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PHENYLPROPANOID GLYCOSIDES OF *PRUNUS SSIORI*

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Key Word Index—*Prunus ssiori*; Rosaceae; bark; phenylpropanoid glucosides; caffeic acid esters.

Abstract—Two new bitter phenylpropanoid glucosides, 2-(3,4-methylenedioxyphenyl)-ethyl-(6-*O*-caffeoyl)-β-D-glucopyranoside and 3-*O*-caffeoyl-β-D-fructofuranosyl, 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside, have been isolated together with the known compounds, 6-*O*-caffeoyl-D-glucopyranoside and 2-(3,4-dihydroxyphenyl)-ethyl-(6-*O*-caffeoyl)-β-D-glucopyranoside, from the bark of *Prunus ssiori*. The structures of the isolated compounds have been established by extensive spectroscopic studies.

INTRODUCTION

Prunus ssiori is reputed to possess therapeutic properties [1–4]. The bark of this plant tastes bitter and is used for the treatment of coughs, headaches, heart and intestinal troubles, and as a sedative in Europe and the United States [3, 4].

The present paper reports the isolation and structure elucidation of new bitter glucosides in *P. ssiori*. The occurrence of conjugates containing sucrose as the core sugar, however, is limited to several groups of plants, i.e. Polygonaceae [5], Polygalaceae [6] and Brassicaceae [7] and especially in Liliaceae [8–10], in spite of the widespread occurrence of phenylpropanoids and sucrose.

RESULTS AND DISCUSSION

The methanolic extract of the fresh bark of *P. ssiori*, upon repeated silica gel and sephadex LH-20 column chromatography gave pure **1–4**.

Compound **1** analysed for $C_{24}H_{26}O_{11}$ (SI-MS, *m/z* 491 $[M + H]^+$). It gave a brownish-violet colour with vanillin–sulphuric acid reagent and a positive ferric chloride test for phenols. The ^1H NMR spectrum showed the existence of a *trans*-olefin system, aromatic protons of an ABC system, methylenedioxy protons and sugar protons. The EI-mass spectrum showed a peak at *m/z* 163, a characteristic fragment ion peak due to caffeic acid. The more important fragments [caffeic acid $- H]^-$ at *m/z* 179 and caffeic acid–H–CO_2 at *m/z* 135.

Acid hydrolysis of **1** in refluxing aqueous 2 M HCl–MeOH (1:1) yielded D-glucose and caffeic acid.

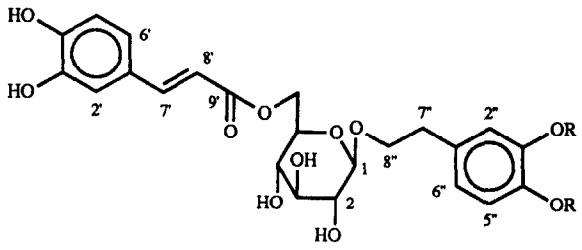
Compound **1** was hydrolysed with sodium methoxide to give methyl caffeate and 2-(3,4-methylene dioxyphenyl)-ethyl-β-D-glucopyranoside **1a**. Comparison of the ^1H NMR and ^{13}C NMR spectral data of **1** with that of **1a** revealed that the signals assignable to C-5 and C-6 of the glucose moiety confirmed location of the caffeoyl group at C-6 in the glucose moiety [11].

Compound **2** was obtained as a white amorphous powder and exhibited a bitter taste. The presence of hydroxyl group (S) (3450 cm^{-1}) carbonyl groups (S) (1755 cm^{-1}), a double bond (1635 cm^{-1}) and an aromatic ring (1605, 1585, 1515 cm^{-1}) was indicated by the IR spectrum. The ^1H NMR spectrum showed the signals assignable to a *trans*-olefine system, aromatic, protons of ABC system, sugar protons and four alcoholic acetyl groups [δ2.08, 2.01 2.00 and 1.98 (each 3H, s)]. Acetylation of **2** with acetic anhydride in pyridine yielded the corresponding peracetate, the ^1H NMR spectrum of which showed two new aromatic acetoxyl and three additional actoxyl signals.

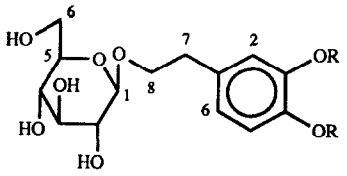
Alkaline methonolysis of **2** with 3% sodium methoxide gave methyl caffeate and sucrose, confirming the suggested structure. Thus, the fundamental structure of **2** was indicative of a caffeoyl ester of sucrose with four alcoholic acetyl moieties. Compound **2** analysed for $C_{29}H_{36}O_{18}$, (SI-MS) *m/z* 673 $[M + H]^+$. The ^{13}C NMR spectra, in comparison with that of sucrose, demonstrated that four hydroxyl groups of the glucose residue were acylated (Table 1). The ^1H 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. Accordingly, the structure of **2** was shown to be 2-*O*-caffeoyl-β-D-fructofuranosyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside.

Facile migration and scission of acyl groups of partially acylated polyhydric alcohols or carbohydrates often occurs under acidic and basic conditions or by merely heating or melting the compounds [12]. In this study, no migration or scission of acyl groups was observed during the isolation and purification procedures.

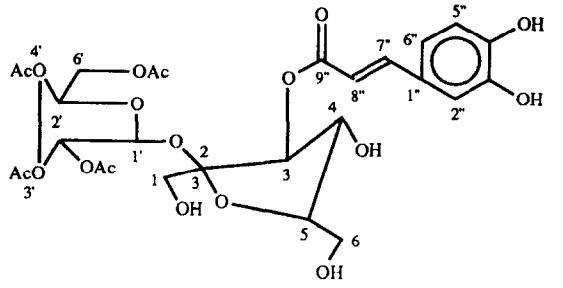
Compound **3**, $C_{23}H_{26}O_{11}$, (SI-MS, *m/z* 479 $[M + H]^+$]) had spectral data similar to those of **1**, the only



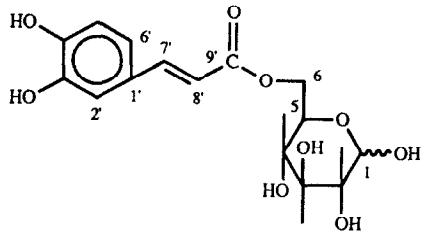
1 R = —CH_2—
3 R = —H—



1a R = —CH_2—
3a R = —H—



2



4

difference in the ^{1}H and ^{13}C NMR spectra was the absence of methylenedioxy protons and carbon signals, respectively. The ^{1}H NMR spectrum indicated the presence of caffeoyl, phenethyl alcohol and sugar moieties. Acid hydrolysis of **3** yielded D-glucose and caffeic acid. Alkaline methanolysis with sodium methoxide gave methyl caffeate and 2-(3,4-dihydroxyphenyl)-ethyl-β-D-glucopyranoside (**3a**). The ^{13}C NMR spectral data (Table 1) revealed that the caffeoyl moiety was located at glucose C-6.

Compound **4**, $C_{15}H_{18}O_9$ (SI-MS *m/z* 342 $[M]^+$) showed chemical shifts of the anomeric carbon signal (δ94.5) in agreement with that of D-glucose. The linkage of the sugar unit was also inferred from the anomeric proton signal at δ5.5 and (J = 8.1 Hz). Alkaline methanolysis of **4** with sodium methoxide gave methyl caffeate and D-glucose. The chemical shift value in the ^{13}C NMR spectrum (δ60.5, C-6) indicated the location of caffeic acid to be at C-6 of the sugar.

EXPERIMENTAL

General. Mps: uncorr. IR spectra were measured in KBr discs. NMR were measured at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts are given on the δ(ppm) scale with TMS as int. standard. MS were measured at 70 eV. TLC was performed on silica gel G (Merck) using $CHCl_3$–MeOH (4:1) as solvent system. Spots were visualized by their fluoresences at 254 nm or by spraying with $FeCl_3$ or with vanillin–H_2SO_4 reagents.

Plant material. Fr. bark of *P. ssiori* was collected from trees growing in the Assiut area in May 1992. The plant was identified by Prof. Dr N. El-Hadidy, Faculty of Science, Cairo University.

Extraction. Fr. bark (3 kg) was extracted with petrol. The bark was further exhaustively extracted with hot MeOH to yield 60 g crude extract. The concd MeOH extract was applied to a column packed with silica gel, eluted with $CHCl_3$–MeOH (4:1) and 100 frs (each *ca* 50 ml) were collected. Repeated Sephadex LH-20 CC was also carried out. Some of the isolated compounds were purified by prep. TLC.

Compound (**1**). Amorphous powder. $[\alpha]^{20}$ $-32.1°$ (MeOH; *c* 1.5). IR ν_{max}^{KBr} cm^{-1}: 3420, 1700, 1650, 1590, 1520, 970. ^{1}H NMR (CD_3OD): caffeoyl moiety δ7.01 (1H, *d*, J = 2.2 Hz, H-2), 6.80 (1H, *d*, J = 8.1 Hz, H-5), 6.90 (1H, *dd*, J = 8.1, 2.1 Hz, H-6'), 7.61 (1H, *d*, J = 16 Hz, H-7'), 6.31 (1H, *d*, J = 16 Hz, H-8'): glucose moiety δ4.29 (1H, *d*, J = 7.8 Hz, H-1) 3.38–4.01, (2H, overlapping, H-2, H-3), 3.26 (1H *t*-like, H-4), 3.56 (1H, *m*, H-5), 4.50 (1H, *dd*, J = 12, 2.3 Hz, H-6α), 4.35 (1H, *dd*, J = 12, 6.2 Hz, H-6β): phenethyl alcohol moiety δ6.71 (1H, *d*, J = 2 Hz, H-2') 6.66 (1H, *d*, J = 8 Hz, H-5'), 6.55 (1H, *dd*, J = 8 Hz, 2 Hz, H-6'), 2.8 (2H *t*-like, H-7), 3.98 (1 H, *m*, H-8α), 3.71 (1H, *m*, H-8β), 5.95 (2H, *s*, -OCH_2O-).

Alkaline methanolysis. Compound **1** (30 mg) was dissolved in 3% NaOMe in MeOH (5 ml) and the soln allowed to stand 1 hr at room temp. The residue was purified by prep. TLC to give Me caffeate and 2-(3,4-methylenedioxyphenyl)-ethyl-β-D-glucopyranoside (**1a**) (5 mg), amorphous powder, mp 171–174 . IR ν^{KBr} cm^{-1}: 3440, 1620, 1530. ^{1}H NMR (CD_3OD): glucose moiety δ4.31 (1H, *d*, J = 7.5 Hz, H-1), 3.3–3.38 (2H, overlapping H-2, H-3), 3.2 (1H, *dd*, J = 8.7, 7.5 Hz, H-4), 3.85 (1H, *dd*, J = 12, 2 Hz, H-6a): phenethyl alcohol moiety δ7.03 (1H, *d*, J = 2, 1 Hz, H-2''), 6.72 (1H, *d*, J = 8.1 Hz, H-5''), 6.82 (1H, *dd*, J = 8.1, 2 Hz, H-6''), 2.81 (2H *t*-like, H-7''), 4.01 (1H, *m*, H-8''α), 3.61–3.71 (3H, overlapping, H-5), H-6β, and H-8β).

Compound **2**. $[\alpha]^{20}$ $+41.5°$ (MeOH; *c* 1.1). EI-MS *m/z* (rel. int.) 673 (2.5), 631 (2), 180 (100), 127 (41), 109 (30). IR ν^{KBr} cm^{-1} 3450 (OH), 2960, 2925 (CH), 1755 (C=O), 1635 (CH=CH), 1605, 1585 (aromatic ring) 1360, 1260, 1515,

Table 1. ^{13}C NMR spectral data of **1–4** and caffeic acid in DMSO-d_6

C	1	2	3	4	Caffeic acid
Phenethyl moiety					
1	131.7 *s*		131.5		
2	116.6 *d*		116.4		
3	146.8 *s*		146.4		
4	144.3 *s*		144.5		
5	117.3 *d*		117.2		
6	121.1 *d*		121.6		
7	36.2 *t*		36.6		
8	72.3 *t*		72.4		
Caffeoyl moiety					
1′	126.9 *s*	125.8	127.6	125.8	126.3
2′	115.1 *d*	113.3	114.5	113.3	114.5
3′	149.1 *s*	145.2	149.3	146.8	145.3
4′	146.2 *s*	148.3	146.5	148.6	145.3
5′	115.9 *d*	115.1	116.2	114.8	114.5
6′	122.9 *d*	121.9	123.1	121.5	121.5
7′	147.3 *d*	116.5	147.6	115.7	115.8
8′	115.4 *d*	146.1	115.1	146.8	144.9
9′	169.3 *s*	170.0	169.4	165.2	167.2
Fructose moiety					
1	—	64.7	—	—	—
2	—	105.1	—	—	—
3	—	78.9	—	—	—
4	—	73.5	—	—	—
5	—	84.2	—	—	—
6	—	62.4	—	0.2	—
Glucose moiety					
1″	104.3 *d*	89.6	104.5	94.2	—
2″	75.2 *d*	71.2	75.1	72.4	—
3″	77.7 *d*	70.9	77.8	77.7	—
4″	71.3 *d*	69.2	71.9	69.5	—
5″	75.6 *d*	68.1	75.3	76.4	—
6″	64.1	63.2	64.3	60.5	—
Methylenedioxy	102.1 *t*	—	—	—	—
Acetyl moiety		170.7, 170.5			
		170.1, 170			
		20.2, 20.1			
		20.5, 20.3			

860. UV λ^{MeOH} nm (log ε) 230 (4.1), 315 (4.5). ^{1}H NMR (CD_3OD): caffeoyl moiety δ7.01 (1H, *d*, J = 2.2 Hz, H-2′), 6.71 (1H, *d*, J = 8.2 Hz, H-5′), 6.88 (1H, *d*, J = 28.2, 2.2 Hz, H-6′), 7.55 (1H, *d*, J = 16 Hz, H-7′), 6.31 (1H, *d*, J = 16 Hz, H-8′): fructose moiety 4.21 (1H, *d*, J = 12 Hz, H-1α), 4.04 (1H, *d*, J = 12 Hz, H-1β), 6.36 (1H, *d*, J = 7.9 Hz, H-3), 4.92 (1H, *dd*, J = 7.9, 7.9 Hz, H-4), 4.55 (1H, *ddd*, 7.9, 4.5 Hz, H-5), 4.30 (1H, *d*, J = 4.5 Hz, H-6): glucose moiety δ6.2 (1H, J = 3.8, H-1′), 5.15 (1H, *dd*, J = 9.5, 3.8 Hz, H-2′), 5.90 (1H, *dd*, J = 9.5, 9.5 Hz, H-3′), 5.42 (1H, *dd*, J = 9.5, 9.5 Hz, H-4′), 4.81 (1H, *ddd*, J = 9.5, 4.5, 4.5 Hz, H-5′), 4.84 (1H, *br d*, J = 4.5 Hz, H-6): acetyl moieties δ2.08, 2.01, 2.0, 1.98 (3H, each, *s*).

Compound **3**. Amorphous powder (150 mg). $[\alpha]^{20}$ − 20° (MeOH; *c* 0.9). IR ν^{KBr} cm^{-1}: 3425, 1690, 1635, 1605, 1525, 960. ^{1}H NMR (CH_3OD): caffeoyl moiety δ7.03 (1H, *d*, J = 2 Hz, H-2), 6.75 (1H, *d*, J = 8.5 Hz, H-5), 6.88 (1H, *dd*, J = 8.5, 2 Hz, H-6′), 7.55 (1H, *d*, J = 16 Hz, H-7′), 6.31 (1H, *d*, J = 2, 16 Hz, H-8′): glucose moiety δ4.33 (1H, *d*, J = 7.8 Hz, H-1), 3.33–3.40 (2H, overlapping H-2, H-3), 3.25 (1H *t*-like, H-4), 3.25 (1H, *m*, H-5), 4.45 (1H, *dd*, J = 11.9, 2 Hz, H-6α), 4.32 (1H, *dd*, J = 11.9, 6 Hz, H-6′ B): phenethyl alcohol moiety δ6.66 (1H, *d*, J = 2 Hz, H-2″), 6.61 (1H, *d*, J = 8 Hz, H-5″), 6.53 (1H, *dd*, J = 8, 2 Hz, H-6″), 3.81 (2H *t*-like, H-7″), 3.98 (1H, *m*, H-8″α), 3.74 (1H, *m*, H-8″β). Alkaline methanolysis. Compound **3** (30 mg) was treated in the same manner as **1** to give Me caffeate and 2-(3,4-dihydroxyphenyl)-ethyl-D-glucopyranoside, **3a**. Amorphous pale yellow powder. IR ν^{KBr}_{max} cm^{-1}: 3410, 1620, 1525, 1500, ^{1}H NMR (CD_3OD): glucose moiety δ4.22 (1H, *d*, J = 7.9 Hz, H-1), 3.30–3.33 (2H, overlapping H-2, H-3), 3.2 (1H, *dd*, J = 8.8, 7.9 Hz, H-4), 3.88 (1H, *dd*, J = 11.9, 2 Hz, H-6α): phenethyl alcohol moiety δ6.9 (1H, *d*, J = 2 Hz, H-2″), 6.68 (1H, *dd*, J = 8, 2 Hz, H-6″), 2.79 (2H *t*-like, H-7″), 4.01 (1H, *m*, H-8″a), 3.06–3.74 (3H, overlapping, H-5, H-6β and H-8″β).

Compound **4**. Amorphous pale yellow powder (2g). $[\alpha]^{20}$ + 25.4 (MeOH; *c* 1.1). IR ν_{max}^{KBr} cm^{-1}: 3425, 1640, 1635, 1610, 1525, 960. ^1H NMR (CD_3OH): caffeoyl moiety, δ7.58 (*d*, *J* = 16 Hz, H-7′), 7.04 (*d*, *J* = 1.9 Hz, H-2′), 6.94 (*d*, *J* = 8, 1.9 Hz, H-6′), 6.80 (*d*, *J* = 8 Hz, H-5′), 6.29 (*d*, *J* = 16 Hz, H-8′): glucose moiety, 5.5 (*d*, *J* = 8.1 Hz, aromatic-H), 3.18-4.5 (sugar protons). *Alkaline methanolysis.* Compound **4** (200 mg) was treated in the same manner as **1** to give D-glucose and Me caffeate.

Acid hydrolysis. Compounds **1**–**4** were each refluxed in 2 M HCl–MeOH (1:1, 5 ml) at 80° for 3 hr to afford caffeic acid and D-glucose. Both compounds were identified by TLC comparison with authentic samples.

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