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ARTICLE *in* JOURNAL OF NATURAL PRODUCTS · FEBRUARY 2002

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New Cyanogenic and Alkyl Glycoside Constituents from *Phyllagathis rotundifolia*

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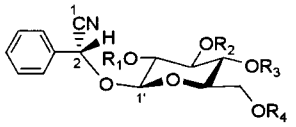
Received August 10, 2001

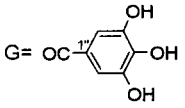
Methanolic extracts of the leaves, stems, and roots of *Phyllagathis rotundifolia* collected in Malaysia yielded seven galloylated cyanogenic glucosides based on prunasin, with six of these being new compounds, prunasin 2′,6′-di-*O*-gallate (**3**), prunasin 3′,6′-di-*O*-gallate (**4**), prunasin 4′,6′-di-*O*-gallate (**5**), prunasin 2′,3′,6′-tri-*O*-gallate (**6**), prunasin 3′,4′,6′-tri-*O*-gallate (**7**), and prunasin 2′,3′,4′,6′-tetra-*O*-gallate (**8**). Also obtained was a new alkyl glycoside, oct-1-en-3-yl α-arabinofuranosyl-(1→6)-*β*-glucopyranoside (**9**). For compounds **3**−**8**, the galloyl groups were individually linked to the sugar moieties via ester bonds. All new structures were established on the basis of NMR and MS spectroscopic studies. In addition, prunasin (**1**), gallic acid and its methyl ester, *β*-glucogallin, 3,6-di-*O*-galloyl-D-glucose, 1,2,3,6-tetra-*O*-galloyl-*β*-D-glucose, strictinin, 6-*O*-galloyl-2,3-*O*-(*S*)-hexahydroxydiphenoyl-D-glucose, praecoxin B, and pterocarinin C were isolated and identified. The isolation of **1** and its galloyl derivatives (**3**−**8**) from a Melastomataceous plant are described for the first time.

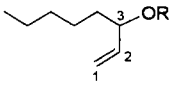
Plants in the family Melastomataceae are widely distributed in tropical and subtropical regions of South America, Southeast Asia, and the southern parts of mainland China. Some of these plants have been employed as remedies for skin diseases, dysentery, and diarrhea and as astringents and hemostatics in the People's Republic of China, Malaysia, and Indonesia.[1] The presence of hydrolyzable tannins of the oligomeric, dimeric, and tetrameric types has been reported in plants of this family, from genera such as *Bredia*, *Heterocentron*, *Medinilla*, *Melastoma*, and *Tibouchina*.[2−10] *Phyllagathis rotundifolia* (Jack) Bl., known as "Tapak Sulaiman" in Malaysia, is a creeper with a short stem and heart-shaped leaves and is commonly found on the damp forest floor throughout Malaysia and Sumatra. All parts of this plant are used in the form of a decoction for the treatment of malaria, fever, and stomachache and for childbirth and as a tonic in the traditional medicinal system of Malaysia.[11,12] A literature survey, however, indicated no previously reported phytochemical studies on this plant. During the course of our chemical study of Malaysian medicinal plants, we have investigated the leaves and the stems and roots of this plant, leading to the isolation of eight cyanogenic glucosides, one alkyl glycoside, two aromatic compounds, and seven hydrolyzable tannins. The following describes the isolation and structural characterization of these compounds.

Results and Discussion

The methanol extracts of the leaves and the combined stems and roots of *P. rotundifolia* were fractionated separately by solvent−solvent partitioning. A combination of column chromatography using MCI gel CHP 20P, Chromatorex ODS, Sephadex LH-20, silica gel, and C_{18}-20 MPLC led to the isolation of seven acylated cyanogenic glucosides (**2**−**8**) (including six new compounds (**3**−**8**)) and one new alkyl glycoside (**9**), in addition to 10 known compounds, which were identified as prunasin (**1**),[13] gallic acid and its methyl ester, *β*-glucogallin,[14] 3,6-di-*O*-galloyl-D-glucose,[15] 1,2,3,6-tetra-*O*-galloyl-*β*-D-glucose,[3] strictinin,[16] 6-*O*-galloyl-2,3-*O*-(*S*)-hexahydroxydiphenoyl-D-glucose,[3] praecoxin B,[17] and pterocarinin C[3] by comparison with authentic samples or literature data.







1: R_1, R_2, R_3, R_4 = H
2: R_1, R_2, R_3 = H; R_4 = G
3: R_2, R_3 = H; R_1, R_4 = G
4: R_1, R_3 = H; R_2, R_4 = G
5: R_1, R_2 = H; R_3, R_4 = G
6: R_3 = H; R_1, R_2, R_4 = G
7: R_1 = H; R_2, R_3, R_4 = G
8: R_1, R_2, R_3, R_4 = G

9: R = α-Ara(1"→6')-β-Glc
9a: R = β-Glc

Compounds **2**−**8** exhibited spectral features closely resembling those of prunasin (**1**).[18] Each of the ^{1}H NMR spectra (Table 1) exhibited five aromatic protons (*δ* 7.27−7.64) and a singlet for one oxymethine proton, along with the signals arising from a *β*-glucopyranosyl moiety. These structural features were supported by their ^{13}C NMR spectra (Table 2), where six aromatic carbon signals in the *δ* 128.0−134.7 range, a methine carbon, and that of a *β*-glucopyranosyl moiety, as well as a quaternary carbon, the chemical shift of which suggested a nitrile function, were observed. The presence of the nitrile group was supported by the IR absorption band (2249−2260 cm^{-1}) and by the elemental analysis of each of the compounds. In accordance with these data, the aglycons were each established as a monosubstituted aromatic ring linked to the methine carbon, which in turn formed a glycosidic linkage with the anomeric carbon, as well as a linkage with the nitrile function. All the aglycon chiral centers were determined as having *R* configuration on the basis of the downfield shifts of the C-2 protons after alkaline isomerization.[19,20] However, the ^{1}H and ^{13}C NMR spectral data of compounds **2**−**8** were different from those of **1** as a result of the presence of galloyl ester signals and the deshielded proton signals of the glucose moiety attributed to acylation.

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10.1021/np010393v CCC: $22.00
Published on Web 01/18/2002

Table 1. ^{1}H NMR Spectral Data of Compounds **2**−**8**[a]

position	**2**[b]	**3**[c]	**4**[c]	**5**[c]	**6**[c]	**7**[c]	**8**[c]
aglycon							
2	5.70 s	5.88 s	5.93 s	5.91 s	5.95 s	5.97	6.00 s
4, 8	7.48−7.51 m	7.27−7.41 m	7.59−7.62 m	7.59−7.62 m	7.29−7.44 m	7.61−7.64 m	7.31−7.46 m
5, 7	7.39−7.42 m	7.27−7.41 m	7.46−7.49 m	7.46−7.49 m	7.29−7.44 m	7.46−7.50 m	7.31−7.46 m
6	7.39−7.42 m	7.27−7.41 m	7.46−7.49 m	7.46−7.49 m	7.29−7.44 m	7.46−7.50 m	7.31−7.46 m
glucose							
1′	4.26 d (8.0)	4.79 d (8.1)	4.64 d (7.8)	4.54 d (7.8)	5.02 d (7.8)	4.78 d (8.1)	5.18 d (8.1)
2′	3.34−3.50 m	5.09 dd (8.1, 9.0)	3.70 dd (7.8, 9.3)	3.55 dd (7.8, 9.0)	5.31 dd (7.8, 9.6)	3.86 dd (8.1, 9.0)	5.46 d (8.1, 9.6)
3′	3.34−3.50 m	3.66−3.79 m	5.19 dd (8.7, 9.3)	3.78 dd (9.0, 9.3)	5.47 dd (8.7, 9.6)	5.51 dd (9.0, 9.6)	5.80 t (9.6)
4′	3.34−3.50 m	3.66−3.79 m	3.86 dd (8.7, 9.9)	5.17 dd (9.3, 10.2)	4.05 dd (8.7, 9.0)	5.40 dd (9.6, 9.9)	5.58 t (9.6)
5′	3.34−3.50 m	3.66−3.79 m	3.79 m	3.94 m	3.98 m	4.18 m[e]	4.37 m
6′	4.58 dd (1.8, 12.0)	4.46 dd (5.1, 12.0)	4.52 dd (5.1, 12.0)	4.23 dd (3.0, 12.3)	4.60 dd (4.5, 12.0)	4.37 dd (5.4, 12.3)	4.44 dd (4.5, 12.0)
	4.85 dd (5.4, 12.0)	4.66 dd (1.5, 12.0)	4.63 dd (2.1, 12.0)	4.51 dd (2.1, 12.3)	4.63 dd (2.1, 12.0)	4.50 dd (2.4, 12.3)	4.55 dd (2.1, 12.0)
galloyl							
2′, 6′	7.15 s	7.11, 7.22 s	7.16, 7.24 s	7.13, 7.21 s	7.01, 7.03, 7.20 s	7.01, 7.04, 7.23 s	6.94, 7.02, 7.03, 7.25 s

[a] Measured at 300 MHz. [b] Measured in CD_3OD. [c] Measured in acetone-d_6.

Table 2. ^{13}C NMR Spectral Data of Compounds **2**−**8**[a]

position	**2**[b]	**3**[c]	**4**[c]	**5**[c]	**6**[c]	**7**[c]	**8**[c]
aglycon							
1	119.3	118.4	118.8	118.8	118.3	118.7	118.3
2	68.6	68.4	68.3	68.2	68.6	68.4	68.8
3	134.7	134.1	134.4	134.3	134.2	134.3	134.1
4, 8	129.3	128.0	128.5	128.6	128.1	128.6	128.2
5, 7	130.4	129.8	129.8	129.9	129.8	129.9	129.9
6	131.3	130.5	130.6	130.6	130.6	130.7	130.7
glucose							
1′	101.9	100.2	102.0	101.7	100.2	101.8	100.0
2′	75.0	75.4	72.8	74.5[d]	72.2	72.9[f]	72.2
3′	77.8	74.2	78.5	73.4[d]	75.4[e]	73.3[f]	73.1[g]
4′	71.7	71.0	69.4	71.7	69.3	69.5	69.4
5′	76.2	77.0	75.3	75.2[d]	75.8[e]	75.4[f]	73.4[g]
6′	64.9	64.1	63.9	63.5	63.6	63.1	62.8
galloyl							
1″	121.7	121.2, 121.3	121.7, 121.9	120.9, 121.2	120.8, 121.2, 121.6	120.6, 121.2, 121.5	120.4, 120.5, 120.6, 121.4
2′, 6′	110.5	109.8, 109.9	110.0, 110.1	109.9, 110.0	110.0 × 2, 110.1	110.0, 110.1 × 2	110.0, 110.1 × 2, 110.2
3′, 5′	146.8	145.9, 146.0	145.8, 146.0	145.9, 146.0	145.8, 145.9, 146.0	145.8 × 2, 146.0	145.8, 145.9 × 2, 146.0
4′	140.0	138.9 × 2	138.6, 138.8	138.9, 139.1	138.8, 138.9, 139.1	138.8, 138.9, 139.1	139.0, 139.1, 139.2, 139.3
C=O	168.5	165.9, 167.0	166.4, 166.6	166.3, 166.7	165.4, 166.1, 166.6	165.7, 166.0, 166.4	165.3, 165.5, 165.8, 166.4

[a] Measured at 75 MHz. [b] Measured in CD_3OD. [c] Measured in acetone-d_6. [d−g] Values with same superscript may be interchanged.

Compound **2** displayed a prominent $[M + H]^+$ peak at *m*/*z* 448 in the FABMS, which in combination with the ^{13}C NMR spectroscopic and elemental analysis data, suggested the molecular formula $C_{21}H_{21}NO_{10}$. The molecular weight was 152 units higher than that of **1**, corresponding to a galloyl moiety, as evidenced by the ^{1}H and ^{13}C NMR spectral data, where a singlet at δ 7.15 for two aromatic protons, one carbonyl carbon signal at δ 168.5, and six aromatic carbon signals in the δ 110.5−146.8 range were observed (Tables 1 and 2). The location of the galloyl moiety was found to be at C-6′ of the glucose unit in **2** on the basis of the downfield shifts of C-6′ and H-6′, as well as the upfield shift of C-5′ in **2** relative to those in **1**. Compound **2** was thus designated as prunasin 6′-*O*-gallate, which was recently isolated from *Monochaetum multiflorum*.[21]

Compound **3** showed a protonated molecular ion peak $[M + H]^+$ at *m*/*z* 600, in the positive FABMS, which corresponded to the molecular formula $C_{28}H_{25}NO_{14}$. The observed molecular weight was 152 units higher than **2**, indicating the presence of an additional galloyl moiety, which was confirmed from the ^{1}H and ^{13}C NMR spectra (Tables 1 and 2). The downfield shifts of H-2′ and H-6′, as well as their corresponding carbons, and the upfield shifts of C-1′, C-3′, and C-5′ indicated that the two galloyl moieties were attached at the C-2′ and C-6′ positions of **3** via ester linkages. Thus compound **3** was characterized as prunasin 2′,6′-di-*O*-gallate.

Compounds **4** and **5** exhibited the same protonated molecular ion peaks $[M + H]^+$ as **3** at *m*/*z* 600, in the positive FABMS, indicating that all three compounds have the same molecular formula. In the ^{1}H and ^{13}C NMR spectra of **4** (Tables 1 and 2), the protons and carbons at positions 3′ and 6′ were shifted downfield, while the C-2′, C-4′, and C-5′ signals were shifted upfield, suggesting that the galloyl moieties are located at C-3′ and C-6′. On the other hand, compound **5** displayed downfield shifts of H-4′ and H-6′ and upfield shifts of C-3′ and C-5′, indicating that the C-4′ and C-6′ were esterified. Accordingly, compounds **4** and **5** were designated as prunasin 3′,6′-di-*O*-gallate and prunasin 4′,6′-di-*O*-gallate, respectively.

Compounds **6** and **7** are structural isomers, as exemplified by the FABMS, which showed the same protonated molecular ion peaks $[M + H]^+$ at *m*/*z* 751, corresponding to the molecular formula $C_{35}H_{29}NO_{18}$. Their molecular weights were 152 units more relative to **3**−**5**, indicating the presence of an additional galloyl moiety in **6** and **7**.

This was confirmed by comparison of their ^{1}H and ^{13}C NMR spectral data (Tables 1 and 2). The positions of the galloyl ester units were determined to be at C-2′, C-3′, and C-6′ for **6** and at C-3′, C-4′, and C-6′ for **7**, based on the ^{1}H NMR downfield shifts for H-2′, H-3′, and H-6′ in **6** and for H-3′, H-4′, and H-6′ in **7**, respectively. Compounds **6** and **7** were assigned therefore as prunasin 2′,3′,6′-tri-*O*-gallate and prunasin 3′,4′,6′-tri-*O*-gallate, respectively.

Compound **8** exhibited a $[M + H]^+$ peak at *m*/*z* 904 in the positive FABMS, which was 152 units more than that of **6** or **7**, indicating an additional galloyl moiety in the molecule. The molecular formula was thus deduced to be $C_{42}H_{33}NO_{22}$. The corresponding signals of the four galloyl moieties were observed in the ^{1}H and ^{13}C NMR spectra (Tables 1 and 2). The esterification by galloyl groups at the four hydroxyl groups of prunasin was verified by the downfield shifts of H-2′, H-3′, H-4′, and H-6′, respectively. From these spectral observations, compound **8** was deduced to be prunasin 2′,3′,4′,6′-tetra-*O*-gallate.

Compound **9** showed a $[M + Na]^+$ peak at *m*/*z* 445 in the positive FABMS, which corresponded to the molecular formula $C_{19}H_{34}O_{10}$. The ^{1}H and ^{13}C NMR spectral data showed 11 carbon sugar signals including two anomeric proton doublets at δ 4.31 (J = 8.0) and δ 4.95 (J = 1.0), which is indicative of the presence of two sugar units besides an eight-carbon aglycon moiety. The coupling constant of one of the anomeric protons (δ 4.31, dd, J = 8.0, H-1′) and the sequential *trans* diaxial relationship of H-1′ to H-5′ (J = 9.0−9.5) with the corresponding carbon signals established that the sugar unit was that of a β-glucopyranosyl moiety. The other sugar moiety, having a small coupling constant for the anomeric proton (δ 4.95, dd, J = 1.0, H-1″), and the remaining five carbon signals were consistent with data on α-arabinofuranose. The correlations observed in the H−H COSY, HSQC, and HMBC spectra established that the aglycon was oct-1-en-3-ol (matsutake alcohol), an important flavor compound present in some mushrooms.[22] The glycosidic linkage of the glucopyranosyl moiety to the C-3 position of the aglycon was revealed from the H−C long-range correlation between the glucosyl anomeric proton signal and the C-3 carbon, and vice versa in the HMBC spectrum. Similarly, the interglycosidic linkage between the arabinofuranosyl and the glucopyranosyl unit was deduced from a downfield shift of C-6′ (δ 67.9) and HMBC correlations between H-1″ and C-6′, and vice versa. It was difficult to determine unambiguously the absolute configuration at C-3, since hydrolysis of **9** by hesperidinase afforded only the glucoside (**9a**), which displayed $[\alpha]^{20}_D$ −37.2°, in contrast to that of the known compound having an 3*R* configuration, $[\alpha]^{21}_D$ +10.0° (MeOH).[23] This observation however should favor an *S* configuration at C-3 in the present compound despite the fact that naturally occurring oct-1-en-3-ol has been isolated only in the *R* form so far. Accordingly, compound **9** was concluded to be oct-1-en-3-yl α-arabinofuranosyl-(1→6)-β-glucopyranoside.

Prunasin (**1**) is known to occur in many species of plants, in families such as the Compositae,[13] Labiatae,[24] Rosaceae,[25,26] and Rubiaceae.[27] However, this is the first report of this compound from a Melastomataceous plant as well as the galloyl derivatives of this cyanogenic glucoside (**3**−**8**). Previous reports on prunasin derivatives include 4′-*O*-*p*-coumarate and 4′-*O*-caffeate isolated from *Microlepia strigosa*[28] and caffeoyl esters at C-6 of the glucose from *Prunus* sp.[26] We found that prunasin was present in both the leaf, and the stem and root extracts of *P. rotundifolia*. However, all of its galloyl esters were isolated only from the leaf extract, though gallic acid was found to be present in both the leaf extract and the combined stem and root extract. In terms of biosynthesis, the biogenetic precursor of prunasin is most likely phenylalanine,[29] and the galloyl ester derivatives (**2**−**8**) are each derived by acylation with gallic acid. On the other hand, oct-1-en-3-ol is known to occur as one of the volatile components in many plants as well as several mushrooms.[22] However, the occurrence of glycosidically bound oct-1-en-3-ol is infrequent, and only a few examples have been reported from plants.[23,30] The presence of the glycosylated oct-1-en-3-yl metabolite (**9**) in *P. rotundifolia* is therefore of chemotaxonomic interest.

Experimental Section

General Experimental Procedures. Optical rotations were measured with a JASCO DIP-370 digital polarimeter. UV and IR spectra were recorded with a JASCO V-560 and a JASCO FT/IR-410K spectrometer, respectively. ^{1}H and ^{13}C NMR spectra were recorded in ppm (δ) in CD_3OD or acetone-d_6 with TMS as the internal standard, employing Varian Unity plus 500 and Varian Gemini 300 spectrometers operating at 500 and 300 MHz for ^{1}H and 125 and 75 MHz for ^{13}C. Positive FABMS were recorded using a JEOL JMS DX-303 spectrometer, with glycerol as the matrix. Column chromatography was performed with MCI gel CHP 20P (75−150 μm, Mitsubishi Chemical Industries, Ltd.), Chromatorex ODS (Fuji Silysia), Sephadex LH-20, and silica gel 60 (0.040−0.063 mm, 0.063−0.200 mm, Merck). Medium-pressure liquid chromatography (MPLC) was carried out with a prepacked column, C_{18}-20, equipped with a JASCO PU-986 preparative pump. TLC was performed on precoated silica gel 60 F_{254} plates (0.2 mm thick, Merck) with $CHCl_3$−MeOH−H_2O (8:2:0.1 or 7:3:0.5 v/v) or C_6H_6−HCOOEt−HCOOH (1:7:1 v/v), and spots were detected by UV illumination and by spraying with 10% H_2SO_4 followed by heating, or by spraying with 2% ethanolic $FeCl_3$ reagent.

Plant Material. *Phyllagathis rotundifolia* was collected from the Pasoh Forest Reserve, Negeri Sembilan, Malaysia, in March 2000. A voucher specimen (FRI 45415) was deposited at the Herbarium of Forest Research Institute Malaysia (FRIM), Kuala Lumpur, Malaysia.

Extraction and Isolation. Dried ground leaves (428 g), and stems and roots together (378 g), were extracted with MeOH by soaking repeatedly (three times). The concentrated extracts (97 and 57 g, respectively) were suspended in H_2O and partitioned successively with hexane, ethyl acetate, and butanol for the leaves, and ethyl acetate and butanol for the stems and roots. Each fraction upon concentration, except for the hexane fraction, was subsequently chromatographed over MCI gel CHP 20P, using H_2O with increasing amounts of MeOH (20−100%). The resulting fractions were further purified by a combination of column chromatography employing MCI gel CHP 20P, Chromatorex ODS, Sephadex LH-20, silica gel, as well as MPLC using C_{18}-20. From the leaves, the ethyl acetate fraction afforded prunasin (**1**, 46.6 mg), prunasin 6′-*O*-gallate (**2**, 200.4 mg), **3** (15.0 mg), **4** (36.8 mg), **5** (7.8 mg), **6** (30.3 mg), **7** (33.2 mg), **8** (27.7 mg), gallic acid (335.4 mg) and its methyl ester (73.9 mg), 1,2,3,6-tetra-*O*-galloyl-β-D-glucose (138.2 mg), 6-*O*-galloyl-2,3-*O*-(*S*)-hexahydroxydiphenoyl-D-glucose (31.4 mg), and pterocarinin C (28.2 mg). The butanol fraction afforded prunasin 6′-*O*-gallate (**2**, 22.9 mg), **9** (60.5 mg), strictinin (16.0 mg), 6-*O*-galloyl-2,3-*O*-(*S*)-hexahydroxydiphenoyl-D-glucose (81.6 mg), and praecoxin B (102.8 mg). From the stems and roots, 6-*O*-galloyl-2,3-*O*-(*S*)-hexahydroxydiphenoyl-D-glucose (66.8 mg) and praecoxin B (122.4 mg) were obtained from the ethyl acetate fraction, while the butanol fraction gave prunasin (**1**, 22.1 mg), gallic acid (21.1 mg), β-glucogallin (22.0 mg), 3,6-di-*O*-galloyl-D-glucose (21.9 mg), 6-*O*-galloyl-2,3-*O*-(*S*)-hexahydroxydiphenoyl-D-glucose (569.7 mg), and praecoxin B (46.9 mg). 6-*O*-Galloyl-2,3-*O*-(*S*)-hexahydroxydiphenoyl-D-glucose (68.6 mg) was also obtained from the water fraction. The known compounds were identified by

comparison of their physical and spectral data with the authentic samples or literature data.

Prunasin 6′-*O*-gallate (2): pinkish amorphous powder; $[\alpha]^{27}_D$ −81.2° (*c* 0.22, MeOH); −76.9° (*c* 0.28, EtOAc); UV (MeOH) λ_{max} (log ϵ) 276 (3.98) nm; IR (dry film) ν_{max} 3170, 2255, 1705, 1495, 1456 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; positive FABMS *m/z* 448 $[M + H]^+$; *anal*. C 54.50%, H 5.00%, N 3.24%, calcd for $C_{21}H_{21}NO_{10}\cdot H_2O$, C 54.20%, H 4.98%, N 3.01%.

Prunasin 2′,6′-di-*O*-gallate (3): tan amorphous powder; $[\alpha]^{27}_D$ −77.2° (*c* 0.12, MeOH); UV (MeOH) λ_{max} (log ϵ) 278 (4.31) nm; IR (dry film) ν_{max} 3206, 2257, 1714, 1496, 1455 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; positive FABMS *m/z* 600 $[M + H]^+$; *anal*. C 52.22%, H 4.40%, N 1.74%, calcd for $C_{28}H_{25}O_{14}N\cdot 2^1/_2H_2O$, C 52.18%, H 4.69%, N 2.17%.

Prunasin 3′,6′-di-*O*-gallate (4): tan amorphous powder; $[\alpha]^{27}_D$ −8.2° (*c* 0.27, MeOH); UV (MeOH) λ_{max} (log ϵ) 276 (4.28) nm; IR (dry film) ν_{max} 3300, 2260, 1700, 1497, 1451 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; positive FABMS *m/z* 600 $[M + H]^+$; *anal*. C 53.92%, H 4.50%, N 2.45%, calcd for $C_{28}H_{25}NO_{14}\cdot 1^1/_2H_2O$, C 53.68%, H 4.51%, N 2.24%.

Prunasin 4′,6′-di-*O*-gallate (5): tan amorphous powder; $[\alpha]^{27}_D$ −73.1° (*c* 0.12, MeOH); UV (MeOH) λ_{max} (log ϵ) 277 (4.21) nm; IR (dry film) ν_{max} 3218, 2260, 1714, 1455 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; positive FABMS *m/z* 600 $[M + H]^+$; *anal*. C 52.84%, H 4.52%, N 2.18%, calcd for $C_{28}H_{25}O_{14}N\cdot 2H_2O$, C 52.92%, H 4.60%, N 2.20%.

Prunasin 2′,3′,6′-tri-*O*-gallate (6): tan amorphous powder; $[\alpha]^{27}_D$ +57.0° (*c* 0.16, MeOH); UV (MeOH) λ_{max} (log ϵ) 278 (4.39) nm; IR (dry film) ν_{max} 3071, 2260, 1731, 1468 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; positive FABMS *m/z* 752 $[M + H]^+$; *anal*. C 52.42%, H 4.25%, N 1.89%, calcd for $C_{35}H_{29}NO_{18}\cdot 2^3/_4H_2O$, C 52.47%, H 4.34%, N 1.75%.

Prunasin 3′,4′,6′-tri-*O*-gallate (7): tan amorphous powder; $[\alpha]^{27}_D$ −65.0° (*c* 0.23, MeOH); UV (MeOH) λ_{max} (log ϵ) 278 (4.49) nm; IR (dry film) ν_{max} 3213, 2257, 1715, 1496, 1454 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; positive FABMS *m/z* 752 $[M + H]^+$; *anal*. C 52.62%, H 4.24%, N 1.58%, calcd for $C_{35}H_{29}NO_{18}\cdot 2^3/_4H_2O$, C 52.47%, H 4.34%, N 1.75%.

Prunasin 2′,3′,4′,6′-tetra-*O*-gallate (8): tan amorphous powder; $[\alpha]^{27}_D$ +14.2° (*c* 0.25, MeOH); UV (MeOH) λ_{max} (log ϵ) 279 (4.58) nm; IR (dry film) ν_{max} 3207, 2260, 1725, 1497, 1454 cm^{-1}; ^{1}H NMR, Table 1; ^{13}C NMR, Table 2; positive FABMS *m/z* 904 $[M + H]^+$; *anal*. C 51.78%, H 4.22%, N 1.69%, calcd for $C_{42}H_{33}NO_{22}\cdot 4H_2O$, C 51.70%, H 4.24%, N 1.44%.

Alkaline Isomerization of 2−8.[18,19] A solution of each individual compound (5.0−20.0 mg/2.0 mL H_2O) was combined with one drop of 1.48 M NH_4OH and incubated at room temperature with stirring for 2 h. Each reaction mixture was evaporated and chromatrographed over Sephadex LH-20 gel, eluting with MeOH to afford the *R* and *S* epimers of the aglycon.

Oct-1-en-3-yl α-arabinofuranosyl-(1→6)-β-glucopyranoside (9): colorless syrup; $[\alpha]^{27}_D$ −82.2° (*c* 0.48, MeOH); UV (MeOH) λ_{max} (log ϵ) 225 (2.71) nm; IR (dry film) ν_{max} 3261, 1645 cm^{-1}; ^{1}H NMR (CD_3OD, 500 MHz) δ 5.85 (1H, ddd, J = 7.0, 10.5, 17.5 Hz, H-2), 5.20 (1H, dd, J = 1.0, 17.5 Hz, H-1a), 5.11 (1H, dd, J = 1.0, 10.5 Hz, H-1b), 4.95 (1H, d, J = 1.0 Hz, H-1″), 4.31 (1H, d, J = 8.0 Hz, H-1′), 4.08 (1H, q, J = 7.0, 13.0 Hz, H-3), 3.97 (1H, m, H-2″), 3.96 (1H, m, H-4″), 3.94 (1H, dd, J = 2.5, 11.0 Hz, H-6a′), 3.82 (1H, dd, J = 3.5, 5.5 Hz, H-3″), 3.74 (1H, dd, J = 3.5, 12.0 Hz, H-5a″), 3.64 (1H, dd, J = 5.5, 12.0 Hz, H-5b″), 3.58 (1H, dd, J = 6.0, 11.0 Hz, H-6b′), 3.36 (1H, m, H-5′), 3.33 (1H, dd, J = 9.0, 9.5 Hz, H-3′), 3.27 (1H, dd, J = 9.0, 9.5 Hz, H-4′), 3.17 (1H, dd, J = 8.0, 9.0 Hz, H-2′), 1.68 (1H, m, H-4a), 1.50 (1H, m, H-4b), 1.38 (2H, m, H-5), 1.32 (2H, m, H-7), 1.28 (2H, m, H-6), 0.90 (3H, t, J = 7.0 Hz, H-8); ^{13}C NMR (CD_3OD, 125 MHz) δ 140.8 (C-2), 116.3 (C-1), 109.8 (C-1″), 103.3 (C-1′), 86.0 (C-4″), 83.2 (C-3), 83.1 (C-2″), 79.0 (C-3″), 78.1 (C-3′), 76.6 (C-5′), 75.3 (C-2′), 71.9 (C-4′), 67.9 (C-6′), 63.1 (C-5″), 35.7 (C-4), 33.0 (C-6), 25.6 (C-5), 23.6 (C-7), 14.4 (C-8); positive FABMS *m/z* 445 $[M + Na]^+$; *anal*. C 53.49%, H 8.05%, calcd for $C_{19}H_{34}O_{10}\cdot {}^1/_4H_2O$, C 53.45%, H 8.14%.

Enzymatic Hydrolysis of 9. A solution of compound **9** (30.0 mg/15.0 mL H_2O) was incubated with 20 mg of hesperidinase (0.01 units/mg, *Aspergillus niger*, Sigma) at 37 °C for 20 days. The reaction mixture was partitioned with diethyl ether. The organic layer was evaporated under reduced pressure and chromatographed over silica gel, eluting with $CHCl_3$, $CHCl_3$−MeOH (19:1 v/v), and $CHCl_3$−MeOH−H_2O (9:1:0.1 v/v) to afford **9a** (2.2 mg).

Oct-1-en-3-yl β-glucopyranoside (9a): colorless syrup; $[\alpha]^{20}_D$ −37.2° (*c* 0.17, MeOH); ^{1}H NMR (CD_3OD, 300 MHz) δ 5.88 (1H, ddd, J = 7.2, 10.5, 17.1 Hz, H-2), 5.20 (1H, dd, J = 1.0, 17.1 Hz, H-1a), 5.09 (1H, dd, J = 1.0, 10.5 Hz, H-1b), 4.31 (1H, d, J = 7.8 Hz, H-1′), 4.12 (1H, q, J = 7.2, 13.2 Hz, H-3), 3.81 (1H, dd, J = 2.4, 12.0 Hz, H-6a′), 3.64 (1H, dd, J = 5.7, 12.0 Hz, H-6b′), 3.15−3.36 (4H, m, H-2′, H-3′, H-4′, H-5′), 0.90 (3H, t, J = 6.9 Hz, H-8); ^{13}C NMR (CD_3OD, 75 MHz) δ 141.0 (C-2), 116.0 (C-1), 103.2 (C-1′), 82.8 (C-3), 78.2 (C-5′), 77.8 (C-3′), 75.3 (C-2′), 71.6 (C-4′), 62.7 (C-6′), 35.6 (C-4), 33.0 (C-6), 25.6 (C-5), 23.7 (C-7), 14.4 (C-8); positive FABMS *m/z* 313 $[M + Na]^+$.

Acknowledgment. S.-K.L. acknowledges the Forest Research Institute Malaysia (FRIM), Kuala Lumpur, Malaysia, for study leave, and the Ministry of Education, Science, Sports and Cultures of Japan for a scholarship. We thank Mr. K. Inada and Mr. N. Yamaguchi for NMR and MS measurements. Our thanks are also due to Mr. Y.-C. Chang, Mr. J. Ghazali, and Mrs. Hj. A. B. Siti Asha of FRIM, for species authentification and sample processing.

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(18) Prunasin (**1**): colorless needles (EtOAc); $[\alpha]^{27}_D$ −76.7° (*c* 0.15, MeOH); −29.2° (*c* 0.22, H_2O); IR (dry film) ν_{max} 3199, 2249, 1495, 1455 cm^{-1}; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.57−7.60 (2H, m, H-4, H-8), 7.43−7.47 (3H, m, H-5, H-6, H-7), 5.90 (1H, s, H-2), 4.25 (1H, d, J = 8.0 Hz, H-1′), 3.91 (1H, dd, J = 2.5, 12.0 Hz, H-6a′), 3.71 (1H, dd, J = 6.0, 12.0 Hz, H-6b′), 3.30 (1H, overlapped, H-4′), 3.27 (1H, overlapped, H-2′), 3.25 (1H, overlapped, H-3′), 3.22 (1H, m, H-5′); ^{13}C NMR (CD_3OD, 125 MHz) δ 134.8 (C-3), 130.9 (C-6), 130.1 (C-5, C-7), 128.9 (C-4, C-8), 119.4 (C-1), 102.0 (C-1′), 78.3 (C-5′), 77.8 (C-3′), 74.7 (C-2′), 71.4 (C-4′), 68.4 (C-2), 62.8 (C-6′); positive FABMS *m/z* 296 $[M + H]^+$, *m/z* 318 $[M + Na]^+$; *anal*. C 55.33%, H 5.93%, N 4.16%, calcd for $C_{14}H_{17}NO_6\cdot {}^1/_2H_2O$, C 55.26%, H 5.96%, N 4.60%.
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NP010393V