Phytochemistry, Vol. 21, No. 11, pp. 2746–2747, 1982.
Printed in Great Britain.

0031–9422/82/112746–02$03.00/0

A GLUCOSIDE OF UROSPERMAL A*

N. A. Abdel Salam, Zeinab F. Mahmoud, Jürgen Ziesche† and Ferdinand Bohlmann†

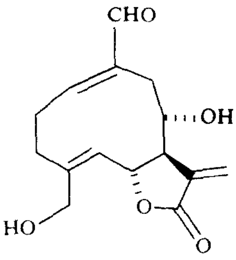
Faculty of Pharmacy, Alexandria University, Egypt; †Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany

(*Received* 21 *December* 1981)

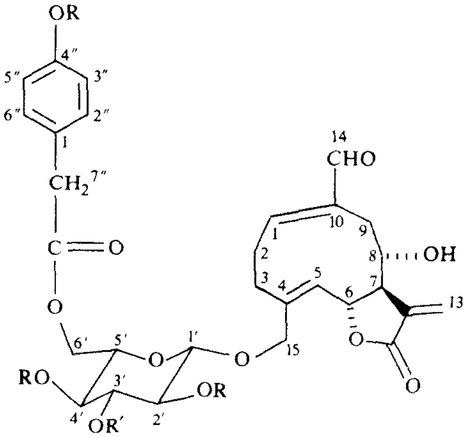
Key Word Index—*Urospermum picroides*; Compositae; sesquiterpene lactone; melampolide glucoside.

Abstract—The aerial parts of *Urospermum picroides* afforded, in addition to urospermal A a *p*-hydroxylphenyl acetate of a glucoside of urospermal A.

The aerial parts of *Urospermum picroides* (L.) Scop. ex F. W. Schmidt (tribe Lactuceae) afforded Urospermal A (**1**) [1], in which the 1, 10-double bond has been shown to be *cis* [Halsall, T. G., unpublished work] and a very polar compound, which turned out to be the glucoside **2**. Acetylation of **2** gave the triacetate **3** and the tetra-acetate **4**, whose ^{1}H NMR spectra (Table 1) with spin decoupling allowed assignment of the structure of **2**. Starting with the H-7 signal those of H-6, H-8 and H-13 were assigned. Irradiation of the H-6 signal collapsed the broadened doublet at δ 5.12 to a singlet. The latter, therefore, was the H-5 signal. Its irradiation allowed the assignment of H-15 and H-15′, already indicating that an oxygen function was at C-15. The remaining sig-



1



2 R = R′ = H

3 R = Ac, R′ = H

4 R = R′ = Ac

Table 1. ^{1}H NMR spectral data of compounds **2–4** (400 MHz, TMS as int. standard)

	2 (acetone d_6)	**3**	**4**
H-1	6.98 *ddd*	6.81 *br dd*	6.79 *br dd*
H-5	5.25 *br d*	5.15 *br d*	5.12 *br d*
H-6	4.85 *dd*	4.56 *dd*	4.53 *dd*
H-7	2.65 *dddd*	2.46 *dddd*	2.44 *dddd*
H-8	4.03 *br ddd*	3.90 *br ddd*	3.87 *br ddd*
H-9	2.97 *dd*	2.74 *dd*	2.68 *dd*
H-9′	2.28 *br d*	2.37 *br d*	2.34 *br d*
H-13	6.36 *dd*	6.53 *dd*	6.51 *dd*
H-13′	6.05 *dd*	6.31 *dd*	6.28 *dd*
H-14	9.48 *s*	9.45 *s*	9.43 *s*
H-15	4.37 *s*	4.23 *d*	4.22 *d*
H-15′		4.17 *d*	4.13 *d*
H-1′	4.39 *d*	4.37 *d*	4.47 *d*
H-2′	3.23 *dd*	4.72 *dd*	4.98 *dd*
H-3′	3.39 *dd*	3.60 *dd*	5.19 *dd*
H-4′	3.32 *dd*	4.61 *dd*	5.03 *dd*
H-5′	3.51 *ddd*	3.54 *ddd*	3.65 *ddd*
H-$6'_1$	4.42 *dd*	4.37 *dd*	4.28 *dd*
H-$6'_2$	4.20 *dd*	4.15 *dd*	4.20 *dd*
H-3″,H-5″	6.75 *d*	7.05 *d*	7.02 *d*
H-2″, H-6″	7.12 *d*	7.30 *d*	7.29 *d*
H-$7''_1$	3.55 *br s*	3.67 *d*	3.66 *d*
H-$7''_2$		3.63 *d*	3.62 *d*

J (Hz): 1, 2 = 9; 1, 2′ = 8; 1, 9 ~ 1; 5, 6 = 10.5; 6, 7 = 10; 7, 8 = 10; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 5; 8, 9′ = 11; 9, 9′ = 16; 13, 13′ = 2; 15, 15′ = 12; 1′, 2′ = 8.5; 2′, 3′ = 3′, 4′ = 9.5; 4′,5′ = 9; 5′, $6'_1$ = 2.5; 5′, $6'_2$ = 5; $6'_1$, $6'_2$ = 12; 2″, 3″ = 8.5; $7''_1$, $7''_2$ = 14.

---

*Part 450 in the series "Naturally Occurring Terpene Derivatives". For Part 449 see Bohlmann, F., Ates, N., Jakupovic, J., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 2691.

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);

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

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