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DIHYDROPYRANOCOUMARINS FROM ROOTS OF *PEUCEDANUM JAPONICUM*

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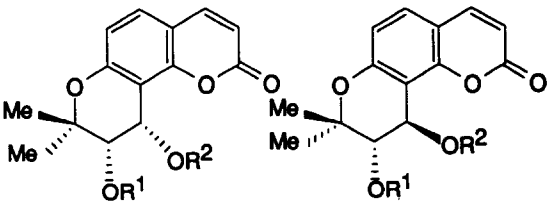
Key Word Index—*Peucedanum japonicum*; Umbelliferae; roots; dihydropyranocoumarins; peujaponisin;(−)-visnadin; ^{13}C NMR.

Abstract—Two new angular-type dihydropyranocoumarins, peujaponisin and (−)-visnadin, were isolated from the roots of *Pencedanum japonicum* and the structures determined as 3′(*S*)-senecioyloxy-4′(*S*)-isovaleryloxy-3′,4′-dihydroseselin and 3′(*S*)-2-methylbutyryloxy-4′(*S*)-acetoxy-3′,4′-dihydroseselin, respectively, by spectroscopic analysis and chemical reactions.

INTRODUCTION

The dried roots (Shoku-Bohfuu in Japanese) of *Peucedanum japonicum* (Umbelliferae), are used for coughs, colds, heachaches and as an antifebrile and anodyne in Japan. In our previous study [1], we isolated a mixture of acetylangeloyloxy-3′,4′-dihydroseselin and acetyltigloyloxy-3′,4′-dihydroseselin from roots of this plant. From the roots, three dihydropyranocoumarins were subsequently isolated, 3′(*S*), 4′(*S*)-diisovaleryloxy-3′,4′-dihydroseselin (**1**), 3′(*S*),4′(*S*)-disenecioyloxy-3′,4′-dihydroseselin (**2**) [2] and (+)-samidin (**3**) [3]. Recently, three angular-type dihydropyranocoumarin derivatives have been isolated from this crude drug and identified as antihistaminic, calcium-blocking and cytotoxic natural products [4, 5]. The constituents of roots of *P. japonicum* were studied and two new angular-type dihydropyranocoumarins, peujaponisin (**4**) and (−)-visnadin (**5**), were isolated along with four known dihydropyranocoumarins, **1**–**3** and (+)-anomalin (**6**) [1, 6, 7]. This study was conducted in order to isolate these related compounds and to determine their structures.



1 R^1=R^2=$COCH_2CH(Me)_2$
2 R^1=R^2=COCH=$C(Me)_2$
3 R^1=COCH=$C(Me)_2$, R^2=COMe
4 R^1=COCH=$C(Me)_2$, R^2=$COCH_2CH(Me)_2$
5 R^1=COCH(Me)CH_2Me, R^2=COMe
6 R^1=R^2=COC(Me)=CHMe
7 R^1=R^2=H
8 R^1=R^2=H
9 R^1=H, R^2=C_2H_5
10 R^1=H, R^2=C_2H_5
11 R^1=COCH=$C(Me)_2$, R^2=C_2H_5
12 R^1=COCH(Me)CH_2Me, R^2=COMe

RESULTS AND DISCUSSION

Compound **4** was found to have the molecular formula, $C_{24}H_{28}O_7$ ([M]$^+$ *m/z* 428.1593). Its UV spectrum with maxima at 216 (sh), 245 (sh), 255, 297 (sh) and 323 nm, indicated it to possess a 7-oxycoumarin moiety and its IR spectrum showed absorption for a carbonyl group (1730 cm^{-1}) and an aromatic ring (1605 cm^{-1}), both characteristic of the coumarin skeleton. The ^{1}H NMR spectrum showed three AB quartet systems at δ6.24, 7.60 (each 1H, *d*, J=9.5 Hz, H-3, H-4), δ7.36, 6.79 (each 1H, *d*, J=8.6 Hz, H-5, H-6) and δ5.32, 6.58 (each 1H, *d*, J=5.0 Hz, H-3′, H-4′), and *gem*-dimethyl groups at δ1.42, 1.46 (each 3H, *s*). The complex signals at δ1.89, 2.23 (each 3H, *d*, J=1.3 Hz) and δ5.63 (1H, *m*) were due to a senecioyl group, while those at δ0.94–2.24 were ascribed to an *iso*valeryl moiety.

Alkaline hydrolysis of **4** gave (−)-*cis*-khellactone (**7**) and (+)-*trans*-khellactone (**8**) as artifacts from epimerization at the benzylic 4′-position, along with senecioic and isovaleric acids. Ethanolic alkaline hydrolysis of **4** gave (−)-*cis* (**9**) and (+)-*trans*-ethylkhellactone (**10**). By partial hydrolysis with 1 N ethanolic NaOH [8, 9], **4** gave the khellactone ester as a viscous oil (**11**), subsequently identified as 3′(*S*)-senscioyloxy-4′(*S*)-ethoxy-3′,4′-dihydroseselin, based on a comparison (TLC, IR, ^{1}H NMR, ^{13}C NMR and mass spectra) with an authentic sample prepared from **3**. The isovaleryl group of **4** is thus linked to the 4′-hydroxyl group of **7**. It thus follows that the structure of **4** is 3′(*S*)-senecioyloxy-4′(*S*)-isovaleryloxy-3′,4′-dihydroseselin.

Compound **5** had the molecular formula, $C_{21}H_{24}O_7$ ($[M]^+$ *m/z* 388). Its ^1H NMR and mass spectra were quite similar to those of peucedanocoumarin I (**12**) [10]. Chemical shifts of the ^{13}C NMR signals of **5** were in good agreement with those of **12**, except for those arising due to its *gem*-dimethyl groups (Table 1). By alkaline hydrolysis, **5** gave **7** and **8** along with 2-methylbutyric acid and acetic acid. Based on the present results, **5** may be considered to have the structure, 3′(*S*)-2-methylbutyryloxy-4′(*S*)-acetoxy-3′,4′-dihydroseselin, which is the C-3′ and C-4′ enantiomer of visnadin [11, 12].

For compound **6**, IR, UV and ^1H NMR spectra were virtually the same as those of (+)-anomalin [1, 7]. By alkaline hydrolysis, **6** gave **7** and **8**, with angelic acid, and was identified by a comparison with authentic (+)-anomalin isolated from *P. formosanum* [1].

EXPERIMENTAL

Mps: uncorr. EIMS: 20 and 70 eV, HRMS: 70 eV. ^1H and ^{13}C NMR: 200, 400 MHz and 50, 100 MHz, respectively, with TMS as an int. std. CC: Mallinckrodt silica gel (100 mesh). TLC and prep. TLC: silica gel 60 GF_{254} plates (0.25 mm) and silica gel 60 PF_{254} plates (0.5 mm). Spots and bands were detected by UV irradiation (254 and 365 nm).

Plant material. Dried roots of *Peucedanum japonicum* Thumb. were cultivated and collected in the botanical garden of this college in September 1987. The crude drug (Shoku-Bohfuu) was supplied by Uchida Wakan-Yaku Company, Ltd. Ogatacho, Niigata.

Extraction and isolation. Finely cut roots (1.5 kg) were extracted with MeOH (3 l × 3) at room temp. for 2 hr. The comb. MeOH extracts were concd in vacuo. The residue (490 g) was dissolved in H_2O and extracted successively with *n*-hexane (200 ml × 3), Et_2O (200 ml × 3), EtOAc (200 ml × 3), and *n*-BuOH (210 ml × 5). An aliquot (63 g) of the *n*-hexane extract (144 g) was subjected to CC on silica gel (900 g) and eluted successively with a *n*-hexane–EtOAc (100:1) mixt. of increasing polarity. A total of 70 frs were collected. Frs 29–38 were repeatedly subjected to prep. TLC (silica gel, *n*-hexane EtOAc, 5:1) to yield the six crude coumarins. Each was further purified by recrystallisation and prep. TLC (*n*-hexane–EtOAc 5:1; 10 developments), yielding in order of increasing polarity: **1** (1.1 g), (+)-anomalin (**6**) (1.15 g), **4** (1.23 g), **5**(13 mg), **2** (75 mg) and (+)-samidin (**3**) (450 mg). Known coumarin compounds were identified by comparison of their spectroscopic properties with lit. values.

Peujaponisin (**4**). Oily $[\alpha]_D^{25}$ −7.0°, $[\alpha]_{578}^{25}$ −9.0°, $[\alpha]_{546}^{25}$ −13.0°, $[\alpha]_{436}^{25}$ −83.0°, $[\alpha]_{365}^{25}$ −603.0° ($CHCl_3$; *c* 1.0). UV λ_{max}^{MeOH} nm (log ε): 216 (sh. 4.56), 245 (sh. 4.00), 255 (3.88), 297 (sh. 4.06), 323 (4.23); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1650, 1605, 1465; ^1H NMR (400 MHz, $CDCl_3$): see Table 2. ^{13}C NMR (100 MHz, $CDCl_3$): see Table 1. EIMS 70 eV, *m/z* (rel. int.): 428 $[M]^+$ (1), 326 (6), 311 (11), 261 (13), 244 (17), 229 (44), 213 (9), 85 (37), 83 (100). HRMS *m/z*: 428.1593 ($[M]^+$, calcd. for $C_{24}H_{28}O_7$: 428.1621), 326.1125 ($C_{19}H_{18}O_5$: 326.1152), 311.0951 ($C_{18}H_{15}O_5$: 311.0918).

(−)-Visnadin (**5**). Oily, $[\alpha]^{22}$ −12.9°, $[\alpha]_{546}^{22}$ −16.2°, $[\alpha]_{436}^{22}$ −45.2°, $[\alpha]_{365}^{22}$ −241.9° ($CHCl_3$; *c* 0.31). UV λ_{max}^{MeOH} nm (log ε): 218 (sh. 4.17), 244 (sh. 3.74), 255 (3.66), 297 (sh. 3.96), 323 (4.10). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1605, 1520, 1485, 1455. ^1H NMR

Table 1. ^{13}C NMR spectral data of compounds **1–6** in $CDCl_3$

C	1	2	3	4*	5*	6
2	159.6 *s*	159.8 *s*	159.8 *s*	159.8 *s*	159.7 *s*	159.7 *s*
3	113.3 *d*	113.2 *d*	113.3 *d*	113.2 *d*	113.3 *d*	113.3 *d*
4	143.2 *d*	143.2 *d*	143.1 *d*	143.1 *d*	143.3 *d*	143.1 *d*
5	129.3 *d*	129.0 *d*	129.2 *d*	129.1 *d*	129.4 *d*	129.2 *d*
6	114.4 *d*	114.4 *d*	114.4 *d*	114.4 *d*	114.5 *d*	114.4 *d*
7	156.6 *s*	156.8 *s*	156.7 *s*	156.7 *s*	156.6 *s*	156.8 *s*
8	107.5 *s*	107.6 *s*	107.5 *s*	107.6 *s*	107.4 *s*	107.6 *s*
4a	112.5 *s*	112.5 *s*	112.6 *s*	112.5 *s*	112.5 *s*	112.5 *s*
8a	154.1 *s*	154.1 *s*	154.1 *s*	154.1 *s*	154.0 *s*	154.2 *s*
2′	77.3 *s*	77.3 *s*	77.4 *s*	77.5 *s*	77.2 *s*	77.5 *s*
3′	70.5 *d*	69.5 *d*	70.8 *d*	70.4 *d*	70.8 *d*	70.3 *d*
4′	60.5 *d*	59.8 *d*	59.6 *d*	59.6 *d*	60.3 *d*	60.2 *d*
gem-Me	22.5 *q*	22.6 *q*	22.2 *q*	22.5 *q*	21.8 *q*	22.5 *q*
	25.4 *q*	25.1 *q*	25.4 *q*	25.3 *q*	25.6 *q*	25.4 *q*
3′-Ester						
1	171.8 *s*	165.2 *s*	165.2 *s*	165.1 *s*	175.6 *s*	166.3 *s*
2	43.3 *t*	115.3 *d*	115.1 *d*	115.2 *d*	41.4 *d*	127.1 *s*
3	25.4 *d*	158.1 *s*	158.0 *s*	157.9 *s*	26.6 *t*	139.7 *d*
4	22.5 *q*	27.4 *q*	27.4 *q*	27.4 *q*	11.6 *q*	15.5 *q*
5	22.5 *q*	20.3 *q*	20.4 *q*	20.4 *q*	16.6 *q*	20.4 *q*
4′-Ester						
1	171.7 *s*	165.1 *s*	169.9 *s*	171.8 *s*	169.7 *s*	166.5 *s*
2	43.1 *t*	115.4 *d*	20.7 *q*	43.1 *t*	20.7 *q*	127.5 *s*
3	25.6 *d*	157.4 *s*	—	25.4 *d*	—	138.3 *d*
4	22.5 *q*	27.4 *q*	—	22.4 *q*	—	15.7 *q*
5	22.2 *q*	20.3 *q*	—	22.4 *q*	—	20.3 *q*

*Assignments confirmed by ^1H–^{13}C COSY experiments.
SFORD and DEPT multiplicity.

Table 2. ^{1}H NMR spectral data of compounds **4** and **5** in $CDCl_3$

H	4	5
3	6.24 *d* (9.5)	6.20 *d* (9.5)
4	7.60 *d* (9.5)	7.60 *d* (9.5)
5	7.36 *d* (8.6)	7.38 *d* (8.6)
6	6.79 *d* (8.6)	6.78 *d* (8.6)
3′	5.32 *d* (5.0)	5.28 *d* (5.0)
4′	6.58 *d* (5.0)	6.48 *d* (5.0)
gem-Me	1.46 *s*	1.45 *s*
	1.42 *s*	1.42 *s*
3′-Ester		
2	5.63 *m*	2.41 *m*
3	—	1.72 *m*
		1.45 *m*
4	2.23 *d* (1.3)	0.94 *t* (7.5)
5	1.89 *d* (1.3)	1.21 *d* (7.0)
4′-Ester		
2	2.24 *m*	2.09 *s*
3	2.11 *m*	—
4	0.97 *d* (6.6)	—
5	0.95 *d* (6.6)	—

All assignments were confirmed by ^{1}H–^{1}H 2D COSY.

Values in parentheses are coupling constants in Hz.

(200 MHz, $CDCl_3$): see Table 2. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 1. EIMS 70 eV, *m/z* (rel. int.): 388 $[M]^+$ (5), 328 (5), 313 (10), 244 (32), 229 (100), 85 (70), 57 (38).

(+)-*Anomalin* (**6**). Needles, mp 173–174°. $[\alpha]_D^{23}$ +38.2° ($CHCl_3$; *c* 2.76). IR, UV and ^{1}H NMR spectra essentially identical with those reported [1, 7, 9]. ^{13}C NMR (50 MHz, $CDCl_3$): see Table 1. EIMS 70 eV, *m/z* (rel. int.): 426 $[M]^+$ (2), 327 (24), 326 (11), 311 (15), 244 (6), 229 (33), 227 (7), 213 (4), 83 (100), 55 (69).

Alkaline hydrolysis of peujaponisin (**4**). Compound **4** (600 mg) was treated with 5% NaOH (60 ml), and the reaction mixt. refluxed for 2 hr. The reaction mixt. was acidified with dil.H_2SO_4, extracted with Et_2O, washed with 10% $NaHCO_3$ soln, dried with Na_2SO_4 and evapd; the residue was subjected to CC (silica gel, *n*-hexane–EtOAc, 2:1) to yield two products. The first eluant gave (−)-*cis*-khellactone (**7**) as needles (85 mg), mp 173–174°. $[\alpha]_D^{27}$ −75.7° ($CHCl_3$; *c* 0.33). ^{13}C NMR: see Table 3. EIMS 70 eV, *m/z* (rel. int.): 262 $[M]^+$ (22), 192 (12), 191 (100), 162 (35), 134 (27), 107 (14). The second eluant gave (+)-*trans*-khellactone (**8**) as needles (105 mg), mp 185–186°. $[\alpha]_D^{25}$ +19.8° ($CHCl_3$; *c* 0.50). ^{13}C NMR (50.10 MHz, $CDCl_3$): see Table 3. EIMS 70 eV, *m/z* (rel. int.): 262 $[M]^+$ (11), 192 (13), 191 (100), 190 (12), 162 (25), 134 (29), 107 (12). These substances **7** and **8** were identified by comparison with respective authentic samples (mmp, IR and ^{1}H NMR). The acidic portion was converted to the *p*-phenylphenacyl ester in the usual way. The crude product was subjected to prep. TLC (C_6H_6) and recrystallized from EtOH to afford *p*-phenylphenacyl isovalerate as lustrous platelets, mp 78.5–79° [11, 13], and *p*-phenylphenacyl senecioate, lustrous platelets, mp 145–146° [1, 11, 14]. These esters were identical to the respective authentic samples (mmp, MS and ^{1}H NMR).

Ethanolic alkaline hydrolysis of peujaponisin (**4**). Compound **4** (300 mg) dissolved in EtOH (10 ml) was added to 1 N ethanolic NaOH (20 ml), and the reaction mixt. refluxed for 1 hr. After work-up in the usual way, the reaction product was subjected to CC on silica gel eluting with *n*-hexane–EtOAc (1:1) to give (−)-*cis-ethylkhellactone* (**9**) as needles (15.4 mg), mp 126–127°. $[\alpha]_D^{23}$ −77.04° ($CHCl_3$; *c* 1.35). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.24 (1H, *d*, *J* = 9.5 Hz, H-3), 7.62 (1H, *d*, *J* = 9.5 Hz, H-4), 7.30 (1H, *d*, *J* = 8.6 Hz, H-5), 6.74 (1H, *d*, *J* = 8.6 Hz, H-6), 3.84 (1H, *d*, *J* = 5.0 Hz, H-3′), 4.82 (1H, *d*, *J* = 5.0 Hz, H-4′), 1.40, 1.46 (each 3H, *s*, *gem*-Me_2), 3.98 (2H, *qm*, *J* = 8.0 Hz, $-CH_2Me$), 1.34 (3H, *t*, *J* = 8.0 Hz, $-CH_2Me$). ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3. EIMS 70 eV, *m/z* (rel. int.): 290 $[M]^+$ (13), 219 (34), 218 (60), 191 (51), 190 (32), 162 (62), 149 (12), 134 (36), 107 (10), 77 (19), 57 (22), 43 (100).

(+)-*trans*-Ethylkhellactone (**10**). Needles (113 mg), mp 157–158°. $[\alpha]_D^{25}$ +84.5° ($CHCl_3$; *c* 0.64). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.18 (1H, *d*, *J* = 9.5 Hz, H-3), 7.56 (1H, *d*, *J* = 9.5 Hz, H-4), 7.26 (1H, *d*, *J* = 8.6 Hz, H-5), 6.74 (1H, *d*, *J* = 8.6 Hz, H-6), 3.88 (1H, *d*, *J* = 3.0 Hz, H-3′), 4.63 (1H, *d*, *J* = 3.0 Hz. H-4′), 1.48, 1.44 (each 3H, *s*, *gem*-Me_2), 4.06 (2H, *qm*, *J* = 8.0 Hz, $-CH_2Me$), 1.28 (3H, *t*, *J* = 8.0 Hz, $-CH_2Me$). ^{13}C NMR (50 MHz, $CDCl_3$): see Table 3. EIMS 70 eV, *m/z* (rel. int.): 290 $[M]^+$ (23), 219 (49), 218 (84), 191 (95), 190 (50), 189 (16), 176 (15), 175 (14), 162 (100), 149 (12), 134 (61), 107 (14), 77 (19), 59 (26), 43 (83), identified by direct comparison with authentic samples (mmp, IR and ^{1}H NMR). The acid portion was worked-up as described above to afford *p*-phenylphenacyl senecioate and *p*-phenylphenacyl isovalerate.

Partial hydrolysis of peujaponisin (**4**). Compound **4** (300 mg) was treated with 1 N ethanolic NaOH (20 ml) and the mixt. stirred at room temp. for 10 min. After working up in the usual way, the reaction product was subjected to prep. TLC (silica gel) with *n*-hexane–EtOAc (5:1) to give viscous oil (**11**) (120 mg), $[\alpha]_D^{23}$ −94.2° $CHCl_3$; *c* 1.08). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.22 (1H, *d*, *J* = 9.5 Hz, H-3), 7.58 (1H, *d*, *J* = 9.5 Hz, H-4), 7.30 (1H, *d*, *J* = 8.6 Hz, H-5), 6.77 (1H, *d*, *J* = 8.6 Hz, H-6), 4.54 (1H, *d*, *J* = 2.5 Hz, H-3′), 5.18 (1H, *d*, *J* = 2.5 Hz, H-4′), 1.49, 1.42 (each 3H, *s*, *gem*-Me_2), 5.60 (1H, *q*, *J* = 1.3 Hz, $-CH=C(Me)_2$), 2.14, 1.84 (each 3H, *d*, *J* = 1.3 Hz, 2 × Me), 4.04 (2H, *q*, *J* = 8.0 Hz, $-CH_2Me$), 1.30 (3H, *t*, *J* = 8.0 Hz, $-CH_2Me$). ^{13}C NMR (50 MHz. $CDCl_3$): see Table 3. EIMS 70 eV, *m/z* (rel. int.): 372 $[M]^+$ (2), 327 (18), 257 (30), 229 (20), 83 (100), 55 (15). The acid portion was worked-up as described above to afford *p*-phenylphenacyl isovalerate. Identification with 3′-(*S*)-senecioyloxy-4′ (*S*)-ethoxy-3′,4′-dihydroseselin from **3** by the same reaction as above was established by comparison of MS, $[\alpha]_D$, ^{1}H NMR and ^{13}C NMR spectra.

Alkaline hydrolysis of (−)-*visnadin* (**5**). Compound **5** (12 mg) was treated with 5% NaOH (10 ml) and the reaction mixt. refluxed for 2 hr. Working up as described above yielded a product, which was subjected to prep. TLC (*n*-hexane–EtOAc, 2:1, 4 developments) to yield **7** (2.6 mg) and **8** (3.8 mg). The acid portion was worked-up as described above to afford *p*-phenylphenacyl acetate, lustrous platelets, mp 110–111° [1] and *p*-phenylphenacyl 2-methylbutyrate, lustrous platelets, mp 68–70° [11]. These substances were identical to the respective authentic samples by ^{1}H NMR comparison.

Alkaline hydrolysis of (+)-*anomalin* (**6**). Compound **6** (350 mg) was treated in the same manner as described for **4** to give **7**

Table 3. ^{13}C NMR spectral data of compounds 7–11 in $CDCl_3$

C	7	8	9	10	11
2	161.2 *s*	161.5 *s*	160.7 *s*	160.9 *s*	160.8 *s*
3	112.1 *d*	112.0 *d*	112.6 *d*	112.8 *d*	112.4 *d*
4	144.3 *d*	144.4 *d*	143.8 *d*	143.6 *d*	143.6 *d*
5	128.6 *d*	128.4 *d*	128.8 *d*	128.5 *d*	128.5 *d*
6	114.9 *d*	114.8 *d*	114.6 *d*	114.6 *d*	114.6 *d*
7	156.6 *s*	156.4 *s*	156.8 *s*	156.3 *s*	156.2 *s*
8	111.1 *s*	111.8 *s*	109.7 *s*	109.3 *s*	108.6 *s*
4a	112.2 *s*	112.5 *s*	112.4 *s*	112.6 *s*	112.8 *s*
8a	154.6 *s*	154.3 *s*	154.8 *s*	155.1 *s*	155.0 *s*
2′	79.1 *s*	79.5 *s*	78.8 *s*	78.4 *s*	79.7 *s*
3′	71.2 *d*	74.8 *d*	70.3 *d*	72.7 *d*	69.9 *d*
4′	61.1 *d*	66.4 *d*	69.6 *d*	71.4 *d*	69.5 *d*
gem-Me	21.6 *q*	20.3 *q*	22.2 *q*	23.7 *q*	23.6 *q*
	25.3 *q*	25.4 *q*	25.1 *q*	24.2 *q*	25.4 *q*
3′-Ester					
1	—	—	—	—	165.3 *s*
2	—	—	—	—	115.3 *d*
3	—	—	—	—	158.9 *s*
4	—	—	—	—	27.4 *q*
5	—	—	—	—	20.4 *q*
4′-OC_2H_5	—	—	68.5 *t*	68.8 *t*	66.4 *t*
			15.8 *q*	15.8 *q*	15.6 *q*

Assignment by selective decoupling.
SFORD and DEPT multiplicity.

(45 mg), **8** (56 mg) and *p*-phenylphenacyl angelate, lustrous platelets, mp 87–88° [9]. These substances were identified by comparison with the respective authentic samples.

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