CHEMICAL CONSTITUENTS FROM
POLYGONATUM KINGIANUM COLL. & HEMSL.

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Abstract. Six compounds, including two homoisoflavanones 3-(2’-hydroxy-4’-methoxy-benzyl)-5,7-dihydroxy-8-methyl-chroman-4-one (1), disporopsin (2) along with 2-O-methyl-α-D-fructofuranose (3), (E,E)-9-oxooctadeca-10,12-dienoic acid (4), 1-palmitoylglycerol (5), 5α,8α-ergosterol peroxide (6) were isolated from the rhizomes of Polygonatum kingianum of Viet Nam. Their structures were determined by 1D- and 2D-NMR spectra and by comparison with the reported spectral data. Compounds 3, 4 and 6 are first reported from the genus Polygonatum. Compound 1 and 5 are reported for the first time from Polygonatum kingianum.

Keywords: Polygonatum kingianum, homoisoflavanone, 2-O-methyl-α-D-fructofuranose, (E,E)-9-oxooctadeca-10,12-dienoic acid, 5α,8α-ergosterol peroxide.

Classification numbers: 1.1.1, 1.1.6.

1. INTRODUCTION

Polygonatum kingianum Coll. & Hems. belonging to the genus Polygonatum (Liliaceae), is originated in Asian temperate and subtropical regions. The species is distributed mainly in China, Laos, and Viet Nam. In traditional Vietnamese medicine, the rhizomes of P. kingianum has been used to treat some diseases such as tuberculosis, hemoptysis, angina, coronary artery disease, diabetes, hypotension, autonomic nervous system disorders [1]. On the other hand, P. kingianum is also used as a tonic and a remedy to treat lung diseases, upset stomachs, hyperlipidemia and related metabolic syndrome, ringworm in China [2 - 4]. Some previous studies on the rhizomes of P. kingianum in the world have resulted in the isolation of steroidal saponins, flavonoids, alkaloids, phenolics, fructose derivatives, and phytosterols [3 - 6]. However, in Viet Nam, there have not been any publication on chemical constituents of P. kingianum so far. In the present paper, we report the isolation and structural identification of...
six compounds including 3-(2'-hydroxy-4'-methoxy-benzyl)-5,7-dihydroxy-8-methyl-chroman-4-one (1), disporopsin (2), 2-O-methyl-α-D-fructofuranose (3), (E,E)-9-oxooctadeca-10,12-dienoic acid (4), 1-palmitoylglycerol (5), 5α,8α-ergosterol peroxide (6) from the rhizomes of *P. kingianum* of Viet Nam.

2. MATERIALS AND METHODS

2.1. Plant materials

The rhizomes of *Polygonatum kingianum* Coll. & Hemsl. were collected at Ha Giang, Viet Nam in September 2017, and identified by Dr. Nguyen Van Du, Institute of Ecology and Biological Resources, Vietnam Academy of Science and Technology (VAST). A voucher specimen (HTHD - 09.2017) has been deposited at Institute of Natural Products Chemistry, VAST.

2.2. General experimental procedures

The 1H-NMR (500 MHz) and 13C-NMR (125 MHz) spectra were recorded on a Bruker AM500 FT-NMR spectrometer and tetramethylsilane was used as an internal standard. ESI-MS spectra were obtained from an Agilent 1100 Series LC/MSD Trap SL. The optical rotation was conducted on Jasco P2000 instrument. Column chromatography (CC) was performed using silica gel (0.040 - 0.063 mm) and YMC RP-18 resins (30 - 50 μm). Thin layer chromatography (TLC) used pre-coated silica gel 60 F254 and RP-18 F254S plates. Compounds were visualized by UV light at 254 and 365 nm, and by spraying with the solution of 10 % H2SO4 in ethanol and heating for 1-3 minutes.

2.3. Extraction and isolation

The dried and powdered rhizomes of *P. kingianum* (3.0 kg) were extracted with hot methanol three times using bath sonicator to yield 350 g of dark crude residue, which was then suspended in water and successively partitioned with n-hexane, ethyl acetate (EtOAc) to obtain the corresponding extracts: n-hexane (25.0 g), EtOAc (45.0 g) and water layer.

The n-hexane extract (25.0 g) was applied to silica gel CC eluting with a gradient of n-hexane : EtOAc (50:1, 20:1, 5:1,1:1, 0:1; v:v) to provide five fractions (H1 to H5). Fraction H1 (3.2 g) was fractionated on silica gel CC using the mobile phase of n-hexane : EtOAc (25:1; v:v) to give three smaller fractions (H1.1 to H1.3). Fraction H1.2 (0.8 g) was further purified by silica gel CC eluting with n-hexane : acetone (15:1; v:v) to afford compound 5 (12.0 mg). Fraction H2 (1.5 g) was firstly subjected to silica gel CC with the eluent of n-hexane : EtOAc (10:1; v:v) and then recrystallized in n-hexane : acetone (4:1; v:v) to yield compound 6 (15.0 mg). Fraction H3 (2.0 g) was separated into four smaller fractions (H3.1 to H3.4) by silica gel CC using n-hexane : EtOAc (15:1; v:v) as eluent. Compound 4 (10.0 mg) was obtained from fraction H3.2 using silica gel CC and the eluent of dichloromethane : EtOAc (40:1; v:v).

The EtOAc extract (45.0 g) was subjected to silica gel CC eluting with a gradient of n-hexane : EtOAc (10:1, 4:1, 1:1,1:2, 0:1; v:v) to produce five fractions (E1 to E5). Fraction E1 (5.7 g) was subsequently separated using silica gel CC and n-hexane : acetone (15:1; v:v) to give four smaller fractions (E1.1 to E1.4). Fraction E1.1 (1.2 g) was passed through silica gel CC using the mobile phase of dichloromethane : EtOAc (10:1; v:v) to yield five sub-fractions.
Chemical constituents from Polygonatum kingianum Coll. & Hemsl.

(E1.1.1 to E1.1.5). Purification of sub-fraction E1.1.3 on YMC RP-18 CC with the solvent system of methanol : water (1:3, v:v) gave compound 1 (12.0 mg). Fraction E1.2 (0.9 g) was chromatographed on silica gel CC with dichloromethane : acetone (15:1; v:v) and then on silica gel CC with the solvent mixture of chloroform : methanol : water (8:1:0.05; v:v:v) to achieve compound 2 (9.0 mg). Fraction E5 (2.8 g) was separated into four smaller fractions (E5.1 to E5.4) by silica gel CC using the solvent mixture of chloroform : methanol : water (7:1:0.1; v:v:v). Fraction E5.3 (0.6 g) was purified by YMC RP-18 CC using methanol : water (2:1, v:v) to afford compound 3 (11.0 mg).

3-(2'-hydroxy-4'-methoxy-benzyl)-5,7-dihydroxy-8-methyl-chroman-4-one (1): yellow powder. ESI-MS: m/z 331.1 [M+H]⁺, C₁₈H₁₈O₆. [α]D²⁵ = −12.5 (c 0.2, MeOH). ¹H-NMR (500 MHz, CD₂OD), δ (ppm): 1.94 (3H, s, CH₃); 2.63 (1H, dd, J = 13.5, 5.0 Hz, Ha-9); 2.97 (1H, m, H-3); 3.20 (1H, dd, J = 13.5, 5.0 Hz, Hb-9); 3.76 (3H, s, OCH₃); 4.15 (1H, dd, J = 11.5, 7.5 Hz, Ha-2); 4.30 (1H, dd, J = 11.5, 7.5 Hz, Hb-2); 5.94 (1H, s, H-6); 6.38 (1H, dd, J = 8.5, 2.5 Hz, H-5'); 6.40 (1H, d, J = 2.5 Hz, H-3'); 7.00 (1H, d, J = 8.5 Hz, H-6'). ¹³C-NMR (125 MHz, MeOD), δ (ppm): 7.4(CH₃); 28.2(C-9); 28.2(C-3); 46.4(C-3); 55.6(OCH₃); 70.7(C-2); 96.2(C-6); 102.4(C-3'); 102.9(C-4a); 104.2(C-8); 105.7(C-5'); 118.3(C-1'); 132.6(C-2'); 157.6(C-2'); 161.2(C-4'); 161.7(C-8a); 163.3(C-5); 166.0(C-7); 200.5(C-4).

Disporopin (2): white powder. ESI-MS: m/z 303.4 [M+H]⁺, C₁₈H₁₈O₆. [α]D²⁵ = −24.5 (c 0.1, MeOH). ¹H-NMR (500 MHz, CD₂OD), δ (ppm): 2.59 (1H, d, J = 14.0 Hz, Ha-9); 3.15 (1H, d, J = 14.0 Hz, Hb-9); 4.09 (1H, d, J = 11.5 Hz, Ha-2); 4.23 (1H, d, J = 11.0 Hz, Hb-2); 5.80 (1H, d, J = 2.0 Hz, H-8); 5.83 (1H, d, J = 2.0 Hz, H-6); 6.26 (1H, dd, J = 8.0, 2.5 Hz, H-5'); 6.32 (1H, d, J = 2.5 Hz, H-3'); 6.89 (1H, d, J = 8.0 Hz, H-6'). ¹³C-NMR (125 MHz, MeOD), δ (ppm): 28.3(C-9); 46.1(C-3); 70.5(C-2); 96.6(C-8); 97.8(C-6); 102.2(C-4a); 103.6(C-3'); 107.5(C-5'); 117.0(C-1'); 132.6(C-2'); 157.6(C-2'); 158.3(C-4'); 164.8(C-8a); 165.8(C-5); 170.5(C-7); 199.6(C-4).

2-O-methyl-α-D-fructofuranose (3): pale yellow oil. ESI-MS: m/z 195.2 [M+H]⁺, C₉H₁₄O₆. [α]D²⁵ = +27.0 (c 0.15, MeOH). ¹H-NMR (500 MHz, CD₂OD), δ (ppm): 3.30 (3H, s, OCH₃); 3.65 (1H, d, J = 12.0 Hz, Ha-1); 3.66 (1H, dd, J = 3.0, 12.0 Hz, Ha-6); 3.73 (1H, d, J = 12.0 Hz, Hb-1); 3.77 (1H, d, J = 3.0, 12.0 Hz, Hb-6); 3.87 (1H, m, H-5); 3.92 (1H, m, H-4); 4.05 (1H, d, J = 4.5 Hz, H-3).¹³C-NMR (125 MHz, MeOD), δ (ppm): 49.0(OCH₃); 60.5(C-1); 62.8(C-6); 78.9(C-4); 82.5(C-8); 84.6(C-5); 109.2(C-2).

(E,E)-9-oxoacteada-10,12-dienoic acid (4): colorless oil. ESI-MS: m/z 295.2 [M+H]⁺, C₁₇H₁₇O₃. ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 0.88 (3H, t, J = 6.5 Hz, H-18); 1.27 – 1.33 (10H, H-4, H-5, H-6, H₁₆, H₁₇); 1.43 (2H, m, H-15); 1.61 (2H, m, H-7); 1.63 (2H, m, H-3); 2.18 (2H, m, H-14); 2.34 (2H, t, J = 7.5 Hz, H-2); 2.53 (2H, t, J = 7.5 Hz, H-8); 6.07 (1H, d, J = 15.0 Hz, H-10); 6.16 (1H, m, H-13); 6.17 (1H, m, H-12); 7.13 (1H, dm, J = 15.0 Hz, H-11).¹³C-NMR (125 MHz, CDCl₃), δ (ppm): 14.0(C-18); 22.5(C-17); 24.4(C-19); 24.6(C-3); 28.4(C-15); 28.9-29.1(C-4 to C-6); 31.4(C-16); 33.1(C-14); 33.8(C-2); 40.5(C-8); 127.9(C-10); 128.9(C-12); 143.1(C-11); 145.8(C-13); 178.6(C-1); 201.1(C-9).

1-palmitoylgllycerol (5): white powder. ESI-MS: m/z 331.3 [M+H]⁺, C₁₉H₃₉O₄. ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 0.88 (3H, t, J = 7.0 Hz, H-16'); 1.26 (2H, m, H-4' to H-15'); 1.60 (2H, m, H-3'); 2.35 (2H, t, J = 7.5 Hz, H-2'); 3.59 (1H, dd, J = 3.5, 11.5 Hz, H-3a); 3.69 (1H, dd, J = 6.0, 11.5 Hz, Hb-3); 3.92 (1H, m, H-2'); 4.17 (2H, m, H-1).¹³C-NMR (125 MHz, CDCl₃), δ
from ESI cytotoxic against a series of human cancer cell lines (HCT15, T24S, MCF7, Bowes) [9]. Compound = spectrum of of from ESI - first time. with the published data [8], C methyl group (group (group (H NMR (500 MHz, CDCl 3)); 51.1 (C 23); 18); 1.90 (1H, m, Ha-11); 1.35 (1H, m, Ha-16); 1.41 (1H, m, Ha-15); 1.46 (1H, m, H-25); 1.49 (1H, m, H-9); 1.50 (1H, m, Hb-11); 1.53 (1H, m, Ha-2); 1.57 (1H, m, H-14); 1.59 (1H, m, Hb-15); 1.69 (1H, m, Ha-1); 1.75 (1H, m, Hb-16); 1.84 (2H, m, Hb-2, H-24); 1.90 (1H, m, Ha-4); 1.95 (2H, m, Hb-1, Hb-12); 2.01 (1H, m, H-20); 2.10 (1H, m, Hb-4); 3.96 (1H, m, H-3); 5.15 (1H, m, H-22); 5.23 (1H, m, H-23); 6.24 (1H, d, J = 8.5 Hz, H-6); 6.50 (1H, d, J = 8.5 Hz, H-7). 13C-NMR spectrum of 1 showed 18 carbon signals. Twelve of them were assigned to two aromatic rings (δC from 96.2 to 166.0 ppm). Besides, the presence of a carbonyl group (δC 200.5), a methylene (δC 28.2), an oxygenated methylene (δC 70.7), and a methine (δC 46.4) suggested compound 1 was a homoisoflavanone [7]. The HMBC cross-peaks from the methyl group (δH 1.94) to C-7 (δC 166.0), C-8 (δC 104.2), C-8a (δC 161.7) and from the methoxy group (δH 3.76) to C-4′ (δC 161.2) established the methyl and methoxy groups were attached to C-8 and C-4′, respectively. According to the analysis, specific rotation value and comparison with the published data [8], compound 1 was determined to be 3-(2′-hydroxy-4′-methoxybenzyl)-5,7-dihydroxy-8-methyl-chroman-4-one, which was isolated from P. kingianum for the first time.

Compound 2 was obtained as a white powder. The molecular ion peak at m/z 303.4 [M+H] + from ESI-MS spectrum of 2 suggested its molecular formula C18H18O6. The 13C-NMR spectrum of 2 showed the presence of 16 carbon signals typical of a homoisoflavane skeleton [28.3(C-9); 46.1 (C-3); 70.5 (C-2), 199.6 (C-4)], the others from δC 96.6 to 170.5 ppm [7]. The 1H-NMR spectrum of 2 exhibited five aromatic protons at δH 5.80 (1H, d, J = 2.0 Hz, H-8), 5.83 (1H, d, J = 2.0 Hz, H-6); 6.26 (1H, d, J = 8.0, 2.5 Hz, H-5′); 6.32 (1H, d, J = 2.5 Hz, H-3′); 6.89 (1H, d, J = 8.0 Hz, H-6′). Based on the spectroscopic evidence and specific rotation value, the structure of compound 2 was identified as disporopin by comparison with the published data [9]. Disporopin was previously isolated from the rhizomes of P. kingianum [10] and found to be cytotoxic against a series of human cancer cell lines (HCT15, T24S, MCF7, Bowes) [9].

Compound 3 was obtained as pale yellow oil. The molecular ion peak at m/z 195.2 [M+H] + from ESI-MS spectrum of 3 suggested its molecular formula C7H14O6. Detailed analysis of the

3. RESULTS AND DISCUSSION

Compound 1 was obtained as a yellow powder. The molecular ion peak at m/z 331.1 [M+H] + from ESI-MS spectrum of 1 suggested its molecular formula C18H18O6. Detailed analysis of the 1H-NMR and HSQC spectra of 1 revealed four aromatic protons [5.94 (1H, s, H-6), 6.38 (1H, dd, J = 8.5, 2.5 Hz, H-5′), 6.40 (1H, d, J = 2.5 Hz, H-3′), 7.00 (1H, d, J = 8.5 Hz, H-6′)], a singlet methyl signal (δH 1.94), a methoxy group (δH 3.76), two methylene groups and a methine proton. The 13C-NMR spectrum of 1 showed 18 carbon signals. Twelve of them were assigned to two aromatic rings (δC from 96.2 to 166.0 ppm). Besides, the presence of a carbonyl group (δC 200.5), a methylene (δC 28.2), an oxygenated methylene (δC 70.7), and a methine (δC 46.4) suggested compound 1 was a homoisoflavanone [7]. The HMBC cross-peaks from the methyl group (δH 1.94) to C-7 (δC 166.0), C-8 (δC 104.2), C-8a (δC 161.7) and from the methoxy group (δH 3.76) to C-4′ (δC 161.2) established the methyl and methoxy groups were attached to C-8 and C-4′, respectively. According to the analysis, specific rotation value and comparison with the published data [8], compound 1 was determined to be 3-(2′-hydroxy-4′-methoxybenzyl)-5,7-dihydroxy-8-methyl-chroman-4-one, which was isolated from P. kingianum for the first time.

Compound 2 was obtained as a white powder. The molecular ion peak at m/z 303.4 [M+H] + from ESI-MS spectrum of 2 suggested its molecular formula C18H18O6. The 13C-NMR spectrum of 2 showed the presence of 16 carbon signals typical of a homoisoflavane skeleton [28.3(C-9); 46.1 (C-3); 70.5 (C-2), 199.6 (C-4)], the others from δC 96.6 to 170.5 ppm [7]. The 1H-NMR spectrum of 2 exhibited five aromatic protons at δH 5.80 (1H, d, J = 2.0 Hz, H-8), 5.83 (1H, d, J = 2.0 Hz, H-6); 6.26 (1H, d, J = 8.0, 2.5 Hz, H-5′); 6.32 (1H, d, J = 2.5 Hz, H-3′); 6.89 (1H, d, J = 8.0 Hz, H-6′). Based on the spectroscopic evidence and specific rotation value, the structure of compound 2 was identified as disporopin by comparison with the published data [9]. Disporopin was previously isolated from the rhizomes of P. kingianum [10] and found to be cytotoxic against a series of human cancer cell lines (HCT15, T24S, MCF7, Bowes) [9].

Compound 3 was obtained as pale yellow oil. The molecular ion peak at m/z 195.2 [M+H] + from ESI-MS spectrum of 3 suggested its molecular formula C7H14O6. Detailed analysis of the
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$^1$H-, $^{13}$C-NMR and HSQC spectra of 3 displayed signals of three oxygenated methines [3.87 (1H, m, H-5)/ 84.6 (C-5), 3.92 (1H, m, H-4)/ 78.9 (C-4), 4.05 (1H, d, J = 4.5 Hz, H-3)/ 82.5 (C-3)], two oxygenated methylenes [3.65 (1H, d, J = 12.0 Hz, Ha-1), 3.73 (1H, d, J = 12.0 Hz, Hb-1)/ 60.5 (C-1) and 3.66 (1H, dd, J = 3.0, 12.0 Hz, Ha-6), 3.77 (1H, dd, J = 3.0, 12.0 Hz, Hb-6)/ 62.8 (C-6)], a dioxygenated non-protonated carbon [109.2 (C-2)]. The above evidence suggested the presence of a fructofuranose moiety, which was supported by correlations observed from the COSY and HMBC spectra. Furthermore, a singlet signal at $\delta_H$ 3.30 (3H, s) was assigned to a methoxy group. The location of the methoxy group at C-2 was deduced by the HMBC cross-peak between $\delta_H$ 3.30 and $\delta_C$ 109.2 (C-2). The NOESY correlation of the methoxy protons with H-3 suggested $\alpha$ configuration at C-2 [11]. The prediction was further confirmed by the positive optical rotation value of 3 as $\left[\alpha\right]_{D}^{25} = + 27.0 \ (c 0.15, \text{MeOH})$ [11]. Therefore, the structure of 3 was determined as 2-$O$-methyl-$\alpha$-D-fructofuranose by comparison with the published literature [11]. This is the first report on the isolation of 2-$O$-methyl-$\alpha$-D-fructofuranose from the genus Polygonatum.

**Figure 1.** Chemical structures of isolated compounds (1-6).

Compound 4 was obtained as a colorless oil. The molecular ion peak at $m/z$ 295.2 [M+H]$^+$ from ESI-MS spectrum of 4 suggested its molecular formula C$_{18}$H$_{30}$O$_3$. The $^1$H-NMR data of 4 revealed four olefinic protons [6.07 (1H, d, J = 15.0 Hz, H-10); 6.16 (1H, m, H-13); 6.17 (1H, m, H-12); 7.13 (1H, dd, J = 15.5, 9.5Hz, H-11)], a triplet methyl signal [0.88 (3H, t, J = 6.5 Hz, H-18)], and an overlap signal at $\delta_H$ from 1.27 to 1.33 (10H, m). The $^{13}$C-NMR and HSQC spectra of 4 showed 18 carbon signals including two carbonyl group [178.6 (C-1), 201.1 (C-9)], four olefinic methines [127.9 (C-10), 128.9 (C-12), 143.1 (C-11), 145.8 (C-13)], a methyl group [14.0 (C-18)] and eleven methylenes from at $\delta_C$ 22.5 to 40.5. The above spectroscopic data suggested 4 was an oxooctadecadienoic acid [12]. The spectroscopic data of 4 was identical to those of (E,E)-9-oxooctadeca-10,12-dienoic acid [13]. The cross-peaks obtained from HMBC and COSY spectra of 4 further confirmed the identified structure. Therefore, the structure of 4
was deduced to be \((E,E)\)-9-oxooctadecano-10,12-dienoic acid, which was first reported from the genus *Polygonatum*. Compound 4 was previously reported to show acetyl-CoA carboxylase inhibitory activity thus retard fat accumulation and avoid obesity which is a risk factor of many chronic diseases [12].

Compound 5 was obtained as a white powder. The molecular ion peak at *m/z* 331.3 [M+H]+ from ESI-MS spectrum of 5 suggested its molecular formula \(\text{C}_{19}\text{H}_{30}\text{O}_{4}\). The \(^1\)H-NMR spectrum of 5 showed a triplet methyl signal [0.88 (3H, t, \(J = 7.0\) Hz, H-16')] and an overlap signal [1.26 (24H, H-4' to H-15')], suggesting the presence of a long chain aliphatic moiety. Besides, five protons [3.59 (1H, dd, \(J = 3.5, 11.5\) Hz, Ha-3)], 3.69 (1H, dd, \(J = 6.0, 11.5, \text{Hb-3}\)), 3.92 (1H, J = 7.0 Hz, H-2), 4.17 (2H, m, H-1')] were assigned to a glycerol moiety. The \(^{13}\)C-NMR spectrum of 5 exhibited a carbonyl group [174.4 (C-1')] along with three carbon of a glycerol moiety [63.4 (C-3), 65.1 (C-1), 70.3 (C-2)] and the others belonging to a long chain aliphatic moiety [14.1 (C-16'), 22.7 (C-15'), 24.9 (C-3'), 29.1-29.8 (C-4' to C-13'), 31.9 (C-14'), 34.2(C-2')]. These predictions are completely based on the data obtained from the HSQC, HMBC and COSY spectra of 5. Based on the spectroscopic evidence and by comparison with the published data [14], compound 5 was identified as 1-palmitoylglycerol, which was obtained from *P. kingianum* for the first time.

Compound 6 was obtained as white crystals. The molecular ion peak at *m/z* 429.2 [M+H]+ from ESI-MS spectrum of 6 suggested its molecular formula \(\text{C}_{28}\text{H}_{46}\text{O}_{6}\). The \(^1\)H-NMR spectrum of 6 displayed the presence of four olefinic protons [6.24 (1H, d, \(J = 8.5\) Hz, H-6), 6.50 (1H, d, \(J = 8.5\) Hz, H-7), 5.15 (1H, m, H-22), 5.23 (1H, m, H-23)], an oxygenated methine proton [3.96 (H-3)] and six methyl groups [0.81 (3H, d, \(J = 7.0\) Hz, H-19), 0.83 (3H, d, \(J = 7.0, \text{H-27}, 0.88 (3H, s, \text{H-18}), 0.90 (3H, d, \(J = 7.0, \text{H-28}, 1.00 (3H, d, \(J = 6.5\) Hz, H-21)]. The \(^{13}\)C-NMR and DEPT spectra of 6 showed signals of 28 carbons (6 x CH, 7 x CH\(_2\), 11x CH\(_3\), 4 x non-protonated C). Four olefinic carbons [130.8 (C-7), 132.3 (C-23), 135.2 (C-22), 135.4 (C-6)] and three oxygenated carbons [79.4 (C-8), 82.2 (C-5), 66.5 (C-3)] are characteristic for a 5a,8a-epidioxy sterol skeleton [15]. Detailed analysis of HSQC, HMBC and COSY spectra of 6 further confirmed the predicted structure. Based on the above evidence and literature [16], compound 6 was identified to be 5a,8a-ergosterol peroxide, which was reported to have antibacterial, anti-inflammatory, antiviral, antioxidant, antitumor and immunosuppressive properties [17]. 5a,8a-Ergosterol peroxide is a known compound obtained from a variety of fungi, lichens, sponges, and marine organisms [18] but this is the first time this compound was isolated from the genus *Polygonatum*.

4. CONCLUSION

From the \(n\)-hexane and EtOAc extracts of the rhizomes of *P. kingianum* (Liliaceae), six compounds were isolated and identified of structures including 3-(2’-hydroxy-4’-methoxybenzyl)-5,7-dihydroxy-8-methyl-chroman-4-one (1), disporopin (2), 2-O-methyl-\(\alpha\)-D-fructofuranose (3), \((E,E)\)-9-oxooctadecano-10,12-dienoic acid (4), 1-palmitoylglycerol (5), and 5a,8a-ergosterolperoxide (6). Among them, compound 1 and 5 were isolated from *P. kingianum* for the first time, compounds 3, 4 and 6 were first reported from the genus *Polygonatum*. To date, this is the first phytochemical investigation of *P. kingianum* of Viet Nam.

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REFERENCES


