#### DOI: 10.11931/guihaia.gxzw201505031

韩冰洋,张宇,田新雁,等. 类芒齿黄芪地下部分化学成分研究 [J]. 广西植物,2016,36(11):1382-1388 HAN BY, ZHANG Y, TIAN XY, et al. Chemical constituents from underground part of Astragalus camptodontoides [J]. Guihaia, 2016, 36(11):1382-1388

# 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'-hydroxyisolonchocarpin (2), 5-deoxyeuchrenone (3), shinflavanone (4), khonklonginols 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 isodibutyl ester (14), butul isobutyl phthalate (15),  $\beta$ -sitosterol (16), daucosterol (17), oleanic 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 CLC number: Q946.8 Document code: A Article ID: 1000-3142(2016)11-1382-08

## 类芒齿黄芪地下部分化学成分研究

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摘 要:为了解类芒齿黄芪(*Astragalus camptodontoides*)主要化学成分,从其地下部分甲醇提取物的乙酸乙酯部 位分离出 19个单体化合物,通过现代波谱分析及理化性质等手段分别鉴定为异补骨脂黄酮 (1),4'-hydroxy-isolonchocarpin (2),5-去氧山豆根黄酮(3),shinflavanone (4),khonklonginols H (5),4'-O-methylpreglabridin (6), 3'-hydroxy-4'-O-methylglabridin (7),4'-O-methylglabridin (8),8-prenyl-phaseollinisoflavan (9),xambioona (10),光 甘草酚 (11),粗毛甘草素 H (12),methylnissolin (13),邻苯二甲酸异丁酯 (14),邻苯二甲酸丁酯异丁酯 (15),  $\beta$ -谷甾醇(16),胡萝卜苷(17),齐墩果酸(18),(2*S*,3*S*,4*R*,9*E*)-1,3,4-trihydroxy-2- [(2'R)-2'- hydr-oxytetraco-sanoylamino]-9-octadecene (19)。化合物 1~19 均为首次从该植物中获得,化合物 1~7 为首次从黄芪属(*Astragalus*)植物中分离得到。

关键词:类芒齿黄芪,地下部分,化学成分,分离与鉴定

收稿日期: 2015-07-29 修回日期: 2015-12-20

基金项目: 国家自然科学基金(31170313) [Supported by the National Natural Science Foundation of China (31170313)]。

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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'-hydroxyisolonchocarpin (2), 5deoxyeuchrenone (3), shinflavanone (4), khonklonginols 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 isodibutyl ester (14), butul isobutyl phthalate (15),  $\beta$ -sitosterol (16), daucosterol (17), oleanic acid (18), and (2S, 3S, 4R, 9E) - 1, 3, 4trihydroxy-2- [(2'R)-2'-hydroxytetracosanoylamino]-9octadecene (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. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker-400 MHz Spectrometer using TMS as an internal standard. TLC was performed on silica gel G and  $GF_{254}$  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  $\mu$ m; J. T. Baker). TLC spots were visualized by 10% H<sub>2</sub>SO<sub>4</sub> 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  $CHCl_3$ -Me<sub>2</sub>CO (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-Me<sub>2</sub>CO 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-Me<sub>2</sub>CO 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-Me<sub>2</sub> CO to yield Compound 11 (8.2 mg). Fr. 6 (8 g) was subjected to a RP-18 chromatographic column and eluted with MeOH-H<sub>2</sub>O 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;  $C_{25} H_{26} O_4$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.76 (1H, d, J = 8.7Hz, H-5), 6.96 (2H, d, J = 2.2 Hz, H-2', 6'), 6.69



Fig. 1 Chemical structures of compounds 1-19

(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"); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 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;

 $C_{20}H_{18}O_4$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.74 (1H, d, J = 8.7 Hz, H-5), 7.20 (2H, d, J = 8.6)Hz, H-2', 6'), 6.81 (2H, d, J = 2.0 Hz, H-3', 5'), 6.64 (1H, d, J = 10.5 Hz, H-1"), 6.49 (1H, d, J = 8.7 Hz, H-6), 5.55 (1H, d, J = 10.0 Hz, H-2''), 5.35 (1H, dd, J = 13.2, 2.8 Hz, H-2), 3.00 (1H, dd, J = 13.3, 3.6 Hz, H-3b), 2.79(1H, dd, J = 16.8, 2.9 Hz, H-3a), 1.46 (6H, s)H-4", 5");  ${}^{13}$ C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 190.5 (s, C-4), 159.6 (s, C-9), 157.8 (s, C-7), 155.4 (s, C-4'), 131.3 (s, C-1'), 128.8 (d, C-5), 127.9 (d, C-2"), 127.1 (d, C-2', 6'), 124.3 (d, C-3', 5'), 122.0 (d, C-1"), 116.5 (s, C-8), 116.0 (s, C-10), 111.1 (d, C-6), 79.6 (d, C-2), 77.3 (s, C-3"), 44.1 (t, C-3), 28.4 (q, C-4"), 28.1 (q, C-5"). Its <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data were in accordance with those reported in the literature (Ryu et al, 2012). Therefore, Compound 2 was identified as 4'-hydroxyisolonchocarpin.

5-Deoxyeuchrenone (3) Yellow oil;  $C_{30}H_{32}O_4$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.66 (1H, s, H-5), 7.13 (1H, dd, J = 2.2, 8.2 Hz, H-6'), 7.01 (1H, d, J = 2.2 Hz, H-2'), 6.74 (1H, m, H-5'), 6.57  $(1H, d, J = 10.0 \text{ Hz}, H-\alpha), 6.27 (1H, d, J = 9.8)$ Hz, H- $\alpha'$ ), 5.59 (1H, d, J = 9.8 Hz, H- $\beta$ ), 5.50  $(1H, d, J = 10.0 \text{ Hz}, H-\beta'), 5.30 (1H, dd, J =$ 2.8, 13.3 Hz, H-2), 5.27 (1H, bt, H-2"), 3.60 (1H, d, J = 4.5 Hz, H-1''), 2.94 (1H, m, H-3b),2.72 (1H, dd, J = 2.9, 16.8 Hz, H-3a), 1.50  $(6H, s, 2 \times CH_3)$ , 1.18 (12H, s,  $4 \times CH_3$ ); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 192.7 (s, C-4), 166.5 (s, C-7), 156.7 (s, C-9), 152.3 (s, C-4'), 131.4 (s, C-1'), 130.3 (s, C-3"), 130.1 (d, C-2'), 129.9 (d, C-β'), 127.8 (d, C-β), 127.8 (d, C-6'), 126.9 (t, C-2"), 126.1 (d, C-α), 123.3 (s, C-5'), 120.9 (d, C-5), 115.4 (s, C-6), 115.0 (d, C-3'), 113.7 (d,  $C-\alpha'$ ), 110.1 (s, C-8), 108.3  $(s, C-10), 78.6 (s, 2 \times Me_2 C), 76.3 (d, C-2),$ 43.1 (t, C-3), 30.9 (t, C-1"), 29.9 (q, C-CH<sub>3</sub>), 28.7 (q, C-CH<sub>3</sub>), 28.3 (q, C-CH<sub>3</sub>), 27.4 (q, C-*C*H<sub>3</sub>), 26.7 (q, C-4"), 18.1 (q, C-5"). Its <sup>1</sup>H NMR and <sup>13</sup>C NMR data were identical with those reported in the literature (Mali et al, 1998). Thus, Compound 3 was identified as 5-deoxyeuchrenone.

Shinflavanone (4) Yellow powder:  $C_{25}H_{26}O_4$ : <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 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 = 6.7Hz, 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'''); <sup>13</sup>C-NMR (CDCl<sub>2</sub>, 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<sup>'''</sup>), 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-4"), 17.9 (q, C-5"). Compound 4 was identified as shinflavanone since its <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data agreed with those reported literatures (Suh et al, 1999).

Khonklonginols H (**5**) Yellow oil;  $C_{26}H_{28}O_6$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 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<sub>3</sub>), 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"");

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ: 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,

4 ' - O - Methylpreglabridin ( 6 ) Yellow oil ;  $C_{21}H_{24}O_4$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 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 = 9.1Hz, H-2b), 3.90 (3H, s,  $-0CH_3$ ), 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, ddd, J)= 15.8, 10.2, 2.0 Hz, H-4), 1.81 (3H, s, H-5"), 1.74 (3H, s, H-4"); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 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, -0*C*H<sub>3</sub>), 31.6 (d, C-3), 31.0 (t, C-4), 25.8 (g, C-5"), 22.3 (t, C-1"), 17.9 (g, C-4"). Its <sup>1</sup>H-NMR and <sup>13</sup>C-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-methylglabridin (7) White oil;  $C_{21}H_{22}O_5$ ; <sup>1</sup>H-NMR (Acetone- $d_6$ , 400 MHz)  $\delta$ : 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, - $OCH_3$ , 3.51 (m, 1H, H-3), 3.04 (dd, 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"); <sup>13</sup>C-NMR (Acetone- $d_6$ , 100 MHz)  $\delta$  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,  $-0CH_3$ ), 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*-methyl-glabridin by comparison of the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data with those reported in the literature (Kinoshita et al, 1996).

4'-O-Methylglabridin (8) White oil;  $C_{21}H_{22}O_4$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 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, ddd, J = 10.4, 3.3, 2.0 Hz, H-2a), 4.02 (1H, t, J = 10.4 Hz, H-2b), 3.89 (6H, s,  $-0CH_3$ ), 3.47 (1H, overlap, H-3), 3.00 (1H, dd, J = 10.9, 15.7 Hz, H-4b), 2.89(1H, dd, J = 15.7, 5.3 Hz, H-4a), 1.45 (3H, s,H-4"), 1.44 (3H, s, H-5"); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 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, -OCH<sub>3</sub>), 32.0 (t, C-4), 30.4 (t, C-3), 27.8 (q, C-4"), 27.5 (q, C-5"). Its <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data were in accordance with those reported in the literature (Kinoshita et al, 1996). Therefore, Compound 8 was identified as 4'-O-methylglabridin.

8-Prenyl-phaseollinisoflavan (**9**) Yellow oil;  $C_{25} H_{28} O_4$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 6.90 (1H, d, J = 8.2 Hz, H-5), 6.81 (1H, d, J = 8.2Hz, 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 = 8.2Hz, H-5'), 5.54 (1H, d, J = 9.8 Hz, H-2"), 5.28 (1H, m, H-2"'), 4.35 (1H, ddd, 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 = 6.8Hz, H-1"'), 2.94 (1H, ddd, 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"); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 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-phase-ollinisoflavan by comparison of the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data with those reported in the literature (Kinoshita et al, 1996).

Xambioona (10) Yellow powder;  $C_{25} H_{24} O_4$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.74 (1H, d, J = 8.7 Hz, H-5, 7.20 (1 H, 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- $\alpha$ ), 6.49 (1H, d, J = 8.7 Hz, H-6), 6.34 (1H, d, J = 9.8)Hz, H- $\alpha'$ ), 5.66 (1H, d, J = 9.8 Hz, H- $\beta$ ), 5.56  $(1H, d, J = 10.0 \text{ Hz}, H-\beta'), 5.36 (1H, dd, J =$ 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) $4 \times CH_3$ ; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 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  $(d, C-6'), 127.9 (d, C-\beta'), 127.1 (d, C-\beta'),$ 124.3 (d, C-2'), 122.0 (d, C-α), 121.3 (s, C-3'), 116.5 (d, C-5'), 116.0 (d, C-α'), 114.7 (s, C-8), 111.1 (d, C-6), 109.4 (s, C-10), 79.6 (d, C-2), 77.5 (s,  $2 \times -Me_2C$ ), 44.1 (t, C-3), 28.4 (q,  $C-CH_3$ , 28.2 (q, C-CH<sub>3</sub>), 28.1 (q, 2 × C- $CH_3$ ). These data are consistent with the literature values (Mizuno et al, 1989). Therefore, Compound 10 was identified as xambioona.

Glabrol (**11**) Yellow oil;  $C_{25}H_{28}O_4$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 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", 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"'); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 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 <sup>1</sup>H-NMR and <sup>13</sup>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;  $C_{22}H_{24}O_5$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 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-2a), 3.99 (1H, d, J = 9.2)Hz, H-2b), 3.89 (6H, s,  $2 \times OCH_3$ ), 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<sub>3</sub>, 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, 2'-OCH<sub>3</sub>), 56.2 (q, 4'-OCH<sub>3</sub>), 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 <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data with those reported in the literature (Sairafianpour et al, 2002).

Methylnissolin (13) White oil;  $C_{17}H_{16}O_5$ ; <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 400 MHz)  $\delta$ : 7.47 (1H, d, J = 8.5Hz, H-1), 7.01 (1H, d, J = 4.2 Hz, H-7), 6.66 (1H, d, J = 2.2 Hz, H-8), 6.55 (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<sub>3</sub>), 3.82 (3H, s, 10-OCH<sub>3</sub>), 3.81 (1H, m, H-6a), 3.33 (1H, m, H-6); <sup>13</sup>C-NMR (CD<sub>3</sub>OD, 100

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MHz)  $\delta$ : 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, -OCH<sub>3</sub>), 55.5 (q, -OCH<sub>3</sub>), 39.8 (d, C-6a). Compound **13** was identified as methylnissolin by comparison of the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data with the data reported in the literature (Lee et al, 2008).

Phthalic acid isodibutyl ester (14) Yellow powder;  $C_{16}H_{22}O_4$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 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'); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 167.6 (s, C- $\alpha$ ), 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 <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data were identical with those reported in the literature (Zhang et al, 2003). So, Compound **14** was identified as hthalic acid isodibutyl ester.

Butul isobutyl phthalate (**15**) Yellow oil; C<sub>16</sub> H<sub>22</sub>O<sub>4</sub>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 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'); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 167.8 (s, C- $\alpha$ ), 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 butul isobutyl phthalate.

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

Daucosterol (17) White powder. This compound was identified by co-TLC experiments and it showed the same  $R_f$  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  $R_f$  values with oleanic acid standard in different elution systems.

(2S, 3S, 4R, 9E)-1, 3, 4-Trihydroxy-2- [(2'R)-2'hydroxytetracosanoylamino]-9-octadecene (19) White powder;  $C_{42}$  H<sub>83</sub> O<sub>5</sub> N; EI-MS: 681 [M]<sup>+</sup>; <sup>1</sup>H-NMR  $(CD_3OD, 400 \text{ MHz}) \delta$ : 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');  $^{13}$ C-NMR (CD<sub>2</sub> OD, 100 MHz)  $\delta$ : 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 (methylens), 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'-hydroxytetracosanoylamino]-9-octadecene by comparison of the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data above with those reported in the literature (Su et al, 2002).

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