3 βOH



4 R = R¹ = H, R² = Me
5 R = R² = H, R¹ = Me
6 R = Ac, R¹ = H, R² = Me
7 R = Ac, R² = H, R¹ = Me

Table 2. ^{1}H NMR spectral data of compounds 6 and 7 (400 MHz, C_6D_6, TMS as internal standard)

	6	7
H-3	4.78 *dd*	4.75 *dd*
H-9	2.02 *d*	1.93 *d*
H-11	5.77 *dd*	5.73 *dd*
H-12	5.60 *d*	5.45 *d*
Me	1.36 *s*	1.21 *s*
	1.03 *s* (6H)	1.00 *s*
	0.97 *s*	0.98 *s*
	0.96 *s*	0.93 *s*
	0.95 *s* (6H)	0.91 *s*
	0.87 *s*	0.88 *s*
		0.98 *d*
		0.93 *d*
OAc	1.80 *s*	1.79 *s*
	1.74 *s*	1.78 *s*

J (Hz): 2, 3 = 11; 2', 3 = 5; 9, 11 = 8.5; 11, 12 = 3.5; compound 7: 19, 29 = 20, 30 = 6.

which, however, could only be separated as their diacetates by HPLC (reversed phase). One of these diacetates was identical with 11α-acetoxy-β-amyrin acetate (**6**) [4] while the second one showed two methyl doublets in the ^{1}H NMR spectrum (Table 2). The other signals were close to those of **6** especially those of H-9, H-11 and H-12. Therefore the second diacetate most probably is **7**. The minute amount did not allow chemical transformations to establish the proposed structure. However, the similarity of the ^{1}H NMR spectra of **6** and **7** and comparison with the spectra of α- and β-amyrin acetate strongly supported the structure which also was in agreement with the mass spectral fragmentation pattern.

EXPERIMENTAL

The air dried aerial parts (320 g) (voucher T. S. F. 892) were extracted with Et_2O–petrol, 1:2, and the resulting extract was separated by CC (silica gel) and further by repeated TLC (silica gel). The petrol fraction gave 5 mg γ-cadinene, that one with Et_2O–petrol (1:10) 20 mg β-amyrin acetate, that one with Et_2O–petrol (1:3), 150 mg lupeol, 150 mg of its Δ^{12} isomer, 10 mg spathulenol, 10 mg α-cadinol, 20 mg **1** and 20 mg **3** while that one with Et_2O after acetylation (Ac_2O, 1 hr, 70°) afforded a mixture of 3 mg **6** and 3 mg **7** (Et_2O–petrol, 1:3) which was separated by HPLC (reversed phase, MeOH–H_2O, 50:1).

Compound **6**. Colourless crystals, mp. 214° (lit. 216° [4]); ^{1}H NMR: see Table 2.

Compound **7**. Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730, 1250 (OAc); MS *m/z* (rel. int.): 526.402 $[M]^+$ (3) ($C_{34}H_{54}O_4$), 466 $[M - HOAc]^+$ (100), 451 $[466 - Me]^+$ (12), 406 $[466 - HOAc]^+$ (6), 391 $[406 - Me]^+$ (12), 276 [$C_{18}H_{28}O_2$, RDA]$^+$ (14), 234 $[276 - ketene]^+$ (20).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-26 \quad -27 \quad -32 \quad -58} (c\ 0.2, CHCl_3).$$

4β-Hydroxygermacra-1(10),5-diene (**3**). Colourless oil, $bp_{0.1\,Torr}$ 110°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3603 (OH), 3060, 1630, 980 (CH=CH); MS *m/z* (rel. int.): 222.198 $[M]^+$ (2) ($C_{15}H_{26}O$), 207 $[M - Me]^+$ (5), 204 $[M - H_2O]^+$ (3), 189 $[207 - H_2O]^+$ (6), 161 $[204 - C_3H_7]^+$ (13), 81 $[C_6H_9]^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-109 \quad -116 \quad -133 \quad -235} (c\ 0.62, CHCl_3).$$

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