Phytochemistry, Vol 27, No 11, pp 3688–3689, 1988
Printed in Great Britain

0031 9422/88 \$3.00+0.00

A DIHYDROFURANOCOUMARIN FROM *PEUCEDANUM OREOSELINUM*

ELSE LEMMICH and LENE GYLLE

Department of Chemistry BC, Royal Danish School of Pharmacy, 2 Universitetsparken, DK-2100 Copenhagen Ø, Denmark

(*Received* 29 *February* 1988)

Key Word Index—*Peucedanum oreoselinum*, Umbelliferae, angular dihydrofuranocoumarin, (8*S*,9*R*)-2′-angeloyloxy-9-isovaleryloxydihydrooroselol, 2′-(2-methylbutyryloxy)-8,9-dihydrooroselol

Abstract—A new dihydrofuranocoumarin has been isolated from the roots of *Peucedanum oreoselinum*, and the structure established as (8*S*,9*R*)-2′-angeloyloxy-9-isovaleryloxy-8,9-dihydrooroselol mainly on the basis of spectroscopic evidence.

INTRODUCTION

During previous phytochemical investigations [1–3] of *Peucedanum oreoselinum* (L.) Moench we observed a blue fluorescent minor constituent with the polarity equal to vaginidin, in the ether extract of the root material. Recently this compound (**1**) has been reisolated and the structure of it elucidated.

RESULT AND DISCUSSION

Compound **1** remained after purification a non-crystalline substance. The molecular ion at *m/z* 444 (EIMS) corresponded to $C_{24}H_{28}O_8$ (high resolution measurement). The angular dihydrofuranocoumarinic structure of **1** was evident from the ^1H NMR spectrum (Table 1), the ^{13}C NMR spectrum (Table 2) [4] and was supported by the EI mass spectrum [5]. Moreover, the characteristic chemical shift data and coupling patterns in the ^1H and ^{13}C NMR spectra, combined with the ions $[M-102]^+$ and $[M-100-102]^+$ and corresponding acylium ions in the EIMS, showed that **1** was an angelate and an isovalerate.

The ^1H NMR spectrum of **1** was close to that of vaginidin (**2**) [1], but instead of the two methyl groups in vaginidin, one methyl group and an acylated hydroxymethyl group were present in **1**. The ^{13}C NMR spectra of the two compounds are, save for the chemical shift of C-2′, quite similar as well.

The location of the acyl groups was demonstrated by a hydrogenation experiment under conditions as previously used [1] to obtain hydrogenolyses of the benzylic acyloxy group without hydrogenation of the C-3 double bond. The molecular ion of the hydrogenation product **3** was, as expected, *m/z* 346 (EIMS) corresponding to $C_{19}H_{22}O_6$ (high resolution measurement). The ^1H NMR spectrum of **3** confirmed that no acyloxy group was present at C-9 and showed that the acyloxy group left was 2-methylbutyryloxy arising from hydrogenation of the angeloyloxy group. On basis of this it could be concluded that **1** is 2′-angeloyloxy-9-isovaleryloxy-8,9-dihydrooroselol.

Like the previously isolated dihydrofuranocoumarins [1] with a benzylic acyloxy group, the value of the coupling constant $J_{7,8}$ in **1** is 6.5 Hz, which is consistent with a *cis*-configuration at C-8 and C-9. By correlation of the CD spectrum of **3** with that of dihydrooroselol (**4**), which is the hydrogenolysis product from vaginidin **2** [1], the configuration at C-8 could be determined and the configuration of **1** is thus 8*S*,9*R*.

The configuration at C-1′ has not been established.

EXPERIMENTAL

Collection of plant material, extraction and gross fractionation has previously been described [1]. Isolation and final purification of **1** was carried out by chromatography on silica gel

Table 1. ^1H NMR spectral data of compounds **1** and **3** (500 MHz, $CDCl_3$, TMS as internal standard)

H	1	3
3	6.24 *d*	6.15 *d*
4	7.63 *d*	7.60 *d*
5	7.44 *d*	7.20 *d*
6	6.88 *d*	6.68 *d*
8	4.72 *d**	4.85 *t*†
9	7.07 *d*	3.29 *dd*
		3.38 *dd*
Me-1′	1.45 *s*	1.20 *s*
2′a	4.30 *d*	4.07 *d*†
2′b	4.34 *d*	4.27 *d*†
O-Angeloyl	6.13 *qq*	*O*-α-Me- 2.39 *m*
	2.02 *dq*	butyryl 1.45 *m*
	1.92 *dq*	1.65 *m*
		1.12 *d*
O-Isovaleryl	2.25 *m*	0.86 *t*
	2.15 *m*	
	0.96 *d*	

J (Hz) compound **1:** 3,4 = 9.5, 5,6 = 8.5, 8,9 = 6.5, 2′a, 2′b = 11.0. **3:** 3,4 = 9.5, 5,6 = 8.5, 8,9 = 9.0, 9α,9β = 16, 2′a, 2′b = 11.0

*The chemical shift of H-8 in vaginidin was erroneously reported as δ 5.55 [1]. The correct value is δ 4.55

†Compound **3** is a mixture of two epimers. The marked signals are doubled, Δδ ~ 0.01 ppm or less

Table 2. ^{13}C NMR spectral data of compounds **1** and **2** (125 8 MHz, $CDCl_3$)

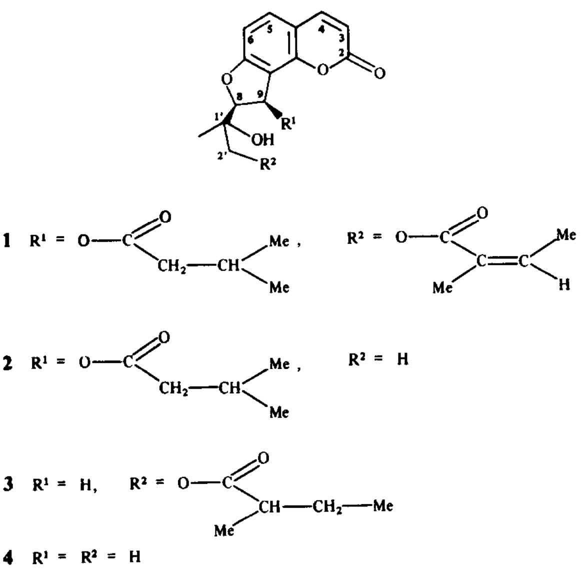
C	**1**	**2**
2	160.2	160.0
3	108.5	108.4
4	144.1	144.1
4a	133.3[a]	113.9[a]
5	132.2	132.1
6	114 0	113.9
6a	164.3	164.5
8	69.5	69.6
9	88.8	92 1
9a	114.1[a]	114.0[a]
9b	152 6	152.4
1′	73 2	71.9
2′	68.2	27.0
Me-1′	22.9[b]	27.5
O-Isovaleryl	171 7	172.1
	44 1	44.1
	26.2	26.2
	22 7[b]	23 0
	22.8[b]	23.1
O-Angeloyl	168.2	
	128.0	
	139.9	
	16.5	
	21.2	

[a], [b] Interchangeable assignments

(eluent· toluene–EtOAc, 1:9 → 1 3) and by prep. HPLC (column· Lichrosorb RP 18, 5μm, 8 × 200 mm, eluent: $MeOH-H_2O$, 7:3, UV detection 330 nm).

(8R,9S)-2′-*Angeloyoxy-9-isovaleryloxy-dihydrooroselol* (**1**). The substance did not crystallize. $[\alpha]_D^{20} + 124.0°$, $[\alpha]_{436}^{20} + 317.8°$ (MeOH; *c* 0.4). IR ν_{max}^{KBr} cm^{-1}· 3500 (OH), 1740 (C=O), 835 (C=C). EIMS (probe) 70 eV, *m/z* (rel. int): 444 177 $[M]^+$(9) (calc. for $C_{24}H_{28}O_8$· 444.178), 342 $[M-\text{isoval OH}]^+$ (2), 341 (4), 242 $[342-\text{Ang OH}]^+$(24), 241 (11), 229 (41), 213 (5), 203 (34), 187 (79), 186 (100), 158 (29), 85 [sat. $RC{\equiv}O]^+$(36), 83 [unsat. $RC{\equiv}O]^+$(97), 57 $[85-CO]^+$(44), 55 $[83-CO]^+$(59).

(8R)-2′-(*Methylbutyryloxy*)-8,9-*dihydrooroselol* (**3**) Compound **1** (5 mg) was added to a prereduced suspension of PtO_2 (10 mg) in EtOH (10 ml). A stream of H_2 was passed through at 0° for 25 min. The reaction was followed on TLC and was interrupted when 10–20% of **1** was left. The catalyst and the solvent were removed and the product was purified on silica gel with toluene–EtOAc (1.9 → 1.4) as eluent The product was compound **3** (3 mg), which crystallized, but as it was a mixture of two epimers the mp and $[\alpha]_D^{20}$ of **3** were not determined. EIMS (probe) 70 eV, *m/z* (rel. int.). 346.141 $[M]^+$ (30) (calc. for $C_{19}H_{22}O_6$· 346 142), 244 $[M-\text{Mebutyr OH}]^+$ (5), 242 (5), 231 (26), 229 (35), 213 (17), 203 (5), 188 (87), 187 (100), 186 (12), 159 (13), 85 $[RC{\equiv}O]^+$(55), 57 $[85-CO]^+$(73). CD.$\Delta\varepsilon_{325} + 4.4$ (MeOH) [dihydrooroselol (**4**) $\Delta\varepsilon_{325} + 4\,9$ (MeOH)]



Acknowledgements—The author is grateful to Dr K Bock (The Technical University of Denmark) and to Dr J Møller (Odense University) for recording the NMR and mass spectra, respectively. Thanks are due to the Danish Natural Science Research Council for the provision of NMR and MS facilities.

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