# TRITERPENES FROM THE STEMS AND LEAVES OF MYXOPYRUM SMILACIFOLIUM (WAll.) BLUME

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## TÓM TẮT

# CÁC HỢP CHẤT TRITERPENE TỪ THÂN VÀ LÁ CỦA CÂY NHƯƠNG LE KIM CANG (*MYXOPYRUM SMILACIFOLIUM* (WAll.) BLUME)

*Năm hợp chất triterpene đã biết bao gồm ursolic acid (**1**), uvaol (**2**), oleanolic (**3**), betulinic acid (**4**) và betulin (**5**) đã được phân lập từ thân và lá loài Nhương lê kim cang (Myxopyrum smilacifolium (Wall.) Blume). Cấu trúc của chúng đã được làm sáng tỏ bằng các phương pháp phổ khối (MS) và phổ cộng hưởng hưởng từ hạt nhân (NMR). Các hợp chất **(2 – 5)** đã được phân lập lần đầu tiên từ chi Myxopyrum.*

***Keywords.*** *Myxopyrum smilacifolium, triterpenes, ursolic acid, uvaol, oleanolic, betulinic acid, betulin.*

## 1. INTRODUCTION

*Myxopyrum smilacifolium* (Wall.) Blume belongs genus *Myxopyrum* (Oleaceae) found four species distributed at tropical and subtropical East Asia. In Viet Nam, there are 3 species, *M. nervosum* (Nhuong le gan), *M. pierrei*, (Nhuong le pierrei) and *M. smilacifolium* (Nhuong le kim cang) [1, 2]. *M. smilacifolium* is also known as "Sam xuyen da" growing at high rock mountains (with altitude around 700 - 1000 m). It was a well-known herbal medicine traditionally used for the treatment of cough, rheumatism, cephalalgia, notalagia, and otopathy [2, 3]. Phytochemical studies of the leaves of *M. smilacifolium* showed the presence of terpenoids, flavones, anthraquinones, sugars, alkaloids, tannins and saponins [2, 3], iridoid glycosides [4]. In Viet Nam, the roots of *M. smilacifolium* is widely used among people for health promotion. Recently, in our project, six new iridoid glycosides and one new phenylpropanoid glycoside isolated from the roots of *M. smilacifolium* were reported [5, 6]. In this paper, we present the isolation and structural elucidation of five known triterpenes from the stems and leaves of *M. smilacifolium* including, ursolic acid (**1**), uvaol (**2**), oleanolic (**3**), betulinic acid (**4**) and betulin (**5**) (Figure 1).

## 2. MATERIALS AND METHODS

### 2.1. Plants materials

The stems and leaves of *M. smilacifolium* was collected in Vi Xuyen district, Ha Giang province in November 2019 and identified by Dr. Do Van Hai, Institute of Ecology and Biological Resources, VAST. A voucher specimen (DVH3692019) was deposited at the Institute of Ecology and Biological Resources, VAST.

### 2.2. General experimental procedures

All NMR spectra, including $^{1}$H-NMR (600 MHz), $^{13}$C (150 MHz), HSQC and HMBC were recorded on a Bruker AvanceNEO 600 MHz spectrometer and TMS was used as an internal standard. ESI-MS were recorded on an Agilent 1100 Series LC/MSD Trap SL. Column chromatography (CC) was performed using a silica gel (Kieselgel 60, 70-230 mesh and 230-400 mesh, Merck), RP-18 resins (30-50 µm, Fuji Silysia Chemical Ltd.) and sephadex LH-20 (Merck). Thin layer chromatography (TLC) was done using pre-coated silica gel 60 $F_{254}$ (0.25 mm, Merck) and RP-18 $F_{254S}$ plates (0.25 mm, Merck). HPLC was carried out using an AGILENT 1100 HPLC system.

### 2.3. Extraction and separation

The pulverized dry stems and leaves of *M. smilacifolium* (1.7 kg) were sonicated in 85 % MeOH (5 L × 4, each in 30 minus) at 50 °C. The solvent was removed in reduced pressure to give a crude MeOH extract (150 g). The MeOH extract was suspended with water (400 mL), then successively partitioned with *n*-hexane and ethyl acetate (EtOAc) to give *n*-hexane (MH, 12 g) and EtOAc (ME, 35.0 g) residues and a water layer (MW). The ME residue was applied on a silica gel CC eluting with $CH_2Cl_2$/EtOAc (20/1, 10/1, v/v) and MeOH to give five fractions (fr. ME1–ME2, ME3–ME4) and ME5, respectively.

The fraction ME2 (2.5 g) was chromatographed on a silica gel column eluting with *n*-hexane/acetone (10/1, v/v) to give five fractions (ME2.1–ME2.5). The fraction ME2.2 (0.8 g) was chromatographed on an RP-18 column eluting with acetone/$H_2O$ (2/1, v/v) to give three fractions (ME2.2.1–ME2.2.3). The fractions ME2.2.1 and ME2.2.3 were purified further by CC on a sephadex LH-20 eluting with MeOH to give compound **1** (5.0 mg) and compound **2** (4.0 mg). The fraction ME2.4 (1.8 g) was chromatographed on an RP-18 column, then on a sephadex LH-20 column eluting with MeOH to obtain compound **4** (6.0 mg).

The fraction ME3 (2.8 g) was chromatographed on a silica gel column eluting with $CH_2Cl_2$/MeOH (100/1, v/v) to give three fractions ME3.1-ME3.3. The fraction ME3.2 (1.5 g) was chromatographed on a RP-18 silica gel column eluting with MeOH/$H_2O$ (1/1, v/v) to give four fractions (ME3.2.1-ME3.2.4). The fraction ME3.2.2 (175 mg) was isolated by semi-preparative HPLC using an YMC column eluted wih 45% ACN to give **1** (5 mg) and **3** (4 mg).

Compound **1** (Ursolic acid): White powder. ESI-MS: *m/z* 457 $[M+H]^+$. $^{1}$H-NMR ($CD_3OD$, 600 MHz): $\delta_H$ 5.13 (1H, t, *J* = 3.6 Hz, H-12), 3.06 (1H, dd, *J* = 11.5, 4.2 Hz, H-3α), 2.11 (1H, d, *J* = 11.5 Hz, H-18β), 1.94 (1H, td, *J* = 13.8, 4.2 Hz, H-16), 1.83 (2H, dd, *J* = 8.4, 4.2 Hz, $H_2$-11), 1.02 (3H, s, $H_3$-27), 0.88 (3H, s, $H_3$-23), 0.87 (3H, d, *J* = 3.6 Hz, $H_3$-30), 0.86 (3H, s, $H_3$-25), 0.79 (3H, d, *J* = 6.6 H, $H_3$-29), 0.76 (3H, s, $H_3$-26), 0.68 (3H, s, $H_3$-24), 0.65 (1H, dd, *J* = 12.6, 1.2 Hz, H-5α); and $^{13}$C-NMR ($CD_3OD$, 150 MHz) see Table 1.

Compound **2** (Uvaol): White powder. ESI-MS: *m/z* 443 $[M+H]^+$. $^{1}$H-NMR ($CDCl_3$, 600 MHz): $\delta_H$ 5.14 (1H, t, *J* = 3.6 Hz, H-12), 3.53 and 3.19 (2H, 2 × d, each *J* = 11.4 Hz, $H_2$-28), 3.23 (1H, dd, *J* = 10.8, 4.8 Hz, H-3α), 1.10 (3H, s, $H_3$-27), 1.00 and 0.99 (6H, 2 × s, $H_3$-23 and $H_3$-26), 0.95 (3H, s, $H_3$-25), 0.94 (3H, d, *J* = 6.6 Hz, $H_3$-30), 0.81(3H, d, *J* = 6.0 Hz, $H_3$-29), 0.79 (3H, s, $H_3$-24), 0.73 (1H, dd, *J* = 12.0, 1.2 Hz, H-5); and $^{13}$C NMR ($CDCl_3$, 150 MHz,) see Table 1.

Compound **3** (Oleanolic acid): White powder. ESI-MS: *m/z* 457 $[M+H]^+$. $^{1}$H-NMR ($CD_3OD$, 600 MHz): $\delta_H$ 5.26 (1H, dd, *J* = 4.2, 3.0 Hz, H-12), 3.17 (1H, dd, *J* = 11.4, 4.8 Hz, H-3α), 2.87 (1H, dd, *J* = 13.8, 4.2 Hz, H-18β), 2.03 (1H, td, *J* = 7.8, 4.2 Hz, H-16a), 1.18 (3H, s, $H_3$-27), 1.00 (3H, s, $H_3$-23), 0.97 (3H, s, $H_3$-25), 0.96 (3H, s, $H_3$-30), 0.93 (3H, s, $H_3$-29), 0.84 (3H, s, $H_3$-26), 0.80 (3H, s, $H_3$-24), 0.77 (dd, *J* = 11.4, 4.2 Hz, H-5α); and $^{13}$C-NMR ($CD_3OD$, 150 MHz) see Table 1.

Compound **4** (Betulinic acid): White powder. ESI-MS: *m/z* 457 $[M+H]^+$ . $^{1}$H-NMR ($CD_3OD$, 600 MHz): $\delta_H$ 4.73 and 4.61 (2H, 2 × d, each *J* = 2.4 Hz, $H_2$-29), 3.15 (1H, dd, *J* = 11.4, 4.8 Hz, H-3α), 3.04 (1H, ddd, *J* = 11.4, 4.8 Hz, H-19), 1.71 (3H, s, $H_3$-30),1.03 (3H, s, $H_3$-27), 0.99 (3H, s, $H_3$-26), 0.97 (3H, s, $H_3$-23), 0.88 (3H, s, $H_3$-25), 0.77 (3H, s, $H_3$-24), 0.74 (1H, m, H-5); and $^{13}$C-NMR ($CD_3OD$, 150 MHz) see Table 1.

Compound **5** (Betulin): White powder. ESI-MS: *m/z* 442 $[M+H]^+$ . $^1$H-NMR ($CDCl_3$, 600 MHz): $\delta_H$ 4.68 and 4.58 (2H, 2 × d, each *J* = 10.8 Hz, $H_2$-29), 3.80 and 3.35 (2H, 2 × d, mỗi *J* = 10.8 Hz, $H_2$-28), 3.19 (1H, dd, *J* = 12.0, 4.8 Hz, H-3α), 1.68 (3H, s, $H_3$-30),1.03 (3H, s, $H_3$-27), 0.98 (3H, s, $H_3$-26), 0.97 (3H, s, $H_3$-23), 0.83 (3H, s, $H_3$-25), 0.76 (3H, s, $H_3$-24), 0.74 (1H, m, H-5); and $^{13}$C-NMR ($CDCl_3$, 150 MHz) see Table 1.

## 3. RESULTS AND DISCUSSIONS

Compound **1** was isolated as a white powder. The ESI-MS spectrum of **1** gave the pseudomolecular ion peak at m/z 457 $[M+H]^+$ suggested for molecular formula of **1** is $C_{30}H_{48}O_3$ (M = 456). The $^1$H, $^{13}$C NMR of **1** (Table 1) indicated signals of an ursane triterpene. The $^1$H NMR spectrum showed signals of an olefinic proton at $\delta_H$ 5.13 (1H, t, *J* = 3.6 Hz, H-12); one proton of oxymethine at $\delta_H$ 3.06 (1H, dd, *J* = 11.5, 4.2 Hz, H-3ax); one methine proton at $\delta_H$ 2.11 (d, *J* = 11.5 Hz, H-18β); and seven methyls including five singlet methyls at $\delta_H$ 0.88 (s, $H_3$-23), 0.68 (s, $H_3$-24), 0.86 (s, $H_3$-25), 0.76 (s, $H_3$-26), and 1.02 (s, $H_3$-27), and two doublet methyl at $\delta_H$ 0.79 (d, *J* = 5.5 Hz, $H_3$-29) and 0.87 (d, *J* = 5.5 Hz, $H_3$-30). The large proton coupling constant $J_{H\text{-}2/H\text{-}3}$ = 11.5 Hz indicated that the H-3 proton was *axial* orientation and the 3β-OH. The $^{13}$C NMR, DEPT, HSQC and HMBC spectra of **1** indicated signals of 30 carbon, including a carbonyl at $\delta_C$ 181.5 (C-28, identified by HMBC spectrum); seven methines, one oxymethine at $\delta_C$ 79.7 (C-3), one olefnic methine at $\delta_C$ 126.9 (C-12), and five saturated methines at $\delta_C$ 56.8 (C-5), 49.0 (C-9), 54.4 (C-18), 40.5 (C-19), and 40.4 (C-20); nine methylenes at $\delta_C$ 40.0 (C-1), 27.9 (C-2), 19.5 (C-6), 34.4 (C-7), 24.4 (C-11), 29.3 (C-15), 25.4 (C-16), 31.8 (C-21), and 38.1 (C-22); and seven methys at $\delta_C$ 28.8 (C-23), 16.4 (C-24), 16.0 (C-25), 17.9 (C-26), 24.1 (C-27) 17.7 (C-29) and 21.6 (C-30); six quaternary carbons at $\delta_C$ 39.8 (C-4), 40.8 (C-8), 38.2 (C-10), 139.7 (C-13), 43.3 (C-14), and 49.0 (C-17). The HMBC correlations between H-3 (δ 3.06) and C-1/C-24/C-23, H-12 ($\delta_H$ 5.13) and C-27/C-14/C-9, H-18β ($\delta_H$ 2.11) and C-12/C-13/C-28/C-17/C-19, $H_3$-23/$H_3$-24 and C-4, $H_3$-25 and C-5/C-9, $H_3$-26 and C-8/C-9/C-14, $H_3$-27 and C-13/C-14/C-8/C-15, $H_3$-29 and C-18/C-19/C-20, and $H_3$-30 and C-19/C-18/C-21 revealed the positions of the groups 3β-OH, 12-CH=, H-18, H-19, and methyls respectively. The ESI-MS and 1D, 2 D NMR spectral data analysis of **1** and comparison with those in literature (Table 1) [7] determined the compound **1** as ursolic acid (3β-hydroxyurs-20-en-28-oic acid).

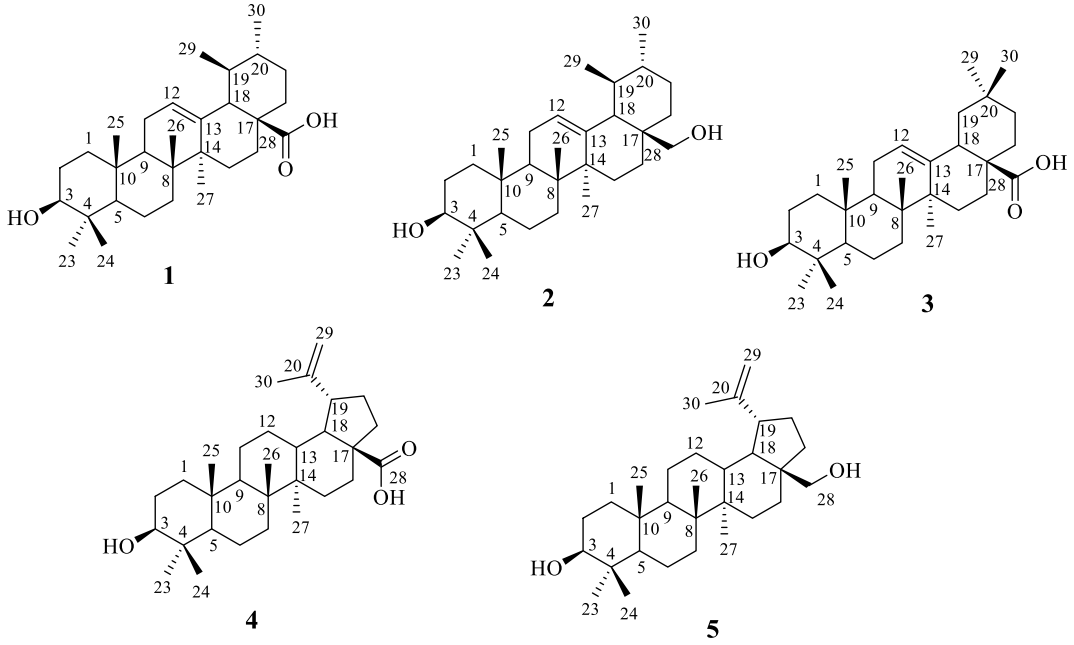


*Figure 1. Chemical structure of compounds 1-5*

*Table 1. $^{13}$C-NMR spectral data of compounds **1-5** and references*

| C | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| | $\delta_C$ [a] | $\delta_C$ [b] | $\delta_C$ [a] | $\delta_C$ [a] | $\delta_C$ [b] |
| 1 | 40.0 | 38.8 | 39.8 | 40.1 | 38.7 |
| 2 | 27.9 | 27.3 | 28.9 | 28.1 | 27.4 |
| 3 | 79.7 | 79.1 | 79.7 | 79.7 | 79.0 |
| 4 | 39.8 | 38.8 | 39.8 | 40.0 | 38.9 |
| 5 | 56.8 | 55.2 | 56.8 | 56.9 | 55.3 |
| 6 | 19.5 | 18.4 | 19.5 | 19.5 | 18.3 |
| 7 | 34.4 | 32.9 | 34.0 | 35.6 | 34.3 |
| 8 | 40.8 | 40.0 | 39.8 | 41.9 | 40.9 |
| 9 | 49.0 | 47.7 | 49.1 | 52.0 | 50.4 |
| 10 | 38.1 | 36.9 | 38.2 | 38.3 | 37.2 |
| 11 | 24.4 | 23.4 | 24.1 | 22.1 | 20.9 |
| 12 | 126.9 | 125.1 | 123.6 | 26.9 | 25.2 |
| 13 | 139.7 | 138.7 | 145.3 | 39.7 | 37.3 |
| 14 | 43.3 | 42.1 | 42.9 | 43.6 | 42.7 |
| 15 | 29.3 | 26.0 | 27.9 | 30.8 | 27.1 |
| 16 | 25.4 | 23.3 | 24.5 | 33.4 | 29.2 |
| 17 | 48.9 | 38.0 | 47.3 | 57.5 | 47.8 |
| 18 | 54.4 | 54.1 | 42.8 | 50.5 | 48.8 |
| 19 | 40.5 | 39.5 | 47.3 | 48.6 | 47.8 |
| 20 | 40.4 | 39.4 | 31.6 | 152.0 | 150.5 |
| 21 | 31.8 | 30.6 | 34.9 | 31.7 | 29.8 |
| 22 | 38.2 | 35.2 | 33.9 | 38.1 | 34.0 |
| 23 | 28.8 | 28.1 | 28.8 | 28.6 | 28.0 |
| 24 | 16.4 | 15.7 | 16.3 | 16.1 | 15.4 |
| 25 | 16.0 | 15.6 | 15.9 | 16.6 | 16.1 |
| 26 | 17.9 | 16.8 | 17.8 | 16.7 | 16.0 |
| 27 | 24.1 | 23.3 | 26.4 | 15.1 | 14.8 |
| 28 | #181.5 | 70.0 | #181.4 | 180.1 | 60.6 |
| 29 | 17.7 | 17.4 | 33.6 | 110.2 | 109.7 |
| 30 | 21.6 | 21.3 | 24.0 | 19.6 | 19.1 |

*[a]Recorded in $CD_3OD$, [b]$CDCl_3$, at 150 MHz, [#]Signal identified by HMBC spectrum.*

Compound **2** was obtained as a white powder. The $^1$H and $^{13}$C-NMR (Table 1) of **2** gave the very similary signals to those of **1** except the absence of the 28-carbonyl, which was replaced by an oxymethylene at $\delta_H$ 3,53 (1H, d, *J* = 9.5 Hz, H-28β) and 3.19 (1H, d, *J* = 9.5 Hz, H-28α)/$\delta_C$ 70.0 (C-28). The signals of an ursane triterpene of **2** indicated with 30 carbons including: seven methyls, in which five singlet methyls and two doublet methyls, seven methines, ten methylenes, six quaternary carbons. The ESI-MS spectrum of **2** gave the pseudomolecular ion peak at m/z 443 $[M+H]^+$ together its $^{13}$C NMR spectrum suggested for molecular formula of **2** was $C_{30}H_{50}O_2$ (M = 442). The ESI-MS and the NMR spectral data analysis of **2** and comparison to those in literature (Table 1) [8] determined the compound **2** as uvaol (3β,28-dihydroxyurs-12-ene).

Compound **3** was isolated as a white powder. The $^{1}$H NMR spectra of **3** gave signals of an oleane triterpene including one olefinic proton at $\delta_H$ 5.26 (dd, *J* = 4.2, 3.0 Hz, H-12), a proton of an oxymethine at $\delta_H$ 3.17 (dd, *J* = 11.4, 4.8 Hz, H-3α), and seven singlet methyls at $\delta_H$ 1.18 ($H_3$-27), 1.00 ($H_3$-23), 0.97 ($H_3$-25), 0.96 ($H_3$-30), 0.93 ($H_3$-29), 0.84 ($H_3$-26), 0.80 ($H_3$-24). The large proton coupling constant $J_{H\text{-}2/H\text{-}3}$ = 11.4 Hz revealed the orientation of the 3β-OH. The $^{13}$C NMR, DEPT, HSQC and HMBC spectra of **3** showed signals of 30 carbons, including one carbonyl at $\delta_C$ 181.4 (C-28); five methines, in which one oxymethine at $\delta_C$ 79.7 (C-3), one olefinic methine at $\delta_C$ 123.6 (C-12) and three saturated methines at $\delta_C$ 56.8 (C-5), 49.1 (C-9), 42.8 (C-18); ten methylenes at $\delta_C$ 39.8 (C-1), 28.9 (C-2), 19.5 (C-6), 34.0 (C-7), 24.1 (C-11), 27.9 (C-15), 24.1 (C-16), 47.3 (C-19), 34.9 (C-21), and 33.9 (C-22); seven methyls at $\delta_C$ 28.8 (C-23), 16.3 (C-24), 15.9 (C-25), 17.8 (C-26), 26.4 (C-27), 33.6 (C-29) and 24.0 (C-30); and seven quaternary carbons at $\delta_C$ 39.8 (C-4), 39.8 (C-8), 38.2 (C-10), 145.3 (C-13), 42.9 (C-14), 47.3 (C-17), and 30.7 (C-20). The HMBC correlations between H-3 (δ 3.17) and C-2/C-24/C-23; H-12 ($\delta_H$ 5.26) and C-13/C-14/C-9/C-18; H-18 ($\delta_H$ 2.87) and C-12/C-13/C-17/C-19; $H_3$-23/$H_3$-24 and C-3/C-4/C-5; $H_3$-25 and C-5/C-9; $H_3$-26 and C-8/C-9/C-14; $H_3$-27 and C-13/C-14/C-8/C-15; $H_3$-29/$H_3$-30 and C-19/C-20/C-21; indicated the locations of the goups 3β-OH, 12-CH=, H-18, and methyls, respectively. The ESI-MS spectrum of **3** gave the pseudomolecular ion peak at m/z 457 $[M+H]^+$ together its $^{13}$C NMR spectrum suggested for molecular formula of **3** as $C_{30}H_{48}O_3$ (M = 456). The ESI-MS and the 1D, 2D NMR spectral data analysis of **3** and comparison to those in literature (Table 1) [7] determined the compound **3** as oleanolic acid (3β-Hydroxyolean-12-en-28-oic acid).

Compound **4** is a white powder. The $^{1}$H, $^{13}$C NMR and DEPT spectra of **4** showed signals of lupane triterpene with 30 carbons, including one isopropylene at $\delta_H$ 4.73 and 4.61/$\delta_C$ 110.2 (29-$CH_2$=) and $\delta_C$ 152.0 (C-20), and $\delta_H$ 1.71/$\delta_C$ 19.6 (30-$CH_3$); one oxymethine at $\delta_H$ 3.15 (dd, *J* = 11.4 4.8 Hz, H-3α)/$\delta_C$ 79.7 (C-3); five singlet methyl $\delta_H$ 1.03 0.99 0.97 0.88 0.77; five methines at $\delta_C$ 56.9 52.0 39.7 50.5 48.6; ten methylenes tại $\delta_C$ 40.1 28.1 19.5 35.6 22.1 26.9 30.8 33.4 31.7 38.1; and five quaternary carbons at $\delta_C$ 40.0 41.9 38.3 43.6 57.5. The ESI-MS together $^{13}$C NMR of **4** suggested the molecular formula as $C_{30}H_{48}O_3$ (M = 456). The ESI-MS and NMR spectral data analysis of **4** and comparison to those in literature (Table 1) [9] determined the compound **4** as betulinic acid (3β-Hydroxylup-20(29)-en-28-oic acid).

Compound **5** is a white powder. The $^{1}$H and $^{13}$C-NMR (Table 1) of **5** gave the very similary signals to those of **4** except the absence of the 28-carbonyl, which was replaced by a new hydroxymethylene at $\delta_H$ 3.80 and 3.35 (2 × d, each *J* = 10.8 Hz, $H_2$-28)/$\delta_C$ 60.6 (C-28). The ESI-MS together $^{13}$C NMR of **5** suggested the molecular formula as $C_{30}H_{50}O_2$ (M = 442). The ESI-MS and NMR spectral data analysis of **5** and comparison to those in literature (Table 1) [10] determined the compound **5** as betulin (lup-20(29)-ene-3β,28-diol)

## 4. CONCLUSION

From the stems and leaves of *M. smilacifolium*, five known triterpenes including, ursolic acid (**1**), uvaol (**2**), oleanolic (**3**), betulinic acid (**4**) and betulin (**5**) were isolated. The structures were elucidated by means of ESI-MS and NMR spectroscopic methods. The compounds **(2 – 5)** were isolated for the first time from the genus *Myxopyrum*.

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