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Studies on Coumarins from the Root of *Angelica pubescens* Maxim. IV.[1] Structures of Angelol-Type Prenylcoumarins

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The root of *Angelica pubescens* Maxim. (Umbelliferae) afforded seven new coumarins, angelols B—H (**2**—**8**), together with a known coumarin, angelol A (formerly simply called angelol). The structures of these coumarins were determined on the basis of spectral and chemical evidence as 6-(1-acyloxy-2,3-dihydroxy-3-methylbutyl)-7-methoxycoumarins and 6-(2-acyloxy-1,3-dihydroxy-3-methylbutyl)-7-methoxycoumarins.

Furthermore, in the course of this investigation we revised the reported structure of angelol A (**1**)

Keywords——*Angelica pubescens* Maxim.; Umbelliferae; coumarins; 6-(1-acyloxy-2,3-dihydroxy-3-methylbutyl)-7-methoxycoumarins; 6-(2-acyloxy-1,3-dihydroxy-3-methylbutyl)-7-methoxycoumarins; ^{13}C-NMR

We are interested in the coumarins of the root of *Angelica pubescens* Maxim., which is a plant related to the Chinese crude drug Du Huo. In the previous paper, we reported the isolation of the thirteen coumarins from this root, as well as the structure elucidation of these compounds.[2]

Recently, we have been able to isolate the angelol-type coumarins and to elucidate those structures. Though they are the principal coumarin component of this root, only the structure of angelol A (**1**)[3] had been determined previously because of the difficulty of isolating these compounds. This paper deals with the isolation and the structure elucidation of these compounds. Furthermore, although the structure of **1** had hitherto been assumed to be **1a**, in the course of the chemical and spectral investigations of the analogous compounds **2**—**8** as described below, it became clear that **1b** should be preferred as the structure of **1**. Therefore, we also present a revision of the structure of **1**.

The angelol-type coumarins fraction, isolated from the ethyl acetate extract of the root of this plant after repeated chromatographic separation, afforded seven coumarins, namely angelol B (**2**), angelol C (**3**), angelol D (**4**), angelol E (**5**), angelol F (**6**), angelol G (**7**) and angelol H (**8**) in addition to angelol A (**1**). The ultraviolet (UV) and proton magnetic resonance (^{1}H-NMR) spectral data of **2**—**8** indicated that they were coumarins having a methoxyl and a trihydroxyisopentyl group at the C-7 and C-6 positions, respectively, and that one of the hydroxyl groups on the isopentyl group is esterified with one of the following acids: angleic acid, tiglic acid, isovaleric acid and 2-methylbutyric acid.

Angelol B (**2**), colorless prisms, mp 143—144°C, $C_{20}H_{24}O_7$. The optical rotatory dispersion (ORD) spectrum of **2** showed a negative plane curve similar to that of **1**. The ^{1}H-NMR spectrum (δ ppm, $CDCl_3$) of **2** exhibited signals due to protons of the C-3 and C-4 positions of the coumarin ring at 6.18 (1H, d, J=9.5 Hz) and 7.55 (1H, d, J=9.5 Hz), signals assignable to the protons of the C-5 and C-8 positions at 7.55 (1H, s) and 6.71 (1H, s), signals due to a methoxyl group at 3.89 (3H, s) and signals arising from a trioxyisopentyl group at 5.60 (1H, br s), 5.06 (1H, br s), 4.72 (1H, br s), 3.10 (1H, br s), 1.53 (3H, s) and 1.22 (3H, s). This signal pattern was very similar to that of **1**. The ^{1}H-NMR spectrum of **2** showed signals arising from a tigloyl group at 6.75 (1H, m), 1.70 (3H, m) and 1.65 (3H, s), in contrast to that of **1**, which showed the presence of an angeloyl group. **2** was treated with conc. H_2SO_4 (or P_2O_5) in acetone to yield a 12,13-isopropylidene derivative (**9**) similar to that formed from **1**,

and **9** afforded two alcohols **10** and **11** having different configurations at the C-11 position (benzyl position) and tiglic acid upon alkali hydrolysis. The chemical properties and the spectral data of **9**, **10** and **11** were identical with those of the isopropylidene derivative and two alcohols prepared from **1** in the same way. The finding that the isopropylidenation of **1** and **2** gave the same product was attributed to the isomerization of the acyl group (from angeloyl to tigloyl) under these conditions. On oxidation with lead tetraacetate in benzene, **2** afforded an aldehyde (**12**), whose ^{1}H-NMR spectrum (δ ppm, $CDCl_3$) still showed the signals assignable to the tigloyl group at 7.00 (1H, m), 1.90 (3H, m) and 1.85 (3H, m), and coincided with those of an aldehyde prepared from **1** by the same reaction except for the proton signals due to the acid moiety. Furthermore, the ORD spectrum of **12** showed a negative plane curve. From the above results, it became clear that **2** had the same absolute structure as **1** except that the acid forming the ester was tiglic acid.

Angelol C (**3**), colorless plates, mp 113—114°C, $C_{20}H_{26}O_7$. The ORD spectrum of **3** also showed a negative plane curve like those of **1** and **2**. The ^{1}H-NMR signals (δ ppm, $CDCl_3$) of **3** were very similar to those of **2** except that complicated signals assignable to a 2-methylbutyryl group at 2.25 (1H, m), 1.37 (2H, m), 1.02 (3/2H, d, J=7.5 Hz), 0.77 (3/2H, d, J=7.5 Hz), 0.74 (3/2H, t, J=7.0 Hz) and 0.49 (3/2H, t, J=7.0 Hz) were observed instead of the signals due to the tigloyl group of **2**. Therefore, it was presumed that **3** had the same coumarin moiety as **2**, and had 2-methylbutyric acid as the ester moiety. Furthermore, in view of the fact that in the ^{1}H-NMR of **3** the signals due to this ester moiety appeared as a complicated pattern, and that the hydrolysis of **3** afforded *dl*-2-methylbutyric acid, it was considered that **3** was a mixture of two diastereoisomers which were formed by esterification of the optically active isopentylcoumarin with a racemate of this acid. This presumption was confirmed by the fact that the chemical properties and spectral data of **2** were identical with those of the dihydro derivative of **3** (diastereoisomer) prepared from angelol A (**1**) by catalytic reduction. However, attempts to separate these diastereoisomers were unsuccessful.

Angelol D (**4**), colorless viscid oil, $C_{20}H_{24}O_7$. The ORD spectrum of **4** showed a negative plane curve. The ^{1}H-NMR spectrum (δ, ppm, $CDCl_3$) of **4** exhibited signals due to the protons of the C-3 and C-4 positions of the coumarin ring at 6.13 (1H, d, J=9.5 Hz) and 7.59 (1H, d, J=9.5 Hz), signals due to the protons of the C-5 and C-8 position at 7.39 (1H, s) and 6.75 (1H, s), signals arising from a methoxyl group at 3.91 (3H, s), signals assignable to a trioxyisopentyl group at 6.40 (1H, br s), 3.64 (1H, d, J=7.5 Hz), 3.05 (1H, d, J=7.5 Hz), 2.58 (1H, br s), 1.31 (3H, s) and 1.29 (3H, s), and signals due to a tigloyl group at 7.02 (1H, m), 1.88 (3H, s) and 1.81 (3H, m). These spectral data indicated that **4** was an ester derivative of 7-methoxy-6-trihydroxyisopentylcoumarin having a tigloyl group as the acyl moiety. However, the signal pattern of the ^{1}H-NMR spectrum of **4** was very different from those of **1**—**3**. Like **1**—**3**, **4** readily afforded a 12,13-isopropylidene derivative, which was identical with **9**.

Furthermore, the oxidation of **4** with lead tetraacetate in benzene gave an aldehyde, which was identical with **12** prepared from **2**. These findings suggested that **2** and **4** were isomers which differed in the position of the acyl moiety. Consequently, it appears that one of the compounds, whose acyl group was linked at the C-12 position, underwent acyl migration during the isopropylidenation and the oxidation with lead tetraacetate in the presence of acid, then it reacted in the same way as the compound bearing the acyl group at the C-11 position from the first. On comparison of the ^{1}H-NMR spectra of **2** and **4**, the signals due to two methine protons were observed at 5.06 and 5.60 (each 1H, br s) in the former, but at 3.64 (1H, d, J=7.5 Hz, $+D_2O$ br s) and 6.40 (1H, br s) in the latter, respectively. From the above evidence, the structure **4** was apparently preferred to **2**. In order to clarify the position of the acyl group, the glycol cleavage with sodium metaperiodate in ethanol was carried out, and it was confirmed that, as expected, **4** was easily cleaved to afford **12**, whereas **2** was unreactive. Similarly, **1** and **3** were also unreactive. Furthermore, on oxidation with CrO_3–pyridine complex, **2** readily gave a ketone (**13**), while **4** was merely recovered unchanged from this reaction. From

the above results, it was decided that **2** and **4** contained tigloyl group at the C-12 position of isopentylcoumarin and tigloyl group at the C-11 position of the same coumarin, respectively. Consequently, although Hata and Kozawa proposed that the structure of **1** was the angelate at the C-11 position (**1a**),[2] on the basis of the above results we revise the structure of **1** to the angelate at the C-12 position (**1b**). As regards acyl migration between **2** and **4**, it was observed that each compound was partly isomerized to the other by refluxing in acetic acid. Furthermore, on heating in 50% AcOH, the isopropylidene derivative (**9**) reverted to **2** and **4** during cleavage of the isopropylidene group, but in this case the formation of **2** is larger than that of **4**. For this acyl migration mechanism, two pathways can be considered, as shown in Chart 2.[4] In view of the fact that the ORD spectrum of **4** prepared from **2** through the acyl

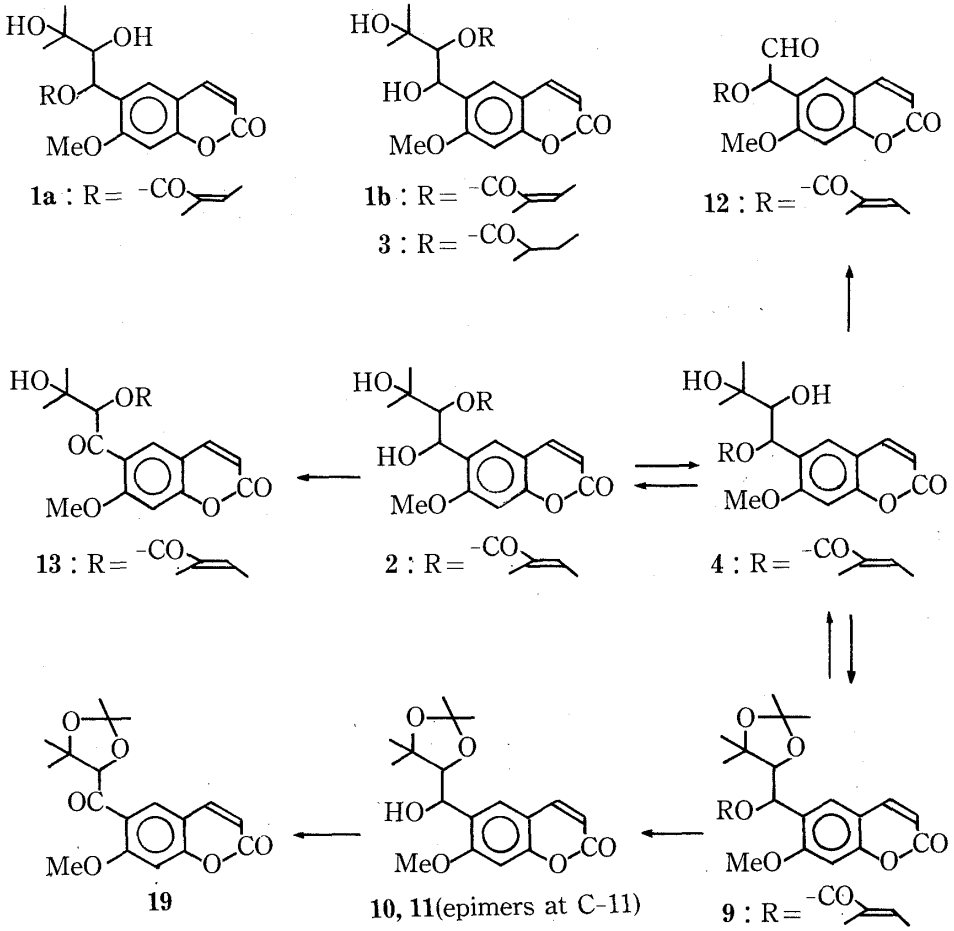


Chart 1

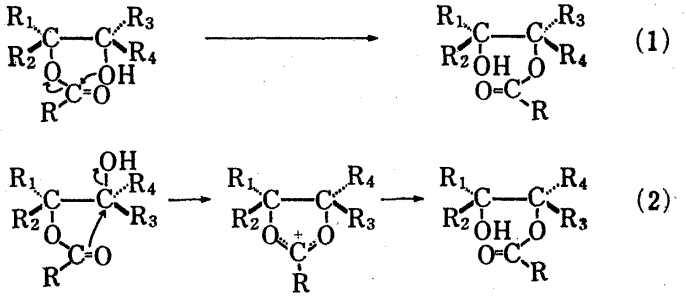


Chart 2

migration showed a negative plane curve like that of **2**, inversion of the configuration at C-11 presumably did not occur, and in this case, it is clear that the reaction proceeded by pathway (1).

Angelol E (**5**), colorless needles, mp 83—84°C, $C_{20}H_{26}O_7$. The ORD spectrum of **5** showed a negative plane curve. The ^{1}H-NMR spectrum (δ ppm, $CDCl_3$) of **5** exhibited signals arising from a trioxyisopentyl group at 5.15 (2H, br s), 3.90 (1H, br s), 3.28 (1H, br s), 1.40 (3H, s) and 1.23 (3H, s), and signals assignable to an isovaleryl group at 1.86 (2H, m), 1.28 (1H, m), 0.72 (3H, d, J=6.5 Hz) and 0.64 (3H, d, J=6.5 Hz), in addition to signals due to a 6,7-disubstituted coumarin ring and a methoxyl group. These spectral data indicated that **5** was also a 7-methoxy-6-trihydroxyisopentylcoumarin derivative having a isovaleryl group as the acyl moiety. However, the ^{1}H-NMR spectrum differed from those of **1**—**4**, and signals assignable to a gem-dimethyl group and two methine protons appeared at 1.23, 1.40 (each 3H, s) and 5.15 (2H, br s), respectively. Like **1** and **2**, on treating with conc. H_2SO_4 in acetone **5** gave a 12,13-isopropylidene derivative (**15**). However, **5** was unreactive in the oxidation with sodium metaperiodate. Accordingly, **5** should have the structure differing from **1** and **2** in the configuration at either C-11 or C-12. The alkali hydrolysis of **15** afforded two alcohols **16** and **17** which were isomeric at the C-11 position, and isovaleric acid. The IR, ^{1}H-NMR spectra and the melting points of **16** and **17** were identical with those of **10** and **11** prepared from **2**, but the ORD spectra showed opposite plane curves (Table I). On oxidation with CrO_3–pyridine complex, **16** and **17** gave a ketone (**18**), whose IR and ^{1}H-NMR spectra were identical with those of a ketone (**19**) prepared from **10** and **11** in the same way, except that the ORD spectra showed opposite Cotton effects. From the above evidence, it became claer that **5** was a compound having an isopentylcoumarin portion which differed from **1**—**3** only in the configuration at the C-12 position.

Angelol F (**6**), colorless viscid oil, $C_{20}H_{26}O_7$. The ORD spectrum of **6** showed a negative plane curve. The ^{1}H-NMR spectrum (δ ppm, $CDCl_3$) was very similar to that of **5** except that complicated signals arising from a 2-methylbutyryl group like that of **3** were observed instead of the signals due to an isovaleryl group as in **5**. Therefore, it was assumed that **6** had the same

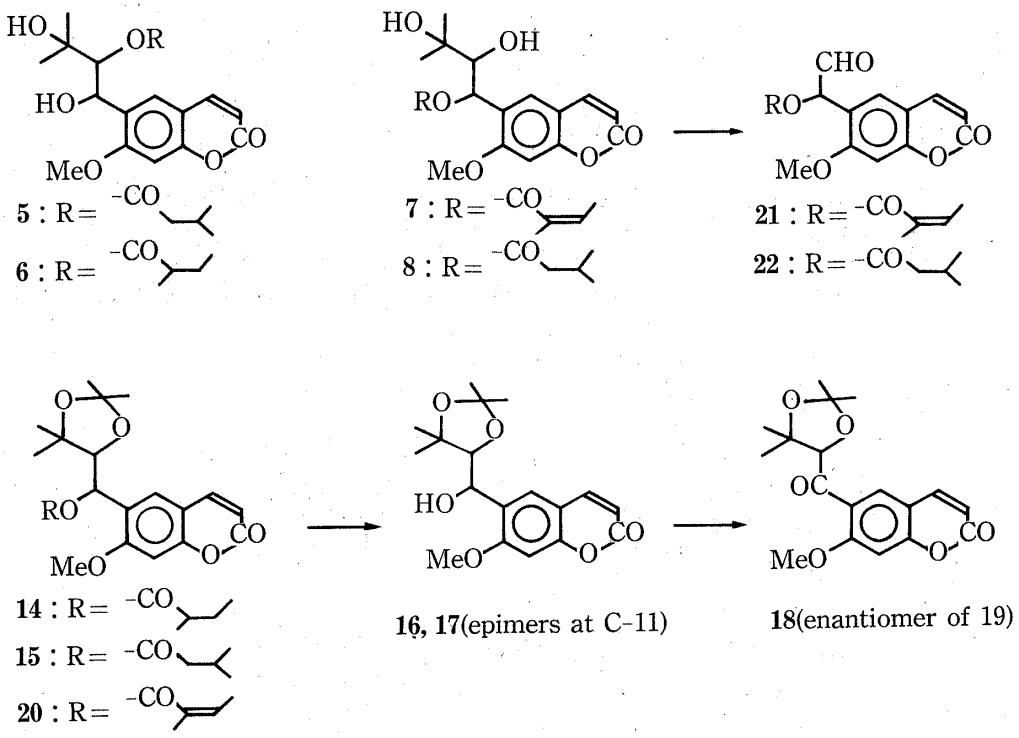


Chart 3

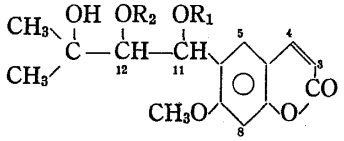
coumarin portion as **5** and a mixture of two diastereoisomers having *dl*-2-methylbutyryl groups as the acyl moiety. However, attempts to separate them were unsuccessful as in the case of **3**.

Angelol G (**7**), colorless viscid oil, $C_{20}H_{24}O_7$. The ORD spectrum of **7** showed a negative plane curve. The ^{1}H-NMR spectrum (δ ppm, $CDCl_3$) exhibited signals arising from a trioxyiso-

Table I. ORD Data for Derivatives

Compd.	c	Solvent	°C	[α] (nm)			
10	0.503	Ethanol	24	−95.4° (589)	−143.1° (500)	−270.4° (400)	−548.7° (375)
11	0.419	Ethanol	24	+19.1° (589)	+23.9° (500)	+66.8° (400)	+105.5° (375)
16	0.550	Ethanol	25	+80.0° (589)	+130.9° (500)	+298.2° (400)	+589.1° (375)
17	0.598	Ethanol	25	−13.4° (589)	−20.1° (500)	−60.4° (400)	−107.4° (375)
18	0.177	Dioxane	22	+22.6° (500)	+56.5° (400)	+146.9° (370)	+237.3° (360)
				+508.5° (351, p)	+372.9° (349)		
19	0.111	Dioxane	22	−18.0° (500)	−54.1° (400)	−144.1° (370)	−234.3° (360)
				−486.5° (351, tr)	−414.4° (349)		

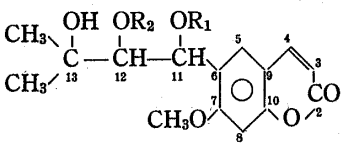
Table II. ^{1}H-NMR Data for Angelol-Type Coumarins, **1**—**8**, (δ ppm, J=Hz, $CDCl_3$)

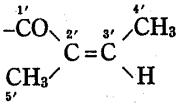


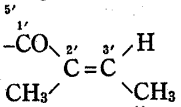
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
3-H	6.18 (d, J=9.5)	6.18 (d, J=9.5)	6.20 (d, J=9.5)	6.13 (d, J=9.5)	6.17 (d, J=9.5)	6.22 (d, J=9.5)	6.15 (d, J=9.5)	6.18 (d, J=9.5)
4-H	7.58 (d, J=9.5)	7.55 (d, J=9.5)	7.60 (d, J=9.5)	7.59 (d, J=9.5)	7.55 (d, J=9.5)	7.60 (d, J=9.5)	7.62 (d, J=9.5)	7.62 (d, J=9.5)
5-H	7.58(s)	7.55(s)	7.61(s)	7.39(s)	7.45(s)	7.47(s)	7.53(s)	7.53(s)
8-H	6.73(s)	6.71(s)	6.72(s)	6.75(s)	6.70(s)	6.75(s)	6.75(s)	6.78(s)
11-H	5.63 (br s)	5.60 (br s)	5.60 (br s)	6.40 (br s)	5.15 (br s)	5.20 (br s)	6.30 (d, J=6.0)	6.27 (d, J=6.0)
12-H	5.13 (br s)	5.06 (br s)	5.10 (br s)	3.64 (d, J=7.5)	5.15 (br s)	5.20 (br s)	3.95 (d, J=6.0)	3.90 (d, J=6.0)
OH	4.75 (br s)	4.72 (br s)	4.78 (br s)	3.05 (d, J=7.5)	3.90 (br s)	4.35—3.00 (br)	3.30—2.55 (br)	2.80 (br s)
OH	3.15 (br s)	3.10 (br s)	3.20 (br s)	2.58 (br s)	3.28 (br s)	4.35—3.00 (br)	3.30—2.55 (br)	2.45 (br s)
CH_3	1.53(s)	1.53(s)	1.55(s)	1.31(s)	1.40(s)	1.40(s)	1.30(s)	1.30(s)
CH_3	1.25(s)	1.22(s)	1.22(s)	1.29(s)	1.23(s)	1.23(s)	1.24(s)	1.24(s)
CH_3O	3.92(s)	3.89(s)	3.90(s)	3.91(s)	3.89(s)	3.92(s)	3.95(s)	3.95(s)
Acyl moiety	5.88 (m, 1H)	6.75 (m, 1H)	2.25 (m, 1H)	7.02 (m, 1H)	1.86 (m, 2H)	2.00 (m, 1H)	6.10 (m, 1H)	2.20 (m, 2H)
	1.75 (m, 3H)	1.70 (m, 3H)	1.37 (m, 2H)	1.88 (s, 3H)	1.80 (m, 1H)	1.30 (m, 2H)	2.02 (m, 3H)	2.05 (m, 1H)
	1.70 (m, 3H)	1.65 (s, 3H)	1.02 (d, J=7.5, 3/2H)	1.81 (m, 3H)	0.72 (d, J=6.5, 3H)	0.88 (d, J=7.5, 3/2H)	1.93 (s, 3H)	0.92 (d, J=6.5, 6H)
			0.77 (d, J=7.5, 3/2H)		0.64 (d, J=6.5, 3H)	0.70 (d, J=7.5, 3/2H)		
			0.74 (t, J=7.0, 3/2H)			0.69 (t, J=7.0, 3/2H)		
			0.49 (t, J=7.0, 3/2H)			0.50 (t, J=7.0, 3/2H)		

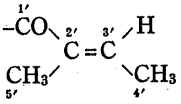
pentyl group at 6.30 (1H, d, J=6.0 Hz), 3.95 (1H, d, J=6.0 Hz), 3.30—2.55 (2H, br), 1.30 (3H, s) and 1.24 (3H, s) in addition to signals due to a 6, 7-disubstituted coumarin ring, a methoxyl group and an angeloyl group. Therefore, it was assumed that **7** was the ester derivative of 7-methoxy-6-trihydroxyisopentylcoumarin having an angeloyl group as the acyl moiety. But, the ^{1}H-NMR spectrum (δ ppm, $CDCl_3$) of **7** differed greatly from those of **1**—**6**, and the signals due to a *gem*-dimethyl group and two methine protons were seen at 1.30, 1.24 (each 3H, s) and 6.30, 3.95 (each 1H, d, J=6.0 Hz), respectively. On treatment with conc. H_2SO_4 in acetone, **7** yielded a 12,13-isopropylidene derivative (**20**), which afforded two alcohols **16** and **17**, and angelic acid upon alkali hydrolysis. The oxidation of **7** with sodium metaperiodate readily gave an aldehyde (**21**), whose ^{1}H-NMR spectrum still revealed signals arising from an angeloyl group at 6.25 (1H, m), 2.05 (3H, m) and 2.00 (3H, m), and was identical with that of the aldehyde obtained from **1** by oxidation with lead tetraacetate. On the basis of the above

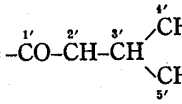
Table III. ^{13}C-NMR Spectral Data for **1**, **2**, **4**, **5**, **7** and **8** (δ in $CDCl_3$)

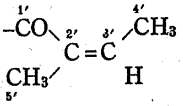


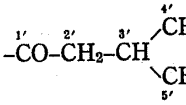
1: R_1=H, R_2=  , 11(R), 12(S)

2: R_1=H, R_2=  , 11(R), 12(S)

4: R_1=  , R_2=H, 11(R), 12(S)

5: R_1=H, R_2=  , 11(R), 12(R)

7: R_1=  , R_2=H, 11(R), 12(R)

8: R_1=  , R_2=H, 11(R), 12(R)

	1	2	4	5	7	8
C-2	161.33	161.33	160.95	160.92	160.86	160.98
C-3	126.49	126.52	126.20	125.99	128.22	128.28
C-4	143.60	143.55	143.58	143.31	143.52	143.49
C-5	112.92	112.83	112.95	113.59	112.31	112.98
C-6	127.25	127.78	128.28	128.23	126.84	124.56
C-7	159.08	158.96	158.73	160.42	160.16	160.19
C-8	98.47	98.41	98.82	99.14	98.53	98.91
C-9	111.81	111.78	111.93	112.13	111.55	111.96
C-10	155.16	155.04	155.13	155.51	154.78	155.19
C-11	75.74	76.09	77.64	73.37	77.91	78.46
C-12	67.43	67.49	68.55	70.18	69.28	69.39
C-13	74.43	74.51	72.70	77.00	72.09	72.35
CH_3	27.92	27.77	26.51	27.74	26.57	26.80
CH_3	26.31	26.34	25.31	24.64	23.94	24.38
CH_3O	56.14	56.05	56.09	56.23	55.85	56.20
C-1′	166.54	166.77	166.27	171.25	165.98	171.57
C-2′	126.49	126.52	125.32	43.07	124.62	43.36
C-3′	137.69	137.58	138.69	25.17	138.84	25.46
C-4′	15.36	14.23	14.46	22.12	15.34	22.18
C-5′	20.34	11.91	12.00	22.12	20.11	22.18

results, it was found that **7** had the same coumarin portion, including the absolute configuration, as **5** and **6**, but the acyl moiety was linked at the C-11 position, that is, **7** was a diastereoisomer which differed from **4** in the configuration at the C-12 position.

Angelol H (**8**), colorless viscid oil, $C_{20}H_{26}O_7$. The ORD spectrum of **8** showed a negative plane curve. The ^{1}H-NMR spectrum (δ ppm, $CDCl_3$) was very similar to that of **7** except that signals assignable to an isovaleryl group were observed instead of the signals due to an angeloyl group as in **7**. On being treated with conc. H_2SO_4 in acetone, **8** gave a 12, 13-isopropylidene derivative, which was identical with **15** prepared from **5** in all respects. Furthermore, the oxidation of **8** with sodium metaperiodate readily afforded an aldehyde (**22**), whose ^{1}H-NMR spectrum ($CDCl_3$) exhibited signals due to an isovaleryl group and was very similar to that of **21** except for the signals arising from the acyl moiety. Accordingly, it became evident that **8** had the same isopentylcoumarin moiety as **7**, but with isovaleric acid as the acyl moiety. Acyl migration between **5** and **8** occurred under reflux in acetic acid, as with **2** and **4**. As regards cleavage of the isopropylidene group by treatment in 50% AcOH, **15** differed from **9** in extent of reaction; that is, **8** was the major product and **5** was a minor product. This is presumably due to a conformational difference between **9** and **15**.

During this investigation, the plane structures and the relative configurations of **1**—**8** were elucidated. In terms of the ^{1}H-NMR spectra, these coumarins could be classified into four groups I (**1**—**3**), II (**4**), III (**5**, **6**) and IV (**7**, **8**) depending on the signal patterns of the two methine protons and *gem*-dimethyl protons in the hydroxyisopentyl group. Furthermore, these four groups can also be distinguished by chemical shifts of the ^{13}C-NMR signals arising from the hydroxyisopentyl carbons, as shown in Table III. The absolute configuration of these compounds will be reported in a subsequent paper.

Experimental

All melting points were measured on a Büchi melting point apparatus and are uncorrected. The UV spectra were recorded with a Shimadzu UV-200S spectrometer, infrared (IR) spectra with a Hitachi EPI-G2 spectrometer, and ORD spectra with a JASCO ORD/UV-5 spectrometer. The ^{1}H-NMR spectra were taken with a Hitachi R-40 (90 MHz) spectrometer with tetramethylsilane as an internal standard and ^{13}C-NMR spectra with a Nihondenki JEOL FX-100 (25 MHz) spectrometer. For medium pressure column chromatography on silica gel and for column chromatography on silica gel, we used Merck silica gel 60 (230—400 mesh) and silica gel 60 (70—230 mesh), respectively. For thin-layer chromatography and preparative thin-layer chromatography, Merck plate silica gel 60 F_{254} (0.25 mm and 2 mm) was employed and the developed spots were detected under a UV lamp (253.7 nm and 365 nm), and measured with Shimadzu high speed TLC scanner, model CS-920.

Isolation of the Compounds——The dried and crushed roots (8 kg) of *Angelica pubescens* Maxim. were extracted 3 times by refluxing with 15 l of hexane and with 15 l of ethyl acetate for 5 h (for each extraction). Each solution was concentrated under reduced pressure to give the corresponding extract: hexane extract (173.8 g) and ethyl acetate extract (215 g). The hexane extract was further treated with hexane at room temperature and divided into soluble (77.5 g) and insoluble (96.3 g) portions. The insoluble part was added to the ethyl acetate extract, then this (311 g) was chromatographed on silica gel (2 kg) with a mixture of hexane and ethyl acetate as the eluent. The part eluted with hexane–EtOAc (3: 1) was divided into three fractions, F-1 (79.1 g), F-2 (51.1 g) and F-3 (53.5 g), containing angelol-type coumarins. F-1 was rechromatographed on silica gel (1.5 kg) with $CHCl_3$–MeOH (100: 1) to give **1** (3.2 g), **3** (1.8 g), a mixture of **1** and **3** (51.8 g) and crude **4** (4 g), which was purified by medium pressure column chromatography on silica gel (200 g) with hexane–EtOAc (3: 1) to give **4** (1.8 g). F-2 was rechromatographed on silica gel (1.5 kg) with $CHCl_3$–MeOH (50: 1) to afford **2** (10.6 g) and a mixture of **5** and **6** (30.8 g), which was further rechromatographed on silica gel (1 kg) with hexane–EtOAc (2: 1) to give **5** (4.2 g) and **6** (3.1 g) and a mixture of the two (23.5 g). F-3 was rechromatographed on silica gel (1.5 kg) with $CHCl_3$–MeOH (50: 1) to give a mixture of **7** and **8** (40 g), which was rechromatographed on silica gel (1 kg) with hexane–EtOAc (2: 1) to afford **7** (6.8 g), **8** (3.6 g) and a mixture of the two (26 g).

Angelol A (**1**)——Recrystallized from Et_2O to give colorless needles. mp 108—109°C. The melting point showed no depression on admixture with an authentic sample of angelol A. The IR, ORD and ^{1}H-NMR spectra were identical with those of the authentic sample.

Angelol B (**2**)——Recrystallized from hexane–EtOAc to give colorless prisms. mp 143—144°C. UV λ_{max}^{EtOH} nm (log ε): 223 (4.34), 250 (3.62), 298 (3.85), 326 (4.12). IR ν_{max}^{nujol} cm^{-1}: 3400 (OH), 1710, 1680 (CO),

1605, 1561 (arom.). ORD (c=0.576, EtOH) $[\alpha]^{22}$ (nm): −229.1° (589), −291.6° (550), −395.8° (500), −590.2° (450), −935.5° (410). The ^{1}H-NMR and ^{13}C-NMR data are summarized in Tables II and III, respectively. *Anal.* Calcd for $C_{20}H_{24}O_7$: C, 63.82; H, 6.43. Found: C, 63.88; H, 6.29.

Angelol C (3)——Recrystallized from Et_2O to give colorless plates. mp 113—114°C. UV λ_{max}^{EtOH} nm (log ε): 223 (4.38), 250 (3.68), 297 (3.88), 325 (4.10). IR ν_{max}^{nujol} cm^{-1}: 3500 (OH), 1720 (CO), 1610, 1550 (arom.). ORD (c=0.703, EtOH) $[\alpha]^{18}$ (nm): −119.8° (589), −219.6° (500), −339.4° (450), −559.0° (400). The ^{1}H-NMR data are summarized in Table II. *Anal.* Calcd for $C_{20}H_{26}O_7$: C, 63.48; H, 6.93. Found: C, 63.48; H, 6.78. The IR, ORD and ^{1}H-NMR spectra were identical with those of dihydroangelol-A.

Angelol D (4)——Colorless viscid oil. UV λ_{max}^{EtOH} nm (log ε): 223 (4.59), 250.5 (3.89), 297 (4.04), 325 (4.29). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550 (OH), 1720, 1690 (CO), 1620, 1560, 1490 (arom.). ORD (c=0.559, EtOH) $[\alpha]^{22}$ (nm): +3.6° (589), 0° (450), −17.9° (400), −64.4° (370). The ^{1}H-NMR and ^{13}C-NMR data are summarized in Tables II and III, respectively. *Anal.* Calcd for $C_{20}H_{24}O_7$: C, 63.82; H, 6.43. Found: C, 63.97; H, 6.23.

Angelol E (5)——Recrystallized from Et_2O to give colorless needles. mp 83—84°C. UV λ_{max}^{EtOH} nm (log ε): 223.5 (4.31), 250 (3.68), 298 (3.92), 324 (4.15). IR ν_{max}^{Nujol} cm^{-1}: 3300 (OH), 1730, 1680 (CO), 1610, 1560 (arom.). ORD (c=0.465, EtOH) $[\alpha]^{22}$ (nm): −51.6° (589), −68.8° (550), −86.0° (500), −137.6° (450), −240.8° (400), −670.9° (360). The ^{1}H-NMR and ^{13}C-NMR data are summarized in Tables II and III, respectively. *Anal.* Calcd for $C_{20}H_{26}O_7$: C, 63.48; H, 6.93. Found: C, 63.34; H, 7.22.

Angelol F (6)——Colorless viscid oil. UV λ_{max}^{EtOH} nm (log ε): 223 (4.15), 250 (3.48), 298 (3.72), 327.5 (3.92). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3350 (OH), 1720, 1690 (CO), 1615, 1560, 1490 (arom.). ORD (c=0.526, EtOH) $[\alpha]^{22}$ (nm): −38.0° (589), −53.2° (550), −76.0° (500), −121.7° (450), −228.1° (400), −418.3° (365). The ^{1}H-NMR data are summarized in Table II. *Anal.* Calcd for $C_{20}H_{26}O_7$: C, 63.48; H, 6.93. Found: C, 63.49; H, 6.84.

Angelol G (7)——Colorless viscid oil. UV λ_{max}^{EtOH} nm (log ε): 223 (4.56), 250 (3.86), 298 (4.06), 323 (4.33). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1720, 1690 (CO), 1620, 1570, 1490 (arom.). ORD (c=0.605, EtOH) $[\alpha]^{21}$ (nm): −82.6° (589), −105.8° (550), −145.4° (500), −204.9° (450), −343.8° (400), −515.7° (375). The ^{1}H-NMR and ^{13}C-NMR data are summarized in Tables II and III, respectively. *Anal.* Calcd for $C_{20}H_{24}O_7$: C, 63.82; H, 6.43. Found: C, 63.57; H, 6.72.

Angelol H (8)——Colorless viscid oil. UV λ_{max}^{EtOH} nm (log ε): 222 (4.18), 250 (3.53),298 (3.78), 324 (3.98). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1710, 1690 (CO), 1610, 1550, 1480 (arom.). ORD (c=0.696, EtOH) $[\alpha]^{22}$ (nm): −74.7° (589), −91.9° (550), −120.6° (500), −178.1° (450), −293.1° (400), −448.2° (375). The ^{1}H-NMR and ^{13}C-NMR data are summarized in Tables II and III, respectively. *Anal.* Calcd for $C_{20}H_{26}O_7$: C, 63.48; H, 6.93. Found: C, 63.54; H, 7.03.

12,13-Isopropylideneangelol B (9)——Ten drops of conc. H_2SO_4 were added to a solution of **2** (4.5 g) in dry acetone (500 ml). After being stirred, the mixture was allowed to stand at room temperature overnight and was then neutralized with Na_2CO_3. After removal of Na_2CO_3 by filtration, the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent, and recrystallized from hexane–EtOAc to give **9** (3.2 g), colorless plates, mp 193—194°C. IR ν_{max}^{nujol} cm^{-1}: 1720, 1700 (CO), 1620, 1560 (arom). ORD (c=0.613, EtOH) $[\alpha]^{20}$ (nm): −16.3° (589), −17.9° (550), −21.2° (500), −26.1° (450), −32.6° (400), −39.3° (360). ^{1}H-NMR ($CDCl_3$) δ ppm: 7.67 (1H, d, J=9.5 Hz), 7.49 (1H, s), 7.00 (1H, m), 6.85 (1H, s), 6.28 (1H, d, J=9.5 Hz), 6.22 (1H, d, J=6.0 Hz), 4.18 (1H, d, J=6.0 Hz), 3.95 (3H, s), 1.85 (3H, s), 1.82 (3H, m), 1.50, 1.34, 1.18, 1.04 (each 3H, s). *Anal.* Calcd for $C_{23}H_{28}O_7$: C, 66.33; H, 6.78: C, 66.14; H, 6.63.

12,13-Isopropylideneangelol D——Five drops of conc. H_2SO_4 were added to a solution of **4** (500 mg) in dry acetone (100 ml). The mixture was treated in the same way as described above. The product was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent, and recrystallized from hexane–EtOAc to give colorless plates (350 mg), mp 193—194°C, which were identified as **9** by comparison of the IR, ORD and ^{1}H-NMR spectra with those of **9**. The melting point showed no depression on admixture with **9**.

12,13-Isopropylideneangelol E (15)——Five drops of conc. H_2SO_4 were added to a solution of **5** (1 g) in dry acetone (100 ml). The mixture was treated in the same way as described above. The product was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent, and recrystallized from hexane–EtOAc to give **15** (700 mg), colorless needles, mp 138—139°C. IR ν_{max}^{nujol} cm^{-1}: 1730 (CO), 1610, 1560 (arom.). ORD (c=0.474, EtOH) $[\alpha]^{22}$ (nm): −33.7° (589), −42.2° (550), −59.1° (500), −75.9° (450), −109.7° (400), −194.1° (365). ^{1}H-NMR ($CDCl_3$) δ ppm: 7.67 (1H, d, J=9.5 Hz), 7.49 (1H, s), 6.84 (1H, s), 6.28 (1H, d, J=9.5 Hz), 6.15 (1H, d, J=9.0), 4.21 (1H, d, J=9.0 Hz), 3.95 (3H, s), 2.19 (2H, m), 2.10 (1H, m), 1.40, 1.37, 1.27, 1.26 (each 3H, s), 0.92 (6H, d, J=6.5 Hz), *Anal.* Calcd for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 66.11; H, 7.25.

12,13-Isopropylideneangelol F (14)——Five drops of conc. H_2SO_4 were added to a solution of **6** (1 g) in dry acetone (100 ml). The mixture was treated in the same way as described above. The product was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent, and recrystallized from hexane–EtOAc to give **14** (670 mg), colorless needles, mp 118—119°C. IR ν_{max}^{nujol} cm^{-1}: 1730 (CO), 1610, 1560 (arom.). ORD (c=0.452, EtOH) $[\alpha]^{22}$ (nm): −44.2° (589), −66.4° (500), −88.5° (450), −123.9° (400), −221.2° (360). ^{1}H-NMR ($CDCl_3$) δ ppm: 7.66 (1H, d, J=9.5 Hz), 7.48 (1H, s), 6.86 (1H, s), 6.28 (1H, d, J=9.5 Hz), 6.14 (1H, d, J=9.0 Hz), 4.22 (1H, d, J=9.0 Hz), 3.95 (3H, s), 2.30 (1H, m), 1.55 (2H, m), 1.40,

1.38 (each 3H, s), 1.27 (6H, s), 1.13, 1.10 (each 3/2H, d, J=7.0 Hz), 0.89, 0.80 (each 3/2H, t, J=6.0 Hz). *Anal.* Calcd for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 65.86; H, 7.04.

12,13-Isopropylideneangelol G (20)——Five drops of conc. H_2SO_4 were added to a solution of **7** (1 g) in dry acetone (100 ml). The mixture was treated in the same way as described above. The product was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent, and recrystallized from hexane–EtOAc to give **20** (800 mg), colorless viscid oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720 (CO), 1620, 1560, 1500 (arom.). ORD (c=0.725, EtOH) $[\alpha]^{22}$ (nm): −49.7° (589), −60.7° (550), −77.2° (500), −110.3° (450), −171.0° (400), −292.4° (365). ^{1}H-NMR ($CDCl_3$) δ ppm: 7.66 (1H, d, J=9.5 Hz), 7.48 (1H, s), 6.83 (1H, s), 6.26 (1H, d, J=9.5 Hz), 6.22 (1H, m), 6.21 (1H, d, J=9.0 Hz), 4.24 (1H, d, J=9.0 Hz), 3.95 (3H, s), 1.97 (3H, m), 1.93 (3H, s), 1.39, 1.36 (each 3H, s), 1.26 (6H, s). *Anal.* Calcd for $C_{23}H_{28}O_7$: C, 66.33; H, 6.78. Found: C, 66.09; H, 6.52.

12,13-Isopropylideneangeleol H——Five drops of conc. H_2SO_4 were added to a solution of **8** (1 g) in dry acetone (100 ml). The mixture was treated in the same way as described above. The product was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent, and recrystallized from hexane–EtOAc to give colorless needles (800 mg), mp 138—139°C. The IR, ORD and ^{1}H-NMR spectral data were identical with those of **15**. The melting point showed no depression on admixture with **15**.

Hydrolysis of 9——A 5% NaOH solution (50 ml) was added dropwise to a solution of **9** (3 g) in pyridine (20 ml) with stirring in a stream of N_2 at room temperature. After being stirred for 30 min, the mixture was cooled and diluted with water (50 ml) then acidified with 20% H_2SO_4. The solution was extracted with Et_2O, and the extract was separated into the neutral and acidic portions in the usual way. The neutral portion was washed with water, dried and concentrated *in vacuo*. The residue was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent to give **10** (750 mg) and **11** (150 mg). The acidic portion was led to *p*-phenylphenacyl ester in the usual way. The crude product was chromatographed on silica gel with hexane–EtOAc (10: 1) and recrystallized from hexane to afford colorless needles (370 mg), mp 103—104°C. The IR and ^{1}H-NMR spectra were identical with those of an authentic sample of *p*-phenylphenacyl tiglate. The melting point showed no depression on admixture with the authentic sample.

Compound 10——Recrystallized from hexane–EtOAc to give colorless needles, mp 187—188°C. IR ν_{max}^{Nujol} cm^{-1}: 3400 (OH), 1720 (CO), 1610, 1560 (arom.). The ORD data are summarized in Table I. ^{1}H-NMR ($CDCl_3$) δ ppm: 7.63 (1H, d, J=9.5 Hz), 7.53 (1H, s), 6.78 (1H, s), 6.22 (1H, d, J=9.5 Hz), 5.04 (1H, dd, J=6.0 and 6.0 Hz, +D_2O d, J=6.0 Hz), 3.97 (1H, d, J=6.0 Hz), 3.89 (3H, s), 3.09 (1H, d, J=6.0 Hz), 1.50, 1.35, 1.25, 1.08 (each 3H, s). *Anal.* Calcd for $C_{18}H_{22}O_6$: C, 64.65; H. 6.63. Found: C, 64.62; H, 6.57.

Compound 11——Recrystallized from hexane–EtOAc to give colorless needles, mp 147—148°C. IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 1700 (CO), 1600, 1550 (arom.). The ORD data are summarized in Table I. ^{1}H-NMR ($CDCl_3$) δ ppm: 7.66 (1H, d, J=9.5 Hz), 7.49 (1H, s), 6.83 (1H, s), 6.24 (1H, d, J=9.5 Hz), 4.98 (1H, dd, J=6.0 and 8.5 Hz, +D_2O d, J=8.5 Hz), 4.07 (1H, d, J=8.5 Hz), 3.94 (3H, s), 2.85 (1H, d, J=6.0 Hz), 1.39, 1.31 (each 3H, s), 1.37 (6H, s). *Anal.* Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63. Found: C, 64.54; H, 6.68.

Oxidationof 2 with Lead Tetraacetate——Lead tetraacetate (200 mg) was added to a solution of **2** (200 mg) in dry benzene (10 ml), and the mixture was stirred for 4 h at room temperature, then Et_2O (50 ml) was added. The whole was washed with 5% $NaHCO_3$ and water successively, dried and concentrated. The residue was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent and recrystallized from hexane–EtOAc to afford **12** (85 mg,) colorless needles, mp 109—110°C. ORD (c=0.550, $CHCl_3$,) $[\alpha]^{24}$ (nm): −32.7° (589), −47.3° (500), −64.5° (450), −94.5° (500), −170.9° (360). ^{1}H-NMR ($CDCl_3$) δ ppm: 9.71 (1H, s), 7.64 (1H, d, J=9.5 Hz), 7.47 (1H, s), 7.00 (1H, m), 6.88 (1H, s), 6.29 (1H, d, J=9.5 Hz), 6.40 (1H, s), 3.95 (3H, s), 1.90, 1.85 (each 3H, m). *Anal.* Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10. Found: C, 64.27; H, 4.83.

Oxidation of 4 with Lead Tetraacetate——Lead tetraacetate (200 mg) was added to a solution of **4** (200 mg) in dry benzene (10 ml). The mixture was treated in the same way as described above to give colorless needles (120 mg), mp 109—110°C. The ORD and ^{1}H-NMR spectra of the product were identical with those of **12**. The melting point showed no depression on admixture with **12**.

Oxidation of 4 with $NaIO_4$——$NaIO_4$ (140 mg) was added to a solution of **4** (200 mg) in 50% EtOH (30 ml). The mixture was allowed to stand at room temperature for 2 h, diluted with water (50 ml), and extracted with ether. The ether layer was washed with water, dried and concentrated *in vacuo*. The residue was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent, and recrystallized from hexane–EtOAc to give colorless needles (100 mg), mp 109—110°C. The ORD and ^{1}H-NMR spectra were identical with those of **12**. The melting point showed no depression on admixture with **12**.

Oxidation of 2 with CrO_3–pyridine Complex——A solution of **2** (300 mg) in dry pyridine (3 ml) was added dropwise to a CrO_3–pyridine complex which had been prepared from dry pyridine (3 ml) and CrO_3 (300 mg) under ice cooling, and stirred. The mixture was allowed to stand at room temperature for 4 h and then diluted with ice water (200 ml), acidified with 20% H_2SO_4, and extracted with Et_2O. The extract was dried, and evaporated to dryness. The residue was collected and recrystallized from hexane–EtOAc to give **13** (130 mg), colorless crystalline powder, mp 113—114°C. IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 1750, 1705, 1650 (CO), 1620 (arom.). ORD (c=0.488, $CHCl_3$) $[\alpha]^{23}$ (nm): −139.3° (589), −180.3° (550), −221.3° (500), −321.9° (450), −524.6° (400), −778.7° (370). ^{1}H-NMR ($CDCl_3$) δ ppm: 7.94 (1H, s), 7.70 (1H, d, J=9.5 Hz), 6.85

(1H, s), 6.28 (1H, d, J=9.5 Hz), 6.93 (1H, m), 5.96 (1H, s), 3.95 (3H, s), 2.80 (1H, br s), 1.85, 1.82 (each 3H, m), 1.30 (6H, s). *Anal.* Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.35; H, 5.88.

Hydrolysis of 3——A 5% NaOH solution (20 ml) was added dropwise to a solution of **3** (500 mg) in pyridine (10 ml) with stirring in a stream of N_2 at room temperature. After being stirred for 30 min, the mixture was treated in the same way as for **9** and separated into neutral and acidic portions in the usual way. The acidic portion (55 mg) was led to the *p*-phenylphenacyl ester in the usual way. The product was purified by chromatography on silica gel with hexane–EtOAc (10: 1) as a solvent and recrystallized from hexane to afford colorless plates (18 mg), mp 67—70°C, optically inactive. The IR and ^{1}H-NMR spectra were identical with those of an authentic sample of *p*-phenylphenacyl *dl*-2-methylbutyrate. The melting point showed no depression on admixture with the authentic sample.

Hydrolysis of 15——A 5% NaOH solution (20 ml) was added dropwise to a solution of **15** (500 mg) in pyridine (10 ml) with stirring in a stream of N_2 at room temperature. After being treated in the same way as described above, the mixture was separated into the neutral and acidic portions in the usual way. The neutral portion was washed with water, dried and concentrated *in vacuo*. The residue (310 mg) was purified by chromatography on silica gel with hexane–EtOAc (3: 1) to give **16** (155 mg) and **17** (40 mg). The acidic portion was led to the *p*-phenylphenacyl ester in the usual way. The product was purified by chromatography on silica gel, using hexane–EtOAc (10: 1) as a solvent and recrystallized from hexane to afford colorless plates (23 mg), mp 78—79°C. The IR and ^{1}H-NMR spectra were identical with those of an authentic sample of *p*-phenylphenacyl isovalerate. The melting point showed no depression on admixture with the authentic sample.

Compounds 16——Recrystallized from hexane–EtOAc to give colorless needles, mp 187—188°C. The IR and ^{1}H-NMR spectra were identical with those of **10**. The ORD data are summarized in Table I. *Anal.* Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63. Found: C, 64.44; H, 6.49.

Compound 17——Recrystallized from hexane–EtOAc to give colorless needles, mp 147—148°C. The IR and ^{1}H-NMR spectra were identical with those of **11**. The ORD data are summarized in Table I. *Anal.* Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63. Found: 64.51; H, 6.64.

Oxidation of 10 with CrO_3–Pyridine Complex——A solution of **10** (300 mg) in dry pyridine (3 ml) was added dropwise to a CrO_3–pyridine complex which had been prepared from dry pyridine (3 ml) and CrO_3 (300 mg) under ice cooling, and treated in the same way as for **2**. The product was recrystallized from hexane–EtOAc to give **19** (150 mg), colorless plates, mp 124—125°C. IR ν_{max}^{Nujol} cm^{-1}: 1740, 1700 (CO), 1610, 1600, 1570 (arom.). The ORD data are summarized in Table I. ^{1}H-NMR ($CDCl_3$) δ ppm: 7.69 (1H, s), 7.63 (1H, d, J=9.5 Hz), 6.84 (1H, s), 6.28 (1H, d, J=9.5 Hz), 5.17 (1H, s), 3.95 (3H, s), 1.50, 1.43, 1.36, 1.10 (each 3H, s). *Anal.* Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 65.10; H, 5.81.

Oxidation of 16 with CrO_3–Pyridine Complex——A solution of **16** (300 mg) in dry pyridine (3 ml) was added dropwise to a CrO_3–pyridine complex which had been prepared from dry pyridine (3 ml) and CrO_3 (300 mg) under ice cooling, and treated in the same way as described above. The product was recrystallized from hexane–EtOAc to give **18** (110 mg), colorless plates, mp 123—124°C. The IR and ^{1}H-NMR spectra were identical with those of **19**. The ORD data are summarized in Table I. *Anal.* Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 65.14; H, 6.07.

Hydrolysis of 20——A 5% NaOH solution (20 ml) was added dropwise to a solution of **20** (500 mg) in pyridine (10 ml) with stirring in a stream of N_2 at room temperature. After being treated in the same way as described above, the mixture was separated into the neutral and acidic portions. The neutral portion was washed with water, dried and concentrated *in vacuo*. The residue (270 mg) was purified by chromatography on silica gel with hexane–EtOAc to give **16** (120 mg) and **17** (25 mg). The acidic portion was led to the *p*-phenylphenacyl ester in the usual way. The product was purified by chromatography on silica gel with hexane–EtOAc (10: 1) as a solvent, and recrystallized from hexane to give colorless plates (300 mg), mp 86—87°C. The IR and ^{1}H-NMR spectra were identical with those of an authentic sample of *p*-phenylphenacyl angelate. The melting point showed no depression on admixture with the authentic sample.

Oxidation of 7 with $NaIO_4$——$NaIO_4$ (140 mg) was added to a solution of **7** (200 mg) in 50% EtOH (30 ml). The mixture was treated in the same way as for **4**. The product was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent, and recrystallized from hexane–EtOAc to give **21** (90 mg), colorless plates, mp 110—111°C. ORD (c=0.595, $CHCl_3$) $[\alpha]^{24}$ (nm): −107.5° (589), −127.7° (550), −161.3° (500), −228.6° (450), −369.7° (400), −598.3° (370). ^{1}H-NMR ($CDCl_3$) δ ppm: 9.71 (1H, s), 7.64 (1H, d, J= 9.5 Hz), 7.46 (1H, s), 6.87 (1H, s), 6.42 (1H, s), 6.25 (1H, m), 6.24 (1H, d, J=9.5 Hz), 3.95 (3H, s), 2.05 (3H, m), 2.00 (3H, s).

Oxidation of 8 with $NaIO_4$——$NaIO_4$ (140 mg) was added to a solution of **8** (200 mg) in 50% EtOH (30 ml). The mixture was treated in the same way as described above. The product was purified by chromatography on silica gel with hexane–EtOAc (3: 1) as a solvent and recrystallized from hexane–EtOAc to give **22** (55 mg), colorless viscid oil. ORD (c=0.445, $CHCl_3$) $[\alpha]^{24}$ (nm): −8.9° (589), −13.5° (500), −22.5° (450), −44.9° (400), −80.9° (360). ^{1}H-NMR ($CDCl_3$) δ ppm: 9.70 (1H, s), 7.65 (1H, d, J=9.5 Hz), 7.46 (1H, s), 6.87 (1H, s), 6.39 (1H, s), 6.28 (1H, d, J=9.5 Hz), 3.95 (3H, s), 2.35 (2H, m), 2.28 (1H, m), 1.02 (6H, d, J=6.5 Hz).

Heating of 2, 4, 5 and 8 in AcOH (Acyl Migration)——A solution of **2** (5 mg) in AcOH (1 ml) was heated on a boiling water bath for 1 h, and the mixture was subjected to thin layer chromatography (TLC) (silica

gel) with hexane–EtOAc (1: 2) as a developing solvent. The ratio of the starting material to the migrated material was measured with a TLC scanner (Hg lamp, excited wavelength at 313 nm). **4**, **5** and **8** were also treated in the same way. The results can be summarized as follows (numbers in parentheses show the ratio of formation). **2**→**2**+**4** (4: 1), **4**→**2**+**4** (2: 1), **5**→**5**+**8** (3: 1), **8**→**5**+**8** (1: 1.3).

Heating of 9 and 15 in 50% AcOH——A solution of **9** (5 mg) in 50% AcOH (1 ml) was heated on a boiling water bath for 1.5 h, and the mixture was treated in the same way as described above. **15** (5 mg) was also treated in the same way as for **9**. The results of measurement with the TLC scanner were as follows. **9**→**2**+**4** (2: 1), **15**→**5**+**8** (1: 16).

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References and Notes

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3) Compound **1** had been reported as angelol. However, we have its name to angelol A since the analogs of **1** were isolated and structure of **1** was revised.
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