Polyphenolic Glycosides and Oligosaccharide Multiesters from the Roots of *Polygala dalmaisiana*

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Four new polyphenolic glycosides, dalmaisiones A−D (**1**−**4**), 16 new oligosaccharide multiesters, dalmaisioses A−P (**5**, **7**−**21**), and one known tetrasaccharide multiester, reiniose G (**6**), were isolated from the roots of *Polygala dalmaisiana*. The structures of the new compounds were elucidated on the basis of chemical and spectroscopic evidence.

In the course of conducting a research program on the oligosaccharide esters from *Polygala* species,[1] we have investigated *P. dalmaisiana* (*P. oppositifolia* × *P. myrtifolia*) (Polygalaceae). No previous investigation has been reported on the oligosaccharide esters of *P. dalmaisiana*. We now report on an investigation of the roots of *P. dalmaisiana*, which led to isolation of four new compounds (**1**−**4**), 16 new oligosaccharide esters (**5**, **7**−**21**), and a known oligosaccharide ester, reiniose G (**6**) (Chart 1). Known compounds were identified by comparison of their spectral data with reported data.[2]

Results and Discussion

The roots of *P. dalmaisiana* were extracted with MeOH. The MeOH extract was partitioned between H_2O and diethyl ether. The H_2O layer was passed through a porous polymer gel (Mitsubishi Diaion HP-20) column and eluted with a mixture of H_2O and MeOH. The 70% MeOH elute was separated further to afford compounds **1**−**21**.

The FABMS of dalmaisione A (**1**) gave pseudo molecular ion peaks at *m*/*z* 589 $[M + H]^+$ and 611 $[M + Na]^+$, compatible with a molecular formula $C_{28}H_{28}O_{14}$. The ^1H NMR and $^1H-^1H$ COSY spectra showed the presence of a 1,2-disubstituted benzene ring [δ 7.86 (1H, dd, $J = 7.5$, 1.5 Hz), 7.90 (1H, td, $J = 7.5$, 1.5 Hz), 7.58 (1H, td, $J = 7.5$, 1.5 Hz), 8.12 (1H, dd, $J = 7.5$, 1.5 Hz) in this order] and a 1,2,3-trisubstituted benzene ring [δ 7.66 (1H, dd, $J = 7.5$, 1.5 Hz), 7.46 (1H, t, $J = 7.5$ Hz), 7.92 (1H, dd, $J = 7.5$, 1.5 Hz) in this order] and two anomeric protons [δ 5.45 (1H, d, $J = 7.5$ Hz), 5.24 (1H, d, $J = 1.5$ Hz)]. The $^1H-^1H$ COSY and HOHAHA difference spectra on irradiation at each anomeric proton signal and ROE experiments involving irradiation at each anomeric proton signal enabled us to assign all proton signals. Acid hydrolysis afforded **1a** as an aglycone and D-glucose and L-rhamnose as sugar moieties.[3] Compound **1a** was methylated by diazomethane to afford the methyl ether **1b**. Compound **1b** was identified as frutinone B by comparison of spectral data with reported data.[4] The sugar sequence and the glycosidic site were decided by ROE and HMBC. In the ROE difference spectra of **1**, when the proton signals at δ 5.45 due to H-1 of Glc and δ 5.24 due to H-1 of Rha were irradiated, ROEs were observed at δ 7.66 due to H-3′ and δ 3.68 due to H-2 of Glc, respectively. In the HMBC spectrum of **1**, long-range correlations were observed between the proton signal due to H-1 of Rha and the carbon signal due to C-2 (δ 76.2) of Glc and between the proton signal due to H-1 of Glc and the carbon signal due to C-2′ (δ 143.8), respectively. Thus, the structure of dalmaisione A was determined to be **1**.

Dalmaisione B (**2**) gave a pseudo molecular ion peak at *m*/*z* 979 $[M + Na]^+$ in a FABMS compatible with molecular formula $C_{45}H_{48}O_{23}$. The ^1H NMR spectrum showed the presence of an aglycone (**1a**), three monosaccharides [δ 5.56 (1H, d, $J = 2$ Hz), 5.18 (1H, d, $J = 7.5$ Hz), 4.43 (1H, d, $J = 7.5$ Hz)], and a sinapoyl residue [δ 7.20 (1H, d, $J = 16$ Hz), 6.56 (2H, s), 6.02 (1H, d, $J = 16$ Hz), 3.76 (6H, s)]. Acid hydrolysis afforded **1a**, D-glucose, L-rhamnose, and sinapinic acid. The $^1H-^1H$ COSY and HOHAHA difference spectra on irradiation at each anomeric proton signal and ROE experiments involving irradiation at each anomeric proton signal enabled us to assign all proton signals. In the ROE difference spectra of **2**, when the proton signals at δ 5.18 due to H-1 of Glc (inner), at δ 4.43 due to H-1 of Glc (terminal), and at δ 5.56 due to H-1 of Rha were irradiated, ROEs were observed at δ 7.79 due to H-3′, at δ 4.08 due to H-6 of Glc (inner), and at δ 3.85 due to H-2 of Glc (inner), respectively. In the HMBC spectrum of **2**, long-range correlations were observed between the proton signal at δ 5.18 due to H-1 of Glc (inner) and the carbon signal at δ 145.9 due to C-2′; between the proton signal δ 5.56 due to H-1 of Rha and the carbon signal δ 77.3 due to C-2 of Glc (inner); between the proton signal δ 4.43 due to H-1 of Glc (terminal) and the carbon signal δ 71.6 due to C-6 of Glc (inner); between the proton signals δ 4.15 and 4.78 due to H_2-6 of Glc (terminal) and the sinapoyl carbonyl carbon signal δ 168.5, respectively. Thus, the structure of dalmaisione B was determined to be **2**.

Dalmaisione C (**3**) gave NMR data similar to those of **1**. In the $^1H-^1H$ COSY spectrum, a 1,2-disubstituted benzene ring [δ 7.43 (1H, dd, $J = 8$, 1.5 Hz), 7.84 (1H, td, $J = 8$, 1.5 Hz), 7.55 (1H, td, $J = 8$, 1.5 Hz), 8.45 (1H, dd, $J = 8$, 1.5 Hz) in this order] and a 1,2,3-trisubstituted benzene ring [δ 7.70 (1H, dd, $J = 8$, 1.5 Hz), 7.49 (1H, t, $J = 8$ Hz), 7.91 (1H, dd, $J = 8$, 1.5 Hz) in this order] were observed other than two anomeric protons [δ 5.47 (1H, d, $J = 7.5$ Hz), 5.38 (1H, d, $J = 2$ Hz)]. Compound **3** afforded D-glucose and L-rhamnose on acid hydrolysis. After assignment of all proton signals by $^1H-^1H$ COSY and HOHAHA difference spectra, the sugar sequence was determined to be α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl using ROE and HMBC spectra. On irradiation of the glucosyl anomeric proton signal at δ 5.47, ROE was observed at the aromatic proton signal at δ 7.70, which had an HMBC correlation to the carbon signal at δ 120.3. The carbon signal at δ 120.3 was correlated to the proton signal δ 7.91 in the HMQC

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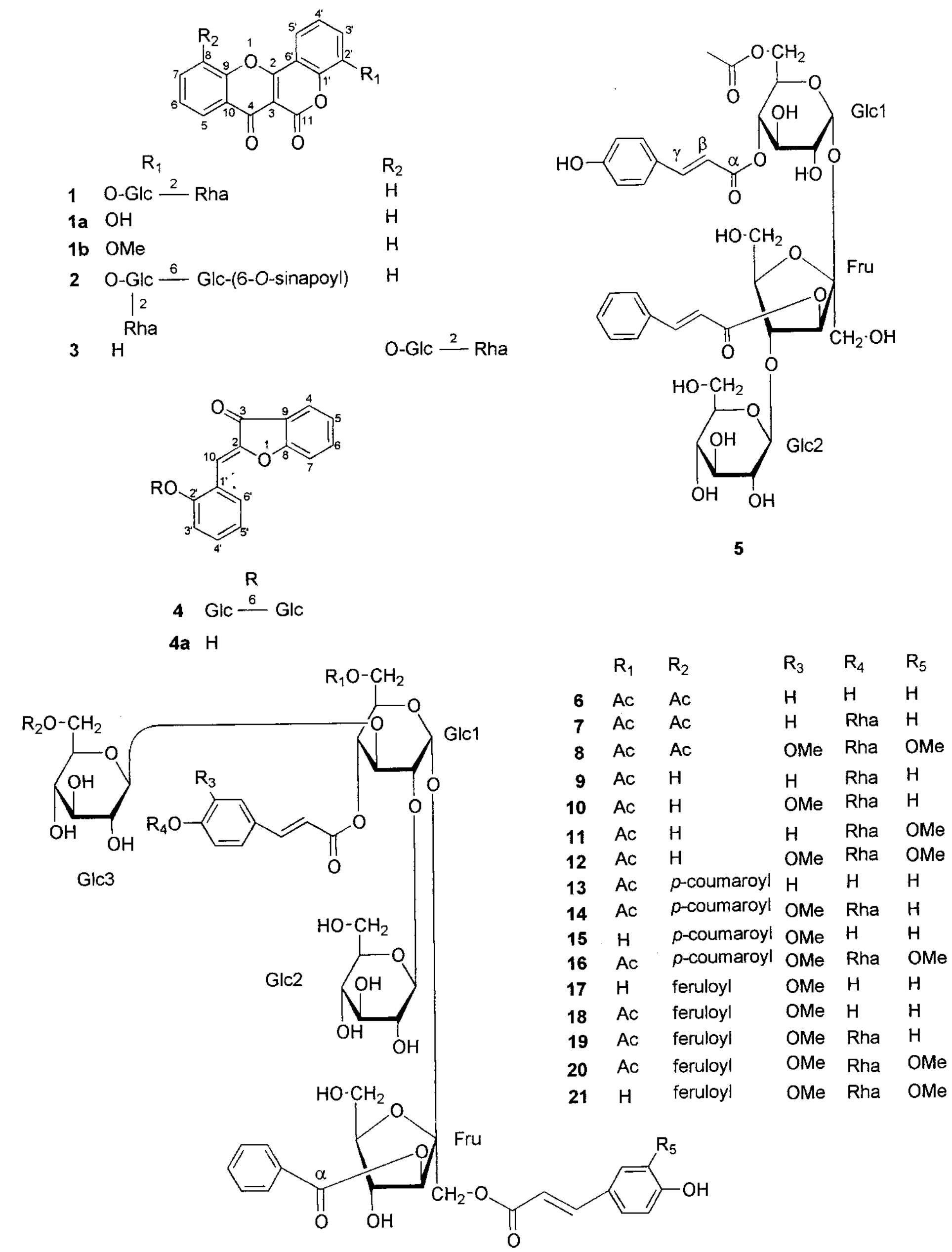
Chart 1



	R_1	R_2	R_3	R_4	R_5
6	Ac	Ac	H	H	H
7	Ac	Ac	H	Rha	H
8	Ac	Ac	OMe	Rha	OMe
9	Ac	H	H	Rha	H
10	Ac	H	OMe	Rha	H
11	Ac	H	H	Rha	OMe
12	Ac	H	OMe	Rha	OMe
13	Ac	*p*-coumaroyl	H	H	H
14	Ac	*p*-coumaroyl	OMe	Rha	H
15	H	*p*-coumaroyl	OMe	H	H
16	Ac	*p*-coumaroyl	OMe	Rha	OMe
17	H	feruloyl	OMe	H	H
18	Ac	feruloyl	OMe	H	H
19	Ac	feruloyl	OMe	Rha	H
20	Ac	feruloyl	OMe	Rha	OMe
21	H	feruloyl	OMe	Rha	OMe

spectrum. The proton signal at δ 7.91 had a correlation to the carbon signal at δ 175.3 due to C-4 of the aglycone. Thus, the structure of dalmaisione C was determined to be **3**.

Dalmaisione D (**4**) was shown to have molecular formula $C_{27}H_{30}O_{13}$ by FABMS ($[M + H]^+$ *m/z* 563), which was consistent with the ^{13}C NMR spectrum. Acid hydrolysis afforded **4a** and D-glucose. Two 1,2-disubstituted benzene rings [δ 8.06 (1H, dd, J = 7.5, 1.5 Hz), 7.50 (1H, td, J = 7.5, 1.5 Hz), 7.82 (1H, td, J = 7.5, 1.5 Hz), 7.73 (1H, dd, J = 7.5, 1.5 Hz) in this order; 7.92 (1H, dd, J = 7.5, 1.5 Hz), 7.22 (1H, td, J = 7.5, 1.5 Hz), 7.57 (1H, td, J = 7.5, 1.5 Hz), 7.49 (1H, dd, J = 7.5, 1.5 Hz) in this order] and an olefinic proton signal at δ 7.10 (1H, s) were observed other than two monosaccharides in the ^1H NMR spectrum. All proton signals were assigned by the aid of $^1H-^1H$ COSY and HOHAHA difference spectra. In the ROE spectra, irradiation at the olefinic proton signal at δ 7.10 enhanced the aromatic proton signal at δ 7.92, and irradiation at the anomeric proton signal at δ 5.10 enhanced the aromatic proton signal at δ 7.49. In the HMBC spectrum, long-range correlations were observed between a proton signal at δ 7.10 and carbon signals at δ 177.1, 123.1 (*W*-type long-range coupling[5]), 160.4, 120.6, 155.3, and an anomeric proton signal at δ 5.10 and carbon signal at δ 116.0, and aromatic proton signals at δ 7.73 and 8.06 (*W*-type long-range coupling) and a carbonyl carbon signal at δ 177.1 (Figure 2). Sugar sequence was decided by the ROE spectrum to be glucopyranosyl-(1→6)-glucopyranosyl. These data led us to assign the structure of dalmaisione D as **4**.

Dalmaisiose A (**5**) has a molecular formula of $C_{38}H_{46}O_{20}$ on the basis of FABMS $[M + Na]^+$ *m/z* 845. The UV and ^1H NMR spectra showed the presence of an acetyl, a cinnamoyl, and a *p*-coumaroyl residue. Hydrolysis with alkali and acid afforded acetic acid, *p*-coumaric acid, and cinnamic acid as ester moieties and D-glucose and D-fructose as sugar moieties.[3,6] All proton signals were assigned by the aid of $^1H-^1H$ COSY and HOHAHA difference spectra. In the HMBC spectrum, correlations were observed at the signals H_2-6 (δ 4.14, 4.09) of Glc1/acetyl carbonyl carbon (δ 172.7), H-4 (δ 4.85) of Glc1/carbonyl carbon at δ 167.5 which was assigned to the

Table 1. ^{1}H NMR and ^{13}C NMR Data of Compound **1**−**3** at 35 °C[d]

	1[a]		**2**[b]		**3**[b]	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
aglycon moiety						
2		164.8[G]		166.6[G]		166.9[G]
3		104.7		105.4		105.7
4		172.5[A]		174.9[A]		175.3[A]
5	8.12 (dd, 7.5, 1.5)[A]	125.5	8.15 (dd, 8, 2)[A]	127.1	7.91 (dd, 8, 1.5)[A]	120.3
6	7.58 (td, 7.5, 1.5)[B]	126.5	7.52 (td, 8, 2)[B]	127.7	7.49 (t, 8)[B]	127.6
7	7.90 (td, 7.5, 1.5)[C]	135.0	7.83 (td, 8, 2)[C]	136.4[A]	7.70 (dd, 8, 1.5)[C,#]	123.8
8	7.86 (dd, 7.5, 1.5)[D]	118.4	7.65 (dd, 8, 2)[D]	119.3		147.3[B,C,H]
9		154.1[A,C]		155.9[A]		147.2[C]
10		124.0[B,D]		125.2[B,D]		126.5[B]
11		154.9		158.4		158.6
1′		143.6[E,G]		145.4[E,G]		155.6[D,F,G]
2′		143.8[F,H]		145.9[F,H]	7.43 (dd, 8, 1.5)[D]	118.1
3′	7.66 (dd, 7.5, 1.5)[E,†]	120.1	7.79 (dd, 8, 2)[E,#]	124.4	7.84 (td, 8, 1.5)[E]	137.1
4′	7.46 (t 7.5)[F]	124.5	7.31 (t, 8)[F]	126.3	7.55 (td, 8, 1.5)[F]	126.7
5′	7.92 (dd, 7.5, 1.5)[G]	116.5	7.70 (dd, 8, 2)[G]	118.3	8.45 (dd, 8, 1.5)[G]	126.4
6′		114.2[F]		115.2[F]		114.8[D,F,G]
sugar moiety						
Glc-1	5.45 (d, 7.5)[H,#]	97.3	5.18 (d, 7.5)[H,#]	101.2	5.47 (d, 7.5)[H,#]	101.4
2	3.68 (dd, 8.5, 7.5)*	76.2[I]	3.85 (dd, 9, 7.5)*	77.3[L]	3.86 (dd, 9.5, 7.5)*	80.8[I]
3	3.54 (dd, 8.5, 8.5)	77.6	3.71 (dd, 9, 9)	79.7	3.69 (dd, 9.5, 9.5)	78.6
4	3.27 (dd, 8.5, 8.5)	69.6	3.35 (dd, 9, 9)	72.4	3.51 (dd, 9.5, 9.5)	71.4
5	3.42 (m)	77.0	3.95 (m)	77.1	(3.46 (m)	78.3
6	3.47[c]	60.4	3.90 (br d, 12)[I]	71.6	3.69 (dd, 12.5, 5)	62.4
	3.66[c]		4.08 (br d, 12)[I,§]		3.83 (dd, 12.5, 2.5)	
Glc (terminal)-1			4.43 (d, 7.5)[§]	105.9[I]		
2			3.28[c]	75.5		
3			3.40 (dd, 9, 9)	77.9		
4			3.52 (dd, 9, 9)	71.2		
5			3.45 (m)	75.5		
6			4.15 (dd, 12.5, 3.5)[J]	63.0		
			4.78[c,K]			
Rha-1	5.24 (d, 1)[I,*]	100.1	5.56 (d, 2)[L,*]	101.2	5.38 (d, 2)[I,*]	103.0
2	3.73 (dd, 3, 1)	70.4	3.99 (dd, 3.5, 2)	72.3	4.04 (dd, 3, 2)	72.2
3	3.34 (dd, 9, 3)	70.4	3.85 (dd, 10, 3.5)	72.4	3.64 (dd, 10, 3)	72.2
4	3.15 (dd, 9, 9)	72.0	3.42 (dd, 10, 10)	74.4	3.26 (dd, 10, 10)	73.9
5	3.73 (m)	68.5	4.20 (m)	70.3	3.78 (m)	70.2
6	1.14 (d, 6)	18.0	1.34 (d, 6)	18.5	0.92 (d, 6)	17.9
acid						
(at C-6 of Glc2) α				168.5[J,K,N]		
β			6.02 (d, 16)[M,†]	115.6		
γ			7.20 (d, 16)[N,†]	146.5[O]		
1				126.3[M]		
2,6			6.56 (s)[O,†,‡]	106.5		
3,5				149.0[P]		
4				139.4[O]		
OMe			3.76 (s)[P,‡]	56.9		

[a] In DMSO-d_6. [b] In CD_3OD. [c] Overlapped with other signals. [d] Assigned with the aid of HOHAHA difference, ^{1}H−^{1}H COSY, HMQC, and HMBC spectra. ROEs were observed between protons that have the same (#,*,§,†,‡,¶) in each column. Long-range correlations were observed between protons and carbons that have the same letter (A,B,...,P) in the same compounds.

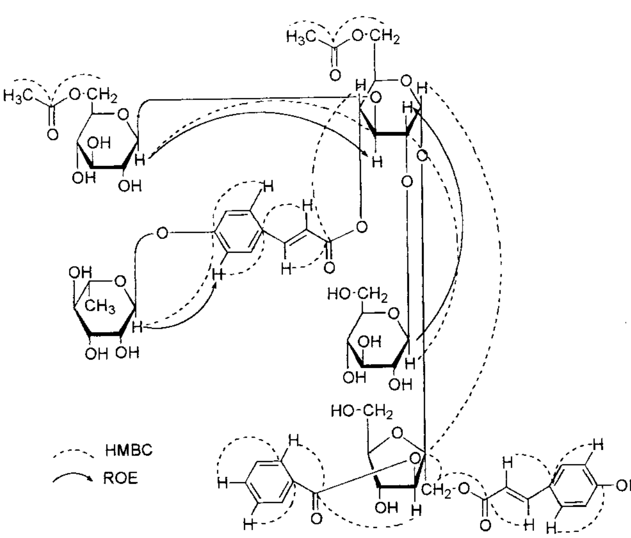


Figure 1. ^{1}H−^{13}C long-range correlations and ROEs of **7**.

α-carbon of a *p*-coumaroyl residue by HMBC correlation with sequence of the aromatic proton, H-3 (*δ* 5.77) of Fru/

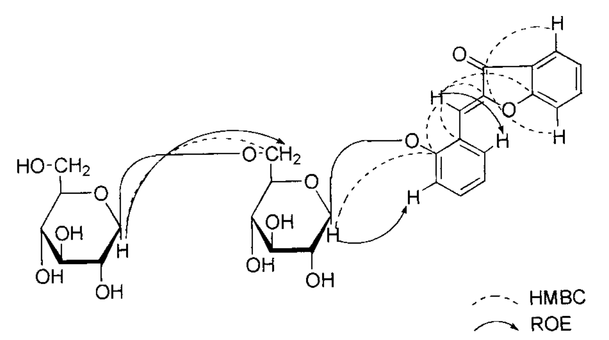


Figure 2. ^{1}H−^{13}C long-range correlations and ROEs of **4**.

carbonyl carbon at *δ* 167.8 which was assigned to the α-carbon of a cinnamoyl residue, and H-1 (*δ* 5.42) of Glc1/anomeric carbon (*δ* 107.2) of Fru and H-1 (*δ* 4.43) of Glc2/C-4 (*δ* 84.4) of Fru. Accordingly, **5** was confirmed to be *β*-D-glucopyranosyl-(1→4)−(3-*O*-cinnamoyl)-*β*-D-fructofuranosyl-(2→1)-(6-*O*-acetyl-4-*O*-*p*-coumaroyl)-α-D-glucopyranoside.

The NMR spectra of dalmaisiose B (**7**) were similar to those of reiniose G (**6**)[2] except for the presence of a rhamnosyl residue. After assignment of all proton signals

Table 2. ^{1}H NMR Data of Compounds **7**−**11** in CD_3OD at 35 °C[b]

		7	**8**	**9**	**10**	**11**
sugar moiety						
	Glc1-1	5.85 (d, 3)[A]	5.86 (d, 3.5)[A]	5.86 (d, 3.5)[A]	5.86 (d, 3.5)[A]	5.86 (d, 5)[A]
	-2	3.81 (dd, 8.5, 3)[#]	3.82 (dd, 10, 3.5)[#]	3.81 (dd, 10, 3.5)[#]	3.81 (dd, 9, 3.5)	3.81 (dd, 10, 5)[#]
	-3	3.95 (dd, 8.5, 8.5)*	3.97 (dd, 10, 10)*	4.03 (dd, 10, 10)*	4.03 (dd, 9, 9)	4.03 (dd, 10, 10)*
	-4	5.01 (dd, 10, 8.5)[B]	5.02 (dd, 10, 9)[B]	5.00 (dd, 10, 8.5)[B]	5.00 (dd, 9, 9)[B]	5.00 (dd, 10, 10)[B]
	-5	4.39 (m)	4.39 (m)	4.39 (m)	4.39 (m)	4.39 (m)
	-6	4.14 (dd, 12, 5.5)[C]	4.14 (dd, 12.5, 5.5)[C]	4.14 (dd, 12.5, 5)[C]	4.14 (dd, 12.5, 5.5)[C]	4.14 (dd, 12.5, 5)[C]
		4.20[a]	4.20 (dd, 12.5, 3.5)	4.20 (dd, 12.5, 3.5)[C]	4.21 (dd, 12.5, 3)	4.20[a]
	Glc2-1	4.60 (d, 7.5)[D,#]	4.60 (d, 7.5)[D,#]	4.59 (d, 7.5)[D,#]	4.59 (d, 7.5)[D]	4.59 (d, 7.5)[D,#]
	-2	3.32[a]	3.32[a]	3.31[a]	3.32[a]	3.32[a]
	-3	3.32[a]	3.32[a]	3.31[a]	3.32[a]	3.32[a]
	-4	3.32[a]	3.32[a]	3.31[a]	3.32[a]	3.32[a]
	-5	3.32[a]	3.32[a]	3.31[a]	3.31[a]	3.32[a]
	-6	3.71 (m)	3.72 (dd, 12.5, 5.5)	3.71 (d, 12)	3.71 (d, 12)	3.72[a]
		3.94[a]	3.95[a]	3.93 (d, 12)	3.93[a]	3.93 (d, 11)
	Glc3-1	4.49 (d, 8)[E,*]	4.50 (d, 7.5)[E,*]	4.46 (d, 7.5)[E,*]	4.46 (d, 7.5)[E]	4.46 (d, 7.5)[E,*]
	-2	2.99 (dd, 9, 8)	3.00 (dd, 8.5, 7.5)	3.01 (dd, 8.5, 7.5)	3.01 (dd, 8.5, 7.5)	3.01 (dd, 8.5, 7.5)
	-3	3.17 (dd, 9, 9)	3.18 (dd, 8.5, 8.5)	3.20 (dd, 8.5, 8.5)	3.20 (dd, 8.5, 8.5)	3.20 (dd, 8.5, 8.5)
	-4	3.18[a]	3.21 (dd, 8.5, 8.5)	3.17 (dd, 8.5, 8.5)	3.15 (dd, 8.5, 8.5)	3.16 (dd, 8.5, 8.5)
	-5	3.08 (m)	3.10 (m)	3.02[a]	3.03 (m)	3.02[a]
	-6	3.95[a,F]	3.98 (dd, 12.5, 5.5)[F]	3.43 (dd, 12, 5)	3.44 (dd, 12, 5)	3.43 (dd, 12.5, 5)
		4.03[a]	4.07 (dd, 12.5, 3.5)	3.58 (dd, 12, 4)	3.61 (dd, 12, 3)	3.58 (dd, 12.5, 2.5)
	Fru-1	4.20 (d, 12)[G]	4.21 (d, 12.5)[G]	4.20 (d, 12.5)[F]	4.19 (d, 12.5)[F]	4.20 (d, 12)[F]
		4.70 (d, 12)[G]	4.72 (d, 12.5)[G]	4.71 (d, 12.5)[F]	4.70 (d, 12.5)[F]	4.70[a,F]
	-3	5.73 (d, 8)[H]	5.73 (d, 8)[H]	5.74 (d, 8)[G]	5.74 (d, 8)[G]	5.74 (d, 8)[G]
	-4	4.43 (dd, 8, 8)	4.43 (dd, 8, 8)	4.43 (dd, 8, 8)	4.43 (dd, 8, 8)	4.44 (dd, 8, 8)
	-5	4.07 (m)	4.07[a]	4.07 (m)	4.07 (m)	4.08 (m)
	-6	3.86[a]	3.86[a]	3.86[a]	3.86[a]	3.87[a]
		3.86[a]	3.86[a]	3.86[a]	3.86[a]	3.87[a]
	Rha-1	5.53 (d, 2)[I,§]	5.48 (d, 2)[I,§]	5.52 (d, 2)[H,§]	5.46 (d, 2)[H,§]	5.52 (d, 2)[H,§]
	-2	4.02 (dd, 3, 2)	4.09 (dd, 3, 2)	4.02 (dd, 3, 2)	4.08 (dd, 3, 2)	4.02 (dd, 3, 2)
	-3	3.85 (dd, 9, 3)	3.91[a]	3.85 (dd, 9, 3)	3.90 (dd, 9, 3)	3.85 (dd, 9, 3)
	-4	3.48 (dd, 9, 9)	3.47 (dd, 9, 9)	3.48 (dd, 9, 9)	3.47 (dd, 9, 9)	3.48 (dd, 9, 9)
	−5	3.62 (m)	3.75 (m)	3.63 (m)	3.75 (m)	3.63 (m)
	−6	1.23 (d, 6)	1.24 (d, 6)	1.24 (d, 6)	1.24 (d, 6)	1.24 (d, 6)
ester moiety						
(at C-6 of Glc1)	Ac	2.06 (s)[J]	2.06 (s)[J]	2.07 (s)[I]	2.07 (s)[I]	2.07 (s)[I]
(at C-6 of Glc3)	Ac	1.59 (s)[K]	1.58 (s)[K]			
(at C-4 of Glc1)	β	6.31 (d, 16)[L]	6.34 (d, 16)[L]	6.41 (d, 16)[J]	6.44 (d, 16)[J]	6.41 (d, 16)[J]
	γ	7.59 (d, 16)[M]	7.59 (d, 16)[M]	7.62 (d, 16)[K]	7.61 (d, 16)[K]	7.62 (d, 16)[K]
	2	7.56 (d, 8)[N]	7.27 (d, 2)[N,†]	7.60 (d, 8)[L]	7.31 (d, 1.5)[L,†]	7.60 (d, 8)[L]
	3	7.15 (d, 8)[O]		7.15 (d, 8)[M,§]		7.15 (d, 8)[M,§]
	5	7.15 (d, 8)[O,§]	7.19 (d, 8)[O,§]	7.15 (d, 8)[M,§]	7.19[a,M]	7.15 (d, 8)[M,§]
	6	7.56 (d, 8)[N]	7.13 (dd, 8, 2)[P]	7.60 (d, 8)[L]	7.19[a,N,§]	7.60 (d, 8)[L]
	OMe		3.93 (s)[Q,†]		3.93 (s)[O,†]	
(at C-6 of Glc3)	β					
	γ					
	2					
	3					
	5					
	6					
	OMe					
(at C-1 of Fru)	β	6.37 (d, 16)[P]	6.40 (d, 16)[R]	6.36 (d, 16)[N]	6.36 (d, 16)[P]	6.41 (d, 16)[N]
	γ	7.68 (d, 16)[Q]	7.48 (d, 16)[S]	7.68 (d, 16)[O]	7.68 (d, 16)[Q]	7.68 (d, 16)[O]
	2	7.43 (d, 8)[R]	7.20 (d, 2)[T,‡]	7.43 (d, 8)[P]	7.43 (d, 8)[R]	7.20 (d, 2)[P,†]
	3	6.81 (d, 8)[S]		6.81 (d, 8)[Q]	6.81 (d, 8)[S]	
	5	6.81 (d, 8)[S]	6.81 (d, 8)[U]	6.81 (d, 8)	6.81 (d, 8)	6.82 (d, 8)[Q]
	6	7.43 (d, 8)[R]	7.02 (dd, 8, 2)[V]	7.43 (d, 8)	7.43 (d, 8)	7.04 (dd, 8, 2)[R]
	OMe		3.91 (s)[W,‡]			3.91 (s)[S,†]
(at C-3 of Fru)	2, 6	8.18 (dd, 7.5, 1)[T]	8.18 (dd, 7.5, 1)[X]	8.16 (dd, 8, 2)[R]	8.16 (dd, 7.5, 1)[T]	8.16 (dd, 7.5, 1)[T]
	3, 5	7.59 (t, 7.5)[U]	7.59 (t, 7.5)[Y]	7.58 (t, 8)[S]	7.58 (t, 7.5)[U]	7.58 (t, 7.5)[U]
	4	7.71 (tt, 7.5, 1)	7.61 (t, 7.5)	7.65 (tt, 8, 2)	7.61 (tt, 7.5, 1)	7.63 (tt, 7.5, 1)

[a] Overlapped with other signals ROEs were observed between protons that have the same letter (#,*,§,†,‡,¶) in each column. Long-range correlations were observed between protons and carbons that have the same letter (A,B,...,γ,δ) in the same compounds in Table 5. [b] Assigned with the aid of HOHAHA difference, ^{1}H−^{1}H COSY, HMQC, and HMBC spectra.

by ^{1}H−^{1}H COSY and HOHAHA difference spectra, irradiation of a rhamnosyl anomeric proton signal at δ 5.53 (1H, d, J = 2 Hz) enhanced the signal area of an aromatic proton signal at δ 7.15 (2H, d, J = 8 Hz), which was assigned to H-3 and H-5 of the *p*-coumaroyl residue attached to C-4 of α-D-glucose (Figure 1). Hydrolysis with alkali and acid gave acetic acid, *p*-coumaric acid, and benzoic acid as ester moieties and D-glucose, D-fructose, and L-rhamnose as sugar moieties.

The NMR spectra of dalmaisioses C−G (**8**−**12**) were similar to those of **7**, showing acetyl(s), a benzoyl, and two oxycinnamoyl residues as ester moieties and a rhamnosyl, a fructosyl, and three glucosyl residues as sugar moieties. The binding sites of these residues were decided with the aid of ROE and HMBC after assignment of all proton signals by ^{1}H−^{1}H COSY and HOHAHA difference spectra. The structures of dalmaisioses C−G were determined to be **8**−**12**, respectively.

Table 3. [1]H NMR Data of Compounds **12**−**16** in CD_3OD at 35 °C[b]

		12	**13**	**14**	**15**	**16**
sugar moiety						
	Glc1-1	5.86 (d, 3.5)[A]	5.84 (d, 3.5)[A]	5.84 (d, 3.5)[A]	5.82 (d, 3.5)[A]	5.84 (d, 3)[A]
	-2	3.82 (dd, 9, 3.5)[#]	3.82 (dd, 10, 3.5)[#]	3.82 (dd, 10, 3.5)[#]	3.79 (dd, 9, 3.5)[#]	3.83 (dd, 9, 3)
	-3	4.03 (dd, 9, 9)*	3.99 (dd, 10, 10)*	3.97 (dd, 10, 10)*	3.99 (dd, 9, 9)*	3.97 (dd, 9, 9)
	-4	5.00 (dd, 10.5, 9)[B]	5.02 (dd, 10, 9)[B]	5.03 (dd, 10, 10)[B]	5.03 (dd, 9, 9)[B]	5.03 (dd, 9, 9)[B]
	-5	4.39 (m)	4.38 (m)	4.38 (m)	4.20[a]	4.38 (m)
	-6	4.14 (dd, 12.5, 5.5)[C]	4.13[a,C]	4.14[a,C]	3.54 (dd, 12.5, 5)	4.14[a,C]
		4.21 (dd, 12.5, 3)[C]	4.13[a]	4.14[a]	3.66 (dd, 12.5, 3.5)	4.14[a]
	Glc2-1	4.60 (d, 7.5)[D,#]	4.62 (d, 7.5)[D,#]	4.63 (d, 8)[D,#]	4.62 (d, 7.5)[C,#]	4.63 (d, 7.5)[D]
	-2	3.32[a]	3.35[a]	3.34[a]	3.33[a]	3.34 (dd, 10, 7.5)
	-3	3.32[a]	3.35[a]	3.34[a]	3.33[a]	3.31[a]
	-4	3.32[a]	3.35[a]	3.34[a]	3.33[a]	3.31[a]
	-5	3.32[a]	3.35[a]	3.34[a]	3.33[a]	3.31[a]
	-6	3.72 (dd, 12, 3.5)	3.72[a]	3.72[a]	3.73 (dd, 12.5, 5.5)	3.72 (dd, 12, 3)
		3.93[a]	3.94 (dd, 12, 2)	3.94 (br d, 12.5)	3.93 (dd, 12.5, 5)	3.94 (br d, 12)
	Glc3-1	4.47 (d, 8)[E,*]	4.52 (d, 8)[E,*]	4.52 (d, 8)[E,*]	4.50 (d, 8)[D,*]	4.53 (d, 8)[E]
	-2	3.01 (dd, 8.5, 8)	3.06 (dd, 9, 8)	3.06 (dd, 9, 8)	3.06 (dd, 9, 8)	3.06 (dd, 9, 8)
	-3	3.20 (dd, 8.5, 8.5)	3.21 (dd, 9, 9)	3.21 (dd, 9, 9)	3.20 (dd, 9, 9)	3.21 (dd, 9, 9)
	-4	3.15 (dd, 8.5, 8.5)	3.30 (dd, 9, 9)	3.34 (dd, 9, 9)	3.33[a]	3.33 (dd, 9, 9)
	-5	3.05 (m)	3.15 (m)	3.12 (m)	3.10 (m)	3.13 (m)
	−-6	3.44 (dd, 12, 5)	4.09 (dd, 12.5, 3)	4.07[a,F]	4.08 (dd, 12.5, 2.5)	3.04 (dd, 12, 2.5)
		3.61 (dd, 12, 3)	4.18 (dd, 12.5, 4)[F]	4.23[a,F]	4.19 (dd, 12.5, 3.5)[E]	4.23 (dd, 12, 3.5)[F]
	Fru-1	4.19 (d, 12)[F]	4.22 (d, 12)[G]	4.22 (d, 12)[G]	4.22 (d, 12)[F]	4.22 (d, 2.5)[G]
		4.72 (d, 12)[F]	4.71 (d, 12)[G]	4.70 (d, 12)[G]	4.72[a]	4.72[a,G]
	-3	5.u75 (d, 8)[G]	5.73 (d, 8)[H]	5.73 (d, 8)[H]	5.72 (d, 8)[G]	5.74 (d, 8)[H]
	-4	4.44 (dd, 8, 8)	4.43 (dd, 8, 8)	4.44 (dd, 8, 8)	4.50 (dd, 8, 8)	4.43 (dd, 8, 8)
	-5	4.08[a]	4.06 (m)	4.06[a]	4.03[a]	4.07[a]
	-6	3.86[a]	3.86[a]	3.86[a]	3.86[a]	3.85[a]
		3.86[a]	3.86[a]	3.86[a]	3.86[a]	3.87[a]
	Rha-1	5.46 (d, 2)[H,§]		5.42 (d, 2)[I,§]		5.42 (d, 2)[I,§]
	-2	4.09 (dd, 3, 2)		4.07 (dd, 3, 2)		4.07 (dd, 3.5, 2)
	-3	3.91[a]		3.90 (dd, 9, 3)		3.90 (dd, 9, 3.5)
	-4	3.48 (dd, 9, 9)		3.48 (dd, 9, 9)		3.48 (dd, 9, 9)
	-5	3.76 (m)		3.79 (m)		3.78 (m)
	-6	1.24 (d, 6.5)		1.27 (d, 6)		1.26 (d, 6)
ester moiety						
(at C-6 of Glc1)	Ac	2.07 (s)[I]	2.04 (s)[I]	2.04 (s)[J]		2.04 (s)[J]
(at C-6 or Glc3)	Ac					
(at C-4 of Glc1)	*β*	6.44 (d, 16)[J]	6.18 (d, 15.5)[J]	6.28 (d, 16)[K]	6.21 (d, 16)[H]	6.28 (d, 16)[K]
	γ	7.16 (d, 16)[K]	7.50 (d, 15.5)[K]	7.50 (d, 16)[L]	7.49 (d, 16)[I]	7.50 (d, 16)[L]
	2	7.30 (d, 1)[L,†]	7.31 (d, 8)[L]	7.04 (d, 2)[M,†]	7.00 (d, 2)[J]	7.04 (d, 2)[M,†]
	3		6.71 (d, 8)[M]			
	5	7.19[a,M,§]	6.71 (d, 8)	7.03 (d, 8)[N,§]	6.69 (d, 8)[K,§]	7.03 (d, 8)[N,§]
	6	7.19[a,N]	7.31 (d, 8)	6.97 (dd, 8, 2)[O]	6.90 (dd, 8, 2)[L]	6.97 (dd, 8, 2)[O]
	OMe	3.92 (s)[O,†]		3.76 (s)[P,†]	3.81 (s)[M,§]	3.76 (s)[P,†]
(at C-6 of Glc3)	*β*		5.98 (d, 15.5)[N]	5.89 (d, 16)[Q]	5.92 (d, 16)[N]	5.89 (d, 16)[Q]
	γ		7.35 (d, 15.5)[O]	7.26 (d, 16)[R]	7.27 (d, 16)[O]	7.26 (d, 16)[R]
	2		7.24 (d, 8)[P]	7.20 (d, 8)[S]	7.20 (d, 8)[P]	7.21 (d, 8)[S]
	3		6.77 (d, 8)[Q]	6.76 (d, 8)[T]	6.76 (d, 8)[Q]	6.76 (d, 8)
	5		6.77 (d, 8)	6.76 (d, 8)	6.76 (d, 8)	6.76 (d, 8)
	6		7.24 (d, 8)	7.20 (d, 8)	7.20 (d, 8)	7.21 (d, 8)
OMe						
(at C-1 of Fru)	*β*	6.41 (d, 16)[P]	6.36 (d, 15.5)[R]	6.36 (d, 16)[U]	6.36 (d, 16)[R]	6.41 (d, 16)[U]
	γ	7.68 (d, 16)[Q]	7.68 (d, 15.5)[S]	7.78 (d, 16)[V]	7.68 (d, 16)[S]	7.68 (d, 16)[V]
	2	7.20 (d, 2)[R,‡]	7.42 (d, 8)[T]	7.42 (d, 8)[W]	7.42 (d, 8)[T]	7.20 (d, 2)[W,‡]
	3		6.81 (d, 8)[U]	6.81 (d, 8)[X]	6.81 (d, 8)[U]	
	5	6.81 (d, 8)[S]	6.81 (d, 8)	6.81 (d, 8)	6.81 (d, 8)	6.82 (d, 8)[X]
	6	7.04 (dd, 8, 2)[T]	7.42 (d, 8)	7.42 (d, 8)	7.42 (d, 8)	7.02 (dd, 8, 2)[Y]
	OMe	3.90 (s)[U,‡]				3.91 (s)[Z,‡]
(at C-3 of Fru)	2, 6	8.16 (dd, 8, 2)[V]	8.17 (dd, 7.5, 1)[V]	8.18 (dd, 7.5, 1)[Y]	8.20 (dd, 8, 1)[V]	8.18 (dd, 7.5, 1)[α]
	3, 5	7.58[a,W]	7.57 (t, 7.5)[W]	7.60 (t, 7.5)[Z]	7.60 (t, 8)[W]	7.60 (t, 7.5)[β]
	4	7.60[a]	7.68 (tt, 7.5, 1)	7.71 (tt, 7.5, 1)	7.70 (tt, 8, 1)	7.71 (tt, 7.5, 1)[γ]

[a] Overlapped with other signals ROEs were observed between protons that have the same letter ([#,*,§,†,‡,¶]) in each column. Long-range correlations were observed between protons and carbons that have the same letter ([A,B,...,γ,δ]) in the same compounds in Table 5. [b] Assigned with the aid of HOHAHA difference, $^1H-^1H$ COSY, HMQC, and HMBC spectra.

Dalmaisioses H−K (**13**−**16**) are tetrasaccharides having the same sugar sequence as that of reiniose G (**6**) and with a *p*-coumaroyl residue at C-6 of Glc3. Dalmaisioses L−P (**17**−**21**) are also tetrasaccharides, but these have a feruloyl residue at C-6 of Glc3. In these compounds, the positions of each residue were confirmed by the same method as for previously mentioned compounds.

Tetrasaccharide multiesters having a sugar sequence of *β*-D-fructofuranosyl-(2→1)-[*β*-D-glucopyranosyl-(1→2)]-[*β*-D-glucopyranosyl-(1→3)]-α-D-glucopyranoside are most widely distributed in *Polygala* species. The sugar sequence of *β*-D-glucopyranosyl-(1→4)-*β*-D-fructofuranosyl-(2→1)-α-D-glucopyranoside in dalmaisiose A (**5**) is the first example in *Polygala* species.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter at

Table 4. ^{1}H NMR Data of Compounds **17**−**21** in CD_3OD at 35 °C[b]

		17	**18**	**19**	**20**	**21**
sugar moiety						
	Glc1-1	5.82 (d, 3)[A]	5.84 (d, 3.5)[A]	5.85 (d, 3)[A]	5.85 (d, 3.5)[A]	5.83 (d, 3.5)[A]
	-2	3.79[a,#]	3.82 (dd, 10, 3.5)[#]	3.82 (dd, 9, 3)[#]	3.82 (dd, 10, 3.5)[#]	3.79 (dd, 9, 3.5)[#]
	-3	3.98 (dd, 9, 9)*	3.98 (dd, 10, 10)*	3.97 (dd, 9, 9)*	3.97 (dd, 10, 10)*	3.98 (dd, 9, 9)*
	-4	5.02 (dd, 10.5, 9)[B]	5.02 (dd, 10, 8.5)[B]	5.03 (dd, 10.5, 9)[B]	5.03 (dd, 10, 9)[B]	5.04 (dd, 9, 9)[B]
	-5	4.23[a]	4.38 (m)	4.38 (m)	4.38 (m)	4.22 (m)
	-6	3.54 (dd, 12.5, 5)	4.13[a,C]	4.14[a,C]	4.14[a,C]	3.54 (dd, 12.5, 5.5)
		3.66 (dd, 12.5, 2.5)	4.13[a]	4.14[a]	4.14[a]	3.67 (dd, 12.5, 3.5)
	Glc2-1	4.62 (d, 7.5)[C,#]	4.62 (d, 8)[D,#]	4.63 (d, 7.5)[D,#]	4.63 (d, 7.5)[D,#]	4.63 (d, 7.5)[C,#]
	-2	3.33[a]	3.32[a]	3.35 (dd, 7.5, 7.5)	3.37[a]	3.33[a]
	-3	3.33[a]	3.32[a]	3.33[a]	3.34[a]	3.33[a]
	-4	3.33[a]	3.32[a]	3.33[a]	3.34[a]	3.33[a]
	-5	3.33[a]	3.32[a]	3.33[a]	3.34[a]	3.33[a]
	-6	3.73 (dd, 12, 6)	3.72 (br d, 12.5)	3.72[a]	3.73[a]	3.73[a]
		3.93 (dd, 12, 2)	3.93 (br d, 12.5)	3.94 (dd, 11, 2.5)	3.94 (dd, 11, 2.5)	3.94[a]
	Glc3-1	4.51 (d, 7.5)[D,*]	4.53 (d, 8)[E,*]	4.53 (d, 7.5)[E,*]	4.53 (d, 7.5)[E,*]	4.51 (d, 7.5)[D,*]
	-2	3.06 (dd, 9, 7.5)	3.06 (dd, 9, 8)	3.06 (dd, 9, 7.5)	3.07 (dd, 9, 7.5)	3.06 (dd, 9, 7.5)
	-3	3.20 (dd, 9, 9)	3.21 (dd, 9, 9)	3.22 (dd, 9, 9)	3.22 (dd, 9, 9)	3.20 (dd, 9, 9)
	-4	3.35 (dd, 9, 9)	3.35 (dd, 9, 9)	3.36 (dd, 9, 9)	3.35 (dd, 9, 9)	3.35 (dd, 9, 9)
	-5	3.10 (m)	3.12 (m)	3.13 (m)	3.14 (m)	3.11 (m)
	-6	4.07 (dd, 12, 3)	4.08[a]	4.03 (dd, 12, 2)[F]	4.03 (dd, 12, 2)	3.84[a]
		4.20 (dd, 12, 3)	4.21 (dd, 12, 3.5)[F]	4.25 (dd, 12, 3.5)	4.25 (dd, 12, 3)[F]	4.03[a,E]
	Fru-1	4.23 (d, 12)[F]	4.21 (d, 12)[G]	4.22 (d, 12)[G]	4.22 (d, 12)[G]	4.32 (d, 12)[F]
		4.79 (d, 12)[F]	4.72 (d, 12)[G]	4.71 (d, 12)[G]	4.72 (d, 12)[G]	4.73 (d, 12)[F]
	-3	5.72 (d, 8)[G]	5.73 (d, 8)[H]	5.73 (d, 8)[H]	5.74 (d, 8)[H]	5.72 (d, 8)[G]
	-4	4.50 (dd, 8, 8)	4.42 (dd, 8, 8)	4.43 (dd, 8, 8)	4.44 (dd, 8, 8)	4.51 (dd, 8, 8)
	-5	4.03 (m)	4.07[a]	4.08[a]	4.09 (m)	4.04[a]
	-6	3.85[a]	3.85[a]	3.86[a]	3.85[a]	3.86[a]
		3.85[a]	3.85[a]	3.86[a]	3.85[a]	3.86[a]
	Rha-1			5.42 (d, 2)[I,§]	5.42 (d, 2)[I,§]	5.42 (d, 2)[H,§]
	-2			4.07 (dd, 3, 2)	4.06 (dd, 3.5, 2)	4.06 (dd, 3, 2)
	-3			3.89 (dd, 9, 3)	3.89 (dd, 9, 3.5)	3.91[a]
	-4			3.48 (dd, 9, 9)	3.48 (dd, 9, 9)	3.47 (dd, 9, 9)
	-5			3.77 (m)	3.77 (m)	3.76[a]
	-6			1.25 (d, 6)	1.26 (d, 6)	1.25 (d, 6)
ester moiety						
(at C-6 of Glc1)	Ac		2.04 (s)[I]	2.04 (s)[J]	2.05 (s)[J]	
(at C-6 of Glc3)	Ac					
(at C-4 of Glc1)	β	6.20 (d, 16)[H]	6.19 (d, 16)[J]	6.28 (d, 16)[K]	6.28 (d, 16)[K]	6.28 (d, 16)[I]
	γ	7.48 (d, 16)[I]	7.48 (d, 16)[K]	7.50 (d, 16)[L]	7.50 (d, 16)[L]	7.50 (d, 16)[J]
	2	6.97 (d, 2)[J,§]	6.98 (d, 2)[L,§]	7.01 (d, 2)[M,†]	7.01 (d, 2)[M,†]	7.00 (d, 2)[K,†]
	3					
	5	6.67 (d, 8)[K]	6.68 (d, 8)[M]	7.03 (d, 8)[N,§]	7.03 (d, 8)[N,§]	7.03 (d, 8)[L,§]
	6	6.84 (dd, 8, 2)[L]	6.89 (dd, 8, 2)[N]	6.97 (dd, 8, 2)[O]	6.97 (dd, 8, 2)[O]	6.97 (dd, 8, 2)[M]
	OMe	3.88 (s)[M,§]	3.80 (s)[O,§]	3.72 (s)[P,†]	3.73 (s)[P,†]	3.72 (s)
(at C-6 of Glc)	β	5.95 (d, 16)[N]	5.96 (d, 16)[P]	5.93 (d, 16)[Q]	5.94 (d, 16)[Q]	5.93 (d, 16)[O]
	γ	7.23 (d, 16)[O]	7.24 (d, 16)[Q]	7.23 (d, 16)[R]	7.23 (d, 16)[R]	7.23 (d, 16)[P]
	2	6.90 (d, 2)[P,†]	6.90 (d, 2)[R,†]	6.92 (d, 2)[S,‡]	6.92 (d, 2)[S,‡]	6.92 (d, 2)[Q,‡]
	3					
	5	6.77 (d, 8)[Q]	6.76 (d, 8)[S]	6.78 (d, 8)[T]	6.78 (d, 8)[T]	6.78 (d, 8)[R]
	6	6.88 (dd, 8, 2)[R]	6.84 (dd, 8, 2)[T]	6.85 (dd, 8, 2)[U]	6.85 (dd, 8, 2)[U]	6.86 (dd, 8, 2)[S]
	OMe	3.80 (s)[S,†]	3.87 (s)[U,†]	3.87 (s)[V,‡]	3.87 (s)[V,‡]	3.88 (s)[T,‡]
(at C-1 of Fru)	β	6.36 (d, 16)[T]	6.35 (d, 16)[V]	6.36 (d, 16)[W]	6.41 (d, 16)[W]	6.41 (d, 16)[U]
	γ	7.68 (d, 16)[U]	7.68 (d, 16)[W]	7.68 (d, 16)[X]	7.69 (d, 16)[X]	7.69 (d, 16)[V]
	2	7.42 (d, 8)[V]	7.42 (d, 8)[X]	7.42 (d, 8)[Y]	7.20 (d, 2)[Y,¶]	7.21 (d, 2)[W,¶]
	3	6.81 (d, 8)[W]	6.81 (d, 8)[Y]	6.81 (d, 8)[Z]		
	5	6.81 (d, 8)	6.81 (d, 8)	6.81 (d, 8)	6.82 (d, 8)[Z]	6.82 (d, 8)[X]
	6	7.42 (d, 8)	7.42 (d, 8)	7.42 (d, 8)	7.01 (dd, 8, 2)[α]	7.03 (dd, 8, 2)[Y]
	OMe				3.91 (s)[β,¶]	3.91 (s)[Z,¶]
(at C-3 of Fru)	2, 6	8.20 (dd, 8, 1)[X]	8.18 (dd, 7.5, 1)[Z]	8.18 (dd, 7.5, 1)[α]	8.18 (dd, 7.5, 1)[γ]	8.20 (dd, 8, 1)[α]
	3, 5	7.61 (t, 8)[Y]	7.60 (t, 7.5)[α]	7.60 (t, 7.5)[β]	7.60 (t, 7.5)[δ]	7.60 (t, 8)[β]
	4	7.71 (tt, 8, 1)	7.71 (tt, 7.5, 1)	7.71 (tt, 7.5, 1)	7.71 (tt, 7.5, 1)	7.71 (tt, 8, 1)

[a] Overlapped with other signals ROEs were observed between protons that have the same letter (#,*,§,†,‡,¶) in each column. Long-range correlations were observed between protons and carbons that have the same letter (A,B,...,γ,δ) in the same compounds in Table 5. [b] Assigned with the aid of HOHAHA difference, ^{1}H−^{1}H COSY, HMQC, and HMBC spectra.

23 °C. UV spectra were recorded on a Hitachi U-3410 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL α-400 FT-NMR spectrometer with TMS as an internal standard. Inverse-detected heteronuclear correlations were measured using HMQC (optimized for $^1J_{C-H}$ = 145 Hz) and HMBC (optimized for $^nJ_{C-H}$ = 8 Hz) pulse sequences with a pulse-field gradient. Positive-mode FABMS were recorded on a JEOL JMS-SX102 spectrometer, using a *m*-nitrobenzyl alcohol as matrix. GC was carried out with a HEWLETT PACKARD 5890 gas chromatograph. HPLC was performed using a JASCO System 800.

Plant Material. The seedling of *Polygala dalmaisiana* (*P. oppositifolia* × *P. myrtifolia*) was purchased from Sakata Seed (Yokohama, Japan) in April 1998 and grown in the botanical garden of the University of Shizuoka. The roots of *P. dalmaisiana* were harvested in November 2000.

Extraction and Isolation. The plant material (fresh roots, 1.7 kg) was extracted twice with hot MeOH. After evaporation

Table 5. ^{13}C NMR Data of Compounds **7**−**20** in CD_3OD at 35 °C[a]

		7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
sugar moiety																
	Glc1-1	93.0	93.0	93.0	92.9	93.0	92.9	93.1	93.1	93.3	93.1	93.3	93.0	93.0	93.1	93.3
	2	81.4[D]	81.4[D]	81.0[D]	81.1[D]	81.1[D]	81.1[D]	81.3[D]	81.3[D]	81.5[C]	81.3[D]	81.5[C]	81.4[D]	81.4[D]	81.4[D]	81.5[C]
	3	79.1[E]	79.0[E]	79.5[E]	79.5[E]	79.5[E]	79.5[E]	79.3[E]	79.1[E]	79.4[D]	79.1[E]	79.3[D]	79.0[E]	79.1[E]	79.1[E]	79.4[D]
	4	70.6	70.5	71.1	71.0	70.9	71.0	70.5	70.5	70.2	70.5	70.3	70.4	70.5	70.5	70.3
	5	69.7	69.7	69.6	69.6	69.6	69.6	69.7	69.7	72.4	69.7	72.4	69.7	69.7	69.7	72.3
	6	64.4	64.3	64.4	63.8	64.3	64.4	64.4	64.3	62.1	64.3	62.1	64.3	64.3	64.3	62.1
	Glc2-1	105.4	105.4	105.5	105.5	105.5	105.4	105.4	105.4	105.4	105.4	105.5	105.4	105.4	105.4	105.3
	2	75.3	75.3	75.3	75.3	75.3	75.3	75.3	75.3	75.3	75.3	75.3	75.3	75.3	75.3	75.3
	3	78.6	78.5	78.5	78.5	78.5	78.5	78.6	78.6	78.5	78.6	78.5	78.6	78.6	78.6	78.5
	4	71.7	71.7	71.8	71.7	71.8	71.7	71.7	71.7	71.7	71.7	71.7	71.7	71.7	71.7	71.7
	5	78.6	78.5	78.5	78.5	78.5	78.5	78.6	78.6	78.5	78.6	78.5	78.6	78.6	78.6	78.5
	6	63.1	63.1	63.1	63.0	63.1	63.1	63.1	63.1	63.1	63.1	63.1	62.9	63.1	63.1	63.2
	Glc3−1	104.5	104.4	104.7	104.6	104.7	104.6	104.6	104.5	104.5	104.5	104.5	104.5	104.5	104.5	104.5
	2	75.6	75.5	75.7	75.7	75.7	75.6	75.6	75.5	75.5	75.5	75.5	75.6	75.5	75.5	75.5
	3	77.9	78.0	77.9	78.0	77.9	77.9	78.0	78.1	78.0	78.1	78.1	78.1	78.1	78.1	78.1
	4	71.1	71.0	71.7	71.9	72.0	71.7	71.1	71.1	70.9	71.1	70.9	70.9	71.1	70.8	71.0
	5	74.8	74.8	77.2	77.3	77.2	77.3	75.0	74.9	74.9	74.9	74.9	74.9	74.9	74.9	74.9
	6	64.4	64.3	62.9	63.1	62.9	63.0	64.2	64.0	64.0	64.0	64.0	63.8	64.0	64.0	64.0
	Fru-1	66.0	65.9	65.8	65.7	65.8	65.8	65.9	65.9	65.9	65.9	66.0	66.0	66.0	65.9	66.0
	2	104.0[A,B]	104.0[A,G]	104.0[A,F]	104.0[A,F]	104.1[A,F]	104.0[A,F]	104.0[A,G]	104.0[A,G]	103.9[A,F]	104.0[A,G]	103.9[A,F]	104.0[A,G]	104.0[A,G]	104.0[A,G]	103.9[A,F]
	3	80.2	80.1	80.0	80.0	80.0	80.0	80.2	80.2	80.2	80.2	80.3	80.2	80.2	80.2	80.2
	4	74.0	74.0	74.0	74.0	74.0	74.0	74.1	74.1	73.7	74.1	73.7	74.1	74.1	74.1	73.8
	5	84.7	84.7	84.7	84.7	84.7	84.7	84.8	84.8	84.6	84.8	84.7	84.8	84.8	84.8	84.6
	6	63.8	63.8	63.8	63.8	63.8	63.8	63.9	63.9	63.2	63.9	63.2	63.1	63.8	63.8	63.2
	Rha-1	99.7	100.9	99.8	101.1	99.8	100.9		101.1		101.1			101.0	101.1	101.0
	2	71.9	72.0	72.0	72.0	71.7	72.0		72.0		72.0			72.0	72.0	72.0
	3	72.3	72.2	72.3	72.2	72.3	72.2		72.3		72.3			72.2	72.3	72.2
	4	73.8	73.8	73.8	73.8	73.8	73.8		73.9		73.9			73.8	73.8	73.8
	5	70.9	71.0	70.9	71.0	71.1	71.0		70.9		70.9			70.8	71.1	71.0
	6	18.0	18.0	18.1	18.0	18.1	18.0		18.0		18.1			18.0	18.0	18.0
ester moiety																
(at C-6 of Glc1)	Ac	172.5[C,J]	172.5[C,J]	172.5[C,I]	172.5[C,I]	172.5[C,I]	172.5[C,I]	172.5[C,I]	172.5[C,J]		172.5[C,J]		172.5[C,I]	172.5[C,J]	172.5[C,J]	
		20.5	20.8	20.8	20.8	20.8	20.8	20.7	20.7		20.7		20.7	20.7	20.7	
(at C-6 of Glc3)	Ac	172.6[F,K]	172.5[F,K]													
		20.8	20.5													
(at C-4 of Glc1)	α	167.6[B,M]	167.6[B,M]	167.8[B,K]	167.7[B,K]	167.8[B,K]	167.7[B,K]	168.1[B,K]	167.7[B,L]	168.2[B,I]	167.7[B,L]	168.2[B,I]	168.1[B,K]	167.7[B,L]	167.7[B,L]	167.8[B,J]
	β	116.9	117.2	117.1	117.6	117.1	115.2	114.9	116.9	115.1	116.9	115.1	114.9	116.9	116.9	117.1
	γ	146.1[N]	146.4[N,P]	146.3[L]	146.5[L,N]	146.3[L]	146.5[L,N]	147.0[L]	146.5[M,O]	147.0[J,L]	146.2[M,O]	147.0[J]	147.3[L,N]	146.5[M,O]	146.5[M,O]	146.4[K,M]
	1	129.7[L,O]	131.0[L,O]	129.8[J,M]	130.9[J,M]	129.8[J,M]	130.9[J,M]	127.0[J,M]	130.7[K,N]	127.5[H,K]	130.7[K,N]	127.5[H,K]	127.4[J,M]	130.7[K,N]	130.7[K,N]	130.7[I,L]
	2	131.1	112.6	131.3	112.8	131.1	112.8	131.2	112.8	111.6	112.8	111.7	111.7	112.9	112.9	112.8
	3	118.0	152.2[O,Q]	117.9	152.1[M,O]	117.9	152.1[M,O]	116.9	152.0[N,P]	149.2[K,M]	152.1[N,P]	149.2[K,M]	149.2[M,O]	152.0[N,P]	152.0[N,P]	152.0[L,N]
	4	159.8[I,N]	150.8[I,N,P]	159.8[H,L]	149.3[H,L]	159.8[H,L]	159.8[H,L,N]	161.3[L]	149.2[I,M,O]	150.7[J,L]	149.2[I,M,O]	150.7[J,L]	150.7[L,N]	149.1[I,M,O]	149.1[I,M,O]	149.0[H,K,M]
	5	118.0	118.9	117.9	118.8	117.9	118.8	116.9	119.2	116.5	119.2	116.5	116.5	119.2	119.2	119.2
	6	131.1	123.6	131.3	123.4	131.1	123.4	131.2	123.2	124.3	123.2	124.2	124.3	123.1	123.1	123.0
	OMe		56.6		56.7		56.6		56.3	56.2	56.3	56.2	56.2	56.2	56.3	56.2
(at C-6 of Glc3)	α							169.0[F,O]	168.8[F,R]	168.9[E,O]	168.8[F,R]	168.9[O]	168.9[F,Q]	168.8[F,R]	168.8[F,R]	168.7[E,P]
	β							114.8	114.8	114.8	115.2	115.1	115.0	115.1	115.1	115.2
	γ							146.5[P]	146.2[S]	146.3[P]	146.5[S]	146.5[P]	146.5[R,T]	146.4[S,U]	146.4[S,U]	146.3[Q,S]
	1							127.1[N,Q]	127.1[Q,T]	127.1[N,Q]	127.1[Q,T]	127.7[N,Q]	127.7[P,S]	127.7[Q,T]	127.7[Q,T]	127.7[O,R]
	2							131.2	131.1	131.1	131.1	111.7	111.7	111.8	111.8	111.8
	3							116.7	116.9	116.7	116.8	149.2[Q,S]	149.2[S,U]	149.2[T,V]	149.3[T,V]	149.2[R,T]
	4							161.2[P]	161.1[S]	161.1[P]	161.1[S]	150.5[P,R]	150.5[R,T]	150.5[S,U]	150.5[S,U]	150.5[Q,S]
	5							116.7	116.9	116.7	116.8	116.4	116.4	116.5	116.5	116.5
	6							131.2	131.1	131.1	131.1	124.0	124.0	124.0	124.0	124.0
	OMe											56.5	56.5	56.6	56.6	56.6

Table 5 (Continued)

		7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
(at C-1 of Fru)	α	$168.4^{G,Q}$	$168.4^{G,S}$	$168.4^{F,O}$	$168.4^{F,Q}$	$168.4^{F,O}$	$168.4^{F,Q}$	$168.4^{G,S}$	$168.4^{G,V}$	$168.5^{F,S}$	$168.4^{G,V}$	$168.5^{F,U}$	$168.4^{G,W}$	$168.4^{G,X}$	$168.4^{G,X}$	$168.5^{F,V}$
	β	114.9	115.2	114.9	114.9	115.2	115.2	114.9	114.9	114.9	114.8	114.9	114.9	114.9	115.2	115.2
	γ	147.0^{R}	$147.3^{T,V}$	147.0^{P}	147.1^{R}	$147.3^{P,R}$	$147.3^{R,T}$	147.0^{T}	147.0^{W}	147.0^{T}	$147.3^{W,Y}$	147.0^{V}	147.0^{X}	147.0^{Y}	$147.3^{Y,\alpha}$	$147.3^{W,Y}$
	1	$127.2^{P,S}$	$127.7^{R,U}$	$127.2^{N,Q}$	$127.2^{P,S}$	$127.8^{N,Q}$	$127.7^{P,S}$	$127.2^{R,U}$	$127.2^{U,X}$	$127.2^{R,U}$	$127.7^{U,X}$	$127.2^{T,W}$	$127.2^{V,Y}$	$127.2^{W,Z}$	$127.7^{W,Z}$	$127.7^{U,X}$
	2	131.1	111.8	131.1	131.3	111.8	111.8	131.3	131.1	131.2	111.8	131.2	131.2	131.1	111.8	111.8
	3	116.9	$149.5^{U,W}$	116.9	116.9	$149.5^{Q,W}$	$149.4^{S,U}$	116.9	116.8	116.9	$149.5^{X,Z}$	116.9	116.9	116.9	$149.5^{Z,\beta}$	$149.4^{X,Z}$
	4	161.4^{R}	$149.3^{T,V}$	161.3^{P}	161.3^{R}	$150.8^{P,R}$	$150.8^{R,T}$	161.3^{T}	161.3^{W}	161.3^{T}	$150.8^{W,Y}$	161.3^{V}	161.3^{X}	161.4^{Y}	$150.8^{Y,\alpha}$	$150.8^{W,Y}$
	5	116.9	116.5	116.9	116.9	116.5	116.5	116.9	116.8	116.9	116.5	116.9	116.9	116.9	116.5	116.5
	5	131.1	124.4	131.1	131.3	124.4	124.4	131.3	131.1	131.2	124.4	131.2	131.2	131.1	124.4	124.4
	OMe		56.6			56.6	56.6				56.6				56.6	56.6
(at C-3 of Fru)	α	$167.3^{H,T}$	$167.3^{H,X}$	$167.4^{G,R}$	$167.4^{G,T}$	$167.4^{G,T}$	$167.3^{G,V}$	$167.3^{H,V}$	$167.3^{H,Y}$	$167.3^{G,V}$	$167.3^{H,\alpha}$	$167.3^{G,X}$	$167.2^{H,Z}$	$167.2^{H,\alpha}$	$167.3^{H,\gamma}$	$167.3^{G,\alpha}$
	1	131.1^{U}	130.7^{Y}	131.0^{S}	131.0^{U}	130.9^{U}	130.9^{W}	131.0^{W}	131.1^{Z}	131.1^{W}	131.1^{β}	131.1^{Y}	131.0^{α}	131.1^{β}	131.1^{δ}	131.1^{β}
	2,6	131.2	131.0	131.0	131.0	131.0	131.0	131.0	131.2	131.1	131.1	131.1	131.1	131.2	131.1	131.1
	3,5	130.0	129.9	130.0	129.9	130.0	129.9	129.9	129.9	129.9	129.9	129.9	129.9	129.9	129.9	129.9
	4	134.9^{T}	134.8^{X}	134.8^{R}	134.7^{T}	134.8^{T}	134.7^{V}	134.9^{V}	134.9^{Y}	134.8^{V}	134.9^{α}	134.8^{X}	134.8^{Z}	134.9^{α}	134.9^{T}	134.8^{α}

[a] Long-range correlations were observed between protons and carbons that have the same letter ($^{A,B,...,\gamma,\delta}$) in the same compounds in Tables 2−4.

of MeOH under reduced pressure, the extract was suspended in H_2O and extracted with diethyl ether. The H_2O layer was passed through a Mitsubishi Diaion HP-20 column (9 cm × 36 cm). The absorbed material was eluted with 50% aqueous MeOH, 70% aqueous MeOH, and MeOH, successively. The 70% MeOH eluate (16 g) was submitted to column chromatography on silica gel (500 g) and eluted with $CHCl_3$−MeOH−H_2O (72:25:3) to afford 13 fractions (A−M). Fractions E + F (1215 mg) were chromatographed over ODS [5 cm × 50 cm, CH_3CN−H_2O (15:85 to 23:77) linear gradient] to afford **1** (412 mg), **3** (6.4 mg), **4** (106 mg), **5** (32 mg), **6** (14 mg), and fraction N (128 mg). Fraction N (128 mg) was chromatographed over Ph-A [2 cm × 25 cm, MeOH−H_2O (60:40)] to give fraction N-a (19 mg) and N-b (13 mg). Fraction N-a was chromatographed over Ph-A [2 cm × 25 cm, MeOH−H_2O (52:48)] to afford **13** (26 mg), and fraction N-b was chromatographed over Ph-A [2 cm × 25 cm, MeOH−H_2O (60:40)] to afford **18** (6.9 mg). Fractions G + H (1074 mg) were chromatographed over ODS [5 cm × 50 cm, CH_3CN−H_2O (15:85 to 31:69) linear gradient] to afford 19 fractions (a−s). Fractions j (187 mg), n (316 mg), and p (22 mg) were chromatographed over Ph-A [2 cm × 25 cm, MeOH−H_2O (50:50)] to afford **8** (19 mg) from fraction j, **16** (79 mg) and **20** (184 mg) from fraction n, and **15** (3.3 mg) and **17** (4.7 mg) from fraction p. Fraction f (17 mg) was chromatographed over Ph-A [2 cm × 25 cm, CH_3CN−H_2O (45:55)] to afford **2** (5.4 mg). Fraction l (63 mg) was chromatographed over ODS [2 cm × 25 cm, CH_3CN−H_2O (22.5:77.5)] to afford **19** (5.1 mg). Fraction I (2047 mg) was chromatographed over ODS [5 cm × 100 cm, CH_3CN−H_2O (21:79)] to afford 10 fractions (O−X). Fraction P (248 mg) was chromatographed over Ph-A [2 cm × 25 cm, CH_3CN−H_2O (22.5:77.5)] to afford **9** (36 mg), **10** (24 mg), and **21** (15 mg). Fractions Q (271 mg), S (229 mg), and U (244 mg) were chromatographed over Ph-A [2 cm × 25 cm, MeOH−H_2O (50:50)] to afford **11** (51 mg) and **12** (103 mg) from fractions Q, **7** (50 mg) from fraction S, and **14** (94 mg) from fraction U. Fraction R (208 mg) was separated by HPLC [Ph-A, 2 cm × 25 cm, CH_3CN−H_2O (20:80)] to afford **12** (18 mg). Fraction V (115 mg) was separated successively by Ph-A [2 cm × 25 cm, CH_3CN−H_2O (22.5:77.5)] and Ph-A [2 cm × 25 cm, MeOH−H_2O (50:50)] to afford **14** (6.6 mg).

Dalmaisione A (1): amorphous powder, $[\alpha]^{23}_{D}$ −62.0° (*c* 1.0, pyridine); UV (MeOH) λ_{max} (log ϵ) 245 (4.26), 266 (4.23), 305 (4.20); ^1H and ^{13}C NMR, see Table 1; FABMS *m/z* 589 [M + H]$^+$, 611 [M + Na]$^+$.

Dalmaisione B (2): amorphous powder, $[\alpha]^{23}_{D}$ −42.4° (*c* 0.59, pyridine); UV (MeOH) λ_{max} (log ϵ) 240 (4.33), 308 (4.25); ^1H and ^{13}C NMR, see Table 1; FABMS *m/z* 979 [M + Na]$^+$.

Dalmaisione C (3): amorphous powder, $[\alpha]^{23}_{D}$ −110.2° (*c* 0.64, pyridine); UV (MeOH) λ_{max} (log ϵ) 272 (4.09), 314 (3.85); ^1H and ^{13}C NMR, see Table 1; FABMS *m/z* 589 [M + H]$^+$, 611 [M + Na]$^+$.

Dalmaisione D (4): amorphous powder, $[\alpha]^{23}_{D}$ −19.7° (*c* 1.0, pyridine); UV (MeOH) λ_{max} (log ϵ) 235 (3.97), 248 (4.01), 306 (4.04); ^1H NMR (DMSO-d_6) δ 8.06 (1H, dd, *J* = 7.5, 1.5 Hz, H-7), 7.92 (1H, dd, *J* = 7.5, 1.5 Hz, H-6′), 7.82 (1H, td, *J* = 7.5, 1.5 Hz, H-5), 7.73 (1H, dd, *J* = 7.5, 1.5 Hz, H-4), 7.57 (1H, td, *J* = 7.5, 1.5 Hz, H-4′), 7.50 (1H, td, *J* = 7.5, 1.5 Hz, H-6), 7.49 (1H, dd, *J* = 7.5, 1.5 Hz, H-3′), 7.22 (1H, td, *J* = 7.5, 1.5 Hz, H-5′), 7.10 (1H, s, H-10), 5.10 (1H, d, *J* = 7 Hz, H-1 of Glc1), 4.24 (1H, d, *J* = 7.5 Hz, H-1 of Glc2), 4.02 (1H, br d, *J* = 11 Hz, H-6 of Glc1), 3.68 (1H, dd, *J* = 9, 7.5 Hz, H-4 of Glc1), 3.65 (1H, dd, *J* = 12.5, 4 Hz, H-6 of Glc2), 3.63 (1H, br d, *J* = 11 Hz, H-6 of Glc1), 3.42 (1H, dd, *J* = 12.5, 6 Hz, H-6 of Glc2), 3.42 (overlapped, H-5 of Glc1), 3.34 (1H, dd, *J* = 9, 7 Hz, H-2 of Glc1), 3.20 (1H, dd, *J* = 9, 9 Hz, H-3 of Glc1), 3.12 (1H, dd, *J* = 8, 8 Hz, H-3 of Glc2), 3.06 (1H, dd, *J* = 8, 8 Hz, H-4 of Glc2), 3.03 (overlapped, H-5 of Glc2), 2.99 (1H, dd, *J* = 8, 7.5 Hz, H-2 of Glc2); ^{13}C NMR (DMSO-d_6) δ 177.1 (C-3), 160.4 (C-2), 155.9 (C-9), 155.3 (C-2′), 134.0 (C-5), 132.9 (C-4′), 128.9 (C-6′), 125.2 (C-6), 124.6 (C-7), 123.1 (C-8), 121.9 (C-5′), 120.6 (C-1′), 118.4 (C-4), 116.0 (C-3′), 112.0 (C-10), 103.3 (C-1 of Glc2), 100.2 (C-1 of Glc1), 76.8 (C-3 of Glc2), 76.8 (C-5 of Glc2), 76.6 (C-4 of Glc1), 76.1 (C-5 of Glc1), 73.5 (C-2 of Glc2), 73.3 (C-2 of Glc1), 70.1 (C-4 of Glc2), 69.7 (C-3 of Glc1), 68.4 (C-6 of Glc1), 61.0 (C-6 of Glc2); FABMS *m/z* 563 [M + H]$^+$.

Dalmaisiose A (5): amorphous powder, $[\alpha]^{23}_{D}$ −5.8° (*c* 0.77, MeOH); UV (MeOH) λ_{max} (log ϵ) 224 (4.43), 284 (4.46), 317 (4.29); ^{1}H NMR (CD_3OD) δ 7.73 (1H, d, J = 16 Hz, $H\gamma$ of *p*-cou.), 7.55 (1H, d, J = 16 Hz, $H\gamma$ of cin.), 7.52 (2H, d, J = 8 Hz, H-2, 6 of *p*-cou.), 7.34 (overlapped, H-2, 3, 4, 5, 6 of cin.), 6.74 (2H, d, J = 8 Hz, H-3, 5 of *p*-cou.), 6.41 (1H, d, J = 16 Hz, H_β of *p*-cou.), 6.07 (1H, d, J = 16 Hz, H_β of cin.), 5.77 (1H, d, J = 5 Hz, H-3 of Fru), 5.42 (1H, d, J = 3.5 Hz, H-1 of Glc1), 4.85 (1H, dd, J = 10, 10 Hz, H-4 of Glc1), 4.44 (1H, dd, J = 5, 5 Hz, H-4 of Fru), 4.43 (1H, d, J = 7.5 Hz, H-1 of Glc2), 4.31 (1H, m, H-5 of Glc1), 4.18 (1H, m, H-5 of Fru), 4.14 (1H, dd, J = 12.5, 3 Hz, H-6 of Glc1), 4.09 (1H, dd, J = 12.5, 5 Hz, H-6 of Glc1), 3.81 (overlapped, H-6 of Fru), 3.78 (overlapped, H-6 of Glc2), 3.75 (1H, dd, J = 10, 10 Hz, H-3 of Glc1), 3.73 (overlapped, H-6 of Fru), 3.67 (2H, br s, H-1 of Fru), 3.62 (1H, dd, J = 12.5, 5 Hz, H-6 of Glc2), 3.52 (1H, dd, J = 10, 3.5 Hz, H-2 of Glc1), 3.31 (overlapped, H-3 of Glc2), 3.31 (overlapped, H-4 of Glc2), 3.24 (1H, m, H-5 of Glc2), 3.18 (1H, dd, J = 9, 7.5 Hz, H-2 of Glc2), 2.04 (3H, s, Ac); ^{13}C NMR (CD_3OD) δ 172.7 (Ac), 167.8 (C_α of cin.), 167.5 (C_α of *p*-cou.), 161.6 (C-4 of *p*-cou.), 147.6 (C_γ of *p*-cou.), 147.1 (C_γ of cin.), 135.4 (C-1 of cin.), 131.6 (C-4 of cin.), 131.4 (C-2, 6 of *p*-cou.), 130.1 (C-3, 5 of cin.), 129.3 (C-2, 6 of cin.), 127.1 (C-1 of *p*-cou.), 118.0 (C_β of cin.), 117.1 (C-3, 5 of *p*-cou.), 114.7 (C_β of *p*-cou.), 107.2 (C-2 of Fru), 104.5 (C-1 of Glc2), 93.5 (C-1 of Glc1), 85.0 (C-5 of Fru), 84.4 (C-4 of Fru), 78.6 (C-3 of Fru), 77.9 (C-4 of Glc2), 77.9 (C-5 of Glc2), 75.0 (C-2 of Glc2), 73.0 (C-2 of Glc1), 72.8 (C-4 of Glc1), 72.5 (C-3 of Glc1), 71.2 (C-3 of Glc2), 70.0 (C-5 of Glc1), 65.1 (C-1 of Fru), 64.6 (C-6 of Glc-1), 63.2 (C-6 of Fru), 62.4 (C-6 of Glc2), 20.9 (Ac); FABMS *m/z* 823 [M + H]$^+$, 845 [M + Na]$^+$.

Dalmaisiose B (7): amorphous powder, $[\alpha]^{23}_{D}$ −46.0° (*c* 0.49, MeOH); UV (MeOH) λ_{max} (log ϵ) 210 (4.43), 228 (4.55), 300 (4.64), 309 (4.66); ^{1}H NMR, see Table 2; ^{13}C NMR, see Table 5; FABMS *m/z* 1293 [M + H]$^+$, 1315 [M + Na]$^+$.

Dalmaisiose C (8): amorphous powder, $[\alpha]^{23}_{D}$ −67.8° (*c* 0.20, MeOH); UV (MeOH) λ_{max} (log ϵ) 220 (4.53), 232 (4.54), 298 (4.48), 323 (4.54); ^{1}H NMR, see Table 2; ^{13}C NMR, see Table 5; FABMS *m/z* 1375 [M + Na]$^+$.

Dalmaisiose D (9): amorphous powder, $[\alpha]^{23}_{D}$ −41.3° (*c* 0.99, MeOH); UV (MeOH) λ_{max} (log ϵ) 228 (4.50), 300 (4.59), 309 (4.62); ^{1}H NMR, see Table 2; ^{13}C NMR, see Table 5; FABMS *m/z* 1273 [M + Na]$^+$.

Dalmaisiose E (10): amorphous powder, $[\alpha]^{23}_{D}$ −69.0° (*c* 0.29, MeOH); UV (MeOH) λ_{max} (log ϵ) 230 (4.61), 299 (4.64), 313 (4.68); ^{1}H NMR, see Table 2; ^{13}C NMR, see Table 5; FABMS *m/z* 1303 [M + Na]$^+$.

Dalmaisiose F (11): amorphous powder, $[\alpha]^{23}_{D}$ −45.7° (*c* 0.44, MeOH); UV (MeOH) λ_{max} (log ϵ) 229 (4.58), 298 (4.62), 310 (4.64); ^{1}H NMR, see Table 2; ^{13}C NMR, see Table 5; FABMS *m/z* 1281 [M + H]$^+$, 1303 [M + Na]$^+$.

Dalmaisiose G (12): amorphous powder, $[\alpha]^{23}_{D}$ −41.4° (*c* 0.89, MeOH); UV (MeOH) λ_{max} (log ϵ) 219 (4.46), 233 (4.48), 297 (4.43), 323 (4.51); ^{1}H NMR, see Table 3; ^{13}C NMR, see Table 5; FABMS *m/z* 1311 [M + H]$^+$, 1333 [M + Na]$^+$.

Dalmaisiose H (13): amorphous powder, $[\alpha]^{23}_{D}$ −11.5° (*c* 0.86, MeOH); UV (MeOH) λ_{max} (log ϵ) 211 (4.64), 229 (4.74), 300 (4.85), 313 (4.91); ^{1}H NMR, see Table 3; ^{13}C NMR, see Table 5; FABMS *m/z* 1273 [M + Na]$^+$.

Dalmaisiose I (14): amorphous powder, $[\alpha]^{23}_{D}$ −66.2° (*c* 1.07, MeOH); UV (MeOH) λ_{max} (log ϵ) 230 (4.73), 300 (4.80), 315 (4.84); ^{1}H NMR, see Table 3; ^{13}C NMR, see Table 5; FABMS *m/z* 1427 [M + H]$^+$, 1449 [M + Na]$^+$.

Dalmaisiose J (15): amorphous powder, $[\alpha]^{23}_{D}$ −14.5° (*c* 0.37, MeOH); UV (MeOH) λ_{max} (log ϵ) 230 (4.70), 301 (4.77), 316 (4.83); ^{1}H NMR, see Table 3; ^{13}C NMR, see Table 5; FABMS *m/z* 1239 [M + H]$^+$, 1261 [M + Na]$^+$.

Dalmaisiose K (16): amorphous powder, $[\alpha]^{23}_{D}$ −60.3° (*c* 0.68, MeOH); UV (MeOH) λ_{max} (log ϵ) 220 (4.64), 231 (4.67), 300 (4.69), 318 (4.73); ^{1}H NMR, see Table 3; ^{13}C NMR, see Table 5; FABMS *m/z* 1457 [M + H]$^+$, 1479 [M + Na]$^+$.

Dalmaisiose L (17): amorphous powder, $[\alpha]^{23}_{D}$ −19.9° (*c* 0.47, MeOH); UV (MeOH) λ_{max} (log ϵ) 220 (4.60), 231 (4.62), 300 (4.64), 319 (4.73); ^{1}H NMR, see Table 4; ^{13}C NMR, see Table 5; FABMS *m/z* 1291 [M + Na]$^+$.

Dalmaisiose M (18): amorphous powder, $[\alpha]^{23}_{D}$ −10.7° (*c* 0.29, MeOH); UV (MeOH) λ_{max} (log ϵ) 220 (4.62), 231 (4.63), 300 (4.65), 320 (4.74); ^{1}H NMR, see Table 4; ^{13}C NMR, see Table 5; FABMS *m/z* 1311 [M + H]$^+$, 1333 [M + Na]$^+$.

Dalmaisiose N (19): amorphous powder, $[\alpha]^{23}_{D}$ −67.9° (*c* 0.40, MeOH); UV (MeOH) λ_{max} (log ϵ) 231 (4.58), 300 (4.57), 318 (4.63); ^{1}H NMR, see Table 4; ^{13}C NMR, see Table 5; FABMS *m/z* 1479 [M + Na]$^+$.

Dalmaisiose O (20): amorphous powder, $[\alpha]^{23}_{D}$ −61.5° (*c* 1.17, MeOH); UV (MeOH) λ_{max} (log ϵ) 219 (4.68), 234 (4.69), 297 (4.65), 325 (4.75); ^{1}H NMR, see Table 4; ^{13}C NMR, see Table 5; FABMS *m/z* 1487 [M + H]$^+$, 1509 [M + Na]$^+$.

Dalmaisiose P (21): amorphous powder, $[\alpha]^{23}_{D}$ −61.8° (*c* 0.33, MeOH); UV (MeOH) λ_{max} (log ϵ) 219 (4.63), 232 (4.63), 298 (4.59), 323 (4.67); ^{1}H NMR, see Table 4; ^{13}C NMR, see Table 5; FABMS *m/z* 1467 [M + Na]$^+$.

Acid Hydrolysis of Compounds 1−4. Compound **1** (30 mg) was stirred with 2 N aqueous HCl (3 mL) and dioxane (3 mL) at 100 °C for 1 h. The reaction mixture was extracted with diethyl ether. From the H_2O layer, D-glucose (t_R 12.1 min) and L-rhamnose (t_R 7.6 min) were detected by GC (Supelco SPB-1, 0.25 × 30 m, 215 °C). The diethyl ether layer afforded compound **1a** (7 mg) as an alycone. **1a** was dissolved in methanol and methylated by diazomethane−diethyl ether solution to afford methyl ether **1b** (7 mg). Compounds **2** (2 mg), **3** (2 mg), and **4** (10 mg) were hydrolyzed in the same way. The sugar residues from **1−4** were identified in the same way as described for the oligosaccharide mentioned below. Compound **2** afforded **1a** (1 mg), D-glucose, L-rhamnose, and sinapinic acid, and **1a** was identified by HPLC [ODS, 4.6 mm × 25 cm, CH_3CN-H_2O (32.5:67.5), 1.0 mL/min, UV 260 nm] and sinapinic acid (t_R 8.4 min) was identified by HPLC [ODS, 4.6 mm × 25 cm, CH_3CN-H_2O (22.5:77.5), 1.0 mL/min, UV 260 nm]. Compound **3** afforded D-glucose and L-rhamnose. Compound **4** afforded **4a** (4 mg) as an aglycone and D-glucose. **1a:** amorphous powder, ^{1}H NMR (DMSO-d_6) δ 8.13 (1H, dd, J = 8, 1.5 Hz, H-5), 7.91 (1H, td, J = 8, 1.5 Hz, H-7), 7.86 (1H, dd, J = 8, 1.5 Hz, H-5′), 7.72 (1H, dd, J = 8, 1.5 Hz, H-8), 7.58 (1H, td, J = 8, 1.5 Hz, H-6), 7.33 (1H, t, J = 8 Hz, H-4′), 7.31 (1H, overlapped, H-3′); ^{13}C NMR (DMSO-d_6) δ 172.5 (C-4), 165.1 (C-2), 155.3 (C-11), 154.0 (C-9), 144.9 (C-1′), 142.7 (C-2′), 134.9 (C-7), 126.4 (C-6), 125.4 (C-5), 124.7 (C-4′), 123.9 (C-10), 121.2 (C-3′), 118.3 (C-8), 114.0 (C-6′), 113.8 (C-5′), 104.6 (C-3); FABMS *m/z* 281 [M + H]$^+$. **4a:** amorphous powder, ^{1}H NMR (DMSO-d_6) δ 8.05 (1H, dd, J = 8, 2 Hz, H-7), 7.92 (1H, dd, J = 8, 2 Hz, H-6′), 7.82 (1H, td, J = 8, 2 Hz, H-5), 7.74 (1H, dd, J = 8, 2 Hz, H-4), 7.49 (1H, td, J = 8, 2 Hz, H-6), 7.40 (1H, td, J = 8, 2 Hz, H-4′), 7.13 (1H, s, H-10), 7.07 (1H, dd, J = 8, 2 Hz, H-3′), 7.02 (1H, td, J = 8, 2 Hz, H-5′); ^{13}C NMR (DMSO-d_6) δ 177.1 (C-3), 160.7 (C-2), 156.5 (C-9), 155.8 (C-2′), 134.0 (C-5), 132.5 (C-4′), 128.5 (C-6′), 125.1 (C-6), 124.6 (C-7), 123.1 (C-8), 119.4 (C-5′), 118.3 (C-4), 117.7 (C-1′), 117.0 (C-3′), 111.0 (C-10); FABMS *m/z* 239 [M + H]$^+$.

Hydrolysis of Oligosaccharides 5 and 7−21. Each sample (2 mg) was stirred with 1 N aqueous NaOH (50 μL) at 65 °C for 1 h. After acidification with 1 N HCl (100 μL), the reaction mixture was diluted with H_2O (500 μL) and extracted with EtOAc (100 μL). The EtOAc layer was washed with H_2O (500 μL). To the EtOAc layer was added *O*-(4-nitrobenzyl)-*N*,*N*′-diisopropylisourea (NBDI) (3 mg), and the reaction mixture was stirred for 1 h at 65 °C. From the reaction mixture, acetic acid (t_R 9.4 min) was detected from **5**, **7−14**, **16**, and **18−20**, *p*-coumaric acid (t_R 14.9 min) was detected from **5**, **7**, **9**, **10**, **11**, and **13−19**, ferulic acid (t_R 15.8 min) was detected from **8**, **10**, **11**, **12**, and **14−21**, benzoic acid (t_R 22.8 min) was detected from **7−21**, and cinnamic acid (t_R 31.9 min) was detected from **5** by HPLC [Develosil Ph-A, 4.6 mm × 25 cm, CH_3CN-H_2O (45:55), 1.0 mL/min, UV 273 nm]. The H_2O layer was passed through a column equipped with Amberlite IRA-60E + IR-120B (1:1) (7 mm × 7 cm) and eluted with H_2O. The H_2O elute was concentrated and dried in a small sample tube, 0.5 N HCl (50 μL) was added, and the mixture was warmed for 10 min at 100 °C. The reaction mixture was passed though a column equipped with Amberlite IRA-60E (7 mm × 5 cm), eluted with H_2O, and concentrated and dried in a small tube. D-Cysteine methyl ester in pyridine (3 mg/25 μL) was added, and the mixture was stirred for 1.5 h at 65 °C. To the reaction mixture were added hexamethyldisilazane (15 μL) and trimethylsilyl chloride (15 μL), and the mixture was stirred for 30 min at 65 °C. The reaction mixture was diluted with H_2O and extracted with hexane. From the hexane extract, D-glucose (t_R 12.1 min) and D-fructose (t_R 8.9 min) were detected from **5** and **7**−**21**, and L-rhamnose (t_R 7.4 min) was detected from **7**−**12**, **14**, **16**, **19**, **20**, and **21** by GC (Supelco SPB-1, 0.25 mm × 30 m, 215 °C). The t_R of L-glucose, l-fructose, and D-rhamnose was 11.3, 9.8, and 7.6 min, respectively.[7]

References and Notes

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