6 mg **2** was heated with 0.5 ml Ac_2O at 80° for 1 hr. TLC gave 3.5 mg **4** and 1.5 mg **3** (^1H NMR spectra, see Table 1).

11α, 13-*dihydrozaluzanin C* (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3470 (OH), 1785 (γ-lactone); MS *m/z* (rel. int.): 248 $[M]^+$ (9), 230 $[M-H_2O]^+$ (4), 177 (28), 157 (12), 152 (37), 134 (41), 121 (12), 105 (27), 81 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-12 \quad -10 \quad +4 \quad +86.4} \quad (c = 0.25,\ CHCl_3)$$

Acknowledgements—Z.-L. C. thanks the Alexander von Humboldt foundation for a stipendium and Mrs. S. L. Huang, Shanghai, Institute of Materia Medica, Chinese Academy of Sciences for identification of the plant material.

REFERENCES

1. Editor in chief: Institute of Botany, Chinese Academy of Sciences (1975) *Iconogr. Cormophyt. Sin.* **4**, 663.
2. Vivar, A. R. de, Cabrera, A., Ortega, A. and Romo, J. (1967) *Tetrahedron* **23**, 3903.
3. Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21**, 647.
4. Bohlmann, F. and LeVan, N. (1977) *Phytochemistry* **16**, 487.

Phytochemistry, Vol. 21, No. 8, pp. 2122–2124, 1982.
Printed in Great Britain.

0031-9422/82/082122–03$03.00/0

GERMACRANOLIDES FROM *DICOMA TOMENTOSA**

FERDINAND BOHLMANN, PAHUP SINGH and JASMIN JAKUPOVIC

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

(*Received* 16 *October* 1981)

Key Word Index—*Dicoma tomentosa*; Compositae; Mutisieae; sesquiterpene lactones; germacranolides; melampolides.

Abstract—An investigation of the aerial parts of *Dicoma tomentosa* afforded four new germacranolides and four melampolides together with urospermal A and its 11β,13-dihydroderivative. The structures were elucidated by spectroscopic methods. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

The genus *Dicoma* (Compositae, tribe Mutisieae) is placed in the subtribe Gochanatiinae [1] Chemical investigations have shown that 14, 15-oxygenated germacranolides are present [2] in one species, while two others only afforded acetylenic compounds and an allenic acid [2, 3]. We have now investigated a further species, *D. tomentosa*, which again gave germacranolides.

RESULTS AND DISCUSSION

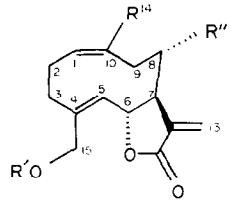
While the roots of *Dicoma tomentosa* only afforded the triterpenes taraxasterol, stigmasterol, sitosterol and lupeyl acetate, the aerial parts gave taraxasterol, urospermal A (**1**) [3] where the configuration of the 1,10 double bond has to be changed [Halsall T. G., unpublished], 11β,13-dihydrourospermal A (**10**) [4] and eight further sesquiterpene lactones, the melampolides **2–5** and the germacranolides **6–9**. The structure of **2** followed from the ^1H NMR spectral data (Table 1) which were close to those of **1**. As expected the H-15 signals were shifted downfield. The spectra of **8** and **9** (Table 1) showed that we were dealing with the mono- and diacetate of albicolide. All signals in the spectrum of **9** were assigned by spin decoupling. If the spectrum of **3** (Table 1) is compared with that of **8** the difference in the configuration of the 1, 10-double bond becomes obvious. The downfield shift of the H-1 signal in the spectrum of **3**, if compared with the H-1 shift of **8**, supported a *cis*-1, 10-double bond. The same is true in the spectrum of a diacetate isolated previously from a *Dicoma* species [2]. The configuration of the 1, 10-double bond has to be changed to 1,10-*cis*. The spectra of **4** and **5** (Table 1) showed that these lac-

*Part 428 in the series "Naturally Occurring Terpene Derivatives". For Part 427 see Bohlmann, F., Singh, P., Joshi, K. C. and Singhi, C. L. (1982) *Phytochemistry* **21**, 1441.

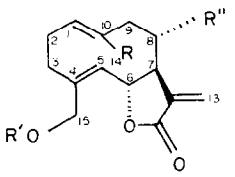
Table 1. ^{1}H NMR spectral data of compounds **2–9** (400 MHz, $CDCl_3$, TMS as internal standard)

	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
H-1	6.84 *br dd*	5.56 *br t*	6.53 *ddd*	6.54 *ddd*	6.24 *br dd*	5.23 *dd*	5.18 *br t*	6.18 *br t*
H-2	2.61 *m*	—	2.52 *m*	2.50 *m*	—	2.35 *m*	2.33 *m*	2.35 *m*
H-2′	2.38 *m*	—	2.35 *m*	2.42 *m*	—	2.27 *m*	—	—
H-3	2.67 *ddd*	2.59 *ddd*	2.64 *ddd*	2.77 *ddd*	—	2.59 *ddd*	—	2.57 *ddd*
H-3′	2.10 *br dd*	1.85 *dd*	2.10 *br dd*	2.02 *ddd*	—	2.16 *m*	—	2.15 *m*
H-5	5.23 *br d*	5.22 *br d*	5.28 *br d*	5.17 *br d*	5.12 *br d*	4.98 *br d*	4.89 *br d*	5.01 *br d*
H-6	4.60 *dd*	4.83 *dd*	4.67 *dd*	4.78 *dd*	4.51 *dd*	4.73 *dd*	4.80 *dd*	4.62 *dd*
H-7	2.48 *dddd*	2.60 *ddddd*	2.28 *ddddd*	2.28 *ddddd*	2.54 *m*	2.93 *dddd*	2.62 *m*	2.63 *ddddd*
H-8	3.98 *ddd*	2.30 *m*	2.93 *dddd*	2.92 *dddd*	—	4.15 *br dd*	—	2.15 *m*
H-8′		1.60 *m*	1.53 *m*	1.53 *dddd*	—		—	1.73 *m*
H-9	2.52 *m*	2.20 *m*	2.44 *br dd*	2.41 *ddd*	—	2.87 *br d*	—	2.75 *dd*
H-9′		2.05 *m*	2.10 *m*	2.22 *ddd*	—	2.46 *dd*	—	2.15 *m*
H-13	6.54 *dd*	6.20 *d*	6.19 *d*	6.18 *d*	6.29 *d*	6.44 *dd*	6.28 *d*	6.31 *d*
H-13′	6.33 *dd*	5.45 *d*	5.50 *d*	5.50 *d*	5.50 *d*	6.37 *dd*	5.53 *d*	5.57 *d*
H-14	9.47 *s*	4.62 *d*	9.48 *s*	9.48 *s*	9.90 *br s*	4.57 *dd*	4.55 *dd*	4.50 *d*
H-14′		4.48 *d*				4.53 *d*	4.39 *d*	4.28 *d*
H-15	4.82 *d*	4.49 *d*	4.81 *d*	4.48 *d*	4.48 *br s*	4.51 *d*	4.21 *br d*	4.55 *d*
H-15′	4.71 *d*	4.25 *d*	4.77 *d*	4.30 *d*		4.23 *d*	4.09 *br d*	4.60 *d*
OAc	2.14 *s*	2.05 *s*	2.12 *s*	—	2.10 *s*	2.14 *s* 2.10 *s*	2.06 *s*	2.13 *s* 2.08 *s*
OH	5.64 *d*							

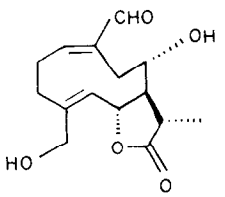
J(Hz): 5, 6 = 6, 7 = 10; 14, 14′ = 14; 15, 15′ = 12.5; compound **2**: 1, 2 = 7; 1, 2′ = 9; 2, 3 = 6; 2′, 3 = 2; 3, 3′ = 12.5; 7, 8 = 10; 7, 13 = 3; 8, 9 = 3; 8, 9′ = 4; 8, OH = 11; 13, 13′ = 1.5; compound **3**: 1, 2 = 8.5; 2, 3 = 6; 2′, 3 = 2; 2′, 3′ = 12; 3, 3′ = 12.5; 7, 8 = 3; 7, 8′ = 11; 7, 13 = 3.5; 7, 13′ = 3; compound **4**: 1, 2 = 7; 1, 2′ = 9; 1, 14 = 1.5; 2, 3 = 6; 2′, 3 = 2; 2′, 3′ = 3, 3′ = 12; 7, 8 = 3; 7, 8′ = 11; 7, 13 = 3.5; 7, 13′ = 3; 8, 8′ = 12; 8, 9 = 6.5; 8, 9′ = 10; 9, 9′ = 14; compound **5**: 1, 2 = 7; 1, 2′ = 9; 1, 14 = 1.5; 2, 3 = 6; 2, 3′ = 2; 2′, 3 = 2.5; 2′, 3′ = 3, 3′ = 12; 7, 8 = 3; 7, 8′ = 12; 7, 13 = 3.5; 7.13′ = 3; 8, 9 = 6.5; 8, 9′ = 12; 8, 8′ = 14; 8′, 9 = 2; 8′, 9′ = 6; 9, 9′ = 14; 9′, 14 = 1.5; compound **6**: 1, 2 = 5; 1, 2′ = 12.5; 7, 13 = 3.5; 7, 13′ = 3; compound **7**: 1, 2 = 5; 1, 2′ = 2, 2′ = 12; 2′, 3 = 4; 2′, 3′ = 12; 2, 3 = 2.5; 3, 3′ = 12; 7, 8 = 8, 9′ = 10; 9, 9′ = 13; 7, 13 = 3.5; 7, 13′ = 3; 13, 13′ = 1.5; compounds **8** and **9**: 1, 2 = 8.5; 2, 3 = 2′, 3 = 3.5; 3, 3′ = 12; 7, 8 = 4; 7, 8′ = 10; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 6.5; 8, 9′ = 10; 9, 9′ = 13.



	1	**2**	**3**	**4**	**5**
R	CHO	CHO	CH_2OAc	CHO	CHO
R′	H	Ac	H	Ac	H
R″	OH	OH	H	H	H



	6	**7**	**8**	**9**
R	CHO	CH_2OAc	CH_2OAc	CH_2OAc
R′	Ac	Ac	H	Ac
R″	H	OH	H	H



10

tones only differed at C-15, the former being an acetate and the latter the corresponding hydroxy compound. The *cis*-configuration of the 1, 10-double bond followed from the chemical shift of H-14. All signals could be assigned by spin decoupling, although some signals were overlapping multiplets. Small differences in the conformation of **4** and **5** led to some unexpected differences, namely the presence of a clear allylic coupling in the spectrum of **5** not visible in that of **4**. A slight downfield shift of H-3 in the spectrum of **5** was due to the more pronounced deshielding effect of the 15-hydroxy group. The ^{1}H NMR spectrum of **6** (Table 1) showed that this lactone was the 1, 10 *trans*-isomer of **4** as indicated by the chemical shift of H-14. The spectral data of **7** showed that this lactone was the 8α-hydroxy derivative of **9**. As usual in 8α-hydroxy germacranolides the H-13′ signal was shifted downfield and a coupling $J_{13,13'}$ was visible. Also H-7 was slightly deshielded by the 8-hydroxy group.

Further *Dicoma* species must be investigated to see whether sesquiterpene lactones of types **1–9** are characteristic for the genus and perhaps for the subtribe as similar lactones have been isolated from *Actinoseris* [4], *Cnicothamnus* [5], *Gochnatia* [6] and *Wunderlichia* [4], while from *Pertya* [7] guaianolides were reported. By contrast *Oldenburgia* and *Onoseris* [8] have so far yielded no lactones. However, the constituents of the latter species indicated that this genus may be better placed in the *Nassauviinae*, while those of *Pleiotaxis* showed that it perhaps should be placed in the *Cynareae* [9].

EXPERIMENTAL

The air-dried plant material (collected in Transvaal, voucher 81/42, deposited in the Botanic Research Institute, Pretoria) was extracted with Et_2O–petrol (1:2) and the resulting extract was separated by repeated TLC (Si gel). The aerial parts (10 g) afforded 20 mg taraxasterol, 5 mg **1**, 10 mg **2**, 1.5 mg **3**, 3.5 mg **4**, 3 mg **5**, 1.5 mg **6**, 4 mg **7**, 1 mg **8**, 6.4 mg **9** and 1.5 mg **10** (solvent: C_6H_6–CH_2Cl_2–Et_2O, 2:2:1), while the roots (2 g) gave 5 mg lupeyl acetate, 4 mg taraxasterol, 1 mg stigmasterol and 2 mg sitosterol. Known compounds were identified by comparing their ^{1}H NMR spectra with those of authentic material. Due to the small amounts no mp could be determined.

Urospermal A-15-O-acetate (**2**). Colourless solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420 (OH), 1780 (γ-lactone), 1750 (OAc), 1690, 1630 (C=CCHO); MS *m/z* (rel. int.): 320 [M]$^+$ (0.5) ($C_{17}H_{20}O_6$), 260 [M − HOAc]$^+$ (55), 242 [260 − H_2O]$^+$ (25), 214 [242 − CO]$^+$ (31), 213 [242 × CHO]$^+$ (31), 69 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+91 \quad +97 \quad +111 \quad +218} \quad CHCl_3;\ c = 1.0.$$

1, 10-cis-*Albicolide*-14-O-*acetate* (**3**). Colourless solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1770 (γ-lactone), 1740 (OAc); MS *m/z* (rel. int.): 306 [M]$^+$ (0.1), 246.126 [M − HOAc]$^+$ (21) ($C_{15}H_{18}O_3$), 228 [246 − H_2O]$^+$ (19), 91 (63), 81 (63), 53 (100); $[\alpha]_D$ = +8.5° ($CHCl_3$; *c* = 0.14).

8-*Desoxy urospermal A*-15-O-*acetate* (**4**). Colourless solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 (γ-lactone), 1745 (OAc), 1690, 1630 (C=CCHO); MS *m/z* (rel. int.): 304 [M]$^+$ (0.1), 244.110 [M − HOAc]$^+$ (100), 216 [244 − CO]$^+$ (24), 215 [244 − CHO]$^+$ (37).

8-*Desoxy urospermal A* (**5**). Colourless solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1770 (γ-lactone), 1690, 1630 (C=CCHO); MS *m/z* (rel. int.): 262 [M]$^+$ (2), 244.110 [M − H_2O]$^+$ (8) ($C_{15}H_{16}O_3$), 216 [244 − CO]$^+$ (12), 215 [244 − CHO]$^+$ (15), 53 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-20 \quad -26 \quad -32 \quad -52} \quad CHCl_3;\ c = 0.26.$$

8α-*Hydroxy albicolide*-14-O-*acetate* (**7**). Colourless solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1760 (γ-lactone), 1730 (OAc); MS *m/z* (rel. int.): 305.139 [M − OAc]$^+$ (82) ($C_{17}H_{21}O_5$), 245 [305 − HOAc]$^+$ (16), 244 [M − 2 × HOAc]$^+$ (15), 227 [245 − H_2O]$^+$ (15), 226 [244 − H_2O]$^+$ (13), 55 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+41 \quad +63 \quad +74 \quad +142} \quad CHCl_3;\ c = 0.32.$$

Albicolide-14-O-*aceate* (**8**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1770 (γ-lactone), 1740 (OAc); MS *m/z* (rel. int.): 246.126 [M − HOAc]$^+$ (4) ($C_{15}H_{18}O_3$), 228 [246 − H_2O]$^+$ (4), 57 (100).

Albicolide diacetate (**9**). Colourless solid, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1750 (OAc); MS *m/z* (rel. int.): 348 [M]$^+$ (0.1), 289 [M − OAc]$^+$ (100), 229 [289 − HOAc]$^+$ (72), 228.115 [M − 2 × HOAc]$^+$ (27) ($C_{15}H_{16}O_2$).

Acknowledgements—We thank Dr. B. de Winter and Miss M. Welman, Botanic Research Institute, Pretoria, for their help during plant collection and identification of the plant material, the Deutsche Forschungsgemeinschaft for financial support and Dr. T. G. Halsall for the ^{1}H NMR data of urospermal.

REFERENCES

1. Cabrera, A. L. (1977) in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., Eds.) p. 1042. Academic Press, London.
2. Bohlmann, F. and Le Van, N. (1978) *Phytochemistry* **17**, 570.
3. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 239.
4. Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 1631.
5. Bohlmann, F. and Zdero, C. (1979) *Phytochemistry* **18**, 95.
6. Bohlmann, F., Jakupovic, J., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 109.
7. Nagumo, S., Izawa, K., Hagahiyama, K. and Nagai, M. (1980) *Yakugaku Zasshi* **100**, 427.
8. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, 689.
9. Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21**, 1434.