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OLEFINIC AND ACETYLENIC BUTENOLIDES FROM *PEUCEDANUM ALSATICUM*

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Key Word Index—*Peucedanum alsaticum*; Apiaceae; unsaturated fatty acid derivatives; butenolides.

Abstract—The lipophilic root extract of *Peucedanum alsaticum* afforded four highly unstable butenolides which could be separated by HPLC. Whereas the stereochemistry of three olefinic derivatives, previously isolated only as their methyl ethers, were now established by ^{1}H NMR, the structure of a new acetylenic lactone was additionally confirmed by ^{13}C NMR. The compounds are probably formed by condensation of unsaturated C_{18}-acids with pyruvate.

INTRODUCTION

Peucedanum alsaticum L. is a thermophilic, perennial plant centred in SE and Central Europe [1]. Previous investigations have shown that highly unstable olefinic butenolides are accumulated in the roots and aerial parts of this speices and of the closely related *P. venetum* (Spreng.) Koch [2]. The same types of butenolide were also reported to occur in *Seseli hippomarathrum* Jacq. where, in contrast, they were found in the aerial parts only [2]. However, the stereochemistry of the triene part of the main constituents, isolated as their methyl ethers, were not established. Regarding the many chemical data already reported for the Apiaceae [3, 4], the distribution of these compounds seems to be restricted and hence, might be of some systematic relevance. More recently, a closely related acetylenic lactone was isolated from the stem bark of *Sapranthus palanga* R. E. Fries (Annonaceae) [5].

In the present paper, a re-investigation of the roots of *P. alsaticum* has been carried out in order to obtain more detailed information of the stereochemistry of the olefinic butenolides as well as the occurrence of further derivatives.

RESULTS AND DISCUSSION

The petrol–ether extract of the roots of *P. alsaticum* again afforded an unstable mixture of butenolides which could be separated by HPLC to give the previously isolated compounds **1–3** [2], and a new acetylenic butenolide (**4**). All four lactones exhibited a strong tendency to polymerize. High field ^{1}H NMR spectra allowed the assignment of the configurations of the double bonds of all compounds. Furthermore, most signals could be assigned by spin decoupling although some were still overlapping multiplets. The ^{1}H NMR spectral data of compounds **1–3** are presented here for the first time, since they were previously isolated as their methyl ethers only (Table 1) [2].

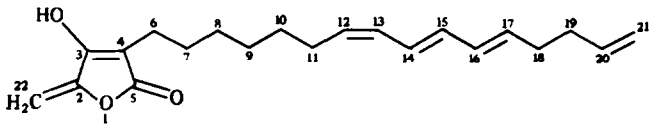
The structure of the new acetylenic lactone **4** followed from the ^{1}H NMR spectrum: a broadened doublet at δ3.07, typical for a methylene group, collapsed to a singlet on irradiation of the multiplet at δ5.45 (3H). Furthermore, the double triplet at δ5.83 became a triplet which was also

Table 1. ^{1}H NMR spectral data of compounds **1–4** (400 MHz, $CDCl_3$)

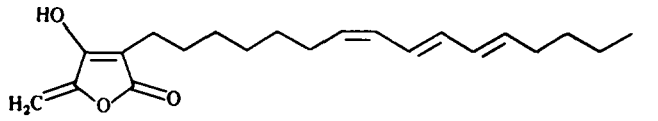
H	1	2	3	4
6	2.26 *t*	2.25 *t*	2.26 *t*	2.26 *t*
7	1.54 *tt*	1.53 *tt*	1.53 *tt*	1.52 *tt*
8–10	1.34 *m*	1.33 *m*	1.30 *m*	1.32 *m*
11	2.14 *br q*	2.14 *br q*	2.03 *br dt*	2.04 *br dt*
12	5.40 *dt*	5.38 *dt*	5.35 *m**	5.83 *dt*
13	5.99 *br t*	5.99 *br t*		5.43 *br d*
14	6.38 *dd*	6.36 *dd*	2.76 *br t*	—
15	6.17 *dd**	6.17 *dd**	5.35 *m**	—
16	6.12 *dd**	6.09 *dd**		3.07 *br d*
17	5.71 *br dt*	5.71 *br dt*	2.04 *br dt*	5.45 *m**
18	2.17 *t*	2.10 *br q*	1.30 *m*	
19		1.33 *m*		2.25 *br q*
20	5.82 *ddt*			1.42 *tt*
21t	5.03 *br d*	0.90 *t*	0.89 *t*	0.92 *t*
21c	4.97 *br d*			
22	5.07 *d*	5.04 *d*	5.05 *d*	5.08 *s*
	5.01 *d*	5.02 *d*	5.02 *d*	

*Not first order.

Typical splitting of *cis*-olefinic protons; *J* (Hz): 6, 7 = 7, 8 = 11, 12 = 7; 12, 13 = 10; 22, 21 = 2.7; compounds **1** and **2**: 13, 14 = 11; 14, 15 = 14; 15, 16 ~ 10; 16, 17 ~ 14; 16, 17 = 18, 19 = 7; (compound **1**: 19, 20 = 6; 20, 21t = 17; 20, 21c = 10; compound **2**: 20, 21 = 6.5); compound **3**: 13, 14 = 14, 15 = 6; 16, 17 = 17, 18 = 20, 21 = 6.5; compound **4**: 16, 17 = 5; 18, 19 = 19, 20 = 20, 21 = 7.



1



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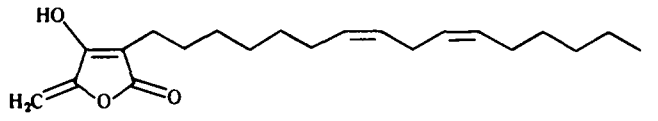

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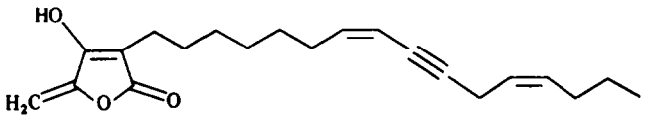

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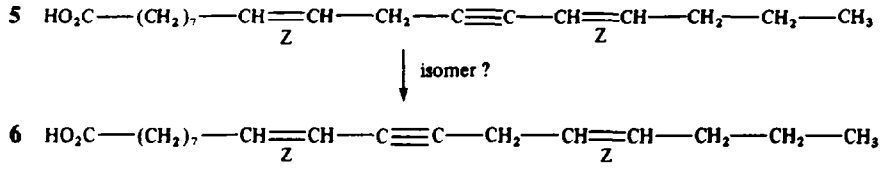

coupled with a broadened quartet at δ2.04. The coupling of the olefinic signals indicated at *Z*-configuration of the Δ^{12} and Δ^{17} double bonds. Whilst in the spectra of the butenolides **1**–**3** a pair of doublets for H-22 were visible, in that of compound **4** a singlet was observed. The structure of this acetylenic butenolide was also confirmed by ^{13}C NMR (see Experimental).

Biogenetically, this set of unstable butenolides is most likely formed by condensation of unsaturated C_{18}-acids with pyruvate. Whereas the C_{18}-acids with triene parts may be derived from linoleic acid, the corresponding acetylenic acid of the new compound **4** has not yet been isolated. The presumed precursor **6** may be formed by isomerization of dehydrocrepenynic acid (**5**).

EXPERIMENTAL

Peucedanum alsaticum was collected near Vienna, Austria (F. Hadaček, 27 July 1985). Voucher specimens have been deposited at the Herbarium of the Institute of Botany, University of Vienna (WU).

Fresh air-dried roots (77 g) were cut into small pieces and extracted with petrol(60–80°)–Et_2O (2:1) for 2 days at room temp. The conc. extract was roughly fractionated on a silica gel column eluting with petrol–Et_2O mixtures, with Et_2O increasing from 0 to 100%.

A tenth of the polar fraction obtained by CC (silica gel, Et_2O–petrol, 1:1) afforded by HPLC (RP 8, MeOH–H_2O, 17:3, *ca.* 100 bar) 20 mg **4** (R_t 7.8 min), 40 mg **1** (R_t 9.7 min), 5 mg **2** (R_t 10.2 min) and 3 mg **3** (R_t 11.1 min). All data were obtained with freshly separated material as all compounds rapidly polymerized.

Compound **4**. Colourless oil; UV $\lambda_{max}^{Et_2O}$ nm: 260 (sh), 235, 227; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550, 3400, 1780, 1750, 1645, 1445, 1380, 1320, 1120, 1090, 1045, 954, 845; MS *m/z* (rel. int.): 328.204 [M]$^+$ (9) (calc. for $C_{21}H_{28}O_3$: 328.204), 299 (5), 133 (27), 119 (28), 105 (50), 91 (92), 55 (100); ^{13}C NMR ($CDCl_3$, C-2–C-22): 149.6 *s*, 171.5 *s*, 109.3 *s*, 161.3 *s*, 18.0 *t*, 21.4 *t*, 28.9 *t*, 27.8 *t*, 27.1 *t*, 109.3 *d*, 142.8 *d*, 77.2 *s*, 92.4 *s*, 32.1 *t*, 131.6 *d*, 124.4 *d*, 29.2 *t*, 22.1 *t*, 13.7 *q*, 92.0 *t*.

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(+)-ISOBICYCLOGERMACRENAL FROM *ARISTOLOCHIA MANSHURIENSIS*

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Key Word Index—*Aristolochia manshuriensis*; Aristolochiaceae; (+)-isobicyclogermacrenal.

Abstract—The previously unknown (+)-isobicyclogermacrenal was isolated from *Aristolochia manshuriensis*. Its structure was elucidated by spectroscopic means and X-ray analysis.

By separation of the petrol–ether extract (1:1) of the stems of *Aristolochia manshuriensis* Komarov, a crystalline substance (**1**) with mp 54–56° was isolated [1]. The IR, ^{1}H NMR, ^{13}C NMR and mass spectral data are identical with those of (−)-isobicyclogermacrenal (**2**), which was isolated from the liverwort *Lepidozia vitrea* as an oil [2]. Reduction of **1** affords isobicyclogermacrenol (**3**) as does **2**. The optical rotation of **1** is positive; probably it is (+)-isobicyclogermacrenal. However, the rotation value of **1** is twice as high as that of **2** (**1**: $[\alpha]_D^{20} + 341°$ ($c = 0.7$, $CHCl_3$), **2**: $[\alpha]_D^{20} - 168°$ ($c = 1$; $CHCl_3$ [2]).

X-Ray diffraction analysis (Fig.1) indicates that **1** must be the (+)-(6*S*,7*R*)-enantiomer of (−)-(6*R*,7*S*)-6,11-cyclogermacra-1(10)*E*,4*E*-dien-14-al, (**2**) [2]. It is interesting to note that in **1** and **3** [2] the C=C double bonds are strongly elongated [1.343(6) and 1.353(6)Å], whereas the C–C single bonds C5–C6 (1.451(6) Å) and C4–C15 (1.451 (6) Å) are likely to be shortened. Furthermore the bonds C1–C2, C3–C4, C9–C10 and C7–C8 are somewhat shortened. Least squares planes calculations for molecule fragments reveal that the planes formed by C5–C6–C7–C8 and C6–C7–C11 intersect an angle of 113°. As expected, the methyl groups C12 and C13 intersect an angle of nearly 90° with the plane formed by atoms C6–C7–C11. The double bonds have identical configurations in **1** and **3**; C1=C10 is established as *trans* and C4=C5 as *cis*.

The 10-membered macro-cyclus (C1–C10) shows nearly the same configuration in both molecules. A list of the torsion angles is given in Table 1. Compounds **1** and **3** only differ in the conformation of the cyclopropane ring (C6–C7–C10) which results in the enantiomeric stereochemistry at atoms C6 and C7.

Crystal data

Compound **1** crystallized orthorhombically with the lattice constants: $a = 8.677(3)$ Å, $b = 11.717(4)$ Å, $c = 13.704(5)$ Å in the space group $p2_12_12_1$. The cell volume was calculated as 1393.3 (8) Å^3, the number of formula units in the elementary cell amounted to $Z = 4$,

Table 1. Torsion angles (°)

	3 [2]	1
C10–C1–C2–C3	94.5	85.3
C2–C1–C10–C15	9.2	9.5
C1–C2–C3–C4	−61.2	−61.6
C2–C3–C4–C5	87.4	89.2
C3–C4–C5–C6	2.3	8.6
C4–C5–C6–C7	−113.4	−117.8
C5–C6–C7–C8	4.0	5.3
C6–C7–C8–C9	90.2	93.3
C7–C8–C9–C10	−69.9	−70.6
C8–C9–C10–C1	89.5	88.4
C9–C10–C1–C2	−163.8	−163.5