(2:1); 75–85, EtOAc and 86–91, EtOH. Fraction 61 solidified and was recrystallized from C_6H_6 to give 110 mg **1a**, mp 132–134°. IR bands as given in the Discussion; ^{1}H NMR ($CDCl_3$) (identified by spin decoupling): δ 5.59 (H-2), 5.93 *dq* (4, 1.5 Hz, H-5), 5.3 *tq* (4, 1.5 Hz, H-6), 3.70 *m* (H-7), θ5.25 *ddd* (5.5, 4, 2 Hz, H-8), 2.53 *dd* (15, 5.5 Hz, H-9a), 2.29 *dd* (15, 4 Hz, H-9b), 6.36 *d* (3 Hz, H-13a), 5.69 *qd* (3 Hz, H-13b), 1.48 (3H, H-14), 1.80 *quint* (3p, 1.5 Hz, H-15), 5.11 *qq* (7, 1.5 Hz, H-3′), 1.93 *dq* (3p, 7, 1.5 Hz, H-4′), 1.80 *quint* (3p, 1.5 Hz, H-5′); CD (MeOH): $[\theta]_{323}+5900$ ($\Delta\epsilon$ + 1.79), $[\theta]_{288}-5220$ ($\Delta\epsilon-1.58$), $[\theta]_{256}+3000$ (sh, $\Delta\epsilon$ 10.91), $[\theta]_{236.5}+6700$ ($\Delta\epsilon+2.03$). [Calculated for $C_{22}H_{22}O_6$; MW, 358.1415. Found: MW (MS), 358.1427.]

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REFERENCES

1. Goulart, E. G. *et al. Rev. Bras. Farm.* (in press).
2. Ortega, A., Romo de Vivar, A., Diaz, E. and Romo, J. (1970) *Rev. Latinoam. Quim.* **1**, 81.
3. Bjeldanes, L. F. and Geissman, T. A. (1970) *Phytochemistry* **11**, 327.
4. Bohlmann, F. and Dutta, L. N. (1979) *Phytochemistry* **18**, 676.
5. Guerrero, C., Santana, M. and Ramo, J. (1976) *Rev. Latinoam. Quim.* **7**, 41.
6. Romo de Vivar, A., Guerrero, C., Diaz, E., Bratoeff, E. A. and Jimenez, L. (1976) *Phytochemistry* **15**, 525.
7. Herz, W. and Kumar, N. (1981) *Phytochemistry* **20**, 93.

NOTE ADDED IN PROOF

Compound **1a**, also in noncrystalline form, has been reported recently among the lactone constituents of *Calea pilosa* and *C. morii* (Bohlmann, F., Fritz, W., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 743).

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LABDANE DERIVATIVES FROM *PLANALTOA LYCHNOPHOROIDES**

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Key Word Index—*Planaltoa lychnophoroides*; Compositae; Eupatorieae; diterpenes; *ent*-labdane derivatives; toxol derivative.

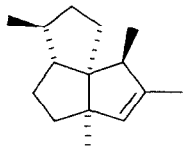
Abstract—The investigation of a representative of the small Brazilian genus *Planaltoa* afforded, in addition to known compounds, a new toxol derivative and two *ent*-labdane derivatives, closely related to austrofolin. The structures were elucidated by high field ^{1}H NMR spectroscopy. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

In continuation of our chemosystematic studies of the tribe Eupatorieae, we have now studied the constituents of *Planaltoa lychnophoroides* Barroso, one of the two Brazilian species of the genus belonging to the subtribe Alomiinae[1]. The aerial parts afforded germacrene D, bicyclogermacrene, α-humulene, lupeyl acetate, stigmasterol, the dehydronerolidol derivatives **3**[2] and **4**[3], the euparin derivative **5**[4], the toxol derivative **7**[5] and the corresponding dimethyl ether **8**, the structure of which followed from the molecular formula and the ^{1}H NMR data (see Experimental). The configuration at C-2 and C-3 was deduced from the coupling $J_{2,3}$, while the position of the methoxy groups clearly followed from the chemical shift of the aromatic proton. The polar fractions afforded two diterpenes, the *ent*-labdanes **10** and **11**. The structures of which followed from the ^{1}H NMR data (Table 1), the molecular formulae and

*Part 386 in the series "Naturally Occurring Terpene Derivatives". For Part 385, see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 147.

1



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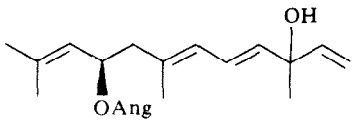

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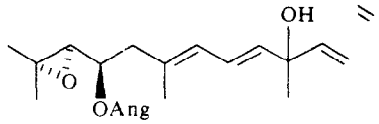

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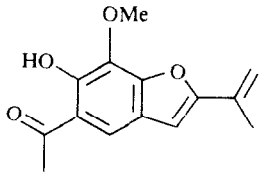

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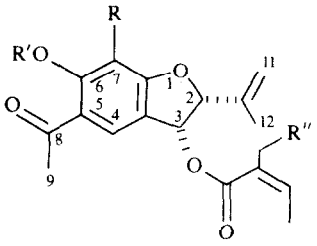
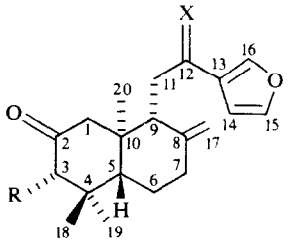


	6	7	8
R	H	OMe	OMe
R′	H	H	Me
R″	OAc	H	H



	9	10	11	12
R	H	OH	OH	OAc
X	=O	=O	OH,H	OAc,H

from the data of the diacetate (**12**) obtained on acetylation of **11**. The ^{1}H NMR data of **10** were similar to those of austrofolin (**9**)[6]; only the signals of H-1 and H-3 were different. One of the pairs of doublets was replaced by a broadened doublet at δ4.27, which was coupled with a broadened doublet at δ3.13. Deuterium exchange showed that this coupling was due to a coupling with a hydroxy group. All the signals were assigned by spin decoupling. Therefore, the diterpene was 1- or 3-hydroxyaustrofolin. The ^{1}H NMR data of **11** showed that the C-12 keto group was replaced by a hydroxyl group. Consequently, manganese dioxide oxidation afforded a diketone identical with **10**. Acetylation of **11** gave the diacetate **12**. When the ^{1}H NMR data of **10** and **12** were compared, it was obvious that the hydroxy group deshielded two of the methyl groups. This, however, required a 3-α-position of the hydroxyl group. Consequently, **10** was 3α-hydroxyaustrofolin, while **11** was 3α, 12-dihydroxy-12-desoxoaustrofolin. The MS of **10** and **12** also supported these structures. In the spectrum of **10**, elimination of water was

Table 1. ^{1}H NMR spectral data of compounds **10–12** (400 MHz, $CDCl_3$, TMS as internal standard)

	10	**11**	**12**
H-1α	2.52 *d*	2.45 *m*	2.35 *d*
H-1β	2.41 *d*		2.14 *d*
H-3β	4.27 *d*	4.30 (*br*)	4.86 *s*
H-5β	1.63 *dd*	1.6 *m*	1.55 *dd*
H-6α	1.53 *dddd*		1.43 *dddd*
H-6β	1.78 *dddd*	1.8 *m*	1.66 (*br*)
H-7α	2.45 *ddd*	2.45 *m*	2.42 *ddd*
H-7β	2.16 *ddd*(*br*)	2.0 *m*	1.90 *ddd*(*br*)
H-9β	2.77 *dd*(*br*)		2.04 *m*
H-11	3.09 *dd*	1.6 *m*	1.69 *dd*(*br*)
H-11′	2.55 *dd*		2.06 *m*
H-12	—	4.72 *dd*	5.79 *dd*
H-14	6.80 *dd*	6.44 *dd*	6.39 *d*(*br*)
H-15	7.47 *dd*	7.44 *dd*	7.42 *dd*
H-16	8.09 *dd*	7.33 *dd*	7.33 (*br*)
H-17	4.83 (*br*)	5.01 *s*(*br*)	5.01 *s*(*br*)
H-17′	4.44 *s*(*br*)	4.83 *s*(*br*)	4.96 *s*(*br*)
H-18	1.12 *s*	1.08 *s*	0.89 *s*
H-19	1.11 *s*	1.06 *s*	0.88 *s*
H-20	0.91 *s*	0.79 *s*	0.92 *s*
OAc	—	—	2.12 *s* 2.03 *s*
OH	3.13 *d*(*br*)	—	—

J (Hz): 1α, 1β = 16.5; 3, OH = 4; 5β, 6α = 12; 5β, 6β = 2.5; 6α, 6β = 13; 6α, 7α = 4; 6α, 7β = 12; 6β, 7α = 2; 6β, 7β = 4; 7α, 7β = 13; 9β, 11 = 10; 9β, 11′ = 2.5; 11, 11′ = 16.5; 14, 15 = 1.7; 14, 16 = 1; 15, 16 = 1.5; diacetate **12**. 11, 12 = 11; 11′, 12 = 4.5.

followed by splitting of the 9, 11-bond (*m*/*z* 203) and the base peak was at *m*/*z* 95 [$\overset{+}{O}$≡C–(C_4H_3O)]; in the spectrum of **12** the base peak was at *m*/*z* 97 [H$\overset{+}{O}$=CH–(C_4H_3O)]. The roots afforded **1**, **2**[7], **5–6**[4], **7** and **8**.

The constituents of the *Planaltoa* species showed relationships to those of other so far investigated genera which are placed in the subtribe Alomiinae. *Ent*-labdanes, dehydronerolidol and toxol derivatives have also been isolated from *Brickellia* species [3, 8], and *ent*-labdanes are also present in *Pleurocoronis* [9, 10], while *Pseudokirsteniopsis* so far only gave coumarin [9].

EXPERIMENTAL

The air-dried plant material, collected in February 1981 in north-eastern Brazil (voucher RMK 8821, deposited in the U. S. National Herbarium) was extracted with Et_2O–petrol (1:2). The resulting extracts were separated by CC (Si gel) and by repeated TLC (Si gel). Known compounds were identified by comparing their ^{1}H NMR spectra (400 MHz) with those of authentic materials. The aerial parts (150 g) finally gave 4 mg germacrene D, 2 mg bicyclogermacrene, 5 mg α-humulene, 10 mg lupeyl acetate, 3 mg stigmasterol, 0.1 mg **1**, 2 mg **3**, 5 mg **4**, 4 mg **5**, 80 mg **7**, 5 mg **8** (Et_2O–petrol, 2:1), 5 mg **10** (Et_2O–petrol, 3:1) and 4 mg **11** (Et_2O), while the roots (25 g) gave 2 mg **1**, 5 mg **2**, 10 mg **7**, 5 mg **6**, 50 mg **7** and 10 mg **8**.

6,7-*Dimethoxytoxol angelate* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 (C=CCO_2R), 1675, 1610 (PhCO); MS *m*/*z* (rel. int.): 360.157 [M]$^+$ (**9**) ($C_{20}H_{24}O_6$), 345 [M − ·Me]$^+$ (0.1), 260 [M − HOAng]$^+$ (34), 245 [260 − ·Me]$^+$ (12), 83 [C_4H_7CO]$^+$ (100), 55 [83 − CO]$^+$ (88); ^{1}H NMR ($CDCl_3$): δ5.24 (*d*, H-2), 6.43 (*d*, H-3), 7.57 (*s*, H-4), 2.59 (*s*, H-9), 5.22 and 5.10 [*s*(*br*), H-11], 1.81 [*s*(*br*), H-12], 4.01 and 3.99 (*s*, OMe), 6.14 (*qq*), 1.95 (dq) and 1.81 [*s*(*br*), OAng] [*J* (Hz): 2,3 = 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.3].

3α-*Hydroxyaustrofolin* (**10**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 3480 (OH), 1720 (C=O), 1690 (furan ketone); MS *m*/*z* (rel. int.): 330.183 [M]$^+$ (5) ($C_{20}H_{26}O_4$), 312 [M − H_2O]$^+$ (2), 297 [312 − Me]$^+$(2), 279 [297 − H_2O]$^+$ (4), 269 [297 − CO]$^+$ (2), 203 [312 − $CH_2CH_2C_4H_3O$]$^+$ (6), 95 [O≡C–(C_4H_3O)]$^+$ (100), 67 (95 − CO)$^+$(26);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{-24 \quad -25 \quad -27 \quad -54} \quad (c = 0.19, CHCl_3).$$

3α,12-*Dihydroxy*-12-*desoxoaustrofolin* (**11**). Colourless gum, which was purified as its diacetate **12** (1 hr Ac_2O, 70°), colourless gum, IR $\nu_{max}^{CCl_4}$ cm^1: 3080, 1640 (C=CH_2), 1750, 1240 (OAc), 1720 (C=O); MS *m*/*z* (rel. int.): 374.209 [M − ketene]$^+$ (4) ($C_{22}H_{30}O_5$), 356 [M − HOAc]$^+$ (61), 341 [356 − Me]$^+$ (6), 332 [374 − ketene]$^+$ (1), 314 [374 − HOAc]$^+$ (10), 296 [356 − HOAc]$^+$ (51), 281 [341 − HOAc]$^+$ (30), 253 [281 − CO] (14), 97 [HO=CH–(C_4H_3O)]$^+$ (100), 69 [97 − CO] (41);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+18 \quad +22 \quad +22 \quad +30} \quad (c = 0.05, CHCl_3).$$

1 mg **11** in 1 ml Et_2O was stirred with 20 mg MnO_2. TLC (Et_2O–petrol, 3:1) afforded 0.5 mg **10**, identical with the natural diketone (^{1}H NMR).

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REFERENCES

1. King, R. M. and Robinson, H. (1980) *Phytologia* **46**, 446.
2. Bohlmann, F. and Zdero, C. (1971) *Chem. Ber.* **107**, 964.
3. Bohlmann, F. and Zdero, C. (1976) *Chem. Ber.* **109**, 1436.
4. Bohlmann, F., Knoll, K.-H., Zdero, C., Mahanta, P. K., Grenz, M., Suwita, A., Ehlers, D., LeVan, N., Abraham, W.-R. and Natu, A. A. (1979) *Phytochemistry* **16**, 965.
5. Bohlmann, F., Dhar, A. K., Jakupovic, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1077.
6. Bohlmann, F., Zdero, C. and Grenz, M. (1977) *Chem. Ber.* **110**, 1034.
7. Bohlmann, F. and Jakupovic, J. (1980) *Phytochemistry* **19**, 259.
8. Bohlmann, F., Bapuji, M., Jakupovic, J., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 181.
9. Bohlmann, F., Suwita, A. and Mabry, T. J. (1978) *Phytochemistry* **17**, 763.
10. Bohlmann, F., Borthakur, N., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 2433.