# Five new iridoïd dimers from the fruits of Canthium subcordatum DC (syn. Psydrax subcordata DC)

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# Five new iridoïd dimers from the fruits of *Canthium subcordatum* DC (syn. *Psydrax subcordata* DC)

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**Abstract**

Five new iridoid dimmers, canthiumosides 1-5 (**1-4** and **5a**), together with nine known compounds, shanzhigenin methyl ester (**6),** 1-epishanzhigenin methyl ester **(6'**), linearin (**7),** 1-epilinearin (**7'**), mussaenoside (**8**), shanzhiside methyl ester (**9**), 3',4',7- trihydroxyflavone (**10**), betulinic acid (**11**), and oleanolic acid (**12**) were isolated from the fruits of *Canthium subcordatum* DC (Syn. *Psydrax subcordata* (DC) Bridson). The structures of these compounds were established by interpretation of their spectral data, mainly HR-TOFESIMS, 1D-NMR ($^{1}$H, $^{13}$C and DEPT) and 2D-NMR ($^{1}$H-$^{1}$H COSY, HSQC, HMBC, and NOESY), and by comparison with the literature.

*Keywords*: *Canthium subcordatum/Psydrax subcordata*; Rubiaceae; iridoid dimers; canthiumoside; structure elucidation.

## 1. Introduction

*Canthium subcordatum* (formely *Psydrax subcordata*) is a tree which grows in central and western Africa and reaches a height of more than 10 m (Irvine, 1961). Its roots, leaves and stem bark are used for medicinal purposes (Ampofo, 1977). Alcoholic extracts of the stem bark have potential antidiabetic properties (Ampofo, 1977) and the roots are used to treat malaria fever, inflammation and cardiovascular disease (Awah et al., 2012). Previous work on this genus revealed the presence of iridoids (Achenbach et al., 1980, 1981), peptidic alkaloids (Dongo al., 1989; Achenbach et al., 1986), terpenoids and miscellaneous compounds (Patro et al., 2014). In the course of our continuing search for secondary metabolites of biological importance from Cameroonian medicinal plants, we investigated the *iso*BuOH, EtOAc and *n*-hexane extracts of the fruits of *C. subcordatum*. In the present paper, we report the isolation and structural elucidation of five new iridoid dimers using chemical and spectroscopic methods.

## 2. Results and Discussion

Purification of the *iso*BuOH, EtOAc and *n*-hexane soluble fractions of the crude MeOH extract afforded five new compounds, canthiumosides 1-5 (**1-4** and **5a)**, and nine known compounds (**6-12**). The structures of the known compounds were determined by means of co-TLC and by comparative analysis of their physical and spectral data with those reported in the literature for shanzhigenin methyl ester (**6)** and 1-epishanzhigenin methyl ester (**6'**) (Guo et al., 2001), linearin (**7)** and 1-epilinearin (**7'**) (Khatri et al., 1979), mussaenoside (**8**) (Takeda et al., 1997), shanzhiside methyl ester (**9**) (Takeda et al., 1997), 3',4',7-trihydroxyflavone (**10**) (Bickoff et al., 1965), betulinic acid (**11**) (Sholichin et al., 1980), and oleanolic acid (**12**) (Hossain et Ismail, 2013) (Figure 1).

Compound **1** (canthiumoside 1) was obtained as a waxy solid. Its HR-TOFESIMS exhibited a pseudo-molecular ion peak at *m/z* 485.1428 $[M+Na]^+$ (calcd. for $C_{23}H_{26}O_{10}Na$. 485.1424), indicating the molecular formula $C_{23}H_{26}O_{10}$ with twelve degrees of unsaturation. The $^1H$ and $^{13}C$ NMR spectra (Tables 1 and 2) showed mainly doubled peaks suggesting that compound **1** was an iridoid dimer. The two iridoid moeities are hereafter referred to as units a and b. The proton and carbon signals of these two units closely resembled those of the ulmoidosides (Yahara et al., 1990). The $^1H$ NMR spectrum showed four olefinic protons at $\delta_H$ 7.55 (H-3a, s), $\delta_H$ 7.61 (H-3b, s) and $\delta_H$ 5.91 (H-7a and b, br s); four methylene protons at $\delta_H$ 2.06 (H-α-6a and b, m) and $\delta_H$ 2.87 (H-β-6a and b, m); a methoxy group at $\delta_H$ 3.73 (11a-OMe, s); six methine protons at $\delta_H$ 4.84 (H-1a, d, $J$ = 8.6 Hz), 4.82 (H-1b, d, $J$ = 8.6 Hz), 3.18 (H-5a q, $J$ =

8.5 Hz), 3.21 (H-5b, q, $J$ = 8.5 Hz) and $\delta_H$ 2.56 (H-9a and b, t, $J$ = 8.5 Hz); two oxymethylenes at $\delta_H$ 4.91 (H-10a, d, $J$ = 14.4 Hz), $\delta_H$ 4.78 (H-10a, d, $J$ = 14.4 Hz), 4.81 (H-10b, d, $J$ = 14.5 Hz) and $\delta_H$ 4.76 (H-10b, d, $J$ = 14.5 Hz) attributable to an iridoid framework (Patro et al., 2014; Cui-lian et al., 2010; Demirezer et al., 2006) as summarized in Table 1. This was confirmed by the $^{13}$C NMR spectrum, which exhibited 23 carbon signals due to 10 pairs of carbons of the main iridoid skeleton (Quang et al., 2002), including two *α,β*-unsaturated ester groups at *δ*c 168.4 (C-11a) and *δ*c 167.6 (C-11b), eight olefinic carbons at *δ*c 153.2 (C-3b), 152.9 (C-3a), 110.2 (C-4a and b), 139.3 (C-8a), 139.1 (C-8b), 129.3 (C-7a) and *δ*c 129.7 (C-7b); an acetyl group at *δ*c 171.3 (C-10b-$\underline{C}OCH_3$) and $\delta_C$ 19.4 (C-10b-CO$\underline{C}H_3$) and a methoxyl carbon at $\delta_C$ 50.3 (11a-OMe) (Table 2). The two hemiacetal protons at $\delta_H$ 4.82 (H-1b) and $\delta_H$ 4.84 (H-1a) correlated in the HSQC spectrum with carbons at $\delta_C$ 96.3 (C-1b) and 96.2 (C-1a), respectively. Comparison of these chemical shifts with those of linearin (Guo et al., 2001) and shanzhigenin methyl ester (Khatri et al., 1979) indicated that the two hydroxy groups at C-1a and C-1b were not involved in any ether bond.

In the COSY spectrum, protons at $\delta_H$ 4.82 (H-1b) and 4.84 (H-1a) correlated with protons at $\delta_H$ 2.56 (2H, t, $J$ = 8.5 Hz) attributed to H-9a and H-9b, which correlated to protons at $\delta_H$ 3.18 (H-5a, q, $J$ = 8.5 Hz) and $\delta_H$ 3.21 (H-5b, q, $J$ = 8.5 Hz). In addition these two protons showed cross peaks with protons at $\delta_H$ 2.06 (H-6αa and H-6αb, m) and $\delta_H$ 2.87 (H-6βa and H-6βb, m) which correlated with the olefinic protons at $\delta_H$ 8.91 (H-7a, H-7b). The corresponding carbons of these protons were assigned by analysis of the HSQC spectrum (Table 1). In the HMBC spectrum the vinyl protons H-7a and H-7b showed cross-peaks with carbons at $\delta_C$ 139.3 (C-8a), 139.1 (C-8b), 38.8 (C-6a), 38.7 (C-6a), 35.9 (C-5a), 36.0 (C-5b) and with the hemiacetal carbons C-1a and C-1b. The protons at $\delta_H$ 4.78 and 4.91 (H-10a, d, $J$ = 14.4 Hz), showed long-rang correlations with carbon C-7a (*δ*c 129.3). Similarly, protons 2H-10b ($\delta_H$ 4.76 and 4.81, d, $J$ = 14.5 Hz) showed long-rang correlations with carbon C-7b ($\delta_C$ 127.9). The presence of cross-peaks between 2H-10b and the carbonyl carbon at $\delta_C$ 171.2 revealed the attachment of the acetate to C-10b (Patro et al., 2014; Yahara et al., 1990; Cui-Lian et al., 2010).

In the HMBC spectrum, vinyl proton H-3a ($\delta_H$ 7.55) correlated with C-1a ($\delta_C$ 96.2), C-4a ($\delta_C$ 110.1), C-11a ($\delta_C$168.3) and C-5a (*δ*C 35.9) while vinyl proton H-3b at $\delta_H$ 7.61 showed correlations with C-1b (*δ*c 96.3), C-4b ($\delta_C$ 110.2), C-11b ($\delta_C$ 167.6) and C-5b ($\delta_C$ 36.0). The position of the methoxy group ($\delta_C$ 50.3) was revealed by a cross-peak between the methoxyl protons at ($\delta_H$ 3.73) and the carbonyl carbon at $\delta_C$168.3 (C-11a). The position of the ester

linkage between units a and b was determined by the presence of cross-peaks between protons 2H-10a ($\delta_H$ 4.91 and 4.78) and the carbonyl carbon C-11b ($\delta_C$ 167.6) (Sui-Kiong et al., 2002) Confirmation of the stereochemistry of the stereogenic centers was achieved by analysis of *J* values and comparison of $^{13}C$ chemical shifts with literature data, especially those for the chiral centers at C-5a, C-9a and C-5b, C-9b, which indicated the beta-configuration of H-9 as in geniposide (Inouye et al., 1974; Bailleul et al., 1977). The data were also consistent with the normal *cis* junction between the two rings and the beta-configurations of the hydroxyl residue at C-1 (Hamerski et al., 2003; Zapesochnaya et al., 1991). This was confirmed by NOESY correlations between H-5 and H-9, as well as H-6β, in both units. Thus structure **1** was assigned to the iridoid dimmer canthiumoside 1 (Figure 1).

Compound **2** was obtained as a waxy solid. Its HR-TOFESIMS exhibited a pseudo-molecular ion peak at *m/z* 647.1946 $[M+Na]^+$ (calcd. for $C_{29}H_{36}O_{15}Na$. 647.1952), indicating a molecular formula $C_{29}H_{36}O_{15}$ with thirteen degrees of unsaturation. The $^1H$ and $^{13}C$-NMR spectra (Tables 1 and 2) displayed two sets of signals typical of a dimeric iridoid and showed similar chemical shifts to those of compound **1**, apart from additional signals for a glucose moiety at $\delta_H$ 4.74 (H-1'b, d, *J* = 7.8 Hz), 3.24 (H-2'b, dd, *J* = 9.1, 7.8 Hz), 3.40 (H-3'b, t, *J* = 9.1 Hz), 3.31 (H-4'b, m), 3.31 (H-5'b, m), 3.67 (H-6'b, dd, *J* = 11.7, 5.8 Hz), 3.89 (H-6'b, dd, *J* = 11.7, 1.7 Hz) and at $\delta_C$ 99.0 (C-1'b), 73.4 (C-2'b), 76.5 (C-3'b), 70.1 (C-4'b), 77.0 (C-5'b) and 61.4 (C-6'b). Analysis of COSY and HSQC spectra revealed the presence of a glucopyranose moiety (Patro et al., 2014; Cui-Lian et al., 2010) (Tables 1 and 2) characterized by coupling constants up to 7 Hz for protons H-2', H-3' and H-4'. The anomeric configuration of the glucose was determined to be beta from the $J_{H\text{-}1'\text{-}H\text{-}2'}$ = 7.5 Hz (Kanchanpoom et al., 2002). Acid hydrolysis followed by column chromatography over silica gel with MeCN/$H_2O$ as eluent, afforded D-glucose.

The linkage of the glucopyranosyl moiety to C-1b of the aglycone was clearly indicated by the cross-peak between the anomeric carbon ($\delta_C$ 99.0, C-1'b) and H-1b ($\delta_H$ 5.22, d, *J* = 7.7 Hz). Compound **2** afforede the hexa-acetate **2a** on acetylation, confirming the presence of a free hydroxyl group at C-1a. Thus structure **2** was assigned to canthiumoside 2 (Figure 1).

Compound **3,** a waxy solid, had a molecular formula $C_{35}H_{46}O_{20}$, deduced from the pseudo-molecular ion peak at *m/z* 809.2477 $[M+Na]^+$ (calcd. for $C_{35}H_{46}O_{20}Na$. 809.2480) in its HR-TOFESIMS spectrum. The $^1H$ and $^{13}C$-NMR spectra (Tables 1 and 2) displayed two sets of signals typical of a dimeric iridoid and showed similar chemical shifts to those of compound **2**, except for the presence of signals of a second hexose moiety. A *β*-glucopyranose moiety was identified starting from the anomeric proton at $\delta_H$ 4.73 (H-1'a, d, *J* = 7.8 Hz) in the

COSY spectrum (Patro et al., 2014; Cui-Lian et al., 2010) and confirmed by the carbon chemical shifts (Kanchanpoom et al., 2002). Again acid hydrolysis afforded only *D*-glucose.
The attachment of the second glucopyranose moiety to C-1a was clearly indicated by the cross-peak between the anomeric carbon ($\delta_C$ 98.9, C-1'a) and H-1a at $\delta_H$ 5.24. In addition, comparison of the $^{13}C$ data of **3** with those of related compounds (Zeng et al., 2010) supported structure **3** for canthiumoside 3 (Figure 1).
Compound **4** was obtained as a waxy solid. Its HR-TOFESIMS exhibited a pseudo-molecular ion peak at *m/z* 767.2369 $[M+Na]^+$ (calcd. for $C_{33}H_{44}O_{19}Na$. 767.2374), indicating that the molecular formula $C_{33}H_{44}O_{19}$ and twelve degree of unsaturation. The $^1H$ and $^{13}C$ NMR spectra were very similar to those of **3**, except the absence of the acetyl group at C-10b. Acid hydrolysis again afforded only *D*-glucose. Structure **4** for canthiumoside 4 (Figure 1) was also supported by the literature data of related compounds (Zeng et al., 2010).

Compound **5** was obtained pure only as its acetate **5a** and its structure elucidation was carried out with the acetate. However, NMR spectra of the mixture containing the compound **5** were in complete agreement with the proposed structure. The general appearance of the $^1H$ and $^{13}C$ NMR spectra of the mixture suggested that **5** was an iridoid dimmer with a glycosyl moiety. The $^1H$ NMR spectrum contained three hemiacetal proton doublets whose HMBC correlations were also consistent with a dimeric iridoid skeleton. Comparison with NMR data of compounds **2** and **3** showed that compound **5** possessed the same unit a glucosylated at C-1a but differed in the structure of unit b. The HR-TOFESIMS of the pentaacetate **5a** showed a pseudo-molecular ion peak at *m/z* 801.2592 $[M+Na]^+$ (calcd. 801.2582) corresponding to the elemental composition $C_{37}H_{46}O_{18}$. This was consistent with the $^{13}C$ NMR spectrum which displayed thirty seven carbons (Table 2). The $^1H$ NMR spectrum contained six methyl signals, five of which at $\delta_H$ 2.15, 2.11, 2.05, 2.02 and 1.99 were due to acetates. The structure of **5a** was confirmed by analysis of the 2D NMR (COSY, HSQC and HMBC) data. A beta-glucopyranose moiety was identified in the COSY spectrum starting from the anomeric proton at $\delta_H$ 4.90 (H-1'a, $J$ = 7.9 Hz). The expected HMBC correlations confirmed that unit a, with a glucopyranose unit attached to C-1a, was the same as in compounds **1**-4 and was connected to unit b *via* the same ester link. In the COSY spectrum, H-1b at $\delta_H$ 6.05 (d, $J$ = 7.7 Hz) correlated with H-9b ($\delta_H$ 2.25) which, in turn, showed a cross-peak with H-8b ( $\delta_H$ 2.35). A further cross-peak from H-8b to a methyl group Me-10b ($\delta_H$ 1.05, d, $J$ = 5.1 Hz) revealed the structure of unit b. The assignments of all the protons and carbons of unit B followed readily from analysis of the HMBC spectrum (Tables 1 and 2). The relative stereochemistry

of **5a** was supported by its NOESY spectrum which showed correlations between H-5bβ and H-9bβ, and between Me-10b and H-1bα showing that the methyl group is alpha. Comparison of the $^{13}C$ data of **5a** with those of related compounds S(Zhang et al., 2009) supported structure **5** for canthiumoside 5 (Figure 1).

## 3. Experimental

### 3.1. General

The melting points were recorded with a Reichert microscope (Reichert Technologies, Depew, New York USA) and are uncorrected. IR spectra were recorded with a Shimadzu FT-IR-8400S (Shimadzu, France) spectrophotometer. $^{1}H$ (500 MHz) and $^{13}C$ (125 MHz) NMR spectra were recorded on a BRUKER Avance DRX-500 spectrometer (Bruker, Wissembourg, France) equipped with a BBFO+5 mm probe. $^{1}H$ (600 MHz) and $^{13}C$ (150 MHz) NMR spectra were recorded on a BRUKER Avance III-600 spectrometer (Bruker, Wissembourg, France) equipped with a cryoplatform using $CD_3OD$ with TMS as the internal standard. TOF-ESIMS and HR-TOF-ESI experiments were performed using a Micromass Q-TOF micro instrument (Manchester, UK) with an electrospray source. The samples were introduced by direct infusion in a solution of MeOH at a rate of 5µl $min^{-1}$. The optical rotations were measured on a Bellingham & Stanley ADP 220) polarimeter (Bellingham + Stanley Ltd, United King-Dom). Column chromatography was run on Merck silica gel (VWR, France ) 60 (70-230 mesh) and gel permeation on Sephadex LH-20 (VWR, France ), while TLC was carried out on silica gel $GF_{254}$ pre-coated plates with detection accomplished by spraying with 50% $H_2SO_4$ followed by heating at 100 °C or by visualizing with a UV lamp at 254 and 365 nm.

### 3.2. Plant material

The fruits of *Canthium subcordatum* DC (syn. *Psydrax subcordata* DC Bridson) were collected in Foto village (Menoua Division, Western region of Cameroon), in April 2012. Authentication was performed by Victor Nana, a botanist of the Cameroon National Herbarium, Yaoundé, where a voucher specimen (N° 19579/SRF/CAM) has been deposited.

### 3.3. Extraction and isolation

The dried fruits of *C. subcordatum* (3.5 kg) were extracted with MeOH at room temperature for 3 days, and the extract was concentrated to dryness under reduced pressure (130 g). Part of the residue (122 g) was suspended in water and successively extracted with *n*-hexane, ethyl acetate and *iso*butanol to obtain, after evaporation of solvent, 53.8 g, 6.6 g and 35 g respectively. Part of the *iso*butanol-solute extract (32 g) was subjected to silica gel CC eluting with EtOAc containing increasing MeOH (0%, 5%, 10%, 15%, 20% and 30%, each

500 ml) to give eight sub fractions (A to H). Fraction D (6.6 g) was purified by silica gel CC eluting with an EtOAc-MeOH (5%) mixture to give compound **8** (40 mg). Fraction H (8 g) was purified by silica gel CC eluting with an EtOAc-MeOH (15%) mixture to give compounds **4** (39 mg) and **3** (42 mg). G (1.4 g) was purified by silica gel CC eluting with an EtOAc-MeOH (15%) mixture to give compound **9** (36 mg). Fractions A to C were combined with the EtOAc-soluble extract (8.6 g) and the whole was eluted with *n*-hexane containing increasing EtOAc (0%, 5%, 10%, 15%, 20%, 30% and 70%), EtOAc and EtOAc-MeOH (5%) mixtures. Eight sub fractions, 1-8, were obtained. Fraction 5 (1.5 g) was purified by silica gel CC eluting with a Hex-EtOAc (15%) mixture to give compounds **1** (24 mg) and **7** (35 mg). Fraction 6 (430 mg) was purified by silica gel CC eluting with a Hex-EtOAc (80%) mixture to give compound **2** (36 mg). Fraction 7 (2 g) was purified by silica gel CC eluting with a *n*-Hex-EtOAc (40%) mixture to give compounds **10** (22 mg), **6** and **6'** (32 mg). Fraction 8, containing compound **5**, could not be purified and was acetylated (acetic anhydridre:pyridine 1:1). The pentaacetate **5a** was isolated by silica gel CC. Part of *n*-hexane-solute extracts (50 g) was eluted with *n*-hexane containing increasing EtOAc (0%, 10%, 20%, 30%, 60%), EtOAc and EtOAc-MeOH (5%) mixtures to give five sub fractions A to E. The portion eluted with 20% ethyl acetate in *n*-hexane (fraction C) was chromatographed over silica gel with the same system to give compounds **11** (50 mg) and **12** (40 mg).

### 3.4. New Compound Data

Canthiumoside 1 **1.** Waxy solid, $[\alpha]_D^{23}$ - 43.2 (*c* 0.50, MeOH). IR (NaCl) $\nu_{max}$ ($cm^{-1}$):3500; 1754; 1640; 1602. $^1H$ (500 MHz) and $^{13}C$-NMR (125 MHz) data in $CD_3OD$ see Tables 1 and 2. HR-TOFESIMS *m/z*: 485.1428 $[M+Na]^+$ (calcd. for $C_{23}H_{26}O_{10}Na$, 485.1424)

Canthiumoside 2 **2.** Waxy solid, $[\alpha]_D^{23}$ – 17.6 (*c* 0.50, MeOH). IR (NaCl) $\nu_{max}$ ($cm^{-1}$):3540; 1744; 1643; 1622. $^1H$ (600 MHz) and $^{13}C$-NMR (150 MHz) data in $CD_3OD$, see Tables 1 and 2. HR-TOFESIMS *m/z*: 647.1946 $[M+Na]^+$ (calcd. for $C_{29}H_{36}O_{15}Na$, 647.1952)

Canthiumoside 3 **3.** Waxy solid, $[\alpha]_D^{23}$ -0.6 (*c* 0.46, MeOH). IR (NaCl) $\nu_{max}$ ($cm^{-1}$):3500; 1754; 1630; 1612. $^1H$ (500 MHz) and $^{13}C$-NMR (125 MHz) data in $CD_3OD$, see Tables 1 and 2. HR-TOFESIMS *m/z*: 809.2477 $[M+Na]^+$ (calcd. for $C_{35}H_{46}O_{20}Na$, 809.2480)

Canthiumoside 4 **4**. Waxy solid, $[\alpha]_D^{23}$ -3.9 (*c* 0.55, MeOH). IR (NaCl) $\nu_{max}$ ($cm^{-1}$):3550; 1750; 1645; 1610. $^1H$ (500 MHz) and $^{13}C$-NMR (125 MHz) data in $CD_3OD$, see Tables 1 and 2. HR-TOFESIMS *m/z*: 767.2369 $[M+Na]^+$ (calcd. for $C_{33}H_{44}O_{19}Na$, 767.2374)

Canthiumoside 5a **5a**. Waxy solid, $[\alpha]_D^{23}$ –11.2 (*c* 0.50, $CHCl_3$). IR (NaCl) $\nu_{max}$ ($cm^{-1}$):1754; 1640; 1602. $^1H$ (600 MHz) and $^{13}C$-NMR (150 MHz) data in $CDCl_3$, see Tables 1 and 2. HR-TOFESIMS *m/z*: 801.2592 $[M+Na]^+$ (calcd. for $C_{37}H_{46}O_{18}Na$, 801.2582)

### 3.6. Acetylation of 2, 6 and 6', 7 and 7'

Compound **2** (13 mg) was acetylated with $Ac_2O$–pyridine and the reaction mixture was purified over a silica gel column, eluting with a Hex-EtOAc (20%) mixture to give compound **2a** (Waxy solid, 6 mg). $[\alpha]_D^{23}$ -14.1 (*c* 0.58, $CHCl_3$). IR (NaCl) $\nu_{max}$ ($cm^{-1}$): 1754; 1640; 1602. HR-TOFESIMS *m/z*: 857.2488 $[M+Na]^+$ (calcd. for $C_{39}H_{46}O_{20}Na$, 857.2480). $^1H$ NMR ($CDCl_3$, 600 MHz) $\delta_H$: 7.91 (1H, s, H-3b), 7.48 (1H, s, H-3a), 5.94 (1H, d, 6.9, H-1a), 5.92 (1H, br s, H-7a), 5.92 (1H, br s, H-7b), 5.88 (1H, d, 7.4, H-1b), 5.25 (1H, t, 9.3, H-3'b), 5.15 (1H, dd, 9.5, 9.3, H-4'b), 5.05 (1H, dd, 8.1, 9.3, H-2'b), 4.90 (1H, d, 8.1, H-1'b), 4.86 (1H, d, 13.5, H-10b), 4.85 (1H, d, 13.7), 4.72 (1H, d, 13.7, H-10a), 4.70 (1H, d, 13.5, H-10b), 4.27 (1H, dd, 13.0, 2.4), 4.16 (1H, dd, 13.0, 5.9, H-6'b), 3.75 (3H, s, C-11a -OMe), 3.75 (1H, m, H-5'b), 3.30 (1H, m, H-5a), 3.23 (1H, m, H-5b), 2.90 (1H, m, H-6-β-a), 2.89 (1H, t, 7.4, H-9b), 2.88 (1H, t, 8.2, H-9a), 2.87 (1H, m, H-6-β-b), 2.20 (1H, m, H-6-α-a), 2.18 (3H, s, C-1a-OAc). $^{13}C$ NMR ($CDCl_3$, 150 MHz) $\delta_C$: 170.6 (C-10b-OAc), 170.5 (C-6'-OAc), 170.2 (C-3'-OAc), 169.4 (C-4'-OAc), 169.3 (C-1a-OAc), 169.1 (C-2'-OAc), 167.2 (C-11a), 166.4 (C-11b), 151.6 (C-3a), 151.4 (C-3b), 137.2 (C-8b), 136.6 (C-8a), 132.3 (C-7a), 130.8 (C-7b), 111.7 (C-4b), 111.3 (C-4a), 96.9 (C-1'b), 96.1 (C-1b), 91.5 (C-1a), 72.4 (C-3'), 72.0 (C-5'b), 70.7 (C-2'b), 68.2 (C-4'b), 62.5 (C-10b), 61.6 (C-6'b), 61.5 (C-10a), 51.4 (C-11a-OMe), 46.7 (C-9b), 45.3 (C-9a), 38.6 (C-6b), 38.4 (C-6a), 34.4 (C-5a), 34.0 (C-5b), 20.7 (C-4'-OAc; C-6'-OAc), 20.6 (C-3'-OAc), 20.5 (C-10b-OAc; C-1a-OAc), and 20.3 (C-2'-OAc).

Mixture **6 and 6'** (30 mg) was acetylated with $Ac_2O$–pyridine and the reaction mixture was purified over a silica gel column, eluting with a Hex-EtOAc (20%) mixture to give only the compound **6a** (Waxy solid, 10 mg). IR (NaCl) $\nu_{max}$ ($cm^{-1}$): 3500; 1754; 1640; 1602. HR-TOFESIMS *m/z*: 309.0943 $[M+Na]^+$ (calcd. for $C_{13}H_{18}O_7Na$, 309.0950). $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta_H$: 7.38 (1H, s, H-3), 6.15 (1H, d, 7.4, H-1), 4.13 (1H, m, H-6), 3.74 (3H, s, C-11-$OCH_3$), 3.09 (1H, m, H-5), 2.66 (1H, t, 7.4, H-9), 2.10 (3H, s, C-1-OAc) 2.04 (1H, m, H-7β), 1.96 (1H, m, H-7α), 1.31 (3H, s, H-10). $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta_C$: 169.2 (C-1-OAc), 168.1 (C-11), 151.2 (C-3), 109.8 (C-4), 89.5 (C-1), 78.8 (C-6), 77.0 (C-8), 50.7 (C-11-OMe), 50.1 (C-9), 47.1 (C-7), 41.3 (C-5), 23.8 (C-1-OAc), 20.9 (C-10),

Mixture **7** and **7'** (120 mg) was acetylated with $Ac_2O$–pyridine and the reaction mixture was purified over a silica gel column, eluting with a Hex-EtOAc (80%) mixture to give compounds **7a** (20 mg) and **7b** (30 mg).

Compound **7a** was obtained as a waxy solid. IR (NaCl) $\nu_{max}$ ($cm^{-1}$): 3500; 1754; 1640; 1602. HR-TOFESIMS *m/z*: 293.1006 $[M+Na]^+$ (calcd. for $C_{13}H_{18}O_6Na$, 293.1001). $^1H$ NMR

($CDCl_3$, 600 MHz) $\delta_H$: 7.35 (1H, s, H-3), 6.15 (1H, d, 7.3, H-1), 3.74 (3H, s, C-11-$OCH_3$), 3.21 (1H, m, H-5), 2.35 (1H, m, H-6), 2.29 (1H, t, 8.5, H-9), 2.10 (3H, s, C-1-OAc), 1.73 (2H, m, H-7), 1.52 (1H, m, H-6), 1.32 (3H, s, H-10). $^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta_C$: 169.5 (C-1-OAc), 167.2 (C-11), 150.2 (C-3), 112.0 (C-4), 89.8 (C-1), 79.6 (C-8), 51.3 (C-9), 50.1 (C-11-OMe), 40.3 (C-7), 30.5 (C-5), 29.5 (C-6), 24.3 (C-10), 21.5 (C-1-OAc).

Compound **7b** was obtained as a waxy solid. $^1$H and $^{13}$C NMR spectra showed similar chemical shifts to those of compound **7a** except for the additional peaks of an acetyl group, due to acetylation of the tertiary hydroxyl group at C-8. IR (NaCl) $\nu_{max}$ ($cm^{-1}$): 1754; 1640; 1602. HR-TOFESIMS *m/z*: 335.1111 $[M+Na]^+$ (calcd. for $C_{15}H_{20}O_7Na$, 335.1107]. $^1$H NMR ($CDCl_3$, 600 MHz) $\delta_H$: 7.41 (1H, s, H-3), 6.15 (1H, d, 7.5, H-1), 3.75 (3H, s, C-11-OMe), 3.16 (1H, m, H-5), 2.68 (1H, t, 7.5, H-9), 2.30 (1H, m, H-6), 2.10 (3H, s, C-1-OAc), 2.05 (1H, m, H-7), 2.04 (3H, m, C-8-OAc) 1.85 (1H, m, H-7), 1.55 (3H, s, H-10), 1.39 (1H, m, H-6). $^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta_C$: 170.7 (C-8-OAc), 169.2 (C-1-OAc), 166.9 (C-11), 151.2 (C-3), 111.0 (C-4), 89.5 (C-1), 88.6 (C-8), 51.3 (C-11-OMe), 48.7 (C-9), 38.5 (C-7), 30.9 (C-5), 28.8 (C-6), 22.2 (C-8-OAc), 21.0 (C-1-OAc), 20.5 (C-10).

### 3.7. Acid Hydrolysis

15 mg of each compound (**2-4**) was individually refluxed in 2N HCl (5.0 mL) at 80 °C for 3h. Each reaction mixture was extracted with $CHCl_3$ (3 × 5mL), and the $H_2O$ phase was dried using a $N_2$ stream (Gournelis et al., 1989). The residues were separately subjected to CC over silica gel with MeCN/$H_2O$ (8:1) as the eluent to yield glucose (2 mg, 3.3 mg and 3.5 mg respectively), $[\alpha]^{20}_D$ +35.9 (*c* 1.0, $H_2O$). The solvent system MeCN/$H_2O$ (6:1) was used for TLC identification of glucose (Zhang et al., 2008).

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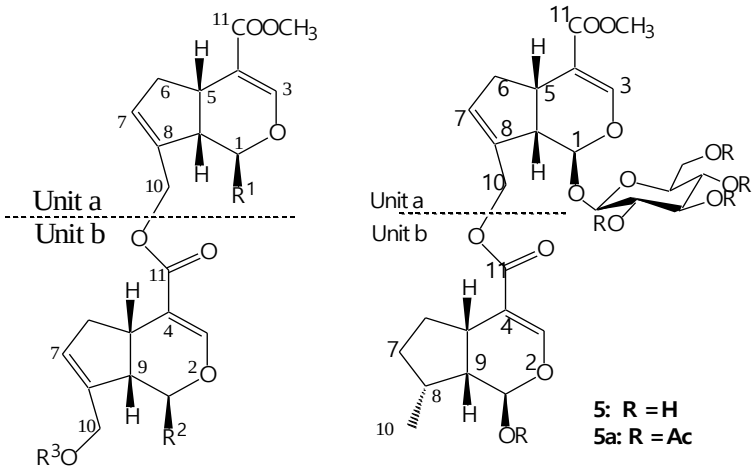
Table 1: $^{1}$H-NMR Spectral data of Compounds **1-4** ($CD_3OD$) and **5a** ($CDCl_3$)

| Positions | Compounds | | | | |
|---|---|---|---|---|---|
| | **1** (500 MHz) | **2** (600 MHz) | **3** (500 MHz) | **4** (500 MHz) | **5a** (600 MHz) |
| 1a | 4.84 (1H, d, 8.6) | 4.84 (1H, d, 8.6) | 5.24 (1H, d, 7.5) | 5.24 (1H, d, 7.5) | 5.22 (1H, d, 7.8) |
| 3a | 7.55 (1H, s) | 7.55 (1H, d, 0.7) | 7.54 (1H, d, 0.9) | 7.54 (1H, d, 1.1) | 7.43 (1H, s) |
| 4a | - | - | - | - | - |
| 5a | 3.18 (1H, q, 8.5) | 3.18 (1H, m) | 3.23 (1H, m) | 3.23 (1H, m) | 3.22 (1H, m) |
| 6a | 2.87 (1H, m, H-β)<br>2.06 (1H, m, H-α) | 2.87 (1H, m, H-β)<br>2.08 (1H, m, H-α) | 2.15 (1H, ddt, 16.4, 7.8, 2.3, H-α)<br>2.87 (1H, dd, 16.4, 7.8, H-β) | 2.13 (1H, ddt, 16.4, 7.7, 2.3, H-α)<br>2.87 (1H, dd, 16.4, 7.7, H-β) | 2.88 (1H, m, H-β)<br>2.21 (1H, m, H-α) |
| 7a | 5.91 (1H, br s) | 5.91 (1H, br s) | 5.87 (1H, brs) | 5.83 (1H, brs) | 5.89 (1H, br, s) |
| 8a | - | - | - | - | - |
| 9a | 2.56 (1H, t, 8.5) | 2.57 (1H, t, 7.8) | 2.81 (1H, t, 7.7) | 2.81 (1H, t, 7.7) | 2.94 (1H, t, 7.8) |
| 10a | 4.91 (1H, d, 14.4)<br>4.78 (1H, d, 14.4) | 4.91 (1H, d, 14.2)<br>4.82 (1H, d, 14.2) | 4.82 (1H, d, 13.9)<br>4.94 (1H, d, 13.9) | 4.81 (1H, dd, 14.1, 1.4)<br>4.95 (1H, d, 14.1) | 4.85 (1H, d, 13.8)<br>4.72 (1H, d, 13.8) |
| 11a | - | - | - | - | - |
| 11a-OMe | 3.73 (3H, *s*) | 3.72 (3H, *s*) | 3.74 (3H, s) | 3.74 (3H, s) | 3.75 (3H, s) |
| 1'a | - | - | 4.73 (1H, d, 7.8) | 4.75 (1H, d, 7.9) | 4.90 (1H, d, 7.9) |
| 2'a | - | - | 3.25 (1H, dd, 9.2, 7.8) | 3.25 (1H, dd, 9.2, 7.9) | 5.05 (1H, dd, 8.6, 7.9) |
| 3'a | - | - | 3.40 (1H, t, 8.8) | 3.40 (1H, t, 9.1) | 5.25 (1H, t, 8.6) |
| 4'a | - | - | 3.31 (1H, m) | 3.32 (1H, m) | 5.13 (1H, dd, 9.5, 8.6) |
| 5'a | - | - | 3.31 (1H, m) | 3.32 (1H, m) | 3.75 (1H, m) |
| 6'a | - | - | 3.67 (1H, dd, 12.0, 5.5)<br>3.89 (1H, d, 12.0) | 3.67 (1H, dd, 11.8, 5.6)<br>3.89 (1H, d, 11.8) | 4.15 (1H, dd, 12.2, 5.8)<br>4.28 (1H, dd, 12.2, 2.3) |
| 1b | 4.82 (1H, d, 8.6) | 5.22 (1H, d, 7.7) | 5.21 (1H, d, 7.7) | 5.21 (1H, d, 7.6) | 6.05 (1H, d, 7.7) |
| 3b | 7.61 (1H, s) | 7.60 (1H, s) | 7.61 (1H, d, 0.8) | 7.60 (1H, d, 1.1) | 7.43 (1H, s) |
| 4b | - | - | - | - | - |
| 5b | 3.21 (1H, q, 8.5) | 3.25 (1H, m) | 3.24 (1H, m) | 3.23 (1H, m) | 2.98 (1H, m) |
| 6b | 2.06 (1H, m, H-α)<br>2.87 (1H, m, H-β) | 2.17 (1H, m, H-α)<br>2.88 (1H, m, H-β) | 2.18 (1H, ddt, 16.4, 8.1, 2.1, H-α)<br>2.90 (1H, dd, 16.4, 8.1, H-β) | 2.13 (1H, ddt, 16.4, 7.7, 2.3, H-α)<br>2.86 (1H, dd, 16.4, 7.7, H-β) | 2.18 (1H, m, H-β)<br>1.59 (1H, m, H-α) |
| 7b | 5.91 (1H, br s) | 5.88 (1H, br s) | 5.89 (1H, brs) | 5.83 (1H, brs) | 1.87 (1H, m, H-β)<br>1.39 (1H, m, H-α) |
| 8b | - | | - | - | 2.35 (1H, m) |
| 9b | 2.56 (1H, t, 8.5) | 2.80 (1H, t, 7.8) | 2.80 (1H, t, 7.0) | 2.77 (1H, t, 7.9) | 2.25 (1H, m) |
| 10b | 4.81 (1H, d, 14.5)<br>4.76 (1H, d, 14.5) | 4.80 (2H, brs) | 4.81 (2H, m) | 4.21 (1H, dd, 14.3, 1.5)<br>4.34 (1H, d, 14.3) | 1.05 (3H, d, 5.1) |
| 10b-OAc | 2.21 (3H, *s*) | 2.10 (3H, s) | 2.09 (3H, s) | - | - |
| 11b | - | - | - | | - |
| 1'b | - | 4.74 (1H, d, 7.8) | 4.74 (1H, d, 7.9) | 4.73 (1H, d, 7.8) | - |
| 2'b | - | 3.24 (1H, dd, 9.1, 7.8) | 3.24 (1H, dd, 8.7, 7.8) | 3.25 (1H, dd, 9.0, 7.8) | - |
| 3'b | - | 3.40 (1H, t, 9.1) | 3.39 (1H, t, 8.9) | 3.41 (1H, t, 9.0) | - |
| 4'b | - | 3.31 (1H, m) | 3.31 (1H, m) | 3.32 (1H, m) | - |
| 5'b | - | 3.31 (1H, m) | 3.31 (1H, m) | 3.32 (1H, m) | - |
| 6'b | - | 3.67 (1H, dd, 11.7, 5.8)<br>3.89 (1H, dd, 11.7, 1.7) | 3.67 (1H, m)<br>3.89 (1H, d, 12.1) | 3.68 (1H, dd, 12.0, 5.6)<br>3.89 (1H, d, 12.0) | - |
| 1b-OAC ($GlcAc_4$) | | - | - | - | 2.15 (3H, s)<br>2.11, 2.07, 2.03, 1.98 |

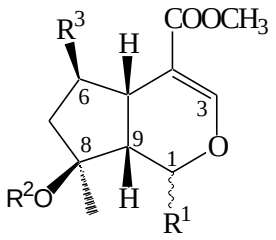
Table 2: $^{13}$C-NMR Spectral data of Compounds **1-4** ($CD_3OD$) and **5a** ($CDCl_3$)

| **Positions** | **Compounds** | | | | |
|---|---|---|---|---|---|
| | **1** (125 MHz) | **2** (150 MHz) | **3** (125 MHz) | **4** (125 MHz) | **5a** (150 MHz) |
| 1a | 96.2 | 96.1 | 96.8 | 96.8 | 95.5 |
| 3a | 152.9 | 152.9 | 151.9 | 152.0 | 150.9 |
| 4a | 110.2 | 110.1 | 111.0 | 111.0 | 112.1 |
| 5a | 35.9 | 35.9 | 34.9 | 34.9 | 33.5 |
| 6a | 38.8 | 38.7 | 38.6 | 38.5 | 38.4 |
| 7a | 129.3 | 129.4 | 129.7 | 127.0 | 130.8 |
| 8a | 139.3 | 139.3 | 138.1 | 138.3 | 136.9 |
| 9a | 47.2 | 47.2 | 46.3 | 46.3 | 46.8 |
| 10a | 62.1 | 62.1 | 61.9 | 61.9 | 61.4 |
| 11a | 168.4 | 168.0 | 168.0 | 168.1 | 167.3 |
| 11a-OMe | 50.3 | 50.3 | 50.4 | 50.4 | 51.3 |
| 1’a | - | - | 98.9 | 98.9 | 96.1 |
| 2’a | - | - | 73.4 | 73.4 | 70.7 |
| 2a’-OAc | | | | | 20.3 and 169.1 |
| 3’a | - | - | 76.4 | 76.4 | 72.5 |
| 3’a-OAc | | | | | 20.6 and 170.2 |
| 4’a | - | - | 70.1 | 70.0 | 68.1 |
| 4’a-OAc | | | | | 20.7 and 169.4 |
| 5’a | - | - | 77.0 | 77.0 | 72.1 |
| 6’a | - | - | 61.3 | 61.3 | 61.7 |
| 6’a-OAc | | | | | 20.7 and 170.6 |
| 1b | 96.3 | 96.8 | 96.8 | 96.9 | 90.7 |
| 3b | 153.2 | 152.2 | 152.2 | 152.3 | 151.1 |
| 4b | 110.2 | 111.0 | 111.0 | 111.2 | 111.8 |
| 5b | 36.0 | 35.0 | 35.0 | 35.2 | 33.7 |
| 6b | 38.7 | 38.6 | 38.2 | 38.4 | 31.2 |
| 7b | 129.7 | 129.9 | 130.0 | 129.7 | 31.8 |
| 8b | 139.1 | 138.4 | 138.3 | 143.3 | 36.2 |
| 9b | 47.0 | 46.0 | 45.9 | 45.7 | 42.0 |
| 10b | 62.5 | 62.3 | 62.3 | 60.0 | 16.0 |
| 11b | 167.6 | 167.3 | 167.4 | 167.5 | 166.4 |
| 10b-OAc | 171.3 | 171.4 | 171.4 | - | - |
| 10b-OAc | 19.4 | 19.4 | 19.4 | - | - |
| 1’b | - | 99.0 | 99.2 | 99.2 | - |
| 2’b | - | 73.4 | 73.5 | 73.5 | - |
| 3’b | - | 76.5 | 76.5 | 76.5 | - |
| 4’b | - | 70.1 | 70.1 | 701 | - |

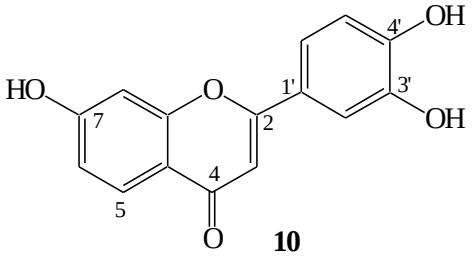
| | | | | | |
|---|---|---|---|---|---|
| 5’b | - | 77.0 | 77.0 | 77.0 | - |
| 6’b | - | 61.4 | 61.4 | 61.4 | - |



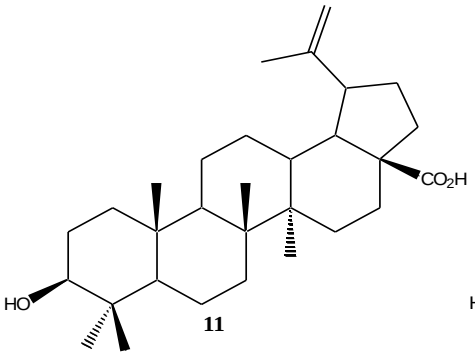

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **1** | OH | OH | Ac |
| **2** | OH | *O*-Glc | Ac |
| **2a** | OAc | *O*-GlcAc$_4$ | Ac |
| **3** | *O*-Glc | *O*-Glc | Ac |
| **4** | *O*-Glc | *O*-Glc | H |



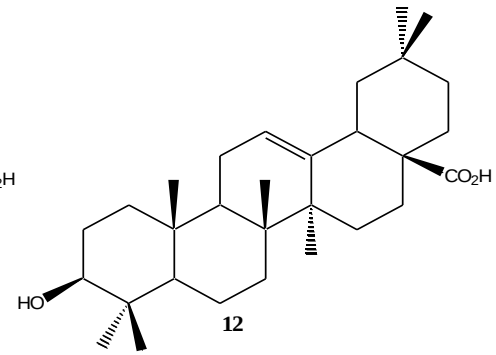
| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **6** | β-OH | OH | H |
| **6'** | α-OH | OH | H |
| **6a** | β-OAc | OH | H |
| **7** | β-OH | H | H |
| **7'** | α-OH | H | H |
| **7a** | β-OAc | H | H |
| **7b** | β-OAc | H | Ac |
| **8** | β-*O*-Glc | H | H |
| **9** | β-*O*-Glc | OH | H |



**10**



**11**



**12**

**Fig. 1. Chemical structure of the isolated compounds (1-12).**