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AN ISOMER OF XANTHANOL FROM *XANTHIUM ORIENTALE**

FERDINAND BOHLMANN and CHRISTA ZDERO

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

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

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

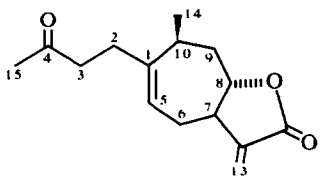
From the genus *Xanthium* several xanthanolides were isolated [1–11], which seem to be characteristic for this genus, though this type of sesquiterpene lactone has been reported from other genera too. We now have re-investigated the aerial parts of *Xanthium orientale* from which the presence of xanthine 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)

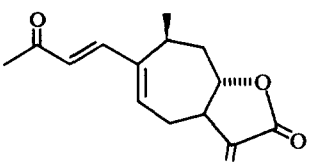
	4	**5**	**6**
H-2	5.22 *dd*	5.41 *dd*	5.19 *dd*
H-3	2.10 *m*	1.85 *ddd*	1.88 *ddd*
H-3′	1.72 *m*	1.59 *ddd*	1.75 *m*
H-4	4.85 *ddq*	3.75 *ddq*	4.91 *ddq*
H-5	5.87 *br dd*	5.96 *br dd*	5.93 *br dd*
H-6α	2.53 *ddd*	2.57 *ddd*	2.53 *ddd*
H-6β	2.10 *m*	2.14 *ddd*	2.13 *ddd*
H-7	2.52 *m*	2.48 *dddd*	2.44 *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*	2.12 *s*	2.04 *s*
	2.04 *s*		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).

* 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.



1



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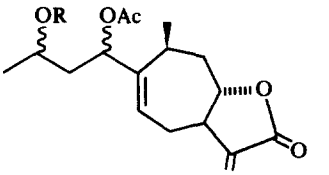

3 R = H 5 R = H(2-*epi*)
4 R = Ac 6 R = Ac(2-*epi*)

nevertheless, xanthanolides are present in *Iva* species [14, 15] also placed in this subtribe.

EXPERIMENTAL

The fresh aerial parts (120 g) (Botanical Garden Berlin-Dahlem) were extrd with Et_2O–petrol, 1:2, and the resulting extract was sepd by CC (Si gel). The fractions obtained with Et_2O were further sepd by TLC (Si gel, Et_2O–petrol, 3:1, ×2) affording 5 mg **1**, 10 mg **2** and 2 mg **5**.

2-*Epixanthanol* (**5**). Colourless gum, MS *m/z* (rel. int.): 248.140 (M − AcOH, 5) ($C_{15}H_{20}O_3$), 230 (248–H_2O, 7), 204 (248 − C_2H_4O, 100), 189 (204 − Me, 33), 176 (204 − CO, 43); CI (isobutane): 309 (M + 1, 72), 249 (309 − AcOH, 100), 234 (249 − Me, 87), 205 (249 − C_2H_2O, 86).

To 2 mg **5** in 1 ml $CHCl_3$ were added 5 mg 4-pyrrolidinopyridine [16] and 0.1 ml Ac_2O. Usual work-up after 12 hr and TLC (Et_2O–petrol, 1:1) afforded 1.5 mg **6**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (γ-lactone), 1750, 1250 (OAc); MS *m/z* (rel. int.): 308 (M − ketene, 2), 293 (308 − Me, 22), 290.152 (M − AcOH, 18) ($C_{17}H_{22}O_4$), 248 (290 − C_2H_2O, 42), 230 (290 − AcOH, 51), 215 (230 − Me, 14), 175 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-43 \quad -44 \quad -50 \quad -81} \quad (c = 0.07, CHCl_3).$$

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