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Study on C6-C3 Skeleton Derivatives from the Flower Buds of *Magnolia denudata*

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The chemical constituents of flower buds of *Magnolia denudata* Desr. were investigated. We isolated and identified five furofurans type lignan (**1**, **2**, **3**, **4**, **5**), three Phenylpropanoid type derivatives (**6**, **7**, **8**), one dihydrofuran type lignan (**9**), one flavonoid glycoside (**10**) and dibutyl phthalate (**11**) from *M. denudate*. The structures of these compounds were elucidated based on the chemical and ^{1}H NMR, ^{13}C NMR and MS spectroscopic evidence.

Keywords: *Magnolia denudata* Desr, Lignan, Phenylpropanoid, Flavonoid glycoside.

INTRODUCTION

Magnolia flower buds are a traditional Chinese medicine known as the name "XinYi", which has been used for thousands of years to treat headache, chronic infection of sinus, stuffy nose and tooth ache disease[1]. This crude drug has also been applicable for a general antiallergic and antioxidative agents and traditionally used to treat lowering blood pressure, stimulating uterus and inhibiting fungi and its essential oil possesses antiinflammatory effect[2]. Recently, traditional folk medicine is becoming increasingly popular in many medical contexts, particularly among patients with anti-inflammatory effect. Recent researches demonstrated the relevant pharmacological effects as regards with various *Magnolias* and the main pharmacological active compounds. A number of chemical investigations on the lignans and neolignans from the leaves, flower and twigs have been performed. In connection with our studies on the genera *Magnoliaceae* that has diverse biological activities, we have surveyed the constituents of the flower buds of *M. denudata* to isolate five furofurans type lignan, three Phenylpropanoid type derivatives, one dihydrofuran type lignan, one flavonoid glycoside and dibutyl phthalate from *M. denudate*. The chemical constituents have been identified as (7S,8R,8'R)-lariciresinol demethy ether (**1**)[3], magnostellin A (**2**)[4], 9-O-acetyl-(7R,8S,7'S,8'S)-fargesol (**3**)[5], galgravin (**4**)[1], veraguensin (**5**)[6], syringin (**6**)[7], benzyl α-D-mannopyranoside (**7**)[8], allyl catechol (**8**)[9], 3',4-O-dimethylcedrusin (**9**)[10], biondnoid I (**10**)[11], dibutyl phthalate (**11**)[12] by analysis of their ^{1}H NMR and ^{13}C NMR spectra and comparison with published data.

EXPERIMENTAL

The flower buds of *M. denudata* were obtained by Hubei Jin-Gui Crude Drug Medicin Co. Ltd., China, in May 2010. A voucher specimen (MD 102010) was deposited in the Herbarium of the college of pharmacy, South Central University for Nationalities, Wuhan, China.

Optical rotations were determined on a JASCO DIP-1000 polarimeter. ESI-MS and HR-ESI-MS were obtained using a JEOL JMS-DX300 and JMS-DX303HF spectrophotomer, respectively. NMR spectra were measured in $CDCl_3$ on a JEOL α-500 spectrometer (500 MHz) and chemical shifts were referenced to TMS. Column chromatography was carried out on silica gel 60 (230-400 mesh, Merck) and Chromatorex ODS (30-50 μm, Fuji Silysia Chemical Ltd.). Preparative HPLC was carried on an ODS column (Nihon Waters Ltd.) using the MeOH-H_2O solvent system. TLC was performed on precoated silica gel 60 F254 (0.2 mm, Merck)

The dry flower buds (3.2 kg) of *M. denudata* were extracted with 95 % EtOH three times under reflux. The ethanolic extract (470 g) was partitioned between hexane, $CHCl_3$, EtOAc, BuOH and H_2O, respectively. The $CHCl_3$-soluble portion (75 g) was repeatedly subjected to silica gel column chromatography with $CHCl_3$-MeOH (50:1-2:1) to afford 6 fractions (Frs.1-6). Fraction 5 was repeatedly subjected to silica gel column chromatography with $CHCl_3$-MeOH (20:1-10:1) to afford **1** (40.2 mg), **2** (25.4 mg), **3** (30.3 mg), **4** (10.7 mg) and **5** (11.4 mg). The EtOAc-soluble portion (35 g) was repeatedly subjected to silica gel and ODS column chromatography with $CHCl_3$-MeOH (50:1-2:1) and MeOH (20-100 %), respectively, to afford **10**

(500.5 mg), **11** (10.4 mg). The BuOH-soluble portion (23 g) was subjected to silica gel column chromatography with hexane-EtOAc (20:1-10:1) to afford **8** fractions (frs 3-1-8). Fraction 3-2 was purified by preparative HPLC (ODS, 70 % CH_3OH) to afford **9** (15.3 mg). Fractions 3-3 (720 mg) and 3-4 (826 mg) were repeatedly subjected to silica gel column chromatography with haxane-acetone (1:1) and hexane-EtOAc (3:1), then were purified with preparative HPLC (ODS, 70 % CH_3OH) to afford **6** (35.2 mg), **7** (51.5 mg) and **8** (13.4 mg).

RESULTS AND DISCUSSION

Compound 1: (7S, 8R, 8'R)-Lariciresinol demethy ether, yellow powder, ESI-MS *m/z*: 388 $(M)^+$ ($C_{22}H_{28}O_6$). ^{1}H NMR (400MHz, $CDCl_3$): δ 2.45 (1H, m, H-8'), 2.58 (1H, dd, *J* = 13.4, 10.7 Hz, H-7a), 2.76 (1H, m, H-8), 2.95 (1H, dd, *J* = 13.4, 5.1Hz, H-7b), 3.76 (1H, m, H-9a, 9'a), 3.81(12H, s, 4OCH_3), 3.92 (1H, m, H-9'b), 4.10 (1H, dd, *J* = 8.5, 6.6 Hz, H-9b), 4.85 (1H, d, *J* = 6.2Hz, H-7'), 6.76-6.93 (6H, m, H-2, 5, 6, 2', 5', 6'); ^{13}C NMR (100 MHz, $CDCl_3$): 33.2 (C-7), 42.3 (C-8); 52.5 (C-8'), 55.9, 60.85 (OCH_3), 60.8 (C-9'), 72.9 (C-9), 82.8 (C-7'), 109.1 (C-2'), 111.1 (C-5'), 111.5 (C-5), 112.0 (C-2), 118.0 (C-6'), 120.5 (C-6), 133.0 (C-1), 135.5 (C-1'), 147.5 (C-4), 149.0 (C-3), 148.4 (C-4'), 149.1 (C-3').

Compound 2: Magnostellin A, amorphous powder, ESI-MS *m/z*: 388 $(M)^+$ ($C_{22}H_{28}O_6$). ^{1}H NMR (400MHz, $CDCl_3$): δ 6.88-6.95 (6H, m, H-2, 5, 6, 2', 5', 6'), 4.88 (1H, d, *J* = 6.8Hz, H-7'), 4.66(1H, d, *J* = 6.4Hz, H-7), 4.28(1H, dd, *J* = 8.6, 16.4 Hz, H-9'e), 4.18 (1H, dd, *J* = 6.9, 15.7Hz, H-9'a), 3.94 (12H, s, OCH_3), 2.78 (1H, m, H-8'), 2.18 (1H, m, 8-H), 1.17 (3H, d, *J* = 7.2 Hz, H-9); ^{13}C NMR (100 MHz, $CDCl_3$): 87.8 (C-7), 44.0 (C-8); 48.1 (C-8'), 55.9 (OCH_3), 69.5 (C-9'), 13.0 (C-9), 73.1 (C-7'), 109.6 (C-2'), 111.0 (C-5'), 111.2 (C-5), 109.1 (C-2), 118.0 (C-6'), 118.4 (C-6), 136.3 (C-1), 135.5 (C-1'), 149.2 (C-4), 148.5 (C-3), 149.0 (C-4'), 148.3 (C-3').

Compound 3: 9-*O*-acetyl-(7R, 8S, 7'S, 8'S)-fargesol, Amorphous powder, ESI-MS *m/z*: 446 $(M)^+$ ($C_{24}H_{30}O_8$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85-6.97 (6H, m, H-2, 5, 6, 2', 5', 6'), 4.63 (1H, d, *J* = 8.2 Hz, H-7), 4.56 (1H, d, *J* = 7.7 Hz, H-7'), 4.38 (1H, dd, *J* = 4.5, 9.2 Hz, H-9'e), 4.02 (1H, dd, *J* = 7.2, 9.2 Hz, H-9'a), 3.89 (2H, m, H-9), 3.95 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 3.91 (6H, s, OCH_3), 2.54 (1H, m, H-8'), 2.16 (1H, m, H-8), 1.95 (3H, s, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): 84.0 (C-7), 49.0 (C-8); 49.9 (C-8'), 55.9 (OCH_3), 70.0 (C-9'), 63.8 (C-9), 75.7 (C-7'), 109.4 (C-2'), 111.1 (C-5'), 111.1 (C-5), 109.4 (C-2), 118.6 (C-6'), 118.9 (C-6), 135.2 (C-1), 133.6 (C-1'), 149.2 (C-4), 148.8 (C-3), 149.1(C-4'), 148.6 (C-3'), 170.7 (CO), 20.6 (OAc).

Compound 4: Galgravin, amorphous powder, ESI-MS *m/z*: 372 $(M)^+$ ($C_{22}H_{28}O_5$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (2H, d, *J* = 1.8 Hz, H-2, 2'), 6.86 (2H, d, *J* = 7.8 Hz, H-5, 5'), 6.96 (2H, dd, *J* = 1.8, 7.8 Hz, H-6,6'), 4.52 (2H, d, *J* = 6.1 Hz, H-7, 7'), 2.33 (2H, m, H-8, 8'), 1.04 (6H, d, *J* = 6.7 Hz, H-9, 9'), 3.88 (6H, s, 3, 3'-OMe), 3.85 (6H, s, 4, 4'-OMe); ^{13}C NMR (100MHz, $CDCl_3$): 134.9 × 2 (C-1', l), 111.1 × 2 (C-2', 2), 149 × 2 (C-3,3'), 148.5 × 2 (C-4', 4), 109.9 × 2 (C-5', 5), 118.6 × 2 (C-6',6), 87.3 × 2 (C-7',7), 44.4 × 2 (C-8', 8), 13 × 2 (C-9, 9'), 55.9 × 2 (3, 3'-OMe), 55.8 × 2 (4', 4-OMe).

Compound 5: Veraguensin, amorphous powder, ESI-MS *m/z*: 372 $(M)^+$ ($C_{22}H_{28}O_5$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (2H, m, H-2, 2'), 6.87 (4H, m, H-5', 5, 6', 6), 5.13 (1H, d, *J* = 9.2 Hz, H-7), 4.42 (1H, d, *J* = 9.4 Hz, H-7'), 2.24 (1H, m, H-8), 1.77 (1H, m, H-8'), 1.07 (3H, d, *J* = 6.7 Hz, H-9), 0.66 (3H, d, *J* = 7.3 Hz, H-9'), 3.91, 3.87 (6H, s, 3',3-OMe), 3.87, 3.86 (6H, s, 4', 4-OMe); ^{13}C NMR (100 MHz, $CDCl_3$): 133.9, 133.5 (C-1', 1), 110.5, 110.7 (C-2', 2), 148.9 × 2 (C-3', 3), 149 × 2 (C-4, 4'), 111.2, 118.7 (C-5', 5), 119.2, 110.1 (C-6, 6'), 87.3, 83.0 (C-7', 7), 46.0, 48.0 (C-8', 8), 15 × 2 (C-9, 9'), 55.9 × 2 (3', 3-OMe), 55.8 × 2 (4', 4-OMe).

Compound 6: Syringin, white amorphous powder, ESI-MS *m/z*: 372 $(M)^+$ ($C_{17}H_{24}O_9$). ^{1}H NMR (400 MHz, DMSO): δ 6.78 (2H, s, H-3, 5), 6.52 (1H, d, *J* = 15.9 Hz, H-7), 6.40 (1H, m, H-8), 4.16 (2H, m, H-9), 3.83 (6H, s, 2OCH_3), 4.97 (1H, d, *J* = 7.3 Hz, H-1'), 3.63, 3.45 (2H, m, H-6'), 3.35 (1H, m, H-3'), 3.26 (1H, m, H-4'), 3.19 (1H, m, H-5'), 3.10 (1H, m, H-2'). ^{13}C NMR (100 MHz, DMSO): δ 153.2 (C-2, 6), 134.3 (C-7), 133.0 (C-4), 130.6 (C-8), 128.9 (C-1), 104.9 (C-3, 5), 103.1 (C-1'), 77.7 (C-5'), 77.0 (C-2'), 74.6 (C-3'), 70.4 (C-4'), 61.9 (C-6'), 61.36 (C-9), 56.8 (2OCH_3).

Compound 7: Benzyl α-D-mannopyranoside, white Amorphous powder, ESI-MS *m/z*: 270 $(M)^+$ ($C_{13}H_{18}O_6$). ^{1}H NMR (400 MHz, MeOD): δ 7.49 (2H, d, *J* = 7.3 Hz, H-2, 6), 7.37-7.48 (2H, m, H-3, 5), 7.34 (1H, m, H-4), 5.01 (1H, d, *J* = 11.7 Hz, H-CH_2Bn), 4.73 (1H, d, *J* = 11.7 Hz, H-CH_2Bn), 3.38-4.14 (6H, m, H-Man); ^{13}C NMR (100 MHz, MeOD): δ 137.8 (C-1), 127.92 (C-2, 3), 127.8 (C-3, 5), 127.3 (C-4), 99.6, 74.1, 71.5, 71.0, 67.6 (C- Man), 61.8 (C-CH_2Bn).

Compound 8: Allyl catechol, white amorphous powder, ESI-MS *m/z*: 150 $(M)^+$ ($C_9H_{10}O_2$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.27 (2H, d, *J* = 6.7Hz, H-7), 5.04 (2H, m, H-9), 5.32 (2H, m, OH), 5.92 (1H, m, H-8), 6.62 (1H, dd, *J* = 1.8, 7.9 Hz, H-6), 6.71 (1H, d, *J* = 1.8 Hz, H-2), 6.78 (1H, d, *J* = 7.9 Hz, H-5).

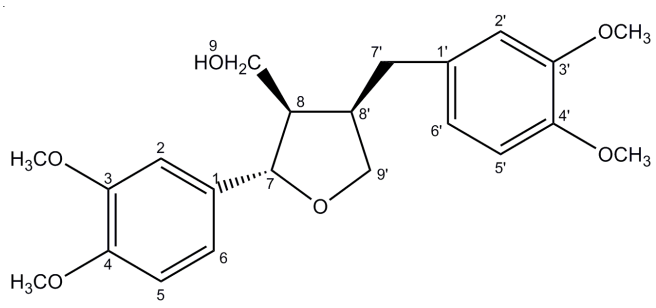
Compound 9: 3',4-*O*-Dimethylcedrusin, yellow amorphous powder, ESI-MS *m/z*: 374 $(M)^+$ ($C_{21}H_{26}O_6$). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.01-7.03 (2H, m, H-2, 6), 6.89 (2H, d, *J* = 8.7 Hz, H-5), 2.75 (1H, s, H-2'), 2.74 (1H, s, H-6'), 5.62 (1H, d, *J* = 7.2 Hz, H-7), 4.03 (1H, m, H-9a), 3.97 (1H, m, H-9b), 3.95 (3H, s, 3'-OCH_3), 3.93 (3H, s, 3-OCH_3), 3.92 (3H, s, 4-OCH_3), 3.75 (2H, m, H-9'), 3.67 (1H, m, H-7), 2.74 (2H, m, H-7'), 1.94 (2H, m, H-8'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2 (C-3), 149.0 (C-4), 146.6 (C-4'), 144.2 (C-3'), 135.4 (C-1'), 133.8 (C-1), 127.8 (C-5'), 118.7 (C-6), 116.0 (C-6'), 112.6 (C-2'), 111.1 (C-5), 109.4 (C-2), 87.7 (C-7), 64.0 (C-9), 62.3 (C-9'), 53.8 (C-8), 34.6 (C-8'), 32.0 (C-7'), 56.1, 56.0 (OCH_3).

Compound 10: Biondnoid I, yellow amorphous powder, ESI-MS *m/z*: 594 $(M)^+$ ($C_{30}H_{26}O_{13}$). ^{1}H NMR (400 MHz, MeOD): δ 6.19 (1H, s, H-6), 6.37 (1H, s, H-8), 8.05 (2H, d, *J* = 7.4 Hz, H-2', 6'), 6.88 (4H, m, H-3', 5', 3''', 5'''), 5.31 (1H, m, H-1''), 3.54 (1H, m, H-3''), 7.35 (2H, m, H-2''', 6'''), 7.50 (1H, d, *J* = 16.0 Hz, H-7'''), 6.13 (1H, d, *J* = 16.0 Hz, H-8''), 3.50-5.46 (the protons of suger); ^{13}C NMR (100 MHz, MeOD): δ 156.99 (C-2), 133.79 (C-3), 178.01 (C-4), 161.53 (C-5), 98.60 (C-6), 164.15 (C-7), 93.44 (C-8), 157.97 (C-9), 104.21 (C-10), 121.32 (C-1'), 130.08 × 2 (C-2''', 6''') 115.39 × 2 (C-3', 5'), 159.75 (C-4'), 102.56 (C-1''), 74.32 (C-2''), 74.39 (C-5''), 76.61 (C-3''), 70.33 (C-4''), 62.92 (C-6''), 125.69 (C-1''') 129.76 × 2 (C-2', 6'), 115.09 × 2 (C-3''', 5'''), 160.10 (C-4'''), 145.15 (C-7'''), 113.34 (C-8'''), 167.40 (C-9''').

Compound 11: Dibutyl phthalate, yellow amorphous powder, ESI-MS *m/z*: 278 $(M)^+$ ($C_{16}H_{22}O_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.79 (2H, m), 7.60 (2H, m), 4.38 (4H, t), 1.79 (4H, m), 1.53 (4H, m), 1.03 (6H, t).

Conclusion

As a part of our study, we have surveyed the constituents of the flower buds of *M. denudate*. The constituents of the original plant have systematically been examined in detail and showed so different pattern among the respective origins. The constituents contained five furofurans type lignan (**1**, **2**, **3**, **4**, **5**, Fig. 1), three phenylpropanoid type derivatives (**6**, **7**, **8**, Fig. 2), one dihydrofuran type lignan (**9**, Fig. 3), one flavonoid glycoside (**10**, Fig. 4) and aromatic compound as dibutyl phthalate (**11**, Fig. 5) carrying C-6 skeleton added to C-3.



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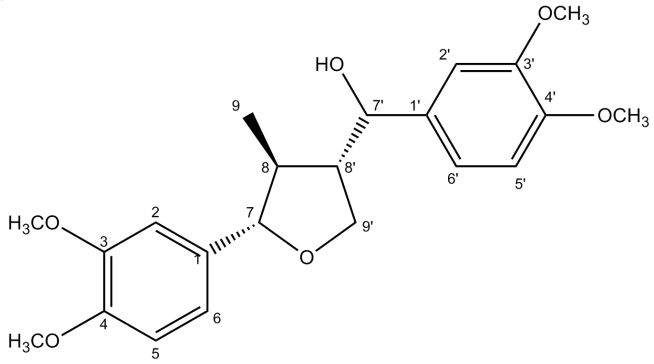

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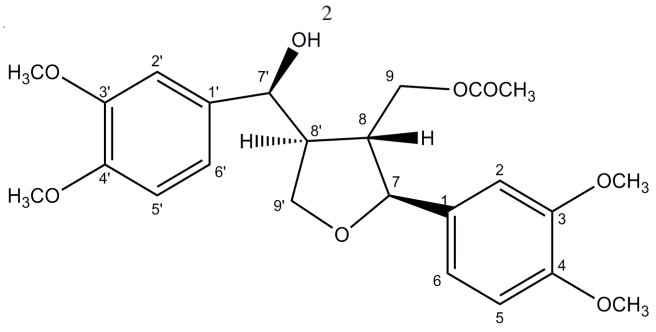

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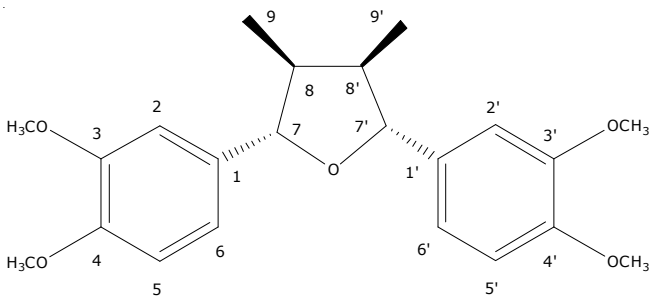

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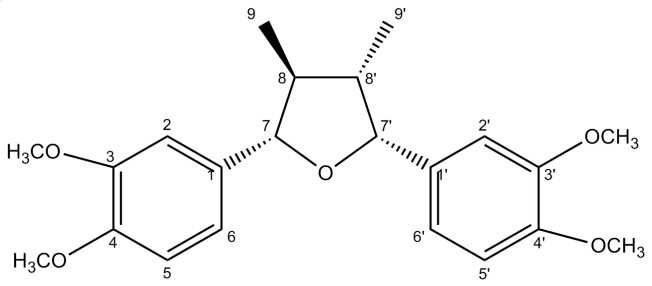

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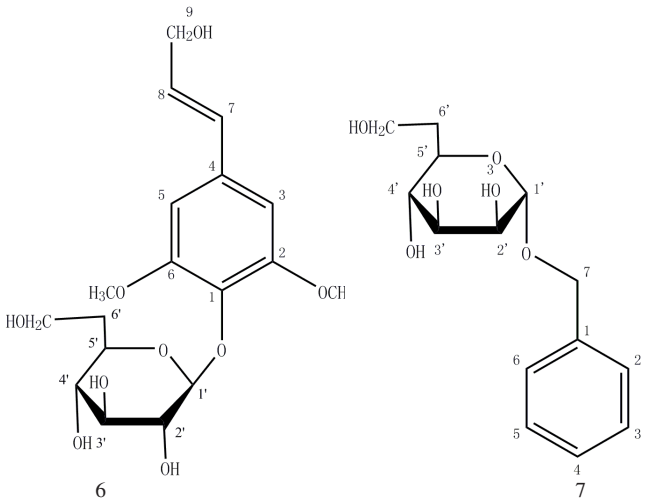
Fig. 1. Furofurans type lignan from the buds of *M. denudate*



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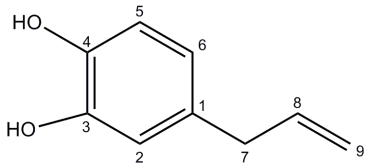

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Fig. 2. Phenylpropanoid type derivatives from the buds of *M. denudate*

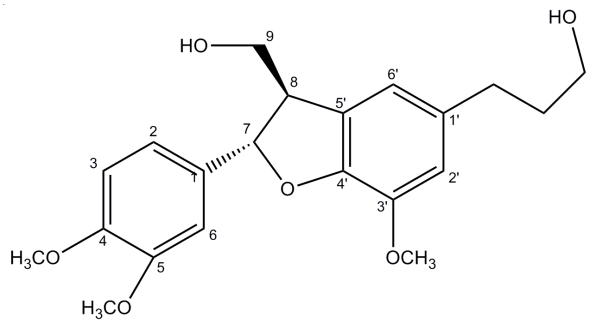

Fig. 3. Dihydrofuran type lignan from the buds of *M. denudate*

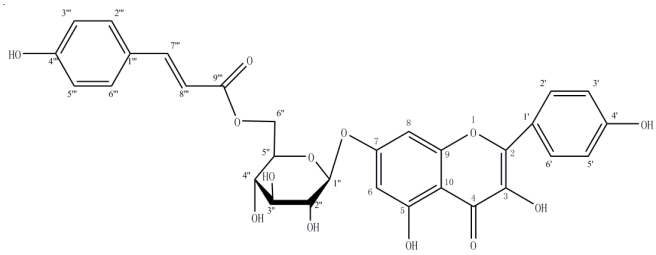

Fig. 4. Flavonoid glycoside from the buds of *M. denudate*

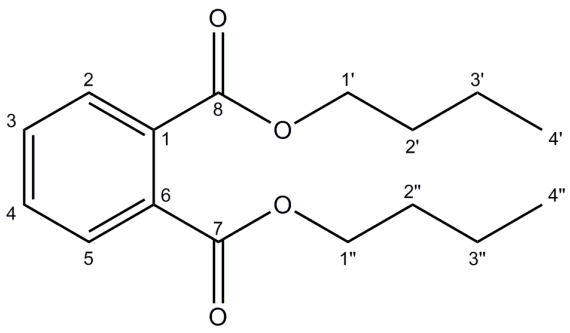

Fig. 5. Aromatic compound from the buds of *M. denudate*

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