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## Cycloartane glycosides from Leaves of *Oxyanthus pallidus*

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**Abstract-** From the MeOH extract of leaves of *Oxyanthus pallidus*, three cycloartane glycosides, named pallidiosides A-C, were isolated together with two known compounds, oleanolic acid and 3-*O*- $\beta$ -D-glucopyranosyl- $\beta$ -sitosterol. The structures of pallidiosides A-C were assigned on the basis of spectral studies and comparison with published literature data. The known compounds were identified by means of *Co* TLC and confirmed by their physical constants.

**Key Word Index-** *Oxyanthus pallidus*/*Oxyanthus sankuruensis*/*Oxyanthus schubotzianus*, Rubiaceae, pallidioside, cycloartane glycoside.

## 1. Introduction

Plants of the genus *Oxyanthus*, occupy a prominent position in traditional African medicine (Kawukpa et Angoyo, 1994; Chaaib, 2004; Bouquet, 1969; Adjanohoun *et al.*, 1988; Iwu, 1988). The genus *Oxyanthus*, belongs to the family Rubiaceae and consists of more than 40 species distributed in the African continent, south of the Sahara (Hallé, 1970). *Oxyanthus pallidus* Hiern/*Oxyanthus sankuruensis* De Wild/*Oxyanthus schubotzianus* K. Krause, is a small shrub widespread from Senegal to Nigeria, and extending from Sudan to Ethiopia (Hallé, 1970). *Oxyanthus pallidus*, has not been the object of any chemical investigation. The present contribution reports the isolation and the structure elucidation of three new cycloartane glycosides from the plant.

## 2. Results and discussion

Pallidioside A (**3**), was obtained as a white fine powder. HR-ESI-MS data showed a molecular ion peak at  $m/z$  675.3884  $[M+Na]^+$  in agreement with the molecular formula  $C_{36}H_{60}O_{10}Na$ . The IR spectrum exhibited strong absorptions at  $\nu_{max}$  3375 and 1703  $cm^{-1}$  representing, respectively the -OH groups and a carbonyl group. The  $^1H$ -NMR spectrum of **3** (table 1) showed highly shielded signals characteristic of methylene protons of a cyclopropane ring as an AX system ( $\delta_H$  0.17, 0.84, each d,  $J=4.4$  Hz, H2-19), and signals due to six tertiary methyls ( $\delta_H$  0.80, 0.92, 0.97, 1.16, 1.30, 1.30) and a secondary methyl group ( $\delta_H$  0.93, d,  $J=8.4$  Hz). The  $^{13}C$ -NMR spectrum of pallidioside A (**3**), exhibited signals of 36 carbons, of which 30 accounted for the aglycone moiety. The six remaining signals were in good accordance, with the presence of a hexose unit, identified after analysis of COSY and

HSQC spectra, as a glucose (table 1). The 1,2-diaxial coupling of anomeric proton (H-1') at  $\delta_{\text{H}}$  4.32 (d,  $J = 7.8 \text{ Hz}$ ) indicated the  $\beta$ -configuration of the glucose unit. Acid hydrolysis of **3** and *Co* TLC of the water-soluble fraction of the reaction mixture, using methanol-ethyl acetate-water (8.1.1), allowed the identification of D-glucose with a retention factor 0.23. By analysing the HSQC spectrum, the resonances assigned to the aglycone moiety consisted of seven methylys, nine methylenes, seven methines and seven quaternary carbons among these one  $\text{sp}^2$  ( $\delta_{\text{C}}$  219.16) and one  $\text{sp}^3$  bearing oxygen ( $\delta_{\text{C}}$  77.9). The signals at  $\delta_{\text{C}}$  73.4, 79.2 and 81.3 were attributed to methine carbons, each bearing a hydroxyl group. Thus, pallidioside A (**3**), was considered to be a cycloartane-type triterpene monoglycoside (Kaipnazarov et al., 2004; Kucherbaev et al., 2002; Gutierrez-Lugo et al., 2002; Özipek et al., 2005; Calis et al., 1999; Zhao et al., 1996; Uteniyazov et al., 1999; Zhao et al., 2008). The assignments of the proton and carbon signals, and the positions of the hydroxyl groups of **3** were established by analysis of the COSY, HSQC and HMBC spectra. In the HMBC spectrum, the correlation between H<sub>3</sub>-28 and 29 ( $\delta_{\text{H}}$  0.80, 0.97, respectively) and  $\delta_{\text{C}}$  79.2 placed one of the hydroxyl groups at the 3-position, and the position of the second hydroxyl was determined to be at the 7-position from the coupling pattern of the H-5 ( $\delta_{\text{H}}$  1.43, dd,  $J = 13.3, 3.5 \text{ Hz}$ ) and H-8 ( $\delta_{\text{H}}$  2.07, d,  $J = 7 \text{ Hz}$ ). The hydroxyl group at the 16-position was proved by the HMBC correlations of H-8 with C-15 ( $\delta_{\text{C}}$  47.8) and then H-15 ( $\delta_{\text{H}}$  2.32) with C-16 ( $\delta_{\text{C}}$  73.4). The remaining hydroxyl group and the carbonyl groups were placed at the 25 and 24-positions respectively based on the HMBC correlations for H<sub>3</sub>-26 and 27 ( $\delta_{\text{H}}$  1.30) with C-24 ( $\delta_{\text{C}}$  219.6) and 25 ( $\delta_{\text{C}}$  77.9). Other HMBC correlations were also supportive of the positions of hydroxyl group on the cycloartane skeleton (figure 1). The long-range correlation observed between the anomeric proton of the glucose unit ( $\delta_{\text{H}}$  4.32) and C-7 ( $\delta_{\text{C}}$  81.3) of the aglycone moiety indicated the position of the sugar linkage on the hydroxyl at C-7 position. The stereochemistry of **3** was determined by analysis of the NOESY spectrum and the  $^1\text{H}$ - $^1\text{H}$

coupling constants (figure 2, table 1). The orientation of the hydroxyl group at C-3 was concluded to be  $\beta$  on the basis of the coupling constant of H-3, since the H-3 ( $\delta_{\text{H}}$  3.20) signal was observed as a doublet of doublets due to 1,2-diaxial ( $J=11.1$  Hz) and axial-equatorial coupling ( $J=4.4$  Hz) with H-2ax and H-2eq, respectively. The 1,2-diaxial coupling of H-8 ( $\delta_{\text{H}}$  2.07, d,  $J=7$  Hz) and H-7, was supported by the Noe effect observed between H-7 and H-5, and suggested the  $\beta$ - configuration for the hydroxyl at C-7. In the case of H-16 ( $\delta_{\text{H}}$  4.45), the large coupling constant of H-16 with H-15ax-like ( $\delta_{\text{H}}$  2.32,  $J=7.6$  Hz) and the small coupling constant of H-16 with H-15eq-like ( $\delta_{\text{H}}$  1.62, d,  $J=5.1$  Hz), and also the large coupling constant ( $J=7.6$  Hz) with H-17 indicated the  $\beta$ -configuration for the hydroxyl at this position. These observations were further confirmed by the correlations observed in the NOESY spectrum, in which H<sub>3</sub>-30 ( $\delta_{\text{H}}$  0.92) showed correlations with H-7 ( $\delta_{\text{H}}$  3.61) and H-16 (figure 2). The position of the sugar linkage was confirmed to be the hydroxyl group at C-7 by the Noe effect observed between H-1' and H-7. Therefore, the structure of pallidioside A (**3**) was elucidated to be 7-*O*- $\beta$ -D-glucopyranosylcycloart-3 $\beta$ ,16 $\beta$ ,25-trihydroxy-24-one.

Pallidioside B (**4**) was obtained as white powder. Its positive HR-ESI-MS, gives the  $[\text{M}+\text{Na}]^+$  at  $m/z$  677.4028, corresponding to the molecular formula  $\text{C}_{36}\text{H}_{62}\text{O}_{10}\text{Na}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of **4** (tables 1 and 2), were almost superimposable to those of compound **3**. Consequently, pallidioside B (**4**) was considered to be a cycloartane-type triterpene monoglycoside. The main difference observed between these two compounds appeared on the lateral chain, where, the carbonyl at C-24 ( $\delta_{\text{C}}$  = 219.6), observed in the structure of **3** was transformed in to an alcohol ( $\delta_{\text{C}}$  = 78.5) in compound **4**. This was confirmed by  $^{13}\text{C}$  NMR spectrum of **4** on which, signal characteristic for a ketone was not observed. The hydroxyl group was fixed at the 24-position based on the HMBC correlations for H<sub>3</sub>-27 and 26 ( $\delta_{\text{H}}$  1.14, 1.16) with C-24 ( $\delta_{\text{C}}$  78.5) and 25 ( $\delta_{\text{C}}$  73.8) (figure 3). The configuration of the C-24 hydroxyl group was indicated to be 24*S* on the comparison with the chemical shift values of

cyclocantogenin (24*S*, C-24:  $\delta_C$  76.99, Kucherbaev et al. 2002) (**6**) and tarecilioside A (24*R*, C-24:  $\delta_C$  80.5, Zhao et al. 2008) (**7**). This observation was further confirmed by the correlation observed in the NOESY spectrum, on which H-24 ( $\delta_H$  3.37) showed correlation with H-23 $\beta$  ( $\delta_H$  1.62) (figure 4). The position of the sugar linkage was confirmed to be the hydroxyl group at C-7 by the Noe effect observed between H-1' and H-7. Therefore, the structure of pallidioside B (**4**) was elucidated to be 7-*O*- $\beta$ -D-glucopyranosylcycloart-3 $\beta$ ,16 $\beta$ ,24(*S*),25-tetraol.

Pallidioside C (**5**) possess the same molecular formula as **4** as observed by the molecular ion at  $m/z$  677.4028  $[M+Na]^+$  in the positive HR-ESI-MS. Thus Pallidiosides B (**4**) and C (**5**) are two isomers. The analysis of the NMR spectral data of compound **5**, showed the signals characteristic of cycloartane skeleton with a sugar moiety as in **4**. Significant difference between these two isomers, were observed on the lateral chain, particularly, from C-20 to C-24. The configuration of the C-24 hydroxyl group was indicated to be 24*R* on the comparison with the chemical shift values of cyclocantogenin (24*S*, C-24:  $\delta_C$  76.99, Kucherbaev et al. 2002) (**6**) and tarecilioside A (24*R*, C-24:  $\delta_C$  80.5, Zhao et al. 2008) (**7**). The position of the sugar linkage was confirmed to be the hydroxyl group at C-7 by the Noe effect observed between H-1' and H-7. Therefore, the structure of pallidioside C (**5**) was elucidated to be 7-*O*- $\beta$ -D-glucopyranosylcycloart-3 $\beta$ ,16 $\beta$ ,24(*R*),25-tetraol.

Compound **1**, was identified by means of *Co* TLC, using hexane-ethyl acetate (7.5: 2.5) as oleanolic acid, with a retention factor, 0.57. For compound **2**, *Co* TLC has been done, using ethyl acetate, and 3-*O*- $\beta$ -D-glucopyranosyl- $\beta$ -sitosterol was detected with a retention factor, 0.27. Identification of these compounds was confirmed by determining their melting point: 307°C for **1** and 283°C for **2**, which were compatible with those of the literature.

### 3. EXPERIMENTAL

#### 3.1. General Experimental Procedures.

All melting points were recorded with a Reichter microscope and uncorrected. IR spectra were recorded with a Shimadzu FTIR-8400S spectrometer.  $^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) spectra were recorded in  $\text{CD}_3\text{OD}$  on a Bruker Avance DRX-500 spectrometer. Chemical shifts ( $\delta$ ) are reported in parts per million with solvent signals  $\delta_{\text{H}}$  3.31 and  $\delta_{\text{C}}$  49.1 as references, while the coupling constants ( $J$ ) are given in Hertz. HR-ESI-MS experiments were performed using a Micromass Q-TOF.micro instrument (Manchester, UK) with an electrospray source. Column chromatography was run on Merck silica gel 60, while TLC were carried out on silica gel GF<sub>254</sub> precoated plates with detection accomplished by spraying with 50%  $\text{H}_2\text{SO}_4$  followed by heating at 100°C.

#### 3.2. Plant material.

Leaves of *Oxyanthus pallidus* were collected in the city of Bandjoun, Cameroon, in February 2005 and identified by Mr. Nana François of the National Herbarium of Cameroon. A voucher specimen (n° 7335 / SFR / CAM) was deposited at the National Herbarium of Cameroon, Yaounde, Cameroon (YA).

#### 3.3. Extraction and isolation

The air-dried and finely powdered material (2 kg) was extracted with MeOH (7 l) in a glass tank at room temperature. After complete removal of solvent under vacuum evaporation, a dark green residue (154.5 g) was obtained. Part of this, (54.4 g), was fractionated on silica gel (40-63  $\mu\text{m}$ , 110 g) column chromatography, eluted with a mixture of cyclohexane:ethyl acetate (3:7), followed by ethyl acetate and a mixture of EtOAc containing 1 to 3% amounts of MeOH, yielding three fractions (I-III). Fraction I (3 g) obtained with the mixture of cyclohexane-ethyl acetate (3:7) was chromatographed on a silica gel column, using the same solvent to yield compound **1** (274 mg). Fraction II was obtained with ethyl acetate; when this

solvent was distilled off, a precipitate was formed in the bottom flask and recuperated with cyclohexane; under vacuum filtration of crude crystal, 770 mg of compound **2** were obtained. Fraction III (2.5 g), obtained with a mixture of ethyl acetate and MeOH (9:1) was purified over silica gel using the same system to yield **3** (430 mg). The re-examination of sub-fraction III-c (1 g), over the silica gel column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub>: MeOH (8.5:1.5) yielded compounds **4** (308 mg) and **5** (20 mg).

### **3.4. Acid hydrolysis of saponins**

5 mg of each compound were hydrolysed by methanolic H<sub>2</sub>SO<sub>4</sub> (3 ml, 0.15%) with heating on a boiling water bath for 8 h. The reaction mixture was cooled and poured into water (3 ml). The methanol was distilled off. The solid was filtered and washed with water. After neutralization with BaCO<sub>3</sub> and evaporation, thin layer chromatography of the water-soluble fraction using methanol-ethyl acetate-water (8:1:1) was done, and revealed the presence of glucose, which was identical to an authentic sample (tr. 0.23). The D-glucose was identified after preparative TLC in the same solvent and by measurement of the optical rotation  $[\alpha]^{21}_D$  +56.4 (*c* 0.975, H<sub>2</sub>O).

### **3.5. Pallidioside 3**

Mp 144°;  $[\alpha]_D$  +17.2 (CH<sub>3</sub>OH, *c* 0.471x10<sup>-2</sup>); IR  $\nu_{\max}$  (NaCl) cm<sup>-1</sup>: 3375 (OH), 1703 (C=O), 1250 (C-O); <sup>1</sup>H and <sup>13</sup>C (CD<sub>3</sub>OD): see Tables 1 and 2; HR-ESI-MS (positive-ion mode) *m/z* 675.3884 [M+Na]<sup>+</sup> (calculated for C<sub>36</sub>H<sub>60</sub>O<sub>10</sub>Na: 675.3874).

### **3.6. Pallidioside 4**

Mp 176°C;  $[\alpha]_D$  +33.8° (CH<sub>3</sub>OH, *c* 0.461x10<sup>-2</sup>); IR  $\nu_{\max}$  (NaCl) cm<sup>-1</sup>: 3465 (OH), 1250 (C-O); <sup>1</sup>H and <sup>13</sup>C (CD<sub>3</sub>OD): see Tables 1 and 2; HR-ESI-MS (positive-ion mode) *m/z* 677.4028 [M+Na]<sup>+</sup> (calculated for C<sub>36</sub>H<sub>62</sub>O<sub>10</sub>Na: 677.4031).

### **3.7. Pallidioside 5**

Mp 259°C;  $[\alpha]_D +19.2^\circ$  (CH<sub>3</sub>OH,  $c$  0.448x10<sup>-2</sup>); IR  $\nu_{\max}$  (NaCl) cm<sup>-1</sup>: 3477 (OH), 1250 (C-O); <sup>1</sup>H and <sup>13</sup>C (CD<sub>3</sub>OD): see Tables 1 and 2; HR-ESI-MS (positive-ion mode)  $m/z$  677.4028 [M+Na]<sup>+</sup> (calculated for C<sub>36</sub>H<sub>62</sub>O<sub>10</sub>Na: 677.4031).

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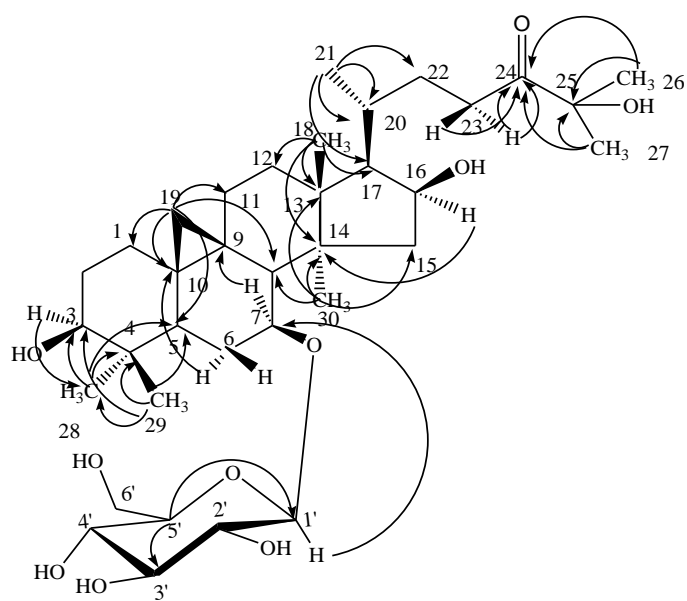
**Table 1:  $^1\text{H}$  NMR of pallidosides A (3), B (4) and C (5)**

	<b>3</b>	<b>4</b>	<b>5</b>
<b>H</b>	$\delta_{\text{H}}, J$ (Hz)	$\delta_{\text{H}}, J$ (Hz)	$\delta_{\text{H}}, J$ (Hz)
1ax	1.58 (1H, m)	1.59 (1H, m)	1.58 (1H, m)
1eq	1.38 (1H, m)	1.39 (1H, m)	1.40 (1H, m)
2ax	1.60 (1H, m)	1.59 (1H, m)	1.58 (1H, m)
2eq	1.69 (1H, m)	1.69 (1H, m)	1.71 (1H, m)
3	3.20 (1H, dd, 11.1, 4.4)	3.20 (1H, dd, 11.0, 4.3)	3.20 (1H, dd, 11.0, 4.3)
4		-	
5	1.43, (1H, dd, 13.3, 3.5)	1.39, (1H, dd, 13.3, 3.5)	1.40, (1H, dd, 13.3, 3.5)
6ax	1.11 (1H, m)	1.11 (1H, m)	1.10 (1H, m)
6eq	2.16 (1H, m)	2.15 (1H, m)	2.15 (1H, m)
7	3.61 (1H, ddd, 12, 7, 5.5)	3.64 (1H, ddd, 12, 7, 5.5)	3.63 (1H, ddd, 12, 7, 5.5)
8	2.07 (1H, d, 7)	2.08 (1H, d, 6.0)	2.10 (1H, d, 6.5)
9		-	-
10		-	-
11ax	1.50 (1H, m)	1.56 (1H, m)	1.56 (1H, m)
11eq	1.67 (1H, m)	1.67 (1H, m)	1.68 (1H, m)
12a	1.56 (1H, m)	1.58 (1H, m)	1.54 (1H, m)
12b	1.58 (1H, m)	1.59 (1H, m)	1.56 (1H, m)
13		-	
14		-	
15ax	2.32 (1H, dd, 7.6; 5.0)	2.32 (1H, dd, 7.6; 5.0)	2.30 (1H, dd, 7.6; 5.0)
15eq	1.62 (1H, dd, 7.6, 5.0)	1.59 (1H, dd, 7.6, 5.0)	1.60 (1H, dd, 7.6; 5.0)
16	4.45 (1H, ddd, 7.7, 7.6, 5.0)	4.41 (1H, ddd, 7.8, 7.6, 5.0)	4.40 (1H, ddd, 7.8, 7.6, 5.0)
17	1.60 (1H, dd, 12.5, 7.7)	1.62 (1H, dd, 12.5, 7.8)	1.62 (1H, dd, 12.5, 7.8)
18	1.16 (3H, s)	1.17 (3H, s)	1.17 (3H, s)
19 $\alpha$	0.16 (1H, d, 4.4)	0.15 (1H, d, 3.9)	0.15 (1H, d, 4.6)
19 $\beta$	0.84 (1H, d, 4.4)	0.84 (1H, d, 3.9)	0.85 (1H, d, 4.6)
20	1.71 (1H, m)	1.89 (1H, m)	1.84 (1H, m)
21	0.95 (3H, d, 6)	0.94, (3H, d, 7.4)	0.95 (3H, d, 7.8)
22 $\alpha$	1.21 (1H, m)	1.21 (1H, m)	1.89 (1H, m)
22 $\beta$	1.94 (1H, m)	1.80 (1H, m)	1.01 (1H, m)
23 $\alpha$	2.80 (2H, m)	1.39 (1H, m)	2.15 (1H, m)
23 $\beta$		1.62 (1H, m)	1.10 (1H, m)
24		3.37 (1H, dd, 11.8, 5)	3.24 (1H, dd, 8.8, 5.4)
25		-	-
26	1.30 (3H, s)	1.16 (3H, s)	1.17 (3H, s)
27	1.30 (3H, s)	1.14 (3H, s)	1.14 (3H, s)
28	0.97 (3H, s)	0.96 (3H, s)	0.97 (3H, s)
29	0.80 (3H, s)	0.79 (3H, s)	0.80 (3H, s)
30	0.92 (3H, s)	0.91 (3H, s)	0.91 (3H, s)
1'	4.32 (1H, d, 7.8)	4.31 (1H, d, 7.8)	4.31 (1H, d, 7.7)
2'	3.16 (1H, dd, 9, 7.8)	3.16 (1H, dd, 9, 7.8)	3.17 (1H, dd, 9, 7.8)
3'	3.34 (1H, dd, 9, 9)	3.34 (1H, dd, 9, 9)	3.34 (1H, dd, 9, 9)
4'	3.29 (1H, dd, 9, 9)	3.30 (1H, dd, 9, 9)	3.28 (1H, dd, 9, 9)
5'	3.27 (1H, m)	3.26 (1H, m)	3.26 (1H, m)
6'a	3.83 (1H, dd, 12, 2.1)	3.84 (1H, dd, 11.7, 2.1)	3.84 (1H, dd, 11.7, 2.1)
6'b	3.66 (1H, dd, 12, 2.1)	3.67 (1H, dd, 11.7, 2.2)	3.67 (1H, dd, 11.7, 2.2)

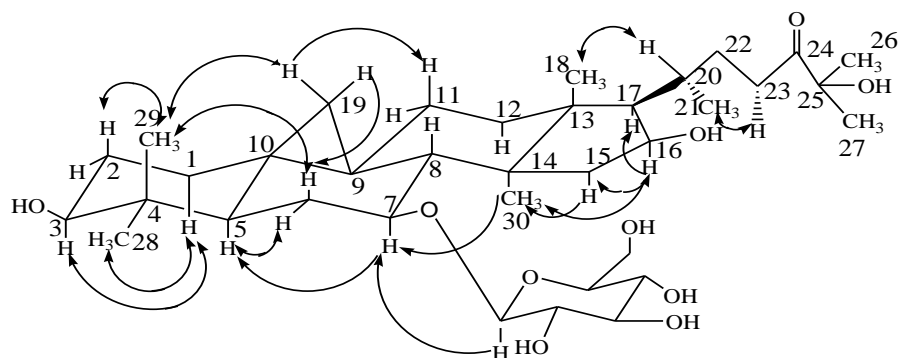
Assignments were performed by means of COSY, HSQC and HMBC experiments. s: singlet, d: doublet, dd: doublet of doublets, m: multiplet. Position was assigned from the HSQC spectrum

**Table 2:**  $^{13}\text{C}$  NMR of compounds **3**, **4**, **5**, **6** and **7**

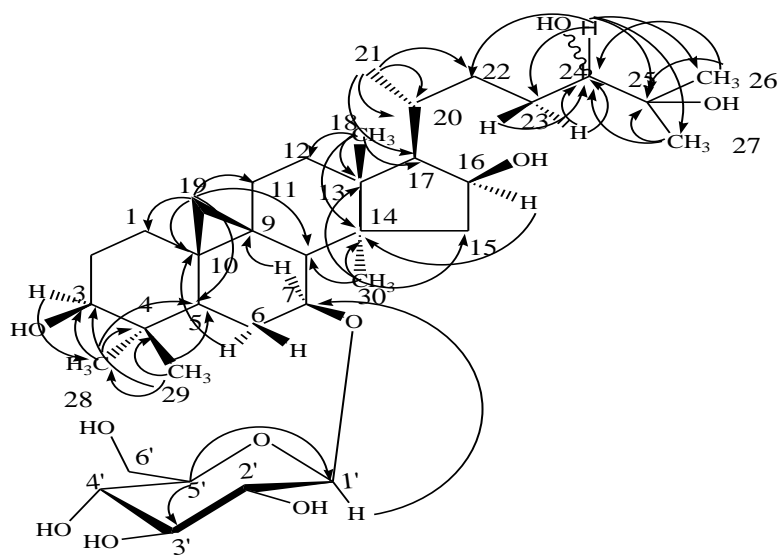
	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
<b>C</b>	$\delta_{\text{C}}/\text{CD}_3\text{OD}$	$\delta_{\text{C}}/\text{CD}_3\text{OD}$	$\delta_{\text{C}}/\text{CD}_3\text{OD}$	$\delta_{\text{C}}/\text{C}_5\text{D}_5\text{N},$ TMS	$\delta_{\text{C}}/\text{C}_5\text{D}_5\text{N},$ TMS
1	31.8	31.7	31.7	32.54	31.8
2	30.6	30.5	30.5	31.17	29.8
3	79.2	79.2	79.2	78.10	88.6
4	41.2	41.2	41.2	42.18	40.9
5	45.6	45.5	45.5	53.73	46.4
6	29.4	29.4	29.4	68.04	31.9
7	81.3	81.3	81.3	38.33	70.3
8	51.5	51.1	51.2	46.94	55.3
9	21.6	21.6	21.6	21.02	20.3
10	27.7	27.7	27.7	29.71	26.9
11	28.0	28.0	28.0	26.17	26.8
12	33.8	33.7	33.8	32.95	33.2
13	48.0	48.3	48.0	45.47	46.1
14	46.7	46.7	46.6	46.67	47.1
15	47.8	47.7	47.7	48.16	50.7
16	73.4	73.3	73.2	71.75	72.2
17	57.4	57.3	57.3	57.11	56.8
18	17.6	17.5	17.4	18.03	18.8
19	26.1	25.8	25.8	29.09	28.6
20	31.1	29.8	32.0	28.44	31.6
21	18.5	18.6	19.0	18.77	18.9
22	31.0	33.7	35.3	32.81	35.0
23	28.4	28.4	29.4	27.67	29.4
24	<b>219.6</b>	<b>78.5</b>	<b>80.7</b>	<b>76.99</b>	<b>80.5</b>
25	77.9	73.8	73.8	72.88	72.8
26	26.8	25.3	25.8	25.48	26.1
27	26.8	25.3	24.8	26.07	25.8
28	26.0	26.0	26.0	19.93	15.3
29	14.2	14.2	14.2	29.34	25.8
30	19.9	19.7	19.8	15.87	20.0
1'	104.1	104.0	104.1	-	106.7
2'	75.4	75.3	75.3	-	75.7
3'	78.6	78.4	78.6	-	78.7
4'	71.7	71.6	71.6	-	71.8
5'	77.6	77.5	77.6	-	78.1
6'	62.9	62.8	62.8	-	63.0



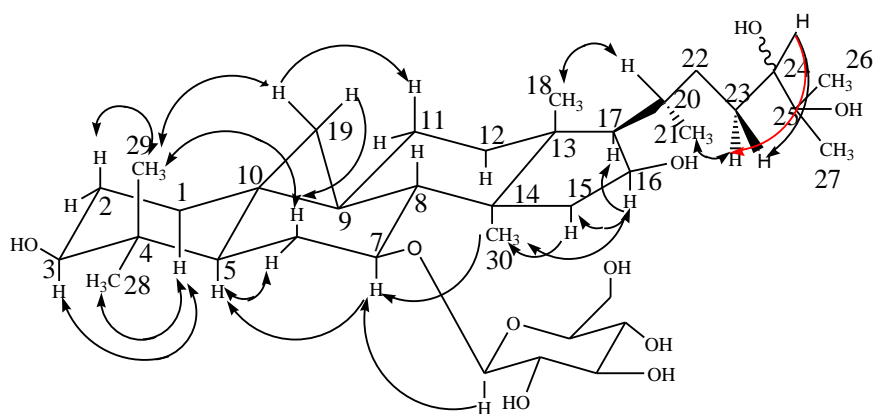
**Fig. 1. HMBC correlations of pallidioside (A) 3**



**Fig. 2. NOESY correlations for Pallidioside A (3)**



**Fig. 3 HMBC correlations of pallidiosides B (4) and C (5)**



**Fig. 4. NOESY correlations for pallidiosides B (4) ↘ and C (5) ↘**