

**OLEANANE SAPONINS FROM  
POLYSCIAS GUILFOYLEI BAIL. (ARALIACEAE)**

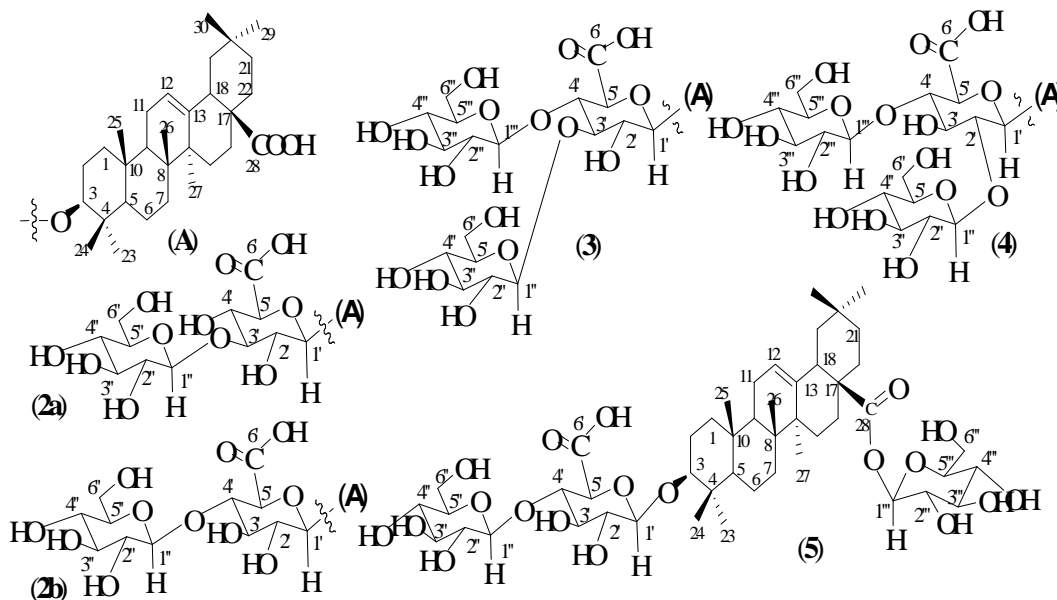
Nguyen Thi Anh Tuyet<sup>(1)</sup>, Nguyen Thuy Anh Thu<sup>(3)</sup>, Nguyen Thi Thuy Hang<sup>(2)</sup>,  
Nguyen Ngoc Suong<sup>(3)</sup>, Nguyen Kim Phi Phung<sup>(3)</sup>

(1) University of Pedagogy of Ho Chi Minh City; (2) An Giang University

(3) University of Science, VNU-HCM

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**ABSTRACT:** *Polyscias guilfoylei* Bail has just studied by our group. From leaves of this plant, four compounds had been isolated: isophytol, oleanolic acid, 3-O- $\beta$ -D-glucopyranosylspinasterol and 3-O- $\beta$ -D-glucopyranosyloleanolic acid<sup>[5]</sup>. Now we presented five saponins isolated from leaves of this plant:  $\beta$ -D-glucuronopyranosyloleanolic acid (1), a mixture of two saponins of 3-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyloleanolic acid (2a) and 3-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)- $\beta$ -D-glucuronopyranosyloleanolic acid (2b) with the ratio of (2:3), 3-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-[ $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)]- $\beta$ -D-glucuronopyranosyloleanolic acid (3), 3-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 2)-[ $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)]- $\beta$ -D-glucuronopyranosyloleanolic acid (4) and 3-O- $\beta$ -D-glucopyranosyl-28-O- $\beta$ -D-glucopyranosyl ester (5). Their chemical structures were established by spectroscopic analysis.



**Key words:** Araliaceae, *Polyscias*, oleanane saponin, glucuronic acid.

## 1. INTRODUCTION

*Polyscias* plants (Araliaceae family) are considered as a rich source of oleanane-type triterpene glycosides<sup>[1,2,3,4]</sup>. In a program of studying phytochemistry on some plants of the genus *Polyscias* growing in Viet Nam, from *P. guilfoylei* Bail., that hasn't yet been studied, we

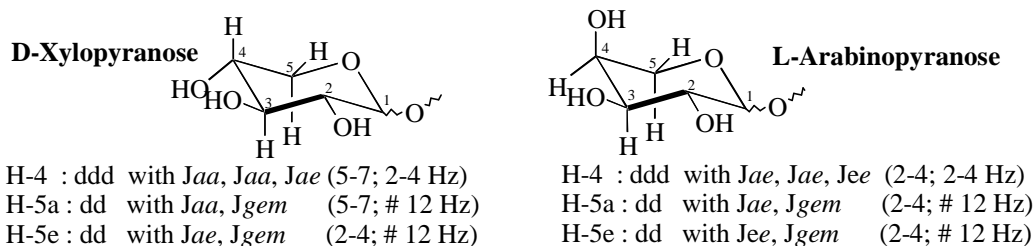
isolated four compounds: isophytol, oleanolic acid, 3-*O*-*b*-D-glucopyranosylspinasterol and 3-*O*-*b*-D-glucopyranosyloleanolic acid<sup>[5]</sup>. On the continuation of the study on this plant, after extensive chromatography of the butanol extract, we isolated five oleanane-type saponins: *b*-D-glucuronopyranosyloleanolic acid (**1**), a mixture with the ratio of (2:3) of two saponins of 3-*O*-*b*-D-glucopyranosyl-(1→3)-*b*-D-glucuronopyranosyloleanolic acid and 3-*O*-*b*-D-glucopyranosyl-(1→4)-*b*-D-glucuronopyranosyloleanolic acid (**2**), 3-*O*-*b*-D-glucopyranosyl-(1→3)-[*b*-D-glucopyranosyl-(1→4)]-*b*-D-glucuronopyranosyloleanolic acid (**3**), 3-*O*-*b*-D-glucopyranosyl-(1→2)- [ *b*-D-glucopyranosyl-(1→4)]-*b*-D-glucuronopyranosyloleanolic acid (**4**) and 3-*O*-*b*-D-glucopyranosyl-(1→4)-*b*-D-glucuronopyranosyloleanolic acid 28-*O*-*b*-D-glucopyranosyl ester (**5**). The present paper reports the spectroscopic analyses which lead to the elucidation of their structures.

## 2. RESULTS AND DISCUSSION

In the elucidation of the structure of saponins, it was very difficult to determine the type of each sugar as well as the position of one sugar linking to other one. Our survey on the NMR spectrums (pyridine-*d*<sub>5</sub>), presented in the figure 1, showed that <sup>13</sup>C- and DEPT-NMR signals could be used as a preliminary guide to solve the above mentioned problem. The number of signals in the zone of 107-94 ppm showed the total number of sugars in the structure and especially, the zone of 96-94 ppm revealed the presence of sugar(s) connected at C-28 of the aglycone. The survey on saponins of some plants of the genus *Polyscias* growing in Viet Nam showed that these saponins composed of an oleanolic acid as aglycone and carbon C-3 of this aglycone often connected to a *b*-D-glucuronic acid and this one further linked to one and/or two, three other sugars at its hydroxyl(s) at C-2' and/or C-3' and/or C-4'. If there was another sugar connecting to C-3', this carbon had chemical shift at δppm 87.9–84.5, the zone of 84.0–82.0 ppm was ascribed for C-4' and of 81.7–78.7 ppm for C-2'. If DEPT-NMR spectrum showed a –CH<sub>2</sub>O– group signal in the zone of 67.5-64.4 ppm, perhaps that was C-5 of D-xylose or L-arabinose, and a –CH<sub>2</sub>O– group signal in the zone of 63.3-62.0 ppm was ascribed for C-6 of D-glucose or D-galactose. Each pair could be further distinguished by their <sup>1</sup>H-NMR spectrum by the coupling constants of their H-4 and H-5, with example presented in the figure 2.

Signal of anomeric carbon(s) of sugar(s)	C-28 of aglycone linking to sugar(s)	glucuronic acid linking to aglycone at C-3, then, it connect to another sugar by its carbon ...						C-5 of Xyl or Ara	C-6 of Glc or Gal	C-6 of Rhm	δ ppm
		C-3 aglycone	C-3'	C-4'	C-2'						
(-O-CH-O-)	(-O-CH-O-)	(-CH-O-)	(-CH-O-)	(-CH-O-)	(-CH-O-)	(-CH <sub>2</sub> -O-)	(-CH <sub>2</sub> -O-)	(-CH <sub>3</sub> )			
107-100	96.0-94.0	89.6-88.0	87.9-84.5	84.0-82.0	81.7-78.7	67.5-64.4	63.3-62.0	18.7-17.6			

**Figure 1.** Particular zone (δ<sub>c</sub>) and DEPT-NMR signals of some carbons of saponins as a preliminary guide to determine the type of sugar and the position of one sugar linking to other one.



**Figure 2.** Type of  $^1\text{H}$  resonant signal of H-4, H-5 of D-xylopyranose and L-arabinopyranose.

Compound (2) was isolated as amorphous white powder.  $^{13}\text{C}$ , DEPT-NMR spectra showed that it was an oleanane type saponin with two typical olefinic carbons at  $\delta\text{ppm}$  144.6, 122.3. A preliminary view showed that perhaps (2) contained four sugars because of the presence of four anomeric carbons at  $\delta\text{ppm}$  105.9, 105.6, 104.6, 104.1. The profound observation confirmed that (2) was a mixture of two saponins and each contained two sugars because of the two signals close at hand at  $\delta\text{ppm}$  89.3 and 89.2 of C-3 of the aglycone. The LC-spectrum of (2) showed a sharp peak but its top was split into two that meant (2) was composed of two compounds with the similar structures. The mass spectrum, negative mode, of (2) with the molecular ion peak at  $m/z = 793.5$  [M-H] $^-$  was consistent with the molecular formula of  $\text{C}_{42}\text{H}_{66}\text{O}_{14}$  (M=794). This formula was suitable for the structure of an oleanolic acid containing one glucuronic acid and one glucose. In HMBC spectra, there were no signals to prove which moiety, glucose or glucuronic acid, linked to the aglycone, but the survey of saponins of some plants of the genus *Polyscias* growing in Viet Nam showed that if there was a presence of a glucuronic acid, this one priorly connected to the aglycone at C-3. HMBC spectra showed that two anomeric protons at  $\delta\text{ppm}$  4.77 and 4.76 had long-range couplings with the  $^{13}\text{C}$  peak at  $\delta\text{ppm}$  89.3 and 89.2 ppm so each saponin had one glucuronic acid linking to its aglycone at C-3, as usual. HMBC spectra also showed that two anomeric protons at  $\delta\text{ppm}$  5.18 and 5.03 had long-range couplings with the  $^{13}\text{C}$  peak at  $\delta\text{ppm}$  86.4 and 83.1, respectively, that meant each mentioned above glucuronic acid connected to one glucose at its C-3' and C-4', respectively. So, (2) was a mixture of 3-*O*- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyloleanolic acid and 3-*O*- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)- $\beta$ -D-glucuronopyranosyloleanolic acid (2) with the ratio of (2:3) owing to the integrations of corresponding protons as well as the height of  $^{13}\text{C}$  signals.

**Table 1.**  $^{13}\text{C}$ -NMR (pyridine- $d_5$ ) data of five saponins isolated in *P. guilfoylei* Bail..

N $^\circ$	(1)	(2a)	(2b)	(3)	(4)	(5)
1	38.7	38.5	38.5	38.5	38.3	38.6
2	26.2	26.0	26.0	25.6	25.7	26.2
3	89.2	89.2	89.3	89.3	90.3	89.5
4	39.7	39.5	39.5	39.1	39.2	39.9
5	55.9	55.6	55.6	55.2	55.6	55.8
6	18.4	18.3	18.3	17.9	18.1	18.4
7	33.1	33.0	33.0	32.5	32.8	32.5
8	39.3	39.2	39.2	38.8	39.0	39.3
9	47.9	47.7	47.7	47.4	47.7	47.9
10	36.9	36.7	36.7	36.3	36.4	36.9
11	23.7	23.5	23.5	23.2	23.3	23.4
12	122.5	122.3	122.3	121.9	121.1	122.9

13	144.6	144.6	144.6	144.4	145.7	144.0
14	42.1	41.9	41.9	41.6	41.9	42.1
15	28.2	28.1	28.1	27.7	28.2	28.2
16	23.7	23.4	23.4	22.3	23.8	23.7
17	46.6	46.6	46.6	47.4	47.6	47.0
18	41.9	41.8	41.8	41.6	42.3	41.7
19	46.5	46.4	46.4	46.2	47.2	46.3
20	30.7	30.6	30.6	30.3	30.5	30.6
21	34.2	34.1	34.1	33.7	34.4	34.0
22	33.2	33.0	33.0	32.5	33.3	33.1
23	28.2	28.0	28.0	27.6	27.5	28.2
24	16.8	16.7	16.7	16.4	16.2	16.9
25	15.3	15.2	15.2	14.8	14.9	15.4
26	17.3	17.2	17.2	16.9	17.2	17.4
27	26.0	25.9	25.9	25.6	25.8	26.0
28	180.3	180.6	180.6	178.0	184.6	176.5
29	33.1	33.0	33.0	32.8	33.2	33.0
30	23.7	23.6	23.6	23.3	23.7	23.6
(Glucuronic acid) 1'	106.3	105.6	105.9	105.6	103.2	106.0
2'	75.1	74.2	74.1	74.2	78.8	74.6
3'	77.9	86.4	77.0	85.5	76.0	78.8
4'	76.0	76.2	83.1	82.6	82.1	83.7
5'	73.3	74.7	74.6	75.8	77.0	76.6
6'	171.9	171.3	172.0	167.9	174.7	175.4
(2 <sup>nd</sup> glucose linking to glcA at C-2') 1''	-	-	-	-	103.8	-
2''	-	-	-	-	75.3	-
3''	-	-	-	-	76.5	-
4''	-	-	-	-	71.2	-
5''	-	-	-	-	77.2	-
6''	-	-	-	-	61.4	-
(2 <sup>nd</sup> glucose linking to glcA at C-3') 1''	-	104.6	-	103.8	-	-
2''	-	74.5	-	73.9	-	-
3''	-	77.5	-	77.2	-	-
4''	-	71.0	-	71.0	-	-
5''	-	78.0	-	77.2	-	-
6''	-	62.0	-	61.4	-	-
(2 <sup>nd</sup> glucose linking to glcA at C-4') 1''	-	-	104.1	-	-	104.6
2''	-	-	74.5	-	-	74.7
3''	-	-	77.0	-	-	78.4
4''	-	-	71.0	-	-	71.1
5''	-	-	77.6	-	-	76.9
6''	-	-	61.9	-	-	62.2
(3 <sup>rd</sup> glucose linking to glcA at C-4') 1'''	-	-	-	103.7	103.6	-
2'''	-	-	-	74.2	74.1	-
3'''	-	-	-	76.5	76.4	-
4'''	-	-	-	70.4	70.4	-
5'''	-	-	-	76.5	76.8	-

6''	-	-	-	61.4	62.2	-
(3 <sup>rd</sup> glucose linking to aglycone at C-28)	-	-	-	-	-	95.6
1''	-	-	-	-	-	73.8
2''	-	-	-	-	-	77.9
3''	-	-	-	-	-	71.3
4''	-	-	-	-	-	77.1
5''	-	-	-	-	-	62.1
6''	-	-	-	-	-	

Compound (**4**) was isolated as amorphous white powder.  $^{13}\text{C}$ , DEPT-NMR spectra showed that it had 48 carbons. Among them, seven in low field at  $\delta\text{ppm}$  184.6, 174.7, 145.7, 121.1, 103.8, 103.6 and 103.2, fifteen in the middle field at  $\delta\text{ppm}$  90.3, 82.1, 78.8, 77.2, 77.0, 76.8, 76.5, 76.4, 76.0, 75.3, 74.1, 71.2, 70.4, 62.2 and 61.4 and twenty six carbons in high field from  $\delta\text{ppm}$  55.5 to 14.9. These NMR data revealed that it was a saponin with oleanolic acid as the aglycone moiety (30 carbons with one carboxyl group at  $\delta\text{ppm}$  184.6, two typical olefinic carbons at  $\delta\text{ppm}$  145.7 and 121.1) with three sugars (18 carbons with three anomeric carbons at  $\delta\text{ppm}$  103.8, 103.6 and 103.2). Among these three sugars, one was glucuronic acid (the carboxyl group at  $\delta\text{ppm}$  174.7) and two were glucoses ( $\delta\text{ppm}$  62.2 and 61.4, -CH<sub>2</sub>OH). This chemical structure was consistent to the molecular formula of C<sub>48</sub>H<sub>76</sub>O<sub>19</sub> (M=956) and was well supported by the mass spectrum, negative mode, with the molecular ion peak at  $m/z = 955.4$  [M-H]. As mentioned above, if there was a glucuronic acid, this one should connect to C-3 of the aglycone oleanolic acid, this connection was well confirmed by HMBC spectra with the correlations between  $^1\text{H}$  signal at  $\delta\text{ppm}$  4.67 with  $^{13}\text{C}$  signal at  $\delta\text{ppm}$  90.3 of C-3. In the low field, there were two signals at  $\delta\text{ppm}$  82.1 and 78.8 that meant two carbons of glucuronic acid, C-2' and C-4', each connected further with a glucose. These two  $^{13}\text{C}$  signals had long-range couplings with peaks at  $\delta\text{ppm}$  4.93 and 5.21, respectively. The anomeric protons of the three sugars had signals as doublets with coupling constants of about 7.5-8.0 Hz that meant they had the *b*-configurations. So, (**4**) was 3-*b*-O-D-glucopyranosyl-(1 $\rightarrow$ 2)-[*b*-D-glucopyranosyl-(1 $\rightarrow$ 4)]-*b*-D-glucuronopyranosyloleanolic acid.

Compound (**3**) was isolated as amorphous white powder. On TLC, it was slightly less polar than (**4**) and indeed, it was eluted out of a reversed phase silica gel column right after (**4**). In the low field of  $^1\text{H}$ -NMR spectra, (**3**) showed signals similar to that of (**4**) with one broad singlet at  $\delta\text{ppm}$  5.36 of H-12, three anomeric protons at  $\delta\text{ppm}$  5.25 (d, J=8.0 Hz, H-1''), 5.01 (d, J=8.0 Hz, H-1''') and 4.77 (d, J= 7.5 Hz, H-1'). The  $^{13}\text{C}$ , DEPT, HSQC-NMR spectra showed two carboxyl carbons at  $\delta\text{ppm}$  178.0 and 167.9, three anomeric carbons at  $\delta\text{ppm}$  105.6 and 103.7 (two carbons), one oxygenated carbon of C-3 at  $\delta\text{ppm}$  89.3, twelve oxygenated methine carbons at  $\delta\text{ppm}$  85.5, 82.6, 77.2, 77.0, 76.5, 75.8, 74.2, 74.2, 73.9, 71.6, 70.5, 70.4 and two oxygenated methylene carbons at  $\delta\text{ppm}$  61.4. These informations suggested that (**4**) was also a saponin with oleanolic acid as the aglycone moiety and one glucuronic acid, two glucoses as sugar moiety. If in (**3**), two glucoses linked to glucuronic acid at its C-2' and C-4', in (**4**) they linked at C-3' and C-4' because of the presence of two signals at  $\delta\text{ppm}$  85.5, 82.6 as shown in the figure 1. These two  $^{13}\text{C}$  signals had long-range couplings with the peak at  $\delta\text{ppm}$  5.25 and 5.01, respectively. The anomeric protons of the three sugars had signals as doublets with coupling constants of about 7.5-8.0 Hz that meant they had the *b*-configurations. So, (**3**) was 3-O-*b*-D-glucopyranosyl-(1 $\rightarrow$ 3)-[*b*-D-glucopyranosyl-(1 $\rightarrow$ 4)]-*b*-D-glucuronopyranosyloleanolic acid.

Compound (**5**) was also a saponin. With the information from the figure 1, (**5**) was immediately recognized with a glucuronic acid and this one linked to another glucose at its C-4' ( $\delta_c = 83.7$  ppm) and the seconde glucose linked to aglycone at C-28. The HMBC spectrum showed long-range couplings of  $^1\text{H}$  signals at  $\delta_{\text{ppm}}$  6.14, 5.05 and 4.77 with  $^{13}\text{C}$  signals at  $\delta_{\text{ppm}}$  176.5 (C-28 aglycone), 83.7 (C-4' glucuronic acid) and 89.5 (C-3 aglycone), respectively. The anomeric protons of the three sugars had signals as doublets with coupling constants of about 7.5-8.0 Hz that meant they had the *b*-configurations. So, (**5**) was 3-*b*-*O*-D-glucopyranosyl-(1 $\rightarrow$ 4)-*b*-D-glucuronopyranosyloleanolic acid 28-*O*-*b*-D-glucopyranosyl ester.

Compounds (**2b**), (**4**) and (**5**) were also found in *Polyscias fruticosa* with compounds N $^{\circ}$ 1, 3 and 6, respectively [3].

### 3. EXPERIMENTAL

#### General

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR were recorded on Bruker Avance 500 MHz and 125 MHz, respectively, in pyridine- $d_5$ . LC-MS spectra were carried out on Agilent-MSD-Trap-SL with the column of Adserbphere UHF C18. All spectrums were recorded in the Institute of Chemistry, Vietnamese Academy of Science and Technology, Cau Giay Dist., Ha Noi.

#### Plant material

The leaves of *Polyscias guilfoylei* Bail were collected in Binh Duong province in June 2005. A voucher specimen was prepared and deposited by Mrs. Lieu Ho My Trang, University of Medicine–Ho Chi Minh City.

#### Extraction and isolation

Dried and powdered leaves (1.1 kg) of *P. guilfoylei* were successively exhaustedly extracted with ethanol at room temperature to yield the crude ethanolic extract (25g). This extract was partitioned successively in petroleum ether, chloroform, ethyl acetate and finally butanol to give corresponding extracts. The butanolic extract (29.5 g) was subjected to silica gel column chromatography, eluted with chloroform and then chloroform: methanol from 1 to 100% methanol to yield 8 fractions. Fraction 2 (1.2 g) was chromatographed by normal silica gel with chloroform: methanol: water (40:10:1.2) yielded (**1**, 32.3mg). Fraction 3 (1.4 g) was chromatographed by normal silica gel with chloroform: methanol: water (80:20:2.5), yielded (**2**, 22.5 mg). Fraction 4 (1.7 g) was chromatographed with normal silica gel, eluted with chloroform: methanol: water (48:16:3) then with RP-18 silica gel, eluted with water: methanol (26:24), yielded (**4**, 40 mg) and then (**3**, 55 mg). Fraction 5 (2.3g) was chromatographed with normal silica gel, eluted with chloroform: methanol: water (48:16:3) then with RP-18 silica gel eluted with water: methanol (6:4) yielded (**5**, 52 mg).

#### *b*-D-Glucuronopyranosyloleanolic acid (**1**)

32.3mg, amorphous white powder. LC/MS ESI (negative mode)  $m/z$ : 631.3 [ $\text{M}-\text{H}$ ] $^-$  (calc. for  $\text{C}_{36}\text{H}_{56}\text{O}_9$ ).  $^1\text{H}$ - and COSY-NMR (Pyridine- $d_5$ ),  $\delta_{\text{ppm}}$ : 5.41 (1H, brs, H-12), 4.78 (1H, d, 7.5 Hz, H-1'), 4.22 (H-4'), 4.17 (H-5'), 4.11 (1H, t,  $J=7.5$  Hz, H-3'), 3.92 (1H, d, 8.5 Hz, H-2'), 3.35 (1H, dd,  $J=4.0, 12.0$  Hz, H-3), 3.20 (1H, dd, 3.5, 13.5 Hz, H-18), 1.26 (s, H-27), 1.23 (s, H-23), 0.98 (s, H-30), 0.94 (s, H-26), 0.93 (s, H-24), 0.92 (s, H-29), 0.80 (s, H-25).  $^{13}\text{C}$ -NMR (Pyridine- $d_5$ ) see Table 1.

**Mixture of 3-O-b-D-glucopyranosyl-(1®3)-b-D-glucuronopyranosyloleanolic acid (2a) and 3-O-b-D-glucopyranosyl-(1®4)-b-D-glucuronopyranosyloleanolic acid (2b)**

22.5 mg, amorphous white powder. LC/MS ESI (negative mode)  $m/z$ : 793.5 [M-H]<sup>-</sup> (calc. for C<sub>42</sub>H<sub>66</sub>O<sub>14</sub>, M= 794). <sup>1</sup>H- and COSY-NMR (Pyridine-d<sub>5</sub>), δppm: 5.40 (2H, brs, H-12a, H-12b), 5.18 (hidden in the signal of solvent, H-1''a), 5.03 (hidden in the signal of solvent, H-1''b), 4.77 (d, J=7.5 Hz, H-1'b), 4.76 (d, J=8.5 Hz, H-1'a), 4.36 (m, H-4'a, H-6''a), 4.28 (m, H-4'b, H-6''b), 4.16 (m, H-3'a), 4.09 (m, H-6''a, H-3'b, H-3''b), 4.01 (m, H-6''b), 3.94 (m, H-2'a, H-2''a, H-2''b), 3.90 (m, H-2'b, H-4''a, H-4''b), 3.84 (m, H-5'a, H-5'b, H-5''a), 3.80 (m, H-5''b), 3.30 (dd, J= 3.5, 11.5, H-3a), 3.24 (dd, J= 3.5, 11.5, H-3b), 3.17 (d br, H-18<sup>a</sup>, H-18b), 1.24 (s, H-27), 1.19 (s, H23), 0.95 (s, H-30), 0.90 (s, H-24, H-29), 0.89 (s, H-26) and 0.74 (s, H-25). <sup>13</sup>C-NMR (Pyridine-d<sub>5</sub>) sees Table 1.

**3-O-b-D-glucopyranosyl-(1®3)-[b-D-glucopyranosyl-(1®4)]-b-D-glucuronopyranosyl oleanolic acid (3)**

55.0 mg, amorphous white powder. LC/MS ESI (negative mode)  $m/z$ : 955.1 [M-H]<sup>-</sup> (calc. for C<sub>48</sub>H<sub>76</sub>O<sub>19</sub>, M= 956). <sup>1</sup>H- and COSY-NMR (Pyridine-d<sub>5</sub>), δppm: 5.36 (1H, brs, H-12), 5.25 (1H, d, 8.0 Hz, H-1''), 5.01 (1H, d, 8.0 Hz, H-1'''), 4.77 (1H, d, 7.5 Hz, H-1'), 4.38 (1H, m, H-6''), 4.30 (3H, m, H-3', H-4', H-6'''), 4.30 (3H, m, H-5', H-3'', H-3'''), 4.05 (4H, m, H-2'', H-4'', H-6'', H-6'''), 3.85 (4H, m, H-5'', H-5''', H-2''', H-4'''), 3.26 (1H, dd, 4.0, 14.0 Hz, H-18), 3.13 (1H, dd, 4.0, 11.5 Hz, H-3), 1.17 (s, H-27), 1.07 (s, H-23), 0.90 (s, H-30), 0.84 (s, H-24), 0.82 (s, H-26), 0.80 (s, H-29) and 0.65 (s, H-25).

**3-O-b-D-Glucopyranosyl-(1®2)-[b-D-glucopyranosyl-(1®4)]-b-D-glucuronopyranosyl oleanolic acid (4)**

40.0 mg, amorphous white powder. LC/MS ESI (negative mode)  $m/z$ : 955.4 [M-H]<sup>-</sup> (calc. for C<sub>48</sub>H<sub>76</sub>O<sub>19</sub>, M= 956). <sup>1</sup>H- and COSY-NMR (Pyridine-d<sub>5</sub>), δppm: 5.42 (1H, brs, H-12), 5.21 (1H, d, 8.0 Hz, H-1''), 4.93 (1H, d, 8.0 Hz, H-1'''), 4.66 (1H, d, 7.5 Hz, H-1'), 4.28 (1H, d, J=10.5 Hz, H-6'''), 4.23 (4H, m, H-2', H-4', H-5'', H-6''), 4.11 (1H, m, H-3'), 4.03 (3H, m, H-3'', H-3''', H-6'''), 3.92 (2H, dd, J=5.5, 12.0 Hz, H-6''), 3.80 (3H, m, H-2'', H-2''', H-5'''), 3.75 (3H, m, H-4'', H-4''', H-5'), 3.25 (1H, dd, 4.0, 14.0 Hz, H-18), 3.08 (1H, dd, 4.0, 11.5 Hz, H-3), 1.16 (s, H-27), 1.04 (s, H-23), 0.99 (s, H-26), 0.97 (s, H-30), 0.90 (s, H-24), 0.79 (s, H-29) and 0.72 (s, H-25).

**3-O-b-D-Glucopyranosyl-(1®4)-b-D-glucuronopyranosyloleanolic acid 28-O-b-D-glucopyranosyl ester (5)**

52.0 mg, amorphous white powder. LC/MS ESI (negative mode)  $m/z$ : 793.4 [M-glucose]<sup>-</sup> (calc. for C<sub>48</sub>H<sub>76</sub>O<sub>19</sub>, M= 956). <sup>1</sup>H- and COSY-NMR (Pyridine-d<sub>5</sub>), δppm: 6.14 (1H, d, 8.0 Hz, H-1'''), 5.38 (1H, brs, H-12), 5.05 (1H, d, 8.0 Hz, H-1''), 4.77 (1H, d, 7.5 Hz, H-1'), 4.36 (2H, m, H-5', H-6'''), 4.28 (2H, m, H-4', H-6''), 4.22 (2H, m, H-5''', H-6'''), 4.16 (2H, m, H-3'', H-4''), 4.10 (2H, m, H-5'', H-2'''), 4.02 (2H, m, H-2', H-6''), 3.92 (4H, m, H-3', H-2'', H-3''', H-4'''), 1.23 (s, H-27), 1.20 (s, H-23), 1.00 (s, H-26), 0.92 (s, H-24), 0.89 (s, H-30), 0.87 (s, H-29) and 0.79 (s, H-25).

SAPONINS TỪ CÂY ĐÌNH LĂNG TRỔ (*POLYSCIAS GUIFOYLEI* BAIL) Họ  
NHÂN SÂM (ARALIACEAE)

Nguyễn Thị Ánh Tuyết<sup>(1)</sup>, Nguyễn Thúy Anh Thu<sup>(3)</sup>, Nguyễn Thị Thúy Hằng<sup>(2)</sup>,  
Nguyễn Ngọc Sương<sup>(3)</sup>, Nguyễn Kim Phi Phụng<sup>(3)</sup>

(1) Trường Đại học Sư phạm TP. HCM; (2) Đại học An Giang

(3) Trường Đại học Khoa học Tự nhiên, ĐHQG-HCM

**TÓM TẮT:** Cây Đình lăng trổ *Polyscias guilfoylei* Bail chưa được các tác giả ở Việt Nam cũng như trên thế giới khảo sát. Từ lá cây đã cô lập được bốn hợp chất: isophytol, acid oleanolic, 3-O-b-D-glucopyranosylspinasterol và acid 3-O-b-D-glucopyranosyloleanolic acid<sup>[5]</sup>. Trong báo cáo này chúng tôi trình bày kết quả cô lập và nhận danh 5 hợp chất saponin: acid b-D-glucuronopyranosyloleanolic (1), một hỗn hợp gồm hai saponin, với tỉ lệ (2:3) là: acid 3-O-b-D-glucopyranosyl-(1@3)-b-D-glucuronopyranosyloleanolic (2a) và acid 3-O-b-D-glucopyranosyl-(1@4)-b-D-glucuronopyranosyloleanolic (2b), acid 3-O-b-D-glucopyranosyl-(1@3)-[b-D-glucopyranosyl-(1@4)]-b-D-glucuronopyranosyloleanolic (3), acid 3-O-b-D-glucopyranosyl-(1@2)-[b-D-glucopyranosyl-(1@4)]-b-D-glucuronopyranosyloleanolic (4) và 3-O-b-D-glucopyranosyl-(1@4)-b-D-glucuronopyranosyloleanolic acid 28-O-b-D-glucopyranosyl ester (5). Cấu trúc hóa học của các hợp chất được xác định bằng các phương pháp phổ nghiệm.

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