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The Constituents of *Schizandra chinensis* Baill. III.[1] The Structures of Four New Lignans, Gomisin H and Its Derivatives, Angeloyl-, Tigloyl- and Benzoyl-gomisin H[2]

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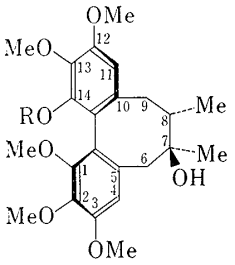
Four new dibenzocyclooctadiene lignans, angeloyl-(**1**), tigloyl-(**2**) and benzoyl-gomisin H(**3**) and gomisin H(**4**), were isolated from the fruits of *Schizandra chinensis* Baill. (Schizandraceae). Their structures were elucidated by chemical and spectral techniques.

Keywords——*Schizandra chinensis* Baill.; Schizandraceae; angeloyl-gomisin H; tigloyl-gomisin H; benzoyl-gomisin H; gomisin H; lignan; dibenzocyclooctadiene

In the previous papers,[1] we reported the structures of the new dibenzocyclooctadiene lignans, gomisin A, B, C, D, F and G, isolated from the fruits of *Schizandra chinensis* Baill. (Schizandraceae). This paper deals with the structures of four additional new lignans, gomisin H (**4**) and its derivatives, angeloyl- (**1**), tigloyl- (**2**) and benzoyl-gomisin H (**3**), isolated from the same source.

The dried fruits of the plant were extracted with petroleum ether and then methanol, and the extracts were treated by the procedure described in the first paper of this series[1a] to give twelve fractions. Fractions 7, 8 and 9 were combined and rechromatographed on



1: R= Me, H, C=C, CO-, Me

2: R= H, Me, C=C, CO-, Me

3: R= C6H4-CO-

4: R= H

5: R= Me

7: R= O_2N-C6H4-NO_2

Chart 1

Table I. UV and IR Spectra of **1**, **2**, **3** and **4**

Compound	UV λ_{max}^{EtOH} nm (log ε)	IR ν_{max}^{KBr} cm^{-1}
1	215(4.72), 248(sh.4.18), 286(sh.3.14)	3500(OH), 1735(C=O), 1645(C=C)
2	215(4.75), 248(sh.4.21), 285(sh.3.47)	3500(OH), 1725(C=O), 1645(C=C)
3	217(4.66), 250(sh.4.20), 282(sh.3.56)	3450(OH), 1735(C=O), 1595, 705 (Aromatic)
4	219(4.81), 247—249(sh.4.32), 276(3.76), 285(sh.3.65)	3530, 3350(OH), 1600, 1579 (Aromatic)

1) *a*) Y. Ikeya, H. Taguchi, I. Yosioka, and H. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **27**, 1383 (1979); *b*) Y. Ikeya, H. Taguchi, I. Yosioka, Y. Iitaka, and H. Kobayashi, *ibid.*, **27**, 1395 (1979).
2) Preliminary communication, see: Y. Ikeya, H. Taguchi, and I. Yosioka, *Chem. Pharm. Bull.* (Tokyo), **26**, 328 (1978).
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TABLE II. PMR Spectral Data for **1**—**5**, **8** and **9** (δ in $CDCl_3$)

Compound	4-H, s 11-H, s	6α-H (J=Hz)	6β-H (J=Hz)	9α-H (J=Hz)	9β-H (J=Hz)	CH_3–C–H (J=Hz) m	CH_3–C–OH s s	OCH_3 s
1[a]	6.67 6.56	2.75, d (13.5)	2.30, d (13.5)	2.37, d, d (13.5/7)	2.75, d, d (13.5/2)	0.83 1.83 (7) ↑ (c)	1.23 1.83	3.53, 3.83(×2) 3.88, 3.90
2[a]	6.68 6.57	2.75, d (13.5)	2.30, d (13.5)	2.35, d, d (13.5/7)	2.75, d, d (13.5/2)	0.84 1.93 (7) ↑ (c)	1.23 1.93	3.50, 3.83(×2) 3.89, 3.90
3[a]	6.77 6.53	2.80, d (13.5)	2.33, d (13.5)	2.40, d, d (13.5/7)	2.78, d, d (13.5/2)	0.88 1.87 (7) ↑ (c)	1.27 1.87	3.53, 3.67, 3.80 3.87, 3.95
4	6.63 6.35	2.70, d (13.5)	2.33, d (13.5)	2.31, d, d (13.5/7)	2.68, d, d (13.5/2)	0.83 1.83 (7)	1.25 1.83	3.63, 3.90(×2) 3.92(×2), 5.78(1H, s, Ar-OH)
5	6.60 6.53	2.70, d (14)	2.32, d (14)	2.33, d, d (14/7)	2.68, d, d (14/2) (c)	0.82 1.80 (7) ↑ (c)	1.25 1.86	3.59(×2) 3.90(×2), 3.92(×2)
8	6.62, s[b] 6.72, s 6.75, s	2.1—2.9(4H, m)				0.87 1.80 (7)	1.25 1.82	3.49, 3.86 3.91(×3)
9	6.59, s (4-H)	2.78, d (15)	2.45, d (15)	2.97, d, d (15/9)	2.12, d, d (15/2) (c)	0.87 1.87 (7) ↑ (c)	1.27 1.68	3.78, 3.87 3.92, 4.05(×2)

a) Other signals: **1**: Me(β) H(α)C=C(α)CO– 1.73(6H, m, α- and β-Me), 5.88(1H, m, β-H); **2**: Me(β) H(α)C=C(α)Me CO– 1.70(6H, m, α- and β-Me), 6.78(1H, m, β-H); **3**: 7.38(3H, m), 7.98(2H, d, d)(C_6H_5CO–).

b) δ in acetone-d_6: 6.70, 6.77 and 6.85 (each singlet).

c) Confirmed by decoupling experiments.

d) d=doublet, m=multiplet, s=singlet.

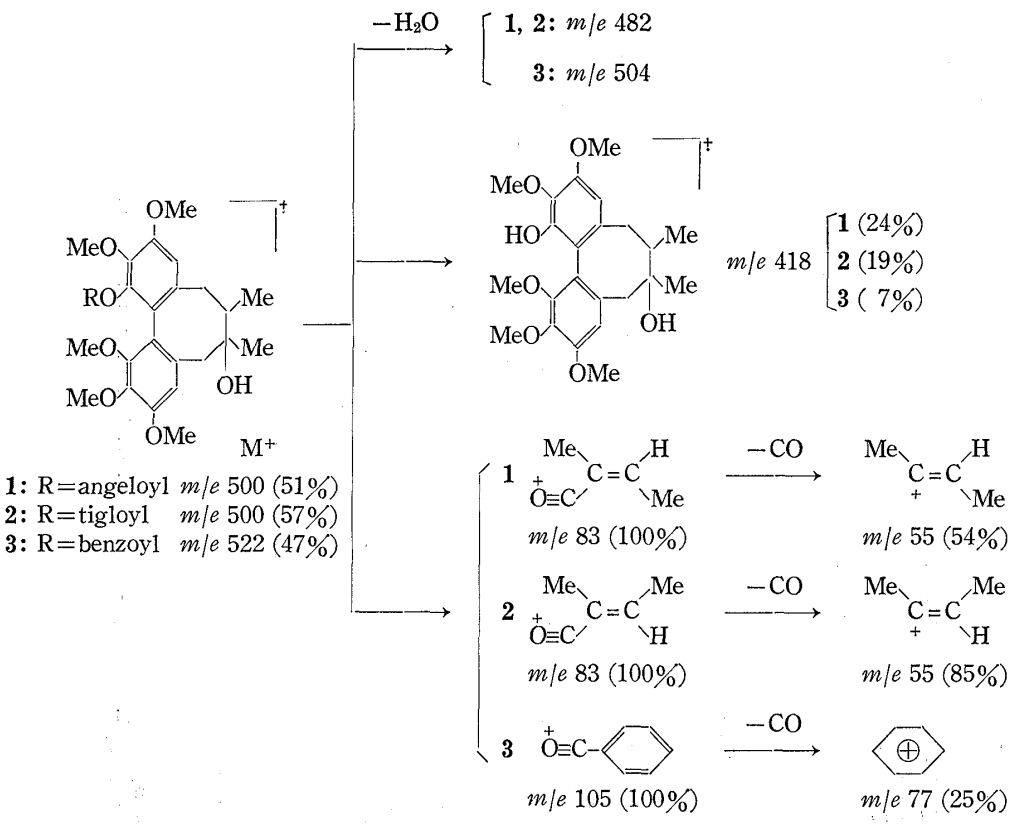

Chart 2. Mass Spectra of **1**, **2** and **3**

silica gel to give **1** (yield, 0.031%), **2** (0.014%) and **3** (0.003%) as amorphous powders, and **4** (0.014%) as colorless plates, mp 144—145°, $[\alpha]_D^{26}$ +41.2° (in $CHCl_3$) (see the experimental section). The molecular formulae of **1**, **2** and **3** were estimated from the high resolution mass spectra to be $C_{28}H_{36}O_8$, $C_{28}H_{36}O_8$ and $C_{30}H_{34}O_8$, respectively, and that of **4** was estimated by elemental analysis to be $C_{23}H_{30}O_7$. The ultraviolet (UV) spectra of these compounds (Table I) showed that they are dibenzocyclooctadiene lignans and the infrared (IR) spectra (Table I) showed that **1**, **2** and **3** possess a hydroxyl and an ester linkage, and **4** possesses two hydroxyls, but no ester linkage [*vide* proton nuclear magnetic resonance (PMR)]. The PMR spectra of these compounds (Table II) revealed that they possess five methoxyls on the aromatic rings, a tertiary methyl group attached to carbon carrying a hydroxyl group (CH_3–$\overset{|}{C}$–OH), a secondary methyl group and two benzylic methylenes. On the other hand, mass spectral and PMR spectral analysis indicated that **1**, **2** and **3** possess an angeloyl, a tigloyl and a benzoyl group, respectively. Although **1** and **2** have the same molecular formulae and gave very similar mass spectra, the chemical shifts of the olefinic protons of the acid moieties in **1** and **2** indicated that **1** possesses an angeloyl group (δ in $CDCl_3$, 5.88) and **2** possesses a tigloyl group (δ 6.78). In fact, on hydrolysis with 3% ethanolic potassium hydroxide, **1**, **2** and **3** afforded angelic acid (it was partly isomerized to tiglic acid during hydrolysis; see the experimental section), tiglic acid and benzoic acid, respectively, and a phenolic compound identical with **4** on direct comparison (mixed mp, IR, PMR and $[\alpha]_D$). Methylation of **4** with dimethylsulfate and potassium carbonate in acetone gave a monomethyl ether, which was identical with schizandrin (**5**) isolated from the same source[1a,4] on direct comparison (mixed mp, IR and TLC), indicating that **4** corresponds to norschizandrin and that the acyl groups in **1**, **2** and **3** are linked to the phenolic hydroxyl in **4**.

4) N.K. Kochetkov, A. Khorlin, O.S. Chizhov, and V.I. Sheichenko, *Tetrahedron Lett.*, **1961**, 730; Y.Y. Chen, Z.B. Shu, and L.N. Li, *Scientia Scinica* (Peking), **19**, 276 (1976).

The following experiments were thus carried out to confirm the position of the hydroxyl group in **4**. First, the intramolecular nuclear Overhauser effects (NOE) in benzyl ether (**6**) of **4** (in C_6D_6) were measured, as in the case of schizandrin.[1a] As shown in Chart 3, both aromatic protons ($C_{(4)}$–H and $C_{(11)}$–H) were affected by irradiation of the methoxyl signals (δ 3.50 and 3.52), indicating that the two methoxyls are located at the positions (C-3 and C-12) adjacent to the aromatic protons. The other results are shown in Chart 3.

Next, treatment of **4** with 2,4-dinitrofluorobenzene in a mixture of benzene and dimethylformamide in the presence of sodium hydride as a catalyst afforded 2,4-dinitrophenyl ether (**7**) (yield, 71.5%) as an oil. Catalytic hydrogenation of **7** over platinum oxide followed by cleavage with sodium in liquid ammonia[5] afforded compound **8**, $C_{23}H_{30}O_6$, mp 121—122.5°, which showed three singlet signals due to aromatic protons in the PMR spectrum, indicating that the hydroxyl in **4** is located at the *para*-position (C-1 or C-14) relative to an aromatic proton.

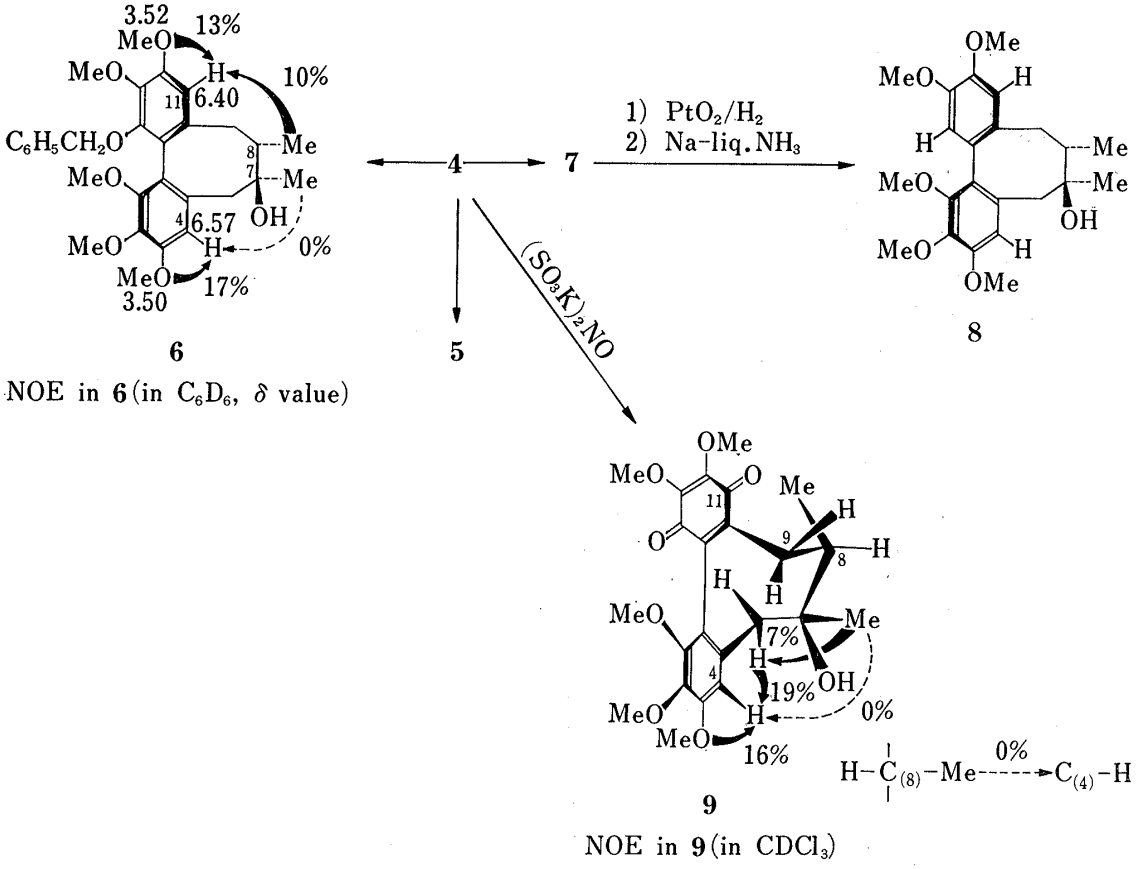

Chart 3

Oxidation of **4** with Fremy salts [$(SO_3K)_2NO$] at 20°[6] afforded compound **9** (yield 97%), $C_{23}H_{28}O_8$, mp 65—66°, which showed absorption bands at 1655 and 1645 cm^{-1} due to *p*-quinone in the IR spectrum and showed only one aromatic proton signal in the PMR spectrum. The structure of **9** was confirmed by measurements of the NOE (in $CDCl_3$) as shown in Chart 3. Irradiation of a methoxyl signal (δ 3.92) and a methylene proton signal (δ 2.45, d, J=15 Hz, $C_{(6\beta)}$–H) caused 16% and 19% increases in the integrated intensity of the aromatic proton signal, respectively. Irradiation of the tertiary methyl signal caused a 7% increase in the integrated intensity of the $C_{(6\beta)}$-proton (δ 2.45), while the aromatic proton

5) W.H. Pirkle and J.L. Zabriskie, *J. Org. Chem.*, **29**, 3124 (1964); W.H. Pirkle and M. Gates, *ibid.*, **30**, 1796 (1965).
6) W. Moser and R.A. Howie, *J. Chem. Soc. A*, **1968**, 3039.

was unaffected by irradiation of both methyl signals. The above results, in comparison with the results of NOE in **5**,[1a] indicated that the phenolic hydroxyl in **4** is located at the C-14 position, and the absolute structure of **9**, including its conformation, is expressed by the formula **9**. These findings are consistent with the J value between the $C_{(8)}$-proton and $C_{(9)}$-methylene protons, which showed extreme downfield ($C_{(9\alpha)}$–H) and highfield ($C_{(9\beta)}$–H) shifts due to the effects of the carbonyl groups in the PMR spectrum ($J_{8,9\alpha}=9$ Hz, $\phi_{8,9\alpha}\fallingdotseq 30°$; $J_{8,9\beta}=2$ Hz, $\phi_{8,9\beta}\fallingdotseq 90°$).

On the basis of the above observations, the absolute structure of gomisin H was elucidated as **4**. Consequently, the structures of angeloyl-, tigloyl- and benzoyl-gomisin H were elucidated as **1**, **2** and **3**, respectively.

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus (a 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 machine. The PMR spectra were recorded with Varian T-60 and JEOL PS-100 spectrometers with tetramethylsilane as an internal standard. Mass spectra were measured with a Hitachi double-focusing mass spectrometer. The specific rotations were measured with a JASCO DIP-SL unit and the circular dichroism (CD) spectrum with a JASCO J-20. Gas liquid chromatography (GLC) was carried out on a Hitachi 073 gas chromatograph with FID. For silica gel column chromatography, Kieselgel 60 (Merck) was used. Thin-layer chromatography (TLC) were carried out on Merck plates precoated with Kieselgel 60 F_{254}. Preparative layer chromatography (PLC) was carried out on plates (20×20 cm, 0.75 mm thick) coated with Kieselgel GF_{254} (Merck).

Isolation of 1, 2 and 3——In the previous paper,[1a] it was reported that the petroleum ether and the methanolic extracts of the fruits of *Schizandra chinensis* (4.67 kg) were column chromatographed on silica gel, developing with *n*-hexane, acetone–benzene, and acetone solvent systems, to give twelve fractions (fr. 1—12). Fr. 7, 8 and 9 were combined and rechromatographed on silica gel, developing with a benzene–ether solvent system, to give nine fractions [fr. (7—9)-a—fr. (7—9)-i] (Table III). Fr. (7—9)-f and -g were combined and a portion (28.5 g) was rechromatographed on silica gel (425 g, 5.5×39 cm), developing with an EtOAc–*n*-hexane solvent system (10% EtOAc–*n*-hexane→EtOAc). The fractions eluted with 35%, 40% and 50% EtOAc–*n*-hexane were combined and concentrated to give a gum (5.48 g), which was separated by PLC with acetone–*n*-hexane (2: 3) as an eluant. The zone with Rf 0.45 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated to give **1** as an amorphous powder (1448 mg, yield 0.031%), $[\alpha]_D^{22}$ +19.4° (c=1.6, $CHCl_3$). High resolution mass spectrum (MS), Calcd. for $C_{28}H_{36}O_8$ (M^+): 500.240. Found: 500.237. The zone with Rf 0.40 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated to give **2** as an amorphous powder (654 mg, 0.014%), $[\alpha]_D^{23}$ +67.7° (c=1.30, $CHCl_3$). High resolution MS, Calcd. for $C_{28}H_{36}O_8$(M^+): 500.240. Found: 500.237. The fractions eluted with 70% EtOAc–*n*-hexane were combined and concentrated to give a gum (1.55 g), which was purified by PLC with acetone–*n*-hexane (2: 3) as an eluant. The zone with Rf 0.38 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated

Table III. Chromatography of Fr. 7—9

Fr. No.	Solvent benzene–ether	Volume (l)	Residue (g)
7—9 a	94:6	0.9	5.32
	92:8	0.3	
7—9 b	90:10	0.5	2.58
7—9 c	88:12	1.0	3.00
7—9 d	86:14	2.4	5.11
7—9 e	84:16	2.6	4.64
7—9 f	82:18	0.7	14.33
7—9 g	80:20	0.3	18.44
	75:25	0.4	
	70.30	0.3	
7—9 h	60:20	0.4	9.80
	50:50	0.4	
	30:70	0.3	
7—9 i	Ether	1.6	1.47

to give **3** as an amorphous powder (140 mg, 0.003%), $[\alpha]_D^{24}$ +96.8° (c=1.25, $CHCl_3$). High resolution MS, Calcd. for $C_{30}H_{34}O_8$(M^+): 522.225. Found: 522.224.

UV and IR spectral data for **1**, **2** and **3** are given in Table I. PMR spectral data are listed in Table II and mass spectral data are given in Chart 2.

Isolation of 4——Fr. 10 (6.07 g)[1a] and fr. (7—9)-i (1.47 g) were combined and rechromatographed on silica gel (120 g, 3.2×35 cm), developing with an acetone–*n*-hexane solvent system. The fractions eluted with 20% acetone–*n*-hexane were concentrated to give a gum (1.632 g), which was separated by PLC with $CHCl_3$–MeOH (19: 1) as an eluant. The zone with *Rf* 0.52 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated and purified by PLC with EtOAc–*n*-hexane (2: 1) as an eluant. The zone with *Rf* 0.51 was further purified by PLC with acetone–*n*-hexane (2: 3) as an eluant. The zone with *Rf* 0.30 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated. The residue was recrystallized from ether–*n*-hexane to give **4** as colorless plates, mp 144—145°, $[\alpha]_D^{26}$ +41.2° (c=0.999, $CHCl_3$) (71 mg, 0.0015%). *Anal.* Calcd. for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 65.78; H, 7.17. UV and IR spectral data are given in Table I and PMR spectral data are given in Table II.

Hydrolysis of 1——A solution of **1** (80 mg) in 3% KOH–EtOH (3 ml) was kept at 70° for 2 hr, then diluted with H_2O (10 ml) 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 purified by PLC with acetone–*n*-hexane (2: 3) as an eluant. The zone with *Rf* 0.30 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated. The residue was recrystallized from ether–*n*-hexane to give a phenolic compound as colorless plates (51 mg), mp 145—146°, $[\alpha]_D^{24}$ +44.5° (c=0.967, $CHCl_3$). *Anal.* Calcd. for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 65.94; H, 7.07. This compound was identified as **4** by direct comparison with authentic material (IR, $[\alpha]_D$ and mixed mp).

The aqueous solution was acidified with 5% H_2SO_4 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°, 15 mmHg) to give colorless needles (4 mg). The presence of angelic acid and tiglic acid in this sublimate in a ratio of 2: 3 was demonstrated by GLC. GLC conditions: column, SP-1200 (10%)+H_3PO_4 (1%) on Chromosorb WAW (80—100 mesh), 3 mm×2 m; column temperature, 130°; injection temperature, 150°; carrier gas, N_2, 25 ml/min; angelic acid, t_R(min), 8.3; tiglic acid, t_R(min), 10.8.

Hydrolysis of 2——A solution of **2** (70 mg) in 3% KOH–EtOH (2.5 ml) was kept at 70° for 2 hr, then the reaction mixture was treated as described for the hydrolysis of **1** to give a phenolic compound and an acid. The former was obtained as colorless plates (50 mg), mp 144.5—146°, $[\alpha]_D^{21}$ +47.1° (c=0.870, $CHCl_3$). *Anal.* Calcd. for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 66.26; H, 7.37. This compound was identified as **4** by direct comparison (IR, $[\alpha]_D$ and mixed mp). The latter was sublimed (70°, 15 mmHg) to give colorless needles (6 mg), mp 61.5—63°. This compound was identified as tiglic acid by direct comparison with an authentic material (GLC, IR and mixed mp, GLC conditions were the same as in the case of **1**).

Hydrolysis of 3——A solution of **3** (30 mg) in 3% KOH–EtOH (2 ml) was kept at 70° for 2 hr, then the reaction mixture was treated as described for the hydrolysis of **1** to give a phenolic compound and an acid. The former was obtained as colorless plates (21 mg), mp 144.5—146°, $[\alpha]_D^{22}$ +45.8° (c=0.677, $CHCl_3$). *Anal.* Calcd. for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 66.30; H, 7.29. This compound was identified as **4** by direct comparison (IR, $[\alpha]_D$ and mixed mp). The latter was sublimed (70°, 15 mmHg) to give colorless prisms (2.5 mg), mp 122—123°. This compound was identified as benzoic acid by direct comparison with authentic material (GLC, IR and mixed mp, GLC conditions: column, SP-1200 (10%)+H_3PO_4 (1%) on Chromosorb WAW (80—100 mesh) 3 mm×2 m; column temperature, 155°; injection temperature, 165°; carrier gas, N_2, 30 ml/min; benzoic acid, t_R(min), 23.5).

Methylation of 4——A solution of **4** (11 mg) in dry acetone (2 ml) containing $(CH_3)_2SO_4$ (0.1 ml) and K_2CO_3 (100 mg) was stirred at 20° for 15 hr, then diluted with H_2O and extracted with ether. The ethereal extract was washed with H_2O, dried over Na_2SO_4 and concentrated. The residue (10 mg) was recrystallized from ether–*n*-hexane to give **5** as colorless prisms, mp 129—131°, $[\alpha]_D^{21}$ +86.9° (c=0.345, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3495 (OH), 1593 (aromatic). *Anal.* Calcd. for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46. Found: C, 66.70; H, 7.48. This compound was identified as **5** by direct comparison (IR, $[\alpha]_D$ and mixed mp).

Benzylation of 4——Benzylchloride (200 mg) and K_2CO_3 (200 mg) were added to a solution of **4** (40 mg) in a mixture of dimethylformamide (DMF) and H_2O (100: 1) (4 ml), and the reaction mixture was heated at 110° for 6 hr, cooled, diluted with H_2O then extracted with ether. The ethereal extract was washed with H_2O, dried over Na_2SO_4 and concentrated to give a residue, which was purified by PLC with benzene–ether (3: 2) as an eluant. The zone with *Rf* 0.28 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated to give **6** (33 mg) as a pale yellow oil, $[\alpha]_D^{23}$ +119° (c=0.787, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 1593, 1578 (aromatic). PMR (δ in C_6D_6): 0.73 (3H, d, J=7 Hz, $C\underline{H}_3$–$\overset{|}{C}$H), 1.23 (3H, s, $C\underline{H}_3$–$\overset{|}{C}$–OH), 1.78 (1H, m, –$\overset{|}{C}$H), 2.03—2.98 (4H, m, 2×Ar–$C\underline{H}_2$–), 3.50, 3.52, 3.62, 3.77, 3.87 (each 3H, s, 5×OCH_3), 4.68, 5.08 (each 1H, d, J=11 Hz, $C_6H_5C\underline{H}_2O$–), 6.40, 6.57 (each 1H, s, arom.-H), 7.05 (5H, s, $C_6\underline{H}_5CH_2O$–). High resolution MS, Calcd. for $C_{30}H_{36}O_7$(M^+): 508.246; Found: 508.248.

Dinitrophenylation of 4——A solution of **4** (65 mg) in dry benzene (4 ml) was stirred under N_2 with NaH (30 mg) until the evolution of H_2 ceased. 2,4-Dinitrofluorobenzene (198 mg) and dry benzene (2 ml) were

added and then DMF (1.6 ml) was added during a period of 10 min. The reaction mixture was stirred for 30 min, refluxed for 30 min, cooled, diluted with H_2O (10 ml) and extracted with ether. The ethereal extract was washed with H_2O, dried over Na_2SO_4 and concentrated. The residue was purified by PLC with EtOAc–*n*-hexane (1: 1) as an eluant. The zone with *Rf* 0.36 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated to give a 2,4-dinitrophenyl ether (**7**) as a yellow oil (65 mg, 71.5%), $[\alpha]_D^{26}$ +49.9° (c=1.021, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 212 (4.70), 250 (4.31), 284 (4.06), 300 (sh 3.98). IR ν_{max}^{KBr} cm^{-1}: 3540 (OH), 1602 (aromatic), 1532, 1343 (NO_2). MS, *m/e* (%): 584 (M^+, 100), 400 [$M^+-C_6H_3(OH)(NO_2)_2$, 19]. PMR (δ in $CDCl_3$): 0.90 (3H, d, J=7 Hz, C<u>H</u>$_3$–CH), 1.27 (3H, s, C<u>H</u>$_3$–C–OH), 1.73 (1H, m, –CH), 1.73 (1H, s, OH, D_2O exchangeable), 2.2—2.9 (4H, m, 2×Ar–C<u>H</u>$_2$–), 3.60, 3.75, 3.80, 3.85, 3.97 (each 3H, s, 5×OCH_3), 6.47 (1H, s, $C_{(11)}$–H), 6.80 (1H, s, $C_{(4)}$–H), 6.77 (1H, d, J=10 Hz), 8.17 (1H, d,d, J=10/2 Hz), 8.60 (1H, d, J=2 Hz) [–$C_6H_3(NO_2)_2$].

Preparation of 8——Compound **7** (65 mg) in a mixture of MeOH (2 ml) and tetrahydrofuran (4 ml) was hydrogenated over PtO_2 (20 mg) at atmospheric pressure for 1 hr. The colorless solution was filtered and concentrated to dryness under reduced pressure. The residue was dissolved in a mixture of liquid ammonia and ether, and treated with small pieces of sodium at −65° until the solution showed a permanent blue color. After standing briefly, NH_4Cl was added to the solution, then NH_3 was evaporated off at room temperature under an N_2 stream. After addition of H_2O (20 ml), the reaction mixture was extracted with ether (15 ml×3). The combined ethereal extract was washed with H_2O, dried over Na_2SO_4 and concentrated to give a residue, which was purified by PLC with acetone–*n*-hexane (2: 3) as an eluant. The zone with *Rf* 0.36 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated. The residue was recrystallized from ether–*n*-hexane to give **8** as colorless plates (23.5 mg, 53%), mp 121—122.5°, $[\alpha]_D^{21}$ +86.0° (c=0.430, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 213 (4.63), 254 (4.14), 282 (3.76), 293 (sh 3.67). IR ν_{max}^{KBr} cm^{-1}: 3480 (OH), 1600 (aromatic). High resolution MS, Calcd. for $C_{23}H_{30}O_6$(M^+): 402.204. Found: 402.203. PMR spectral data are given in Table II.

Oxidation of 4——H_2O (6 ml) was added to a solution of **4** (50 mg) in a mixture of *n*-hexane and $CHCl_3$ (9: 1) (6 ml), and the mixture was stirred at 20° while Fremy salts [$(SO_3K)_2NO$] (100 mg) were added during a period of 2 hr. After adding H_2O (5 ml), the reaction mixture was extracted with $CHCl_3$ and the $CHCl_3$ extract was concentrated to give a residue, which was dissolved in a mixture of *n*-hexane–$CHCl_3$ (9: 1) (6 ml). After adding H_2O (6 ml), the mixture was stirred at 20° while Fremy salts (100 mg) were added during a period of 3 hr, then H_2O (5 ml) was added and the mixture was extracted with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O, dried over Na_2SO_4 and concentrated to give a residue, which was purified by PLC with $CHCl_3$–MeOH (40: 1) as an eluant. The zone with *Rf* 0.47 was extracted with $CHCl_3$–MeOH (4: 1) and the extract was concentrated to give a residue, which was recrystallized from ether–pet. ether to give **9** as reddish needles (50 mg, 97%), mp 65—66°, $[\alpha]_D^{23}$ +85.0° (c=0.635, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 216 (4.59), 241 (sh, 4.16), 274 (4.01), 365 (3.44). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1655, 1645 (*p*-quinone), 1602 (aromatic). CD (c=0.0275, MeOH), $[\theta]^{23}$(nm): −86000(205), +90000(224), +58000(242), −47000(275), +2800(322), −8300(378), +12000(447). MS, *m/e*(%): 432 (M^+, 100), 360(20). PMR spectral data are given in Table II. *Anal.* Calcd. for $C_{23}H_{28}O_8$: C, 63.88, H, 6.53. Found: C, 63.73; H, 6.84.

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