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SESQUITERPENE GLYCOSIDES FROM *DICTAMNUS DASYCARPUS*

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Key Word Index—*Dictamnus dasycarpus*; Rutaceae; sesquiterpene glycosides; dictamnosides A–E.

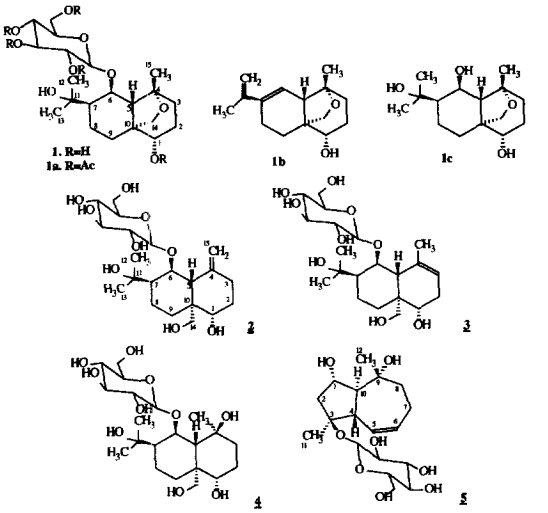
Abstract—Five novel sesquiterpene glycosides named dictamnosides A–E were isolated from the methanol extract of the root bark of *Dictamnus dasycarpus*. Their structures were established on the basis of X-ray diffraction, spectroscopic and chemical methods. © 1997 Elsevier Science Ltd

INTRODUCTION

Dictamnus dasycarpus Turcz. (Bai-Xian-Pi) is a traditional Chinese medicine. The root bark of this plant is used for treatment of jaundice, cough and rheumatism. It has also been widely used to treat some skin diseases [1]. Phytochemical work has been done on the lipophilic components of the genus *Dictamnus*, and various compounds including furoquinoline alkaloids [2, 3], limonoids [4, 5] and a sesquiterpene [6] have been identified. In a previous paper, we have reported the isolation and identification of several antifungal components from the dichloromethane extract of the root bark of *D. dasycarpus* [7]. To our knowledge, the polar components of *Dictamnus* plants have not been well investigated. In order to understand more about the chemistry of the genus *Dictamnus*, we studied the methanol extract of the root bark of *D. dasycarpus*. Here, we report the isolation and structural determination of five novel sesquiterpene glycosides named dictamnosides A–E, respectively.

RESULTS AND DISCUSSION

The root bark of *Dictamnus dasycarpus* (3 kg) was extracted with dichloromethane and methanol, successively. The methanol extract (85 g) was subjected to column chromatography on silica gel with a chloroform–methanol gradient (8:1 → 1:1). The fractions obtained from the chloroform–methanol (5:1 → 3:1) eluents were further filtered through Sephadex LH-20 columns with chloroform–methanol (1:1) and subsequently chromatographed on silica gel [chloroform–methanol–water (10:3:0.3)] and RP-8 Lobar [methanol–water gradient (1:4 → 3:7)] columns to give compounds **1** (150 mg), **2** (50 mg), **3** (120 mg), **4** (30 mg) and **5** (15 mg).



Compound **1** was first purified as an amorphous powder. After crystallization from a mixture of methanol and water (1:1), triclinic crystals were obtained. The positive ion mode D/CI mass spectrum of **1** exhibited a quasimolecular ion adduct at *m/z* 450 $[M+NH_4]^+$ and a fragment ion signal at *m/z* 288 $[M-162+NH_4]^+$. The signal at *m/z* 288 and the high polarity of **1** suggested it to be a glycoside. Acidic hydrolysis of **1** yielded glucose as its sugar component.

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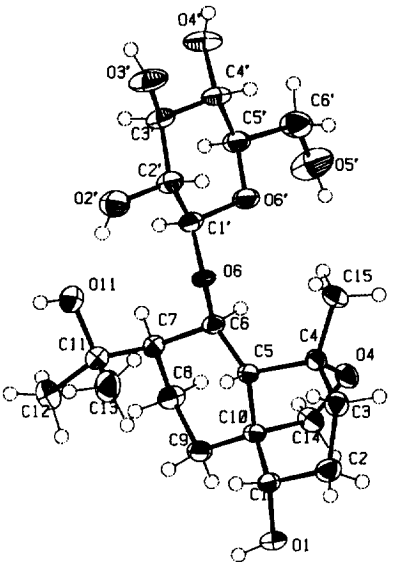

Fig. 1. Perspective view of the molecule of compound **1**; thermal ellipsoids at 50% probability level.

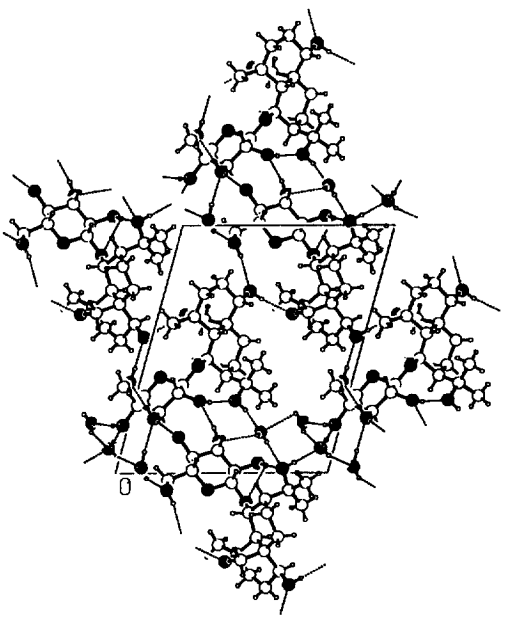

Fig. 2. Crystal packing diagram viewed down the A axis, H-bonds are represented by dashed lines.

In the ^{13}C NMR spectrum of **1**, 21 carbon signals were observed as three methyls, six methylenes, nine methines and three quaternary carbon signals. Therefore, the aglycone of **1** should contain 15 carbons and was supposed to be a sesquiterpene. Combinational analysis of the ^{13}C NMR, DEPT and D/CI mass spectra led to the deduction of its molecular formula as $C_{21}H_{36}O_9$. Hence, the unsaturation degree of **1** is four. In the ^{13}C NMR spectrum of **1**, no signal due to a double bond was found. Thus, three ring systems exist in the aglycone of **1**.

According to the ^{13}C NMR data, five oxygenated carbons were present in the aglycone of **1**. Acetylation of **1** gave compound **1a**. Analysis of the ^{1}H, ^{13}C NMR and mass spectra of **1a** revealed five acetyl groups in **1a**. In addition to the four easily acetylated hydroxyls in the glucose unit, only one hydroxyl in the aglycone of **1** was acetylated. Therefore, an ether bond should exist in the structure of **1**.

Single crystals of **1** were subjected to X-ray diffraction analysis. An ORTEP drawing of the structure of **1** is given in Fig. 1. The crystal packing diagram is shown in Fig. 2. Compound **1** is a new natural product named dictamnoside A.

Acidic hydrolysis of **1** yielded **1b** as the major product. In the ^{1}H NMR spectrum of **1b**, only two methyl signals were observed, and one of them should be connected to an olefinic bond due to its chemical shift at δ 1.91 (3H, *br s*). Furthermore, in the ^{13}C NMR and DEPT spectra of **1b**, four carbon signals corresponding to two olefinic bonds were found at δ 143.1 (*s*), 137.0 (*s*), 121.3 (*d*) and 111.1 (*t*). According to this evidence, **1b** was not the real aglycone of **1**, and the two double bonds were likely located at C-6/C-7 and C-11/C-12 in the structure of **1b**. The above suggestion was further confirmed by ^{1}H-^{1}H COSY, HMQC and HMBC data of **1b**.

In order to obtain the aglycone, compound **1** was subjected to enzymatic hydrolysis with β-glucosidase. No obvious reaction happened after keeping the solution at 35° for three days. Further hydrolysis at room temperature for 30 days afforded **1c**. The structure of **1c** was established on the basis of the ^{1}H, ^{13}C NMR, ^{1}H-^{1}H COSY, HMQC and HMBC spectra, and was identified to be the real aglycone of compound **1**.

Compounds **2** and **3** were obtained as amorphous powders. The positive ion mode D/CI mass spectra of **2** and **3** gave the same quasimolecular ion adducts at *m/z* 450 $[M+NH_4]^+$ and the same fragment ion signals at *m/z* 288 $[M-162+NH_4]^+$, which also suggested them to be glycosides. Acidic hydrolysis of compounds **2** and **3** yielded glucose as their sugar components.

The ^{13}C NMR spectra of both **2** and **3** exhibited 21 carbon signals with certain similarities to those of compound **1**. Therefore, compounds **2** and **3** were presumed to be analogues of **1**. On the basis of the ^{13}C NMR, DEPT and mass spectra, the molecular formulas of **2** and **3** were deduced to be $C_{21}H_{36}O_9$, the same as that of compound **1**. In the ^{13}C NMR spectrum of compound **2**, two olefinic carbon signals at δ 147.2 (*s*) and 106.6 (*t*) along with two methyl signals at δ 31.1 and 28.8 were observed, while in the ^{13}C NMR spectrum of **3**, signals of a trisubstituted double bond were found at δ 121.5 (*d*) and 134.9 (*s*) along with three methyl signals at δ 22.8, 30.1 and 30.6. The unsaturation degrees of **2** and **3** were both four according to their molecular formulas. Therefore, their aglycones should both consist of two ring systems, considering the existence of the olefinic bond and the glucose moiety in their structures. By comparison of the ^{13}C NMR data of compounds **2** and **3**

with those of **1**, and also from a biogenetic point of view, an exo-cyclic olefinic bond has to be located at C-4/C-15 in **2**, while a trisubstituted olefinic bond should be present at C-3/C-4 in **3**. No ether bond exists in the aglycones of **2** and **3**.

In order to confirm the above hypothesis, extensive 2D NMR measurements of **2** and **3** were performed. On the basis of the ^{1}H-^{1}H COSY, TOCSY and HMQC spectra, fragments containing coupled proton systems along with the one bond connections of proton and carbon signals were established (Table 1 and 2). In the HMBC spectra of **2** and **3**, a series of ^{1}H-^{13}C long range correlation signals were observed as shown in Fig. 3. As a result, the linkages among all the fragments were established. Relative configurations of **2** and **3** were determined according to the results of NOESY spectra as shown in Fig. 4. Chemical shifts of all the α and β-protons of each methylene were assigned on the basis of NOE results (Table 1). Compounds **2** and **3** are new natural products, and named dictamnosides B and C, respectively.

Compound **4** was obtained as an amorphous powder. The positive ion mode D/CI mass spectrum of **4** exhibited a quasimolecular ion signal at *m/z* 468 $[M+NH_4]^+$. Due to its high polarity, compound **4** was also suggested to be a glycoside. Acidic hydrolysis of **4** yielded glucose as its sugar component.

The ^{13}C NMR spectrum of **4** exhibited 21 carbon signals. The 15 carbon signals belonging to its aglycone with three methyls, five methylenes, four methines and three quaternary carbon signals, were the same as those of compound **1**. On the basis of the ^{13}C NMR, DEPT and mass spectra, the molecular formula of **4** was deduced to be $C_{21}H_{38}O_{10}$, and therefore, only three unsaturation degrees were present in the structure of **4**. The molecular weight of **4** was 18 daltons higher than that of **1**. Considering the similarities of the ^{13}C NMR data of **1** and **4**, and also from

Table 1. ^{1}H NMR (600 MHz, C_5D_5N) data of compounds **2–5**

No.	2	3	4*	5
1	3.70, *m*	3.97, *m*	3.80, *m*	4.83, *ddd*, 8.0, 6.8, 4.8
2α	2.04, *m*	2.53, *m*	2.19, *m*	2.19, *dd*, 13.6, 4.8
2β	2.11, *m*	2.66, *br d*, 16.1	2.02, *m*	2.91, *dd*, 13.6, 8.0
3α	2.37, *m*	5.40, *d*, 1.8	2.32, *m*	
3β	2.37, *m*		2.09, *m*	
4				2.95, *ddd*, 12.1, 2.5, 2.2
5	2.84, *br d*, 6.6	3.40, *br s*	2.86, *m*	6.09, *dd*, 11.3, 1.9
6	4.946, *dd*, 7.0, 5.1	4.89, *dd*, 4.4, 4.1	5.14, *m*	5.76, *ddd*, 11.3, 5.5, 2.9
7α	2.35, *m*	2.27, *m*	2.15, *m*	2.02, *m*
7β				2.43, *m*
8α	1.80, *m*	2.15, *m*	2.80, *m*	1.94, *m*
8β	2.11, *m*	2.49, *m*	2.49, *m*	1.94, *m*
9α	2.80, *ddd*, 13.9, 7.3, 6.6	2.95, *br dd*, 12.8, 6.2	3.15, *m*	
9β	1.91, *ddd*, 13.9, 6.9, 6.6	1.68, *ddd*, 12.5, 11.6, 7.7	1.81, *m*	
10				2.46, *dd*, 12.1, 6.8
11				1.75, *s*
12	1.55, *s*	1.50, *s*	1.66, *s*	1.45, *s*
13	1.61, *s*	1.60, *s*	1.42, *s*	
14a	3.85, *d*, 11.7	4.17, *dd*, 11.0, 5.9	4.67, *d*, 9.9	
14b	4.33, *d*, 11.3	4.406, *br d*, 11.0	4.19, *m*	
15a	5.11, *br s*	2.13, *br s*	1.28, *s*	
15b	4.98 *br s*			
Glu-1	5.05, *d*, 8.0	5.20, *d*, 8.1	5.39, *m*	5.11, *d*, 7.7
Glu-2	3.96, *dd*, 8.8, 8.1	4.03, *dd*, 8.4, 8.1	4.22, *m*	4.05, *dd*, 8.5, 8.0
Glu-3	4.18, *dd*, 9.1, 8.8	4.25, *m*	4.31, *dd*, 12.5, 8.5	4.30, *dd*, 8.8, 8.8
Glu-4	4.30, *dd*, 9.6, 9.1	4.22, *m*	4.01, *m*	4.25, *dd*, 9.2, 9.1
Glu-5	3.68, *ddd*, 9.6, 4.0, 2.9	3.93, *ddd*, 9.1, 5.2, 3.0	4.23, *m*	3.96, *ddd*, 9.6, 5.5, 2.5
Glu-6a	4.36, *m*	4.44, *br d*, 11.7	4.85, *m*	4.53, *dd*, 11.7, 2.5
Glu-6b	4.36, *m*	4.33, *m*	4.20, *m*	4.35, *dd*, 11.8, 5.5
1-OH		6.44, *d*, 5.5	7.81, *br s*	
4-*OH*			5.01, *br s*	
11-OH	5.24, *s*		5.88, *s*	
14-OH		5.82, *br d*, 4.8		
2′-OH			9.14, *br s*	
3′-OH			8.34, *br s*	
4′-OH			8.05, *br s*	
6′-OH			7.92, *br s*	

* ^{1}H NMR, ^{1}H-^{1}H COSY and NOESY spectra were measured at -38°.

Table 2. ^{13}C NMR (150 Mhz, C_5D_5N) data of compounds **2–5**

No.	2	3	4	5
1	81.4, *d*	78.7, *d*	80.4, *d*	70.5, *d*
2	33.7, *t*	35.2, *t*	30.4, *t*	48.2, *t*
3	36.2, *t*	121.5, *d*	42.3, *t*	84.9, *s*
4	147.2, *s*	134.9, *s*	72.0, *s*	49.7, *d*
5	51.3, *d*	51.4, *d*	59.9, *d*	131.5, *d*
6	77.4, *d*	79.1, *d*	80.5, *d*	130.8, *d*
7	46.1, *d*	44.9, *d*	46.1, *d*	24.0, *t*
8	20.1, *t*	18.2, *t*	18.1, *d*	43.5, *t*
9	28.4, *t*	26.5, *t*	28.5, *t*	74.1, *s*
10	42.9, *s*	42.2, *s*	44.1, *s*	60.1, *d*
11	72.6, *s*	72.4, *s*	71.4, *s*	23.6, *q*
12	31.1, *q*	30.1, *q*	30.4, *q*	22.9, *q*
13	28.8, *q*	30.6, *q*	30.1, *q*	
14	63.8, *t*	61.9, *t*	62.9, *t*	
15	106.6, *t*	22.9, *q*	24.1, *q*	
Glu-1	104.1, *d*	104.8, *d*	105.8, *d*	99.5, *d*
Glu-2	75.0, *d*	75.0, *d*	75.1, *d*	75.2, *d*
Glu-3	78.8, *d*	78.7, *d*	78.8, *d*	78.7, *d*
Glu-4	71.1, *d*	71.7, *d*	72.4, *d*	71.8, *d*
Glu-5	77.9, *d*	78.2, *d*	78.4, *d*	78.1, *d*
Glu-6	62.2, *t*	62.7, *t*	63.3, *t*	62.9, *t*

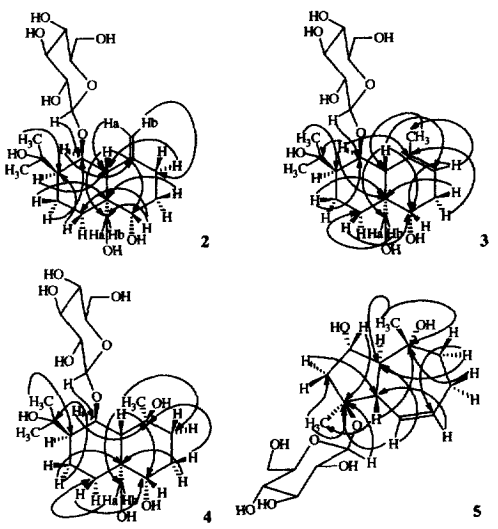

Fig. 3. Main ^1H-^{13}C long-range correlation signals observed in HMBC spectra of compounds **2–5**.

a biogenetic point of view, no ether bond between C-4 and C-14 should exist in **4**. On the basis of the ^1H-^1H COSY, TOCSY, HMQC and HMBC spectra of **4**, the above suggestion was confirmed (Table 2, Fig. 3). However, the relative configuration of **4** was still unknown.

Many hydroxyl proton signals could be clearly observed at lowfield when the ^1H NMR spectrum of **4** was measured at $-38°$. In order to use these hydroxyl proton signals in the determination of its relative configuration, a ^1H-^1H COSY spectrum of **4** was performed again at $-38°$, and the chemical shifts of all proton signals were assigned. The NOESY spectrum

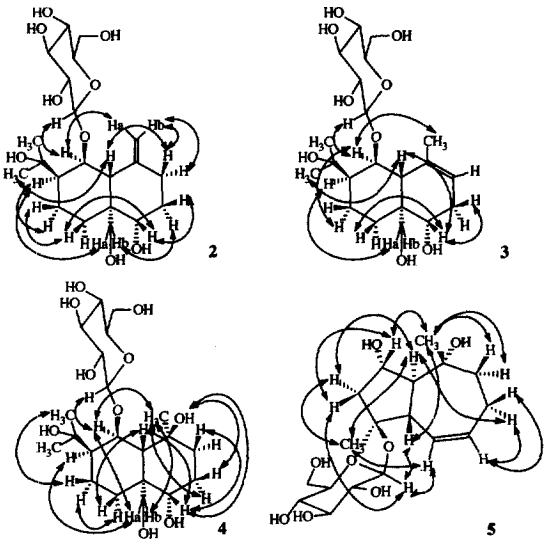

Fig. 4. Main NOE signals observed in NOESY spectra of compounds **2–5**.

of **4** measured at the same temperature enabled the establishment of the relative configuration (Table 1, Fig. 4). Compound **4** is a new natural product named dictamnoside D.

Compounds **1–4** are glycosides with eudesmane-type sesquiterpene aglycones. Glycosides with the same type of aglycones were also found in another Chinese traditional medicine, *Atractylodes lancea* (Asteraceae) by a Japanese group [8].

Compound **5** was obtained as an amorphous powder. The positive ion mode D/CI mass spectrum of **5** gave a quasimolecular ion adduct at *m/z* 392 $[M+NH_4]^+$ and a fragment ion signal at *m/z* 230 $[M-162+NH_4]^+$, which also suggested it to be a glycoside. Acidic hydrolysis of **5** yielded glucose as its sugar component. In the ^1H NMR spectrum of **5**, one anomeric proton signal at δ 5.10 (*d*, J = 7.7 Hz) along with the two methyls at δ 1.75 (*s*), 1.45 (*s*) and two olefinic proton signals at δ 6.08 (*dd*, J = 11.3, 1.9 Hz), 5.76 (*ddd*, J = 11.3, 5.5, 2.9 Hz) were observed. The ^{13}C NMR spectrum of **5** exhibited 18 carbon signals. Among the 12 carbon signals belonging to the aglycone were two methyls, three methylenes, five methines and two oxygen-bearing quaternary carbon signals. On the basis of the ^{13}C NMR, DEPT and mass spectra, the molecular formula of **5** was deduced to be $C_{18}H_{30}O_8$. Two ring systems should exist in the aglycone of **5** according to its unsaturation degree.

Analysis of the ^1H-^1H COSY, TOCSY and HMQC spectra of **5** allowed the establishment of the following fragment: —CH_2—CH(O)—CH—CH—CH=CH—CH_2—CH_2—. The four remaining carbons of the aglycone were the two methyls and two oxygen-bearing quaternary carbons. Since the two methyls appeared as singlets at δ 1.75 (3H, *s*) and 1.45 (3H, *s*) in the ^1H NMR spectrum, they should be linked to the two quaternary carbons, respectively. A HMBC spectrum

allowed to establish the connection of the above fragments and the glucose moiety (Fig. 3). The relative configuration of **5** was determined according to the results of the NOESY spectrum (Fig. 4). Compound **5** is a new natural product and named dictamnoside E.

The aglycone of **5** possess a trinorguaine type skeleton. A related compound, dictamnol, with the same trinorguaine type skeleton was previously reported from *D. dasycarpus* [9]. Dictamnol was also isolated during our investigation of the dichloromethane extract of the root bark of the plant [7].

EXPERIMENTAL

General. $[\alpha]_D$ were measured with a Perkin–Elmer 241 MC polarimeter. NMR spectra of **1** were obtained on Varian VXR 200 and Varian Unity 500 spectrometers. NMR spectra of **2–5** were obtained on a Jeol JNM-LA 600 spectrometer. Chemical shifts were reported in δ (ppm), with residual C_5D_5N signals (7.24/123.5) and $CDCl_3$ signals (7.25/77.0) as int. standards. A Nalorac inverse probe of 5 mm was used for all NMR experiments on **2–5** except for ^{13}C NMR measurements (Jeol probe). D/CI mass spectra were recorded on a Finnigan MAT TSQ 700 instrument. β-Glucosidase from almonds (1000 IU mg^{-1}) was purchased from Fluka AG (no. 49290).

Plant material. The root bark of *Dictamnus dasycarpus* was purchased from Shanghai Medicine Materia Corporation, and identified by Prof. Jixian Guo of School of Pharmacy, Shanghai Medical University. Voucher specimens are deposited in the Herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Sciences and at the Institute of Pharmacognosy and Phytochemistry, University of Lausanne (no. 95143).

Extraction and isolation. The root bark of *Dictamnus dasycarpus* (3 kg) was powdered and then percolated × 3 with CH_2Cl_2 and MeOH, successively, at room temp. (3 × 10 l). the filtrate was evapd to dryness to give CH_2Cl_2 (150 g) and MeOH extracts (90 g), respectively.

The MeOH extract (85 g) was subjected to CC on silica gel with a $CHCl_3$ and MeOH gradient (8:1 → 1:1). The fr. eluted with $CHCl_3$–MeOH (5:1) (6.5 g) was filtered through a Sephadex LH-20 column with $CHCl_3$–MeOH (1:1), and then subjected to CC on silica gel with $CHCl_3$–MeOH–H_2O (10:3:0.3) to give **2** (50 mg) as an amorphous powder. The fr. eluted with $CHCl_3$–MeOH (4:1) (5.0 g) was first filtered through a Sephadex LH-20 column with $CHCl_3$–MeOH (1:1). It was then subjected to CC on silica gel with $CHCl_3$–MeOH–H_2O (10:3:0.3) and RP-18 Lobar columns with a MeOH–H_2O gradient (1:4 → 3:7) to give **1** (150 mg), **3** (120 mg) and **5** (15 mg) as amorphous powders. The fr. eluted with $CHCl_3$–MeOH (3:1) (7.1 g) was filtered through a Sephadex LH-20 column with $CHCl_3$–MeOH (1:1), and then subjected to CC on silica gel with $CHCl_3$–MeOH–H_2O (10:3:0.3) to give **4** (30 mg) as an amorphous powder. Compound **1** was further crystallized from a mixt. of MeOH and H_2O (1:1) to give triclinic crystals.

Acidic hydrolysis of **1–5**. Compounds **1–5** (10 mg) were dissolved in 2N HCl (10 ml), respectively. After heating at 80° in a H_2O bath for 2 hr, the reaction mixts were extracted with EtOAc (3 × 10 ml). Then the aq. phases were concd *in vacuo* and sugar components were identified by TLC chromatography on silica gel with EtOAc–MeOH–H_2O–HOAc (13:3:3:4). Glucose was found as the only sugar component of **1–5**.

Dictamnoside A (**1**). Colourless crystals. $[\alpha]_D^{25}$ −3.6° (MeOH, *c* 0.56). D/CI MS (Positive ion mode) *m/z*: 450 $[M+NH_4]^+$, 288 $[M-glu+NH_4]^+$. ^1H NMR (200 MHz, C_5D_5N): δ 1.41 (3H, *s*), 1.58 (3H, *s*), 1.65 (3H, *s*). ^{13}C NMR (50 MHz, C_5D_5N): δ 106.2 (*d*), 83.3 (*s*), 78.8 (*d*), 78.8 (*d*), 78.6 (*d*), 76.0 (*d*), 74.9 (*d*), 72.0 (*s*), 71.7 (*d*), 70.1 (*t*), 62.7 (*t*), 56.2 (*d*), 49.9 (*s*), 43.9 (*d*), 40.9 (*t*), 30.5 (*q*), 30.3 (*t*), 29.4 (*q*), 22.8 (*t*), 22.6 (*q*), 17.6 (*t*).

Compound **1a**. Compound **1** (20 mg) was dissolved in a mixt. of Ac_2O (3 ml) and anhydrous pyridine (2 ml). The soln was heated at 80° in H_2O bath for 2 hr, and then evapd to dryness *in vacuo*. The residue was purified on a silica gel column, with petrol–Me_2CO (3:2) as eluent to give **1a** (20 mg) as an amorphous powder. $[\alpha]_D^{25}$ −28.4° ($CHCl_3$, *c* 0.05). D/CI MS (Positive ion mode) *m/z*: 660 $[M+NH_4]^+$. ^1H NMR (200 MHz, C_5D_5N): δ 2.53 (1H, *br s*), 2.10 (6H, *s*), 2.02 (9H, *s*), 1.58 (3H, *s*), 1.65 (3H, *s*), 1.60 (3H, *s*). ^{13}C NMR (50 MHz, C_5D_5N): δ 170.4 (*s*), 170.3 (*s*), 170.3 (*s*), 169.8 (*s*), 169.5 (*s*), 100.0 (*d*), 83.4 (*s*), 78.6 (*d*), 76.3 (*d*), 73.5 (*d*), 72.46 (*d*), 72.3 (*d*), 72.0 (*s*), 70.5 (*t*), 69.2 (*d*), 62.5 (*t*), 55.5 (*d*), 48.9 (*s*), 44.0 (*d*), 40.6 (*t*), 30.7 (*q*), 28.8 (*q*), 26.5 (*t*), 22.5 (*q*), 22.1 (*t*), 20.9 (*q*), 20.7 (*q*), 20.6 (*q*), 20.4 (*q*), 20.4 (*q*), 19.1 (*t*).

Compound **1b**. Compound **1** (30 mg) was dissolved in 2N HCl (10 ml) and then 10 ml EtOAc were added. After heating at 80° in a H_2O bath for 2 hr, the mixt. was sepd into EtOAc and H_2O frs by further extraction. The EtOAc fr. was subjected to CC on silica gel with a $CHCl_3$–Me_2CO gradient (5:1 → 3:1) to give **1b** (10 mg) as a colourless oil. $[\alpha]_D^{25}$ −7.0° ($CHCl_3$, *c* 0.72). D/CI MS (Negative ion mode) *m/z*: 233 $[M-H]^-$. ^1H NMR (500 MHz, $CDCl_3$): δ 5.829 (1H, *s*), 5.007 (1H, *s*), 4.897 (1H, *s*), 3.835 (1H, *d*, J = 8.5 Hz), 3.649 (1H, *d*, J = 8.5 Hz), 1.912 (3H, *br s*), 1.278 (3H, *s*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1 (*s*), 137.0 (*s*), 121.3 (*d*), 111.1 (*t*), 81.7 (*s*), 75.4 (*d*), 67.3 (*t*), 50.2 (*d*), 47.2 (*s*), 38.9 (*t*), 29.5 (*t*), 22.9 (*t*), 21.7 (*q*), 21.5 (*t*), 20.7 (*q*).

Compound **1c**. Compound **1** (40 mg) and β-glucosidase (60 mg) were dissolved in 5 ml H_2O. The soln was first kept at 35° for 3 days, and then at room temp. for 30 days until hydrolysis was complete as revealed by TLC analysis. The H_2O soln was extracted with EtOAc (3 × 10 ml). The EtOAc extract was dried *in vacuo* and then chromatographed on a silica gel column with $CHCl_3$–Me_2CO (2:1) to give **1c** (20 mg) as an amorphous powder. $[\alpha]_D^{25}$ +24.7° ($CHCl_3$, *c* 0.14). D/CI MS (Positive ion mode) *m/z* 288

$[M+NH_4]^+$. ^1H NMR (500 MHz, C_5D_5N): δ 4.60 (1H, *dd*, $J = 7.5$, 5.5 Hz), 4.40 (1H, *d*, $J = 8.5$ Hz), 3.96 (1H, *dd*, $J = 9.5$, 7.0 Hz), 3.92 (1H, *d*, $J = 8.5$ Hz), 1.63 (3H, *s*), 1.57 (3H, *s*), 1.52 (3H, *s*). ^{13}C NMR (50 MHz, C_5D_5N): δ 83.8 (*s*), 76.0 (*d*), 74.1 (*s*), 69.7 (*t*), 69.4 (*d*), 55.7 (*d*), 50.5 (*s*), 46.7 (*d*), 40.6 (*t*), 31.4 (*q*), 30.5 (*t*), 30.0 (*q*), 23.5 (*q*), 23.4 (*t*), 20.8 (*t*).

Crystallographic data for compound **1**. $C_{21}H_{36}O_9 \cdot 2H_2O$, triclinic, space group P1 (no. 2), $a = 6.8317(7)$, $b = 12.080(2)$, $c = 14.9623(14)$ Å, $a = 74.988(7)$, $b = 81.253(8)$, $g = 87.711(8)°$, $Z = 2$, 5411 independent reflections, 4894 observed reflections [$I > 2\sigma(I)$], final R_1 0.041, R_{w2} 0.093 (observed data). Goodness of fit 1.118, residual density max/min: 0.223/−0.178 *e* Å^{-3}. Absorption coefficient $m = 0.106$ mm^{-1}.

Intensity data were collected at −50° on a Stoe AED2 4-circle diffractometer using Mo$K\alpha$ graphite monochromated radiation with $2\theta/\omega$ scans in the 2θ range 4–55 β. The structure was solved by direct methods using the program SHELXS-86 [10]. The refinement and all further calculations were carried out using SHELXL-93 [11]. The H-atoms of the H_2O molecules were located from difference maps and refined isotropically. The hydroxyl H-atoms were included in idealized positions with X—O—H angles with maximize the electron density, a rotating group refinement was then applied. The remainder were included in idealized positions and treated as riding atoms. The non-H atoms were refined anisotropically using weighted full-matrix least-squares on F^2.

Bond lengths and angles are normal within experimental error. There are two independent molecules (1 and 2) in the unitcell together with four molecules of H_2O of crystallization. The molecular structure and crystallographic numbering scheme of Molecule 1 of **1** is illustrated in Fig. 1. In the crystal, the two independent molecules and the H_2O molecules are involved in an extensive hydrogen bonding network as shown in Fig. 2.

Full tables of atomic parameters, bond lengths and angles may be obtained from the Cambridge Crystallographic Data Centre, U.K., on quoting the full journal citation. Further details may be obtained from the author H. St-E.

Dictamnoside B (**2**). Amorphous powder. $[\alpha]_D^{25}$ −10.5° (MeOH, *c* 0.55). D/CI MS (Positive ion mode) *m/z*: 450 $[M+NH_4]^+$, 288 $[M-glu+NH_4]^+$. ^1H NMR (600 MHz, C_5D_5N) and ^{13}C NMR (150 MHz, C_5D_5N): Table 1 and 2.

Dictamnoside C (**3**). Amorphous powder. $[\alpha]_D^{25}$ −30.2° (MeOH, *c* 0.57). D/CI MS (Positive ion mode) *m/z*: 450 $[M+NH_4]^+$, 288 $[M-glu+NH_4]^+$. ^1H NMR (600 MHz, C_5D_5N) and ^{13}C NMR (150 MHz C_5D_5N): Table 1 and 2.

Dictamnoside D (**4**). Amorphous powder. $[\alpha]_D^{25}$ −19.5° (MeOH, *c* 0.59). D/CI MS (Positive ion mode) *m/z*: 468 $[M+NH_4]^+$. ^1H NMR (600 MHz, C_5D_5N, room temp.): δ 3.83 (1H, *dd*, $J = 9.1$, 4.7 Hz, H-1), 2.04 (1H, *m*, H-2α), 2.18 (1H, *m*, H-2β), 2.15 (1H, *m*, H-3α), 2.06 (1H, *m*, H-3β), 2.82 (1H, *d*, $J = 2.5$ Hz, H-5), 5.13 (1H, *dd*, $J = 3.3$, 2.5 hz, H-6), 2.24 (1H, *m*, H-7), 2.59 (1H, *m*, H-8α), 2.34 (1H, *m*, H-8β), 1.70 (1H, *m*, H-9α), 3.06 (1H, *m*, H-9β), 1.65 (3H, *s*, H-12), 1.50 (3H, *s*, H-13), 4.60 (1H, *d*, $J = 11.4$ Hz, H-14a), 4.18 (1H, *m*, H-14b), 1.37 (3H, *s*, H-15), 5.31 (1H, *d*, $J = 8.0$ Hz, H_{G-1}), 4.04 (1H, *m*, H_{G-2}), 4.01 (1H, *m*, H_{G-2}), 3.94 (1H, *dd*, $J = 9.5$, 8.8 Hz, H_{G-4}), 4.16 (1H, *m*, H_{G-5}), 4.69 (1H, *dd*, $J = 11.0$, 1.9 Hz, H_{G-6a}), 4.18 (1H, *m*, H_{G-6b}). ^{13}C NMR (150 MHz, C_5D_5N): Table 2.

Dictamnoside E (**5**). Amorphous powder. $[\alpha]_D^{25}$ −6.2° (MeOH, *c* 0.29). D/CI MS (Positive ion mode) *m/z*: 392 $[M+NH_4]^+$, 230 $[M-glu+NH_4]^+$. ^1H NMR (600 MHz, C_5D_5N) and ^{13}C NMR (150 MHz, C_5D_5N): Table 1 and 2.

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