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The Constituents of *Schizandra chinensis* Baill. XI.[1] The Structures of Three New Lignans, Angeloylgomisin O, and Angeloyl- and Benzoylisogomisin O

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Three new dibenzocyclooctadiene lignans, angeloylgomisin O (**1**), and angeloyl-(**2**) and benzoylisogomisin O(**3**) were isolated from the fruits of *Schizandra chinensis* Baill. (Schizandraceae). Their absolute structures were elucidated by means of chemical and spectral studies.

Keywords——*Schizandra chinensis* Baill.; Schizandraceae; dibenzocyclooctadiene; lignan; angeloylgomisin O; angeloylisogomisin O; benzoylisogomisin O; ^{13}C-NMR

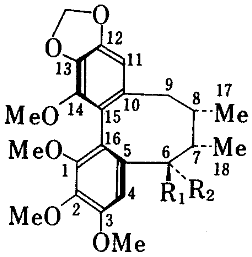
Previously, we reported the isolation and structure elucidation of two dibenzocyclooctadiene lignans named gomisin O(**1a**) and epigomisin O(**6**), which have a hydroxyl group at the C–6 position, from the fruits of *Schizandra chinensis* Baill. (Schizandraceae),[2] and discussed the carbon (^{13}C)-nuclear magnetic resonance (NMR) spectral analysis of these compounds.[3] This paper deals with the isolation and structure elucidation of three new lignans, angeloylgomisin O(**1**), and angeloyl-(**2**) and benzoylisogomisin O(**3**), which may be biosynthetic intermediates between gomisin N type lignans and gomisin B type lignans.[4]

Angeloylgomisin O(**1**) was isolated as an amorphous powder $C_{28}H_{34}O_8$, $[\alpha]_D^{24}$ +47.1° (in $CHCl_3$). The ultraviolet (UV), infrared (IR), proton (^{1}H)- and ^{13}C-NMR spectral analysis of **1** indicate that **1** is a dibenzocyclooctadiene lignan possessing a methylenedioxy moiety and four methoxyls on the aromatic rings, and two secondary methyls and an ester linkage (IR, 1712 cm^{1-}) on the cyclooctadiene ring. One doublet signal at δ 5.74 (1H, J=8 Hz, in $CDCl_3$) in the ^{1}H-NMR spectrum can be assigned to a benzylic methine carrying an acyloxy group. The presence of an angeloyl group in **1** was proved by ^{1}H-NMR [in $CDCl_3$ δ: 1.58 (3H, fine splitted m), 1.83 (3H, dq, J=7/1.5 Hz) and 5.93 (1H, m)], ^{13}C-NMR [in $CDCl_3$ δ: 15.5 (q), 20.0(q), 128.0(s), 138.1(d). 166.8(s)] and mass spectral (*m/z*: 100, 83, 55) analysis.

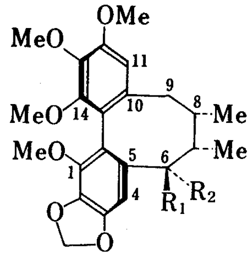
On hydrolysis with 3% ethanolic potassium hydroxide, **1** gave an alcoholic compound (**1a**), $C_{23}H_{28}O_7$, mp 146.5—147.5 °C, $[\alpha]_D^{24}$ −30.1° (in $CHCl_3$), which was identified as gomisin O by direct comparison (IR, ^{1}H-NMR and mixed mp). The structure of angeloylgomisin O was thus elucidated as **1**.

Angeloylisogomisin O(**2**) was isolated as colorless prisms, $C_{28}H_{34}O_8$, mp 122—123 °C, $[\alpha]_D^{24}$ +52.2° (in $CHCl_3$), and benzoylisogomisin O(**3**) was isolated as an amorphous powder, $C_{30}H_{32}O_8$, $[\alpha]_D^{24}$ −14.7° (in $CHCl_3$).[5] The spectral (UV, IR, ^{1}H- and ^{13}C-NMR) data made it clear that **2** and **3** are dibenzocyclooctadiene lignans having the same functional groups as **1**: a methylenedioxy moiety and four methoxyls on the aromatic rings and two secondary methyls, a benzylic methine and an acyloxy group on the cyclooctadiene ring. The presence of an angeloyl group in **2** and a benzoyl group in **3** was proved by ^{1}H- and ^{13}C-NMR spectral analysis (see Table I and Experimental). On hydrolysis with 3% ethanolic potassium hydroxide, **2** and **3** afforded the corresponding acids[6] and the same alcoholic compound **2a**, named isogomisin O, $C_{23}H_{28}O_7$, $[\alpha]_D^{24}$ −27.3° (in $CHCl_3$), IR (in KBr): 3450 cm^{-1} (OH). The circular dichroism (CD) spectrum ($[\theta]_{220}$ +43000, $[\theta]_{229}$ 0, and $[\theta]_{241}$ −75000) of **2a** indicates that **2a** has an *S*-biphenyl configuration.[4]

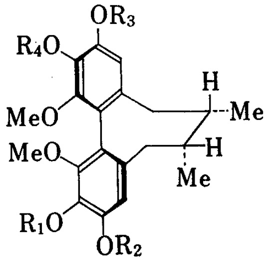
The structure of **2a** was elucidated by ^{13}C-NMR spectral analysis as well as chemical correlation with (±)-γ-schizandrin (**4**) as described below. The presence of an upfield methoxy



1: R_1=-OOC(1′)–C(2′)(CH_3)=C(3′)H–CH_3(4′), R_2=H
1a: R_1=OH, R_2=H
8: R_1+R_2=O



2: R_1=-OOC–C(CH_3)=CH–CH_3, R_2=H
2a: R_1=OH, R_2=H
3: R_1= -OOC–C_6H_5 (1′–6′), R_2=H
5a: R_1+R_2=O
(5: *dl* form of 5a)



7: R_1=R_2=CH_3, R_3+R_4=CH_2
4: R_1+R_2=CH_2, R_3=R_4=CH_3
(*dl* form)

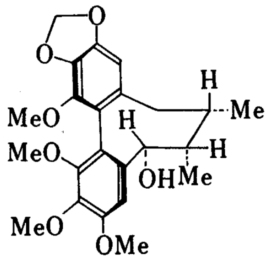


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Chart 1

carbon signal (δ 55.9) and three downfield methoxy carbon signals (δ 59.6, 60.7 and 61.0) indicates that a methoxy (δ 55.9) and a methylenedioxy moiety are located at positions adjacent to the aromatic protons [OCH_3: C-3 or C-12; -OCH_2O-: C-(12—13) or C-(2—3)].[3,7] On comparison of the ^{13}C-NMR spectra of **2a** with those of **1a** and epigomisin O(**6**) (the former has a boat comformation and the latter has a twist-boat-chair conformation of the cyclooctadiene ring), the spectrum of **2a** was seen to be very similar to that of **1a**, except for the chemical shifts of C-4 and C-11, but quite different from that of **6**, as shown in Table I. These observations suggest that **2a** has a methylenedioxy moiety at C-(2—3), and has the same functional groups (a *cis* dimethyl and $C_{(6\beta)}$ -OH) and the same conformational structure as **1a.**[3] The structure of isogomisin O was thus assumed to be **2a**. The coupling constant of the $C_{(6)}$-proton (J=8 Hz) in the ^{1}H-NMR spectrum of **2a** also supports the conformational structure and the presence of a $C_{(6\beta)}$-hydroxyl group in **2a** (*cf.*: **6**, $C_{(6\alpha)}$-H, singlet).

Next, the structure of **2a** was confirmed by chemical correlation with (±)-γ-schizandrin (**4**).[1] In the previous paper,[2] we reported that gomisin N(**7**) was oxidized with $KMnO_4$ in a mixture of pyridine and 2% NaOH at the methylene ($C_{(6)}$-H_2) of the axial methyl side to give a carbonyl compound (**8**). Compound **4** was thus treated with $KMnO_4$ in the same manner to give a carbonyl compound (**5**) as colorless prisms, $C_{23}H_{26}O_7$, mp 164.5—165.5°C, $[\alpha]_D$ ±0°, IR: 1650 cm^{-1} (conjugated carbonyl). In the ^{1}H-NMR spectrum, the aromatic proton signal at δ 6.58 in **5** appears at almost the same region as the C-11 proton of **4** (δ 6.56), whereas the other aromatic proton (δ 7.47) in **5** shows an extreme downfield shift (+$\Delta\delta$ 1.98), compared with the C-4 proton of **4** (δ 6.45). The above observations indicate the presence of a $C_{(6)}$-carbonyl group, which is coplanar with the adjacent aromatic ring.

Table I. ^{13}C-NMR Spectral Data for **1**, **1a**, **2a**, **3** and **6** (δ in $CDCl_3$: ^{13}C, 20 MHz, at 25°C)

Carbon	Compound				
	1	**1a**[3]	**6**[3]	**3**	**2a**
1(s)	151.9	151.9	151.2	141.7	141.6
2(s)	141.7[a]	141.7[a]	140.8[a]	137.0	136.4
3(s)	151.9	152.1	152·3	148.0	148.1
4(d)	111.3	110.2	106.4	106.5	105.5
5(s)	132.8	137.0	136.5	130.8	135.3
6(d)	80.8	81.4	73.4	81.2	81.1
7(d)	37.0	40.1	42.6	36.4	40.2
8(d)	37.2	37.2	39.3	37.7	36.6
9(t)	37.9	38.1	34.7	37.2	37.3
10(s)	135.1	135.5	137.9	136.9	137.2
11(d)	102.3	102.5	102.8	107.1	107.1
12(s)	148.8	149.2	149.2	153.2	153.6
13(s)	134.6	134.6	134.6	140.1	140.1
14(s)	142.0[a]	141.5[a]	140.9[a]	151.8	151.9
15(s)	121.7[b]	120.7[b]	121.3[b]	122.8[a]	121.3[a]
16(s)	123.8[b]	122.2[b]	121.3[b]	122.8[a]	121.6[a]
17(q)	17.8[c]	17.5[c]	20.0[c]	19.2[b]	18.7[b]
18(q)	15.8[c]	16.6[c]	7.8[c]	14.3[b]	15.3[b]
OCH_3 $C_{(1)}$, $C_{(14)}$	60.4, 59.3	60.3, 59.5	60.6, 59.6	59.7, 60.2	59.6, 60.7
OCH_3 $C_{(2)}$, $C_{(13)}$	60.9 —	60.8 —	61.0 —	— 60.7	— 60.9
OCH_3 $C_{(3)}$, $C_{(12)}$	56.0 —	56.0 —	56.0 —	— 56.0	— 55.9
OCH_2O(t)	100.7	100.7	100.8	101.3	101.2
Acid moiety	166.8(s, C-1′)			165.4(C=O)	
	128.0(s, C-2′)			130.2(s, C-1′)	
	138.1(d, C-3′)			129.6(d, C-2′,-6′)	
	15.5(q, C-4′)			128.1(d, C-3′,-5′)	
	20.0(q, C-2′-CH_3)			132.8(d, C-4′)	

a—*c*) Assignments within any column may be reversed.
e) d=doublet, q=quartet, s=singlet, t=triplet.

Finally, oxidation of **2a** with CrO_3 in pyridine gave a carbonyl compound (**5a**) as colorless prisms, mp 149—150 °C, $[\alpha]_D$ +25.1°; this product was identical with **5** in terms of their IR (in $CHCl_3$) and ^{1}H-NMR spectra, and behavior on high performance liquid chromatography (HPLC). The structure of isogomisin O was thus elucidated as **2a**. Therefore, the structures of angeloyl- and benzoylisogomisin O were elucidated as **2** and **3**, respectively. Their ^{1}H-NMR spectral data are in full agreement with the proposed structures, **2** and **3**, respectively.

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus (hot stage type) and are uncorrected. The UV spectra were recorded with a Hitachi 624 digital spectrophotometer and the IR spectra with a Hitachi EPI-G2 unit. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded with Varian T-60 and Varian FT-80A spectrometers, respectively. The mass spectra were measured with a Hitachi RMU-7L double focusing mass spectrometer and a JEOL JMS-DX 300 mass spectrometer. The specific rotations were measured with a JASCO DIP-SL machine and CD spectrum with a JASCO J-20. Gas liquid chromatography (GLC) was carried out on a Hitachi 073 gas chromatograph with FID, and HPLC was carried out on a JASCO Trirotar III. Preparative layer chromatography (PLC) was carried out on plates (20×20 cm, 0.75 mm thick) coated with Kieselgel PF_{254} (Merck). For silica gel column chromatography, Kieselgel 60 (Merck) was used.

Isolation of 1, 2 and 3——Fr. 5-e (11.59 g), reported in the preceding paper,[1] was rechromatographed on silica gel with a hexane–acetone solvent system. The fractions eluted with 4% acetone–hexane were combined and concentrated to give a residue (1.20 g). Repeated PLC of this residue gave **1** (40.7 mg) [i) benzene–

hexane (2: 1), *Rf* 0.85; ii) hexane–acetone–benzene (14: 5: 1), *Rf* 0.54] and **2** (54 mg) [i) benzene–ether (2: 1), *Rf* 0.84; ii) hexane–acetone–benzene (14: 5: 1), *Rf* 0.51].

Fr. 5-g (5.21 g) was rechromatographed on silica gel (120 g) with the hexane–acetone solvent system and the fractions eluted with 10% acetone–hexane were concentrated to give a residue (327 mg), which was purified by repeated PLC [i) hexane–acetone–benzene (14: 5: 1), *Rf* 0.45; ii) benzene–ether (2: 1), *Rf* 0.83, iii) $CHCl_3$–EtOH (99: 1), *Rf* 0.25] to give **3** (50.8 mg).

Angeloylgomisin O (1)——Amorphous powder, $[\alpha]_D^{24}$ +47.1° (c=1.36, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 216 (4.69), 255 (sh 3.95), 275—281 (sh 3.49). IR ν_{max}^{KBr} cm^{-1}: 1712 (C=O), 1645 (C=C), 1617, 1595 (aromatic). ^{1}H-NMR (δ in $CDCl_3$): 0.84 (3H, d, J=7 Hz, C<u>H</u>$_3$–C–H), 0.96 (3H, d, J=7 Hz, C<u>H</u>$_3$–C–H), 1.83 (2H, m, 2×–CH), 2.0—2.4 (2H, m, $C_{(9)}$–H), 3.53 (3H, s), 3.67 (3H, s), 3.92 (6H, s) (4×OCH_3), 5.74 (1H, d, J=8 Hz, $C_{(6)}$–H), 5.93 (2H, s, –OCH_2O–), 6.80 (1H, $C_{(4)}$–H), 6.43 (1H, $C_{(11)}$–H), 1.58 (3H, m), 1.83 (3H, dq, J=7/1.5 Hz), 5.93 (1H, m, not clear due to overlapping with methylenedioxy signal) (angeloyl). MS m/z (%): 498 (M^+, 64), 415 [M^+-CH_3CH=C(CH_3)CO, 9], 398 [M^+-CH_3CH=C(CH_3)COOH, 100], 100 [CH_3CH=C(CH_3)COOH, 38], 83 [CH_3CH=C(CH_3)CO, 71], 55 [CH_3CH=C(CH_3), 68]. *Anal.* Calcd for $C_{28}H_{34}O_8$: C, 67.45; H, 6.87. Found: C, 67.65; H, 6.92. HPLC conditions: column, μ-Bondapak-C_{18} (Waters Assoc.); solvent, MeOH–MeCN–H_2O (1: 1: 1); flow rate, 1 ml/min; t_R (min): 26.8.

Hydrolysis of 1——A solution of **1** (14.1 mg) in 3% KOH–EtOH (2 ml) was kept at 70—75°C for 6 h. The reaction mixture was neutralized with 1 N HCl, diluted with H_2O and extracted with ether. The ethereal extract was washed with 5% $NaHCO_3$, then H_2O, dried over Na_2SO_4 and concentrated to give a residue, which was purified by PLC [hexane–acetone (7: 3), *Rf* 0.38] to give **1a** (10.6 mg) as colorless prisms (from ether–hexane), mp 146.5—147.5°C, $[\alpha]_D^{24}$ −30.1° (c=1.06, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3500 (OH), 1617, 1595 (aromatic). ^{1}H-NMR (δ in $CDCl_3$): 0.92 (6H, d, J=7 Hz, 2×C<u>H</u>$_3$–C–H), 1.75 (2H, m, –CH), 1.92—2.47 (2H, m, $C_{(9)}$–H), 1.63 (1H, s, OH, D_2O exchangeable), 3.53 (3H, s), 3.90 (9H, s) (4×OCH_3), 4.33 (1H, d, J=8 Hz, $C_{(6)}$–H), 5.95 (2H, s, –OCH_2O–), 6.42 (1H, s, $C_{(11)}$–H), 6.57 (1H, s, $C_{(4)}$–H). *Anal.* Calcd for $C_{23}H_{28}O_7$: C, 66.33; H, 6.78. Found: C, 66.28; H, 6.71. HPLC: conditions were the same as in the case of **1**. t_R(min): 8.8. This compound was identified as gomisin O (**1a**) by direct comparison with an authentic sample (IR, ^{1}H-NMR, mixed mp and $[\alpha]_D$).

The 5% $NaHCO_3$ solution was acidified with 1 N HCl and extracted with ether. The ethereal extract was washed with H_2O, dried over Na_2SO_4 and concentrated to give a residue which was sublimed (70°C, 15 mmHg) to give colorless needles. The presence of angelic acid and tiglic acid in a ratio of 1: 33 in this sublimate was demonstrated by GLC.[6] GLC conditions: column, SP-1200 (10%)+H_3PO_4 (1%) on Chromosorb WAW (80—100 mesh), 3 mm×2 m; column temperature, 130°C, injection temperature, 150°C; carrier gas, N_2, 28.8 ml/min. Angelic acid, t_R(min): 6.3; tiglic acid, t_R(min): 8.2.

Angeloylisogomisin O(2)——Colorless prisms from ether–hexane, mp 122—123°C, $[\alpha]_D^{24}$ +52.2° (c=1.80, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 219 (4.91), 255 (sh 4.23), 284 (sh 3.67). IR ν_{max}^{KBr} cm^{-1}: 1702 (C=O), 1639 (C=C), 1610, 1590, 1585 (aromatic). ^{1}H-NMR (δ in $CDCl_3$): 0.83 (3H, d, J=7 Hz, C<u>H</u>$_3$–C–H), 0.96 (3H, d, J=7 Hz, C<u>H</u>$_3$–C–H), 1.88 (2H, m, 2×–CH), 2.27 (center, 2H, m, $C_{(9)}$–H), 3.63, 3.77, 3.85, 3.90 (each 3H, s, 4×OCH_3), 5.78 (1H, d, J=8 Hz, $C_{(6)}$–H), 5.98 (2H, m, –OCH_2O–), 6.50 (1H, s, $C_{(4)}$–H), 6.70 (1H, s, $C_{(11)}$–H), 1.52 (3H, m), 1.82 (3H, dq, J=7/1.5 Hz), 5.91 (1H, m, not clear due to overlapping with methylenedioxy signal) (angeloyl). ^{13}C-NMR (δ in $CDCl_3$): 15.6(q), 20.1(q), 128.0(s), 138.1(d), 166.8(s) (angeloyl). MS m/z(%): 498 [M^+, 82], 415 [M^+-CH_3CH=C(CH_3)CO, 13], 398 [M^+-CH_3CH=C(CH_3)COOH, 100], 100 [CH_3CH=C(CH_3)COOH, 32], 83 [CH_3CH=C(CH_3)CO, 100], 55 [CH_3CH=C(CH_3), 40]. *Anal.* Calcd for $C_{28}H_{34}O_8$: C, 67.45; H, 6.87. Found: C, 67.53; H, 6.90. HPLC: conditions were the same as in the case of **1**. t_R(min): 23.4.

Hydrolysis of 2——A solution of **2** (20.7 mg) in 3% KOH–EtOH (2 ml) was kept at 70—73°C for 6 h. The reaction mixture was treated as described for the hydrolysis of **1** to give **2a** (11.2 mg) as an amorphous powder, $[\alpha]_D^{24}$ −27.3° (c=1.10, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 217 (4.53), 253 (sh 3.90), 283 (sh 3.38). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1615, 1596 (aromatic). CD (c=0.0217, MeOH), $[\theta]^{23}$ (nm): +43000 (220), 0 (229), −75000 (241), −64000 (251, sh). ^{1}H-NMR (δ in $CDCl_3$): 0.86 (3H, d, J=7 Hz, C<u>H</u>$_3$–C–H), 0.99 (3H, d, J=7 Hz, C<u>H</u>$_3$–C–H), 1.77 (2H, m, 2×–CH), 2.20 (center, 2H, m, $C_{(9)}$–H), 3.72 (3H, s), 3.78 (3H, s), 3.85 (6H, s) (4×OCH_3), 4.41 (1H, d, J=8 Hz, $C_{(6)}$–H), 5.97 (2H, s, –OCH_2O–), 6.45 (1H, s, $C_{(4)}$–H), 6.50 (1H, s, $C_{(11)}$–H). MS m/z(%): 416 (M^+, 100), 398 (M^+-H_2O, 44). HPLC: conditions, column; μ-Bondapak-C_{18} (Waters Assoc.), solvent, MeOH–MeCN–H_2O (10: 10: 8); flow rate, 1 ml/min; t_R(min): 7.8. *Anal.* Calcd for $C_{23}H_{28}O_7$: C, 66.33; H, 6.78. Found: C, 66.53; H, 6.90.

The 5% $NaHCO_3$ solution was treated as described for the hydrolysis of **1** to give a sublimate. The presence of angelic acid and tiglic acid in a ratio of 1: 23 was demonstrated by GLC.[6]

Benzoylisogomisin O(3)——Amorphous powder, $[\alpha]_D^{24}$ −14.7° (c=1.70, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 222 (4.75), 257 (sh 4.08), 280 (sh 3.65). IR ν_{max}^{KBr} cm^{-1}: 1712 (C=O), 1618, 1595, 715 (aromatic). ^{1}H-NMR (δ in $CDCl_3$): 0.87 (3H, d, J=7 Hz, C<u>H</u>$_3$–C–H), 0.98 (3H, d, J=7 Hz, C<u>H</u>$_3$–C–H), 1.88 (2H, m, 2×–CH), 2.22 (center, 2H, m, $C_{(9)}$–H), 3.40 (3H, s), 3.80 (6H, s), 3.97 (3H, s) (4×OCH_3), 6.00 (1H, d, J=8 Hz, $C_{(6)}$–H), 6.00 (2H, s, –OCH_2O–), 6.62 (1H, s, $C_{(4)}$–H), 6.73 (1H, s, $C_{(11)}$–H), 7.25—7.67 (5H, m, C_6<u>H</u>$_5$CO). HPLC:

conditions were the same as in the case of **1**. t_R(min): 24.6. *Anal.* Calcd for $C_{30}H_{32}O_8$: C, 69.21; H, 6.20. Found: C, 69.16; H, 6.24.

Hydrolysis of 3——A solution of **3** (15.1 mg) in 3% KOH–EtOH (2 ml) was kept at 70—73°C for 2 h. The reaction mixture was treated as described for the hydrolysis of **1** to give **2a** (8.6 mg) as an amorphous powder, $[\alpha]_D^{24}$ −27.7° (c=0.86, $CHCl_3$), which was identified as **2a** by direct comparison with an authentic sample (IR, ^{1}H-NMR, TLC and $[\alpha]_D$).

The 5% $NaHCO_3$ solution was treated as described for the hydrolysis of **1** to give a sublimate as colorless needles, mp 122—123°C. This compound was identified as benzoic acid by direct comparison with an authentic sample (mixed mp, IR and GLC).

Oxidation of γ-Schizandrin (4) with $KMnO_4$——A solution of **4** (180.4 mg) and $KMnO_4$ (360 mg) in a mixture of pyridine (2 ml) and 2% NaOH (4 ml) was stirred at 55°C for 40 min, then diluted with H_2O (20 ml). The solution was treated with $NaHSO_3$ until no color could be detected, then extracted with ether (15 ml×3). The combined ethereal extract was washed with H_2O, dried over Na_2SO_4 and concentrated. The residue was purified by PLC [hexane–acetone (7: 3)] to give **5** (Rf 0.40, 10.5 mg) and unchanged **4** (Rf 0.61, 64.2 mg). **5**: colorless prisms (from ether–hexane), mp 164.5—165.5°C, $[\alpha]_D^{24}$ 0° (c=0.435, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650 (C=O), 1605, 1592 (aromatic). ^{1}H-NMR (δ in $CDCl_3$): 0.81 (3H, d, J=7 Hz, $C\underline{H}_3$–C–H), 1.00 (3H, d, J=7 Hz, $C\underline{H}_3$–C–H), 1.80 (1H, m, –C$_{(8)}$–H), 1.93—3.07 (3H, m, –C$_{(7)}$–H and C$_{(9)}$–H), 3.60 (3H, s), 3.77 (3H, s), 3.93 (6H, s) (4×OCH_3), 6.07 (2H, s, $-OCH_2O-$), 6.58 (1H, s, C$_{(11)}$–H), 7.47 (1H, s, C$_{(4)}$–H). MS m/z(%): 414 (M^+, 100), 358 (18), 344 (16). High resolution MS, Calcd for $C_{23}H_{26}O_7$(M^+): 414.1679. Found: 414.1659. HPLC: conditions were the same as in the case of **2a**. t_R(min): 7.8.

Oxidation of 2a with CrO_3——CrO_3 (35 mg) was added to a solution of **2a** (10.1 mg) in pyridine (1 ml). The reaction mixture was stirred at room temperature for 3 h, then diluted with H_2O (10 ml) and extracted with ether (15 ml×3). The combined ethereal extract was washed with 1 N HCl (5 ml), then H_2O, dried over Na_2SO_4 and concentrated. The residue was purified by PLC [hexane–acetone (7: 3)] to give **5a** as colorless prisms (from hexane–ether) (6.8 mg), mp 149—150°C, $[\alpha]_D^{25}$ +25.1° (c=0.835, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 208 (4.59), 238 (4.40), 271—273 (sh 3.94). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650 (C=O), 1605, 1592 (aromatic). MS m/z(%): 414 (M^+, 100), 358 (12), 344 (11). High resolution MS, Calcd for $C_{23}H_{26}O_7$(M^+): 414.1679. Found: 414.1708. The IR, ^{1}H-NMR, MS and the retention time on HPLC of this compound were the same as those of **5**.

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References and Notes

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