MRC Letters

Magnetic Resonance in Chemistry

Received: 13 October 2010 Revised: 16 June 2011 Accepted: 29 June 2011 Published online in Wiley Online Library: 6 September 2011

(wileyonlinelibrary.com) DOI 10.1002/mrc.2795

Structure elucidation of two new unusual monoterpene glycosides from *Euphorbia decipiens*, by 1D and 2D NMR experiments

Ozlem Demirkiran,[a]* Gulacti Topcu,[b] Javid Hussain,[c,d] Viqar Uddin Ahmad[e] and M. Iqbal Choudhary[e,f]

Two new unusual monoterpene glycosides, (*Z*)-3,6-dimethyl-3-(β-D-*O*-glucosylmethylene)cyclohept-4-ene-1-one (1) and 3,6-dimethyl-3-(β-D-*O*-glucosylmethylene)cycloheptanone (2) have been isolated along with five known compounds, 3-hydroxy-4-methoxybenzoic acid, 6,7-dihydroxycoumarin, luteolin, apigenin 5-*O*-α-L-rhamnoside, and pinocembrin-7-*O*-rutinoside from ethyl acetate extract of *Euphorbia decipiens*. The structures of the isolated compounds were elucidated by extensive 1D- and 2D-NMR, and mass spectroscopic analyses.

Keywords: NMR spectroscopic analysis; *Euphorbia decipiens*; monoterpene glycosides; phenolics

Introduction

The genus *Euphorbia* is the largest in the spurge family, comprising about 1100 species in the world.[1] Most of the representative *Euphorbia* species are characterized by the occurrence of highly irritant latex.[2] The genus *Euphorbia* is the source of a large number of biologically active compounds. An increasing attention has been paid to *Euphorbia* diterpenes because of their diverse structures and therapeutical importance. Macrocylic diterpenes from *Euphorbia* species have been found to possess cytotoxic, antitumor, antibacterial, and HIV-1 reverse transcriptase-inhibiting activities.[3–6] In recent years, investigations on *Euphorbia* species have been mostly carried out on non-polar fractions, such as hexane and chloroform. In the present study, we report the isolation and structure elucidation of two new monoterpene glucosides with cycloheptane ring, as well as five known phenolic compounds from EtOAc soluble extract of *Euphorbia decipiens* which grows wildly in different regions of Pakistan at high altitudes.[7] Diterpenoids and triterpenoids mostly as esters have been previously reported from *E. decipiens*.[8–15] However, in this study, polar compounds were obtained from EtOAc extract of *E. decipiens*, and their structures were elucidated by extensive 1D- and 2D-NMR, and mass spectroscopic analyses as (*Z*)-3,6-dimethyl-3-(β-D-*O*-glucosylmethyl)-4-cyclohepten-1-one (**1**) and 3,6-dimethyl-3-(β-D-*O*-glucosylmethyl)cycloheptan-1-one (**2**) (Fig. 1). Although about 27 isolated cycloheptane monoterpenes have been reported in the literature,[16] only one cycloheptane monoterpene glycoside has so far been isolated from the nature.[17] The cycloheptane monoterpene glycosides **1** and **2**, isolated from *E. decipiens* herein, are new examples of this class of compounds.

Results and Discussion

Compound **1** was isolated as colorless needles. In the HREI MS no molecular ion peak was present, however, a peak was observed at *m/z* 312.1566, which resulted from the loss of H_2O from the $[M]^+$. The base peak at *m/z* 151.1111 $[C_{10}H_{15}O]$ is formed by cleavage of hexose moiety and a fragment ion at *m/z* 167.1063 for $[C_{10}H_{15}O_2]$ was also observed in EI MS (Fig. 2). HRFAB MS (negative) of compound **1** exhibited the $[M\text{-}H]^-$ at *m/z* 329.1589, consistent with the formula $C_{16}H_{26}O_7$ (calcd. 330.1679), and with four double bond equivalents.

In the ^{1}H NMR spectrum of compound **1**, two overlapped signals at δ 5.45 (1H, d, J = 6.0 Hz, H-4) and (1H, m, H-5) indicated two olefinic protons. In the low-frequency region of ^{1}H NMR spectrum, two methyl signals were observed at δ 0.93 (3H, d, J = 7.1 Hz) and 1.14 (3H, s, H-9). The other proton signals observed at low frequency resonated at δ 2.07 (1H, dd, J = 13.7 Hz, J = 1.5 Hz, H-7α), 2.60 (1H, dd, J = 13.7 Hz, J = 6.5 Hz, H-7β), and 2.38 (1H, m, H-6). Two oxygenated proton signals appeared at δ 3.55 (1H, d, J = 12.0 Hz, H-8a) and 4.27 (1H, d, J = 12.0 Hz, H-8b). The presence of an sugar moiety followed by an anomeric proton signal observed at δ 4.23 as a doublet (J = 7.8 Hz) indicating

* *Correspondence to: Ozlem Demirkiran, Department of Chemistry, Faculty of Science, Trakya University, Edirne 22030, Turkey. E-mail: ozlemdemirkiran@yahoo.com*

a *Department of Chemistry, Faculty of Science, Trakya University, Edirne 22030, Turkey*

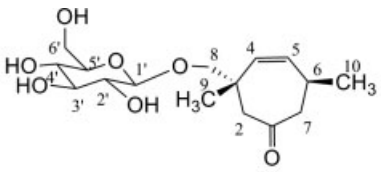
b *Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey*

c *Department of Chemistry, Kohat University of Science and Technology, Kohat 26000, Pakistan*

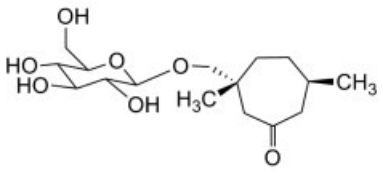
d *Department of Biological Sciences and Chemistry, College of Arts and Sciences, University of Nizwa, Nizwa, Oman*

e *H.E.J. Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi 75270, Pakistan*

f *Dr. Panjwani Center for Molecular Medicine and Drug Research, International Center for Chemical and Biological Sciences, University of Karachi, Karachi 75270, Pakistan*



(Z)-3,6-dimethyl-3-(β-D-glucosylmethyl)cyclohept-4-enone (**1**)



3,6-dimethyl-3-(β-D-glucosylmethyl)cycloheptanone (**2**)

Figure 1. The structures of the new monoterpene glycosides **1** and **2**.

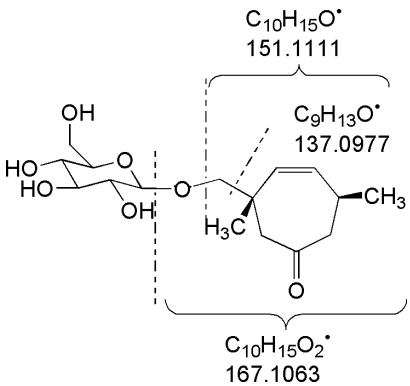


Figure 2. Observed HREI MS fragmantations for compound **1**.

the β-configuration of sugar linkage, besides six proton signals resonating between δ 3.15 and 3.84 in the ^{1}H NMR spectrum.

The presence of a double bond was verified from the signals at δ 128.9 and 129.2 in the ^{13}C-NMR spectrum. The position of the double bond was deduced from the ^{1}H–^{1}H COSY spectrum by the observation a crosspeak between a signal at δ 2.38 (m, H-6) and the olefinic proton at δ 5.45 (m, H-5). The signal at δ 2.38 (m, H-6) also displayed a crosspeak with a methyl signal, appeared as a doublet at δ 0.93 (J = 7.1 Hz, H-10). Therefore, it was deduced that the methyl (H-10) is attached to C-6. The sequences from H-4 to H-10 as well as from H-7 to H-4/H-10 followed by ^{1}H–^{1}H COSY experiment.

In the ^{13}C-NMR (BB decoupled and DEPT) spectra, sixteen carbon atoms were observed consisting of two quarternary, four methylene, eight methine, and two methyl carbon signals. The presence of an isolated keto group inferred from a signal resonated at δ 213.8, besides a glucose moiety with the five oxygenated signals at δ 79.9, 75.3, 73.9, 71.8, and 62.4, as well as an anomeric signal at δ 100.3. The signals for four pairs of methylene carbons were identified based on ^{1}H, DEPT, and HMQC NMR experiments. One of them resonated at δ 4.27 and 3.55 as doublets (J = 12.0 Hz, H-8a and H-8b) and the HMQC spectrum showed its carbon signal at δ 73.8 (CH_2), indicating an oxyganated methylene. The signals of another pair of oxygenated methylene protons (H-6′a and H-6′b) in glucose moiety, resonated at δ 3.84 (dd, J = 11.8 Hz, J = 1.4 Hz) and 3.67 (dd, J = 11.8 Hz, J = 4.8 Hz), respectively. The other two methylene pairs resonated at δ 2.07 (1H, dd, J = 13.7 Hz, J = 1.5 Hz, H-7α), 2.60 (1H, dd, J = 13.7 Hz, J = 6.5 Hz, H-7β),

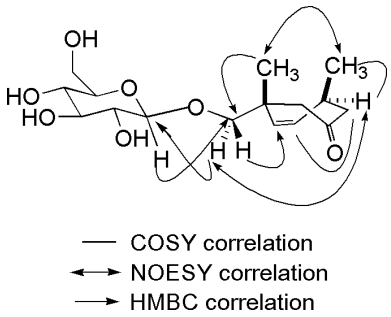


Figure 3. Key COSY, NOESY, and HMBC correlations for compound **1**.

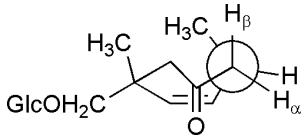


Figure 4. Newman projection for compound **1**, showing angles between H-6 and H-7.

and 3.33 (2H, ovrlpd., H-2α and H-2β. These two methylene pairs (CH_2-2 and CH_2-7) were placed next to carbonyl carbon based on their strong two bond HMBC correlations from both sides of carbonyl carbon, observed at δ 213.8 (C-1).

In the HMBC spectrum, the location of CH_2-8 was deduced by three important HMBC correlations of the signal at δ 3.55 (H-8a) with anomeric carbon of sugar moiety at δ 100.3 (C-1′), olefinic carbon at δ 128.9 (C-4), and methyl carbon at δ 19.1 (C-9). The anomeric proton signal at δ 4.23 showed correlation with C-8 (δ 73.8, CH_2) in the HMBC spectrum. This indicated that sugar moiety was attached to the C-8. Similarly, $^3J_{HC}$ correlations from both olefinic H-4 at δ 5.45 and methyl protons (H-9) at δ 1.14 to C-8 at δ 73.8 (CH_2) were also observed (Fig. 3). These observations unambigously indicated that methyl (H-9) and oxygenated metylene (H-8) were attached to the same carbon (C-3), observed at (δ 26.4).

In the NOESY spectrum, the correlations between methyl protons H-9 (δ 1.14) and H-10 (δ 0.93), as well as a weak correlation between H-6 (δ 2.38) and one of H-8 methylenes (δ 3.55, H-8a) indicated that H-6 and glycosylated side chain are on the same side of the molecular plane (Fig. 3). The study of a Dreiding model helped us in the confirmation of stereochemistry of H-6. The $^3J_{HH}$ values between H-6 and α, β protons of C-7 [$J_{6,7\alpha}$ = 6.5 Hz (φ = 30°) and $J_{6,7\beta}$ = 1.5 Hz (φ = 100°)] indicated that H-6 must have an α configuration (Fig. 4). Therefore, it was deduced that both methyl groups at C-3 and C-6 are on the same side of molecular plane with β configuration. These observations clearly indicated that compound **1** was (*Z*)-3,6-dimethyl-3-(β-D-*O*-glucosylmethylene)cyclohept-4-ene-1-one.

The HRFAB MS (negative) of compound **2** showed a peak $[M - H]^-$ at m/z 331.1698 consistent with the formula $C_{16}H_{28}O_7$ (calcd. 332.1835). In the HREI MS, a peak for $[M - glu]^+$ was at m/z 153.1247 representing the aglycon moiety, consistent with the formula $C_{10}H_{17}O$ (calcd. 153.1279). The ^{1}H and ^{13}C NMR spectra were nearly identical to compound **1**. The only difference was the appearance of the two additional CH_2 protons instead of the olefinic protons. These signals were observed at δ 2.49 and 1.53 for CH_2-4 and at δ 1.92 and 1.39 for CH_2-5. Their carbons were determined at δ 27.9 (C-4) and 34.9 (C-5) by the observed correlations in the HMQC spectrum. Likewise compound

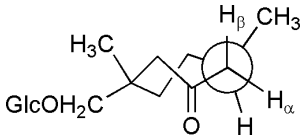


Figure 5. Newman projection for compound **2**, showing angles between H-6 and H-7.

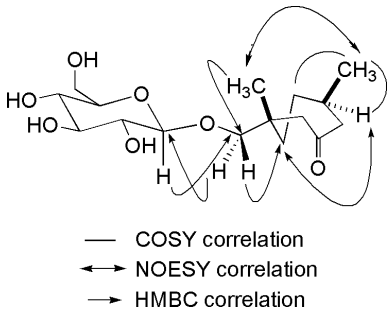


Figure 6. Key COSY, NOESY, and HMBC correlations for compound **2**.

1, the relative configuration of the H-6 was determined by *J* values between H-6 and H-7. Because the seven-member ring is more flexible in the absence of a double bond, and a dihedral angle (φ) between H-7β and H-6 reaches to almost 180° (Fig. 5). Therefore, H-7β appeared as a triplet at δ 2.09 (t, J = 12.0 Hz) formed of two equal overlapping doublets due to H-7α (geminal coupling, J = 12.0 Hz) and H-6 (diaxial coupling, J = 12.0 Hz). The observed important correlations in 2D spectra of compound **2** were shown in Fig. 6. Thus, all 1D and 2D NMR and HREI MS results verified the structure of compound **2** as 3,6-dimethyl-3-(β-D-*O*-glucosylmethylene)cycloheptanone.

The known compounds **3**–**7** were previously reported from various plant sources and their structures were identified by comparison with the reported data.[18,19]

Experimental

General experimental procedures

Optical rotations were measured on a digital polarimeter JASCO DIP-360 in methanol. Infrared spectra were obtained on Vector 22 Bruker spectrophotometer in $CHCl_3$. FAB Mass spectra were recorded on Varian MAT 312 mass spectrometer. Accurate mass measurements were carried out with FAB source using glycerol as matrix and high-resolution-fast-atom-bombardment (HRFAB-MS) on a JEOL HX 110 mass spectrometer, and HREI MS measurements were carried out on a MAT312 instrument; in *m/z* (rel. %). The GC was performed on an ISQ Single Quadrupole GC-MS (Thermo Electron Corporation, USA) with an L-Chirasil-Val column (0.32 mm × 30 m, film thickness: 0.25 µm); detection, FID. Thin-layer chromatography (TLC) was performed on precoated silica gel plates (DC-Alugram 60 UV_{254} E. Merck, Germany), by using ceric sulfate spraying reagent until coloration developed. Purification was carried out on ODS C-18 (63–212 µm, Wako Pure Chemical Industries Ltd, Japan), polyamide-6 DF (Riedel-De Haen AG, Germany), sephadex LH-20, and silica gel (230–400 µm mesh, E. Merck) loaded columns. For final purification, recycling preparative HPLC (LC-908 W, Japan Analytical Industry Co. Ltd) was used with a column YMC ODS H-80 or L-80 (YMC, Japan).

NMR spectra

The ^{1}H NMR, ^{13}C NMR, HMQC, and HMBC spectra were recorded on Bruker AV-500 spectrometer equipped with a 5-mm dual *z*-gradient probe head at room temperature. The sample concentrations were about 2–10 mg in 0.5 ml of CD_3OD solvent. The chemical shifts values were reported in δ (ppm), referenced with respect to the residual solvent signal of CD_3OD, and coupling constants (*J*) were measured in Hz. The pulse conditions were as follows: for the ^{1}H NMR spectra, spectrometer frequency (SF) 500.13 MHz, acqusition time (AQ) 1.586 s, number of transients (NS) 128, spectral width (SW) 10 330.578 Hz, relaxation delay (D1) 1.0 s, flip angle (FA) 30°, pulse width (PW) 4.1 µs; for the ^{13}C NMR spectrum, SF 125.03 MHz, AQ 1.307 s, NS 32 130, SW 25 062.656 Hz, D1 1.0 s, FA 30°, PW 4.1 µs; for the DEPT 135° SF 125.03 Hz, AQ 0.683 s, NS 35 000, DS 2, D1 1.0 s, SW 23 980.814 Hz, DEPT 90° SF 125.03 Hz, AQ 0.6832 s, NS 1100, SW 23 980.814 Hz, DS 2, D1 1.0 s, for the COSY 45° spectrum, SF 500.13 MHz, AQ 0.1425 s, NS 32, SW 3591.954 Hz, D1 1.0 s; for the HMQC spectrum SF 500.13 MHz (^{1}H) and 125.03 MHz (^{13}C), AQ 0.142 s, NS 64, SW 3591.954 Hz, D1 1.0 s; for the HMBC spectrum, SF 500.13 Hz (^{1}H) and 125.03 MHz (^{13}C), AQ 0.142 s, NS 128, SW 3591.954 Hz, D1 1.5 s; for the NOESY spectrum SF 500.13 MHz, AQ 0.227 s, NS 16, SW 8.987 ppm, D1 1.5 s.

^{1}H NMR data were collected with 32k complex data points and were apodized with a Gaussian window function (lb = 0.5 and gb = 0) prior to Fourier transformation. In ^{1}H NMR spectra, the SW was 10 330.578 with a calculated digital resolution of 0.63 Hz/pt at 500 MHz.

^{13}C-jmod spectra with WALTZ 16 H decoupling were aqcuired using 64k data points. A SW of 25 062.656 was chosen, resulting in a digital resolution of 0.73 Hz/pt. Signal-to-noice enhancement was achieved by multiplication of the FID with an exponential window function (lb = 1.5 Hz).

Plant material

E. decipiens (Euphorbiaceae), was collected at the mountain Kandovan, north of Karaj, Iran, in 1998 and identified by Mr. Bahram Zehzad at the Department of Biological Sciences, Shahid Beheshti University, Eveen, Tehran. A voucher specimen (no. 98 112) has been deposited at the herbarium of Biology Department of Shahid Beheshti University, Eveen, Tehran.

Extraction and isolation

The dried and grinded plant material after grinding was extracted with acetone at room temperature. The extract was evaporated under *vacuo* and the residue (62 g) was diluted with water and then defatted by extraction with hexane. The residue (51 g) was extracted with chloroform (44 g). The remaining water extract was then extracted with ethyl acetate. The EtOAc extract (4 g) was fractionated by CC on silica gel and eluted with the mixtures of hexane/EtOAc and EtOAc/MeOH to obtain five subfractions (A–E).

Subfractions A and B were separately subjected to silica gel column by using gradient of hexane/EtOAc. 3-Hydroxy-4-methoxybenzoic acid (4 mg), and 6,7-dihydroxycoumarin (5 mg) were obtained from subfractions A and B, respectively. Polyamide column was used for the purification of subfraction C. Elution was carried out with 100% $CHCl_3$ to 20% MeOH/$CHCl_3$ to give luteolin. Subfraction D was applied to RP HPLC (L-80 column, MeOH/H_2O; 1 : 1, flow rate 4 ml/min) after polyamide column by using gradient solvent system from 100% $CHCl_3$ to 50% MeOH/$CHCl_3$ to obtain compounds **1** (4 mg) and **2** (2 mg). Subfraction E was also loaded

Table 1. ^{1}H, ^{13}C, HMBC, and COSY data for compound **1**

Position	^{1}H NMR	^{13}C NMR	HMBC	COSY
1	–	213.8	–	–
2	3.33 (overlapped)	49.0	C-1	–
3	–	26.4	–	–
4	5.45 (d, $J = 6.0$ Hz)	128.9	C-6, C-9	H-5
5	5.45 (m)	129.2	C-3	H-4, H-6
6	2.38 (m)	32.7	C-4, C-5	H-5, H-10
7α	2.07 (dd, $J = 13.7$, 1.5 Hz)	50.5	C-1	H-6, H-7β, H-10
7β	2.60 (dd, $J = 13.7$, 6.5 Hz)	50.5	C-1	H-7α, H-10
8a	3.55 (d, $J = 12.0$ Hz)	73.8	C-4, C-9, C-2, C-1′	H-8b
8b	4.27 (d, $J = 12.0$ Hz)	73.8	C-1′	H-8a
9	1.14 (s)	19.1	C-2, C-8	–
10	0.93 (d, $J = 7.1$ Hz)	19.2	C-6, C-7	H-6, H-7α, H-7β
1′	4.23 (d, $J = 7.8$ Hz)	100.3	C-8	H-2′
2′	3.15 (t, $J = 7.8$ Hz)	73.9	C-1′, C-4′	H-1′, H-3′
3′	3.38 (m)	79.9	C-1′, C-5′	H-2′, H-4′
4′	3.30 (m)	71.8	C-2′	H-3′, H-5′
5′	3.36 (m)	75.3	C-1′, C-3′	H-4′, H-6′a
6′a	3.84 (dd, $J = 11.8$, 1.4 Hz)	62.4	C-4′	H-6′b
6′b	3.67 (dd, $J = 11.8$, 4.8 Hz)	62.4	C-4′	H-6′a

Table 2. ^{1}H, ^{13}C, HMBC, and COSY data for compound **2**

Position	^{1}H NMR	^{13}C NMR	HMBC	COSY
1	–	212.3	–	–
2	2.50 (s)	58.8	C-1, C-4, C-7	–
3	–	24.8	–	–
4	1.53 (m) and 2.49 (m)	27.9	C-3, C-9	H-5
5	1.39 (m) and 1.92 (m)	34.9	C-4	H-4, H-6
6	1.8 (m)	37.3	C-10	H-5, H-10, H-7β
7α	2.22 (dd, $J = 12.0$, 2.4 Hz)	52.2	C-1, C-10	H-7β
7β	2.09 (t, $J = 12.0$ Hz)	52.2	C-1′	H-7α, H-6
8a	3.42 (d, $J = 12.0$ Hz)	74.5	C-2	H-8b, H-9
8b	4.28 (d, $J = 12.0$ Hz)	74.5	C-1	H-8a, H-1′
9	1.36 (s)	15.6	C-2, C-8	H-8a, H-5
10	1.01 (d, $J = 7.1$ Hz)	22.5	C-5, C-6, C-7	H-6
1′	4.18 (d, $J = 7.8$ Hz)	100.4	C-8	H-2′, H-8b
2′	3.21 (t, $J = 7.8$ Hz)	73.8	C-1′, C-4′	H-1′
3′	3.36 (m)	79.9	C-1′, C-5′	H-2′, H-4′
4′	3.25 (m)	72.0	C-2′	H-3′, H-5′
5′	3.36 (m)	74.5	C-1′, C-3′	H-4′
6′a	3.85 (dd, $J = 11.8$, 1.4 Hz)	62.5	C-4′	H-6′b
6′b	3.68 (dd, $J = 11.8$, 4.8 Hz)	62.5	C-4′	H-6′a

to polyamide column by using gradient solvent system from 100% $CHCl_3$ to 50% MeOH/$CHCl_3$). RP HPLC was used for the purification of the first fraction of subfraction E from polyamide column. From this fraction, apigenin-5-*O*-α-L-rhamnoside (4 mg) was isolated by using ODS column in RP HPLC (L-80 column, MeOH/H_2O; 1 : 1, flow rate 4 ml/min). The later fraction from polyamide column was subjected to sephadex LH-20 column by using H_2O and increasing amount of MeOH to obtain pinocembrin-7-*O*-rutinoside (3 mg).

(Z)-3,6-Dimethyl-3-(β-D-glucosylmethyl)cyclohept-4-enone ***(1)***

White needles, $[\alpha]_D^{20}$ −20° (MeOH, *c* 0.001). UV (MeOH) λ_{max} (log ε): 205 (4.50); IR ($CHCl_3$) ν_{max}: 3220, 3073, 2927, 2850, 1665, 1499, 1320, 1145 cm^{-1}; for ^{1}H NMR, ^{13}C NMR, and 2D NMR data (CD_3OD) (Table 1); EI MS *m/z* (relative intensity): 312 [M − H_2O] (10), 167 (80), 151 (100), 137 (45); HRFAB MS (−) ve [M − H]$^-$ *m/z* 329.1589, (calcd. for $C_{16}H_{26}O_7$, 330.1679); HREI MS *m/z* 312.1566 (calcd. for $C_{16}H_{24}O_6$, 312.1573), 167.1063 (calcd. for $C_{10}H_{15}O_2$, 167.1072), 151.1111 (calcd. for $C_{10}H_{15}O$, 151.1123), 137.0977 (calcd. for $C_9H_{13}O$, 137.0966).

3,6-Dimethyl-3-(β-D-glucosylmethyl)cycloheptanone ***(2)***

White needles, $[\alpha]_D^{20}$ −27° (MeOH, *c* 0.001). UV (MeOH) λ_{max} (log ε): 196 (3.70); IR ($CHCl_3$) ν_{max}: 3150, 2936, 2850, 1660, 1314 cm^{-1}; for ^{1}H NMR, ^{13}C NMR, and 2D NMR data (CD_3OD) (Table 2); EI MS *m/z* (relative intensity): 314 [M − H_2O] (10), 169 (60), 153 (30), 139 (25); HRFAB-MS [M − H]$^-$ *m/z* 331.1698 (calcd. for $C_{16}H_{28}O_7$, 332.1835); HREI MS *m/z* 169.1223 (calcd. for $C_{10}H_{17}O_2$, 169.1229), 153.1247 (calcd. for $C_{10}H_{17}O$, 153.1279), 139.1126 (calcd. for $C_9H_{15}O$, 139.1123).

Acid hydrolysis of compounds 1 and 2

Compounds **1** and **2** (4.0 and 2.0 mg) were hydrolyzed with 2 N HCl (2 ml) at 80 °C for 3 h. The mixture was extracted with $CHCl_3$ (3 × 2 ml). The aqueous layer was neutralized with NaOH (2 N) and evaporated to dryness. The dry powders were dissolved in pyridine (2 ml), and trimethylsilyl imidazole (1.5 ml) was added. The mixture was stirred and heated at 60 °C for 1 h. An aliquot (4 µl) of the supernatant was removed and directly subjected to GC analysis under the following conditions: A temperature gradient system was used for the oven, starting at 150 °C for 1 min and increased up to 280 °C at rate 3°/min, carrier gas N_2 (1 ml/min), injector and detector temperature 250 °C, split ratio 1 : 50. The configurations of D-glucose for compounds **1** and **2** were determined by comparison of the retentions times of the corresponding derivative with standard D-glucose, giving single peaks at 15.20 min for each compounds.

Acknowledgements

One of the authors (Ozlem Demirkiran) is grateful to the H.E.J. Research Institute of Chemistry, International Center for Chemical and Biological Sciences (Pakistan), for financial support, and providing access to the research facilities.

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