New Polyacylated Sucrose Derivatives from the Bark of *Prunus padus*

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Four new polyacylated sucrose derivatives were found in the bark of *Prunus padus*. All the compounds were shown to be derivatives of 3-*O*-*p*-coumaroyl-β-D-fructofuranosyl α-D-glucopyranoside, and their full structures were elucidated on the basis of spectroscopic and chemical evidence.

Keywords *Prunus padus*; Rosaceae; *p*-coumaric acid ester; sucrose ester; bark

A considerable number of mono- and oligosaccharides conjugated with hydroxycinnamoyl groups have been found to occur in many species of higher plants,[1] some of which are noted for their pharmacological and biological activities.[2] The occurrence of conjugates containing sucrose as the core sugar, however, is limited to several groups of plants, *i.e.*, Polygonaceae,[3] Polygalaceae[4] and Brassicaceae[5] plants, and especially in Liliaceae,[6] in spite of the widespread occurrence of phenylpropanoids and sucrose. Recently, galloylsucroses have been detected in Chinese rhubarb as a new class of gallotannins.[7] As a part of our systematic studies on the chemical constituents of the genus *Prunus*,[8] we have now examined the bark of *Prunus padus* and isolated four new phenylpropanoid sucrose esters. This paper provides an account of the structure elucidation of the new components.

The methanolic extract of the fresh bark of *P. padus* was partitioned between water and chloroform, and then between water and *n*-butanol. The *n*-butanol-soluble fraction, upon repeated silica gel and Sephadex LH-20 column chromatographies, gave the pure compounds **1**—**4**.

Compound **1** was obtained as a white amorphous powder and exhibited a bitter taste. The presence of hydroxyl group(s) (3450 cm^{-1}), carbonyl group(s) (1750 cm^{-1}), a double bond (1630 cm^{-1}) and an aromatic ring (1605, 1585, 1510 cm^{-1}) was indicated by the infrared (IR) spectrum. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed typical proton signals of a *p*-coumaroyl moiety [δ 7.98 and 6.67 (each 1H, d, J=15.9 Hz; 7.76 and 7.12 (each 2H, d, J=8.6 Hz)] and four alcoholic acetyl groups [δ 2.08, 2.01, 2.00 and 1.95 (each 3H, s)]. Acetylation of **1** with acetic anhydride in pyridine yielded the corresponding peracetate (**1a**), the ^{1}H-NMR spectrum of which showed a new aromatic acetoxyl and three additional alcoholic acetoxyl signals. Hydrolysis of **1** with 3% sodium methoxide solution afforded methyl *p*-coumarate and sucrose, confirming its constituents. Thus, the fundamental structure of **1** was indicative of a *p*-coumaroyl ester of sucrose with four alcoholic acetyl moieties. The electron impact mass spectrum (EI-MS) of **1a** supported this finding showing a molecular

TABLE I. ^{1}H-NMR Spectral Data for **1**, **1a**, **1b**, **2**—**4** and Sucrose[a]

	1	1a	1b	2	3	4	Sucrose
Fructose moiety							
1a	4.20 d (12.1)	4.41—4.13	4.19 d (12.1)	4.63 d (11.6)	4.70 d (11.8)	4.68 d (11.8)	4.31 d (12.1)
1b	4.00 d (12.1)		4.12 d (12.1)	4.51 d (11.6)	4.61 d (11.8)	4.59 d (11.8)	4.27 d (12.1)
3	6.32 d (7.9)	5.60 d (6.4)	6.23 d (7.9)	6.14 d (8.0)	6.10 d (8.4)	6.13 d (8.6)	4.94 d (7.9)
4	4.98 dd (7.9, 7.9)	5.48 dd (6.4, 6.4)	5.14 dd (7.9, 7.9)	5.05 dd (8.0, 8.0)	5.01 dd (8.4, 8.4)	5.05 dd (8.6, 8.6)	4.98 dd (7.9, 7.9)
5	4.57 ddd (7.9, 4.6, 4.6)	4.41—4.13	4.51 ddd (7.9, 5.4, 3.0)	4.57 ddd (8.0, 6.0, 3.2)	4.55 ddd (8.4, 6.1, 3.0)	4.54 ddd (8.6, 6.2, 2.8)	4.47 m
6a	4.28 d (4.6)	4.41—4.13	4.34 dd (12.4, 5.4)	4.39 dd (12.0, 6.0)	4.34 dd (12.3, 6.1)	4.39 dd (12.1, 6.2)	4.32 dd (12.1, 4.8)
6b			4.24 dd (12.4, 3.0)	4.33 dd (12.0, 3.2)	4.29 dd (12.3, 3.0)	4.31 dd (12.1, 2.8)	4.26 dd (12.1, 3.0)
Glucose moiety							
1′	6.18 d (3.7)	5.67 d (3.6)	6.00 d (3.7)	6.14 d (3.8)	5.97 d (3.6)	5.99 d (3.7)	6.13 d (3.9)
2′	5.23 dd (9.8, 3.7)	4.93 dd (10.0, 3.6)	3.99 dd (9.7, 3.7)	5.23 dd (9.7, 3.8)	4.05 dd (9.5, 3.6)	4.00 dd (9.4, 3.7)	4.11 dd (9.2, 3.9)
3′	5.92 dd (9.8, 9.8)	5.43 dd (10.0, 10.0)	4.47 dd (9.7, 9.7)	6.00 dd (9.7, 9.7)	5.77 dd (9.5, 9.5)	5.83 dd (9.4, 9.4)	4.61 dd (9.2, 9.2)
4′	5.39 dd (9.8, 9.8)	5.04 dd (10.0, 10.0)	4.10 dd (9.7, 9.7)	4.06 dd (9.7, 9.7)	5.30 dd (9.5, 9.5)	3.95 dd (9.4, 9.4)	4.16 dd (9.2, 9.2)
5′	4.78 ddd (9.8, 4.5, 4.5)	4.41—4.13	4.64 ddd (9.7, 4.7, 2.4)	4.75 ddd (9.7, 6.2, 1.5)	4.78 ddd (9.5, 4.5, 4.5)	4.75 br dd (9.4, 5.7)	4.71 ddd (9.2, 4.5, 2.0)
6′a	4.46 br d (4.5)	4.41—4.13	4.42 dd (11.9, 2.4)	4.91 dd (11.6, 1.5)	4.47 br d (4.5)	4.91 br d (10.5)	4.46 dd (11.6, 2.0)
6′b			4.27 dd (11.9, 4.7)	4.61 dd (11.6, 6.2)		4.59 dd (10.5, 5.7)	4.30 dd (11.6, 4.5)
p-Coumaroyl moiety							
2″ and 6″	7.76 d (8.6)	7.63 d (8.5)	7.55 d (8.6)	7.65 d (8.4)	7.63 d (8.5)	7.63 d (8.7)	
3″ and 5″	7.12 d (8.6)	6.14 d (8.5)	7.03 d (8.6)	7.10 d (8.4)	7.11 d (8.5)	7.08 d (8.7)	
7″	7.98 d (15.9)	7.75 d (15.9)	7.95 d (15.9)	7.96 d (15.8)	7.94 d (16.1)	7.93 d (16.1)	
8″	6.67 d (15.9)	6.48 d (15.9)	6.54 d (15.9)	6.63 d (15.8)	6.61 d (16.1)	6.60 d (16.1)	
Acetyl moieties							
	2.08 s	2.31 s		2.10 s	2.11 s	2.10 s	
	2.01 s	2.13 s (×2)		2.06 s	2.02 s	2.02 s	
	2.00 s	2.11 s		2.05 s	1.96 s	1.95 s	
	1.95 s	2.09 s		1.94 s	1.93 s		
		2.07 s					
		1.97 s					
		1.87 s					

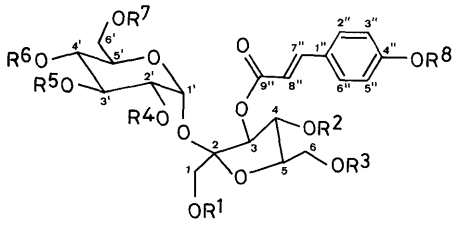
a) Assignments were carried out with the aid of double resonance experiments. Spectra of **1**, **1b**, **2**—**4** and sucrose were measured in C_5D_5N–CD_3OD (4 : 1), and that of **1a** in $CDCl_3$. J values in parentheses are expressed in hertz (Hz). Data for sucrose are cited from reference 6*c*.

TABLE II. ^{13}C-NMR Spectral Data for **1**, **1a**, **1b**, **2**—**4** and Sucrose[a)]

Carbon No.	1	1a	1b	2	3	4	Sucrose
Fructose moiety							
1	64.8	64.6[b)]	65.6	65.4	65.7	65.5	64.6
2	105.6	104.7	104.7	103.2	103.3	103.0	105.4
3	79.0	77.2	79.8	78.9	79.0	78.7	79.8
4	73.8	76.0	73.3	73.5	73.3	72.9	75.5
5	84.7	79.8	84.5	84.6	84.9	84.5	84.0
6	62.8	64.3[b)]	62.4[b)]	63.0	63.1[b)]	62.9	62.8[b)]
Glucose moiety							
1′	89.9	90.9	93.2	90.2	93.0	93.2	93.3
2′	71.1[b)]	70.8[c)]	73.3	71.8[b)]	70.2[c)]	70.8	73.1
3′	70.8[b)]	70.5[c)]	75.2[c)]	71.6[b)]	74.2	77.0	74.8[c)]
4′	69.5[c)]	69.3	71.8	69.2	70.1[c)]	69.5	71.6
5′	68.7[c)]	69.3	75.1[c)]	73.0	69.2	72.0	74.6[c)]
6′	63.0	62.7	62.6[b)]	64.1	63.3[b)]	64.5	62.3[b)]
p-Coumaroyl moiety							
1″	126.1	132.4	126.1	126.0	126.2	126.1	
2″	131.0	130.1	130.8	131.1	131.2	131.1	
3″	116.8	122.7	116.6	116.8	116.9	116.8	
4″	161.6	153.3	161.3	161.8	161.8	161.6	
5″	116.8	122.7	116.6	116.7	116.9	116.8	
6″	131.0	130.1	130.8	131.1	131.2	131.1	
7″	146.4	146.0	145.8	146.7	146.8	146.6	
8″	114.4	117.5	114.8	113.9	114.2	114.1	
9″	167.1	165.8	166.9	167.2	167.8	167.2	
Acetyl moieties							
	170.7	170.5		170.9	171.1	171.0	
	170.5	170.4		170.8	170.7	170.7	
	170.2	170.3		170.4	170.5	170.4	
	170.0	170.2		170.2			
		170.1					
		169.8					
	20.7	20.8		20.7	20.9	21.1	
	20.6	20.6		20.6	20.8	20.8	
	20.5	20.4			20.7	20.6	
	20.4	20.3					

a) Spectra were measured in C_5D_5N. *b*, *c*) Signals bearing the same alphabetical superscript may be interchangeable in each column. Data for sucrose are cited from reference 6*d*.

ion peak at *m/z* 824 ($C_{37}H_{44}O_{21}$) and prominent fragment ion peaks at *m/z* 477, 331 and 189 assignable to the ions of a hexose with four acetyl and one *p*-coumaroyl groups, a tetraacetylhexose, and an acetyl-*p*-coumaroyl group, respectively. Comparison of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra between **1** and **1a**, and between **1** and sucrose demonstrated that all four hydroxyl groups of the glucose residue were acylated (Table II). In addition, the ^{1}H-NMR signals assignable to the fructose H-3 and the glucose H-2, H-3 and H-4 appeared obviously downfield as compared with those of sucrose (Table I). In the 4,6-di-*O*-acylated glucose, no marked downfield shift seems to be observed at the H-6 methylene protons in the ^{1}H-NMR spectrum.[6c)] Thus, compound **1** was a 3,2′,3′,4′,6′-pentaacylated derivative of the sucrose moiety. Mild hydrolysis of **1** with 10% ammonia solution in methanol–water (2:1) for 30 min at room temperature furnished a partial hydrolysis product (**1b**), a *p*-coumaroylsucrose. In the ^{1}H-NMR spectrum of **1b**, the H-3 proton of the fructofuranosyl residue was deshielded to appear at δ 6.23. Compound **1b** was formulated as 3-*O*-*p*-coumaroyl-β-D-fructofuranosyl α-D-glucopyranoside. Accordingly, the structure of **1** was shown to be 3-*O*-*p*-coumaroyl-β-D-fructofuranosyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside.



	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
1	H	H	H	Ac	Ac	Ac	Ac	H
1a	Ac	Ac	Ac	Ac	Ac	Ac	Ac	Ac
1b	H	H	H	H	H	H	H	H
2	Ac	H	H	Ac	Ac	H	Ac	H
3	Ac	H	H	H	Ac	Ac	Ac	H
4	Ac	H	H	H	Ac	H	Ac	H

Chart 1

Compounds **2**, **3** and **4** were obtained as white amorphous powders. A detailed inspection of the IR, ^{1}H- and ^{13}C-NMR spectra indicated that **2** and **3** consist of *p*-coumaric acid, sucrose and four alcoholic acetyl groups, and **4** consists of *p*-coumaric acid, sucrose and three alcoholic acetyl groups. Compounds **2**, **3** and **4** were also concluded to be derivatives of 3-*O*-*p*-coumaroyl-β-D-fructofuranosyl α-D-glucopyranoside, since the IR and ^{1}H-NMR spectra, and the thin-layer chromatographic (TLC) behavior of the peracetates (**2a**—**4a**) of **2**—**4** were in excellent agreement with those of **1a**. The ^{1}H-NMR spectra provided information for the establishment of the positions of the acyl moieties. The downfield shifts due to acylation were observed at the following signals in each compound; the fructose H_2-1, H-3, the glucose H-2, H-3 and H_2-6 in **2**, the fructose H_2-1, H-3, the glucose H-3 and H-4 in **3**, and the fructose H_2-1, H-3, the glucose H-3 and H_2-6 in **4**. In the case of **3**, the significant upfield shifts of the signals of the glucose C-5 (5.4 ppm) compared with that of sucrose in the ^{13}C-NMR spectrum verified that the glucose C-4 and C-6 hydroxyl groups were acylated, but the glucose H_2-6 protons showed no downfield shift in the ^{1}H-NMR spectrum, which seemed to be due to the acylation of the glucose C-4 hydroxyl group as in **1**.

Thus, the respective structures of **2**, **3** and **4** were characterized as 1-*O*-acetyl-3-*O*-*p*-coumaroyl-β-D-fructofuranosyl 2,3,6-tri-*O*-acetyl-α-D-glucopyranoside, 1-*O*-acetyl-3-*O*-*p*-coumaroyl-β-D-fructofuranosyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside, and 1-*O*-acetyl-3-*O*-*p*-coumaroyl-β-D-fructofuranosyl 3,6-di-*O*-acetyl-α-D-glucopyranoside.

The facile migration and scission of acyl groups in partially acylated polyhydric alcohols or carbohydrates often occur under acidic and basic conditions, and merely on heating or melting the compounds.[9)] In this study, no migration or scission of the acyl groups was observed during the isolation and purification procedures.

Compounds **1**—**4** are new natural products, and this is believed to be the first report of polyacylated sucroses from a Rosaceae plant.

Experimental

The following instruments were used for the measurements of the spectral and physical data. Optical rotations were measured with a JASCO DIP-360 automatic digital polarimeter. IR spectra were recorded on a Hitachi 260-36 or a Perkin-Elmer 1710 FT-IR instrument, ultraviolet (UV) spectra on a Hitachi 557 spectrometer, and mass spectra (MS) on a Hitachi

M-80 machine. ^{1}H-NMR and ^{13}C-NMR spectra were taken with a Bruker AM-400 spectrometer. Chemical shifts are given in δ-values referred to internal tetramethylsilane (TMS), and the following abbreviations are used; s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, br = broad. Fuji Davison silica gel, BW-300 and BW-340 (Fuji Davison Co., Ltd.), and Sephadex LH-20 (Pharmacia Fine Chemicals Co., Ltd.) were used for column chromatographies. TLC was carried out on precoated Kiesel gel 60 F_{254} (0.25 mm thick, Merck), and spots were visualized under UV light (254 nm) and by spraying 10% H_2SO_4 followed by heating.

Extraction and Isolation The fresh bark of *Prunus padus* (3.2 kg) collected at Tokachi-kita, Hokkaido (Japan) in May 1988 was extracted with hot MeOH and treated as described in the previous paper[8g] to give **1** (152 mg), **2** (15.9 mg), **3** (31.7 mg) and **4** (32.5 mg) as white amorphous powders.

3-*O*-*p*-Coumaroyl-β-D-fructofuranosyl 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranoside (1) $[\alpha]_D^{27}$ +36.5° (c = 1.04, MeOH). EI-MS m/z (%): 435 (2.8), 331 (3.1), 289 (12), 247 (15), 187 (14), 169 (41), 147 (100), 127 (41), 109 (44). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 2960, 2925 (CH), 1750 (C=O), 1630 (CH=CH), 1605, 1585, 1510 (aromatic ring), 1440, 1370, 1260, 1160, 1030, 860, 800. UV λ_{max}^{MeOH} nm (log ε): 228 (4.31), 300 sh (4.52), 312 (4.60). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Acetylation of 1 A mixture of **1** (19.0 mg), Ac_2O and pyridine was left standing overnight. The crude acetate was chromatographed on silica gel column with $CHCl_3$–EtOAc (5 : 1) to give a white amorphous powder (**1a**) (25.4 mg). EI-MS m/z (%): 824 $[M]^+$ (0.1), 782 (0.8), 331 (81), 189 (99), 169 (99), 147 (100), 109 (99). IR ν_{max}^{KBr} cm^{-1}: 2950 (CH), 1740 (C=O), 1630 (CH=CH), 1595, 1500 (aromatic ring), 1430, 1365, 1220, 1150, 1030, 950, 900, 850, 830, 795. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Alkaline Hydrolysis of 1 A solution of **1** (20.5 mg) in 3% NaOMe–MeOH was left standing at room temperature for 10 min. After dilution with MeOH, the reaction solution was passed through a cation exchange resin (Amberlite IR-120B) and the eluate was subjected to Sephadex LH-20 column chromatography with MeOH as the eluent to furnish methyl *p*-coumarate (4.1 mg) and sucrose (8.3 mg), which were identified by direct TLC comparison with authentic samples. Methyl *p*-coumarate, *Rf* 0.68 ($CHCl_3$–MeOH = 14 : 1). Sucrose, *Rf* 0.15 (*n*-BuOH–AcOH–H_2O = 3 : 1 : 1).

Partial Hydrolysis of 1 Compound **1** (21.7 mg) in 10% NH_3 in MeOH–H_2O (2 : 1) was kept at room temperature for 30 min. The reaction mixture was evaporated to dryness under reduced pressure and the crude product was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (5 : 2 : 0.1) to yield 3-*O*-*p*-coumaroyl-β-D-fructofuranosyl α-D-glucopyranoside (9.3 mg) (**1b**) as a white amorphous powder. $[\alpha]_D^{25}$ −11.0° (c = 1.03, MeOH). EI-MS m/z (%): 308 (0.9), 164 (30), 147 (70), 120 (100), 91 (58). IR ν_{max}^{KBr} cm^{-1}: 3423 (OH), 2930 (CH), 1702 (C=O), 1631 (CH=CH), 1605, 1516 (aromatic ring), 1262, 1171, 1054, 834. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

1-*O*-Acetyl-3-*O*-*p*-coumaroyl-β-D-fructofuranosyl 2,3,6-Tri-*O*-acetyl-α-D-glucopyranoside (2) $[\alpha]_D^{25}$ +18.9° (c = 0.93, MeOH). EI-MS m/z (%): 393 (5), 331 (7), 205 (7), 187 (10), 169 (52), 164 (14), 147 (100), 127 (37), 109 (55). IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 2930 (CH), 1740 (C=O), 1630 (CH=CH), 1605, 1585, 1510 (aromatic ring), 1440, 1370, 1240, 1160, 1040, 835. UV λ_{max}^{MeOH} nm (log ε): 228 (4.34), 300 sh (4.49), 312 (4.56). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

1-*O*-Acetyl-3-*O*-*p*-coumaroyl-β-D-fructofuranosyl 3,4,6-Tri-*O*-acetyl-α-D-glucopyranoside (3) $[\alpha]_D^{27}$ +45.2° (c = 1.12, MeOH). EI-MS m/z (%): 435 (3.2), 331 (2.7), 205 (7), 187 (13), 169 (34), 147 (100), 127 (34), 109 (38). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 2920 (CH), 1740 (C=O), 1625 (CH=CH), 1600, 1580, 1510 (aromatic ring), 1440, 1370, 1240, 1160, 1035, 940, 830. UV λ_{max}^{MeOH} nm (log ε): 228 (4.27), 300 sh (4.47), 312 (4.55). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

1-*O*-Acetyl-3-*O*-*p*-coumaroyl-β-D-fructofuranosyl 3,6-Di-*O*-acetyl-α-D-glucopyranoside (4) $[\alpha]_D^{27}$ +42.2° (c = 1.20, MeOH). EI-MS m/z (%): 435 (2), 331 (1), 205 (11), 187 (16), 169 (29), 164 (16), 147 (100), 127 (43), 109 (35). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 2960, 2920 (CH), 1720 (C=O), 1625 (CH=CH), 1600, 1580, 1510 (aromatic ring), 1440, 1375, 1250, 1160, 1040, 940, 830, 800. UV λ_{max}^{MeOH} nm (log ε): 228 (4.32), 300 sh (4.53), 312 (4.61). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Acetylation of 2, 3 and 4 Treatment of **2** (10.3 mg), **3** (10.3 mg) and **4** (6.7 mg) with Ac_2O in pyridine at room temperature overnight gave the corresponding peracetates, **2a** (8.1 mg), **3a** (12.0 mg) and **4a** (5.1 mg) as white amorphous powders. The IR and ^{1}H-NMR spectra, and the TLC behavior of the peracetates coincided precisely with those of **1a**.

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