nals of the sesquiterpene part were nearly identical with those of **1**. Accordingly the new lactone differed only in the oxygen function at C-15. The nature of this group followed from the ^1H NMR spectral data and from the CI-mass spectrum, which showed $[M+1]^+$-peaks at m/z 701 for **3** and m/z 743 for **4**, in agreement with the molecular formulae $C_{34}H_{40}O_{15}$ and $C_{36}H_{42}O_{16}$, respectively. The presence of a *p*-hydroxyphenyl acetate residue was deduced from the ^1H NMR signals at δ 7.02 (*d*, H-3″, H-5″), 7.29 (*d*, H-2″, H-6″), 3.66 and 3.62 (*d*, H-7″). The presence of a β-glucoside followed from the value of $J_{1'2'}$, while the position of the ester residue was deduced from the downfield shifts of H-6′ in the spectrum of **2** compared with the shifts of glucosides with a free 6-hydroxyl group. Accordingly **2** was urospermal A - 15 - *O* - [4′ - (*p* - hydroxyphenylacetyl)] - β - D - glucopyranoside. Melampolide glucosides esterified with *p*-hydroxyphenylacetic acid have not been detected previously. Urospermal has been isolated only from another *Urospermum* [1] and from a *Dicoma* species [2], which, however, is placed in the tribe Mutisieae.

EXPERIMENTAL

The fresh aerial parts (3 kg) were extracted with 95% EtOH, the extract concd under red. pres. and extracted with $CHCl_3$. The extract (3 g) was separated by CC (Si gel) with $CHCl_3$ and increasing amounts of MeOH. With $CHCl_3$–MeOH (25:1), 50 mg urospermal A (**1**) mp 164–166°, was obtained (^1H NMR of **1** identical with that of an authentic sample) and with MeOH–$CHCl_3$ (1:10), 20 mg **2**, colourless crystals, mp 112–115°. 20 mg **2** on acetylation (Ac_2O, 2 hr 70°) afforded after TLC (Si gel, $CHCl_3$–MeOH, 30:1) 1 mg **3**, colourless gum, MS m/z (rel. int.) (CI, isobutane): 701 $[M+1]^+$ (1) ($C_{34}H_{40}O_{15}+1$), 683 $[701-H_2O]^+$ (7), 641 $[701-HOAc]^+$ (1.5), 623 $[641-H_2O]^+$ (1), 563 $[623-HOAc]^+$ (3) and 20 mg **4**, colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1750 (lactone, CO_2R); MS m/z (rel. int.) (CI, isobutane): 743 $[M+1]^+$ (4) ($C_{36}H_{42}O_{16}+1$), 725 $[743-H_2O]^+$ (10), 683 $[743-HOAc]^+$ (3), 665 $[683-H_2O]^+$ (2), 465 $[C_{22}H_{25}O_{11}]^+$ (53), 331 (73), 279 (100), 249 (40), 191 (47);

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+59.3 \quad +62.0 \quad +71.5 \quad +137.1}\ (CHCl_3;\ c = 2.0).$$

REFERENCES

1. Benthey, R. K., Buchanan, T. G. S. C., Halsall, T. G. and Thaller, V. (1970) *J. Chem. Soc. Chem. Commun.* 435.
2. Bohlmann, F., Singh, P. and Jakupovic, J. (1982) *Phytochemistry* **21**, 2122.

Phytochemistry, Vol. 21, No. 11, pp. 2747–2749, 1982.
Printed in Great Britain.
0031-9422/82/112747-03$03.00/0

A GUAIANOLIDE FROM *CENTAUREA BEHEN*

SEVIL OKSUZ, AYHAN ULUBELEN, YAKOUP AYNECHI* and
HILDEBERT WAGNER†

Faculty of Pharmacy, University of Istanbul, Turkey; *Faculty of Pharmacy, University of Teheran, Iran;
†Institut für Pharmazeutische Biologie der Universitat München, West Germany

(*Revised received* 26 *April* 1982)

Key Word Index—*Centaurea behen*; Compositae; sesquiterpene lactones; guaianolides; circimaritin.

Abstract—Five sesquiterpene lactones of the guaianolide type were isolated from the leaves of *Centaurea behen*. One was identified as a new derivative of solstitialin A. The same extract also yielded a methylated flavone, circimaritin.

In a recent study with *Centaurea behen* collected from Iran (near Teheran) Rustaiyan *et al.* [1] reported the presence of five sesquiterpene lactones. One of them, obtained as its diacetate, was a new compound, 4β, 15-dihydro-3-dehydrosolstitialin A. However, in the present study, this plant, which was collected 25 km east of Teheran, yielded much higher amounts of known compounds such as grosshemin (**1**)[2], cynaropicrin (**2**)[3], aguerin B (**3**)[4] and desacylcynaropicrin (**4**)[5] as well as large amounts of a monoacetyl compound (**5**) which is closely related to solstitialin A. A methylated flavone, circimaritin, was obtained from the same extract.

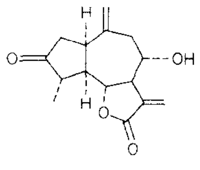
The difference between the two collections of the

Table 1. ^1H NMR spectral data of compounds **5** and **6** (400 MHz, TMS as int. standard)

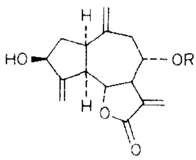
	5 ($CDCl_3$)	Acetyl derivative of **5** (C_6D_6)	**6** (C_6D_6)[1]
H-1α	2.65 *ddd*	2.32 *t*	2.26 *br dd*
H-2α	2.10 *br dd*	1.92 *br dd*	1.90 *dd*
H-2β	2.22 *ddd*	2.17 *dd*	2.13 *ddd*
H-4β	2.25 *dd*	1.97 *brdd*	1.96 *ddq*
H-5α	2.61 *t*	2.15 *ddd*	2.12 *ddd*
H-6β	4.06 *t*	3.73 *t*	3.71 *dd*
H-7α	3.08 *ddd*	3.04 *dtd*	3.03 *ddd*
H-8α	1.43 *dddd*	1.58 *m*	1.58 *dddd*
H-8β	2.29 *ddd*	0.82 *dddd*	0.96 *dddd*
H-9α	2.51 *ddq*	1.48 *ddd*	1.44 *br ddd*
H-9β	2.54 *ddq*	2.03 *dddd*	2.04 *ddd*
H-13	4.33 *d*	4.39 *d*	4.38 *d*
H-13′	4.11 *d*	4.34 *d*	4.34 *d*
H-14	4.99 *br s*	4.59 *br s*	4.56 *br s*
H-14′	4.68 *br s*	4.36 *br s*	4.34 *br s*
H-15	1.24 *d*	1.28 *d*	1.28 *d*
H-15′	—	—	—
OAc	2.06 *s*	1.66 *s* 1.60 *s*	1.62 *s* 1.59 *s*

same plant is in the amounts of known sesquiterpene lactones as well as in the presence of the new compounds. The one previously obtained from *C. behen* is a free alcohol derivative of solstitialin A, while the one obtained in this study is a monoacetate of the same compound.

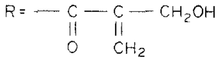
The structure of the new compound was assigned by spectral methods, as well as by comparison of the 400 MHz ^1H NMR spectrum of the acetyl derivative of the new compound to that of compound **6** obtained from *C. behen* previously[1]. They were found to be identical. Table 1 shows the ^1H NMR signals of compound **5** and its acetyl derivative as well as the signals of compound **6**.



1

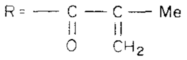


2



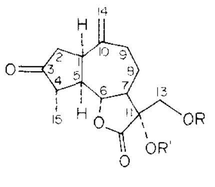
$R = -\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-CH_2OH$

3



$R = -\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-Me$

4 R = H



5 R = Ac, R′ = H

6 R = Ac, R′ = Ac

EXPERIMENTAL

Mps are uncorr. IR spectra were recorded in KBr, UV spectra in MeOH, ^1H NMR spectra were determined on 90 and 400 MHz instruments.

The dried leaves of *Centaurea behen* (1.7 kg) collected from 25 km east of Teheran (voucher No. 41, deposited at the University of Teheran) were extracted with MeOH and evaporated to a small vol. *in vacuo* and the residue (225 g) partitioned between $CHCl_3$ and H_2O (1:1). After evaporation under red. pres. the material was dissolved in 90% aq. MeOH and extracted exhaustively by petrol. The aq. MeOH phase was treated with an aq. soln of 4% lead acetate at room temp. and the resulting ppt was filtered. The filtrate was concd and extracted with $CHCl_3$. The $CHCl_3$ soln, after evaporation, yielded a residue (13 g) which was chromatographed on a Si gel column, eluted with $CHCl_3$ by gradual addition of MeOH[6]. The first fractions yielded circimaritin (450 mg) in a pure state, its structure was established by UV and ^1H NMR spectra, as well as standard sample comparison. While compounds **1** and **5** were obtained as major components (700 and 480 mg, respectively), compounds **2**, **3** and **4** were only obtained in small amounts (45, 20 and 10 mg, respectively) and they were purified by prep. TLC (Si gel). The known compounds were identified by IR, NMR and mass spectral methods.

Identification of compound **5**. Crystallized from MeOH, mp 141–143°. IR ν_{max}^{KBr} cm^{-1}: 3340 (OH), 1775 (γ-lactone), 1735 and 1240 (OAc), 1638 (double bond); UV λ_{max}^{MeOH} nm: 220; MS *m/z* 332 $[M]^+$ ($C_{17}H_{22}O_6$), 262 $[M-C_2H_3O_2]^+$, 250, 218, 165.

Acknowledgement—We thank Professor F. Bohlmann (Berlin) for the 400 MHz NMR spectra.

REFERENCES

1. Rustaiyan, A., Niknejad, A., Zdero, C. and Bohlmann, F. (1981) *Phytochemistry* **20**, 2427.

2. Samek, Z., Holub, M., Vokac, K., Drozdz, B., Jommi, G., Gariboldi, P. and Corbella, A. (1972) *Collect. Czech. Chem. Commun.* **37**, 2611.
3. Suchy, M., Herout, V. and Sorm, F. (1960) *Collect. Czech. Chem. Commun.* **25**, 2777.
4. Gonzales, A. G., Bermejo, J., Cabrera, I., Massanet, G. M., Mansilla, H. and Galindo, A. (1971) *Phytochemistry* **17**, 955.
5. Gonzales, A. G., Bermejo, J., Massanet, G. M. and Perez, J. (1973) *Ann. Quim.* **69**, 1333.
6. Gonzales, A. G., Artega, J. M. and Breton, J. L. (1973) *Phytochemistry* **12**, 2997.

Phytochemistry, Vol. 21, No. 11, pp. 2749–2751, 1982.
Printed in Great Britain.
0031-9422/82/112749–03$03.00/0

A PHYTOECDYSTEROID, TAXISTERONE, FROM *TAXUS CUSPIDATA*

Kimiko Nakano, Toshihiro Nohara, Toshiaki Tomimatsu and Masaru Nishikawa*

Faculty of Pharmaceutical Sciences, Tokushima University, Shomachi 1-78, 770 Tokushima Japan; *Laboratory of Natural Products Chemistry, Otsuka Pharmaceutical Co. Ltd., Kawauchi-cho, 771-01 Tokushima, Japan

(*Revised received* 23 *April* 1982)

Key Word Index—*Taxus cuspidata*; Taxaceae; phytoecdysteroid; taxisterone; 22-deoxyecdysterone.

Abstract—A new phytoecdysteroid, taxisterone, was isolated from *Taxus cuspidata* and the structure was deduced to be 22-deoxyecdysterone by spectral data.

INTRODUCTION

Air-dried leaves and stems of *Taxus cuspidata* have been used in folk medicine for therapy of diabetes. Ecdysterone (**3**) and ponasterone A have been isolated previously from this plant [1]. We have now isolated a new phytoecdysteroid and determined its structure from spectral data.

RESULTS AND DISCUSSION

The methanolic extract was prepared from the dried leaves and stems and separated as described in the Experimental to afford a new phytoecdysteroid, designated taxisterone (**1**). Taxisterone (**1**), a white powder (mp 120–125°), showed IR spectrum absorptions due to the hydroxyl (3400 cm^{-1}) and the α, β-unsaturated carbonyl (1650 cm^{-1}) groups. The ^{1}H NMR spectrum of the acetate (**2**) of **1** ($CDCl_3$) exhibited an analogous pattern to those [2] of phytoecdysteroids. In its spectrum, the respective signals could be assigned as shown in Table 1 by comparison with that [2] of ecdysterone 2, 3, 22-triacetate (**4**).

The signals due to the respective acetoxyls and carbinol methines at C-2 and C-3 were observed but no acetyl carbinol methine ascribable to C-22 was observed and a hydroxyl was assumed to be absent from C-22 in compound **1**. Moreover, the ^{13}C NMR spectrum of **2** ($CDCl_3$) showed five signals at δ 67.0(*d*), 68.7(*d*), 71.0(*s*), 75.0(*s*) and 84.8(*s*) due to the carbons attached to the oxygen function groups (Table 2).

In comparison with the ^{13}C NMR spectrum of **4**, it is evident that no carbon signal attributable to C-22 bearing a hydroxyl was detected. Therefore, **1** is represented as 22-deoxyecdysterone. As for ecdysones lacking the hydroxyl at C-22, 2, 22-dideoxy-20-hydroxyecdysone [3] has been recently obtained from the ovaries of the silkworm *Bombyx mori*. However, taxisterone (**1**) is the first example from the plant kingdom.

Table 1. ^{1}H NMR chemical shifts of compounds **2** and **4** ($CDCl_3$)

	2	**4**
Me-18	0.86	0.86
Me-19	1.04	1.04
Me-21	1.29	1.26
Me-26	1.24	1.21
Me-27	1.24	1.23
H-2	5.04	5.04
H-3	5.32	5.31
H-7	5.84	5.85
H-9	3.10	3.10
H-22	—	4.79
OAc	2.01	1.99
	2.12	2.10
		2.10