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HELIANGOLIDES AND OTHER CONSTITUENTS FROM *BEJARANOA SEMISTRIATA**

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Key Word Index—*Bejaranoa semistriata*; Compositae; sesquiterpene lactones; heliangolides; germacranolides; diterpenes; geranylnerol derivative; nerolidol derivatives.

Abstract—The investigation of *Bejaranoa semistriata*, a new genus in the tribe Eupatorieae, afforded in addition to known compounds a new furanoheliangolide, two epimeric 1-keto-heliangolides, two germacranolides, two nerolidol derivatives and a geranylnerol derivative. The structures were elucidated by spectroscopic methods and a few chemical transformations.

INTRODUCTION

So far, nothing is known of the chemistry of the genus *Bejaranoa* (Compositae, tribe Eupatorieae [1]). In continuation of our chemosystematic studies of representatives of the tribe Eupatorieae, we have investigated *B. semistriata* (Baker) K. et R. The aerial parts afforded several new sesquiterpene lactones, some of a new type, but closely related to those isolated from other genera of this tribe.

RESULTS AND DISCUSSION

The aerial parts of *B. semistriata* afforded bicyclogermacrene, caryophyllene, the chromene **4** [2], the nerolidol derivative **1** [3] and two additional ones, the *E,Z*-isomeric methyl ethers **2** and **3**, which could not be separated. Their structures followed from the ^{1}H NMR spectral data (Table 1). As usual, in the spectrum of **3** the H-2 signal showed a drastic downfield shift. Compounds **2** and **3** were closely related to a corresponding 10,11-epoxide isolated from a *Petravenia* species [4]. We have given the name semistriatin methyl ether to compound **2**. Furthermore, the diterpene diol **5** [5] and a triol (**7**) were present. The latter compound was purified as its triacetate **6**. Again the ^{1}H NMR spectral data (Table 2) supported the structures, especially when compared with those of the corresponding diacetate of **5** [5]. The identical chemical shifts of the signals of H-1, H-2 and H-20 indicated the *Z*-configuration of the 2,3-double bond. The positions of the acetoxy groups were established by spin decoupling and were further supported by the fragmentation pattern in the mass spectrum, though no molecular ion could be detected. Even CI conditions only showed the M − HOAc + 1 peak.

Together with compound **7**, several sesquiterpene lactones were isolated. The main constituent was the furanoheliangolide **10b**. Its structure followed from the ^{1}H NMR spectral data (Table 3), especially if compared with those of **10a** [6], which was also present, and similar lactones, which differ only in the ester group at C-8 [6, 7]. The nature of the ester residue in **10b** was deduced from the typical ^{1}H NMR signals. Heliangin (**8**) [8] was present in minute amounts. Two other lactones, the ketones **11** and **12**, were isolated in larger amounts. Compound **12** was transformed to the acetate **13**. The ^{1}H NMR spectral data of **12** and **13** (Table 3) showed the presence of a germacranolide with a 4,5-*trans* double bond ($J_{5,6}$ and $J_{6,7}$ $\simeq$ 10 Hz), while the small coupling $J_{7,8}$

Table 1. ^{1}H NMR spectral data of compounds **2** and **3** (270 MHz, $CDCl_3$, TMS as internal standard)

	2	**3**
H-1*c*	5.04 *br d*	5.04 *br d*
H-1*t*	5.20 *br s*	5.23 *br d*
H-2	6.39 *dd*	6.94 *dd*
H-4	6.03 *br d*	6.03 *br d*
H-5	6.44 *dd*	6.57 *dd*
H-6	6.65 *d*	5.58 *d*
H-8	2.09 *dd*	2.08 *dd*
H-8′	1.8 *m*	1.8 *m*
H-9	5.76 *ddd*	
H-10	5.14 *dqq*	
H-12	1.75 *br s*	
H-13	1.69 *br s*	
H-14	1.32 *s*	1.31 *s*
H-15	1.86 *br s*	
OAng	5.96 *qq*	
	1.94 *dq*	
	1.83 *dq*	

J (Hz): 1*c*, 2 = 10; 1*t*, 2 = 17; 4, 5 = 11; 5, 6 = 15; 8, 8′ = 14; 8, 9 = 7.5; 8′, 9 = 4.5; 9, 10 = 9.5; 10, 12 = 10, 13 = 1; 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.

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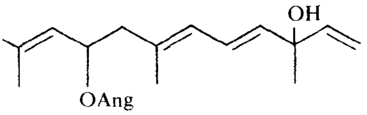
*Part 342 in the series "Naturally Occurring Terpene Derivatives". For Part 341 see Bohlmann, F., Ahmed, M., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1434.

Table 2. ^{1}H NMR spectral data of compounds **6** and **7** (270 MHz, TMS as internal standard)

	6		**7**
	C_6D_6	$CDCl_3$	$CDCl_3$
H-1	4.77 *br d*	4.65 *br d*	4.20 *br d*
H-2	5.67 *br t*	5.63 *br t*	5.68 *br t*
H-4,5	2.22 *m*	2.10 *m*	2.12 *m*
H-6	5.27 *br t*	5.10 *m*	5.10 *m*
H-8,9	2.05 *m*	2.10 *m*	2.03 *m*
H-10	5.20 *br t*	5.10 *m*	5.10 *m*
H-12,13	2.22 *m*	2.10 *m*	2.22 *m*
H-14	5.37 *br s*	5.38 *br t*	5.29 *br t*
H-16	1.77 *br s*	1.74 *br s*	1.78 *br s*
H-17	4.53 *br s*	4.54 *br s*	4.08 *br s*
H-18	1.60 *br s*	1.60 *br s*	1.60 *br s*
H-19	1.62 *br s*		
H-20	4.78 *br s*	4.57 *br s*	4.11 *s*
OAc	1.74 *s*	2.09 *s*	—
	1.73 *s*	2.065 *s*	—
	1.71 *s*	2.06 *s*	—
OH	—	—	3.47 *s*

J (Hz): 1, 2 = 5; 5, 6 = 9, 10 = 13, 14 = 7.

indicated a β-orientated tiglate residue at C-8. The 3α-position of the hydroxyl group and the acetoxy group, respectively, was indicated by the couplings observed and by spin decoupling, which allowed the assignment of the H-2 signals, which were shifted downfield indicating a neighbouring keto group. From spin decouplings it was further shown that two hydrogens were at C-9. Therefore the remaining hydroxy group could be placed only at C-10. The ^{1}H NMR spectral data of the second ketone **11** (Table 3) were very close to those of **12**. However, the H-3 downfield signal was missing and therefore the only hydroxyl group was at C-10 and **11** was the 3-desoxy derivative of **12**. Though the stereochemistry at C-10 could not be determined the proposed one was most likely as this is the normal configuration of lactones of this type. The last two lactones, **9a** and **9b**, isolated in minute amounts only, were also heliangolides, as could be deduced from the ^{1}H NMR spectral data (Table 2). The couplings $J_{6,7}$ and $J_{7,8}$ again were small. The spectra in C_6D_6 at 400 MHz were assigned completely by spin decoupling. Irradiation of the signals at δ 2.64 and 2.56 respectively, collapsed the H-13 signals indicating that they were the H-7 signals. Consequently, the signals of H-6 and H-8 also were changed in the expected way. Irradiation of the H-8 signals allowed the assignment of the H-9 signals. The chemical shift of H-8 showed that the ester group was at C-8, while the hydroxyl must be placed at C-3 as irradiation of the H-5 signal caused a visible sharpening of the H-3 signal. Though the substitution



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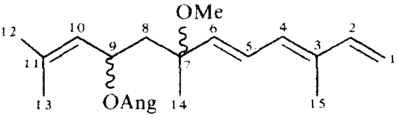

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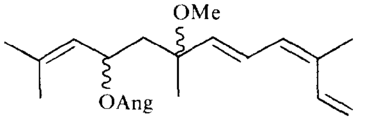

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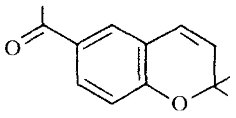

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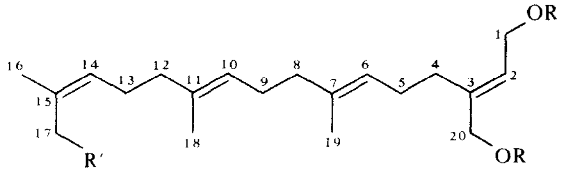
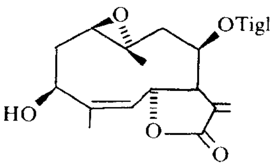


5 R = R′ = H
6 R = Ac, R′ = OAc
7 R = H, R′ = OH



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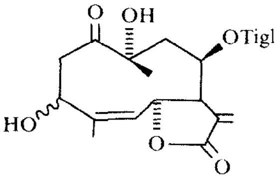
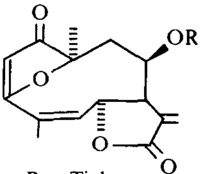
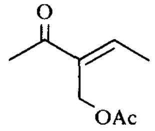


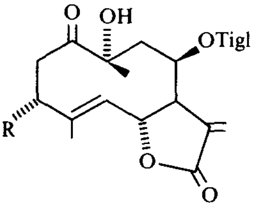
9a 3α-H
9b 3β-H



10a R = Tigl

10b R =





11 R = H
12 R = OH
13 R = OAc

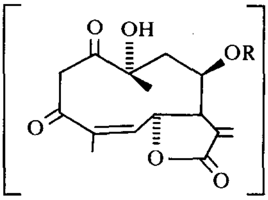


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Table 3. ^{1}H NMR spectral data of compounds 9–13 (270 MHz, TMS as internal standard)

	9a		**9b**					
	(CDCl$_3$)	C$_6$D$_6$*	(CDCl$_3$)	C$_6$D$_6$*	**10b**	**11***	**12**	**13**
H-1	—	—	—	—	—	—	—	—
H-2	2.94 *dd*	2.68 *dd*	3.38 *dd*	2.80 *dd*	5.64 *s*	2.88 *m*	3.07 *dd*	3.06 *dd*
H-2′	2.38 *dd*	2.17 *dd*	2.70 *dd*	2.39 *dd*			2.59 *dd*	2.69 *dd*
H-3	4.63 *dd*	3.90 *dd*	5.24 *br dd*	4.64 *br d*	—	2.35 *m*	4.92 *dd*	5.72 *dd*
H-3′					—	2.22 *m*		
H-5	5.33 *m*	5.14 *dq*	5.36 *br d*	5.12 *br d*	5.95 *dq*	5.12 *dq*	5.20 *br d*	5.31 *br d*
H-6	6.19 *dd*	6.34 *dd*	5.45 *dd*	5.37 *dd*	5.38 *dq*	5.05 *dd*	5.14 *dd*	5.12 *dd*
H-7	2.62 *dddd*	2.64 *dddd*	2.58 *dddd*	2.56 *dddd*	3.65 *dddd*	2.71 *dddd*	2.68 *dddd*	2.69 *dddd*
H-8	5.33 *m*	5.80 *dddd*	5.33 *m*	5.66 *ddd*	5.27 *ddd*	5.76 *ddd*	5.74 *ddd*	5.76 *ddd*
H-9	3.36 *dd*	2.82 *dd*	2.58 *dd*	2.45 *dd*	2.55 *dd*	2.03 *dd*	2.22 *dd*	2.23 *dd*
H-9′	2.89 *dd*	2.46 *dd*	2.29 *dd*	1.80 *dd*	2.33 *dd*	2.18 *dd*	2.04 *dd*	2.00 *dd*
H-13	6.28 *d*	6.33 *d*	6.31 *d*	6.25 *d*	6.36 *d*	6.22 *d*	6.24 *d*	6.25 *d*
H-13′	5.70 *d*	5.17 *d*	5.71 *d*	5.21 *d*	5.70 *d*	5.53 *d*	5.56 *d*	5.55 *d*
H-14	1.42 *s*	1.00 *s*	1.46 *s*	0.98 *s*	1.47 *s*	1.31 *s*	1.33 *s*	1.33 *s*
H-15	1.85 *br s*	1.54 *d*	1.88 *br s*	1.79 *br s*	2.08 *dd*	1.96 *d*	1.97 *br s*	1.92 *d*
OCOR	6.73 *br q* 1.74 *br d* 1.73 *br s*	7.03 *br q* 1.39 *br d* 1.83 *br s*	6.75 *br q* 1.76 *br d* 1.74 *br s*	7.08 *br q* 1.47 *br d* 1.90 *br s*	7.08 *q* 1.95 *d* 4.86 *d* 4.65 *d*	6.75 *qq* 1.79 *br d* 1.78 *br s*	6.77 *br q* 1.81 *br d* 1.80 *br s*	6.76 *br q* 1.80 *br d* 1.79 *br s*
OAc	—	—	—	—	2.05 *s*	—	—	—
OH	3.94 *br s*	3.99 *br s*	3.91 *br s*	3.92 *br s*	—	—	3.91 *br s*	3.84 *br s*

*400 MHz.

J (Hz): Compound **9a**: 2, 2′ = 15; 2, 3 = 4; 2′, 3 = 7; 5, 6 = 10; 5, 15 = 1; 6, 7 = 7, 8 ~ 2; 7, 13 = 2.3; 7, 13′ = 2; 8, 9 = 10; 8, 9′ = 5.5; 9, 9′ = 15; 3′, 4′ = 7; compound **9b**: 2, 2′ = 11.5; 2, 3 = 6; 2′, 3 = 11; 5, 6 = 9; 6, 7 = 7, 8 ~ 2; 7, 13 = 2.3; 7, 13′ = 2; 8, 9 = 5.5; 8, 9′ = 11; 9, 9′ = 15; compound **10**: 5, 6 = 6, 7 = 4; 5, 15 = 6, 15 = 1.5; 7, 8 ~ 1.5; 7, 13 = 2.8; 7, 13′ = 2.4; 8, 9 = 5; 8, 9′ = 3.5; 9, 9′ = 15; 3′, 4′ = 7; $5'_1, 5'_2$ = 12; compound **11**: 5, 6 = 10; 5, 15 = 1.3; 6, 7 = 9; 7, 8 = 2; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 11; 8, 9′ = 5.5; 9, 9′ = 14.5; 3′, 4′ = 7; compounds **12/13**: 2, 2′ = 13; 2, 3 = 11.5; 2′, 3 = 4.5; 5, 6 = 11; 5, 15 = 1.5; 6, 7 = 10; 7, 8 = 1.5; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 5.5; 8, 9′ = 11; 9, 9′ = 15; 3′, 4′ = 7.

pattern in both lactones was the same, characteristic differences in the chemical shifts and in the couplings $J_{2,3}$ were observed. Inspection of models showed that this could be explained by the proposed configurations at C-3. Most probably in both cases a hydrogen bond led to fixed conformations, which would be in good agreement with the observed couplings for $J_{2,3}$. Moreover, the two different conformations of **9a** and **9b** would explain the shift differences for the signals of H-3, H-5 and H-15. Again the configuration at C-10 was assigned by analogy only. We have named **9a**, without an oxygen function at C-3, bejaranolide. Compounds **9a** and **9b** may be the precursors of the widespread furanoheliangolides. Oxidation at C-3 would lead to **14**, which, as its enol, could be transformed to a compound like **10**.

The compounds found in *B. semistriata* support the proposed relationship of this new genus to *Conocliniopsis*, as the sesquiterpene lactones isolated from *C. prasiifolia* are very similar to the main constituents isolated from the *Bejaranoa* species [9].

EXPERIMENTAL

The air-dried plant material, collected in north-eastern Brazil, 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 IR and ^1H NMR spectra with those of authentic material.

Bejaranoa semistriata (Baker) K. et R. (voucher RMK 8032). The aerial parts (390 g) afforded 40 mg bicyclogermacrene, 40 mg caryophyllene, 30 mg **1**, 20 mg **2** (Et_2O–petrol, 1:1), 4 mg **3** (Et_2O–petrol, 1:1), 2 mg **4**, 4 mg **5**, 20 mg **7** (Et_2O), 5 mg **8**, 5 mg **9a** (Et_2O), 4 mg **9b** (Et_2O), 60 mg **10a**, 600 mg **10b** (Et_2O–petrol, 3:1), 60 mg **11** (Et_2O–petrol, 3:1) and 105 mg **12** (Et_2O).

3E *and* Z-*semistriatin methyl ether* (**2** *and* **3**). Colourless oil, which could not be separated, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1720, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 332.235 $[M]^+$ (11), 300 $[M - MeOH]^+$ (2), 232 $[M - AngOH]^+$ (5), 217 $[232 - Me]^+$ (8), 200 $[232 - MeOH]^+$ (15), 185 $[200 - Me]^+$ (9), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (61).

17,20-*Dihydroxygeranylnerol* (**7**). Colourless gum, purified as its triacetate (**6**), colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1237 (OAc); MS m/z (rel. int.): 388.261 $[M - HOAc]^+$ (2), 328 $[388 - HOAc]^+$ (4), 268 $[328 - HOAc]^+$ (4), 253 $(M - MeC(CH_2\text{-}OAc){=}CHCH_2]^+$ (3), 135 $[H_2C{=}C(Me)CH{=}CH_2CH_2C(Me){=}CH{=}CH_2]^+$ (51), 133 $[253 - 2 \times HOAc]^+$ (50), 93 $[C_7H_9]^+$ (100); CIMS (*i*-butane): 389 $[M - HOAc + 1]^+$ (12), 329 $[389 - HOAc]^+$ (54), 269 $[329 - HOAc]^+$ (100).

3β-*Hydroxybejaranolide* (**9a**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1765 (γ-lactone), 1735, 1650 (C=CCO$_2$R), 1710 (C=O); MS m/z (rel. int.): 378 $[M]^+$ (0.2), 278.115 $[M - TiglOH]^+$ (2) ($C_{15}H_{18}O_5$), 260 $[278 - H_2O]^+$ (1), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (78).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{\begin{array}{cccc}589 & 578 & 546 & 436\,\text{nm}\end{array}}{\begin{array}{cccc}-34 & -34 & -38 & -58\end{array}} \quad (c = 0.5, \text{CHCl}_3).$$

3α-*Hydroxybejaranolide* (**9b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630, 3460 (OH), 1770 (γ-lactone), 1715 (C=CCO$_2$R, C=O); MS m/z (rel. int.): 378 $[M]^+$ (0.1), 278.115 $[M - TiglOH]^+$ (1) ($C_{15}H_{18}O_5$), 260 $[278 - H_2O]^+$ (2), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (63); CI (*iso*-butane): 379 $[M + 1]^+$ (61), 361 $[379 - H_2O]^+$ (28), 279 $[379 - TiglOH]^+$ (90), 261 $[279 - H_2O]^+$ (61), 101 $[TiglOH + 1]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{\begin{array}{cccc}589 & 578 & 546 & 436\,\text{nm}\end{array}}{\begin{array}{cccc}-30 & -34 & -37 & -57\end{array}} \quad (c = 0.35, \text{CHCl}_3).$$

8β-[5-*Acetoxytiglinoyloxy*]-*atripliciolide* (**10b**). Colourless crystals, mp 74° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1750 (OAc), 1720 (C=CCO$_2$R, C=O), C=COR (1600); MS m/z (rel. int.): 416.147 $[M]^+$ (20) ($C_{22}H_{24}O_8$), 356 $[M - HOAc]^+$ (2), 258 $[M - RCO_2H]^+$ (5), 141 $[RCO]^+$ (80), 81 $[141 - HOAc]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{\begin{array}{cccc}589 & 578 & 546 & 436\,\text{nm}\end{array}}{\begin{array}{cccc}-91 & -94 & -106 & -155\end{array}} \quad (c = 0.7, \text{CHCl}_3).$$

4,5-trans-*Bejaranolide* (**11**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH), 1775 (γ-lactone), 1715 (C=CCO$_2$R), 1650 (C=C); MS m/z (rel. int.): 362 $[M]^+$ (0.01), 262.121 $[M - TiglOH]^+$ (3) ($C_{15}H_{18}O_4$), 234 $[262 - CO]^+$ (4), 216 $[234 - H_2O]^+$ (2), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (49); CIMS (*iso*-butane): 363 $[M + 1]^+$ (100), 263 $[363 - TiglOH]^+$ (36), 101 $[TiglOH + 1]^+$ (14).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{\begin{array}{cccc}589 & 578 & 546 & 436\,\text{nm}\end{array}}{\begin{array}{cccc}+32 & +34 & +39 & +80\end{array}} \quad (c = 0.95, \text{CHCl}_3).$$

3α-*Hydroxy*-4,5-trans-*bejaranolide* (**12**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1780 (γ-lactone), 1720 (C=CCO$_2$R, C=O), 1650 (C=C); MS m/z (rel. int.): 378 $[M]^+$ (0.1), 278.115 $[M - TiglOH]^+$ (1) ($C_{15}H_{18}O_5$), 260 $[278 - H_2O]^+$ (1.5), 232 $[260 - CO]^+$ (5), 217 $[232 - Me]^+$ (1), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (92).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{\begin{array}{ccc}589 & 578 & 546\,\text{nm}\end{array}}{\begin{array}{ccc}+57 & +59 & +69\end{array}} \quad (c = 1.0, \text{CHCl}_3).$$

Compound **12** (20 mg) was heated for 1 hr with 0.1 ml Ac_2O. TLC (Et_2O–petrol, 3:1) afforded 20 mg **13**, colourless gum. For ^1H NMR spectrum see Table 3.

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