mp 161-163°; $[\alpha]_D^{29} -57.4°$ (EtOAc; $c = 0.406$); R_f 0.70; IR ν_{max}^{nujol} cm^{-1}: 3490, 3300, 3096, 3082, 1745, 1703, 1625, 1152, 1098, 1040, 895, 805, 760; UV λ_{max}^{EtOH} nm (log ϵ): 245 (2.36, sh), 215 (4.19); ^{1}H NMR (100 MHz, pyridine-d_5 TMS int. standard) δ 7.47 (*d*, $J = 2$ Hz, H-3), 7.29 (*d*, $J = 1$ Hz, H-10), 6.38 (*td*, $J = J' = 6$ Hz, $J'' = 2$ Hz, H-6), 5.33 (*d*, $J = 6$ Hz, H-7), 5.33 (*d*, $J = 4$ Hz, H-1), 4.82 (*br q*, $J = 7$ Hz, $J' = 1$ Hz, H-13), 3.94 (*br q*, $J = 8$ Hz, H-5), 3.53 (*s*, $-COOC\underline{H}_3$), 3.10 (*q*, $J = 8$ Hz, $J' = 4$ Hz, H-9), 1.47 (*d*, $J = 7$ Hz, $C\underline{H}_3$-14). Other spectral data are in the text.

Acknowledgement—We thank Dr Chr. Bergner, Halle/S., for the bioassay.

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Phytochemistry, Vol. 21, No. 6, pp. 1439–1441, 1982.
Printed in Great Britain.

0031-9422/82/061439-03$03.00/0

GERMACRANOLIDES FROM *PIPTOLEPIS LEPTOSPERMOIDES**

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(*Received* 18 *August* 1981)

Key Word Index—*Piptolepis leptospermoides*; Compositae; Vernonieae; sesquiterpene lactones; furanoheliangolide; germacranolide.

Abstract—*Piptolepis leptospermoides* afforded, in addition to known compounds, a new eremanthanolide and a germacranolide closely related to piptolepolide.

The small Brazilian genus *Piptolepis* is placed in the subtribe Lychnophorinae [1]. So far the chemistry has supported this assignment, as, in addition to triterpenes derived from lupane, a furanoheliangolide has been isolated [2]. We have now studied the constituents of *Piptolepis leptospermoides* (DC) Sch. Bip. The roots afforded polyisoprene, lupeyl acetate, lupenone, taraxasteryl acetate, taraxasterone and eremanthin (**1**) [3], while the aerial parts gave germacrene D, α-humulene, bisabolene, squalene, lupenone and lupeyl acetate. The polar fractions contained a mixture of small amounts of sesquiterpene lactones which were separated with difficulty into the furanoheliangolides **2** [4] and **3** [5], the eremanthanolides **4** [6], **5** [7] and **6** and the germacranolide **7**. The structures were elucidated by their ^{1}H NMR spectra. The spectrum of **6** (Table 1) showed the typical signal of a furanoheliangolide (5.72 *s*), and those of an eremantholide. Most signals were similar to those of eremantholide C [6, 7]. However, the olefinic methyl group was missing. A broadened two-proton singlet at δ 4.39 indicated a 15-hydroxy group. Accordingly, the H-5 signal was shifted downfield (6.31 *dt*), as in the spectrum of a closely-related eremanthanolide from a *Lychnophora* species [7]. The ^{1}H NMR spectrum of **7** (Table 1) showed the presence of a methylene lactone by the typical downfield doublets at δ 6.32 and 5.70. These protons were coupled with a four-fold doublet at δ 2.94, as was shown by spin decoupling. The latter was further coupled with a three-fold doublet at δ 5.00 and 4.45. Irradiation at δ 5.00 collapsed the double doublet at 2.61 to a doublet and sharpened a broadened doublet at δ 2.15. As these two signals also showed a geminal coupling of 14 Hz partial structure **A** was assigned.

From further decouplings the presence of sequence **B** was deduced. The chemical shifts of H-2 indicated the neighbouring keto group, the position of which

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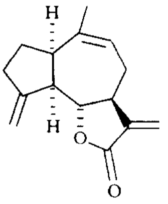
*Part 416 in the series "Naturally Occurring Terpene Derivatives". For Part 415 see Bohlmann, F., Ahmed, M., Robinson, H. and King, R. M. (1982) *Phytochemistry* **21** (in press).

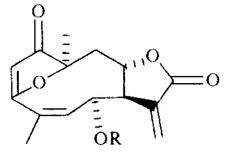
Table 1. ^{1}H NMR spectral data of compounds **6** and **7** (400 MHz, $CDCl_3$, TMS as int. standard)

	6	**7**	(C_6D_6)
H-2 }	5.72 *s*	2.90 *dd*	2.44 *dd*
H-2′ }		3.16 *dd*	2.71 *dd*
H-3	—	4.24 *m*	3.84 *m*
H-4	—	2.06 *m*	2.04 *m*
H-5 }	6.31 *dt*	1.53 *ddd*	1.25 *ddd*
H-5′ }		2.10 *ddd*	1.86 *dd*
H-6	5.06 *dd*	4.45 *ddd*	4.10 *dddd*
H-7	2.81 *dd*	2.94 *dddd*	2.97 *dddd*
H-8	4.16 *ddd*	5.00 *ddd*	4.92 *ddd*
H-9	2.08 *dd*	2.15 *dd*	1.84 *dd*
H-9′	2.42 *dd*	2.61 *dd*	2.57 *dd*
H-13 }	1.20 *s*	5.70 *d*	5.25 *d*
H-13′ }		6.32 *d*	6.23 *d*
H-14	1.51 *s*	1.90 *s*	1.72 *s*
H-15	4.39 *br s*	1.14 *d*	0.84 *d*
H-18	5.08 *dq* }	6.16 *qq* }	5.75 *qq*
H-18′	5.33 *dq* }		
H-19	—	2.00 *dq* }	2.00 *dq*
H-20	1.90 *br s*	1.84 *dq*	1.75 *dq*
OAc	—	2.04 *s*	1.63 *s*

J (Hz): Compound **6**: 5,6 = 2.5; 6,7 = 7; 7,8 = 4; 8,9 = 11; 8,9′ = 2.5; 9,9′ = 13.5; 18,18′ = 18,20 ~ 1; compound **7**: 2,2′ = 19; 2,3 = 10; 2′,3 = 5;4,5 ~ 3; 4,5′ ~ 7.5; 5,5′ = 13; 5,6 ~ 10; 5′,6 ~ 4; 6,7 ~ 7; 7,8 = 4; 7,13 = 2.5; 7,13′ = 2.3; 8,9 ~ 1; 8,9′ = 9; 9,9′ = 14; 18,19 = 7; 18,20 = 19,20 = 1.5.

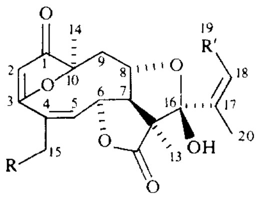


1

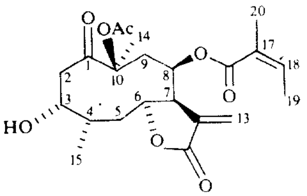


2 R = Ang

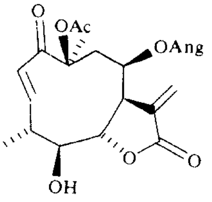
3 R = Mebu



	4	**5**	**6**
R	H	H	OH
R′	H	Me	H



7



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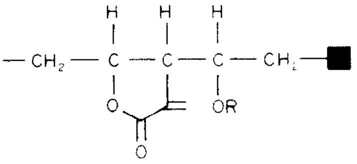
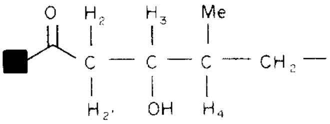


A



B

was further supported by the typical downfield shift of H-14 (1.9 *s*). As it was most probable that a hydrogen bridge was present between the hydroxyl at C-3 and the keto group, inspection of a model allowed the stereochemistry at C-3 to be deduced from the couplings of H-2. Though the coupling $J_{3,4}$ could not be seen directly as H-3 and H-4 were multiplets, spin decoupling showed that this coupling was small and favoured α-orientation of the C-4 methyl group. The stereochemistry at C-6 through C-8 also followed from the couplings observed, expecially when they were compared with those of similar compounds. That at C-10 was only assigned by analogy, since so far all sesquiterpene lactones of this type from Vernonieae seem to have this configuration. Compound **7**, which we have named piptospermolide, is closely related to piptolepolide (**8**) isolated from the same genus[2].

The chemistry of the second *Piptolepis* species again supports the placement of this genus in the subtribe Lychnophorinae, since furanoheliangolides and eremanthanolides are present in all genera except *Albertinia* [8].

EXPERIMENTAL

The air-dried plant material (voucher RMK 8562, deposited in the U.S. National Herbarium, Washington) 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). Compounds were identified by comparing the ^{1}H NMR spectra with those of authentic compounds. The roots (30 g) afforded 20 mg polyisoprene, 150 mg lupeyl acetate, 30 mg lupenone, 80 mg taraxasteryl acetate, 20 mg taraxasterone and 4 mg **1**, while the aerial parts (320 g) gave 2 mg germacrene D, 1 mg α-humulene, 2 mg bisabolene, 5 mg squalene, 30 mg lupeyl acetate, 700 mg lupenone, 3 mg **2**, 3 mg **3**, 2 mg **4**, 2 mg **5**, 2 mg **6** (CH_2Cl_2–C_6H_6–Et_2O, 1 : 1 : 1) and 1 mg **7** (same solvent).

15-*Hydroxyeremantholide C* (**6**). Colourless gum IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3380 (OH), 1780 (γ-lactone), 1695, 1580 (ROC=C–C=O), 910 ($C=CH_2$); MS (CI, *iso*-butane) *m/z* (rel. int.): 363 $[M+1]^+$ (12), 345 $[363 - H_2O]^+$ (63), 180 (100).

Piptospermolide (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3400 (OH), 1780 (γ-lactone), 1720 ($C=CCO_2R$), 1700 (C=O); MS (CI, *iso*-butane) *m/z* (rel. int.): 423 $[M+1]^+$ (14), 405 $[423 - H_2O]^+$ (7), 363 $[423 - HOAc]^+$ (14), 323 $[423 - HOAng]^+$ (34), 263 $[323 - HOAc]^+$ (10), 180 (100).

Acknowledgements—We thank Drs. Scott A. Mori and P. Alvim, Herbario Centro de Pesquisas do Cacau at Itabanu, Bahia, Brazil, for their help during plant collection and the Deutsche Forschungsgemeinschaft for financial support.

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Phytochemistry, Vol. 21, No. 6, pp. 1441–1443, 1982.
Printed in Great Britain.
0031-9422/82/061441-03$03.00/0

XANTHANOLIDES FROM *XANTHIUM INDICUM**

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(*Received* 16 *October* 1981)

Key Word Index—*Xanthium indicum*; Compositae; sesquiterpene lactones; xanthanolides.

Abstract—From the aerial parts of *Xanthium indicum*, in addition to known compounds, two new xanthanolides were isolated and the stereochemistry of xanthumin has been proposed.

From *Xanthium indicum* Koen. ex Roxb., xanthinosin has been isolated[1]. A re-investigation of the aerial parts of this plant afforded germacrene D, β-selinene, phytol, xanthanodiene (**1**)[2], isoalantolactone (**2**)[3], the eudesmanolide (**3**)[4] and its 8-epimer (**4**)[5], 8-epixanthatin (**5**)[1], 2-hydroxytomentosin (**6**)[6], xanthumin (**7**)[7], tomentosin (**10**)[8], large amounts of 4-oxo-bedfordia acid (**11**)[9], isoguaiene (**12**) and two new xanthanolides, the epoxide **9** and the 2-epi-xanthumin (**8**), while xanthinosin was not isolated. The structure of **9** followed from the molecular formula and the ^{1}H NMR spectrum (Table 1), which was similar to that of 8-epi-xanthatin (**5**). The presence of a 4, 5-epoxide was indicated by the doublet at δ 3.05 which was coupled with a pair of three-fold doublets at δ 2.04 and 2.14. Irradiation of the H-7 signal collapsed these signals to double doublets and further decouplings allowed the assignment of the signals of H-7 through H-10. Though the stereochemistry at C-5 could not be established with certainty, inspection of models favoured a β-epoxide if the couplings $J_{5,6}$ were considered. The structure of **8** followed from the ^{1}H NMR spectral data (Table 1) which were similar to those of xanthumin (**7**). However, a few signals were characteristically different. In particular the downfield shifts of the H-2 and H-5 signals were very significant. Inspection of models showed that this effect could be explained only if the side chains of **7** and **8** had fixed conformations.

Table 1. ^{1}H NMR spectral data of compounds **7**–**9** (400 MHz, CDCl$_3$, TMS as int. standard)

	7	**8**	**9**
H-2	5.40 *dd*	5.19 *dd*	6.72 *d*
H-3	2.90 *dd*	2.64 *d*(*br*)	6.25 *d*
H-3′	2.59 *dd*	2.18 *dd*	
H-5	5.83 *dd*	5.52 *dd*	3.05 *dd*
H-6α	2.28 *ddd*	2.18 *ddd*	2.14 *ddd*
H-6β	2.45 *dddd*	2.45 *m*	2.04 *ddd*
H-7	3.28 *ddddd*	3.26 *ddddd*	3.28 *ddddd*
H-8	4.62 *ddd*	4.65 *ddd*	4.60 *ddd*
H-9α	2.03 *ddd*	2.03 *ddd*	1.85 *ddd*
H-9β	1.85 *ddd*	1.94 *ddd*	1.70 *ddd*
H-10	2.65 *ddq*(*br*)	2.45 *ddq*	2.27 *ddq*
H-13	6.25 *d*	6.27 *d*	6.28 *d*
H-13′	5.52 *d*	5.53 *d*	5.65 *d*
H-14	1.12 *d*	1.17 *d*	1.11 *d*
H-15	2.18 *s*	2.19 *s*	2.25 *s*
OAc	2.00 *s*	2.16 *s*	—

J(Hz): Compound **7**: 2, 3 = 9; 2, 3′ = 4.5; 3, 3′ = 16.5; 5, 6α = 5; 5, 6β = 9; 6α, 6β = 14; 6α, 7 = 7; 6β, 7 = 12; 6β, 10 = 1; 7, 8 = 8.5; 7, 13 = 3; 7, 13′ = 2.7; 8, 9α = 2.5; 8, 9β = 12; 9α, 9β = 14; 9α, 10 = 6; 9β, 10 = 12; 10, 14 = 7; compound **8**: 2, 3 = 3; 2, 3′ = 10; 3, 3′ = 15; 5, 6α = 5; 5, 6β = 9; 6α, 6β = 14; 6α, 7 = 7; 6β, 7 = 11; 7, 8 = 8.5; 7, 13 = 3; 7, 13′ = 2.7; 8, 9α = 2.7; 8, 9β = 11.5; 9α, 9β = 14; 9α, 10 = 6; 9β, 10 = 12; 10, 14 = 7; compound **9**: 2, 3 = 15; 5, 6α = 5; 5, 6β = 7.5; 6α, 6β = 14; 6α, 7 = 3.5; 6α, 7 = 3.5; 6β, 7 = 13; 7, 8 = 7.5; 7, 13 = 2.5; 7, 13′ = 2; 8, 9α = 4; 8, 9β = 11.5; 9α, 9β = 14; 9α, 10 = 2.5; 9β, 10 = 12; 10, 14 = 7.

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*Part 427 in the series "Naturally Occurring Terpene Derivatives". For Part 426 see Bohlmann, F. and Chen, Z. L. (1982) *Phytochemistry* **21** (in press).