CHEMICAL CONSTITUENTS OF MACROPANAX MEMBRANIFOLIUS FLOWERS

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TÓM TẮT

THÀNH PHẦN HÓA HỌC CỦA HOA LOÀI ĐẠI LĂNG LÁ MỎNG

Chi Đại lăng (Macropanax) họ Nhân sâm (Araliaceae) gồm hơn 20 loài phân bố ở các nước như Trung Quốc, Ấn độ và các nước Đông Nam Á, trong đó có 11 loài đã được tìm thấy ở Việt Nam. Một số loài Đại lăng được sử dụng trong y học cổ truyền điều trị bệnh tiêu hóa, lưu thông khí huyết, sốt rét. Tuy nhiên có rất ít nghiên cứu về thành phần hóa học và hoạt tính sinh học về các loài thuộc chi Đại lăng. Trong nghiên cứu này, chúng tôi báo cáo phân lập và xác định cấu trúc năm hợp chất từ hoa loài Đại lăng lá mỏng Macropanax membranifolius. Các hợp chất được xác định là serratagenic acid (1), liangwanoside II (2), ciwujianoside C_1 (3), isoquercitrin (4), và quercetin 3-O-α-L-rhamnopyranoside-7-O-β-D-glucopyranoside (5) bằng các phương pháp phổ NMR, MS và so sánh với tài liệu tham khảo. Đây là một trong những công bố đầu tiên của chúng tôi về thành phần hóa học loài Macropanax membranifolius, trong đó các hợp chất 2-5 lần đầu tiên được phát hiện từ chi Macropanax.

Từ khoá: *Đại lăng lá mỏng, axit serratagenic, liangwanoside II, ciwujianoside C_1, flavonoid, triterpene, saponin.*

1. INTRODUCTION

Genus *Macropanax* (Araliacea family) comprising over 20 species distributed in China, India, Nepal, Bhutan, Southeast Asian countries. Among that, 11 species were found in Vietnam and 8 of which are native species [1]. *Macropanax* species have been used in the folk Thai and Myamar medicine for the treatment of digestion, improve blood flow, cough, menopausal fever, and malarial fever [2]. Only few chemical studies of *Macropanax* plants have been described. Previous investigations *M. rosthornii* [3] and *M. disperum* [2,4] reported the presence of triterpenes, triteerpene saponins, sterols, and phenolic compounds. The *M. disperum* plant extracts possess potential thrombolytic, cytotoxic, analgesic, and antipyretic activities [2].

Macropanax membranifolius is a native tree in Vietnam and no chemical studies of this species has been reported. Herein, we reported our investigations of *M. membranifolius* flowers. Five known compounds were isolated and elucidated as serratagenic acid (**1**), liangwanoside

(**2**), ciwujianoside C_1 (**3**), isoquercitrin (**4**), and quercetin 3-*O*-*α*-L-rhamnopyranoside-7-*O*-*β*-D-glucopyranoside (5) (Figure 1) by analysis of NMR and MS spectral data.

2. EXPERIMENTAL

2.1. Plant materials

The flowers were collected at Keo Coong village, Van Tan commune, Gia Binh district, Lang Son province, Vietnam in November 2019 and identified as *Macropanax membranifolius* C.B. Shang by Dr Do Van Hai-Institute of Ecology and Biological Resources, VAST. Voucher specimen (HSB2019MM) was deposited at the Institute of Marine Biochemistry, VAST.

2.2. General procedures

The ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectra were recorded by a Bruker AM500 FT-NMR spectrometer using TMS as an internal standard. HR-ESI-MS were recorded on an ESI Q-TOF MS/MS system (AB SCIEX Triple). ESI-MS were obtained on an Agilent 1260 series single quadrupole LC/MS system. Column chromatography (CC) was performed on silica gel (Merck, 230-400 mesh) or Sephadex® LH-20. Thin layer chromatography used precoated silica gel plates (Merck 60 F_{254}). Compounds were visualized by spraying with 10% sulfuric acid and heating.

2.3. Extraction and isolation

The dried powdered *M. membranifolius* flowers (1 kg) were ultrasonically extracted with MeOH for three times (each time: 3 L of MeOH, at room temperature in 60 minutes). The extracts were collected, and MeOH was removed in reduced pressure to give a crude extract (100 g). The MeOH extract was suspended with water (0.5 L) and successively partitioned with *n*-hexane to give *n*-hexane (MFH, 6.0 g) and a water layer (MFW, 0.3 L). The MFW was subjected to Diaion HP-20 CC, eluting with increasing rate of MeOH in water (water 100%, MeOH 25% and MeOH 100%) to yield MeOH fraction WM (20.3 g) respectively. WM was subjected to silica gel CC, eluted with CH_2Cl_2/EtOAc (1/1, v/v) to give two subfractions, WM1 (3.2 g) and WM2 (1.7 g); then EtOAc/MeOH (1/10, v/v) to give three subfractions WM3 (2.5 g), WM4 (6.1 g) and WM5 (5 g), respectively.

The WM1 fraction was subjected to column chromatography (CC) on silica gel and eluted with *n*- CH_2Cl_2/EtOAc (2:1, v/v) to afford 4 fractions (WM1.1- WM1.4**)**. The WM1.2 fraction (1,2 g) was further separated by silica gel CC eluting with CH_2Cl_2/EtOAc (2:1, v/v) to give compound **1**. The WM3 (2.5 g) fraction was separated by silica gel CC and eluted with EtOAc/MeOH (10:1, v/v) to afford 3 fractions (WM3.1- WM3.3**)**. The WM3.2 fraction (0,8 g) was repeatedly purified by Sephadex CC eluting with MeOH to give compound **4**. The WM4 (6.1 g) fraction was fractionated by silica gel CC and eluted with EtOAc/MeOH (10:1, v/v) to afford 3 fractions (WM4.1-WM4.3**)**. The WM4.4 fraction (4.0 g) was repeatedly purified by Sephadex CC eluting with MeOH to give compound **3**. The WM5 (5.0 g) fraction was chromatographed on a silica gel column and eluted with EtOAc/MeOH (2:1, v/v) to afford 3 fractions (WM5.1- WM5.3**)**. The WM5.2 fraction (1.2 g) was purified by Sephadex CC eluting with MeOH to give compound **5**. The WM5.3 fraction (1.7 g) was purified by Sephadex CC eluting with MeOH, and by reversed phase silica gel CC eluting with MeOH/water (2:1, v/v) to give compound **2**.

Serratagenic acid (1): white armorphous powder, **ESI-MS** *m/z* 487 $[M+H]^+$. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 5.31 (1H, t, *J* = 3.0 Hz, H-12), 3.17 (1H, dd, *J* = 5.0 Hz, 11.5 Hz, H-3), 2.90 (1H, dd, *J* = 4.0, 14.0 Hz, H-18), 2.18 (1H, dd, *J* = 13.5, 14.0 Hz, H-19), 2.05 (1H, td, *J* = 3.5, 13.5 Hz, H-16), 1.27 (3H, s, H-30), 1.19 (3H, s, H-27), 0.99 (3H, s, H-23), 0.97 (3H, s, H-25), 0.84 (3H, s, H-26), 0.80 (3H, s, H-24). **^{13}C-NMR** (125 MHz, $CDCl_3$): Table 1.

Liangwanoside II (2): white armorphous powder, **HR-ESI-MS** *m/z* 1111.5443 $[M+Na]^+$, 1087.5323 $[M-H]^-$ and 1123.5089 $[M+^{35}Cl]^-$. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 5.36 (1H, d, *J* = 8.0 Hz, H-1″), 5.31 (1H, t, *J* = 3.0 Hz, H-12), 4.88 (1H, overlapped, H-1‴″), 4.43 (1H, d, *J* = 8.0 Hz, H-1‴), 4.30 (1H, d, *J* = 7.0 Hz, H-1′), 3.59 (1H, dd, *J* = 6.5 7.5 Hz, H-2′), 3.15 (1H, dd, *J* = 4.5 Hz, 11.5 Hz, H-3), 2.90 (1H, dd, *J* = 4.0, 14.0 Hz, H-18), 2.18 (1H, dd, *J* = 13.5, 14.0 Hz, H-19), 2.12 (1H, td, *J* = 3.5, 13.5 Hz, H-16), 1.29 (3H, d, *J* = 7.0 Hz, H-6 ‴″), 1.27 (3H, s, H-30), 1.19 (3H, s, H-27), 1.05 (3H, s, H-23), 0.98 (3H, s, H-25), 0.87 (3H, s, H-24), 0.82 (3H, s, H-26). **^{13}C-NMR** (125 MHz, $CDCl_3$): Table 1.

Ciwujianoside C_1 (3): white armorphous powder, **HR-ESI-MS** *m/z* 1065.5241 $[M+Na]^+$ and 1043.5421 $[M+H]^+$. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 5.36 (1H, d, *J* = 8.0 Hz, H-1″), 5.36 (1H, m, H-12), 4.87 (1H, d, *J* = 1.5 Hz, H-1‴″), 4.66 and 4.64 (each 1H, br s, H_2-29), 4.41 (1H, d, *J* = 7.5 Hz, H-1‴); 4.30 (1H, d, *J* = 7.0 Hz, H-1′), 3.15 (1H, dd, *J* = 4.5 Hz, 11.5 Hz, H-3), 2.76 (1H, dd, *J* = 4.5, 13.0 Hz, H-18), 2.57 (1H, td, *J* = 13.5, 14.0 Hz, H-19), 2.20 (3H, overlapped, H-16), 1.29 (3H, d, *J* = 6.5 Hz, H-6‴″), 1.21 (3H, s, H-27), 1.07 (3H, s, H-23), 0.98 (3H, s, H-25), 0.87 (3H, s, H-24), 0.82 (3H, s, H-26). **^{13}C-NMR** (125 MHz, $CDCl_3$): Table 1.

Isoquercitrin (**4**) Yellow solid. ESI-MS *m/z* 465 $[M+H]^+$. ^{1}H-NMR (500 MHz, CD_3OD) *δ* (ppm): 7.86 (1H, d, *J* = 2.0 Hz, H-2′), 7.60 (1H, dd, *J* = 2.0 Hz 8.5 Hz, H-6′), 6.88 (1H, d, *J* = 8.5 Hz, H-5′), 6.42 (1H, d, *J* = 2.0 Hz, H-8), 6.23 (1H, d, *J* = 2.0 Hz, H-6), 5.18 (1H, d, *J* = 8.0 Hz, H-1″), 3.87–3.48 (6H, m, H-2"-6"). ^{13}C-NMR (125 MHz, CD_3OD) δ (ppm): 179.5 (C-4), 166.2 (C-7), 163.0 (C-5), 158.8 (C-9), 158.5 (C-2), 149.9 (C-4′), 145.8 (C-3′), 135.7 (C-3), 122.9 (C-6′), 122.8 (C-1′), 117.8 (C-5′), 116.1 (C-2′), 105.6 (C-10), 105.5 (C-1″), 99.9 (C-6), 94.7 (C-8), 77.2 (C-3″), 75.0 (C-5 ″), 73.1 (C-2″), 70.0 (C-4″), 61.9 (C-6″).

Quercetin 3-*O*-*α*-L-rhamnopyranoside-7-*O*-*β*-D-glucopyranoside (**5**) Yellow solid. ESI-MS *m/z* 611 $[M+H]^+$. ^{1}H-NMR (500 MHz, DMSO-d_6) *δ* (ppm): 7.70 (1H, dd, *J* = 2.5 Hz 8.5 Hz, H-6′), 7.57 (1H, d, *J*= 2.5 Hz, H-2′), 6.82 (1H, d, *J* = 8.5 Hz, H-5′), 6.79 (1H, d, *J* = 2.0 Hz, H-8), 6.43 (1H, d, *J* = 2.0 Hz, H-6), 5.55 (1H, d, *J* = 1.5 Hz, H-1″), 5.40 (1H, d, *J* = 8.0 Hz, H-1‴), 3.80-3.42 (10H, m, H-2‴-5‴ ', H-2‴-6‴), 1.12 (1H, d, *J* = 6.5 Hz, H-6″). ^{13}C-NMR (125 MHz, DMSO-d_6) δ (ppm): 177.5 (C-4), 161.5 (C-7), 156.7 (C-5), 155.8 (C-9), 158.5 (C-2), 149.5 (C-4′), 144.8 (C-3′), 133.7 (C-3), 122.1 (C-6′), 120.8 (C-1′), 115.9 (C-5′), 115.1 (C-2′), 105.5 (C-10), 101.5 (C-1‴), 99.3 (C-6), 98.4 (C-1″), 94.3 (C-8), 75.8 (C-3″), 73.1 (C-5″), 71.5 (C-3‴), 71.1 (C-4″), 70.2 (C-2‴), 70.0 (C-5‴), 69.7 (C-2″), 67.8 (C-4‴), 60.0 (C-6″), 17.9 (C-6″).

3. RESULTS AND DISCUSSION

Compound **1** was isolated as a white amorphous solid. The ^{1}H NMR spectrum showed characteristic signals of a triterpene skeleton with six singlet methyls at δ_H 1.27, 1.19, 0.99, 0.97, 0.84, 0.80 (each 3H, s), an olefinic proton at δ_H 5.31 (1H, t, *J* = 3.0 Hz, H-12), and an oxymethine at δ_H 3.17 (1H, dd, *J* = 5.0, 11.5 Hz, H-3). The ^{13}C-NMR and HSQC spectra revealed 30 carbon signals including two carbonyl carbons at δ_C 181.1 (C-29) and 180.0 (C-28), two olefinic carbon at δ_C 143.1 (C-13) and 123.0 (C-12), an oxymethine group at δ_C 78.4 (C-3) and six methyl carbon at δ_C 27.4 (C-23), 25.1(C-27), 18.5 (C-30), 16.4 (C-26), 15.0 (C-24) and 14.6 (C-25). The coupling constants of H-3 (*J* = 5.0 and 11.5 Hz) indicated proton H-3 is in *α*- position. In the HMBC spectrum, the position of methyl group were assigned by correlations of H-23 (δ_H 0.99), H-24 (δ_H 0.80) to C-3 (δ_C 78.4); H-27 (δ_H 1.19) to C-13 (δ_C 143.1); H-30 (δ_H 1.27) to C-29 (δ_C 181.1); H-23, H-24 and H-25 (δ_H 0.80) to C-5 (δ_C 55.3); and H-25, H-26 to C-9 (δ_C 47.7) (Figure 2). The molecular formula of

1 was identified as $C_{30}H_{46}O_5$ (M= 486) by NMR and the protonated molecular ion peak *m/z* 487 $[M+H]^+$. Based on the above spectral evidence, compound **1** was determined as serratagenic acid or 3*β*-hydroxyolean-12-ene-28,29-dioic acid [5]. Serratagenic acid (**1**) have been isolated from *Macropanax rosthornii* [3].

Compound **2** was isolated as a white amorphous solid. The molecular formula of **2** was identified as $C_{53}H_{86}O_{21}$ by the *pseudo*-molecular peak *m/z* 1111.5443 $[M+Na]^+$, 1087.5323 $[M-H]^-$ and 1123.5089 $[M+^{35}Cl]^-$ in the HR-MS spectrum. The NMR spectra showed signals of a triterpene glycoside. The triterpene aglycone was observed with similar signals as those of compound **1** with six singlet methyls at δ_H 1.27, 1.19, 1.05, 0.98, 0.87, 0.82 (each 3H, s), an olefinic proton at δ_H 5.31 (1H, t, *J* = 3.0 Hz, H-12), and an oxymethine at δ_H 3.15 (1H, dd, *J* = 4.5 Hz, 11.5 Hz, H-3*α*). The glycosides were found with 4 anomeric protons at δ_H 5.36 (1H, d, *J* = 8.0 Hz, H-1″)/δ_C 95.8, 4.88 (1H, overlapped, H-1‴″)/δ_C 102.9, 4.43 (1H, d, *J* = 8.0 Hz, H-1‴)/δ_C 104.2; 4.30 (1H, d, *J* = 7.0 Hz, H-1′)/δ_C 107.1. Extensive ^1H-^1H COSY analysis identified 4 sugar moieties as H-1′ (δ_H 4.30)/H-2′ (δ_H 3.59)/H-3′ (δ_H 3.53)/H-4′ (δ_H 3.83)/H-5′ (δ_H 3.53 and 3.85); H-1″ (δ_H 5.36)/H-2″ (δ_H 3.36)/H-3″ (δ_H 3.43)/H-4″ (δ_H 3.42)/H-5″ (δ_H 3.31)/H-6″ (δ_H 4.10 and 3.82); H-1‴ (δ_H 4.43)/H-2‴ (δ_H 3.33)/H-3‴ (δ_H 3.49)/H-4‴ (δ_H 3.56)/H-5‴ (δ_H 3.82)/H-6‴ (δ_H 3.83 and 3.68); H-1‴″ (δ_H 4.88)/H-2‴″ (δ_H 3.86)/H-3‴″ (δ_H 3.52)/H-4‴″ (δ_H 3.41)/H-5‴″ (δ_H 3.99)/H-6‴″ (δ_H 1.29). The NMR data and coupling constants suggested the presence of an *α*-L-arabinose, two *β*-D-glucose and an *α*-L-rhamnose units [6]. The ^{13}C-NMR and HSQC spectra revealed 53 carbon signals, among that 30 carbon signals of aglycone including two carbonyl carbons at δ_C 184.0 (C-29), 177.9 (C-28), two olefinic carbons at δ_C 144.4 (C-13), 124.3 (C-12), an oxymethine group at δ_C 90.7 (C-3); six methyl carbons at δ_C 27.4 (C-23), 25.1(C-27), 18.5 (C-30), 16.4 (C-26), 15.0 (C-24); 14.6 (C-25) and 23 carbon signals of 4 sugar moieties. The HMBC correlations (Figure 2) of H-1′ (δ_H 4.30) to C-3 (δ_C 90.7); H-1″ (δ_H 5.36) to C-28 (δ_C 177.9); H-1‴ (δ_H 4.43) to C-6″ (δ_C 69.4); H-1‴″ (δ_H 4.88) to C-4‴ (δ_C 79.6) confirmed the *α*-L-arabinose linked at 3*β*-hydroxyl and *α*-L-rhamnopyranosyl (1-4)-*β*-D-glucopyranosyl(1-6)-*β*-D-glucoside moiety linked at carboxylic acid group C-28 [6]. Thus, compound **2** was determined as liangwanoside II or 3-*O*-*α*-L-arabinopyranosyl-3*β*-hydroxylolean-12-ene-28,29-dioic acid 28-*O*-[*α*-L-rhamnopyranosyl(1-4)-*β*-D-glucopyranosyl(1-6)-*β*-D-glucosyl] ester [6].

Compound **3** was isolated as a white amorphous solid. The molecular formula of **3** was identified as $C_{53}H_{86}O_{21}$ by the *pseudo*-molecular peak in the HR-MS at *m/z* 1065.5241 $[M+Na]^+$ and 1043.5421 $[M+H]^+$. The NMR spectra also revealed signals of a triterpene glycoside. Similar to compound **2**, four sugar units were found with 4 anomeric protons at δ_H 5.35 (1H, d, *J* = 8.5 Hz, H-1″)/δ_C 95.8, 4.87 (1H, d, *J* = 1.5 Hz, H-1‴″)/δ_C 102.8, 4.41 (1H, d, *J* = 7.5 Hz, H-1‴)/δ_C 104.2; 4.30 (1H, d, *J* = 7.0 Hz, H-1′)/δ_C 107.1. The NMR data and coupling constants also suggested the presence of an *α*-L-arabinose, two *β*-D-glucose and an *α*-L-rhamnose units [6, 7]. The triterpene aglycone was observed with five singlet methyls at δ_H 1.21, 1.07, 0.98, 0.87, 0.80 (each 3H, s), an olefinic proton at δ_H 5.35 (1H, H-12), and an oxymethine at δ_H 3.15 (1H, dd, *J* = 4.5 Hz, 11.5 Hz, H-3). Different from compound **1** and **2**, a terminal methylene group was found at δ_H 4.66 and 4.64 (each 1H, br s, H-29) instead of a methyl of H-30 in the ^1H-NMR spectrum of compound **3**. The ^{13}C-NMR and HSQC spectra revealed 52 carbon signals, including 23 carbon signals of 4 sugar moieties and 29 carbon signals of triterpene aglycone.

The aglycone showed a carbonyl group at δ_C 177.2 (C-28), four olefinic carbons at δ_C 149.3 (C-20), 144.4 (C-13), 124.3 (C-12), 107.6 (C-29), an oxymethine group at δ_C 90.7 (C-3); five methyl carbons at δ_C 28.6 (C-23), 26.4 (C-27), 17.9 (C-26), 17.0 (C-24); 16.1 (C-25). The positions of sugar groups were assigned by HMBC correlations of H-1′ (δ_H 4.30) to C-3 (δ_C 90.7); H-1″ (δ_H 5.35) to C-28 (δ_C 177.2); H-1‴ (δ_H 4.41) to C-6″ (δ_C 69.4); H-1⁗ (δ_H 4.87) to C-4‴ (δ_C 77.9) (Figure 2). Therefore *α*-L-arabinose was linked at 3*β*-hydroxyl and α-L-rhamnopyranosyl(1-4)-*β*-D-glucopyranosyl(1-6)-*β*-D-glucoside moiety was linked at carboxylic acid group at C-28 [6-7]. Therefore, compound **3** was determined as ciwujianoside C_1 or 3-*O*-*α*-L-arabinopyranosyl -30-norolean-12,20(29)-dien-28-oic acid 28-*O*-[*α*-L- (1-4)-*β*-D-glucopyranosyl(1-6)-*β*-D-glucosyl] ester} [7].

Compound **4** was isolated as a yellow solid. The ^{1}H-NMR spectrum displayed the signals of a flavonol glycoside with two *meta* protons at δ_H 6.42 (1H, d, J = 2.0 Hz, H-8), 6.23 (1H, d, J = 2.0 Hz, H-6), three protons of an ABX system at δ_H 7.86 (1H, d, J = 2.0 Hz, H-2′), 7.60 (1H, dd, J = 2.0 Hz 8.5 Hz, H-6′), 6.88 (1H, d, J = 8.5 Hz, H-5′), an anomer proton at δ_H 5.18 (1H, d, J = 8.0 Hz, H-1″) and six protons of a sugar at δ_H 3.87–3.48 (6H, m, H-2"-6"). The ^{13}C-NMR spectrum showed 21 carbon signals including fifteen carbons of a flavonol, and 6 signals of a sugar moiety at δ_C 105.5 (C-1″), 77.2 (C-3 ″), 75.0 (C-5 ″), 73.1 (C-2″), 70.0 (C-4″) and 61.9 (C-6″). The molecular formula of 4 was deduced as $C_{21}H_{20}O_{12}$ based on the protonated molecular ion peak *m/z* 465 $[M+H]^+$ and NMR data. The coupling constant of anomer proton (J = 8.5 Hz) and ^{13}C NMR data suggested the sugar was *β*-glucose. Compound **4** was assigned as isoquercitrin or quercetin-3-*O*-*β*-D-glucopyranoside by comparison of NMR data with those published in literature [8].

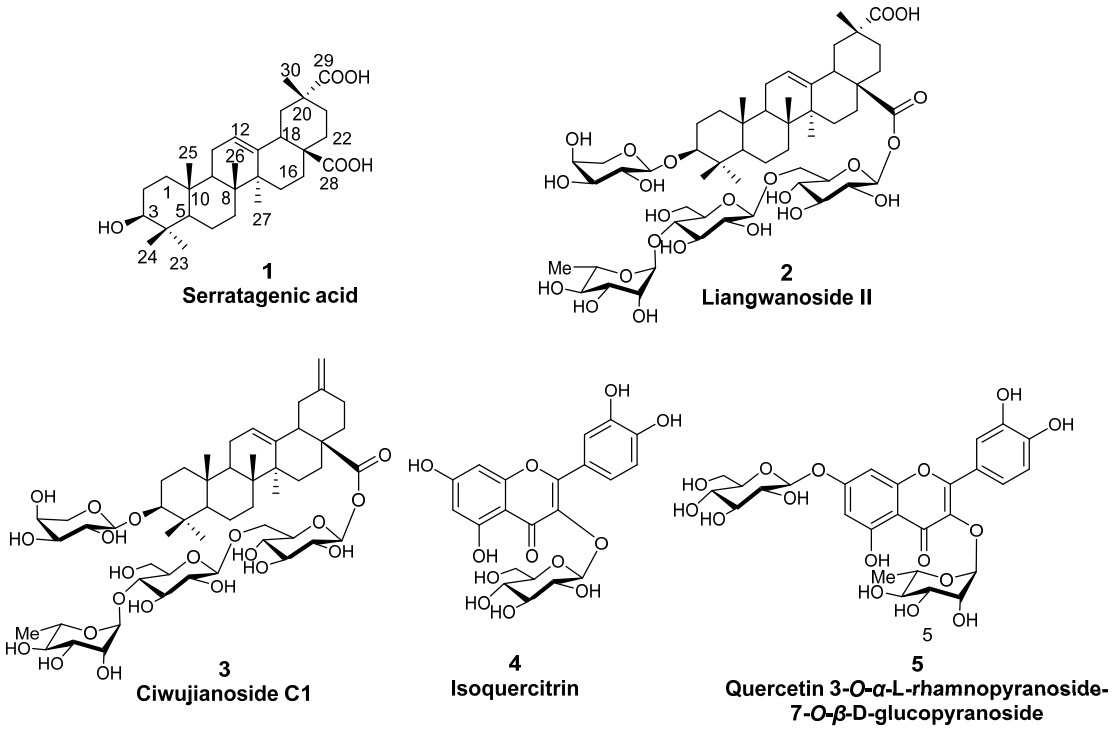

Figure 1. Chemical structures of isolated compounds from M. membranifolius

Table 1. ^{13}C NMR (125 MHz, CD_3OD) data of compounds 1-3

	1	**2**	**3**	**Sugars**	**2**	**3**
C	δ_C	δ_C	δ_C	**C**	δ_C	δ_C
1	38.5	39.8	39.8	3-*O*-Ara		
2	26.5	26.9	26.9	1′	107.1	107.6
3	78.3	90.7	90.6	2′	72.8	72.8
4	38.5	40.2	40.2	3′	74.3	74.2
5	55.3	55.3	57.0	4′	69.5	69.4
6	18.1	19.3	19.3	5′	66.3	66.3
7	32.6	33.9	33.9	28-*O*-Glc		
8	39.2	40.7	40.7	1″	95.8	95.8
9	47.7	48.7	48.5	2″	73.8	73.7
10	36.8	37.9	37.9	3″	78.1	77.9
11	23.2	24.6	24.6	4″	71.0	70.9
12	123.0	124.3	124.3	5″	76.8	76.7
13	143.1	144.4	144.2	6″	69.4	69.4
14	41.5	42.9	42.9	6‴-*O*-Glc		
15	27.3	28.9	28.9	1‴	104.2	104.2
16	22.8	24.1	24.2	2‴	75.3	75.2
17	46.0	47.9	48.3	3‴	76.3	76.6
18	40.2	41.7	49.0	4‴	79.6	79.5
19	39.8	41.7	42.6	5‴	78.2	78.1
20	41.7	43.5	149.3	6‴	61.9	61.9
21	28.2	29.9	30.2	4⁗ -*O*-Rha		
22	31.3	32.5	38.4	1⁗	102.9	102.8
23	27.4	28.6	28.6	2⁗	72.4	72.4
24	15.0	16.1	17.0	3⁗	72.2	72.2
25	14.6	17.0	16.1	4⁗	73.7	73.7
26	16.4	17.8	17.9	5⁗	70.7	70.6
27	25.1	26.2	26.4	6⁗	17.8	17.9
28	180.0	177.9	177.3			
29	181.0	184.0	107.6			
30	18.5	20.2	-			

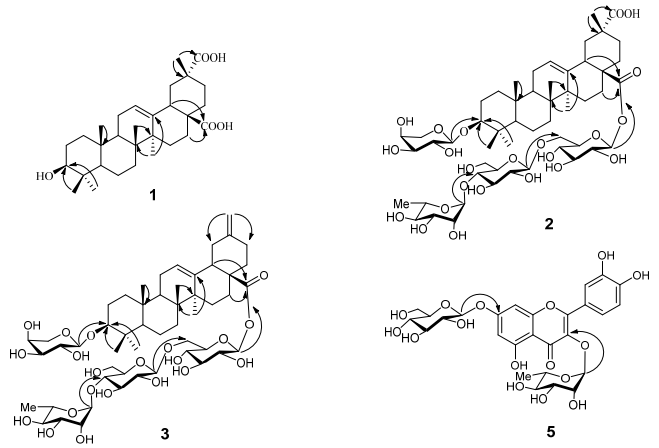

Figure 2. Key HMBC (⟶) correllations of compound 1-3 and 5

Compound **5** was obtained as a yellow solid. The ^{1}H-NMR spectrum also showed the typical signals of a quercetin glycoside with two *meta*-aromatic protons at δ_H 6.79 (1H, d, J = 2.0 Hz, H-8), 6.43 (1H, d, J = 2.0 Hz, H-6), three protons of an ABX system at δ_H 7.70 (1H, dd, J = 2.5 Hz 8.5 Hz, H-6′), 7.57 (1H, d, J = 2.5 Hz, H-2′), 6.82 (1H, d, J= 8.5 Hz, H-5′), two anomer protons at δ_H 5.55 (1H, d, J = 1.5 Hz, H-1″), 5.40 (1H, d, J = 8.0 Hz, H-1‴), a methyl doublet at δ_H 1.12 (1H, d, J = 6.5 Hz, H-6″). The NMR data and coupling constants (J = 1.5 and 8.0 Hz) suggested the presence of an α-rhamnose and a β-glucose units. The ^{13}C-NMR and HSQC spectrum showed 27 carbon signals including fifteen carbons of quercetin, and 12 signals of two sugar units. In the HMBC spectrum, correlations of H-1″ (δ_H 5.55) to C-3 (δ_C 133.7) and H-1‴ (δ_H 5.40) to C-7 (δ_C 161.5) indicated that α-rhamnose and β-glucose attached to C-3 and C-7 positions, respectively. The molecular formula of **5** was assigned as $C_{27}H_{30}O_{16}$ based on the protonated molecular ion peak m/z 611 $[M+H]^+$. Compound **5** was assigned as quercetin 3-*O*-α-L-rhamnopyranoside-7-*O*-β-D-glucopyranoside [9].

4. CONCLUSION

Phytochemical study of *M. membranifolius* flowers led to the isolation of five known compounds including serratagenic acid (**1**), liangwanoside II (**2**), ciwujianoside C_1 (**3**), isoquercitrin (**4**), and quercetin 3-*O*-α-L-rhamnopyranoside-7-*O*-β-D-glucopyranoside (5). To our knowledge, this is the first chemical investigation of *Macropanax membranifolius.* Compound **2-5** have not been reported from *Macropanax* genus before.

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