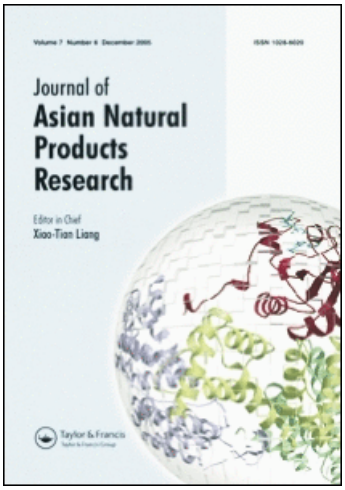

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Acylphloroglucinol glycosides from the fruits of *Pyracantha fortuneana*

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Three new acylphloroglucinol glycosides, namely pyrafortunosides A (**1**), B (**2**) and C (**3**), together with three known glycosides (**4**–**6**), were isolated from the fruits of *Pyracantha fortuneana* (Maxim.) Li. Their sructures were established to be 2,4,6-trihydroxy-acetophenone-6-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside (**1**), 2,4,6-trihydroxy-benzophenone-6-*O*-α-L-rhamno-pyranosyl-(1 → 6)-β-D-gluco-pyran-oside (**2**), 2,4,6-trihydroxy-benzophenone-6-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-gluco-pyranoside (**3**), garcimangosone D (**4**), 2,4,6-trihydroxy-acetophenone-6-*O*-β-D-glucopyranoside (**5**), and 2,4,6-trihydroxy-acetophenone-4-*O*-β-D-glucopyranoside (**6**) by spectral analysis. The three known glycosides (**4**–**6**) were obtained from this genus for the first time.

Keywords: *Pyracantha fortuneana*; Acylphloroglucinol glycosides; Pyrafortunosides

1. Introduction

Pyracantha fortuneana (Maxim.) Li, local Chinese name Huo-ji, is widely distributed throughout the southern and northwest part of China. It is used as a traditional Chinese medicine for treatment of indigestion [1]. Recent studies showed that *P. fortuneana* possessed some antioxidation activities and could significantly improve the lipoprotein metabolism of rats [2–3]. Phytochemical research on the plant resulted in the isolation of several flavonosides [4–6]. Our further investigation on the fruits of this plant led to the isolation and structural determination of three benzophenone glycosides and three acetophenone glycosides.

2. Results and discussion

Pyrafortunoside A (**1**) was obtained as a pale yellow gum. The molecular formula was established as $C_{20}H_{28}O_{13}$ by HRESIMS. The IR absorption band at 3409 cm^{-1} suggested the

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presence of the hydroxyl groups. The broad, intense absorption band at 1627 cm^{-1} was indicative of a conjugated keto group. The unusual low IR absorption frequency of the latter functional group indicated intramolecular hydrogen bonding with a hydroxyl group. The signal of a quaternary carbon at δ 201.4 in the ^{13}C NMR spectrum confirmed the presence of a keto function in the molecule. A three-proton singlet at δ 2.56 in ^{1}H NMR spectrum accounted for acetyl group. Two aromatic proton signals at δ 5.93 (1H, brs) and 5.73 (1H, brs) were deduced to be a couple of *meta* protons in a tetrasubstituted benzene ring on the basis of HMBC correlations of H-3/C-5 (δ 95.5) and H-5/C-3 (δ 97.3). The quaternary carbon signal at δ 104.0 was assigned as C-1 according to its HMBC correlations with H-3 and H-5. C-1 connected to the acetyl group because of the HMBC correlation between methyl protons (δ 2.56) and C-1. The remaining signals in the ^{13}C NMR spectrum were assigned as a rutinosyl residue on the basis of their HSQC and HMBC correlations. The location of the rutiosyl residue was established to be at C-6 (δ 160.9) according to the HMBC cross-peak at H-1′ (δ 4.85)/C-6 and comparison with the NMR spectra of the known compounds **5** and **6**. Thus, **1** was elucidated as 2,4,6-trihydroxy-acetophenone- 6-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside.

Pyrafortunoside B (**2**) was isolated as a pale yellow gum. The molecular formula $C_{25}H_{30}O_{13}$ was established by HRESIMS. The NMR spectra of **2** were similar to those of **1**, except that **2** showed the presence of a mono-substituted benzene ring with the signals at δ 7.65 (2H, d, $J = 7.1$ Hz), 7.46 (2H, t, $J = 7.3$ Hz), and 7.54 (1H, t, $J = 7.3$ Hz) instead of the methyl singlet (δ 2.56) in **1**. This mono-substituted benzene ring was connected to the carbonyl group on the basis of HMBC correlations between H-2′, 6′ (δ 7.46, 2H) and the carbonyl carbon (δ 194.6). The sugar moiety was located at C-6 (δ 157.2) according to the HMBC correlations between H-1″ and C-6. Therefore, **2** was deduced as 2,4,6-trihydroxy-benzophenone-6-*O*-α-L-rhamnopyranosyl-(1 → 6)- β-D-glucopyranoside. It is noted that the H-2″ signal of the glucose moiety in **2** shifted upfield to δ 2.76 due to the shielding effect from the mono-substituted benzene ring [7].

Pyrafortunoside C (**3**) was obtained as a pale yellow gum. It had the molecular formula $C_{24}H_{28}O_{13}$ by HRESIMS analysis. The ^{1}H and ^{13}C NMR spectra of aglycone of **3** were similar to those of tricornoside A, [8] while NMR data of the sugar moiety were consisted with those of dalnigrein-7-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-gluco-pyranoside [9]. The apiosyl residue was located at C-6″ (δ 67.2) of the glucosyl residue due to the obvious glycosylation shift of C-6″. The location of glucosyl residue was established to be at C-6 (δ 157.8) of the aglycone according to the HMBC correlation between anomeric proton H-1″ (δ 4.62) and C-6. The remaining HMBC data were identical to those of **2**. Thus, **3** was deduced as 2,4,6-trihydroxy-benzophenone-6-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside.

Three known compounds were also obtained from the same alcoholic extract. Their structures were determined as garcimangosone D (**4**) [7], 2,4,6-trihydroxy-acetophenone-6-*O*-β-D-glucopyranoside (**5**) [10], and 2,4,6-trihydroxy-acetophenone-4-*O*-β-D-glucopyranoside (**6**) [11] by spectral analysis.

3. Experimental

3.1 General experimental procedures

IR spectra were obtained using a JASCO FT/IR-480 plus spectrometer. Optical rotations were measured on a JASCO P-1020 digital polarmeter. UV spectra were recorded on a

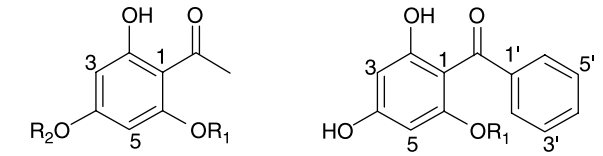
JASCO V-550 UV/Vis spectrometer. ESIMS spectra were taken on a FINIGAN LCQ Advantage MAX mass spectrometer. HRESIMS spectra were acquired using a Micromass Q-TOF mass spectrometer. 1D and 2D NMR spectra were measured with a Bruker AV-400 spectrometer using a DMSO-d_6 solution. The analytical HPLC was performed on a DIONEX system with DAD detector using a Shiseido Capcell Pak ODS column (4.6 × 250 mm) and the preparative HPLC was performed on a Varian system using a Phenomenex Fusion-RP 8 column (21.2 × 250 mm) with UV-Vis detector (ProStar 325). Column chromatography was carried out on silica gel (200–300 mesh) (Qingdao Haiyang Chemical Group Corporation, Qingdao, China), Toyopearl HW-40 (Toyo Soda MFG), Sephadex LH-20 (Amersham Biosciences AB) and ODS (60–80 μm, Merck). Silica gel GF_{254} (Qingdao Haiyang Chemical Group Corporation, Qingdao, China) and RP-18 F_{254} (Merck) were used for analytical TLC.

3.2 Plant material

The plant was collected in Qinling Mountain, Shanxi province, China in November 2003, and was identified as *P. fortuneana*. A voucher specimen (20031202) is deposited in the Institute of Traditional Chinese Medicine and Natural Products, Jinan University, Guangzhou, China.

3.3 Extraction and isolation

The air-dried fruits (5.0 kg) of *P. fortuneana* were refluxed twice with 60% (v/v) aqueous ethanol (30 L) for two hours each time. After filtration, the filtrate was evaporated to dryness under vacuum. The dried extract was suspended in water and successively partitioned with *n*-hexane, chloroform, ethyl acetate, and *n*-butanol to afford 18.4, 36.1, 30.1 and 126.6 g of extracts. From the *n*-butanol extract, 15 fractions were obtained by silica gel column chromatography eluting with a gradient of chloroform-methanol-H_2O (20:1:0 to 5:5:1). Fraction 3 (2.36 g, eluted with chloroform-methanol 10:1) was further separated by reversed-phase column chromatography, eluting with gradient methanol-H_2O, to yield 6 fractions (A1–A6). Fraction A2 (eluted with 30% methanol-H_2O) was fractionated on HW-40 column chromatography eluting with gradient methanol-H_2O to yield 6 subfractions. Compounds **4** (48.3 mg) and **5** (6.4 mg) were obtained from the third subfraction (eluted with 40% methanol-H_2O) after purification by preparative reversed phase HPLC with 15% acetonitrile-H_2O as eluting solvent system. The active fraction 4 (4.47 g, eluted with chloroform-methanol 4:1) was further fractionated by reversed-phase column chromatography eluting with gradient methanol-H_2O to yield 14 fractions (B1-B14). Fraction B1 (eluted with 10% methanol-H_2O) was subjected to column chromatography on HW-40 eluting with gradient methanol-H_2O to yield 8 subfractions. Compounds **1** (3.2 mg) and **6** (19.4 mg) were isolated from the second subfraction (eluted with 20% methanol-H_2O), after purification by preparative HPLC with 15% acetonitrile-H_2O. Fraction B2 (eluted with 30% methanol-H_2O) was subjected to column chromatography on HW-40 eluting with gradient methanol-H_2O to yield 7 subfractions. Compounds **2** (2.4 mg) and **3** (3.5 mg) were obtained from the third subfraction (eluted with 40% methanol-H_2O), after purification by preparative HPLC with 20% acetonitrile-H_2O.



1 R_1 = Glc $\xrightarrow{6\text{-}1}$ Rha, R_2 = H
5 R_1 = Glc, R_2 = H
6 R_1 = H, R_2 = Glc

2 R_1 = Glc $\xrightarrow{6\text{-}1}$ Rha
3 R_1 = Glc $\xrightarrow{6\text{-}1}$ Api
4 R_1 = Glc

Figure 1. Structures of **1**-**6**.

3.3.1 Pyrafortunoside A (1). Pale yellow gum; $[\alpha]_D^{24}$ −55.7 (c 1.58, MeOH); UV (MeOH) λ_{max} (log ε) 204 (4.05), 221 (3.99), 285 (sh) (3.97) nm; IR (KBr) ν_{max} 3409, 1627, 1384, 1074 cm^{-1}; ^{1}H-NMR (400 MHz) and ^{13}C NMR (100 MHz), see table 1; ESIMS (positive ion mode) *m/z* 499 $[M + Na]^+$, 975 $[2M + Na]^+$; ESIMS (negative ion mode) *m/z* 475 $[M\text{-}H]^-$; HRESIMS *m/z* 499.1438 (calcd for $C_{20}H_{28}O_{13}Na$, 499.1428).

3.3.2 Pyrafortunoside B (2). Pale yellow gum; $[\alpha]_D^{25}$ −55.2 (c 1.18, MeOH); UV (MeOH) λ_{max} (log ε) 206 (4.52), 249 (3.78), 300 (3.75) nm; IR (KBr) ν_{max} 3418, 1621, 1384, 1070 cm^{-1}; ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz), see table 2; ESIMS (positive ion mode) *m/z* 561 $[M + Na]^+$, 1099 $[2M + Na]^+$; ESIMS (negative ion mode) *m/z* 537 $[M\text{-}H]^-$; HRESIMS *m/z* 561.1588 (calcd for $C_{25}H_{30}O_{13}Na$, 561.1584).

3.3.3 Pyrafortunoside C (3). Pale yellow gum; $[\alpha]_D^{25}$ −54.1 (c 0.58, MeOH); UV (MeOH) λ_{max} (log ε) 206 (4.42), 250 (3.69), 299 (3.66) nm; IR (KBr) ν_{max} 3430, 1629, 1384, 1075 cm^{-1}; ^{1}H-NMR (400 MHz) and ^{13}C NMR (100 MHz), see table 2; ESIMS (positive ion mode) *m/z* 547 $[M + Na]^+$, 1071 $[2M + Na]^+$; ESIMS (negative ion mode) *m/z* 523 $[M\text{-}H]^-$; HRESIMS *m/z* 547.1412 (calcd for $C_{24}H_{28}O_{13}Na$, 547.1428).

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Table 1. NMR (400 MHz for ^{1}H, 100 MHz for ^{13}C) data of compounds **1, 5** and **6**[†‡].

	1		***5***		***6***	
No.	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	104.0 (s)		103.5 (s)		104.9 (s)	
2	165.9 (s)		166.0 (s)		165.7 (s)	
3	97.3 (d)	5.73(1H, brs)	97.2 (d)	5.73 (1H, d, $J = 1.9$ Hz)	96.6 (d)	5.90 (1H, d, $J = 2.1$ Hz)
4	n.o.[¶]		168.8 (s)		161.1 (s)	
5	95.5 (d)	5.93 (1H, brs)	95.4 (d)	5.97 (1H, d, $J = 1.9$ Hz)	94.3 (d)	6.10 (1H, d, $J = 2.1$ Hz)
6	160.9 (s)		161.1 (s)		164.9 (s)	
C═O	201.4 (s)		201.1 (s)		202.9 (s)	
CH_3	32.5 (q)	2.56 (3H, s)	32.5 (q)	2.57 (3H, s)	32.8 (q)	2.47 (3H, s)
Glc-1′	100.5 (d)	4.84 (1H, d, $J = 7.2$ Hz)	100.6 (d)	4.85 (1H, d, $J = 7.1$ Hz)	100.7 (d)	4.89 (1H, d, $J = 7.3$ Hz)
2′	73.2 (d)	3.29 (1H, m)	73.2 (d)	3.29 (1H, m)	73.1 (d)	3.27 (1H, m)
3′	76.7 (d)	3.27 (1H, m)	77.0 (d)	3.28 (1H, m)	77.1 (d)	3.27 (1H, m)
4′	69.6 (d)	3.12 (1H, m)	69.4 (d)	3.20 (1H, m)	69.4 (d)	3.15 (1H, m)
5′	76.0 (d)	3.44 (1H, m)	76.8 (d)	3.28 (1H, m)	76.7 (d)	3.27 (1H, m)
6′	66.2 (t)	3.80 (1H, d, J = 10 Hz), 3.47 (1H, m)	60.4 (t)	3.67 (1H, brd, $J = 11.8$ Hz), 3.50 (1H, dd, $J = 11.8$, 4.8 Hz)	60.5 (t)	3.68 (1H, d, $J = 11.8$ Hz), 3.50 (1H, dd, $J = 11.8$, 5.3 Hz)
Rha-1″	100.7 (d)	4.58 (1H, brs)				
2″	70.2 (d)	3.64 (1H, m)				
3″	70.6 (d)	3.43 (1H, m)				
4″	72.1 (d)	3.12 (1H, m)				
5″	68.4 (d)	3.43 (1H, m)				
6″	17.7 (q)	1.06 (3H, d, $J = 6.4$ Hz)				

[†] Assignments were based on ^{1}H-^{1}H COSY, HSQC, and HMBC experiments.
[‡] Recorded in DMSO-D_6.
[¶] Not observed.

Table 2. NMR (400 MHz for ^{1}H, 100 MHz for ^{13}C) data of compounds **2-4**[†‡].

	2		***3***		***4***	
No.	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	108.1 (s)		106.2 (s)		108.5 (s)	
2	158.1 (s)		n.o.[¶]		157.3 (s)	
3	97.0 (d)	5.99 (1H, brs)	97.7 (d)	5.78 (1H, brs)	96.7 (d)	6.08 (1H, d, $J = 1.8$ Hz)
4	n.o.[¶]		n.o.[¶]		160.5 (s)	
5	94.8 (d)	6.04 (1H, brs)	94.8 (d)	5.91 (1H, brs)	94.3 (d)	6.16 (1H,d, $J = 1.8$ Hz)
6	157.2 (s)		157.8 (s)		157.0 (s)	
1′	139.2 (s)		140.9 (s)		138.8 (s)	
2′	128.7 (d)	7.65 (1H, d, $J = 7.3$ Hz)	128.2 (d)	7.57 (1H, d, $J = 8.0$ Hz)	128.9 (d)	7.71 (1H, brd, $J = 7.7$ Hz)
3′	128.0 (d)	7.46 (1H, t, $J = 7.3$ Hz)	127.7 (d)	7.40 (1H, t, $J = 8.0$ Hz)	128.1 (d)	7.45 (1H, t, $J = 7.7$ Hz)
4′	131.9 (d)	7.54 (1H, t, $J = 7.3$ Hz)	130.9 (d)	7.49 (1H, t, $J = 8.0$ Hz)	132.4 (d)	7.55 (1H, t, $J = 7.7$ Hz)
5′	128.0 (d)	7.46 (1H, t, $J = 7.3$ Hz)	127.7 (d)	7.40 (1H, t, $J = 8.0$ Hz)	128.1 (d)	7.45 (1H, t, $J = 7.7$ Hz)
6′	128.7 (d)	7.65 (1H, d, $J = 7.3$ Hz)	128.2 (d)	7.57 (1H, d, $J = 8.0$ Hz)	128.9 (d)	7.71 (1H, brd, J = 7.7 Hz)
C═O	194.6 (s)		194.2 (s)		194.9 (s)	
Glc-1″	100.4 (d)	4.70 (1H, d, J = 8.0 Hz)	100.1 (d)	4.62 (1H, d, $J = 8.0$ Hz)	100.6 (d)	4.76 (1H, d, $J = 7.8$ Hz)
2″	73.1 (d)	2.76 (1H, brt)	73.1 (d)	2.62 (1H, t, $J = 8.2$ Hz)	73.1 (d)	2.85 (1H, br t, $J = 8.4$ Hz)
3″	76.4 (d)	3.16 (1H, m)	76.4 (d)	3.13 (1H, t, $J = 8.8$ Hz)	76.5 (d)	3.23 (1H, m)
4″	69.5 (d)	2.98 (1H, brt)	69.7 (d)	2.91 (1H, t, $J = 8.8$ Hz)	69.5 (d)	3.07 (1H,br t, $J = 9.1$ Hz)
5″	75.7 (d)	3.33 (1H, o)	76.2 (d)	3.34 (1H, o)	77.0 (d)	3.25 (1H, m)
6″	66.3 (t)	3.77 (1H, d, $J = 10.3$ Hz), 3.39 (1H, o)	67.2 (t)	3.81 (1H, d, $J = 10.4$ Hz), 3.35 (1H, o)	60.7 (t)	3.68 (1H, brd, $J = 10.0$ Hz), 3.47 (1H, dd, $J = 11.8, 5.4$ Hz)
Rha /Api-1‴	100.7 (d)	4.56 (1H, brs)	109.1 (d)	4.88 (1H, d, $J = 2.8$ Hz)		
2‴	70.3 (d)	3.66 (1H, brs)	75.9 (d)	3.77 (1H, d, $J = 3.0$ Hz)		
3‴	70.6 (d)	3.46 (1H, o)	78.7 (s)	3.88 (1H, d, $J = 9.2$ Hz), 3.56 (1H, d, $J = 9.2$ Hz)		
4‴	72.1 (d)	3.17 (1H, m)	73.3 (t)	3.34 (2H, o)		
5‴	68.3 (d)	3.44 (1H, m)	63.3 (t)			
6‴	17.8 (q)	1.11 (3H, d, $J = 6.0$ Hz)				

[†] Assignments were based on 1H-1H COSY, HSQC and HMBC experiments.
[‡] Recorded in DMSO-D_6.
[¶] Not observed.

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