Phenylpropanoid glycosides from the seeds of *Michelia hedyosperma*

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**Abstract**

The seed of *Michelia hedyosperma* Law (Magnoliaceae) is a commonly used spice by the local people living in the south of Yunnan province, China. From which, six new phenylpropanoid glycosides, michehedyosides A–F (1–6) were obtained, in addition to six known compounds, eugenol, eugenol 4-β-D-glucopyranoside, martynoside, alaschanioside C, 3,4-methylenedioxy-4-C-β-D-glucoside. Their structures were elucidated on the basis of detailed spectroscopic analyses and chemical methods.

**1. Introduction**

Phenylpropanoid glycosides (PPGs) are a group of water soluble natural products widely distributed in the plant kingdom, e.g., Smilacaceae (Zhang et al., 2008), Polygonaceae (Brown, Larson, & Smeden, 1998), and Magnoliaceae (Kelm & Nair, 2000). This class of compounds shows antibacterial, antiviral, analgesic, antispasmodic, neuroprotective, anti-feedant, cytotoxic, anti-inflammatory, antioxidant, enzyme inhibitory activities (Díaza et al., 2004; Xu, Su, & Zhou, 2007). Traditional study on identification of PPGs was carried out by a conventional high-sensitive polarimeter. Recently, rapid resolution liquid chromatography (RRLC) coupled with diode array detection (DAD) and electrospray ionisation time-of-flight mass spectrometry (ESI-TOF MS) method and HPLC–DAD–MS were developed to the exploration of the skeleton and the identity of PPGs in the molecule identification, which provide valuable structural information regarding the PPGs skeleton, fragmentation of the carbohydrate moiety, losses of the hydroxyl and glucose residue units (Qi et al., 2008; Wu et al., 2010). However, these methods appeared insufficient with regard to accurate peak identification in samples and were not sensitive for determination of low-content constituents (Wu et al., 2010). *Michelia hedyosperma* Low (Magnoliaceae), an ornamental plant and important source of timber, is distributed in the southern China (Guan & Zhang, 2004). The seed is a commonly used spice by the local people of its growing area. Previous researches reported sesquiterpene lactones (Iida & Ito, 1982; Jacobsson, Kumar, & Saminathan, 1995; Ogura, Cordell, & Farnsworth, 1978) and alkaloids (Khan, Kihara, & Omoloso, 2002; Nijsiri, Kittisak, & Srirat, 1988; Talapatra, Patra, & Talapatra, 1975) from the genus *Michelia*. However, chemical constituents of *M. hedyosperma* have not been studied. In this paper, we report the isolation and structure elucidation of six new phenylpropanoid glycosides (1–6) from the seeds of *M. hedyosperma* by traditional methods (Fig. 1).

**2. Materials and methods**

**2.1. General procedures**

Optical rotations were measured with a HORIBA SEPA-300 high-sensitive polarimeter. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectra were recorded on a UV 210A Shimadzu spectrometer. 1D- and 2D-NMR spectra were recorded in DMSO-d_6 or CD_3OD with a Bruker DRX-500 instrument operating at 500 MHz for 1H, 125 MHz for 13C, respectively. Coupling constants were expressed in Hertz and chemical shifts were given on a ppm scale with tetramethylsilane as internal standard. FABMS were recorded on a VG Auto Spec-300 spectrometer with glycerol as the matrix. HRESIMS was recorded on an API QSTAR Pulsar-1 mass spectrometer.

**2.2. Chemicals and reagents**

Column chromatography (CC) was performed on silica gel (200–300 mesh; Qingdao Marine Chemical Factory); Diaion HP20SS (Mitsubishi Chemical Industry, Ltd.); MCI-gel CHP20P (75–150 μm; Mitsubishi Chemical Industry, Ltd.); Chromatorex ODS
(100–200 mesh; Fuji Silysia Chemical Co. Ltd.). TLC was carried on silica gel H-precoated plates (0.2–0.25 mm thick, Qingdao Haiyang Chemical Co., Ltd.) with chloroform/methanol/water (7:3:0.5) or 8:2:0.2, v/v/v) and spots were detected by spraying with 10% sulphuric acid reagent followed by heating. GC analysis was run on Agilent Technologies HP5890 gas chromatograph equipped with an H₂ flame ionisation detector. The column was 30QC2/AC-5 quartz capillary column (30 m × 0.32 mm) with the following conditions: column temperature: 180/280 °C; programmed increase, 3 °C/min; carrier gas: N₂ (1 ml/min); injection and detector temperature: 250 °C; injection volume: 4 μl, split ratio: 1:50.

2.3. Plant materials

The seeds of M. hedyosperma were collected from Xishuangbanna, Yunnan, China, in December 2005, where it has been planted widely for seeds as spice.

2.4. Extraction and isolation

Grinded seeds (500 g) of M. hedyosperma were extracted with methanol under reflux condition for three times, and then defatted with petroleum ether. The defatted methanol extract (15 g) was subjected to Diaion column and eluted with H₂O/MeOH (1:0–0:1, v/v, each 800 ml) to give six fractions (I–VI). Fraction I (2.76 g) was chromatographed on a silica gel column, eluted with a gradient solvent system (CHCl₃/CH₂OH/H₂O, 8:2:0–6:4:1, v/v/v), and Rp-8 system (50–70% aq. MeOH) to afforded compounds 2 (591 mg) and 3 (35 mg). Fraction II (1.02 g) was subjected to chromatography of silica gel (CHCl₃/CH₂OH/H₂O, 9:1:0:1–7:3:0:5) and MCI-gel CHP20P (75–100% aq. MeOH) to produced 5 (218 mg). Similarly, compound 4 (45 mg) and alachasinoside C (9 mg) were isolated from fraction III (1.75 g). Compound 1 (223 mg) were obtained from fraction IV (1.3 g), while compound 6 (77 mg), martynoside (176 mg), eugenol 4-O-β-D-glucopyranoside (25 mg) and (+)-pinoreisol 4-O-β-D-glucoside (25 mg) were given from fraction V (2.81 g). Eugenol (8 mg) and 3,4-methylenedioxyxanimyl alcohol (167 mg) were produced from fraction VI (1.89 g) by repeated CC over silica gel (CHCl₃/CH₂OH/H₂O, 8:2:0:2–6:4:1, v/v/v), Rp-8 (50–70% aq. MeOH) and MCI-gel CHP20P (35–100% aq. MeOH).

Michelisedyoside A (1): colourless wax; [α]D₂⁰ − 46.3 (c 0.41, MeOH); IR (KBr) νmax 3357 (OH), 1078, 1602 cm⁻¹; UV (MeOH) λmax nm (log ε): 284 (3.46), 204 (4.41); negative FABMS m/z 311 [M−H]−, 149 [M−H−162]−; HRESIMS m/z 473.1672 [M−H]− (calcd for C₂₁H₂₉O₁₂, 473.1659); ¹H and ¹³C NMR see Tables 1 and 2.

Michelisedyoside C (3): white amorphous powder; [α]D₂⁰ − 52.8 (c 0.12, MeOH); IR (KBr) νmax 3441, 1070, 1599 cm⁻¹; UV (MeOH) λmax nm (log ε): 268 (3.09), 207 (4.67); negative FABMS m/z 503 [M−H]−, 341 [M−H−162]−, 179 [M−H−162]−; HRESIMS m/z 503.1773 [M−H]− (calcd for C₂₂H₃₁O₁₃, 503.1764); ¹H and ¹³C NMR see Tables 1 and 2.

Michelisedyoside D (4): white amorphous powder; [α]D₂⁰ − 53.6 (c 0.43, MeOH); IR (KBr) νmax 3406, 1070, 1612 cm⁻¹; UV (MeOH) λmax nm (log ε): 277 (3.36), 206 (4.57); negative FABMS m/z 341 [M−H]−, 179 [M−H−162]−; HRESIMS m/z 341.1243 [M−H]− (calcd for C₁₃H₁₉O₆, 341.1236). ¹H and ¹³C NMR see Tables 1 and 2.

Michelisedyoside E (5): white amorphous powder; [α]D₂⁰ − 67.0 (c 0.17, MeOH); IR (KBr) νmax 3419, 1069, 1612 cm⁻¹; UV (MeOH) λmax nm (log ε): 279 (3.38), 206 (4.53); negative FABMS m/z 487 [M−H]−, 341 [M−H−146]−, 179 [M−H−146]−; HRESIMS m/z 487.1801 [M−H]− (calcd for C₂₂H₂₉O₁₄, 487.1815). ¹H and ¹³C NMR see Tables 1 and 2.

Michelisedyoside F (6): white amorphous powder; [α]D₂⁰ − 51.2 (c 0.24, MeOH); IR (KBr) νmax 3395, 1075, 1505 cm⁻¹; UV (MeOH) λmax nm (log ε): 296 (3.68), 235 (3.73), 204 (4.39); negative FABMS m/z 359 [M−H]−, 177 [M−H−162]−; HRESIMS m/z 359.1804 [M−H]− (calcd for C₁₀H₁₀O₉, 339.1079). ¹H and ¹³C NMR see Tables 1 and 2.
2.5. Acid hydrolysis of compounds 1–6

A solution of 1–6 (about 5.0 mg) in 2% HCl (dioxane-H₂O, 1:1, 1 ml) was heated at 95 °C for 2 h based on a previous reference (Zhang, Zhang, Jacob, Li, & Yang, 2008). The reaction solution was extracted with chloroform 3 times. The aqueous layer was passed through an Amberlite IRA-401 (OH⁻/C₁₇₆) column and the eluate was condensed to dryness to yield the monosaccharide mixture.

2.6. Sugar analysis of compounds 1–6

The solutions of those sugar parts obtained as described above in pyridine (2 ml) were added to L-cysteine methyl ester hydrochloride (1.5 mg) and kept at 60 °C for 30 min. Supernatant was subjected to GC analysis under the following conditions: Column temperature: 180/280 °C, programmed increase: 3 °C/min, carrier gas: N₂ (1 ml/min), injector and detector temperature: 250 °C, injection volume: 4 μl, split ratio: 1:50. Configuration identification of α-glucose, α-allose, α-rhamnose was carried out by comparison with its derivative’s retention time [Hara et al., 1987], respectively. By comparing with the retention time of the authentic sugars in the form of derivatives under the same condition, the sugar moieties of compounds 1–6 were determined to be α-allose for 1–3, α-glucose for 2–6, and α-rhamnose for 5. All chemical reagents and standard sugars were purchased from Sigma–Aldrich Corporation.

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a Overlapped with each other at the same column.
b Overlapped with each other at the same column.

3. Results and discussion

The MeOH extract of the seeds of M. hedyosperma was defatted with petroleum ether and then applied to repeated column chromatography (CC) on Diaion HP20SS, silica gel, Rp-18 and MCI-gel CHP20P column to afford six new compounds, michehedyosides A–F (1–6). In addition, six known compounds were identified as eugenol (Yamaguchi, Numata, Uemura, Kaneto, & Yokoyama, 1975), eugenol 4-O-β-D-glucopyranoside (Fujita & Nakayama, 1992), martynoside (Jia, Gao, & Liu, 1994), alascosinonide C (Gao & Jia, 1995), trans-3,4-methylenedioxyxycinnamyl alcohol (Kashima, Tanoguchi, Arimoto, & Yamaguchi, 1991) and (+)-pinoresinol 4-O-β-D-glucoside (Chiba, Hisada, Nishibe, & Shima, 1979), respectively, by direct comparison of their spectral and physical data with those of authentic samples and literatures. All compounds were isolated from M. hedyosperma for the first time.

Michehedyoside A (1), obtained as a colourless wax, had a molecular formula C₁₅H₂₀O₇, as derived from the negative HRFABMS (m/z 311.1130 [M–H–162]⁻) and ¹³C NMR (DEPT) spectrum (Table 1). Negative ion FABMS showed fragment ion peak at m/z 149 [M–H–162]⁻, indicating the existence of one hexosyl unit. The IR spectrum of 1 indicated the existence of hydroxyl group (3357, 1078 cm⁻¹) and aromatic ring (1602 cm⁻¹). The ¹³C NMR and DEPT spectra (Table 1) displayed the presence of one methylene at δ 39.8, eight olefinic carbons arising from a phenyl and a terminal double bonds (δ 138.1, 115.5), together with a set of signals due to a hexosyl unit (δ 100.4, 71.2, 70.5, 67.1, 75.0, 61.0). The ¹H NMR spectrum (Table 2) showed three aromatic protons at δ 6.90 (1H, d, J = 1.7 Hz), 6.64 (1H, dd, J = 8.1, 1.7 Hz), and 6.70 (1H, d, J = 8.1 Hz) arising from a 1,3,4-trisubstituted benzene ring, three olefinic protons at δ 5.88 (1H, tdd, J = 6.5, 17.2, 10.2 Hz), 5.02 (1H, J = dd, 17.2, 1.5 Hz), and 5.00 (1H, J = dd, 10.2, 1.5 Hz) referring to a terminal double bonds, a doublet methylene at δ 3.18 (2H, d, J = 6.5 Hz), as well as an anomic proton at δ 4.93 (1H, d, J = 8.0 Hz). These NMR features suggested compound 1 was dihydroxallylbenezene glycoside. Acidic hydrolysis of 1 with 2% HCl afforded α-allose, which was identified by GC analysis of its trimethylsilyl imidazole derivatives (Hara et al., 1987). In the HMBC spectrum of 1, correlations of the methylene (δ 3.18) with the aromatic carbons [δ 116.9 (C-2), 115.8 (C-5)] and the terminal double bond carbons [δ 115.5 (C-9), 138.1 (C-8)] confirmed the connection of the allyl with C-1. Moreover, the HMBC correlation from the anomeric proton (δ 4.93) to C-3 (δ 145.5) and the ROESY...
correlation of the same anumeric proton with H-2 (δ 6.90) determined the connection of allosyl group at C-3. Therefore, the structure of michehedyoside A (1) was elucidated as 3,4-dihydroxy-allylbenezene 3-O-β-D-allopyranoside.

Michehedyoside B (2) was obtained as a colourless wax and possessed a molecular formula C_{23}H_{30}O_{12}, as determined by the negative HRFABMS (m/z 473.1659 [M–H]⁻) and 13C NMR (DEPT) spectrum (Table 1). The negative ion FABMS showed the fragment ion peaks at m/z 473 [M–H]⁻, 311 [M–H–162]⁻ and 149 [M–H–162–162]⁻, indicating the existence of two hexosyl units in 2. The 13C (Table 1) and 1H (Table 2) NMR spectra of 2 were closely related to those of 1, except that 2 had one more β-D-glucopyranosyl unit. Acidic hydrolysis of 2 gave α-glucose and α-allose, as determined by GC analysis as 1. In the HMBC spectrum of 2, correlations from the allosyl anumeric proton at δ 5.02 (1H, d, J = 7.7 Hz) to C-3 (δ 147.7) and the glucosyl anumeric proton at δ 4.71 (1H, d, J = 7.3 Hz) to C-4 (δ 145.7) revealed their connections at C-3 and C-4 of aglycone, respectively. Moreover, the ROESY correlations of the allosyl anumeric proton (δ 5.02) with H-2 (δ 6.95) and the glucosyl anumeric proton (δ 4.71) with H-5 (δ 7.04) confirmed the linkage positions of β-D-allo-pyranosyl to C-3 (δ 147.7) and β-D-glucopyranosyl to C-4 (δ 145.7). In conclusion, michehedyoside B (2) was identified as 3,4-dihydroxy-allylbenezene 3-O-C-β-D-allopyranosyl-4-O-β-D-glucopyranosidase.

Michehedyoside C (3) was isolated as a white amorphous powder and had a molecular formula C_{22}H_{30}O_{13}, as deduced by the HRFABMS (m/z 503.1773 [M–H]⁻) and 13C NMR (DEPT) spectrum (Table 1). The negative FABMS displayed the fragment ion peaks at m/z 503 [M–H]⁻, 341 [M–H–162]⁻ and 179 [M–H–162–162]⁻, indicating the existence of two hexosyl units. Acidic hydrolysis of 3 afforded α-glucose and α-allose as sugar moieties. The NMR data of 3 were similar to 2, except for the appearance of an additional methoxyl group in 3, which led the ABX coupling system in 2 changed to a meta-coupled system in 3 (δ 6.69, dd, J = 1.4 Hz) and 6.55 (dd, J = 1.4 Hz). The linkage position of the additional methoxyl group was determined at C-5 by the HMBC correlation of the methoxyl proton (δ 3.70) with C-5 (δ 152.7) and the ROESY correlation of the methoxyl proton (δ 3.70) with H-6 (δ 6.55) (Fig. 2.). Accordingly, the structure of michehedyoside C (3) was elucidated as 3,4-dihydroxy-5-methoxy-allylbenezene 3-O-β-D-allopyranosyl-4-O-β-D-glucopyranosidase.

Michehedyoside D (4) was obtained as a white amorphous powder. The HRESIMS displayed a quasi-molecular ion peak at m/z 341.1243 [M–H]⁻, corresponding to a molecular formula C_{16}H_{20}O_{5} for 4. In the negative FABMS, the fragment ion peaks at m/z 341 [M–H]⁻ and 179 [M–H–162]⁻ indicated the existence of one hexosyl unit in 4. Acidic hydrolysis of 4 gave α-glucose as a sugar moiety. The 13C (Table 1) and 1H (Table 2) NMR spectra of 4 showed the presence of one 1,3,4,5-tetrasubstituted benzene ring [δ 6.61 and 6.47 (each 1H, d, J = 1.8 Hz), one allyl group with terminal double bonds [δ 3.21 (d, J = 5.0 Hz, H-7), 5.90 (dd, J = 8.3, 17.8, 12.6 Hz, H-8), 5.23 (dd, J = 17.8, 2.8 Hz, H-9a), and 5.00 (dd, J = 12.6, 2.8 Hz, H-9b); δ 3.95 (C-7), 137.9 (C-8) and 115.6 (C-9)], one methoxyl group (δ 55.3), and one hexosyl unit (anumeric proton at δ 4.58 (d, J = 6.9 Hz, H-1')). These NMR features were very similar to those of 3. The only difference was that 4 had only one glucosyl unit in molecule. In the HMBC spectrum of 4, the correlations of the glucosyl H-1 (δ 4.58) with aromatic carbon (δ 145.7, C-5) was observed. Moreover, the ROESY correlations of the glucosyl H-1 with the aromatic H-2 (δ 6.61), and the methoxyl proton (δ 3.70) with the aromatic H-6 (δ 6.47) confirmed the linkage positions of glucosyl and methoxyl groups at C-3 and C-5, respectively. Based on the above evidences, michehedyoside D (4) was determined as 3,4-dihydroxy-5-methoxy-allylbenezene 3-O-β-D-glucopyranosidase.

Michehedyoside E (5), white amorphous powder, displayed a quasi-molecular ion peak at m/z 487.1801 [M–H]⁻ in the HRESIMS, corresponding to a molecular formula C_{23}H_{32}O_{12}. The negative FABMS data at m/z 487 [M–H]⁻, 341 [M–H–162]⁻ and 179 [M–H–162–162]⁻, combining with the 13C NMR data (Table 1), indicated that 5 had one hexosyl and one 6-deoxyhexosyl units. Acidic hydrolysis of 5 yielded l-rhamnose and α-glucose as sugar moieties. The 13C (Table 1) and 1H (Table 2) NMR spectra of 5 were closely related to those of 4, except for the appearance an additional rhamnosyl unit in 5. The HMBC correlations of the glucosyl H-1 (δ 4.57) with C-3 (δ 145.7) and the rhamnosyl H-1 (δ 4.53) with the glucosyl C-6 (δ 66.5), indicated the linkage positions of the glucosyl unit at C-3 and the rhamnosyl unit at glucosyl C-6, respectively. In addition, the ROESY correlations between the glucosyl anumeric proton (δ 4.57) with H-2 (δ 6.46) and the methoxyl proton with H-6 (δ 6.50) further confirmed the glucosyl unit linked at C-3 and the methoxyl group at C-5. Accordingly, michehedyoside E (5) was established as 3,4-dihydroxy-5-methoxy-allylbenezene 3-O-α-L-rhamnopyranosyl-(1–6)-β-D-glucopyranosidase.

Michehedyoside F (6) was isolated as a white amorphous powder. The HRESIMS exhibited a quasi-molecular ion peak at m/z 339.1084 [M–H]⁻, establishing a molecular formula C_{16}H_{18}O_{5} for 6. The negative FABMS displayed fragment ion peaks at m/z 339 [M–H]⁻ and 177 [M–H–162]⁻, suggesting the existence of one hexosyl unit. The 13C (DEPT) (Table 1) and 1H (Table 2) NMR spectra of 6 showed the existence of one 1,2,4,5-tetrasubstituted benzene ring [δ 121.8 (s), 149.5 (d), 99.4 (s), 145.7 (s), 141.9 (d), and 108.5 (s); δ 6.78 and 6.58 (each 1H, s)], one terminal double bonds (δ 137.4 and 115.1), one aliphatic methylene (δ 33.5), and one hexosyl [anumeric proton at δ 4.56 (d, J = 6.4 Hz)] units. Acid hydrolysis of 6 produced α-glucose as the sugar moiety. These NMR data suggested that 6 was an allylbenezene glucoside. However, compared with 1–5, compound 6 showed the presence of a typical methylenedioxy group (δ 5.88 (2H, s), δ 100.7). In the HMBC spectrum of 6, the correlations of the methylenedioxy protons (δ 5.88) with C-4 (δ 145.7) and C-5 (δ 141.9), the allyl methylene protons (δ 3.32 and 3.27) with C-6 (δ 108.5), the aromatic proton (δ 6.58, H-2) with C-1, and the glucosyl anumeric proton (δ 4.56) with C-2 (δ 149.5) were observed. In addition, the ROESY correlations of the allyl methylene protons (δ 3.32 and 3.27) with H-6 (δ 6.58) and the anumeric proton (δ 4.56) with H-3 (δ 6.78) further confirmed the glucosyl unit located on C-2, while the methylenedioxy group was linked between C-4 and C-5 positions. Thus, michehedyoside F (6) was deduced as 2-hydroxy-4,5-methylenedioxy-allylbenezene 2-O-β-D-glucopyranosidase.

![Fig. 2. Key HMBC and ROESY correlations of compound 3.](image-url)
& Sahin-Erdemli, 2002). Our research result supported that the seeds of *M. hedyosperma* could be a healthy plant resource for spice in the view of phytochemistry and the previous pharmacological publications.

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