lactone), 1600 (C=C); MS $m/z$ (rel. int.): 162.068 ($M^+$, 100) ($C_{10}H_{10}O_2$), 133 (M − CHO, 18), 104.060 (M − $CH_2OCO$, 68) ($C_8H_8$).

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# A GUAIANOLIDE FROM *CENTAUREA BEHEN*[*]

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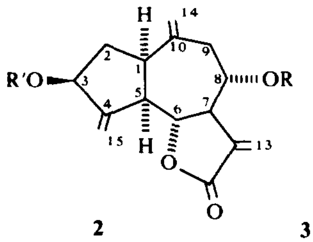
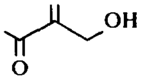
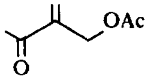
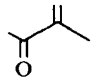
**Key Word Index**—*Centaurea behen*; Compositae; sesquiterpene lactones; guaianolides.

**Abstract**—The aerial parts of *Centaurea behen* afforded in addition to known lactones a new derivative of solstitialin A.



| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| R |  |  |  | H | Ac |
| R' | H | Ac | H | H | Ac |

*Centaurea behen* L., native in Iran, had not been investigated chemically. The aerial parts of this plant afforded several sesquiterpene lactones, the guaianolides cynaropicrin (**1**) [1], arguerin B (**3**) [2], desacylcynaropicrin (**4**) [3], grosshemin (**6**) [4] and minor amounts of the ketone **8**, which is closely related to solstitialin A, the absolute configuration of which had been established [5]. **8** could only be isolated as its diacetate **9**, which still was mixed with the acetate of **6**. The latter, however, could be separated from **9** after transformation to the corresponding pyrazoline derivative. The structures of **1**, the corresponding diacetate **2**, **3**, **4** and **6** were elucidated by their $^1H$ NMR data, which are presented in part in Table 1, as good spectra are not available in the literature. The structure of **8** also followed from the $^1H$ NMR data of the corresponding diacetate **9** (Table 1). At 400 MHz in $C_6D_6$ all signals could be assigned by careful spin decoupling. Starting with the methyl doublet at $\delta$ 1.28 H-4 was assigned. H-4 was coupled with a signal at $\delta$ 2.12 which was assigned to H-5, as it also was coupled with the proton under the lactone oxygen. H-4 further showed a *W*-coupling with the three-fold doublet at $\delta$ 2.13, which obviously was the H-2 $\beta$-signal, as it was further coupled with a proton, which also was coupled with H-5. Finally, by further decoupling all signals could be assigned. The

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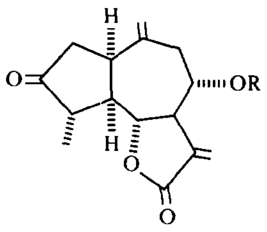
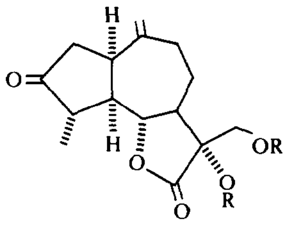
[*] Part 352 in the series "Naturally Occurring Terpene Derivatives". For Part 351 see Bohlmann, F., Zdero, C. and Gupta, R. K. (1981) *Phytochemistry* **20**, 2024.



6 R = H
7 R = Ac



8 R = H
9 R = Ac

Table 1. $^1H$ NMR spectral data of compounds 1–4 and 9 (400 MHz, $CDCl_3$, TMS as internal standard)

| | 1 | 2 | 3 | 4 | 9($C_6D_6$) |
|---|---|---|---|---|---|
| H-1α | 2.98 *ddd* (*br*) | 3.03 *ddd* (*br*) | 2.98 *ddd* (*br*) | 2.95 *ddd* (*br*) | 2.26 *dd* (*br*) |
| H-2α | 1.74 *ddd* | 1.79 *ddd* | 1.73 *ddd* | 1.73 *ddd* | 1.90 *dd* |
| H-2β | 2.24 *ddd* | 2.36 *ddd* | 2.24 *ddd* | 2.23 *m* | 2.13 *ddd* |
| H-3α | 4.56 *t* (*br*) | 5.56 *t* (*br*) | 4.56 *t* (*br*) | 4.55 *t* (*br*) | — |
| H-4β | — | — | — | — | 1.96 *ddq* |
| H-5α | 2.85 *t* (*br*) | 2.86 *t* (*br*) | 2.85 *t* (*br*) | 2.80 *t* (*br*) | 2.12 *ddd* |
| H-6β | 4.27 *dd* | 4.16 *dd* | 4.25 *dd* | 4.15 *dd* | 3.71 *dd* |
| H-7α | 3.20 *dddd* | 3.20 *dddd* | 3.19 *dddd* | 3.07 *dddd* | 3.03 *ddd* |
| H-8α | — | — | — | — | 1.58 *dddd* |
| H-8β | 5.14 *ddd* | 5.16 *ddd* | 5.09 *ddd* | 3.96 *ddd* | 0.96 *dddd* |
| H-9α | 2.72 *dd* | 2.69 *dd* | 2.70 *dd* | 2.67 *dd* | 1.44 *ddd* (*br*) |
| H-9β | 2.40 *dd* | 2.41 *dd* | 2.38 *dd* | 2.29 *dd* | 2.04 *ddd* |
| H-13 | 6.24 *d* | 6.24 *d* | 6.22 *d* | 6.25 *d* | 4.38 *d* |
| H-13′ | 5.63 *d* | 5.63 *d* | 5.61 *d* | 6.15 *d* | 4.34 *d* |
| H-14 | 5.15 *s* (*br*) | 5.14 *s* (*br*) | 5.14 *s* (*br*) | 5.11 *s* (*br*) | 4.56 *s* (*br*) |
| H-14′ | 4.94 *s* (*br*) | 4.96 *s* (*br*) | 4.94 *s* (*br*) | 4.97 *s* (*br*) | 4.34 *s* (*br*) |
| H-15 | 5.49 *dd* | 5.53 *dd* | 5.50 *dd* | 5.46 *dd* | 1.28 *d* |
| H-15′ | 5.37 *dd* | 5.36 *dd* | 5.37 *dd* | 5.33 *dd* | |
| OAc | — | 2.09 *s* | — | — | 1.62 *s* |
| | | | | | 1.59 *s* |
| OR | 6.34 *s* (*br*) | 6.56 *s* (*br*) | 6.19 *s* (*br*) | — | — |
| | 5.97 *s* (*br*) | 5.98 *s* (*br*) | 5.68 *s* (*br*) | — | — |
| | 4.39 *s* (*br*) | 4.84 *s* (*br*) | 2.00 *s* (*br*) | — | — |

*J* (Hz): 1α,2α = 10.5; 1α,2β = 7.5; 1α,5β = 9; 2α,2β = 13.5; 2α,3 = 7.5; 2β,3 = 7.5; 3,15 = 1.5; 3,15′ = 1.5; 5,6 = 10.5; 6,7 = 9; 7,8 = 9.5; 7,13 = 3.5; 7,13′ = 3.0; 8,9α = 5.5; 8,9β = 4; 9α,9β = 14.5; compound **9**: 1α,2α = 9; 1α,2β = 1.5; 1α,5α = 9; 2α,2β = 19; 2β,4β = 1.5; 4β,5α = 10; 4β,15 = 7; 5α,6β = 6β,7α = 9; 7α,8α = 2.5; 7α,8β = 12; 8α,8β = 12; 8α,9α = 5; 8α,9β = 2.5; 8β,9α = 12; 8β,9β = 5; 9α,9β = 13; 13,13′ = 12.

stereochemistry at C-11 was proposed by analogy to that of solstitialin A and by the chemical shift of H-7, which obviously required a *cis*-orientated acetoxy group. **8** therefore is 4β,15-dihydro-3-dehydro solstitialin A.

## EXPERIMENTAL

The fresh plant material (500 g) (collected near Teheran) was extracted with $CHCl_3$. The polar fractions of the CC (Si gel, $Et_2O$ and $Et_2O$–MeOH, 20:1) afforded a mixture of **1**, **3**, **4**, **6** and **8**, which was further separated by TLC (Si gel). While **1** (100 mg) and **3** (30 mg) could be isolated in a pure state, **4** (20 mg) could be separated from **6** and **8** only by HPLC (reversed phase, RP2, MeOH–$H_2O$, 7:3). Acetylation of the remaining mixture (in $CHCl_3$ with $Ac_2O$–4-pyrrolidinopyridine, room temp., 6 hr) gave the acetates **7** and **9**, which again could not be separated (TLC, $Et_2O$–petrol, 3:1). Addition of $CH_2N_2$, however, afforded the pyrazoline derivative of **7** (2 mg), which could be separated from **9** (2 mg) by TLC ($Et_2O$–petrol, 3:1).

*4β,15-Dihydro-3-dehydrosolstitialin A diacetate* (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 1805 (γ-lactone), 1755 (C=O, OAc), 1725 (OAc); MS *m/z* (rel. int.): 364.152 ($M^+$, 4) ($C_{19}H_{24}O_7$), 322 (M − ketene, 2), 304 (M − HOAc, 10), 262 (304 − ketene, 21), 244 (304 − HOAc, 41), 57 (100);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,\text{nm}}{+87 \quad +90 \quad +105 \quad +213 \quad +483}$$

($c \sim 0.15$, $CHCl_3$).

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# AN ISOMER OF XANTHANOL FROM *XANTHIUM ORIENTALE**

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(*Received* 13 *January* 1981)

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

**Abstract**—The aerial parts of *Xanthium orientale* afforded an isomer of xanthanol.

From the genus *Xanthium* several xanthanolides were isolated [1–11], which seem to be characteristic for this genus, though this type of sesquiterpene lactone has been reported from other genera too. We now have reinvestigated the aerial parts of *Xanthium orientale* from which the presence of xanthine was reported [7]. Again, only xanthanolides were isolated, the ketones **1** [3] and **2** [2] and the hydroxy acetate **5**, which was not identical with xanthanol (**3**) [1]. The $^1$H NMR data of **3** and of the corresponding diacetate **4** were nearly identical with those of the new lactone and the diacetate (Table 1), but there were small characteristic differences in the couplings of H-2 and H-3. Also some of the chemical shifts were slightly different. By spin decoupling, all signals could be assigned. As the couplings of the ring protons were identical with those of **3** and **4**, the only possible difference was in the stereochemistry at C-2 or C-4, respectively. The observed shift differences of H-5, however, would favour epimers at C-2. Different stereochemistry at C-10 was unlikely as the couplings of H-10 and the chemical shift of H-14 were nearly identical in **4** and **6**. Also a C-8 epimer was not possible, as these epimers characteristically differ in the $^1$H NMR spectra [12]. Therefore the new lactone most probably is 2-epixanthanol (**5**). Unfortunately, the configuration at C-2 is not known for xanthanol and related lactones, which, however, all seem to have the stereochemistry of xanthanol at C-2, if $J_{2,3}$ is conclusive. These results again show that the chemistry of the genus *Xanthium* is very uniform. This genus is placed in the Heliantheae, subtribe Ambrosiinae, a very distinctive group [13], mainly characterized by pseudoguaianolides;

Table 1. $^1$H NMR spectral data of compounds **4**, **5** and **6** (400 MHz, CDCl$_3$, TMS as internal standard)

| | 4 | 5 | 6 |
|---|---|---|---|
| H-2 | 5.22 *dd* | 5.41 *dd* | 5.19 *dd* |
| H-3 | 2.10 *m* | 1.85 *ddd* | 1.88 *ddd* |
| H-3′ | 1.72 *m* | 1.59 *ddd* | 1.75 *m* |
| H-4 | 4.85 *ddq* | 3.75 *ddq* | 4.91 *ddq* |
| H-5 | 5.87 *br dd* | 5.96 *br dd* | 5.93 *br dd* |
| H-6α | 2.53 *ddd* | 2.57 *ddd* | 2.53 *ddd* |
| H-6β | 2.10 *m* | 2.14 *ddd* | 2.13 *ddd* |
| H-7 | 2.52 *m* | 2.48 *dddd* | 2.44 *dddd* |
| H-8 | 4.38 *ddd* | 4.52 *ddd* | 4.28 *ddd* |
| H-9α | 1.72 *m* | 1.76 *ddd* | 1.79 *m* |
| H-9β | 2.33 *ddd* | 2.35 *ddd* | 2.31 *ddd* |
| H-10 | 2.79 *ddq* | 2.82 *ddq* | 2.79 *ddq* |
| H-13 | 6.17 *d* | 6.20 *d* | 6.17 *d* |
| H-13′ | 5.45 *d* | 5.48 *d* | 5.44 *d* |
| H-14 | 1.11 *d* | 1.18 *d* | 1.10 *d* |
| H-15 | 1.25 *d* | 1.23 *d* | 1.26 *d* |
| OAc | 2.06 *s*<br>2.04 *s* | 2.12 *s* | 2.04 *s*<br>2.03 *s* |

*J* (Hz): 2,3 = 3; 2,3′ = 10.5; 3,3′ = 13.5; 3,4 = 10; 3′,4 = 3; 4,15 = 6.5; 5,6α = 9.5; 5,6β = 3; 6α,7 = 2; 6β,7 = 10; 7,8 = 10; 7,13 = 3; 8,9α = 12; 8,9β = 3; 9α,9β = 12.5; 9α,10 = 9β,10 = 3.5; 10,14 = 7; (compound **4**: 2,3 = 2,3′ = 7).

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*Part 365 in the series "Naturally Occurring Terpene Derivatives". For Part 364 see Dominguez, X. A., Franco, R., Cano, G., Bapuji, M. and Bohlmann, F. (1981) *Phytochemistry* **20**, 2297.