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VERNONIOSIDES AND AN ANDROSTANE GLYCOSIDE FROM *VERNONIA KOTSCHYANA*

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Key Word Index—*Vernonia kostchyana*; Asteraceae; steroidal glycosides; 3β,24β-trihydroxy-21,23:22,28:26,28-triepoxy-5α-stigmasta-8(9),14(15)-dien-3-*O*-β-D-glucopyranoside; 3β,24β-trihydroxy-21,23:22,28:26,28-triepoxy-5α-stigmasta-8(9),14(15)-dien-3-*O*-β-D-xylopyranosyl-(1 → 3)-β-D-glucopyranoside; 3β,24β-trihydroxy-21,23:22,28:26,28-triepoxy-5α-stigmasta-8(9),14(15)-dien-3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside;3β,24β,26,28α-tetrahydroxy-22,28-epoxy-5α-stigmasta-8(9),14(15)-dien-21,23-lactone-3-*O*-β-D-glucopyranoside; 3β,24β,26,28α-tetrahydroxy-22,28-epoxy-5α-stigmasta-8(9),14(15)-dien-21,23-lactone-3-*O*-β-D-xylopyranosyl-(1 → 3)-β-D-glucopyranoside; androst-8-en-glycoside.

Abstract—Five new stigmastane-type steroidal glycosides, vernoniosides D_1, D_2, D_3, F_1, and F_2 and a new androst-8-en glycoside have been isolated from the root of *Vernonia kotschyana*. The aglycones of the first five compounds possess a common 3β-hydroxy-$\Delta^{8,14}$ steroidal nucleus and different side-chains; the glycosidic moieties are made up of one or two monosaccharides (glucose, xylose). Their structures have been elucidated using a combination of 1D and 2D NMR techniques as 3β,24β-trihydroxy-21,23:22,28:26,28-triepoxy-5α-stigmasta-8(9),14(15)-dien-3-*O*-β-D-glucopyranoside; 3β,24β-trihydroxy-21,23:22,28:26,28-triepoxy-5α-stigmasta-8(9),14(15)-dien-3-*O*-β-xylopyranosyl-(1 → 3)-β-D-glucopyranoside; 3β,24β-trihydroxy-21,23:22,28:26,28-triepoxy-5α-stigmasta-8(9),14(15)-dien-3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside; 3β,24β,26,28α-tetrahydroxy-22,28-epoxy-5α-stigmasta-8(9),14(15)-dien-21,23-lactone-3-*O*-β-D-glucopyranoside; 3β,24β,26,28α-tetrahydroxy-22,28-epoxy-5α-stigmasta-8(9),14(15)-dien-21,23-lactone-3-*O*-β-D-xylopyranosyl-(1 → 3)-β-D-glucopyranoside. © 1997 Published by Elsevier Science Ltd

INTRODUCTION

In the course of a search for bioactive principles from African medicinal plants [1–4], we have examined *Vernonia kotschyana* Sch. Bip., a plant used in African folk medicine as a herbal remedy against digestive insufficiency, colitis, dermatosis, tuberculosis and headache. In Mali folk medicine the powdered root of this plant, known by the popular name 'Buayé', is a remedy in the treatment of gastritis and gastroduodenal ulcers. Clinical trials conducted in Mali have corroborated these uses [5]. Pharmacological study of the extracts of the drug showed a gastroprotective effect of the *n*-butanol soluble part of the aqueous extract in different types of experimentally induced gastric ulcers in rats [5]. No phytochemical study has been carried out on this species. The genus *Vernonia* is known to contain a number of stigmastane-type glycosides, namely vernoniosides [6–9], possessing a common $\Delta^{7,9(11)}$-steroidal nucleus, different oxygenated side chains at C-17 and a sugar moiety linked at C-3 of the aglycones made up of glucose.

This report deals with the isolation and structural elucidation of five new stigmastane-type glycosides having a $\Delta^{8(9),14(15)}$-steroid cycle system and one (glucose) or two (glucose and xylose, or two glucose units) sugar units linked at C-3 of the aglycone (**1–5**) from the methanol extract of *V. kotschyana*. A new androst-8-en glycoside (**6**) was also isolated from the same extract.

RESULTS AND DISCUSSION

Sephadex LH-20 column chromatography followed by DCCC and reversed-phase HPLC of the *n*-butanol fraction from the methanol extract of *V. kotschyana* gave compounds **1–6**. Compounds **1–5** displayed the

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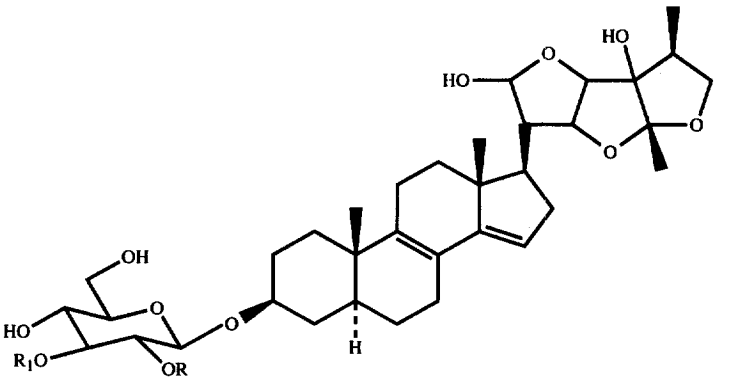
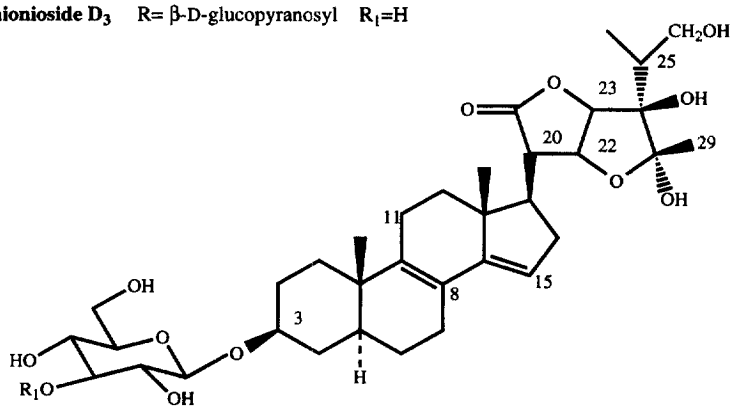


1 Vernionioside D_1 R=H R_1=H

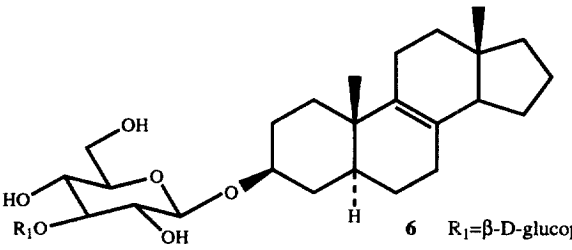
2 Vernionioside D_2 R=H R_1=β-D-xylopyranosyl

3 Vernionioside D_3 R= β-D-glucopyranosyl R_1=H



4 Vernionioside F_1 R_1=H

5 Vernionioside F_2 R_1=β-D-xylopyranosyl



6 R_1=β-D-glucopyranosyl

molecular formulae $C_{35}H_{52}O_{11}$, $C_{40}H_{60}O_{15}$, $C_{41}H_{62}O_{16}$, $C_{35}H_{52}O_{12}$, and $C_{40}H_{60}O_{16}$, respectively, as deduced by FAB mass spectrometry and ^{13}C NMR including DEPT analysis. The FAB mass spectra (negative ion) also showed the loss of a hexose (162 mass units) for compounds **1** and **4**, two hexoses for compound **3**, a hexose and a pentose (132 mass units) for compounds **2** and **5** from the respective quasi-molecular anions $[(M-H)^-$ *m/z* 647, 779, 809, 663 and 795 for **1**–**5**].

The ^1H NMR spectra for the aglycone part of **1**–**3** were typical of a sterol structure displaying the angular methyl singlets at δ 1.06 and 0.92 and a charac-

teristic multiplet at δ 3.77 (H-3) that had correlation with a secondary alcoholic carbon (CH-3) at δ 79.22 in the ^1H–^{13}C HETCOR spectra, although shifted downfield relative to the unglycosylated model [10–11]. The H-3 signal was the starting point which allowed the identification of a first spin system comprising all protons of rings A and B (from H-1 to H-7) through the COSY spectra (Table 1). Also the ^{13}C NMR spectra for the aglycone moieties of **1–3** showed the presence of 29 carbons, 19 of them were assignable to the steroidal nucleus including a glycosylated oxymethine (C-3, δ 79.22) and four $sp^{(2)}$ carbons assignable to a tetrasubstituted double bond at δ 141.33 and 124.43 (each quaternary carbon) and a trisubstituted double bond at δ 151.33 (C) and at 116.62 (CH). The signal at δ 116.62 (C-15) was correlated to a proton signal at δ 5.35 (1H, *br m*, H-15) in the HETCOR spectra. COSY experiments delineated a second spin system which comprised H-15, H_2-16 (δ 2.22 and 2.49), H-17 (δ 2.05), and extended to the side chain protons H-20 (δ 2.30) and H-21 (δ 5.29) (Table 1) leading to the location of the trisubstituted double bond between C-14 and C-15. The tetrasubstituted double bond located between C-8 and C-9 was supported by the observation of the long-range couplings of C-9 with H-7, C-8 with H-11ax and C-8 with H-15 in the HMBC spectrum of the major compound **1** and by comparison with the data reported for a $\Delta^{8,14}$-vernonioside reported previously which was produced by acid hydrolysis of vernonioside B_1 in *V. amygdalina* [6]. Combined analysis of the COSY and HETCOR spectra allowed the assignments (as reported in Table

Table 1. ^1H and ^{13}C NMR data for aglycones of compounds **1** and **4** and ^{13}C NMR data for aglycone of compound **6*** (500 MHz in CD_3OD); (J_{H-H} in Hz)

	Compounds				
		1†		**4**†	**6**
Position	δ_C	δ_H	δ_C	δ_H	δ_C
1	35.42	1.10α	35.50	1.08α	35.80
		1.45β		1.44β	
2	30.79	1.60α	30.80	1.58α	31.90
		1.95β		1.94β	
3	79.22	3.77 *m*	80.00	3.79 *m*	80.05
4	36.70	2.00α	36.50	2.01α	35.80
		1.51β		1.52β	
5	42.30	1.30α	42.30	1.32α	42.50
6	22.75	1.46 *br m*	23.00	1.46 *br m*	23.20
7	36.39	2.10	37.00	2.10	36.80
		1.60		1.60	
8	124.43	—	124.91	—	124.60
9	142.33	—	142.53	—	133.90
10	38.00	—	38.00	—	38.43
11	27.00	2.08	26.90	2.08	27.84
12	26.64	1.39	26.70	1.38	37.40
		1.96		1.93	
13	45.97	—	46.00	—	39.25
14	151.33	—	151.60	5.45	50.00
15	116.62	5.35 *br m*	117.00	2.44	20.13
16	38.00	2.49 *dd*, J = 11.0; 3.0	38.00	2.88	37.33
		2.22 *dd*, J = 11.0; 5.0			
17	50.60	2.05	50.10	2.05	23.20
18	16.72	0.92 *s*	16.80	0.90 *s*	18.51
19	18.80	1.06 *s*	18.50	1.05 *s*	19.40
20	53.84	2.30 *br m*	48.00	2.45 *dd*, J = 11.0, 4.9	—
21	105.61	5.29 *d* J = 6.0	175.80	—	—
22	85.32	4.75 *dd*, J = 2.7; 3.5	79.00	4.51 *dd*, J = 3.6, 4.5	—
23	86.26	4.40 *d*, J = 2.7	86.31	4.44 *d*, J = 3.6	—
24	88.40	—	83.10	—	—
25	41.74	2.18 *br m*	36.00	2.01 *br m*	—
26	73.50	4.00 *dd* J = 9.0, 7.0	67.80	3.51 *dd* J = 11.5, 6.6	—
		3.67 *dd*, J = 9.0, 6.0		3.35 *dd* J = 11.5, 4.9	
27	11.00	1.01 *d* J = 6.0	13.00	1.05 *d* J = 7.0	—
28	118.00	—	107.00	1.07	—
29	21.81	1.33 *s*	25.20	1.39	—

* Assignments were confined by COSY, HETCOR, HMQC.

† Values of the ^1H and ^{13}C NMR resonances for compounds **2** and **3** are almost superimposable to those of compound **1**; values of the resonances of compound **5** are almost superimposable to those of compound **4**.

1) of the remaining protons and carbons of the aglycone moieties of **1–3**, including a $C_{10}H_{15}O_5$ side-chain, and demonstrated that this side-chain was the same as that of vernonioside D, previously isolated from *V. amygdalina* [3].

An extensive use of 1D and 2D NMR techniques indicated the presence of a common steroidal nucleus and a different side-chain in compounds **4** and **5**. A combination of COSY and HETCOR experiments delineated three main connectivities: the first one comprised C-23–C-22–C-20–C-17–C-16–C-15, the second was C-25-C-26 and the third was C-25-C-27. NMR data from COSY and HETCOR of C-20 (^{1}H δ 2.45, ^{13}C δ 48.0), C-22 (^{1}H δ 4.51, ^{13}C δ 79.0), and C-23 (^{1}H δ 4.44, ^{13}C δ 86.31) demonstrated that they were one angular methine adjacent to a carbonyl group and two oxymethine, respectively. A signal at δ 175.80, in the ^{13}C NMR spectra, was assigned to a γ-lactone cyclized between C-21 and C-23 by comparison with the data reported for VE-2 isolated from *V. extensa* [7] and vernonioside B_1 isolated from *V. amygdalina*. [8]. The hemiketal nature of C-28 was indicated by a signal at δ 107.0 and the tertiary alcoholic nature of C-24 was suggested by the resonance at δ 83.10 (quaternary carbon). In accordance with this structure, the ^{1}H NMR signal of Me-29 appeared as a singlet at δ 1.39, indicating a Me linked to a carbon bearing a hydroxyl group while of Me-27 appeared as a doublet at δ 1.05. The presence of a (Me)CH_2OH–CH– group at C-24 instead of the usual terminal isopropyl group of vernoniosides, was shown by the chemical shifts of C-25 (δ 36.00), Me-27 (δ 13.00) and C-26 (δ 67.80), the last one correlated by HETCOR to proton signals at δ 3.51 and 3.35 (each, *dd*, J = 6.6 and 11.5 Hz, and 4.9 and 11.5 Hz, respectively) typical of a $\underline{CH_2OH}$–CH functionality [9]. The relative stereochemistry at the asymmetric carbons of the side-chain of compounds **4** and **5** was established by NOEDS experiments. By irradiation at δ 2.45 (H-20) NOEs were observed for H-22, Me-18 and Me-19; by irradiation at δ 4.51 (H-22), NOEs were observed for both H-20 and H-23 (δ 4.44). No NOEs were observed between H-23 and H-26 or H-27 as well as between H-20 and H-17.

Compound **6** has molecular formula $C_{31}H_{50}O_{11}$ as indicated by FAB mass spectral and NMR data. The ^{13}C NMR spectrum showed the presence of 19 carbon signals for the aglycone moiety ascribable to an androstane nucleus [10] including an oxymethine (δ 80.05, CH, C-3). The ^{1}H NMR spectrum of **6** showed the presence of two angular Me singlets at δ 0.75 and 1.06 [11–13], and the H-3 proton signal at δ 3.80 which was shifted downfield by glycosylation. The sole unsaturated functionality evident from the ^{13}C NMR spectrum was one tetrasubstituted double bond (δ 124.67 and 133.92, each quaternary carbon) which lies between C-8 and C-9 as indicated by their chemical shifts according to Δ^8-steroidal models [14]. All the remaining carbon signals of the molecule were assigned by comparison with steroidal models and according to the substitution effect rules [10, 14] to a 3-β-hydroxy-5α-14α-androst-8-en aglycone. Compound **6** possessed a steroidal cyclic system similar to that of compounds **1–5**, the differences between the sterols were in the absence of the side-chain and of the trisubstituted double bond in **6**. It may be a natural product from a common pathway or a degradation product formed during the extraction and isolation procedure.

The nature and the ratio of the sugars in compounds **1–6** were established by acid methanolysis and GLC analysis of the persylilated methylsugars. The NMR data for the sugar moieties (Table 2) linked at C-3 of the aglycones in compounds **1** and **4** revealed the presence of an unsubstituted β-D-glucopyranosyl unit by comparison with literature data [3]. Compounds **2** and **5** possessed the same disaccharide chain consisting of a glucopyranose and a xylopyranose. On the basis of NMR evidence, it was determined to be β-D-xylopyranosyl-(1 → 3)-β-D-glucopyranoside. Their β-linkages were shown by the coupling constant values (7.5 Hz) of two anomeric proton signals at δ 4.57 an 4.49 and by their chemical shifts in the ^{13}C NMR spectra. COSY, HOHAHA and HETCOR experiments allowed the assignments of all proton and carbon signals and the identification of a terminal β-D-xylopyranose [10, 15] linked at C-3 (δ 83.51) of an inner β-D-glucopyranose (Table 2). In fact the expected glycosylation shifts were observed for C-3 (β-effect) by +6.4 ppm and C-2 (γ-effect) by −0.7 ppm of glucose in compounds **2** and **5** in comparison with the corresponding carbons of terminal sugar model (compounds **1** and **4**). Similarly, the results of COSY, HOHAHA and HETCOR experiments and the chemical shifts upon glycosylation showed that the disaccharide chain was made by a terminal β-D-glucopyranose linked at an inner β-D-glucopyranose through C-2 (δ 81.70) in compound **3** and through C-3 (δ 84.96) in compound **6**. Thus the structure of the disaccharide chain was β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside in **3** and β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside in **6** (Fig 1). The trivial names vernoniosides D_1, D_2 and D_3 were proposed for compounds **1–3** as well as vernoniosides F and F_1 were proposed for **4** and **5**, respectively.

EXPERIMENTAL

General. NMR measurements were determined in CD_3OD solns. COSY, HOHAHA, ^{1}H–^{13}C HETCOR and HMBC experiments were obtained as described previously [4, 16, 17]. Overhauser enhancement effects were evaluated with the NOEDS techniques on samples previously degassed by bubbling Ar in the soln. Optical rotations were measured using a sodium lamp operating at 589 nm in 1% solns in MeOH. FABMS were recorded in glycerol matrix in the negative ion mode. HPLC sepns were achieved using μ-Bondapack C-18 columns and RI detector.

Plant material. The plant *V. kotschyana* was col-

Table 2. ^1H and ^{13}C NMR data for sugar moiety of compounds **2** and **3** and ^{13}C NMR data of compound **1** and **6*** (500 MHz in CD_3OD); (J_{H-H} in Hz)

	Compounds					
	1*	**2***		**3**		**6**
Position	δ_C	δ_C	δ_H	δ_H	δ_C	δ_C
Glc-1	102.12	101.50	4.57 *d*, $J = 7.5$	4.57 *d*, $J = 7.5$	102.50	102.53
2	74.80	73.50	3.22 *dd*, $J = 7.5$; 9.0	3.22 *dd*, $J = 7.5$; 9.0	81.70	73.80
3	78.18	83.51	3.45 *t*, $J = 9.0$	3.43 *t*, $J = 9.0$	76.40	84.96
4	71.00	71.56	3.36 *t*, $J = 9.0$	3.36 *t*, $J = 9.0$	71.20	72.00
5	78.50	77.90	3.47 *m*	3.50 *m*	78.00	78.35
6	62.75	62.75	3.87 *dd*, $J = 12.0$; 5.0	3.90 *dd*, $J = 12.0$; 5	62.80	62.60
			3.70 *dd*, $J = 12.0$; 3.5	3.76 *dd*, $J = 12.0$; 3.5		
Xyl-1		105.60	4.49 *d*, $J = 7.5$			
2		74.00	3.20 *dd*, $J = 7.5$; 9.5			
3		77.78	3.30 *t*, $J = 9.5$			
4		72.00	3.52 *m*			
5		66.70	3.30 *dd*, $J = 10.0$; 5.0			
			3.81 *dd*, $J = 10.0$; 3.0			
Glc-1′				4.62 *d*, $J = 7.5$	106.00	106.70
2′				3.15 *dd*, $J = 7.5$; 9.0	74.90	74.97
3′				3.45 *t*, $J = 9.0$	77.90	77.80
4′				3.39 *t*, $J = 9.0$	71.80	71.00
5′				3.51 *m*	78.10	78.00
6′				3.88 *dd*, $J = 12.0$; 5	63.10	62.38
				3.72 *dd*, $J = 12.0$; 3.5		

* Assignments were confined by COSY, HOHAHA, HETCOR, HMQC.

** Values of the resonances of compound **4** are superimpossible to those of **1**, and of compound **5** to those of **2**.

lected in the belt of Kolakani, Mali. The plant material was identified by the Traditional Medicine Division of Mali and a sample has been deposited in the Division Herbarium for future reference.

Extraction and isolation. The air-dried tuberous roots of *V. kotschyana* (100 g) were defatted with petrol then extracted with MeOH to give 7 g of residue. The MeOH extract was partitioned between H_2O and *n*-BuOH to afford an *n*-BuOH-soluble portion (2.9 g) that was chromatographed on a Sephadex LH-20 column (100 × 5 cm) with MeOH as the eluent. Frs of 8 ml each were collected and checked by TLC. Frs 29–34 (640 mg) from Sephadex were purified by DCCC with $CHCl_3$–MeOH–H_2O (7:13:8) in which the stationary phase consisted of the organic phase (discending mode, flow 10 ml hr^{-1}). About 450 frs (4 ml each) were collected. DCCC fractions 60–168 (200 mg) were sepd by RP-HPLC on a C18 μ-Bondapak column (30 cm × 7.8 mm, flow rate 2.0 ml min^{-1}) with MeOH–H_2O (3:2) as the eluent to yield pure compounds (**1**) (R_t = 12 min, 22.5 mg), (**4**) (R_t = 17 min, 16 mg), (**6**) (R_t = 30 min, 18 mg). DCCC frs 248–380 (220 mg) were further sepd by RP-HPLC on a C18 μ-Bondapak column (30 cm × 7.8 mm, flow rate 2.0 ml min^{-1}) with MeOH–H_2O (1:1) as the eluent to yield compounds (**1**) (R_t = 26 min, 5 mg), (**2**) (R_t = 18 min, 19 mg), (**3**) (R_t = 16 min, 12 mg); (**5**) (R_t = 21 min, 38 mg).

Methanolysis of compounds **1–6**. *Carbohydrate constituents.* A soln of each compound (2 mg) in anhydrous 2N HCl–MeOH (0.5 ml) was heated at 80° in a stoppered reaction vial for 12 hr. After cooling, the soln was neutralized with Ag_2CO_3 and centrifuged, then the supernatant was evapd to dryness under N_2. The residue was reacted with TRISIL-Z and analysed by GLC. R_ts were identical to those of authentic methyl sugars.

Vernionioside D_1 (**1**): $[\alpha]_D^{25} = +35.5°$; $C_{35}H_{52}O_{11}$, negative FABMS *m/z* 647 $[M-H]^-$, 619 $[(M-H)-2Me]^-$, 485 $[(M-H)-162]^-$, 469 $[(M-H)-178]^-$; ^1H NMR for sugar moiety (CD_3OD, 500 MHz): δ 4.52 (1H, *d*, $J = 7.6$ Hz, H-1′); 3.15 (1H, *dd*, $J = 7.6$ and 9.5 Hz, H-2′); 3.40 (1H, *t*, $J = 9.5$ Hz, H-3′); 3.36 (1H, *t*, $J = 9.5$ Hz, H-4′); 3.50 (1H, *m*, H-5′); 3.87 (1H, *dd*, $J = 12.0$; 5.0 Hz, H-6′); 3.70 (1H, *dd*, $J = 12.0$; 3.0 Hz, H-6′); for ^1H and ^{13}C NMR data of aglycone and ^{13}C NMR data of the sugar moiety see Tables 1 and 2, respectively.

Vernionioside D_2 (**2**): $[\alpha]_D^{25} = +54.1°$; $C_{40}H_{60}O_{15}$, negative FABMS *m/z* 779 $[M-H]^-$, 751 $[(M-H)-2Me]^-$, 647 $[(M-H)-132]^-$, 485 $[(M-H)-(132+162)]^-$. NMR data of the aglycone are superimposable to those reported for compound **1**; for ^1H and ^{13}C NMR data of sugar moiety see Table 2.

Vernionioside D_3 (**3**): $[\alpha]_D^{25} = +60.0°$; $C_{41}H_{62}O_{16}$, negative FABMS *m/z* 809 $[M-H]^-$, 781$[(M-H)-2Me]^-$, 647 $[(M-H)-162]^-$, 485 $[(M-H)-(162+162)]^-$. NMR data of the aglycone are superimposable to those reported for compound **1**; for NMR data of sugar moiety see Table 2.

Vernionioside F_1 (**4**): $[\alpha]_D^{25} = +25.7°$; $C_{35}H_{52}O_{12}$, negative FABMS *m/z* 663 $[M-H]^-$, 635 $[(M-H)-$

2Me]$^-$, 501 [(M-H)-162]$^-$, ^{1}H NMR for sugar moiety (CD_3OD, 500 MHz): δ 4.48 (1H, *d*, J = 7.5 Hz, H-1′); 3.18 (1H, *dd*, J = 7.5 and 9.5 Hz, H-2′); 3.39 (1H, *t*, J = 9.5 Hz, H-3′); 3.38 (1H, *t*, J = 9.5 Hz, H-4′); 3.50 (1H, *m*, H-5′); 3.89 (1H, *dd*, J = 12.0; 5.0 Hz, H-6′); 3.72 (1H, *dd*, J = 12.0; 3.0 Hz, H-6′); ^{13}C NMR of sugar moiety are superimposable to those of compound **1**, for ^{1}H and ^{13}C NMR data of aglycone see Table 1.

Vernionioside F_2 (**5**): $[\alpha]_D^{25} = +33.4°$; $C_{40}H_{60}O_{15}$, negative FABMS *m/z* 795 [M-H]$^-$, 765 [(M-H)-2Me]$^-$, 663 [(M-H)-132]$^-$, 501 [(M-H)-(132+162)]$^-$. The NMR data of the aglycone are superimposable to those reported for compound **4**; the NMR data of sugar moiety are superimposable to those of compound **2**.

Compound (**6**): $[\alpha]_D^{25} = +61.4°$; $C_{31}H_{50}O_{11}$, negative FABMS *m/z* 597 [M-H]$^-$, 435 [(M-H)-162]$^-$, 273 [(M-H)-(162+162)]$^-$; ^{1}H NMR for aglycone (CD_3OD, 500 MHz): δ 3.80 (1H, *m*, H-3); 2.35 (1H, *dd*, J = 12.0, 9.0 and 4.5 Hz, H-7a), 2.14 (1H, *dd*, J = 9.0 and 4.0 Hz, H-14); 2.08 (2H, *m*, H-11a); 2.02 (1H, *ddd*, J = 11.5, 9.9, 9.9 Hz, H-4a); 1.98 (1H, *m*, H-15a), 1.97 (1H, *dd*, J = 12.0, 3.0, 5.0 Hz, H-7b), 1.90 (1H, *m*, H-12a), 1.80 (1H, *m*, H-2a), 1.78 (1H, *m*, H-1a), 1.70 (1H, *m*, H-16a), 1.65 (1H, *m*, H-2b), 1.61 (1H, *m*, H-1b), 1.51 (1H, *m*, H-17a), 1.48 (1H, *m*, H-4b), 1.39 (1H, *m*, H-12b), 1.36 (2H, *m*, H-6), 1.34 (1H, *m*, H-15b), 1.32 (1H, *m*, H-5), 1.30 (1H, *m*, H-16b), 1.23 (1H, *m*, H-17b), 1.06 (3H, *s*, Me-19), 0.75 (3H, *s*, Me-18); for ^{13}C NMR data of the aglycone see Table 1; for ^{13}C NMR data of sugar moiety see Table 2.

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