containing 93% *cis*-β-santalol and 5% *epi-cis*-β-santalol) in THF (2 ml) was added $SO_3 \cdot C_5H_5N$ (0.068 g, 0.437 mmol). After stirring for 26 hr at 0°, TLC analysis of the reaction mixture indicated that all of the *cis*-β-santalol had reacted. A soln of $LiAlH_4$ (0.066 g, 1.76 mmol) in THF (2 ml) was added and the mixture stirred at 0° for 30 min and then at 25° for 3 hr. After cooling to 0°, H_2O (0.1 ml), 15% NaOH (0.1 ml), H_2O (0.3 ml) and Et_2O (10 ml) were added consecutively. The solids were removed by filtration and washed with Et_2O, and the combined extracts dried (Na_2SO_4). The solvent was evapd and the residue kugelrohr distilled (130°, 0.5 mm) to give 0.046 g (90% yield) of an oil. GLC analysis indicated 93% of β-santalene (**5**) and 5% of *epi*-β-santalene (**6**). The ^1H NMR and combined GC/MS data for the products are consistent with previously reported data [4, 7].

Reduction of β-santalols from East Indian sandalwood oil. A sample of β-santalols (0.0190 g, 0.086 mmol) isolated from the natural oil was reduced as described above to give 0.011 g of an oil. GLC analysis indicated 76% of β-santalene (**5**) and 12.5% of *epi*-β-santalene (**6**).

REFERENCES

1. Demole, E., Demole, C. and Enggist, P. (1976) *Helv. Chim. Acta* **59**, 737.
2. Klein, E. and Rojahn, W., 6th International Congress of Essential Oils. San Francisco, Calif., 12 September 1974, paper No. 163.
3. Guenther, E. (1952) *The Essential Oils*, Vol. 5, pp. 173–186. Robert Krieger, Huntington, N.Y.
4. Christenson, P. A. and Willis, B. J. (1979) *J. Org. Chem.* **44**, 2012.
5. Brieger, G. (1963) *Tetrahedron Letters* 2123.
6. Hodgson, G. L., MacSweeney, D. F. and Money, T. (1973) *J. Chem. Soc. Perkin Trans.* 1, 2113.
7. Christenson, P. A. and Willis, B. J. (1980) *J. Org. Chem.* **45**, 3068.
8. Corey, E. J. and Achiwa, K. (1969) *J. Org. Chem.* **34**, 3667.

Phytochemistry, Vol. 20, No. 5, pp. 1141–1143, 1981.
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A LABDANE DERIVATIVE FROM *CHROMOLAENA COLLINA* AND A *p*-HYDROXYACETOPHENONE DERIVATIVE FROM *STOMATANTHES CORUMBENSIS**

FERDINAND BOHLMANN†, CHRISTA ZDERO†, LOTHAR FIEDLER†, HAROLD ROBINSON‡ and ROBERT M. KING‡

† Institute for Organic Chemistry, Technical University of Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, West Germany; ‡ Smithsonian Institution, Washington, DC 20560, U.S.A.

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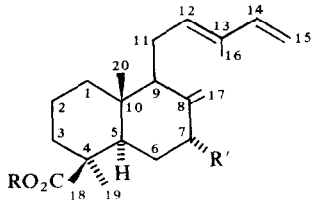
Key Word Index—*Chromolaena collina*; *Stomatanthes corumbensis*; Compositae; Eupatorieae; labdane derivative; *p*-hydroxyacetophenone derivative.

Abstract—A new labdane derivative, 7α-acetoxy-*trans*-communic acid was isolated from *Chromolaena collina*. Extraction of *Stomatanthes corumbensis* yielded a new *p*-hydroxyacetophenone derivative which was identified as 4-methoxy-3-[3′-methyl-4′-angeloyloxy-but-2-en-1′-yl]-acetophenone.

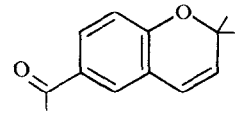
The results obtained so far on the chemistry of the genus *Chromolaena* (*Praxelis* group, tribe Eupatorieae) [1] are not very uniform [2–4]. We have now investigated a further species, *C. collina* (DC) K. et R. The roots only afforded germacrene D and *trans*-communic acid (**1**) [5], while the aerial parts yielded germacrene D, caryophyllene epoxide and **1**, and, in addition, the labdane derivative, **2a**, which on esterification gave **2b**. The structure of **2a** followed from the ^1H NMR data (Table 1). The stereochemistry at C-7 was deduced from the observed small coupling $J_{6,7}$, while the position of the acetoxy group could be established by spin decoupling. As the absolute configuration of **1** was established, **2a** most probably had the same configuration. These results again show the complexity of the chemistry of this genus.

The genus *Stomatanthes* is placed in the Eupatoriinae (tribe Eupatorieae, Compositae) [1]. So far, only the occurrence of coumarin in *S. africanus* has been reported [6]. We have now investigated *S. corumbensis* (B. L.

* Part 325 in the series "Naturally Occurring Terpene Derivatives". For Part 324 see Bohlmann, F., Dhar, A. K., Jakupovic, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1077.



1 R = R′ = H
2a R = H, R′ = OAc
2b R = Me, R′ = OAc



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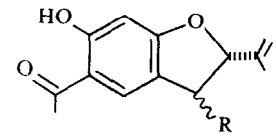
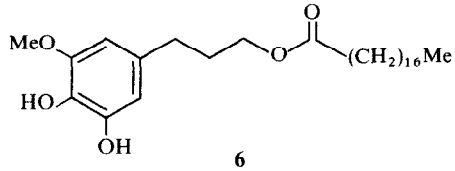


4 R = αOH
5 R = βOMe



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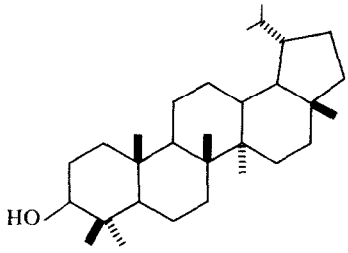
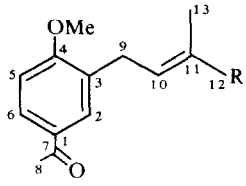


7 Δ9,11 **8** Δ12, 13



9 R = CH_2OAng
10 R = CH_2OH
11 R = CHO

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

	2a ($CDCl_3$)	**2b** (C_6D_6)
7-H	5.51 *br. dd*	5.69 *br. dd*
11-H	2.45 *br. dd*	2.35 *br. dd*
11′-H	2.23 *m*	2.01 *m*
12-H	5.39 *br. t*	5.53 *br. t*
14-H	6.32 *dd*	6.50 *dd*
15*c*-H	4.89 *br. d*	4.97 *br. d*
15*t*-H	5.05 *br. d*	5.13 *br. d*
16-H	1.76 *br. s*	1.73 *d*
17-H	4.86 *br. s*	4.88 *br. d*
17′-H	4.66 *br. s*	4.73 *br. d*
19-H	1.31 *s*	1.16 *s*
20-H	0.99 *s*	1.08 *s*
OAc	1.91 *s*	1.77 *s*
OMe	—	3.26 *s*

J (Hz): 6α, 7 = 4.5; 6β, 7 = 2.5; 7, 17 ~ 1.5; 11, 11′ = 15; 11, 12 = 7; 14. 15 *trans* = 17.5; 14, 15 *cis* = 10.5.

Table 2. ^{1}H NMR spectral data of compounds **9**–**11** ($CDCl_3$)

	9	**10**	**11**
2-H	7.78 *d*	7.78 *d*	7.81 *d*
5-H	6.88 *d*	6.88 *d*	6.91 *d*
6-H	7.85 *dd*	7.85 *dd*	7.89 *dd*
8-H	2.54 *s*	2.54 *s*	2.56 *s*
9-H	3.46 *br. d*	3.43 *br. d*	3.91 *br. d*
10-H	5.54 *br. t*	5.44 *br. t*	6.56 *br. t*
12-H	4.80 *br. s*	4.25 *br. s*	10.36 *s*
13-H	1.82 *dt*	1.83 *dt*	1.79 *dt*
OCOR	6.08 *qq*	—	—
	1.99 *dq*	—	—
	1.90 *dq*	—	—
OMe	3.89 *s*	3.90 *s*	3.90 *s*

J (Hz): 2, 6 = 2; 5, 6 = 8; 9, 10 = 7; 9, 13 = 10, 13 ~ 1.5; 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.

Robins.) K. et R. The roots afforded the chromene derivative **3** [7], the toxol derivatives **4** [8] and **5** [9], lupeyl acetate and tridecapentaynene, while the aerial parts gave germacrene D, bicyclogermacrene, lupeol and its acetate, as well as the isomers **7** and **8**, stigmasterol, the stearate **6** [10] and a new *p*-hydroxyacetophenone derivative, the angelate **9**. Saponification afforded the alcohol **10**, which on manganese dioxide oxidation gave the aldehyde **11**. The ^{1}H NMR data of these three compounds clearly established the structures and the configuration of the double bond, which was indicated by the chemical shift of 10-H in the spectrum of **11**. The substitution pattern of the aromatic ring directly followed from the chemical shifts of the signals of the aromatic protons.

While *Eupatorium* species (placed in the same group) mainly contain sesquiterpene lactones, a few species also afforded *p*-hydroxyacetophenone derivatives. However, compound **6** has, at present, been isolated only from an *Aristeguietia* species [10]. Clearly more species have to be investigated to see whether the chemistry of *Stomatanthes* is related to *Eupatorium* and to the other genera of this group.

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 further by TLC (Si gel). Known compounds were identified by comparing the IR and ^{1}H NMR spectra with those of authentic material.

Chromolaena collina (voucher RMK 7318). The roots (50 g) afforded 14 mg germacrene D and 28 mg **1**, while the aerial parts (75 g) yielded 48 mg germacrene D, 11 mg caryophyllene epoxide, 110 mg **1** and 19 mg **2a** (Et_2O–petrol, 3:1).

Stomatanthes corumbensis (voucher RMK 8244). The roots (200 g) afforded traces of tridecapentaynene, 4 mg lupeyl acetate, 2 mg **3**, 2 mg **4** and 2 mg **5**, while the aerial parts (1 kg) gave 40 mg germacrene D, 2 mg bicyclogermacrene, 60 mg lupeyl acetate, 100 mg lupeol, stigmasterol, 100 mg **6**, 20 mg **7**, 20 mg **8** and 50 mg **9** (Et_2O–petrol, 1:1).

*7α-Acetoxy-*trans*-communic acid* (**2a**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2500, 1695 (CO_2H), 1740 (OAc), 1652, 1620, 995, 900 (C=C); MS *m/z* (rel. int.): 360.230 (M^+, 3) ($C_{22}H_{32}O_4$), 300 (M − HOAc, 28), 255 (300 − CO_2H, 11), 81 (C_6H_9, 100). $[\alpha]_D$ = 0.40 (*c* = 1.75, $CHCl_3$). To 19 mg **2a** excess CH_2N_2 in Et_2O was added. TLC (Et_2O–petrol, 1:1) afforded 15 mg **2b**. For ^{1}H NMR see Table 1.

4-Methoxy-3-[3′-methyl-4′-angelyoxy-but-2-en-1′-yl]-acetophenone (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1650 (C=CCO_2R), 1680, 1603 (PhCO); MS *m/z* (rel. int.): 316 (M^+, 0.2), 216. 115 (M − AngOH, 100) ($C_{14}H_{16}O_2$), 201 (216 − Me, 57), 173 (201 − CO, 87), 83 ($C_4H_7CO^+$, 80), 55 (83 − CO, 98). Compound **9** (5 mg) in 1 ml MeOH was heated for 5 min with 0.2 ml 2 N KOH. TLC (Et_2O–petrol, 3:1) afforded 3 mg **10**, which was stirred for 2 hr with 50 mg MnO_2. TLC (Et_2O–petrol, 1:1) gave 2 mg **11**. For (^{1}H NMR see Table 2).

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REFERENCES

1. Robinson, H. and King, R. M. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) pp. 438–485. Academic Press, London.
2. Bohlmann, F. and Fiedler, L. (1978) *Chem. Ber.* **111**, 408.
3. Bohlmann, F. and Zdero, C. (1977) *Chem. Ber.* **110**, 487.
4. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1979) *Phytochemistry* **18**, 1177.
5. Thomas, B. P. (1966) *Acta Chem. Scand.* **20**, 1074.
6. Wehner, C. (1929–1931) *Die Pflanzenstoffe*, Jena.
7. Bohlmann, F. and Grenz, M. (1970) *Chem. Ber.* **103**, 90.
8. Bohlmann, F., Mahanta, P. K., Suwita, A., Suwita, Ant., Natu, A. A., Zdero, C., Dorner, W., Ehlers, D. and Grenz, M. (1977) *Phytochemistry* **16**, 1973.
9. Bohlmann, F., Zdero, C., Gupta, R. K., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, 2695.
10. Bohlmann, F., Rosenberg, E., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, 977.