Four New Caffeic Acid Metabolites, Yunnaneic Acids E—H, from *Salvia yunnanensis*

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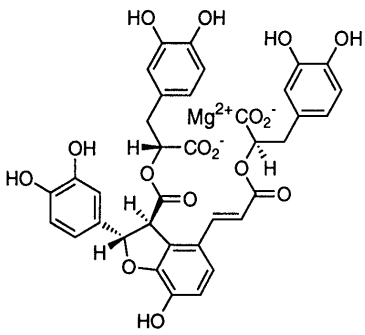
Four new caffeic acid metabolites, named yunnaneic acids E—H were isolated from the root of *Salvia yunnanensis*. Their structures have been established on the basis of spectroscopic and chemical evidence. Yunnaneic acids E and F are biogenetically derived from yunnaneic acid C, which is a Diels–Alder adduct of rosmarinic acid and caffeic acid. On the other hand, yunnaneic acids G and H are arylnaphthalene-type lignan esters derived by oxidative coupling between two molecules of rosmarinic acid. The existence of these compounds indicates that caffeic acid metabolism in *S. yunnanensis* is more complex than that in *S. miltiorrhiza*.

Key words *Salvia yunnanensis*; Labiatae; caffeic acid; polyphenol; lignan; yunnaneic acid

We previously isolated magnesium lithospermate B (**1**), a caffeic acid tetramer derived by oxidative coupling of two molecules of rosmarinic acid (**2**), from the roots of *Salvia miltiorrhiza* BUNGE (Chinese crude drug named "dan shen," Labiatae) as an active principle with an improving effect on renal function in rats with induced renal failure.[1] More recently, we have also reported structure elucidation of four novel caffeic acid metabolites, yunnaneic acids A (**3**), B (**4**), C (**5**) and D (**6**), from the root of *S. yunnanensis* BUNGE,[2] which is used as a substitute for *S. miltiorrhiza* in southern China. Yunnaneic acids C (**5**) and D (**6**) are considered to be Diels–Alder adducts between rosmarinic acid and caffeic acid, and yunnaneic acids A (**3**) and B (**4**) have dimeric structures comprised of **5** and **6**, and two molecules of **5**, respectively. The unique structures of these compounds prompted us to study minor constituents of this plant. Here we describe the isolation and structure determination of four minor caffeic acid metabolites of *S. yunnanensis*.

The aqueous acetone extract of the dried root was first applied on an MCI-gel CHP20P column. Most of the $FeCl_3$-positive substances, however, were not adsorbed on the gel, and were eluted together with sugars and inorganic substances. This result suggested that most of the phenolic constituents are acidic in nature and they exist as salts with inorganic cations. Hence, in order to convert them into free acid form, the first fraction of the column was acidified and immediately subjected to Sephadex LH-20 chromatography as described in a preceding paper.[2] Among the four fractions thus obtained, the third and fourth fractions which contained **3**—**6** were further chromatographed over MCI gel CHP20P, Chromatorex ODS, Toyopearl HW40F and Sephadex LH-20 to yield four new compounds named yunnaneic acids E (**7**), F (**8**), G (**9**) and



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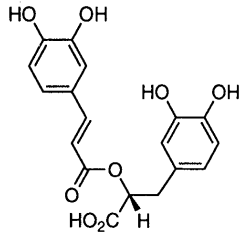

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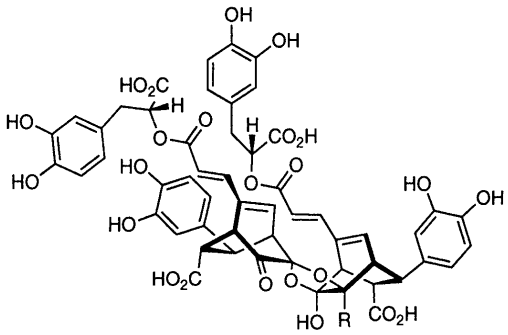
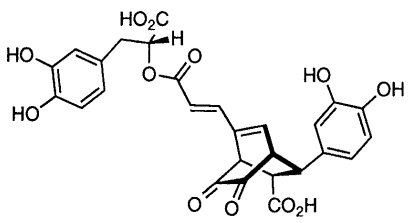


3: R = H
4: R = OH



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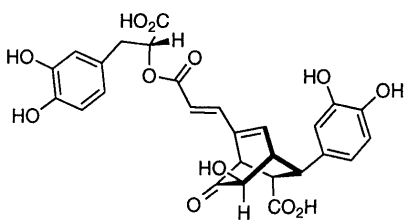

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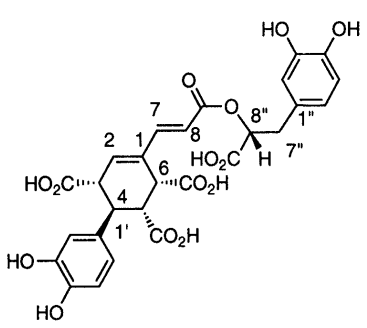

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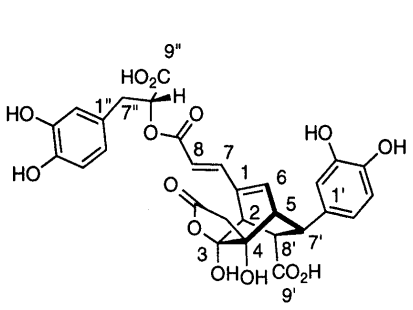

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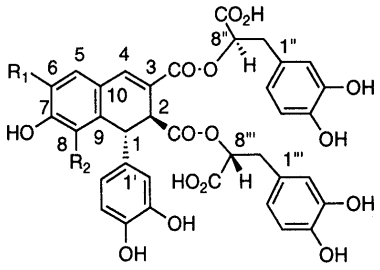
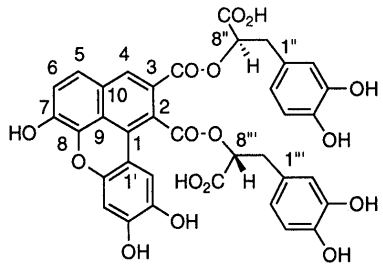


9 : R_1 = H, R_2 = OH
11 : R_1 = OH, R_2 = H



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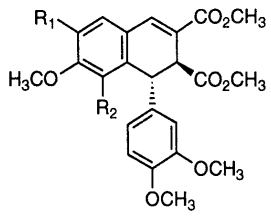
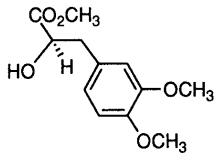


9a : R_1 = H, R_2 = OCH_3
11a : R_1 = OCH_3, R_2 = H



9b

Table 1. ^{1}H-NMR Data for Yunnaneic Acids E (**7**), F (**8**), G (**9**) and H (**10**) (in Acetone-d_6)[a]

	7[b]	8[b]	9[c]	10[c]
H-1			5.09 (br s)	
H-2	6.48 (d, 3)	3.96 (br s)	4.00 (d, 1)	
H-3	3.56 (ddd, 1.5, 3, 10)			
H-4	3.87 (dd, 10, 12)		7.68 (s)	8.21 (s)
H-5	3.26 (dd, 5, 12)	3.13 (d, 7)	6.89 (d, 8)[d]	7.55 (d, 8)
H-6	3.77 (dd, 1.5, 5)	6.87 (br d, 7)	6.80 (d, 8)[d]	7.36 (d, 8)
H-7	7.39 (d, 16)	7.41 (d, 16)		
H-8	6.03 (d, 16)	6.21 (d, 16)		
H-2′	6.85 (d, 2)	6.72 (d, 2)	6.47 (d, 2)	
H-3′				6.65 (s)
H-5′	6.73 (d, 8)	6.70 (d, 8)	6.65 (d, 8)	
H-6′	6.68 (dd, 2, 8)	6.57 (dd, 2, 8)	6.47 (dd, 2, 8)	7.81 (s)
H-7′		4.13 (br d, 7)		
H-8′		2.55 (dd, 2, 7)		
H-2″ (2‴)	6.83 (d, 2)	6.84 (d, 2)	6.78, 6.87 (each d, 2)	6.77, 6.99 (each d, 2)
H-5″ (5‴)	6.77 (d, 8)	6.75 (d, 8)	6.71, 6.76 (each d, 8)	6.68, 6.84 (each d, 8)
H-6″ (6‴)	6.65 (dd, 2, 8)	6.67 (dd, 2, 8)	6.58, 6.66 (each dd, 2, 8)	6.62, 6.80 (each dd, 2, 8)
H-7″ (7‴)	2.99 (dd, 9, 14)	3.04 (dd, 8, 14)	2.99—3.08 (4H, m)	3.08 (dd, 7, 14), 3.30 (dd, 7, 14)
	3.11 (dd, 4, 14)	3.13 (dd, 4, 14)		3.16—3.24 (2H, m)
H-8″ (8‴)	5.16 (dd, 4, 9)	5.23 (dd, 4, 8)	4.99 (dd, 5, 7)	5.35 (dd, 5, 8)
			5.10 (t, 8)	5.45 (dd, 5, 7)
CH_2		2.74 (d, 19)		
		2.80 (d, 19)		

a) Values in parentheses denote coupling constants in Hz. *b*) Measured at 40 MHz. *c*) Measured at 300 MHz. *d*) Assignments may be interchanged.

H (**10**), along with a known compound, rabdosiin (**11**),[3] which was identified by comparison of spectral data with values reported in the literature.[4]

Yunnaneic acid E (**7**) was obtained as a white amorphous powder, and gave a dark green coloration with $FeCl_3$ reagent. The ^{1}H-NMR spectrum (Table 1) showed two sets of ABX aromatic signals due to catechol rings and two doublets due to *trans*-olefin protons (H-7, H-8, J = 16 Hz). The appearance of the signals due to an aliphatic methine (δ 5.16) and a methylene (δ 2.99, 3.11), along with ABX aromatic signals suggested the presence of a 3-(3′,4′-dihydroxyphenyl)lactic acid moiety similar to those of **1**—**6**.[2] With the aid of ^{1}H–^{1}H correlation spectroscopy (COSY) experiments, the coupling between the remaining one olefinic and four aliphatic methine signals ($J_{2,3}$ = 3 Hz, $J_{3,4}$ = 10 Hz, $J_{4,5}$ = 12 Hz, $J_{5,6}$ = 5 Hz, $J_{2,6}$ = 1.5 Hz) revealed the presence of a cyclohexene ring. The relative configuration of the ring protons (3,4-*trans*, 4,5-*trans*, 5,6-*cis*) was deduced from their coupling constants. In the heteronuclear multiple bond connectivity (HMBC) spectrum (8 Hz), the olefinic proton (δ 6.48) of this cyclohexene ring correlated with the carbon signal

Table 2. ^{13}C-NMR Data for Yunnaneic Acids E (**7**), F (**8**), G (**9**) and H (**10**) (in Acetone-d_6+D_2O)[a]

	7[b]	8[b]	9[c]	10[b]
C-1	133.7	142.4[d]	39.6	126.1
C-2	138.5	45.1	47.6	120.5
C-3	52.9	107.3	135.5	124.9
C-4	38.9	76.2	140.3	130.3
C-5	48.5	51.1[e]	122.7	122.5
C-6	44.6	140.4	114.2	120.9
C-7	146.8	142.5[d]	143.8	143.2
C-8	117.3[d]	118.1	148.4	137.8
C-9	166.7	166.5	124.8[d]	124.4
C-10	172.9[e]		125.3[d]	127.4
C-11	173.1[e]		172.0	170.2
C-12	173.5		166.7	166.1
C-1′	134.5	137.2	121.1	110.4
C-2′	116.5	116.0	115.5	148.9
C-3′	145.3	145.7	145.7	104.7
C-4′	144.5	144.5[f]	143.8	147.7
C-5′	115.8	115.5	116.0	142.2
C-6′	120.4	119.8	119.8	113.4
C-7′		38.3		
C-8′		51.3[e]		
C-1″ (1‴)	128.8	128.9	129.0, 129.1	127.9, 128.8
C-2″ (2‴)	117.4[d]	117.3	117.5, 117.6	117.5, 117.7
C-3″ (3‴)	145.6	145.7	145.3, 145.5	145.4, 145.8
C-4″ (4‴)	144.7	144.8[f]	144.7, 144.8	144.7, 144.9
C-5″ (5‴)	116.1	116.0	116.0, 116.1	115.8, 116.1
C-6″ (6‴)	121.5	121.7	121.8, 121.9	121.7, 122.1
C-7″ (7‴)	37.3	37.4	37.2, 37.5	37.2, 37.7
C-8″ (8‴)	74.3	74.1	74.2, 74.5	74.7, 76.1
C-9″ (9‴)	171.8	170.9	170.9, 171.1	171.1, 172.6
CH_2		44.2		
COO		173.1		

a) Values in parentheses denote coupling constants in Hz. b) Measured at 100 MHz. c) Measured at 75 MHz. d–f) Assignments may be interchanged in each column.

attributable to the *trans*-double bond (δ 146.8), through three-bond long-range coupling indicating that these two double bonds were conjugated (Fig. 1). The ^{13}C-NMR spectrum (Table 2) exhibited signals due to five carboxyl carbons. Among them, one (δ 171.8) was assigned as the carboxyl group of the phenyllactic acid moiety, and another (δ 166.7, C-9) was considered to be conjugated with the above mentioned *trans*-double bond. The HMBC spectrum not only confirmed the assignment of these carboxyl groups but also revealed the ester linkage between the conjugated carboxyl carbon and the methine carbon (C-8″) of the phenyllactic acid moiety. The remaining three carboxyl signals were correlated with aliphatic methine proton signals (H-3, 5 and 6), indicating that these carboxyl groups were located on the cyclohexene ring. Furthermore, the C-1′ (δ 128.8) of the remaining catechol ring was correlated with another methine proton at δ 3.87 (H-4), showing that this catechol ring was located at C-4 of the cyclohexene ring. On the basis of these spectroscopic data, the structure of yunnaneic acid E was concluded to be as represented by the formula **7**. It seems reasonable to consider that this compound was generated by oxidative cleavage of the α-diketone part (C-3, C-4) of yunnaneic acid C (**5**) (Chart 1); hence, the chirality of the molecule was also presumed to be similar to that of **5**.

Yunnaneic acid F (**8**) exhibited an $[M-H]^-$ peak at *m/z* 597 in the negative ion FAB-MS, which is 58 mass

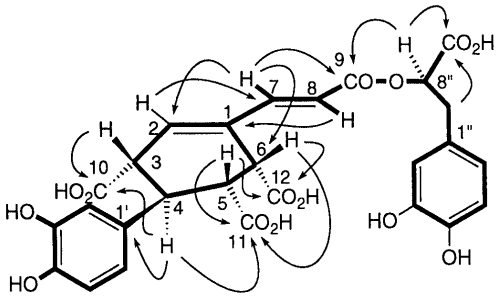


Fig. 1. Selected HMBC Correlations for **7** (H→C)

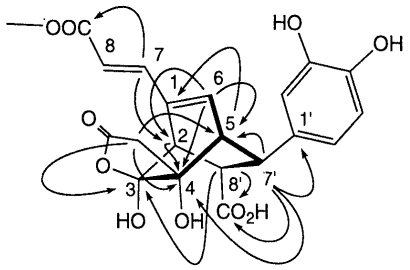


Fig. 2. Selected HMBC Correlations for **8** (H→C)

units larger than that of yunnaneic acid D (**6**). The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) were related to those of **6**, showing the signals arising from a catechol, a carboxyl group and an α,β-unsaturated carboxyl group attached to a bicyclo[2.2.2]octene skeleton, along with the signals due to a 3-(3′,4′-hydroxyphenyl)-lactic acid moiety. The connectivities of these structural units were confirmed by an HMBC experiment, as shown in Fig. 2. The significant difference of the NMR spectra of **8** from those of **6** is the appearance of the signals due to an additional CH_2–COO residue. In the HMBC spectrum, correlations of the methylene protons with C-3, C-4 and C-5 indicated that this methylene was attached to the C-4 position of the bicyclo[2.2.2]octene skeleton. Furthermore, a differential nuclear Overhauser effect (NOE) experiment irradiating the methylene proton signals revealed the NOE between these methylene protons and the olefinic proton H-6, confirming the relative configuration at C-4. In addition, the molecular weight estimated from the FAB-MS suggested that the additional carboxyl group forms a γ-lactone ring with the hemiacetal hydroxyl group at C-3. The circular dichroism (CD) spectrum of **8** showed a large positive Cotton effect at 290 nm and a negative one at 228 nm, which were similar to those of **6**, indicating that the chirality of this compound is the same as that of **6**.[2] On the basis of these spectroscopic findings, the structure of yunnaneic acid F was established as **8**. This compound is probably derived from yunnaneic acid C (**5**) by aldol-type addition of acetic acid to the C-4 carbonyl group.

Yunnaneic acid G (**9**) was found to be an isomer of rabdosiin (**11**),[3,4] because **9** showed an $[M-H]^-$ peak at *m/z* 717 in the negative ion FAB-MS and its ^{1}H-NMR spectrum was closely related to that of **11**, except for the appearance of two aromatic doublets (H-5, H-6, J=8 Hz) instead of two aromatic singlets (H-5, H-8 of **11**). In addition, the benzylic methine proton (H-1) of **9** was observed at lower field (δ 5.09, br s) than that of **11** (δ

4.57, br s). The ^{13}C-NMR spectrum also confirmed the structural relation between these two compounds: that is, **9** and **11** are 1,2-dihydro-1-(3′,4′-dihydroxyphenyl)dihydroxynaphthalene-2,3-dicarboxylic acids with two dihydroxyphenyllactic acid moieties. The lignan units of these compounds might be generated by oxidative coupling between two caffeic acid residues, and the *ortho*-coupling between two aromatic protons of the dihydronaphthalene unit indicated that two phenolic hydroxyl groups were vicinally located at C-7 and -8. Methylation of **9** with dimethyl sulfate followed by methanolysis afforded the methanolysate **9a**, together with (*R*)-methyl 3-(3′,4′-dimethoxyphenyl)lactate (**9b**).[4] The negative specific optical rotation of **9a** ($-105.7°$) suggested that the absolute configuration at C-1 and C-2 is the same as that of **11** (**11a**, $[\alpha]_D$ $-51°$[4,5]). From these results, yunnaneic acid G was concluded to be represented by the formula **9**. Although lignans of aryldihydronaphthalene type sometimes exist with the enantiomeric isomer,[4-6] no other isomers of **9** and **11** were found in this plant.

Yunnaneic acid H (**10**) was isolated as a dark yellow amorphous powder and exhibited an $[M-H]^-$ peak at *m/z* 713 in the negative ion FAB-MS; that is 4 mass units less than that of **9**. The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) indicated the presence of two 3-(3′,4′-dihydroxyphenyl)lactic acid moieties. The remaining part of the molecule consists of 18 sp^2 carbons including five aromatic methines, five oxygen-bearing aromatic carbons and two carboxyl groups. In the ^{1}H-NMR spectrum, three aromatic singlets and two *ortho*-coupled doublet signals were assignable to the protons of this part. In the HMBC spectrum, sixteen correlation peaks between these protons and carbons were appeared as illustrated in Fig. 3: long-range coupling (H→C) of the two doublets (δ 7.55, 7.36) and one singlet (δ 8.21) proton signals suggested the presence of a dicarboxyl naphthalene structure. The remaining two singlet signals (δ 6.65, 7.81) were attributable to aromatic protons of a tri-oxygenated benzene ring attached to the naphthalene nucleus. Taking the molecular weight into account, this observation unequivocally indicated that this lignan unit is an arylnaphthalene type, which has been found as the lignan part of a triterpene-lignan ester isolated from *Rhoiptelea chiliantha*.[6] On the basis of these results, the structure of yunnaneic acid H was concluded to be as shown in formula **10**. This compound is probably an oxidative metabolite derived from **9**.

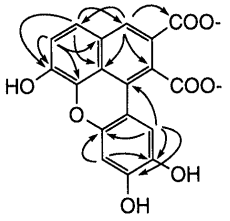


Fig. 3. HMBC Correlations for **10** (H→C)

Caffeic acid metabolism in *S. yunnanensis* is summarized in Chart 1. The phenolic constituents of *S. yunnanensis* are relatively complex as compared with *S. miltiorrhiza*, which contains mainly lithospermic acid B along with lesser amounts of lithospermic acid and rosmarinic acid (**2**). Oxidative coupling between two molecules of rosmarinic acid affords lithospermic acid B (**1**), rabdosiin (**11**) and yunnaneic acid G (**9**), and **9** is further converted to yunnaneic acid H (**10**) by dehydrogenation. On the other hand, two modes of Diels–Alder type coupling between **2** and caffeic acid generate yunnaneic acids C (**5**) and D (**6**). Yunnaneic acids A (**3**) and B (**4**) are dimerization products of these metabolites. Furthermore, yunnaneic acids E (**7**) and F (**8**) are also derived from **5**.

Experimental

The instruments and chromatographic conditions used throughout this work were the same as described in the preceding paper.[2]

Isolation The dried root (1.0 kg) was extracted with 70% aqueous acetone. The extract (300 g) was first subjected to MCI-gel column chromatography (1.5 l) with H_2O containing increasing proportions of MeOH (0→100%, stepwise elution with 10% increase at each step) to give four fractions, the first two of which were positive to $FeCl_3$ reagent. The second fraction (19 g) was separated by Sephadex LH-20 (60→80% MeOH in H_2O) and MCI-gel CHP20P (30→40% MeOH) chromatography to yield lithospermic acid B (**1**, 1.8 g) and rosmarinic acid (**2**, 0.3 g). The first fraction was concentrated to give an aqueous solution, acidified with 2 M HCl to pH 2 at 0 °C, and immediately applied to a column of Sephadex LH-20 (1.5 l) with H_2O. After washing of the column with H_2O to elute inorganic material and sugars, the phenolic substances were eluted with aqueous MeOH (20%→40%→60%) to give four fractions. The third fraction was subsequently chromatographed over MCI-gel CHP20P, Chromatorex ODS (30→40% MeOH), Sephadex

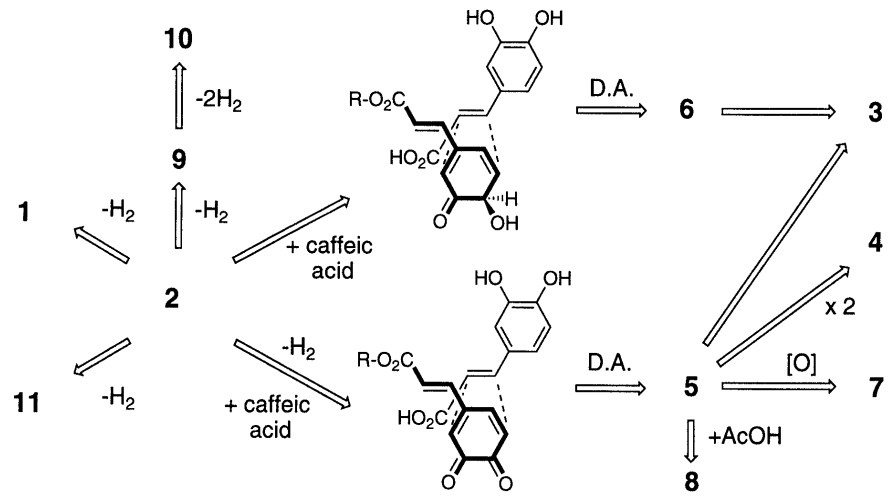


Chart 1. Possible Pattern of Caffeic Acid Metabolism in *S. yunnanensis*

LH-20 (40→60% MeOH) and Toyopearl HW-40F (40→80% MeOH) to afford yunnaneic acids E (**7**, 209 mg), F (**8**, 370 mg), G (**9**, 113 mg) and rabdosiin (**11**, 74 mg), along with **5** (0.61 g) and **6** (0.24 g). The fourth fraction was subjected to Chromatorex ODS chromatography with H_2O containing increasing amounts of MeOH to yield yunnaneic acid H (**10**, 133 mg), together with **3** (0.67 g) and **4** (3.8 g).

Yunnaneic Acid E (**7**): A white amorphous powder, $[\alpha]_D^{26}$ +81.3° (c=0.5, MeOH). *Anal.* Calcd for $C_{27}H_{24}O_{14}\cdot 3/2H_2O$: C, 54.09; H, 4.54. Found: C, 54.00; H, 4.78. Negative ion FAB-MS m/z: 571 $(M-H)^-$, 527 $(M-CO_2H)^-$. UV λ_{max}^{EtOH} nm (ε): 266 (24450). ^{1}H- and ^{13}C-NMR: Tables 1 and 2. HMBC: Fig. 1. CD (9.5×10^{-5} M, EtOH) $\Delta\varepsilon_{282}$ 6.6, $\Delta\varepsilon_{269}$ 4.8, $\Delta\varepsilon_{253}$ 6.07, $\Delta\varepsilon_{239}$ 0, $\Delta\varepsilon_{230}$ −6.5.

Yunnaneic Acid F (**8**): A white amorphous powder, $[\alpha]_D^{26}$ +126.6° (c=0.5, MeOH). *Anal.* Calcd for $C_{29}H_{26}O_{14}\cdot H_2O$: C, 56.50; H, 4.58. Found: C, 56.42; H, 4.88. Negative ion FAB-MS m/z: 597 $(M-H)^-$. IR ν_{max}^{neat} m^{-1}: 3400, 1765 (sh), 1735, 1714, 1629, 1520. UV λ_{max}^{EtOH} nm (ε): 273 (22380). ^{1}H- and ^{13}C-NMR: Tables 1 and 2. HMBC: Fig. 2. CD (9.5×10^{-5} M, EtOH) $\Delta\varepsilon_{290}$ 10.9, $\Delta\varepsilon_{272}$ 3.9, $\Delta\varepsilon_{261}$ 5.1, $\Delta\varepsilon_{239}$ 0, $\Delta\varepsilon_{228}$ −5.0.

Yunnaneic Acid G (**9**): A white amorphous powder, $[\alpha]_D^{23}$ −50.4° (c=0.5, MeOH). *Anal.* Calcd for $C_{36}H_{30}O_{16}\cdot 2H_2O$: C, 57.30; H, 4.54. Found: C, 57.78; H, 5.00. Negative ion FAB-MS m/z: 717 $(M-H)^-$. ^{1}H- and ^{13}C-NMR: Tables 1 and 2.

Methylation and Methanolysis of 9 A mixture of **9** (70 mg), $(CH_3)_2SO_4$ (1.5 ml) and anhydrous K_2CO_3 (1.2 g) in dry acetone (20 ml) was heated under reflux for 1.5 h with stirring. After removal of the inorganic salts by filtration, the filtrate was concentrated to a syrup, which was chromatographed over silica gel 60 (15 g). Elution with benzene–acetone (41 : 9) gave the decamethylate (33.3 mg) as a white amorphous powder, $[\alpha]_D^{23}$ −69.4° (c=0.5, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.67 (1H, s), 7.03 (1H, d, J=8 Hz), 6.81 (1H, d, J=8 Hz), 6.79 (1H, d, J=2 Hz), 6.70—6.73 (4H, m), 6.67 (1H, dd, J=2, 8 Hz), 6.64 (1H, d, J=2 Hz), 6.63 (1H, d, J=8 Hz), 6.47 (1H, dd, J=2, 8 Hz), 5.21 (1H, t, J=6 Hz), 5.11 (1H, t, J=6 Hz), 5.09 (1H, br s), 4.06 (1H, d, J=1.2 Hz), 3.86, 3.84, 3.83 (×2), 3.82, 3.78, 3.74, 3.67, 3.61, 3.55 (each 3H, s), 3.11, 3.05 (each 2H, d, J=6 Hz). The methylate (crude 52 mg) was treated with 2% $NaOCH_3$ at room temperature for 20 h and neutralized with Amberlite IRA 120B (H^+ form). After concentration, the residue was chromatographed over silica gel 60 (15 g). Elution with benzene–acetone (97 : 3) yielded the methanolysate **1a** as a white amorphous powder (15 mg), $[\alpha]_D^{23}$ −69.4° (c=0.5, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.69 (1H, s), 7.13 (1H, d, J=8 Hz), 6.85 (1H, d, J=8 Hz), 6.73 (1H, d, J=2 Hz), 6.64 (1H, d, J=8 Hz), 6.45 (1H, dd, J=2, 8 Hz), 5.11 (1H, s), 4.06 (d, 1.3 Hz), 3.88, 3.80, 3.78, 3.76, 3.65, 3.58 (each 3H, s). CD (1.2×10^{-4} M, EtOH) $\Delta\varepsilon_{346}$ −1, $\Delta\varepsilon_{328}$ 0, $\Delta\varepsilon_{303}$ −7.1, $\Delta\varepsilon_{269}$ −0.7, $\Delta\varepsilon_{250}$ −10.4, $\Delta\varepsilon_{241}$ 0, $\Delta\varepsilon_{220}$ 27. Further elution of the column with benzene–acetone (9 : 1) afforded (*R*)-3-(3′,4′-dimethoxyphenyl)lactate (**9b**) as a white powder (12.5 mg), $[\alpha]_D^{23}$ −4° (c=0.9, MeOH), ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 6.72—6.82 (3H, m), 4.44 (1H, ddd, J=5, 6, 6 Hz), 3.86, 3.85, 3.77 (each 3H, s), 3.10 (1H, dd, J=5, 14 Hz), 2.88 (1H, dd, J=6, 14 Hz), 2.71 (1H, d, J=6 Hz).

Yunnaneic Acid H (**10**): A dark yellow amorphous powder, $[\alpha]_D^{26}$ +55.3° (c=0.2, MeOH). *Anal.* Calcd for $C_{36}H_{26}O_{16}\cdot 3/2H_2O$: C, 58.30; H, 3.94. Found: C, 58.30; H, 4.54. Negative ion FAB-MS m/z: 713 $(M-H)^-$. UV-VIS λ_{max}^{EtOH} nm (ε): 396 (8846), 278 (24423). IR ν_{max}^{KBr} cm^{-1}: 3400, 1720, 1690, 1610, 1520, 1445. ^{1}H- and ^{13}C-NMR: Tables 1 and 2. HMBC: Fig. 3.

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