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CYANOGENIC AND PHENYLPROPANOID GLUCOSIDES FROM *PRUNUS GRAYANA*

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Key Word Index—*Prunus grayana*; Rosaceae; cyanogenic glucoside; mandelonitrile glucoside; phenylpropanoid glucosides; ferulic acid esters; caffeic acid ester; grayanoside A, B; grayanin; prunasin derivative.

Abstract—In a chemical examination of the bark of *Prunus grayana*, three new phenylpropanoid glucosides, grayanoside A, grayanoside B and grayanin, have been isolated. The structures of these compounds have been established to be 2-(4-hydroxyphenyl)ethyl-(6-*O*-feruloyl)-β-D-glucopyranoside, 2-(3,4-dihydroxyphenyl)ethyl-(6-*O*-feruloyl)-β-D-glucopyranoside, and (2*R*)-[(6-*O*-caffeoyl)-β-D-glucopyranosyloxy]benzeneacetonitrile, respectively, on the basis of the spectroscopic studies and the chemical evidence.

INTRODUCTION

The members of the genus *Prunus* (Rosaceae) are particularly rich in flavonoids, but our previous work has established the presence of phenylpropanoid glucosides and a tannin-related compound in the bark of *Prunus grayana* Maxim. [1]. In our further investigation on bitter principles of this plant, three new phenylpropanoid glucosides have been isolated as the minor components. One of them was a prunasin derivative. There have been many reports on the isolation of cyanogenic glucosides from plants [2]. In the family Rosaceae, the compounds commonly found are amygdalin (from *P. persica* and *P. armeniaca*) and prunasin (from *P. macrophylla*). However, few cyanogenic glucosides possessing a phenylpropanoid moiety in the molecule have been reported [3]. This paper deals with the isolation and structure determination of the three new phenylpropanoid glucosides.

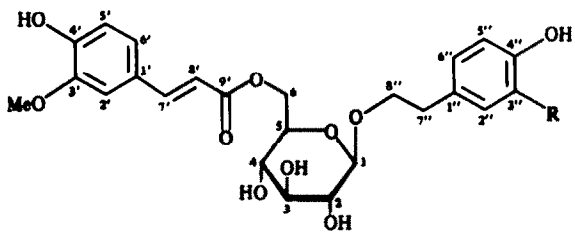
RESULTS AND DISCUSSION

Three new phenylpropanoid glucosides, designated as grayanoside A (**1**) and B (**2**) and grayanin (**3**), were isolated from the methanol extract of the bark of *P. grayana* by a combination of silica gel and Sephadex LH-20 column chromatographies. These compounds were obtained as amorphous pale-yellow powders.

Compound **1** ($C_{24}H_{28}O_{10}$) showed a molecular ion peak at *m/z* 476 in the electron impact mass spectrum (EIMS). The ^{1}H NMR spectrum of **1** revealed the presence of a *trans*-olefin, along with seven aromatic protons ascribable to ABC and AA'BB' systems. An anomeric proton signal (δ4.34, *d*, J = 7.8 Hz) and other sugar proton signals (δ3.24–4.52, 6H) suggested the existance of a β-linked glucose residue in the molecule. On alkaline methanolysis with methanolic sodium methoxide, compound **1** gave methyl ferulate and an amorphous product which was shown to be identical with salidroside, 2-(4-hydroxyphenyl)ethyl-β-D-glucopyranoside (**1a**), by the ^{1}H NMR and ^{13}C NMR spectra [4, 5]. The location of the feruloyl group in **1** was determined to be C-6 in the glucose moiety by comparison of the ^{13}C NMR spectrum of **1** with that of **1a** (see Table 1 and Experimental). The signal easily assignable to the C-6 position of the glucose in **1** was shifted downfield (δ64.8), while the C-5 was shifted upfield (δ75.5) as compared with those in **1a** (C-6, δ62.9; C-5, δ78.2). The above conclusion was also supported by the appearance of the deshielded H-6 proton signals in the ^{1}H NMR spectrum of **1**. The signals in the spectrum of compound **1** attributable to the H-6 methylene protons of the glucose moiety (δ4.52 and 4.36, 1H

Table 1. ^{13}C NMR chemical shift values of compounds **1**, **1a**, **2** and **2a** (100 MHz, CD_3OD, ppm)

Carbon number		**1**	**1a**	**2**	**2a**
Glucose moiety	1	104.6	104.4	104.6	104.4
	2	75.1	75.2	75.1	75.2
	3	78.0	78.0	78.0	78.0
	4	71.9	71.8	71.9	71.7
	5	75.5	78.2	75.5	78.2
	6	64.8	62.9	64.8	62.8
Feruloyl moiety	1′	127.8		127.7	
	2′	111.8		111.7	
	3′	150.7		150.7	
	4′	149.4		149.4	
	5′	116.6		116.6	
	6′	124.3		124.3	
	7′	147.1		147.1	
	8′	115.4		115.3	
	9′	169.1		169.2	
	OCH_3-3′	56.5		56.5	
Phenethylalcohol moiety	1″	130.7	130.9	131.5	131.6
	2″	130.9	131.0	116.4	116.4
	3″	116.2	116.2	146.2	146.2
	4″	156.8	156.8	144.7	144.7
	5″	116.2	116.2	117.1	117.2
	6″	130.9	131.0	121.3	121.3
	7″	36.6	36.4	36.8	36.6
	8″	72.5	72.1	72.5	72.1



1 R = H
2 R = OH

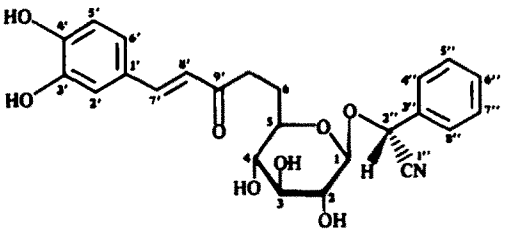
each) showed a downfield shift by *ca* 0.7 ppm as compared with those in the spectrum of **1a** (δ 3.86 and 3.68, 1H each). Accordingly, compound **1** is characterized as 2-(4-hydroxyphenyl)ethyl-(6-*O*-feruloyl)-β-D-glucopyranoside.

The ^{1}H NMR spectrum of **2** ($C_{24}H_{28}O_{11}$; EIMS, *m/z* 492 $[M]^+$) was almost similar to that of **1** except for the aromatic region. On acetylation with acetic anhydride and pyridine, **2** afforded a hexaacetate (**2b**). The ^{1}H NMR spectrum of **2b** exhibited the presence of three aliphatic and three aromatic acetoxyl groups. Treatment of **2** with sodium methoxide in methanol yielded two products, methyl ferulate and 2-(3,4-dihydroxyphenyl)ethyl-β-D-glucopyranoside (**2a**) which were determined by analysis of the ^{1}H NMR and ^{13}C NMR spectra [6]. In the ^{1}H NMR and ^{13}C NMR spectra of **2**, the signal patterns of the glucose moiety were quite similar to those of **1**, indicating that the feruloyl group was attached to the C-6 position of the glucose moiety. Thus, **2** is determined to be 2-(3,4-dihydroxyphenyl)ethyl-(6-*O*-feruloyl)-β-D-glucopyranoside.

Compound **3** ($C_{23}H_{23}NO_9$; EIMS, *m/z* 457 $[M]^+$) is very soluble in methanol and acetone, and insoluble in water. In the ^{1}H NMR spectrum of **3**, *trans*-olefin protons and eight aromatic protons were observed. Five of the eight aromatic protons were at relatively lower field (δ 7.45–7.62) than the others. The residual three were easily assignable to the ABC system of 1,3,4-trisubstituted benzene of caffeic acid. The EIMS of **3** showed peaks at *m/z* 116 (C_8H_6N) and at *m/z* 117 (C_8H_7N), which were characteristic fragment ion peaks due to mandelonitrile [7, 8]. On acid hydrolysis with 1M hydrochloric acid in methanol compound **3** released hydrogen cyanide gas which was indicated by picrate paper test [9]. From these observations, compound **3** was deduced to contain a caffeoyl and a mandelonitrile moiety, joined to glucose through ester and ether linkages respectively. In the ^{13}C NMR spectrum of **3**, the signal ascribable to anomeric carbon (δ 102.7) suggested that the mandelonitrile moiety was located at C-1 of the glucose moiety. Furthermore, the signal attributable to the C-6 of the glucose was remarkably shifted to lower field (δ 64.5), whereas the signal due to C-5 was shifted to upper field (δ 75.8) as compared with those in authentic prunasin, corresponding to the deacylated product of **3** (Table 2.). Therefore, the caffeoyl group was linked to the C-6 position on the glucose moiety. The plane structure of **3** was consequently established to be 2-[(6-*O*-caffeoyl)-β-D-glucopyranosyloxy]benzeneacetonitrile. The nitrile stretching band at 2260 cm^{-1} in the IR spectrum was barely detectable [2, 10].

Table 2. ^{13}C NMR chemical shift values of grayanin (**3**) and prunasin (ppm)

Carbon number		Grayanin (3)		Prunasin	
		CD_3OD	$(CD_3)_2CO$	CD_3OD	$(CD_3)_2CO$
Glucose moiety	1	102.7	102.3	102.1	102.4
	2	74.7	74.5	74.8	74.7
	3	77.7	77.7	78.0	78.0
	4	71.6	71.2	71.6	71.6
	5	75.8	75.4	78.4	78.0
	6	64.5	64.2	62.9	63.1
Caffeoyl moiety	1′	127.8	127.7		
	2′	115.0	115.2		
	3′	149.5	148.8		
	4′	146.7	146.1		
	5′	116.6	116.4		
	6′	123.1	122.6		
	7′	147.3	146.3		
	8′	115.3	115.5		
	9′	169.2	167.5		
Mandelonitrile moiety	1″	69.3	68.5	68.5	68.2
	2″	119.2	118.9	119.5	119.4
	3″	134.7	134.8	134.9	134.9
	4″	130.1	129.8	130.2	129.9
	5″	128.8	128.6	129.0	128.5
	6″	131.0	130.6	131.0	130.6
	7″	128.8	128.6	129.0	128.5
	8″	130.1	129.8	130.2	129.9



3

In order to establish the absolute configuration of the asymmetric carbon atom at the C-2 position of the mandelonitrile moiety, **3** was refluxed with concentrated hydrochloric acid–methanol to afford methyl mandelate (**3a**), methyl caffeate and D-glucose. Comparison of the specific rotation of **3a** with that of the methyl mandelate derived from authentic amygdalin indicated that the C-2 position of **3a** had an *R*-configuration. Based on these findings, the structure of **3** is concluded to be (2*R*)-[6-*O*-caffeoyl)-β-D-glucopyranosyloxy]benzeneacetonitrile.

Application of the degradation method with methanolic sodium methoxide, used for **1** and **2**, was unsuccessful for **3**, since a racemic compound, prulaurasin (DL-mandelonitrile-β-D-glucopyranoside), was afforded in this condition.

In view of the biosynthetic route, the mandelonitrile unit in grayanin (**3**) may be derived from phenylalanine [2]. This class of cyanogenic glucoside is found in many families, but it seems rare that the glucose moiety of cyanogenic glucoside is esterified with phenylpropanoid. Considering the absolute configuration, it seems reasonable that grayanin has an *R*-configuration at the C-2 position of mandelonitrile, since prunasin and amygdalin found in the same family also have an *R*-configuration.

In addition, the cyanogenic glucoside, grayanin (**3**), has a strong bitter taste.

EXPERIMENTAL

NMR spectra were measured at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR. Chemical shifts were given on the δ (ppm) scale with TMS as internal standard.

Details of the extraction and isolation procedure were described in the previous paper [1].

Compound **1**. Amorphous pale yellow powder (110 mg), $[\alpha]_D^{25}$ −30.0° (MeOH; *c* 0.53); UV λ_{max}^{MeOH} nm (log ε): 217 (4.18), 242 sh (3.90), 276 (3.95), 297 (3.99), 326 (4.12); IR ν_{max}^{KBr} cm^{-1}: 3420, 1690, 1630, 1600, 1520; ^{1}H NMR (CD_3OD):glucose moiety: δ4.34 (1H, *d*, *J* = 7.8 Hz, H-1), 3.37–3.41 (2H, overlapping H-2 and H-3), 3.24 (1H, *t*-like, H-4), 3.53 (1H, *m*, H-5), 4.52 (1H, *dd*, *J* = 11.9, 2.2 Hz, H-6a), 4.36 (1H, *dd*, *J* = 11.9, 6.2 Hz, H-6b); feruloyl moiety: δ7.13 (1H, *d*, *J* = 1.8 Hz, H-2'), 6.80 (1H, *d*, *J* = 8.2 Hz, H-5'), 7.00 (1H, *dd*, *J* = 8.2, 1.8 Hz, H-6'), 7.62 (1H, *d*, *J* = 15.9 Hz, H-7'), 6.37 (1H, *d*, *J* = 15.9 Hz, H-8'), 3.85 (3H, *s*, OCH_3-3'); phenethylalcohol moiety: δ7.02 (2H, *d*, *J* = 8.4 Hz, H-2" and H-6"), 6.65 (2H, *d*, *J* = 8.4 Hz, H-3" and H-5"), 2.83 (2H, *t*-like, H-7"), 3.94 (1H, *m*, H-8"a), 3.73 (1H, *m*, H-8"b).

Alkaline methanolysis of compound **1** *with sodium methoxide.* Compound **1** (25 mg) was dissolved in methanolic 1% NaOMe (5 ml) and the soln was allowed to stand for 1 hr at room temp. The mixture was passed through an Amberlite IR-120 (H^+) column and the eluate was concentrated. The residue was purified by Sephadex LH-20 column chromatography to give methyl ferulate and 2-(4-hydroxyphenyl)-ethyl-β-D-glucopyranoside (**1a**). Compound **1a**: amorphous powder (13 mg), IR ν_{max}^{KBr} cm^{-1}: 3400, 1615, 1520; ^{1}H NMR (CD_3OD): glucose moiety: δ4.29 (1H, *d*, *J* = 7.8 Hz, H-1), 3.26–3.33 (2H, overlapping H-2 and H-3), 3.18 (1H, *dd*, *J* = 8.9, 7.8 Hz, H-4), 3.86 (1H, *dd*, *J* = 11.5, 1.4 Hz, H-6a); phenethylalcohol moiety: δ7.06 (2H, *d*, *J* = 8.5 H, H-2" and H-6"), 6.69 (2H, *d*, *J* = 8.5 Hz, H-3" and H-5"), 2.83(2H, *m*, H-7"), 4.03 (1H, *m*, H-8"a), 3.64–3.72 (3H, overlapping H-5, H-6b and H-8"b).

Acetylation of compound **1**. Compound **1** (10 mg) was dissolved in pyridine (0.5 ml) and Ac_2O (2.0 ml) and left at room temp. overnight to afford the pentaacetate (**1b**). Compound **1b**: amorphous powder (12 mg), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1720, 1640, 1605, 1515; ^{1}H NMR ($CDCl_3$): glucose moiety: δ4.51 (1H, *d*, *J* = 7.9 Hz, H-1), 5.02 (1H, *dd*, *J* = 7.9, 9.3 Hz, H-2), 5.20 (1H, *dd*, *J* = 9.3, 9.3 Hz, H-3), 5.14 (1H, *dd*, *J* = 9.3, 9.3 Hz, H-4), 3.76 (1H, *m*, H-5), 4.34 (2H, *d*, *J* = 3.6 Hz, H-6); feruloyl moiety: δ7.11–7.13(2H, overlapping H-2' and H-6'), 7.06 (1H, *d*, *J* = 8.6 Hz, H-5'), 7.67 (1H, *d*, *J* = 16.0 Hz, H-7'), 6.41 (1H, *d*, *J* = 16.0 Hz, H-8'), 3.88 (3H, *s*, OCH_3-3'); phenetylalcohol moiety: δ7.19 (2H, *d*, *J* = 8.5 Hz, H-2" and H-6"), 6.96 (2H, *d*, *J* = 8.5 Hz, H-3" and H-5"), 2.89 (2H, *m*, H-7"), 4.13 (1H, *m*, H-8" a), 3.67 (1H, *m*, H-8"b); acetoxyl groups: δ2.32, 2.27, 2.03, 2.00, and 1.92 (each 3H, *s*, 5 × OAc).

Compound **2**. Amorphous pale yellow powder (170 mg), $[\alpha]_D^{25}$ −34.0° (MeOH; *c* 0.64); UV λ_{max}^{MeOH} nm (log ε): 210 (4.21), 217 (4.21), 232 sh (4.07), 290 (4.05), 325 (4.19); IR ν_{max}^{KBr} cm^{-1}: 3400, 1690, 1630, 1600, 1520; ^{1}H NMR (CD_3OD): glucose moiety: δ4.35 (1H, *d*, *J* = 7.7 Hz, H-1), 3.40–3.44 (2H, overlapping H-2 and H-3), 3.27 (1H, *t*-like, H-4), 3.56 (1H, *m*, H-5), 4.54 (1H, *dd*, *J* = 11.9, 2.1 Hz, H-6a), 4.36 (1H, *dd*, *J* = 11.9, 6.0 Hz, H-6b); feruloyl moiety: δ7.11 (1H, *d*, *J* = 1.9 Hz, H-2'), 6.80 (1H, *d*, *J* = 8.2 Hz, H-5'), 6.99 (1H, *dd*, *J* = 8.2, 1.9 Hz, H-6'), 7.61 (1H, *d*, *J* = 15.9 Hz, H-7'), 6.36 (1H, *d*, *J* = 15.9 Hz, H-8'), 3.84 (3H, *s*, OCH_3-3'); phenethylalcohol moiety: δ6.69 (1H, *d*, *J* = 2.0 Hz, H-2"), 6.65 (1H, *d*, *J* = 8.0 Hz, H-5"), 6.53 (1H, *dd*, *J* = 8.0, 2.0 Hz, H-6"), 2.78 (2H, *t*-like, H-7"), 3.95 (1H, *m*, H-8"a), 3.73 (1H, *m*, H-8"b).

Alkaline methanolysis of compound **2** *with* NaOMe. Compound **2** (26 mg) was treated in the same manner as **1** to give methyl ferulate and 2-(3,4-dihydroxyphenyl)ethyl-β-D-glucopyranoside (**2a**). Compound **2a**: amorphous powder (13 mg), IR ν_{max}^{KBr} cm^{-1}: 3400, 1610, 1530; ^{1}H NMR (CD_3OD): glucose moiety: δ4.29 (1H, *d*, *J* = 7.9 Hz, H-1), 3.30–3.35 (2H, overlapping H-2 and H-3), 3.18 (1H, *dd*, *J* = 9.0, 7.8 Hz, H-4), 3.86 (1H, *dd*, *J* = 11.9, 2.1 Hz, H-6a); phenethylalcohol moiety: δ6.69 (1H, *d*, *J* = 2.0 Hz, H-2"), 6.67 (1H, *d*, *J* = 8.0 Hz, H-5"), 6.55 (1H, *dd*, *J* = 8.0, 2.0 Hz, H-6"), 2.78 (2H, *m*, H-7"), 4.02 (1H, *m*, H-8"a), 3.65–3.72 (3H, overlapping H-5, H-6b, and H-8"b).

Acetylation of compound **2**. Compound **2** (10 mg) was acetylated in the same manner as **1** to give the hexaacetate (**2b**). Compound **2b**: amorphous powder (13 mg), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1720, 1640, 1605, 1510; ^{1}H NMR ($CDCl_3$): glucose moiety: δ4.51 (1H, *d*, *J* = 7.9 Hz, H-1), 5.02 (1H, *dd*, *J* = 7.9, 9.3 Hz, H-2), 5.21 (1H, *dd*, *J* = 9.3, 9.3 Hz, H-3), 5.14 (1H, *dd*, *J* = 9.3, 9.3 Hz, H-4), 3.68 (1H, *m*, H-5), 4.34 (2H, *d*, *J* = 3.5 Hz, H-6); feruloyl moiety: δ7.12–7.13 (2H, overlapping H-2' and H-6'), 7.06–7.07 (3H, overlapping H-5', H-5", and H-6"), 7.67 (1H, *d*, *J* = 16.0 Hz, H-7'), 6.42 (1H, *d*, *J* = 16.0 Hz, H-8'), 3.88 (3H, *s*, OCH_3-3'); phenethylalcohol moiety: δ7.03 (1H, *br s* H-2"), 2.87 (2H, *m*, H-7"), 4.14 (1H, *m*, H-8"a), 3.77 (1H, *m*, H-8"b); acetoxyl groups: δ2.32, 2.26 (× 2), 2.03, 2.00 and 1.93 (each 3H, *s*, 6 × OAc).

Compound **3**. Amorphous pale yellow powder (210 mg), $[\alpha]_D^{25}$ −39.1° (Me_2CO; *c* 0.70); UV λ_{max}^{MeOH} nm (log ε): 215 (4.26),

234 sh (3.99), 245 (4.01), 300 (4.13), 328 (4.24); IR ν_{max}^{KBr} cm^{-1}: 3400, 2260 (quenched), 1690, 1630, 1600, 1525; ^1H NMR (Acetone-d_6): glucose moiety: δ4.45 (1H, *d*, *J* = 7.4 Hz, H-1), 3.36–3.48 (3H,overlapping H-2, H-3 and H-4), 3.57 (1H, *m*, H-5), 4.59 (1H, *dd*, *J* = 11.9, 2.1 Hz, H-6a), 4.32 (1H, *dd*, *J* = 11.9, 6.4 Hz, H-6b); caffeoyl moiety: δ7.20 (1H, *d*, *J* = 2.0 Hz, H-2'), 6.88 (1H, *d*, *J* = 8.1 Hz, H-5'), 7.07 (1H, *dd*, *J* = 8.1, 2.0 Hz, H-6'), 7.64 (1H, *d*, *J* = 16.0 Hz, H-7'), 6.37 (1H, *d*, *J* = 16.0 Hz, H-8'); mandelonitrile moiety: δ5.88 (1H, *s*, H-2"), 7.45–7.63 (5H, overlapping H-4", H-5", H-6", H-7" and H-8").

Treatment of compound **3** *with* 1M HCl. Compound **3** (5 mg) dissolved in MeOH (0.5 ml) was hydrolysed with aqueous 1M HCl (2.0 ml) in a test tube with a sheet of picrate paper hung over the reaction tube. The soln was refluxed for 1 hr, and the yellow colour of the paper turned brown due to the release of HCN.

Treatment of compound **3** *with conc* HCl. A soln of **3** (35 mg) in MeOH (0.5 ml) and conc HCl (2.0 ml) was refluxed for 2 hr. The reaction mixture was evaporated to dryness. The residue was suspended in H_2O, and extracted with Et_2O. The etheral layer was purified by Sephadex LH-20 and Silica gel CC to give *R*-methyl mandelate (**3a**) and methyl caffeate. The H_2O layer contained D-glucose. Methyl caffeate and D-glucose were identified with authentic samples by TLC. Compound **3a** (2 mg): $[\alpha]_D^{28}$ $-6 \times 10°$ (MeOH; *c* 0.09). [authentic *R*-methyl mandelate, $[\alpha]_D^{28}$ $-6.4 \times 10°$ (MeOH; *c* 0.40)]; ^1H NMR (CD_3OD): δ3.69 (3H, *s*, OCH_3-1"), 5.18 (1H, *s*, H-2"), 7.30–7.44 (5H, overlapping H-4", H-5", H-6", H-7" and H-8"); ^{13}C NMR (CD_3OD): δ175.0 (C-1"), 74.4 (C-2"), 140.5 (C-3"), 127.8 (C-4" and C-8"), 129.6 (C-5" and C-7"), 129.4 (C-6"), 52.7 (OCH_3-1").

Acetylation of compound **3**. Compound **3** (20 mg) was acetylated in the same manner as **1** to give the pentaacetate (**3b**). Compound **3b**: amorphous powder (28 mg), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2260 (quenched), 760, 1720, 1640, 1510; ^1H NMR ($CDCl_3$): glucose moiety: δ4.55 (1H, *d*, *J* = 7.5 Hz, H-1), 5.07–5.16 (3H, overlapping H-2, H-3 and H-4), 3.70 (1H, *m*, H-5), 4.36 (1H, *dd*, *J* = 12.0, 2.6 Hz, H-6a), 4.28 (1H, *dd*, *J* = 12.0, 5.3 Hz, H-6b); caffeoyl moiety: δ7.41 (1H, *d*, *J* = 1.9 Hz, H-2'), 7.24 (1H, *d*, *J* = 8.4 Hz, H-5'), 7.70 (1H, *d*, *J* = 16.0 Hz, H-7'), 6.44 (1H, *d*, *J* = 16.0 Hz, H-8'); mandelonitrile moiety: δ5.53 (1H, *s*, H-2"), 7.43–7.46 (6H, overlapping H-4", H-5", H-6", H-7", H-8" and H-6'); acetoxyl groups: δ2.31, 2.30, 2.02 and 2.00 (× 2) (each 3H, *s*, 5 × OAc).

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