Chemical constituents from underground part of *Astragalus camptodontoides*

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Abstract: For understanding the chemical constituents of *Astragalus camptodontoides*, nineteen compounds were isolated from the ethyl acetate fraction of the methanol extract of underground part. By physical-chemical properties and spectroscopic date, their structures were identified as isobavachin (1), 4'-hydroxyisolochocarpin (2), 5-deoxyuechrenone (3), sinflavone (4), khonlonginols H (5), 4',O-methylpreglabridin (6), 3'-hydroxy-4',O-methylglabridin (7), 4'-O-methylglabridin (8), 8-prenyl-phaseollinisosflav (9), xambioona (10), glabrol (11), glyasperin H (12), methylvanilin (13), phthalic acid isobutyl ester (14), butyl isobutyl phthalate (15), β-sitosterol (16), daucosterol (17), oleic acid (18), and (2S,3S,4R,9E)-1,3,4-trihydroxy-2-[(2'R)-2'-hydroxytetracosanoylamino]-9-octadecene (19). All compounds were isolated from this plant for the first time, including compounds 1-7 obtained from *Astragalus* genus for the first time.

Key words: *Astragalus camptodontoides*, underground part, chemical constituents, isolation and identification

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Astragalus camptodontoides, a species of Astragalus genus, grows on grassland with altitude over 3,100 m and is mainly distributed in South Tibet, Southwest Sichuan, and Northwest Yunnan in China (China Flora Editorial Board, 1993; Kunming Institute for Botany, 2006). This plant is often used as substitute of Chinese medicine “Huang Qi” by local folks, and therefore, it is supposed to have the major constituents similar to Huangqi. However, research concerning its chemical composition has not been reported yet. In order to investigate the chemical patterns of its major constituents, a detailed chemical study on the underground part of A. camptodontoides was carried out recently. As a result, nineteen compounds were isolated from the EtOAc fraction of its MeOH extract. Their structures were identified as isobavachin (1), 4′-hydroxyisorholchaoiocarpin (2), 5-deoxyeychecheneone (3), shinflavanone (4), konklonginols H (5), 4′-O-methylpreglabridin (6), 3′-hydroxy-4′-O-methylglabridin (7), 4′-O-methylglabridin (8), 8-prenyl-phaseollinisoflavan (9), xambioona (10), glabrol (11), glyasperin H (12), methylnissolin (13), phthalic acid isodihbutyl ester (14), butul isobutyl phthalate (15), β-sitosterol (16), daucosterol (17), oleic acid (18), and (2S,3S,4R,9E)-1,3,4-tri hydroxy-2-[2′R]-2′-hydroxytetra-cosanoylamino]-9-octadecene (19) (Fig. 1). All of these compounds were isolated from this plant for the first time, and compounds 1-7 were isolated from Astragalus genus for the first time.

1 Materials and Methods

1.1 Plant Materials

Astragalus camptodontoides was collected from Diqing (Yunnan, China) in September 2012 and identified by Dr. ZHANG De-Quan, Laboratory of Pharmacognosy of Dali University. A voucher specimen (20120918-2-A) was deposited in Institute of Materia Medica at Dali University.

1.2 Experimental Instruments

EI-MS spectra were obtained on VG Auto Spec-3000 and API QSTAR Pulsari Spectrometer. 1H-NMR and 13C-NMR spectra were recorded on a Bruker-400 MHz Spectrometer using TMS as an internal standard. TLC was performed on silica gel G and GF254 plates (Qingdao Marine Chemical Factory). Column chromatography was carried out on silica gel (200-300 mesh; Qingdao Marine Chemical Factory), Sephadex LH-20 (Amersham Biosciences), and RP-18 gel (40-75 μm; J. T. Baker). TLC spots were visualized by 10% H2SO4 with heating or by UV light.

2 Extraction and Isolation

The dried and powdered roots of A. camptodontoides (1.05 kg) were extracted with MeOH for six times, 6 h each time. The extracts were combined and concentrated in vacuum to give a crude extract. The crude extract was suspended in water and partitioned with EtOAc and butanol, successively. Removal of the solvent from each phase gave the EtOAc fraction, butanol fraction, and water-soluble extract, respectively. The EtOAc fraction (123.5 g) was subjected to a silica gel column and eluted with CHCl3-Me2CO (1:0:0:1) to provide Fr. 1-7. Fr. 1 (4 g) was subjected repeatedly to column chromatography on silica gel and eluted with petroleum ether-Me2CO to yield compounds 2 (5.4 mg), 3 (12.0 mg), 5 (15.3 mg), 6 (3.2 mg), 9 (5.5 mg), 14 (5.7 mg), 17 (5.6 mg) and 18 (8.7 mg). Fr. 2 (7.5 g) was subjected repeatedly to column chromatography padded with silica gel and eluted with petroleum ether-Me2CO to yield compounds 1 (5.2 mg), 4 (5.4 mg), 7 (8.3 mg), 8 (5.6 mg), 10 (15.3 mg), 12 (5.4 mg), 15 (3.8 mg), and 16 (20.2 mg). Fr. 3 (3 g) was purified repeatedly on silica gel column and eluted with petroleum ether-Me2CO to yield Compound 11 (8.2 mg). Fr. 6 (8 g) was subjected to a RP-18 chromatographic column and eluted with MeOH-H2O and followed by Sephadex LH-20 (MeOH) purification to yield compounds 13 (8.1 mg) and 19 (5.7 mg).

3 Results and Analysis

Isobavachin (1) Yellow powder; C23 H36 O4; 1H-NMR (CDCl3, 400 MHz) δ; 7.76 (1H, d, J = 8.7 Hz, H-5), 6.96 (2H, d, J = 2.2 Hz, H-2′, 6′), 6.69
(2H, d, J = 8.3 Hz, H-3', 5'), 6.36 (1H, d, J = 9.8 Hz, H-6), 5.59 (1H, t, J = 9.8 Hz, H-2'), 5.36 (1H, dd, J = 13.3, 2.8 Hz, H-2), 3.15 (2H, overlap, H-1'), 3.01 (1H, dd, J = 16.8, 13.3 Hz, H-3b), 2.81 (1H, dd, J = 16.8, 2.9 Hz, H-3a), 1.49 (3H, s, H-4'), 1.46 (3H, s, H-5'); 13C-NMR (CDCl₃, 100 MHz) δ: 185.5 (s, C-4), 159.6 (s, C-7), 157.7 (s, C-9), 156.8 (s, C-4'), 131.7 (s, C-3'), 131.1 (s, C-1'), 128.8 (d, C-5), 127.9 (d, C-2', 6'), 121.9 (d, C-2''), 116.0 (d, C-3', 5'), 115.6 (s, C-10), 113.1 (s, C-8), 111.1 (d, C-6), 79.5 (d, C-2), 44.2 (t, C-3), 22.7 (q, C-4''), 22.7 (t, C-1''), 14.1 (q, C-5''). These data are consistent with the literature values (Ali et al., 2011), and hence was identified as isobavachin.

4'-Hydroxyisolonchocarpin (2) Yellow oil;
was identified as 5-deoxyeuchrenone.

Shinflavanone (4) Yellow powder; C_{25}H_{36}O_{4};

\(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.74 (1H, d, J = 8.7 Hz, H-5), 7.22 (1H, d, J = 5.7 Hz, H-2'), 7.20 (1H, s, H-6'), 6.86 (1H, d, J = 8.2 Hz, H-1''), 6.50 (1H, d, J = 8.6 Hz, H-6), 6.63 (1H, d, J = 8.3 Hz, H-5'), 5.56 (1H, d, J = 9.8 Hz, H-2''), 5.38 (1H, t, J = 2.4 Hz, H-2''), 5.35 (1H, dd, J = 3.2, 12.8 Hz, H-2), 3.39 (2H, d, J = 6.7 Hz, H-1''), 3.02 (1H, dd, J = 16.8, 13.3 Hz, H-3b), 2.80 (1H, dd, J = 2.9, 16.8 Hz, H-3a), 1.78 (6H, s, H-4'', 5''), 1.47 (3H, s, H-4''), 1.44 (3H, s, H-5''); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\): 191.3 (s, C-4), 159.7 (s, C-9), 157.9 (s, C-7), 154.8 (s, C-4'), 134.9 (s, C-3'), 130.8 (s, C-1'), 128.8 (d, C-5), 128.0 (d, C-2'), 127.9 (s, C-3'), 127.4 (d, C-2''), 125.4 (d, C-6'), 121.4 (d, C-2''), 116.0 (d, C-1''), 115.8 (d, C-5'), 114.7 (s, C-8), 111.1 (s, C-10), 109.4 (d, C-6), 79.7 (s, C-3''), 77.2 (d, C-2), 44.1 (t, C-3), 29.6 (t, C-1''), 28.4 (q, C-4''), 28.1 (q, C-5''), 25.8 (q, C-14''), 17.9 (q, C-5''). Compound 4 was identified as shinflavanone since its \(^1\)H-NMR and \(^{13}\)C-NMR data agreed with those reported literatures (Suh et al., 1999).

Khonlonginols H (5) Yellow oil; C_{26}H_{30}O_{6};

\(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.18 (1H, d, J = 8.4 Hz, H-6'), 6.87 (2H, d, J = 6.6 Hz, H-1''), 6.64 (1H, dd, J = 8.5, 2.2 Hz, H-5'), 6.32 (1H, d, J = 2.2 Hz, H-3'), 5.82 (1H, dd, J = 12.6, 2.0 Hz, H-2), 5.65 (1H, d, J = 7.0 Hz, H-2''), 5.56 (1H, t, J = 9.7 Hz, H-2''), 3.89 (3H, s, -OCH\(_3\)), 3.20 (2H, t, J = 7.0 Hz, H-1''), 3.01 (1H, dd, J = 17.6, 14.6 Hz, H-3a), 2.91 (1H, dd, J = 17.6, 3.1 Hz, H-3b), 1.76 (6H, s, H-4'', 5''), 1.46 (3H, s, H-4''), 1.44 (3H, s, H-5''); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\): 191.8 (s, C-4), 161.8 (s, C-4'), 159.8 (s, C-7), 158.0 (s, C-9), 157.9 (s, C-5), 154.9 (s, C-2'), 131.2 (s, C-3''), 130.5 (d, C-6'), 128.8 (d, C-2''), 121.6 (d, C-2''), 116.0 (s, C-1''), 115.7 (t, C-1''), 114.6 (s, C-8), 113.1 (d, C-5'), 111.2 (s, C-6), 109.4 (d, C-3'), 108.1 (s, C-10), 79.8 (s, C-3''), 77.6 (d,
C-2), 56.2 (q, -OCH₃), 44.0 (t, C-3), 28.4 (q, C-4″), 28.1 (q, C-5″), 25.9 (q, C-4″), 22.4 (t, C-1″), 17.9 (q, C-5″). Its ¹H-NMR and ¹³C-NMR data were in accordance with those reported in the literature (Sutthivaiyakit et al, 2009). Therefore, Compound 5 was identified as khonklonginols H.

4′-O - Methylpreglabridin (6) Yellow oil; C₂₁H₂₄O₄; ¹H-NMR (CDCl₃, 400 MHz) δ: 6.83 (1H, d, J = 8.2 Hz, H-5), 6.67 (1H, d, J = 8.3 Hz, H-6′), 6.60 (1H, d, J = 8.2 Hz, H-5′), 6.56 (1H, s, H-3′), 6.40 (1H, dd, J = 8.2, 8.3 Hz, H-6), 5.25 (1H, m, H-2″), 4.34 (1H, d, J = 9.1 Hz, H-2b), 3.90 (3H, s, -OCH₃), 3.90 (1H, dd, J = 11.9, 6.0 Hz, H-2a), 3.41 (1H, m, H-3), 3.40 (2H, d, J = 4.8 Hz, H-1″), 2.93 (1H, d/d, J = 15.8, 10.2, 2.0 Hz, H-4), 1.81 (3H, s, H-5″), 1.74 (3H, s, H-4″); ¹³C-NMR (CDCl₃, 100 MHz) δ: 161.9 (s, C-7), 153.8 (s, C-9), 152.6 (s, C-4′), 151.7 (s, C-2′), 134.2 (s, C-3′), 129.1 (d, C-5), 127.6 (d, C-6′), 122.1 (d, C-2″), 120.8 (s, C-1′), 114.4 (s, C-8, 10), 108.1 (d, C-5″), 106.4 (d, C-3′), 97.7 (d, C-6), 69.3 (t, C-2), 56.2 (q, -OCH₃), 31.6 (d, C-3), 31.0 (t, C-4), 25.8 (q, C-5″), 22.3 (t, C-1″), 17.9 (q, C-4″). Its ¹H-NMR and ¹³C-NMR data were identical with those reported in the literature (Castro et al, 1986). Compound 6 was identified as 4′-O-methylpreglabridin.

3′-Hydroxy-4′-O-methylpreglabridin (7) White oil; C₂₁H₂₄O₄; ¹H-NMR (Ace tone-d₆, 400 MHz) δ: 6.85 (1H, d, J = 8.2 Hz, H-5), 6.65 (1H, d, J = 2.3 Hz, H-1″), 6.63 (1H, d, J = 2.3 Hz, H-6′), 6.5 (1H, d, J = 8.6 Hz, H-5″), 6.31 (1H, d, J = 8.2 Hz, H-6), 5.64 (1H, d, J = 9.9 Hz, H-2″), 4.36 (ddd, 1H, J = 2.1, 3.4, 10.3 Hz, H-2a), 4.04 (t, 1H, J = 10.2 Hz, H-2b), 3.81 (3H, s, -OCH₃), 3.51 (m, 1H, H-3), 3.04 (ddd, 1H, J = 11.1, 15.6 Hz, H-4b), 2.83 (ddd, 1H, J = 1.8, 5.1, 15.7 Hz, H-4a), 1.38 (6H, s, H-4″, 5″); ¹³C-NMR (Acetone-d₆, 100 MHz) δ 151.9 (s, C-7), 149.8 (s, C-9), 146.9 (s, C-4′), 143.5 (s, C-2′), 133.4 (s, C-3′), 129.3 (d, C-5), 128.7 (d, C-2″), 120.6 (s, C-1′), 116.9 (d, C-6′), 116.8 (d, C-1″), 114.6 (s, C-10), 109.6 (s, C-8), 108.4 (d, C-6), 102.9 (d, C-5″), 75.2 (s, C-3″), 69.9 (t, C-2), 55.4 (q, -OCH₃), 32.0 (d, C-3), 30.2 (t, C-4), 27.1 (q, C-4″), 26.9 (q, C-5″). Compound 7 was identified as 3′-hydroxy-4′-O-methylpreglabridin by comparison of the ¹H-NMR and ¹³C-NMR data with those reported in the literature (Kinosita et al, 1996).

4′-O-Methylpreglabridin (8) White oil; C₂₁H₂₄O₄; ¹H-NMR (CDCl₃, 400 MHz) δ: 7.20 (1H, d, J = 8.7 Hz, H-5), 7.01 (1H, d, J = 8.7 Hz, H-6′), 6.85 (1H, d, J = 8.3 Hz, H-1″), 6.63 (1H, d, J = 12.5 Hz, H-5″), 6.39 (1H, d, J = 8.2 Hz, H-6), 6.34 (1H, d, J = 2.4 Hz, H-3″), 5.56 (1H, d, J = 9.8 Hz, H-2″), 4.37 (1H, d/d, J = 10.4, 3.3, 2.0 Hz, H-2a), 4.02 (1H, t, J = 10.4 Hz, H-2b), 3.89 (6H, s, -OCH₃), 3.47 (1H, overlap, H-3), 3.00 (1H, d/d, J = 10.9, 15.7 Hz, H-4b), 2.89 (1H, d/d, J = 15.7, 5.3 Hz, H-4a), 1.45 (3H, s, H-4″), 1.44 (3H, s, H-5″); ¹³C-NMR (CDCl₃, 100 MHz) δ: 151.8 (s, C-4′), 149.8 (s, C-2′), 145.7 (s, C-7), 142.2 (s, C-9), 132.2 (d, C-6′), 129.2 (d, C-5), 128.9 (d, C-2″), 120.9 (s, C-1′), 117.7 (d, C-1″), 117.0 (s, C-10), 114.4 (s, C-8), 109.9 (d, C-6), 108.6 (d, C-5″), 102.6 (d, C-3″), 75.6 (s, C-3″), 69.9 (t, C-2), 56.1 (q, -OCH₃), 32.0 (t, C-4), 30.4 (t, C-3), 27.8 (q, C-4″), 27.5 (q, C-5″). Its ¹H-NMR and ¹³C-NMR data were in accordance with those reported in the literature (Kinosita et al, 1996). Therefore, Compound 8 was identified as 4′-O-methylpreglabridin.

8-Preynl-phaseollinisoflavan (9) Yellow oil; C₂₅H₂₈O₄; ¹H-NMR (CDCl₃, 400 MHz) δ: 6.90 (1H, d, J = 8.2 Hz, H-5), 6.81 (1H, d, J = 8.2 Hz, H-6′), 6.64 (1H, d, J = 10.0 Hz, H-1″), 6.49 (1H, d, J = 8.7 Hz, H-6), 6.34 (1H, d, J = 8.2 Hz, H-5″), 5.54 (1H, d, J = 9.8 Hz, H-2″), 5.28 (1H, m, H-2″), 4.35 (1H, d/d, J = 9.8, 3.2, 2.1 Hz, H-2a), 4.08 (1H, dd, J = 9.8, 9.8 Hz, H-2b), 3.66 (1H, m, H-3), 3.34 (2H, d, J = 6.8 Hz, H-1″), 2.94 (1H, d/d, J = 15.4, 5.5, 2.0 Hz, H-4a), 2.72 (1H, m, H-4b), 1.81 (3H, s, H-5″), 1.74 (3H, s, H-4″), 1.46 (6H, s, H-4″, 5″); ¹³C-NMR (CDCl₃, 100 MHz) δ: 159.4 (s, C-7), 157.8...
(s, C-9), 154.0 (s, C-2‘), 153.2 (s, C-4‘), 131.1 (s, C-3") , 131.0 (d, C-2") , 128.9 (d, C-5) , 127.9 (d, C-6‘), 127.1 (d, C-2") , 124.3 (s, C-1‘), 122.0 (d, C-1") , 121.3 (s, C-10) , 116.5 (s, C-8) , 116.0 (s, C-3‘), 111.1 (d, C-6) , 109.4 (d, C-5‘) , 79.6 (d, C-3") , 71.8 (t, C-2) , 44.2 (d, C-3) , 32.0 (t, C-4‘) , 29.7 (q, C-4") , 29.7 (q, C-5‘) , 27.7 (q, C-4") , 22.7 (t, C-1") , 19.2 (q, C-5") . Compound 9 was identified as 8-prenyl-phyto-ellinoliosflavan by comparison of the $^1$H-NMR and $^{13}$C-NMR data with those reported in the literature (Kinoshita et al, 1996).

Xamboona (10) Yellow powder; C$_{25}$H$_{34}$O$_{4}$; $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.74 (1H, d, J = 8.7 Hz, H-5), 7.20 (1H, dd, J = 2.1, 8.3 Hz, H-6‘), 7.08 (1H, d, J = 2.1 Hz, H-2‘), 6.81 (1H, m, H-5‘), 6.64 (1H, d, J = 14.0 Hz, H-1‘), 6.49 (1H, d, J = 8.7 Hz, H-6‘), 6.34 (1H, d, J = 9.8 Hz, H-1‘), 5.66 (1H, d, J = 9.8 Hz, H-1‘), 5.56 (1H, d, J = 10.0 Hz, H-1‘), 5.36 (1H, dd, J = 2.7, 13.2 Hz, H-2‘), 3.01 (1H, m, H-3b), 2.79 (1H, dd, J = 2.9, 16.8 Hz, H-3a), 1.46 (12H, s, 4xCH$_3$); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 191.0 (s, C-4), 159.6 (s, C-9), 157.8 (s, C-7), 153.3 (s, C-4‘), 131.3 (d, C-5), 131.1 (s, C-1‘), 128.8 (d, C-6‘), 127.9 (d, C-1‘), 127.1 (d, C-1‘), 124.3 (d, C-2‘), 122.0 (d, C-1‘), 121.3 (s, C-3‘), 116.5 (d, C-5‘), 116.0 (d, C-1‘), 114.7 (s, C-8), 111.1 (d, C-6‘), 109.4 (s, C-10), 79.6 (d, C-2‘), 77.5 (s, 2xMe$_2$), 44.1 (t, C-2‘), 28.4 (q, C-CH$_3$), 28.2 (q, C-CH$_3$), 28.1 (q, 2xCH$_3$) . These data are consistent with the literature values (Mizuno et al, 1989). Therefore, Compound 10 was identified as Xamboona.

Glabrol (11) Yellow oil; C$_{25}$H$_{34}$O$_{4}$; $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.76 (1H, d, J = 8.7 Hz, H-5), 7.38 (1H, s, H-2‘), 7.17 (1H, d, J = 2.5 Hz, H-6‘), 6.67 (1H, d, J = 8.1 Hz, H-5‘), 6.56 (1H, d, J = 8.6 Hz, H-6‘), 5.33 (2H, dd, J = 2.4, 13.2 Hz, H-2‘), 5.27 (2H, m, H-2‘), 3.75 (2H, m, H-1‘, 1”), 3.34 (1H, dd, J = 8.5, 10.6 Hz, H-3b), 2.82 (1H, dd, J = 16.8, 2.9 Hz, H-3a), 1.62 (6H, s, H-4‘, 5”), 1.61 (6H, s, H-4‘, 5”). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 191.5 (s, C-4), 161.4 (s, C-7), 160.7 (s, C-9), 144.5 (s, C-4‘), 131.8 (s, C-1‘), 131.1 (s, C-3‘, 3”), 126.5 (d, C-6‘), 121.9 (d, C-5), 121.1 (d, C-2‘), 121.1 (d, C-2‘, 2”), 115.5 (s, C-10), 114.9 (d, C-6), 114.5 (s, C-3‘), 112.9 (d, C-5‘), 110.5 (s, C-8), 79.4 (d, C-2‘), 44.0 (t, C-3), 29.2 (t, C-1‘), 25.8 (q, C-5‘, 5”), 22.3 (t, C-1”), 17.9 (q, C-4‘, 4”). The $^1$H-NMR and $^{13}$C-NMR data above were identical with those reported in the literature (Cho et al, 2012). Thus, Compound 11 was identified as glabrol.

Glyasperin H (12) Yellow oil; C$_{22}$H$_{34}$O$_{5}$; $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 6.83 (1H, d, J = 4.5 Hz, H-1‘), 6.65 (1H, d, J = 8.6 Hz, H-6‘), 6.63 (1H, d, J = 9.2 Hz, H-5‘), 6.38 (1H, d, J = 7.0 Hz, H-6‘), 5.58 (1H, d, J = 11.8 Hz, H-2‘), 4.35 (1H, d, J = 8.0 Hz, H-2‘), 3.99 (1H, d, J = 9.2 Hz, H-2b), 3.89 (6H, s, 2xCH$_3$), 3.54 (1H, m, H-3), 2.92 (1H, d, J = 11.1 Hz, H-4b), 2.84 (1H, d, J = 15.8 Hz, H-4a), 1.43 (3H, s, H-5”), 1.42 (3H, s, H-4”), 7.74 (1H, d, J = 8.7 Hz, H-5); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 151.9 (d, C-7), 149.7 (s, C-9), 146.6 (s, C-4‘), 145.3 (s, C-2‘), 138.7 (s, C-3‘), 129.2 (s, C-5), 129.0 (d, C-2‘), 127.5 (s, C-1‘), 117.0 (d, C-6‘), 116.9 (d, C-1‘), 114.4 (s, C-10), 109.9 (s, C-8), 108.7 (d, C-6), 106.5 (d, C-5‘), 75.6 (s, C-3‘), 70.6 (t, C-2‘), 61.1 (q, 2xCH$_3$), 56.2 (q, 4‘- OCH$_3$), 31.6 (d, C-3), 31.6 (t, C-4), 27.8 (q, C-5‘), 27.5 (q, C-4”). Compound 12 was identified as glyasperin H by comparison of the $^1$H-NMR and $^{13}$C-NMR data with those reported in the literature (Sairafi-npour et al, 2002).

Methylmisoisolin (13) White oil; C$_{17}$H$_{16}$O$_{3}$; $^1$H-NMR (CD$_3$OD, 400 MHz) $\delta$: 7.47 (1H, d, J = 8.5 Hz, H-1), 7.01 (1H, d, J = 4.2 Hz, H-7), 6.66 (1H, d, J = 2.2 Hz, H-8), 6.65 (1H, dd, J = 8.2, 2.2 Hz, H-2), 6.48 (1H, d, J = 8.7 Hz, H-4), 5.57 (1H, d, J = 6.2 Hz, H-11a), 4.28 (1H, dd, J = 9.6, 3.4 Hz, H-6e), 3.84 (3H, s, 9-OCH$_3$), 3.82 (3H, s, 9-OCH$_3$), 3.81 (1H, m, H-6a), 3.33 (1H, m, H-6); $^{13}$C-NMR (CD$_3$OD, 100
MHz) δ: 158.6 (s, C-3), 156.5 (s, C-4a), 154.8 (s, C-9), 152.8 (s, C-11b), 131.8 (s, C-10), 129.8 (d, C-1), 122.0 (s, C-6b), 118.5 (d, C-7), 110.3 (s, C-1a), 104.8 (d, C-2), 104.2 (d, C-8), 102.8 (d, C-4), 78.9 (d, C-11a), 66.0 (t, C-6), 61.0( q, -OCH₃), 55.5 (q, -OCH₃), 39.8 (d, C-6a). Compound 13 was identified as methylmethylsulfoxin by comparison of the ¹H-NMR and ¹³C-NMR data with the data reported in the literature (Lee et al., 2008).

Phthalic acid isodibutyl ester (14) Yellow powder; C₁₆H₂₂O₄; ¹H-NMR (CDCl₃, 400 MHz) δ: 7.74 (2H, m, H-3, 6), 7.53 (2H, m, H-4, 5), 4.10 (2H, d, J = 7.2 Hz, H-1'), 2.04 (1H, m, H-2'), 0.99 (6H, d, J = 7.2 Hz, H-1", 3'); ¹³C-NMR (CDCl₃, 100 MHz) δ: 167.6 (s, C-α), 132.3 (s, C-2), 132.3 (s, C-1), 130.8 (d, C-6), 130.8 (d, C-3), 128.7 (d, C-5), 128.7 (d, C-4), 71.8 (t, C-1'), 29.7 (q, C-2'), 19.2 (q, C-3'), 19.2 (q, C-4'). Its ¹H-NMR and ¹³C-NMR data were identical with those reported in the literature (Zhang et al., 2003). So, Compound 14 was identified as phthalic acid isodibutyl ester.

Butyl isobutyl phthalate (15) Yellow oil; C₁₆H₂₂O₄; ¹H-NMR (CDCl₃, 400 MHz) δ: 7.74 (2H, m, H-3, 6), 7.53 (2H, m, H-4, 5), 4.10 (2H, d, J = 7.2 Hz, H-1'), 2.04 (1H, m, H-2'), 0.99 (6H, d, J = 7.2 Hz, H-1", 3'); ¹³C-NMR (CDCl₃, 100 MHz) δ: 167.8 (s, C-α), 132.9 (s, C-1, 2), 130.9 (d, C-4, 5), 128.8 (d, C-3, 6), 71.8 (t, C-1'), 67.7 (t, C-1"), 29.7 (t, C-2'), 27.7 (d, C-2"), 19.2 (q, C-3"), 18.5 (t, C-3'), 14.1 (q, C-4'). These data are consistent with the literature values (Liu et al., 2011), and Compound 15 was therefore identified as butyl isobutyl phthalate.

β-Sitosterol (16) White powder. The compound was developed with β-sitosterol standard on co-TLC experiments eluted with different solvent systems, and they had same Rₜ values. Therefore, it was identified as β-sitosterol.

Daucosterol (17) White powder. This compound was identified by co-TLC experiments and it showed the same Rₜ values with daucosterol standard in different develop systems. Therefore, it was determined as daucosterol.

Oleanic acid (18) White powder. By co-TLC experiments, it was identified as oleanic acid due to the same Rₜ values with oleanic acid standard in different elution systems.

(2S, 3S, 4R, 9E)-1, 3, 4-Trihydroxy-2-[(2'R)-2'-hydroxytetraocasouyaminol]-9-octadecene (19) White powder; C₆₂H₈₃O₃N; EI-MS: 681 [M]+; ¹H-NMR (CD₃OD, 400 MHz) δ: 8.56 (1H, d, J = 8.7 Hz, NH), 5.52 (2H, m, H-9 and H-10), 5.08 (1H, m, H-2), 4.60 (1H, dd, J = 7.5, 3.6 Hz, H-2'), 4.47 (1H, dd, J = 10.8, 4.8 Hz, H-1a), 4.41 (1H, dd, J = 10.8, 4.6 Hz, H-1b), 4.32 (1H, dd, J = 6.2, 5.1 Hz, H-3), 4.26 (1H, m, H-4), 2.15-2.18 (4H, m, H-5a, H-8a, H-9a and H-3'a), 1.94-2.05 (5H, m, H-5b, H-8b, H-9b, H-3'b and H-4'a), 1.71-1.77 (3H, m, H-6a, H-6b and H-4'b), 1.26-1.32 (methylene band), 0.87 (6H, brt, J = 7.0 Hz, H-18 and H-24'); ¹³C-NMR (CD₃OD, 100 MHz) δ: 175.2 (s, C-1'), 131.0 (d, C-9 or C-10), 130.8 (d, C-9 or C-10), 77.0 (d, C-3), 73.0 (d, C-4), 72.6 (d, C-2'), 62.1 (t, C-1), 53.1 (d, C-2), 35.8 (t, C-3'), 34.0 (t, C-5), 33.5 (t, C-8), 33.1 (t, C-11), 32.3 (t, C-16' and C-22'), 29.6-30.4 (methylene), 26.9 (t, C-4'), 26.0 (t, C-6), 23.1 (t, C-17 and C-23'), 14.4 (q, C-18 and C-24'). Compound 19 was identified as (2S, 3S, 4R, 9E)-1, 3, 4-trihydroxy-2-[(2'R)-2'-hydroxytetraocasouyaminol]-9-octadecene by comparison of the ¹H-NMR and ¹³C-NMR data above with those reported in the literature (Su et al., 2002).

References:

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