Costunolide diepoxide. The residue (0.5 g) obtained from fractions 36–50 using 1–2% MeOH afforded, after further fractionation on silica gel (Woelm, 120 g) using C_6H_6–Me_2CO gradient, 20 mg of minute needles; mp 169–170°. Spectral data (IR and MS) indicated identity with costunolide diepoxide [2].

Magnograndiolide (**2**). The residue (0.8 g) obtained from fractions 61–90 using 5–20% MeOH afforded, after further fractionation on silica gel (Woelm, 130 g) using C_6H_6–Me_2CO gradient, 170 mg of colourless prisms; mp 176–177°; IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3480 (OH), 1770 (γ-lactone); MS m/z (rel. int.): 251 $[M - Me]^+$ (9), 248.141 $[M - H_2O]^+$ (11) (calculated for $C_{15}H_{20}O_3$), 233 $[248 - Me]^+$ (8), 230 $[248 - H_2O]^+$ (24), 215 $[230 - Me]^+$ (21), 191 (41), 190 (72), 187 (31), 91 (68), 71 (94), 43 (100).

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XANTHANOLIDES FROM *XANTHIUM SPINOSUM*

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

Abstract—The aerial parts of *Xanthium spinosum* afforded in addition to known xanthanolides three new ones. The structures were elucidated by spectroscopic methods and by partial synthesis. Furthermore one lactone was transformed to a known derivative.

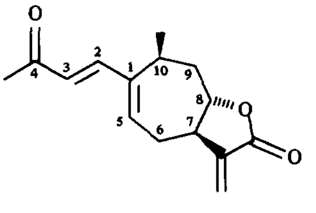
The isolation of only one sesquiterpene lactone, xanthinin, has been reported [1] from *Xanthium spinosum* L. (Compositae, tribe Heliantheae, subtribe Ambrosiinae). A careful reinvestigation afforded also xanthatin (**1**) [1], the epoxide **2** as well as its isomer **3** and the diol **4**. The structures of **2** and **3** followed from the ^{1}H NMR spectra (Table 1) as all signals could be assigned by spin decoupling. Some signals differed typically, especially the couplings of H-5, but those of H-8 and H-9 were also different. The flexibility of the seven membered ring did not allow a clear assignment of the stereochemistry at C-5 though the downfield shift of H-8 in the spectrum of **2**, if compared with the corresponding chemical shift of H-8 in the spectrum of **3**, supported the proposed stereochemistry. Furthermore, inspection of models showed that the couplings observed agreed best with the stereochemistry. The ^{1}H NMR spectrum of **2** also differed clearly from that of the corresponding 8-epimer [2] further supporting the proposed stereochemistry at C-8. Partial epoxidation of **1** afforded a 1:5 mixture of **2** and **3**. The expected favoured addition from the α-face led to an epoxide which was identical with **3** thus establishing the proposed assignment of the stereochemistry of **2** and **3**.

The ^{1}H NMR spectrum of **4** (Table 1) showed that a xanthanolide was present where the keto group was reduced, as an additional methyl doublet at δ1.23 was obviously due to H-15. Irradiation at 4.07 collapsed this doublet to a singlet and also changed the threefold doublets at 1.54 and 1.70 to double doublets. These signals were further coupled with an overlapped signal at 4.30. Accordingly, the side chain at C-1 was very likely to be that proposed. Acetylation afforded the diacetate **5**, identical with a diacetate isolated previously from a *Pulicaria* species [3]. The stereochemistry at C-1 and C-4 could not be determined.

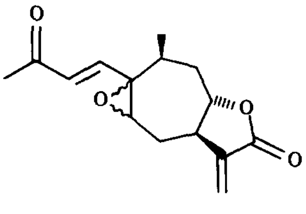
The chemistry of this species again shows that xanthanolides are characteristic for the genus *Xanthium*, where so far these lactones have always been isolated [4]. However, these lactones are also isolated from some *Parthenium* and *Iva* species [4].

EXPERIMENTAL

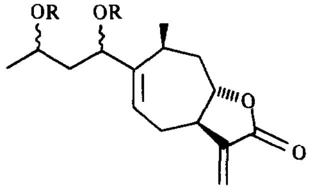
The aerial parts (2.4 kg) of the plant collected near Alexandria were extracted by percolation with Et_2O–petrol (1:2) and the extract was dissolved in 2 l. EtOH (95%). The soln was separated from insoluble waxy material, concd and gradually treated with 0.5 l. H_2O. The soln in EtOH–H_2O (1:1) was extracted with petrol and $CHCl_3$. The petrol extract after evaporation and recrystallization afforded 150 mg xanthinin. The $CHCl_3$ soln was



1



2 1β, 5β epoxide
3 1α, 5α epoxide



	R
4	H
5	Ac

Table 1. ^{1}H NMR spectral data of **2**–**4** (400 MHz, $CDCl_3$, TMS as internal standard)

	2	**3**	**4**
H-2	6.84 *d*	6.92 *d*	4.30 *m*
H-3	6.24 *d*	6.31 *d*	1.70 *ddd*
H-3′			1.54 *ddd*
H-4	—	—	4.07 *ddq*
H-5	2.97 *dd*	3.07 *br d*	5.85 *d*
H-6α	1.81 *ddd*	2.05 *ddd*	2.52 *ddd*
H-6β	2.66 *ddd*	2.70 *dd*	2.11 *ddd*
H-7	2.83 *m*	2.88 *ddddd*	2.43 *ddddd*
H-8	4.25 *ddd*	3.93 *ddd*	4.30 *m*
H-9α	1.96 *ddd*	2.11 *ddd*	1.68 *ddd*
H-9β	2.31 *ddd*	2.23 *ddd*	2.32 *ddd*
H-10	2.83 *m*	2.61 *ddq*	2.84 *ddq*
H-13	6.21 *d*	6.18 *d*	6.15 *d*
H-13′	5.49 *d*	5.46 *d*	5.44 *d*
H-14	1.09 *d*	1.30 *d*	1.18 *d*
H-15	2.27 *s*	2.38 *s*	1.23 *d*

J (Hz): Compound **2**: 2, 3 = 16; 5, 6α = 4.5; 5, 6β = 6; 6α, 6β = 15; 6α, 7 = 3; 6β, 7 = 12; 7, 13 = 3.5; 7, 13′ = 3; 7, 8 = 10; 8, 9α = 10; 8, 9β = 5; 9α, 9β = 14; 9α, 10 = 4; 9β, 10 = 8; 10, 14 = 7; compound **3**: 2, 3 = 16; 5, 6α = 6; 6α, 6β = 16; 6α, 7 = 3; 6β, 7 = 11.5; 7, 8 = 10; 7, 13 = 3.5; 7, 13′ = 3; 8, 9α = 12; 8, 9β = 2.5; 9α, 9β = 13; 9α, 10 = 4; 9β, 10 = 4.5; 10, 14 = 7; compound **4**: 2, 3 = 10; 2, 3′ = 3; 3, 3′ = 14; 3, 4 = 10; 3′, 4 = 2.5; 4, 15 = 6.5; 5, 6α = 3.5; 5, 6β = 9.5; 6α, 6β = 16; 6α, 7 = 2.5; 6β, 7 = 11; 7, 8 = 10.5; 7, 13 = 7, 13′ = 3; 8, 9α = 12.5; 8, 9β = 3.5; 9α, 9β = 13; 9α, 10 = 4.5; 9β, 10 = 4; 10, 14 = 7.5.

separated by CC (silica gel) and prep. TLC (silica gel, Et_2O–petrol, 3:1) affording 100 mg **1**, 50 mg **2**, 30 mg **3**, 100 mg xanthinin and 40 mg **4** (increasing polarity). The structures of **1**, **2** and xanthinin were established by comparing their mp's and their ^{1}H NMR spectra with those of authentic material.

1β,5β-Epoxy-1,5-dihydroxanthatin (**2**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (γ-lactone), 1720, 1690, 1635 (C=C–C=O); MS *m/z* (rel. int.): 219.102 $[M - Me, CO]^+$ (5) (calc. for $C_{13}H_{15}O_3$ 219.102), 109 (100; CI (*i*-butane): 263 $[M + 1]^+$ (100), 245 $[263 - H_2O]^+$ (27).

1α,5α-Epoxy-1,5-dihydroxanthatin (**3**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1700, 1680, 1625 (C=C–C=O); MS *m/z* (rel. int.): 262.121 $[M]^+$ (1) (calc. for $C_{15}H_{18}O_4$ 262.121), 247 $[M - Me]^+$ (1), 244 $[M - H_2O]^+$ (1), 219 $[247 - CO]^+$ (6), 109 (100); CI (*i*-butane): 263 $[M + 1]^+$ (100), 245 $[263 - H_2O]^+$ (12).

Preparation of **2** *and* **3**. To 10 mg **1** in 1 ml $CHCl_3$ 10 mg *m*-chloroperbenzoic acid and 0.1 ml $NaHCO_3$ soln were added. After stirring for 20 hr the usual work-up afforded by TLC (Et_2O) 7.5 mg **3** and 1.7 mg **2**. The ^{1}H NMR spectra were identical with those of the natural compounds.

Desacetyl xanthiuminol (**4**). Colourless crystals, mp 160–161°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590 (OH): 1765 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M - H_2O]^+$ (12) (calc. for $C_{15}H_{20}O_3$ 248.141), 233 $[248 - Me]^+$ (4), 230 $[248 - H_2O]^+$ (7), 207 $[M - MeCH(OH)CH_2]^+$ (27), 189 $[207 - H_2O]^+$ (28), 119 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\text{ nm}}{-50 \quad -55 \quad -63 \quad -108} \ (CHCl_3;\ c\ 0.3)$$

Compound **4** (5 mg) was heated for 30 min with 0.1 ml Ac_2O. TLC (Et_2O–petrol, 3:1) to afford 3 mg **5** (^{1}H NMR spectrum identical with that of authentic diacetate).

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