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.

REFERENCES

1. Robinson, H., Bohlmann, F. and King, R. M. (1980) *Phytologia* **46**, 421.
2. Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 731.
3. Vichnewski, W. and Gilbert, B. (1972) *Phytochemistry* **11**, 2563.
4. Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 2381.
5. Vichnewski, W., Lopes, J. N. C., Filho, D. D. S. and Herz, W. (1976) *Phytochemistry* **15**, 1770.
6. Le Quesne, P. W., Levery, S. B., Menadery, M. D., Brennan, T. F. and Raffauf, R. F. (1978) *J. Chem. Soc. Perkin Trans.* 1 1572.
7. Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1982) *Phytochemistry* **21**, 1087.
8. Bohlmann, F., Singh, P., Zdèro, C., Ruhe, A., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21** (in press).

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*[*]

FERDINAND BOHLMANN, PAHUP SINGH, KRISHNA C, JOSHI† and CHANDRA L. SINGH†

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany;
†Department of Chemistry, University of Rajasthan, Jaipur-302004, India

(*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.

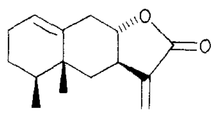
Table 1. ^{1}H NMR spectral data of compounds **7**–**9** (400 MHz, $CDCl_3$, TMS as int. standard)

	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*	—

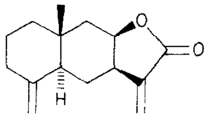
J(Hz): Compound **7**: 2, 3 = 9; 2, 3′ = 4.5; 3, 3′ = 16.5; 5, 6α = 5; 5, 6β = 9; 6α, 6β = 14; 6α, 7 = 7; 6β, 7 = 12; 6β, 10 = 1; 7, 8 = 8.5; 7, 13 = 3; 7, 13′ = 2.7; 8, 9α = 2.5; 8, 9β = 12; 9α, 9β = 14; 9α, 10 = 6; 9β, 10 = 12; 10, 14 = 7; compound **8**: 2, 3 = 3; 2, 3′ = 10; 3, 3′ = 15; 5, 6α = 5;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

---

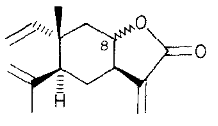
[*] Part 427 in the series "Naturally Occurring Terpene Derivatives". For Part 426 see Bohlmann, F. and Chen, Z. L. (1982) *Phytochemistry* **21** (in press).



1

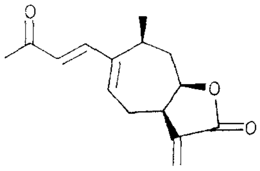


2

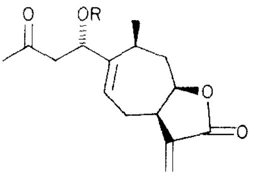


3 8β-H

4 8α-H

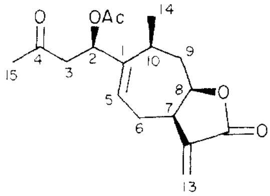


5

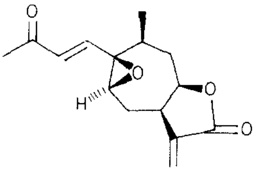


6 R=H

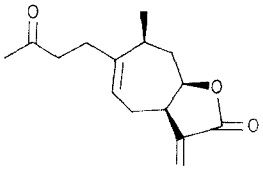
7 R=Ac



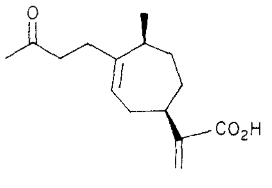
8



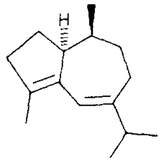
9



10



11



12

Most probably the steric hindrance by the 10-methyl group was important in leading to a conformation of **8** where the acetoxy group deshielded H-5, while **7** had a conformation, where the acetoxyl group deshielded H-10. Accordingly, xanthumin (**7**) would be the 2 *R*-isomer. Analogous epimers of xanthanol are present in *X. orientale* [10]. Following the *Index Kewensis X. indicum* should be identical with *X. strumarium*, which also contains xanthanolides, but not the same ones. *X. indicum* therefore is probably a variety.

EXPERIMENTAL

The air-dried plant material (500 g), collected from the University Campus of Rajasthan, Jaipur (voucher deposited in the RUBL Herbarium), was extracted with Et_2O–petrol (1 : 2) and the resulting extract was separated by CC (Si gel) and further by repeated TLC (Si gel) affording 5 mg germacrene D, 10 mg β-selinene, 20 mg phytol, 100 mg **1**, 7 mg **2**, 5 mg **3**, 5 mg **4**, 20 mg **5**, 10 mg **6**, 1.62 g **7**, 1 mg **8** (Et_2O–petrol, 3 : 1), 5 mg **9** (Et_2O–petrol, 3 : 1), 20 mg **10**, 500 mg **11**, 2 mg **12** and 2 mg **13**.

2-Epi-xanthumin (**8**). Colourless crystals (amount not sufficient to get a clear mp), IR $\nu^{CCl_4}_{max}$, cm^{-1}: 1775 (γ-lactone), 1740 (OAc), 1730 (C=O); MS *m/z* (rel. int.): 246.126 $[M-HOAc]^+$ (38 ($C_{15}H_{18}O_3$), 231 $[246-Me]^+$ (47), 203 $[231-CO]^+$ (38), 135 (100); CI (*iso*-butane): 307 $[M+1]^+$ (100);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589}{+10}\quad\frac{578}{+10}\quad\frac{546}{+22}\quad\frac{436\text{ nm}}{+142}\ (CHCl_3;\ c\ 0.05).$$

8-Epi-xanthatin-1β, 5β-epoxide (**9**). Colourless gum, IR $\nu^{CHCl_3}_{max}$, cm^{-1}: 1760 (γ-lactone), 1700, 1630 (C=CC=O); MS *m/z* (rel. int.): 262 $[M]^+$ (0.5) ($C_{15}H_{18}O_4$), 247 $[M-Me]^+$ (1), 219 $[247-CO]^+$ (7), 109 (100); CI (*iso*-butane): 263 $[M+1]+$ (100), 219 $[M-MeCO]^+$(70);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589}{+29}\quad\frac{578}{+31}\quad\frac{546}{+33}\quad\frac{436\text{ nm}}{+47}\ (CHCl_3;\ c\ 0.4).$$

Acknowledgements—We thank the Deutsche Forschungsgemeinschraft for financial support and the University Grant Commission, New Delhi, for a fellowship to C. L. S.

REFERENCES

1. McMillan, C., Chavez, P. I., Plettman, S. G. and Mabry, T. J. (1975) *Biochem. Syst. Ecol.* 181.
2. Tanaka, N., Yazawa, T., Aayama, K. and Murakami, T. (1976) *Chem. Pharm. Bull.* 1419.
3. Benesova, V., Herout, V. and Sorm, F. (1961) *Collect. Czech. Chem. Commun.* **26**, 2916.
4. Bohlmann, F. and Dutta, N. (1979) *Phytochemistry* **18**, 847.
5. Bohlmann, F. and Dutta, L. N. (1979) *Phytochemistry* **18**, 1228.

6. Bohlmann, F., Jakupovic, J. and Schuster, A. (1981) *Phytochemistry* **20**, 1891.
7. Minato, H. and Horibe, I. (1965) *J. Chem. Soc.* 7009.
8. Julia, M. and Uguen, D. (1976) *Bull. Soc. Chim. Fr.* 513.
9. Bohlmann, F. and LeVan, N. (1978) *Phytochemistry* **17**, 1173.
10. Bohlmann, F. and Zdero, C. (1981) *Phytochemistry* **20** 2429.

Phytochemistry, Vol. 21, No. 6, pp. 1443–1445, 1982.
Printed in Great Britain.
0031-9422/82/061443-03$03.00/0

INEUPATOROLIDE-LIKE SESQUITERPENE LACTONES FROM *DITTRICHIA VISCOSA*[*]

FERDINAND BOHLMANN and RAJINDER K. GUPTA

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany

(*Received* 20 *October* 1981)

Key Word Index—*Dittrichia viscosa*; Compositae; Inuleae; sesquiterpene lactones; germacranolides.

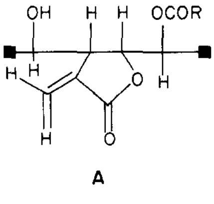
Abstract—*Dittrichia viscosa* afforded, in addition to known compounds, minute amounts of nine sesquiterpene lactones, all closely related to ineupatorolide B, some of which could not be separated from each other. The structures could be elucidated by high field ^{1}H NMR spectroscopy. The chemotaxonomic importance of these compounds is discussed briefly.

INTRODUCTION

The small Mediterranean genus *Dittrichia*, in the subtribe Inulinae [1] has not been investigated chemically. We now have studied the constituents of *D. viscosa* (L.) Greuter. The results are discussed here.

RESULTS AND DISCUSSION

The roots gave the thymol derivative **1** [2] and a mixture of sesquiterpenes, the germacranolides **3a** (main constituent), **3c–3f** and **4a–4c**. The ^{1}H NMR spectrum (Table 1) of **3a** clearly showed that a methyl senecioate was present, which in addition to the keto and methylene lactone group contained two hydroxyl groups. While one of these groups was indicated by the double doublet at δ 3.86, the presence of the second one followed indirectly from the molecular formula and from the IR spectrum of the monoacetate obtained by acetylation. Spin decoupling in the usual way starting with the H-7 signal allowed the assignment of the sequence A:



A

As the hydroxyl at C-6 showed a hydrogen bond, a keto group at C-5 was very likely. The doublet doublet quartet at δ 3.16 was coupled with the methyl doublet at δ 1.18. The chemical shift of the former signal indicated a neighbouring keto group, thus indicating that the secondary methyl group was at C-4. Therefore, the tertiary hydroxyl had to be placed at C-10 leading to the structure **3a**, a lactone closely related to ineupatorolide B (**2**) [3], where, however, the 6-hydroxy group is missing and the ester group is replaced by an angelate residue. Accordingly, the ^{1}H NMR spectral data of **3a** and **2** were in part similar. In particular, the coupling of H-4, H-8 and H-9 were the same, indicating identical stereochemistry at C-4 and C-7 through C-9. The α-orientation of the hydroxyl at C-6 followed from the coupling $J_{6,7}$ while the chemical shift of H-14 indicated the same stereochemistry at C-10 as that of ineupatorolide B, the stereochemistry of which had been established by X-ray analysis [3]. Furthermore, **3a** was closely related to similar lactones isolated from *Inula cuspidata* [4].

In addition to **3a** minute amounts of four other esters were isolated, which could not be separated. The mass spectrum as well as the ^{1}H NMR spectral data, however, indicated the presence of **3c–3f**. Furthermore, three lactones were isolated, the germacranolides **4a–4c**, as followed from the ^{1}H NMR spectrum (Table 1) and the molecular formula. Again **4b** and **4c**, which differed in the ester groups only, could not be separated completely from the isobutyrate **4a**, which was the main constituent of the mixture. Spin decoupling allowed the assignment of the sequence H-4 through H-9. As the molecular

---

[*] Part 434 in the series "Naturally Occurring Terpene Derivatives". For Part 433 see Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21**, (in press).