Tricornoses A−L, Oligosaccharide Multi-esters from the Roots of *Polygala tricornis*

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Twelve new oligosaccharide multi-esters, tricornoses A−L, together with eight known compounds were isolated from the roots of *Polygala tricornis*. The structures of the new compounds were elucidated on the basis of chemical and spectroscopic evidence.

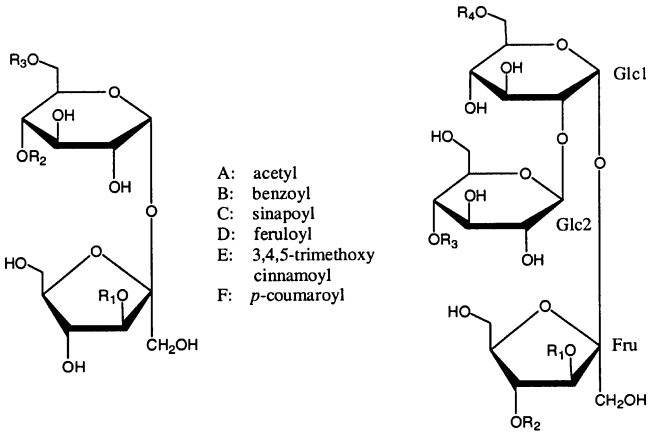
Polygala tricornis Gagnep. is widely distributed in southern China, and its root is used as a tonic and sedative in traditional medicine. No previous investigation has been reported on this plant. Herein we report the isolation and structure elucidation of 12 new oligosaccharide multi-esters, tricornoses A−L (**1**, **2**, and **11**−**20**). Eight known sucrose esters (**3**−**10**) isolated from this plant were identified, by comparison of the spectral data with reported data, as 6-*O*-benzoyl-3′-*O*-3,4,5-trimethoxycinnamoylsucrose (**3**),[1] sibiricose A_6 (**4**),[2] 6-*O*-benzoylsucrose (**5**),[3] 4-*O*-benzoyl-3′-3,4,5-trimethoxycinnamoylsucrose (**7**),[1] tenuifoliside C (**6**),[4] 6-*O*-benzoyl-3′-*O*-sinapoylsucrose (**8**),[1] 3,6′-di-*O*-sinapoylsucrose (**9**),[4] and glomeratose A (**10**).[5]

Results and Discussion

The 95% EtOH extract of the roots of *P. tricornis* was suspended in H_2O and extracted with petroleum ether, $CHCl_3$, and *n*-BuOH. The *n*-BuOH layer was adsorbed on a porous polymer resin (D101) column and eluted with 10%, 30%, and 50% aqueous MeOH and MeOH, successively. The 10%, 30%, and 50% aqueous MeOH eluates were chromatographed on a silica gel column, respectively. The selected fractions were then subjected to semipreparative HPLC, using a reversed-phase (ODS) column, which led to the isolation of 10 sucrose esters (**1**−**10**), four trisaccharide multi-esters (**11**−**14**), and six tetrasaccharide multi-esters (**15**−**20**).

Tricornose A (**1**) was obtained as an amorphous powder, and its HRESIMS gave an $[M + NH_4]^+$ ion peak at *m/z* 622.2343 ($C_{26}H_{40}O_{16}N$). On acid hydrolysis, it afforded D-glucose, D-fructose, and (*E*)-3,4,5-trimethoxycinnamic acid. The NMR spectral data were similar to those of **10** except for the presence of one set of acetyl signals (see Tables 1 and 3). The position of acetyl linkage was determined at C-6 of Glc by the HMBC spectrum, which showed long-range correlations between the proton signals at δ 4.54, 4.12 (H-6 of Glc) and the acetyl carbonyl carbon signal at δ 172.9. From these data, the structure of tricornose A was elucidated as 3-*O*-[(*E*)-3,4,5,-trimethoxycinnamoyl]-β-D-fructofuranosyl-(2→1)-(6-*O*-acetyl)-α-D-glucopyranoside (**1**).

Tricornose B (**2**) was obtained as an amorphous powder, and its HRESIMS gave an $[M + NH_4]^+$ ion peak at *m/z* 726.2608 ($C_{33}H_{44}O_{17}N$). On acid hydrolysis, it afforded D-glucose, D-fructose, benzoic acid, and (*E*)-3,4,5-trimethoxycinnamic acid. Comparison of the NMR spectral data of **2** with that of **3** indicated the presence of an additional acetyl residue in **2** (see Tables 1 and 3). The position of the acetyl linkage was established at C-4 of Glc by the HMBC spectrum, which showed cross-peaks between the proton signal at δ 4.97 (H-4 of Glc) and the acetyl carbonyl carbon signal at δ 170.2. Thus, the structure of Tricornose B was determined as 3-*O*-[(*E*)-3,4,5,-trimethoxycinnamoyl]-β-D-fructofuranosyl-(2→1)-(4-*O*-acetyl)-(6-*O*-benzoyl)-α-D-glucopyranoside (**2**).



	R_1	R_2	R_3
1	E	H	A
2	E	A	B
3	E	H	B
4	C	H	H
5	H	H	B
6	E	H	C
7	E	B	H
8	C	H	B
9	C	H	C
10	E	H	H

	R_1	R_2	R_3	R_4
11	E	H	H	C
12	C	H	H	C
13	E	C	H	C
14	E	D	H	C
15	C	H	Glc	C
16	C	C	Glc	C
17	E	C	Glc	C
18	E	D	Glc	C
19	C	D	Glc	C
20	C	F	Glc	C

Figure 1. Structures of oligosaccharide multi-esters from the roots of *Polygala tricornis*.

Tricornose C (**11**) was obtained as an amorphous powder, and its HRESIMS gave an $[M + NH_4]^+$ ion peak at *m/z* 948.3313 ($C_{41}H_{58}O_{24}N$). On acid hydrolysis, it afforded D-glucose, D-fructose, (*E*)-sinapic acid, and (*E*)-3,4,5-trimethoxycinnamic acid. The ^1H NMR spectrum suggested the presence of two anomeric proton signals, one set of (*E*)-3,4,5-trimethoxycinnamoyl proton signals and one set of (*E*)-sinapoyl proton signals. The ^{13}C NMR spectrum indicated the presence of three anomeric carbon signals, one set of (*E*)-3,4,5-trimethoxycinnamoyl carbon signals and one set of (*E*)-sinapoyl carbon signals (see Tables 1 and 3). The sugar proton and carbon signals in the NMR spectra were assigned by $^1H-^1H$ COSY, HSQC, and HMBC experi-

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Table 1. ^{1}H NMR Spectroscopic Data of Compounds **1**, **2**, and **11**−**14**[a]

sugar	1	2	11	12	13	14
Glc1-1	5.44d(4.0)	5.48d(3.6)	5.78d(3.5)	5.78d(3.5)	5.81d(3.6)	5.82d(3.5)
2	3.43dd(9.5,3.5)	3.60m	3.53dd(10.0,3.0)	3.53dd(10.0,3.5)	3.55dd(9.6,4.2)	3.55dd(10.0,3.5)
3	3.63m	3.81m	3.81m	3.82m	3.83t(9.6)	3.85m
4	3.28dd(9.5)	4.97dd(9.9)	3.38dd(10.0)	3.37dd(9.5)	3.37dd(9.6)	3.38dd(10.0)
5	4.14m	4.32m	4.31m	4.30m	4.38dd(9.6)	4.39dd(8.5)
6	4.54d(10.0)	4.47m	4.70d(10.5)	4.69d(10.5)	4.76d(11.4)	4.76d(16.0)
	4.12dd(12.0,5.5)	4.29m	4.22dd(12.5,6.0)	4.22dd(12.5,6.0)	4.21dd(11.4,7.2)	4.22dd(11.5,7.0)
Glc2-1			4.45d(7.5)	4.45d(8.0)	4.46d(8.4)	4.47d(7.0)
2			3.23m	3.22m	3.23m	3.24m
3			3.34dd(8.5)	3.34dd(8.5)	3.34dd(9.0)	3.35m
4			3.25m	3.24m	3.26(9.0)	3.26m
5			3.27m	3.28m	3.30m	3.30m
6			3.92dd(6.5,2.0)	3.92dd(6.5,2.0)	3.91dd(12.0,3.6)	3.90dd(12.0,4.0)
			3.67dd(12.0,6.0)	3.67dd(12.0,6.0)	3.67dd(12.0,6.0)	3.68dd(12.0,6.0)
Fru-1	3.58d(13.0)	3.56m	3.70d(12.0)	3.71d(12.0)	3.73d(12.0)	3.75d(11.5)
	3.58d(13.0)	3.56m	3.52d(12.0)	3.52(12.0)	3.57d(12.0)	3.57d(12.0)
3	5.47d(8.0)	5.41d(6.6)	5.59d(8.0)	5.58(8.5)	5.90d(8.4)	5.90d(7.5)
4	4.35t(8.0)	4.40m	4.51t(8.5)	4.51t(8.5)	5.67t(7.8)	5.67t(8.0)
5	3.96dt(10.0,3.5)	3.95m	3.99dt(10.5,3.0)	3.99dt(10.5,2.0)	4.19m	4.19m
6	3.88m	3.66m	3.89m	3.89m	3.99dd(11.4,4.8)	3.99(12.0,4.5)
	3.81m	3.66	3.80m	3.81m	3.92m	3.92m
Ac	2.08s	1.79s				
Cinn(C-3 of Fru)						
β	6.52d(16.0)	6.53d(16.0)	6.50d(16.0)	6.44d(16.0)	6.51d(16.2)	6.53d(16.0)
γ	7.69d(16.0)	7.65d(16.0)	7.65d(16.0)	7.63d(16.0)	7.68d(16.2)	7.70d(16.0)
2,6	6.97s	7.02s	6.93s	6.92s	6.90s	6.95s
OMe	3.87s	3.85s	3.86s	3.87s	3.81	3.84
	3.78s		3.77s		3.74	3.77
Cinn(C-4 of Fru)						
β					6.21d(15.6)	6.19d(16.0)
γ					7.41d(15.6)	7.46d(16.0)
2					6.71s	7.01d(1.5)
5						6.74d(8.0)
6					6.71s	6.92d(7.5)
OMe					3.81s	3.77s
Cinn(C-6 of Glc)		Benzoyl				
β		8.02dd(8.4,1.5)	6.44d(16.0)	6.41d(16.0)	6.44d(15.6)	6.44d(16.0)
γ		7.46t(7.5)	7.56d(16.0)	7.56d(16.0)	7.51d(15.6)	7.54d(16.0)
2		7.59t(7.5)	6.86s	6.87s	6.78s	6.81s
6			6.86s	6.87s	6.78s	6.81s
OMe			3.83s	3.83s	3.74	3.77

[a] Compounds **1**, **11**, **12**, and **14** were recorded at 500 MHz in CD_3OD, **2** was recorded at 300 MHz in acetone-d_6, and **13** was recorded at 600 MHz in CD_3OD. Assignments were based on ^{1}H−^{1}H COSY, HSQC, and HMBC experiments.

ments. The sugar and acyl linkages were determined mainly by the HMBC spectrum. In this spectrum, long-range correlations were observed between the proton signal at *δ* 5.78 (H-1 of Glc1) and the carbon signal at *δ* 105.1 (C-2 of Fru); the proton signal at *δ* 4.45 (H-1 of Glc2) and the carbon signal at *δ* 82.2 (C-2 of Glc1); the proton signal at *δ* 5.59 (H-3 of Fru) and the (*E*)-3,4,5-trimethoxycinnamoyl carbonyl carbon signal at *δ* 167.8; and the proton signal at *δ* 4.70, 4.22 (H-6 of Glc1) and the (*E*)-sinapoyl carbonyl carbon signal at *δ* 169.1. Therefore, the structure of tricornose C was established as 3-*O*-[(*E*)-3,4,5,-trimethoxycinnamoyl]-*β*-D-fructofuranosyl-(2→1)-[*β*-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**11**).

Tricornose D (**12**) was obtained as an amorphous powder, and its ESIMS exhibited $[M + Na]^+$ and $[M + NH_4]^+$ ions at *m/z* 939 and 934, respectively. On acid hydrolysis, it afforded D-glucose, D-fructose, and (*E*)-sinapic acid. Comparison of the NMR spectral data of **12** with that of **11** indicated that the (*E*)-3,4,5-trimethoxylcinnamoyl residue in **11** was replaced by an (*E*)-sinapoyl residue in **12** (see Tables 1 and 3). Thus, the structure of tricornose D was identified as 3-*O*-[(*E*)-sinapoyl]-*β*-D-fructofuranosyl-(2→1)-[*β*-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**12**).

Tricornose E (**13**) was obtained as an amorphous powder, and its HRESIMS gave an $[M + H + K]^{2+}$ ion peak at *m/z* 588.1642 ($C_{52}H_{65}O_{28}K$). On acid hydrolysis, it afforded D-glucose, D-fructose, (*E*)-sinapic acid, and (*E*)-3,4,5-trimethoxycinnamic acid. The ^{1}H NMR spectrum suggested the presence of two anomeric proton signals, one set of (*E*)-3,4,5-trimethoxycinnamoyl proton signals and two sets of (*E*)-sinapoyl proton signals. The ^{13}C NMR spectrum indicated the presence of three anomeric carbons, one set of (*E*)-3,4,5-trimethoxycinnamoyl carbons and two sets of (*E*)-sinapoyl carbons (see Tables 1 and 3). The sugar proton and carbon signals in the NMR spectra were assigned by ^{1}H−^{1}H COSY, HSQC, and HMBC spectra. The linkages of sugar and acyl residues were established mainly by the HMBC spectrum. In this spectrum, long-range correlations were observed between the proton signal at *δ* 5.48 (H-1 of Glc1) and the carbon signal at *δ* 105.8 (C-2 of Fru); the proton signal at *δ* 4.46 (H-1 of Glc2) and the carbon signal at *δ* 82.1 (C-2 of Glc1); the proton signal at *δ* 5.90 (H-3 of Fru) and the (*E*)-3,4,5-trimethoxycinnamoyl carbonyl carbon signal at *δ* 167.4; the proton signal at *δ* 5.67 (H-4 of Fru) and the (*E*)-sinapoyl carbonyl carbon signal at *δ*168.1; and the proton signals at *δ* 4.76, 4.21 (H-6 of Glc1) and the (*E*)-sinapoyl carbonyl carbon signal at *δ* 169.2. On the basis of the above data, the structure of tricornose E was determined as 3-*O*-(*E*)-3,4,5,-trimethoxycinnamoyl-[4-*O*-(*E*)-sinapoyl]-*β*-D-fructofuranosyl-(2→1)-[*β*-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**13**).

Tricornose F (**14**) was obtained as an amorphous powder, and its HRESIMS gave an $[M + H + K]^{2+}$ ion peak at

Table 2. ^{1}H NMR Spectroscopic Data of Compounds **15**−**20**[a]

sugar	**15**	**16**	**17**	**18**	**19**	**20**
Glc1-1	5.75d(3.5)	5.80d(3.5)	5.80d(3.5)	5.78d(3.6)	5.79d(3.5)	5.79(3.6)
2	3.51m	3.55m	3.55m	3.53m	3.55m	3.54m
3	3.82m	3.85m	3.85m	3.86m	3.86m	3.87m
4	3.37m	3.40dd(10.0)	3.39dd(10.0)	3.36dd(9.0)	3.38dd(10.0)	3.38dd(9.6)
5	4.32m	4.40m	4.40m	4.37m	4.38m	4.38m
6	4.69d(12.5)	4.76d(12.0)	4.77d(11.0)	4.75d(11.2)	4.75d(11.0)	4.74d(11.2)
	4.22dd(12.0,7.5)	4.23dd(12.0,6.0)	4.22dd(12.0,7.5)	4.21dd(11.2,6.6)	4.23dd(11.5,7.5)	4.24dd(12.0,6.6)
Glc2-1	4.48d(7.5)	4.51d(7.5)	4.51d(7.5)	4.49d(7.2)	4.50d(7.5)	4.51d(7.8)
2	3.29m	3.33m	3.33m	3.32m	3.32m	3.31m
3	3.50m	3.51m	3.52m	3.51m	3.53m	3.52m
4	3.49m	3.51m	3.51m	3.49dd(9.0)	3.51m	3.50m
5	3.41m	3.43m	3.44m	3.42m	3.43m	3.42m
6	3.96m	3.98m	3.99m	3.97m	3.99m	3.98m
	3.86m	3.86m	3.86m	3.85m	3.86m	3.86m
Glc3-1	4.36d(8.0)	4.38d(8.5)	4.38d(8.0)	4.37d(7.2)	4.38d(7.5)	4.37d(7.8)
2	3.21dd(8.0)	3.23dd(9.0)	3.23dd(9.0)	3.20dd(8.4)	3.22dd(9.0)	3.22dd(9.0)
3	3.36m	3.36m	3.37m	3.37m	3.36m	3.36m
4	3.29m	3.34m	3.34m	3.30m	3.33m	3.32m
5	3.34m	3.35m	3.36m	3.35m	3.35m	3.34m
6	3.86m	3.86m	3.87m	3.85m	3.85m	3.85m
	3.64dd(12.5,5.5)	3.65dd(12.0,5.5)	3.65dd(12.0,6.0)	3.63dd(12.0,6.0)	3.65dd(11.5,6.0)	3.64dd(12.0,5.4)
Fru-1	3.69d(12.0)	3.76d(12.0)	3.76d(12.0)	3.72d(12.0)	3.76d(12.0)	3.74d(12.0)
	3.52d(12.0)	3.57d(12.0)	3.56d(12.0)	3.55d(12.0)	3.57d(12.0)	3.57d(12.0)
3	5.57d(8.5)	5.91d(8.0)	5.91d(8.0)	5.89d(8.4)	5.90d(8.0)	5.89d(7.8)
4	4.50t(8.0)	5.69t(8.0)	5.69t(8.0)	5.66t(7.8)	5.68t(8.0)	5.66t(7.8)
5	3.99m	4.20m	4.21m	4.18m	4.20m	4.19m
6	3.84m	3.98m	3.99m	3.95m	3.98m	3.97m
	3.84m	3.98m	3.99m	3.95m	3.98m	3.97m
Cinn(C-3 of Fru)						
β	6.41d(15.5)	6.42d(16.0)	6.52d(16.0)	6.51d(16.2)	6.43d(16.0)	6.45d(16.2)
γ	7.57d(15.5)	7.68d(16.0)	7.69d(16.0)	7.68d(16.2)	7.68d(16.0)	7.68d(16.2)
2,6	6.88s	6.90s	6.92s	6.92s	6.91s	6.93s
OMe	3.88s	3.83s	3.83s	3.82s	3.84s	3.85s
			3.77s	3.75s		
Cinn(C-4 of Fru)						
β		6.21d(16.0)	6.22d(16.0)	6.18d(16.2)	6.19d(16.0)	6.17d(16.2)
γ		7.42d(16.0)	7.43d(16.0)	7.44d(16.2)	7.45d(16.0)	7.48d(16.2)
2		6.72s	6.73s	6.99d(1.8)	6.99d(1.5)	7.30d(9.0)
3						6.74d(9.0)
5				6.73d(8.4)	6.74d(8.0)	6.74d(9.0)
6		6.72s	6.73s	6.91dd(7.8,1.5)	6.91dd(8.0,1.5)	7.30d(9.0)
OMe		3.82s	3.82s	3.83s	3.84s	
Cinn(C-6 of Glc)						
β	6.45d(15.5)	6.44d(16.0)	6.44d(16.0)	6.43d(16.2)	6.44d(16.0)	6.42d(16.2)
γ	7.64d(16.0)	7.53d(16.0)	7.53d(16.0)	7.52d(16.2)	7.53d(16.0)	7.55d(16.2)
2,6	6.94s	6.78s	6.79s	6.78s	6.78s	6.79s
OMe	3.84s	3.76s	3.78s	3.75s	3.76s	3.77s

[a] Compound **15**−**17** and **19** were recorded at 500 MHz in CD_3OD; **18** and **20** were recorded at 600 MHz in CD_3OD. Assignments were based on ^{1}H−^{1}H COSY, HSQC, and HMBC experiments.

m/z 573.1580 ($C_{51}H_{63}O_{27}K$). On acid hydrolysis, it afforded D-glucose, D-fructose, (*E*)-sinapic acid, (*E*)-ferulic acid, and (*E*)-3,4,5-trimethoxycinnamic acid. The NMR spectral data were similar to those of **13** except for the presence of an (*E*)-feruloyl residue instead of an (*E*)-sinapoyl residue (see Tables 1 and 3). The position of the (*E*)-feruloyl residue linkage was determined at C-4 of Fru by the HMBC spectrum, which showed long-range correlations between the proton signal at *δ* 5.67 (H-4 of Fru) and the (*E*)-feruloyl carbonyl carbon signal at *δ* 168.2. Therefore, the structure of tricornose F was deduced as 3-*O*-(*E*)-3,4,5-trimethoxycinnamoyl-[4-*O*-(*E*)-feruloyl]-*β*-D-fructofuranosyl-(2→1)-[*β*-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**14**).

Tricornose G (**15**) was obtained as an amorphous powder, and its HRESIMS gave an $[M + H + K]^{2+}$ ion peak at *m/z* 559.1534 ($C_{46}H_{63}O_{29}K$). On acid hydrolysis, it afforded D-glucose, D-fructose, and (*E*)-sinapic acid. Comparison of the NMR spectral data of **15** with that of **12** suggested the presence of an additional glucose moiety in **15** (see Tables 2 and 3). The position of the additional glucose (Glc3) linkage was established at C-4 of Glc2 by the HMBC spectrum, which showed cross-peaks between the signals at *δ* 4.36 (H-1 of Glc3) and 80.7 (C-4 of Glc2). From these data, the structure of tricornose G was elucidated as 3-*O*-[(*E*)-sinapoyl]-*β*-D-fructofuranosyl-(2→1)-[*β*-D-glucopyranosyl-(1→4)-*β*-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**15**).

Tricornose H (**16**) was obtained as an amorphous powder, and its HRESIMS gave an $[M + 2NH_4]^{2+}$ ion peak at *m/z* 660.2300 ($C_{57}H_{80}O_{33}N_2$). On acid hydrolysis, it afforded D-glucose, D-fructose, and (*E*)-sinapic acid. The NMR spectral data were similar to those of **15** except for the presence of an additional (*E*)-sinapoyl residue in **16** (see Tables 2 and 3). The position of each acyl residue was determined mainly by an HMBC experiment. In this spectrum, long-range correlations were observed between the proton signal at *δ* 5.91 (H-3 of Fru) and the (*E*)-sinapoyl carbonyl carbon signal at *δ* 167.8; the proton signal at *δ* 5.69 (H-4 of Fru) and the (*E*)-sinapoyl carbonyl carbon signal at *δ* 168.1; and the proton signals at *δ* 4.76, 4.23 (H-6 of Glc1) and the (*E*)-sinapoyl carbonyl carbon signal at *δ* 169.3. On the basis of the above evidence, the structure of tricornose H was identified as 3-*O*-(*E*)-sinapoyl-[4-*O*-(*E*)-

Table 3. ^{13}C NMR Spectroscopic Data of Compounds **1**, **2**, and **11**−**20**[a]

sugar	11	12	13	14	15	16	17	18	19	20	1	2
Glc1-1	92.3	92.3	92.6	92.7	92.3	92.6	92.6	92.7	92.7	92.7	92.9	92.8
2	82.2	82.2	82.1	82.1	82.2	82.1	82.1	82.1	82.1	82.1	73.0	72.9
3	73.8	73.8	73.8	73.8	73.8	73.7	73.7	73.7	73.7	73.7	74.9	72.3
4	71.6	71.6	71.6	71.6	71.6	71.7	71.7	71.7	71.7	71.7	71.6	71.5
5	72.2	72.2	72.6	72.6	72.2	72.6	72.6	72.6	72.6	72.6	72.3	69.8
6	65.5	65.6	65.9	65.9	65.5	65.9	65.9	65.9	65.9	65.8	65.5	63.8
Glc2-1	106.0	106.0	105.7	105.7	105.8	105.8	105.8	105.8	105.8	105.8		
2	75.5	75.5	75.5	75.5	75.3	75.3	75.3	75.3	75.2	75.3		
3	77.8	77.8	77.8	77.9	76.1	76.2	76.2	76.3	76.2	76.2		
4	71.6	71.6	71.7	71.7	80.7	80.7	80.6	80.6	80.7	80.7		
5	78.2	78.2	78.2	78.3	76.7	76.7	76.7	76.7	76.7	76.7		
6	62.8	62.8	62.8	62.8	61.9	61.9	61.9	61.9	61.9	61.9		
Glc3-1					104.6	104.6	104.6	104.6	104.6	104.6		
2					74.9	74.9	74.9	74.9	74.9	74.9		
3					77.9	77.8	77.8	77.9	77.8	77.9		
4					71.3	71.3	71.3	71.4	71.3	71.4		
5					78.1	78.1	78.1	78.1	78.1	78.1		
6					62.4	62.4	62.4	62.4	62.4	62.4		
Fru-1	64.8	64.8	64.4	64.4	64.8	64.4	64.4	64.4	64.4	64.4	65.3	65.5
2	105.1	105.1	105.8	105.8	105.2	105.6	105.6	105.7	105.7	105.7	104.8	105.2
3	78.7	78.6	76.5	76.5	78.6	76.4	76.5	76.5	76.4	76.4	79.6	80.2
4	74.0	74.0	76.3	76.3	74.0	76.3	76.3	76.3	76.3	76.3	74.2	73.9
5	84.4	84.4	83.0	83.1	84.4	82.9	82.9	83.0	82.9	83.0	84.3	84.7
6	64.0	64.0	64.2	64.2	64.0	64.2	64.2	64.2	64.2	64.2	63.6	62.2
Cinn(C-3 of Fru)												
1	131.4	126.6	131.3	131.4	126.6	126.4	131.3	131.4	126.4	126.5	131.5	131.0
2	106.7	107.0	107.0	107.0	107.1	107.1	106.9	107.0	107.0	107.1	106.9	106.9
3	154.7	149.4	154.7	154.8	149.4	149.4	154.7	154.7	149.4	149.5	154.8	154.6
4	141.2	139.6	141.3	141.4	139.5	139.8	141.3	141.3	139.8	140.0	141.3	141.5
5	154.7	149.4	154.7	154.8	149.4	149.4	154.7	154.7	149.4	149.5	154.8	154.6
6	106.7	107.0	107.0	107.0	107.1	107.1	106.9	107.0	107.0	107.1	106.9	106.9
7	147.2	147.9	147.7	147.7	147.9	148.2	147.7	147.7	148.0	147.7	147.2	146.6
8	117.7	115.4	117.5	117.5	115.4	115.1	117.5	117.5	115.1	115.0	117.7	117.6
9	167.8	168.2	167.4	167.4	168.2	167.8	167.4	167.4	167.8	167.8	167.7	166.7
MeO	56.8	56.9	56.8	56.8	56.9	56.8	56.8	56.8	56.8	56.8	56.8	56.6
	61.2	56.9	61.2	61.2	56.9	56.8	61.2	61.1	56.8	56.8	61.2	60.6
	56.8		56.8	56.8			56.8	56.8			56.8	56.6
Cinn(C-4 of Fru)												Ac(C-4 of Glc)
1			126.3	127.2		126.3	126.1	127.3	127.3	126.7		20.6
2			106.9	111.6		106.8	107.0	111.6	111.6	131.3		170.2
3			149.3	149.4		149.3	149.4	149.4	149.4	116.9		
4			139.5	150.9		139.8	140.0	151.0	150.9	161.9		
5			149.3	116.5		149.3	149.4	116.4	116.4	116.9		
6			106.9	124.4		106.8	107.0	124.3	124.3	131.3		
7			148.2	148.1		148.4	148.3	148.0	148.4	147.0		
8			114.6	114.1		114.6	114.5	114.1	114.2	113.8		
9			168.1	168.2		168.1	168.1	168.1	168.2	168.2		
MeO			56.8	56.4		56.8	56.8	56.4	56.4			
			56.8			56.8	56.8					
Cinn(C-6 of Glc)											Ac	Benzoyl
1	126.5	126.6	126.6	126.5	126.6	126.5	126.5	126.6	126.6	126.5	20.9	130.7
2	106.9	106.9	107.1	107.1	106.9	107.0	107.1	107.1	107.1	107.2	172.9	130.4
3	149.4	149.4	149.2	149.3	149.4	149.2	149.3	149.3	149.3	149.5		129.3
4	139.5	139.5	139.6	139.8	139.5	139.6	139.7	139.6	139.6	139.8		133.9
5	149.4	149.4	149.2	149.3	149.4	149.2	149.3	149.3	149.3	149.5		129.3
6	106.9	106.9	107.1	107.1	106.9	107.0	107.1	107.1	107.1	107.2		130.4
7	147.3	147.3	147.1	147.1	147.3	147.1	147.1	147.1	147.1	147.1		166.6
8	115.8	115.8	116.1	116.0	115.9	116.0	116.0	116.0	116.0	116.0		
9	169.1	169.1	169.2	169.2	169.1	169.3	169.3	169.2	169.3	169.3		
MeO	56.8	56.9	56.8	56.8	56.9	56.8	56.8	56.8	56.9	56.8		
	56.8	56.9	56.8	56.8	56.9	56.8	56.8	56.8	56.9	56.8		

[a] Compound **1**, **11**, **12**, **15**−**17**, and **19** were recorded at 125 MHz in CD_3OD, **2** was recorded at 75 MHz in acetone-d_6, and **13**, **14**, **18**, and **20** were recorded at 150 MHz in CD_3OD. Assigned by HSQC and HMBC experiments.

sinapoyl]-β-D-fructofuranosyl-(2→1)-[β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**16**).

Tricornose I (**17**) was obtained as an amorphous powder, and its HRESIMS gave an $[M + 2NH_4]^{2+}$ ion peak at *m/z* 667.2387 ($C_{58}H_{82}O_{33}N_2$). On acid hydrolysis, it afforded D-glucose, D-fructose, (*E*)-sinapic acid, and (*E*)-3,4,5-trimethoxycinnamic acid. Comparison of the NMR spectral data of **17** with that of **16** indicated that the (*E*)-sinapoyl residue in **16** was replaced by an (*E*)-3,4,5-trimethoxylcinnamoyl residue in **17** (see Tables 2 and 3). The position of (*E*)-3,4,5-trimethoxylcinnamoyl linkage was established at C-3 of Fru by the HMBC spectrum, which showed cross-peaks between the proton signal at δ 5.91 (H-3 of Fru) and the (*E*)-3,4,5-trimethoxylcinnamoyl carbonyl carbon signal at δ 167.4. From these data, the structure of tricornose I was elucidated as 3-*O*-(*E*)-3,4,5-trimethoxylcinnamoyl-[4-*O*-(*E*)-sinapoyl]-β-D-fructofuranosyl-(2→1)-[β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**17**).

Tricornose J (**18**) was obtained as an amorphous powder, and HRESIMS gave an $[M + H + K]^{2+}$ ion peak at *m/z* 654.1860 ($C_{57}H_{73}O_{32}K$). On acid hydrolysis, it afforded D-glucose, D-fructose, (*E*)-sinapic acid, (*E*)-ferulic acid, and (*E*)-3,4,5-trimethoxycinnamic acid. The NMR spectral data were similar to those of **17** except for the presence of an (*E*)-feruloyl residue instead of an (*E*)-sinapoyl residue (see Tables 2 and 3). The position of (*E*)-feruloyl linkage was deduced at C-4 of Fru by the HMBC spectrum, which showed long-range correlations between the proton signal at δ 5.66 (H-4 of Fru) and the (*E*)-feruloyl carbonyl carbon signal at δ 168.1. Thus, the structure of tricornose J was established as 3-*O*-(*E*)-3,4,5-trimethoxylcinnamoyl-[4-*O*-(*E*)-feruloyl]-β-D-fructofuranosyl-(2→1)-[β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**18**).

Tricornose K (**19**) was obtained as an amorphous powder, and its HRESIMS gave an $[M + H + K]^{2+}$ ion peak at *m/z* 647.1765 ($C_{56}H_{71}O_{32}K$). On acid hydrolysis, it afforded D-glucose, D-fructose, (*E*)-sinapic acid, and (*E*)-ferulic acid. Comparison of the NMR spectral data of **19** with that of **16** indicated that the (*E*)-sinapoyl residue in **16** was replaced by an (*E*)-feruloyl residue in **19** (see Tables 2 and 3). The position of the (*E*)-feruloyl linkage was established at C-4 of Fru by the HMBC spectrum, which showed cross-peaks between the proton signal at δ 5.68 (H-4 of Fru) and the (*E*)-feruloyl carbonyl carbon signal at δ 168.2. Therefore, the structure of tricornose K was identified as 3-*O*-(*E*)-sinapoyl-[4-*O*-(*E*)-feruloyl]-β-D-fructofuranosyl-(2→1)-[β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**19**).

Tricornose L (**20**) was obtained as an amorphous powder, and its ESIMS exhibited $[M + Na]^+$ and $[M + NH_4]^+$ ions at *m/z* 1247 and 1242, respectively. On acid hydrolysis, it afforded D-glucose, D-fructose, (*E*)-sinapic acid, and (*E*)-*p*-coumaric acid. The NMR spectral data were similar to those of **16** except for the presence of an (*E*)-*p*-coumaroyl residue instead of an (*E*)-sinapoyl residue (see Tables 2 and 3). The position of the (*E*)-*p*-coumaroyl linkage was determined at C-4 of Fru by the HMBC spectrum, which showed long-range correlations between the proton signal at δ 5.66 (H-4 of Fru) and the (*E*)-*p*-coumaroyl carbonyl carbon signal at δ 168.2. From these data, the structure of tricornose L was elucidated as 3-*O*-(*E*)-sinapoyl-[4-*O*-(*E*)-*p*-coumaroyl]-β-D-fructofuranosyl-(2→1)-[β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→2)]-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**20**).

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Polatronic D polarimeter. UV spectra were recorded on a UV-2401 spectrophotometer. IR spectra (KBr disks) were recorded on an Avatar-360 spectrophotometer. ^{1}H NMR, ^{13}C NMR, COSY, HMQC, and HMBC spectra were measured on a JEOL JNM-A300, JEOL ECA-600, or Bruker AM-500 spectrometer. ESIMS was obtained on a QSTAR mass spectrometer. HRESIMS was carried out on a Bruker APEX II mass spectrometer. GC analysis was carried out on an Agilent 6890N gas chromatogragh using a HP-5 capillary column (28 m × 0.32 mm, i.d.); detection, FID; detector temperature, 260 °C; column temperature, 180 °C; carrier gas, N_2. D101 resin (Tanjin Chemical Co.). CC: silica gel (200−300 mesh, Qingdao Marine Chemical Factory). Semipreparative HPLC: Waters 600 controller, Waters column (Prep Nova-Pak HR C_{18} 7.8 × 300 mm), Waters 2487 dual λ absorbance detector, detection wavelength 228, 310 nm. Anal. HPLC: Agilent 1100 Series: column, Kromasil C_{18} 4.6 mm × 250 mm.

Plant Material. *P. tricornis* was collected in December 2003, in Yunnan Province, China. The plant was identified by one of the authors (P.F.T.). A voucher specimen (No. 031220) is deposited in the herbarium of Modern Research Center for TCM, Peking University, Beijing, People's Republic of China.

Extraction and Isolation. The dried roots of *P. tricornis* (3.0 kg) were extracted twice with 95% EtOH under reflux. After evaporation of the solvent under reduced pressure, the 95% EtOH extract (800 g) was suspended in H_2O and extracted with petroleum ether, $CHCl_3$, and *n*-BuOH, respectively. The *n*-BuOH layer (250 g) was adsorbed on a porous polymer resin D101 column (9.5 × 50 cm). The adsorbed material was eluted with 10%, 30%, and 50% aqueous MeOH and MeOH successively, after washing with H_2O. The 10% aqueous MeOH eluate (10.5 g) was chromatographed on a silica gel (200−300 mesh, 300 g) column using $CHCl_3$−MeOH−H_2O (70:10:1) as an eluent to afford fractions A−L. Fraction C (0.6 g) was subjected to semipreparative HPLC [MeOH−H_2O (20:80)] to afford **4** (58 mg) and **5** (32 mg). The 30% aqueous MeOH eluate (15.6 g) was chromatographed on a silica gel (200−300 mesh, 400 g) column using $CHCl_3$−MeOH−H_2O (70:10:1 → 80:20:2) as eluent to afford fractions A−P. Fraction C (0.4 g) was subjected to semipreparative HPLC [MeOH−H_2O (41:59)] to afford **6** (28 mg), **7** (12 mg), and **8** (15 mg). Fraction E (0.8 g) was subjected to semipreparative HPLC [MeOH−H_2O (39:61)] to afford **1** (22 mg), **2** (36 mg), **3** (28 mg), **9** (32 mg), and **10** (12 mg). Fraction L (0.5 g) was subjected to semipreparative HPLC [MeOH−H_2O (40:60)] to afford **11** (22 mg) and **12** (36 mg). Fraction O (0.8 g) was subjected to semipreparative HPLC [MeOH−H_2O (42:58)] to afford **15** (18 mg) and **16** (54 mg). The 50% aqueous MeOH eluate (18.5 g) was chromatographed on a silica gel (200−300 mesh, 500 g) column using $CHCl_3$−MeOH−H_2O (80:20:2 → 70:30:3) as eluent to afford fractions A−M. Fraction F (0.5 g) was subjected to semipreparative HPLC [MeOH−H_2O (49:51)] to afford **13** (15 mg) and **14** (9 mg). Fraction H (0.7 g) was subjected to semipreparative HPLC [MeOH−H_2O (49:51)] to afford **17** (18 mg) and **18** (12 mg). Fraction L (0.8 g) was subjected to semipreparative HPLC [MeOH−H_2O (42:58)] to afford **19** (20 mg) and **20** (10 mg).

Tricornose A (1): amorphous powder; $[\alpha]^{25}_D$ +3.4° (*c* 0.96 MeOH); UV (MeOH) λ_{max} nm 308, 232, 205; IR ν_{max} (KBr) 3426 (OH), 2933 (CH), 1719 (C=O), 1634, 1585, 1507, 1458; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz), see Tables 1 and 3; HRESIMS *m/z* 622.2343 $[M + NH_4]^+$ (calcd for $C_{26}H_{40}O_{16}N$, 622.2341).

Tricornose B (2): amorphous powder; $[\alpha]^{25}_D$ −7.8° (*c* 0.87 MeOH); UV (MeOH) λ_{max} nm 306, 232; IR ν_{max} (KBr) 3422 (OH), 2923 (CH), 1720 (C=O), 1644, 1596, 1505; ^{1}H NMR (acetone-d_6, 300 MHz) and ^{13}C NMR (acetone-d_6, 75 MHz), see Tables 1 and 3; HRESIMS *m/z* 726.2608 $[M + NH_4]^+$ (calcd for $C_{33}H_{44}O_{17}N$, 726.2603).

Tricornose C (11): amorphous powder; $[\alpha]^{25}_D$ −33.4° (*c* 0.76 MeOH); UV (MeOH) λ_{max} nm 320, 235; IR ν_{max} (KBr) 3425 (OH), 2934 (CH), 1705 (C=O), 1634, 1591, 1512, 1459; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz), see Tables 1 and 3; HRESIMS *m/z* 948.3313 $[M + NH_4]^+$ (calcd for $C_{41}H_{58}O_{24}N$, 948.3343).

Tricornose D (12): amorphous powder; $[\alpha]^{25}_D$ −23.2° (*c* 0.64 MeOH); UV (MeOH) λ_{max} nm 331, 241, 205; IR ν_{max} (KBr) 3417 (OH), 2934 (CH), 1701 (C=O), 1631, 1601, 1515, 1459; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz), see Tables 1 and 3; ESIMS *m/z* 939 $[M + Na]^+$, 934 $[M + NH_4]^+$.

Tricornose E (13): amorphous powder; $[\alpha]^{25}_D$ −13.4° (*c* 0.96 MeOH); UV (MeOH) λ_{max} nm 323, 235; IR ν_{max} (KBr) 3410 (OH), 2937 (CH), 1711 (C=O), 1632, 1594, 1513, 1460; ^{1}H NMR (CD_3OD, 600 MHz) and ^{13}C NMR (CD_3OD, 150 MHz), see Tables 1 and 3; HRESIMS *m/z* 588.1642 $[M + H + K]^{2+}$ (calcd for $C_{52}H_{65}O_{28}K$, 588.1644).

Tricornose F (14): amorphous powder; $[\alpha]^{25}_D$ −53.4° (*c* 1.02 MeOH); UV (MeOH) λ_{max} nm 324, 235; IR ν_{max} (KBr) 3415 (OH), 2930 (CH), 1710 (C=O), 1632, 1593, 1513, 1459; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 150 MHz), see Tables 1 and 3; HRESIMS *m/z* 573.1580 $[M + H + K]^{2+}$ (calcd for $C_{51}H_{63}O_{27}K$, 573.1591).

Tricornose G (15): amorphous powder; $[\alpha]^{25}_D$ −8.4° (*c* 0.54 MeOH); UV (MeOH) λ_{max} nm 330, 239, 205; IR ν_{max} (KBr) 3418 (OH), 2930 (CH), 1702 (C=O), 1630, 1592, 1515, 1459; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz), see Tables 2 and 3; HRESIMS *m/z* 559.1534 $[M + H + K]^{2+}$ (calcd for $C_{46}H_{63}O_{29}K$, 559.1540).

Tricornose H (16): amorphous powder; $[\alpha]^{25}_D$ −18.2° (*c* 0.84 MeOH); UV (MeOH) λ_{max} nm 331, 240, 207; IR ν_{max} (KBr) 3415 (OH), 2932 (CH), 1706 (C=O), 1630, 1591, 1514, 1459; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz), see Tables 2 and 3; HRESIMS *m/z* 660.2300 $[M + 2NH_4]^{2+}$ (calcd for $C_{57}H_{80}O_{33}N_2$, 660.2316).

Tricornose I (17): amorphous powder; $[\alpha]^{25}_D$ −14.6° (*c* 0.75 MeOH); UV (MeOH) λ_{max} nm 324, 236, 205; IR ν_{max} (KBr) 3408 (OH), 2934 (CH), 1710 (C=O), 1632, 1590, 1513, 1459; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz), see Tables 2 and 3; HRESIMS *m/z* 667.2387 $[M + 2NH_4]^{2+}$ (calcd for $C_{58}H_{82}O_{33}N_2$, 667.2394).

Tricornose J (18): amorphous powder; $[\alpha]^{25}_D$ −22.7° (*c* 0.98 MeOH); UV (MeOH) λ_{max} nm 324, 235; IR ν_{max} (KBr) 3409 (OH), 2934 (CH), 1710 (C=O), 1632, 1593, 1514, 1459; ^{1}H NMR (CD_3OD, 600 MHz) and ^{13}C NMR (CD_3OD, 150 MHz), see Tables 2 and 3; HRESIMS *m/z* 654.1860 $[M + H + K]^{2+}$ (calcd for $C_{57}H_{73}O_{32}K$, 654.1855).

Tricornose K (19): amorphous powder; $[\alpha]^{25}_D$ −12.6° (*c* 0.68 MeOH); UV (MeOH) λ_{max} nm 324, 235; IR ν_{max} (KBr) 3409 (OH), 2929 (CH), 1708 (C=O), 1630, 1599, 1515, 1459; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz), see Tables 2 and 3; HRESIMS *m/z* 647.1765 $[M + H + K]^{2+}$ (calcd for $C_{56}H_{71}O_{32}K$, 647.1777).

Tricornose L (20): amorphous powder; $[\alpha]^{25}_D$ −9.6° (*c* 0.55 MeOH); UV (MeOH) λ_{max} nm 322, 236, 205; IR ν_{max} (KBr) 3403 (OH), 2930 (CH), 1706 (C=O), 1632, 1601, 1515, 1458; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz), see Tables 2 and 3; ESIMS *m/z* 1247 $[M + Na]^+$, 1242 $[M + NH_4]^+$.

Acid Hydrolysis. Each compound (3 mg) was hydrolyzed with 2 N aqueous CF_3COOH (5 mL) at 110 °C for 6 h in a sealed tube. After this period, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 × 5 mL). The combined EtOAc extracts were washed with H_2O and then evaporated to dryness in a vacuum. The residue was dissolved in MeOH and subjected to HPLC [Kromasil C_{18} 4.6 mm × 250 mm, CH_3CN-H_2O-HAc (22.5:77.5:0.5), 1.0 mL/min, UV 228 nm]. Benzoic acid (15.3 min) was detected from **2**; (*E*)-ferulic acid (8.6 min) was detected from **14**, **18**, and **19**; (*E*)-sinapic acid (8.0 min) was detected from **11**−**20**; (*E*)-3,4,5-trimethoxycinnamic acid (26.9 min) was detected from **1**, **2**, **11**, **13**, **14**, **17**, and **18**; (*E*)-*p*-coumaric acid (8.3 min) was detected from **20**. After repeated evaporation to dryness of the aqueous layer with MeOH until neutral, the residue was dissolved in pyridine (0.060 mL), then hexamethyldisilazine (0.060 mL) and trimethylsilyl chloride (0.020 mL) were added, and the reaction mixture was stirred at 60 °C for 30 min. The supernatant was subjected to GC. D-Glucose (12.45 min) and D-fructose (10.30 min) were detected from **1**, **2**, and **11**−**20**.

References and Notes

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