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AN ACYLATED SESQUITERPENE GLYCOSIDE FROM *MORTONIA GREGII*

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Key Word Index—*Mortonia gregii*; Celastraceae; 2-*O*-β-(2′,6′-diacetyl glucopyranosyl) desacetyl mortonol B.

Abstract—A new glycoside has been isolated from *Mortonia gregii* and identified by chemical and spectral means as 2-*O*-β-(2′,6′-diacetyl glucopyranosyl) desacetyl mortonol B.

INTRODUCTION

Previous work on the sesquiterpenoid constituents of *Mortonia gregii* (A. Gray) led to the identification of mortonins A–D and mortonol A [1–3]. Mortonol B (4b) has since been isolated from *M. hidalgensis* (Standl) [4]. Mortonins can be derived biogenetically from a polyhydroxylated dihydro agarofurane structure [1–3]. The present communication deals with the structural determination of a new glycoside 2-*O*-β-(2′,6′-diacetyl glucopyranosyl) desacetyl mortonol B, isolated from the polar fractions of a chloroform extract of *M. gregii*.

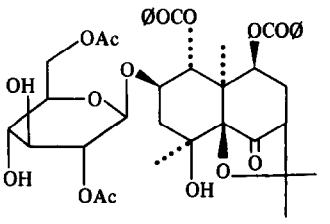
RESULTS AND DISCUSSION

The new glycoside (**1**), mp 263–265°, $[\alpha]_D^{20} = +45.3$, analysed for $C_{39}H_{46}O_{15}$. The mass spectrum showed the loss of the sugar moiety and peaks which correspond to the subsequent loss of two benzoic acid units. The IR spectrum contained bands at 1605 and 1590 cm^{-1}, which confirmed the presence of benzoate esters in **1**; it also showed a broad band at 3400–3450 cm^{-1} which was assigned to hydroxyl groups.

The ^1H NMR ($CDCl_3$) spectrum of **1** showed four singlets at δ1.30–1.75 (Table 1) which were attributed to four tertiary methyl groups. Two singlets (3H each) at δ1.85 and 2.1 were assigned to two acetate methyl groups. A broad absorption at δ3.0–4.5 was attributed to the protons of the sugar moiety. The signals observed at δ4.95 (*dd*, $J = 2$ and 6 Hz) and 5.90 (*d*, $J = 11$ Hz) (1H each), were assigned to the protons attached to the carbon atoms bearing the secondary ester groups. The ^1H NMR spectrum of **1** also showed aromatic signals due to two benzoate esters at δ7.25–8.2 (10H, *m*).

A comparison of the IR, ^1H NMR and ^{13}C NMR (Table 2) spectra of **1** with those of mortonol B, suggested that **1** was an acetylated monosaccharide derivative of mortonol B. The structure proposed for **1**, 2-*O*-β-(2′,6′-diacetyl glucopyranosyl) desacetyl mortonol B, was proved in the following manner. Acetylation of **1** gave the tetra-acetyl derivative **2** which still showed hydroxyl absorption in the IR spectrum. The ^1H NMR spectrum of **2** showed at δ2.65 a signal exchangeable with D_2O, which was attributed to the tertiary hydroxyl group at C-4 common to all the sesquiterpene derivatives isolated so far from *Mortonia* species [1–4]. Dehydration of the tetra-acetyl derivative **2** with $SOCl_2$ in pyridine, gave the anhydro derivative **3**, which did not show hydroxyl absorption in the IR spectrum. The ^1H NMR spectrum of **3** showed the presence of three tertiary methyl groups (Table 1). The newly formed exocyclic methylene was responsible for two broad singlets at δ5.2 and 5.65 (1H each). The formation of **3** proved that the tertiary hydroxyl group was at C-4. Acid hydrolysis of **1** gave the free aglycone, which was identified as 2-desacetyl mortonol B (**4a**), as it gave mortonol B (**4b**), on acetylation.

From these observations the structure of **1** was deduced as a diacetyl glucosyl derivative of 2-desacetyl mortonol B. The location of the two acetyl groups was established by MS and ^{13}C NMR spectral measurements of **1**. The



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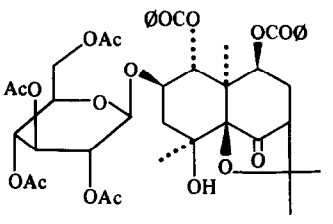

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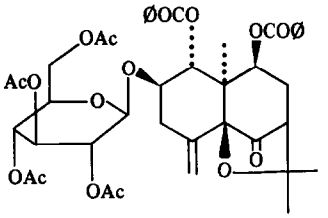
Contribution No. 662, Instituto de Química, U.N.A.M.

Table 1. ^{1}H NMR data for compounds **1**–**4** (80 MHz, $CDCl_3$, TMS as int. standard)

H	1	2	3	4a	4b
1	5.9 *d* (11)	5.9 *d* (11)	6.05 *d* (11)	5.75 *d* (10)	6.0 *d* (11)
2	3.75 *m*	—	—	3.75 *m* (1H)	5.20 *ddd* (10, 11, 6)
9	4.95 *dd* (2, 6)	4.9 *m*	5.0 *m*	5.0 *dd* (3, 6)	5.0 *dd* (2, 6)
C-4 Me	1.75 *s*	1.75 *s*	—	1.75 *s*	1.75 *s*
C-10 Me	1.30 *s*	1.25 *s*	1.47 *s*	1.30 *s*	1.30 *s*
C-11 $(Me)_2$	1.40 *s*	1.35 *s*	1.57 *s* (6H)	1.40 *s*	1.40 *s*
	1.55 *s*	1.55 *s*		1.55 *s*	1.55 *s*
OH	2.75 (1H)	2.70 (1H)	—	2.85 (1H)	2.75 (1H)
OAc	1.85 *s* (3H)	1.85 *s* (3H)	1.80 *s* (3H)	—	1.85 *s*
	2.10 *s* (3H)	1.90 *s* (6H)	1.90 *s* (6H)		
		2.0 *s* (3H)	2.0 *s* (3H)		
Arom.	7.20–8.15 (10H)	7.1–8.1 (10H)	7.15–8.1 (10H)	7.15–8.0 (10H)	7.25–8.2 (10H)
Glc_p	3.0–4.0 (9H)	3.25–3.95 (4H)	3.25–3.75 (4H)	—	—
		4.35–5.20 (5H)	4.70–5.10 (5H)		
Exocyclic–CH_2–	—	—	5.2 *s* (*br*) (1H)	—	—
			5.6 *s* (*br*) (1H)		



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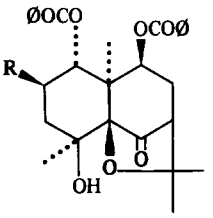

4a R = OH
4b R = OAc

presence of the [diacetyl glucopyranosyl]$^+$ ion peak at m/z 247 and the [M − diacetyl glucopyranosyl-O]$^+$ ion peak at m/z 491, indicated that the two acetyl groups were situated on the glucopyranosyl moiety. Furthermore it was observed that the ^{13}C NMR signal due to C-2′ of **1** was shifted downfield by δ2.26, whilst those of C-1′ and C-3′ were shielded by δ4.2 and δ1.2 respectively, in comparison with those due to the corresponding carbon atoms of methyl-β-D-glucopyranoside [5]. The same behaviour was shown by C-6′, since it was shifted downfield by δ2.0 and C-5′, which was shielded by δ3 in comparison with methyl-β-D-glucopyranoside. Application of the acetylation shift rule [6–9] to the displacements of the above signals showed that the two acetyl groups were located at C-2′ and C-6′ of the glucopyranosyl moiety.

A comparison of the ^{13}C NMR (Table 2) signals of the peracetates of D-glucopyranosyl glycosides found in the literature with the sugar moiety of the tetra-acetyl derivative **2** proved the nature of the sugar [10].

Table 2. ^{13}C NMR data of compounds **1**, **2** and **4b** (20 MHz, TMS as int. standard)

C	4b ($CDCl_3$)	1 (DMSO-d_6)	2 ($CDCl_3$)
1	72.23	72.15	72.02
2	68.99	73.30	73.01
3	44.37	42.79	44.95
4	70.95	69.89	70.74
5	85.77	84.92	85.50
6	211.04	212.67	211.32
7	55.34	55.54	55.38
8	33.14	32.59	33.10
9	72.08	72.15	72.02
10	55.84	55.54	55.83
11	78.55	77.46	78.72
12	22.24	23.05	22.36
13	17.88	17.36	17.93
14	23.63	23.33	23.58
15	29.62	28.60	29.63
OCO	165.53	164.82	165.66
OCO	165.41	163.60	163.94
CO	170.21	169.75	170.19
CO		168.89	169.07, 168.94
CH_3CO	20.76	20.92	
CH_3CO		20.37	
1		99.70	99.86
2		75.56	71.87
3		75.52	73.01
4		69.89	68.38
5		73.70	71.87
6		63.00	61.85

EXPERIMENTAL

Mps. are uncorr. Analyses were determined by Dr. Pascher, Bonn, Germany.

Isolation of 2-O-β-(2′,6′-*diacetyl glucopyranosyl*) *desacetyl mortonol B* (**1**). The dried leaves and stems of *Mortonia gregii* (A. Gray) (voucher deposited in the National Herbarium, MEXU 346253), collected near Matehuala (S.L.P.) (4 kg) were extracted as previously described [1–3]. The $CHCl_3$ extract was chromatographed on silica gel. Elution with $CHCl_3$–MeOH (9:1) gave 2-*O*-β-(2′,6′-diacetyl glucopyranosyl) desacetyl mortonol B (**1**). The analytical sample showed mp 263–265° (EtOAc); UV $\lambda_{max}^{95\%\ EtOH}$ nm: 228 ($\varepsilon = 41\,300$); $[\alpha]_D^{20}$ +45.3 (*c* 2.6; EtOH); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1760, 1735, 1700, 1600, 1580. [Found: C, 61.65; H, 6.29; 0, 32.0; $C_{39}H_{46}O_{15}$ requires: C, 62.0; H, 6.1; 0, 31.8%.] MS *m/z* (rel. int.): 491 (1.2), 473 (1.2), 369 (5), 247 (10), 105 (100), 43 (16), 187 (5), 127 (10); $C_{39}H_{46}O_{15}$ requires: $[M]^+$ at *m/z* 754.

Acetylation of **1**. Treatment of **1** with Ac_2O–C_5H_5N gave the tetra acetate, which was crystallized from $CHCl_3$–isopropyl ether. Mp 180–182°; UV $\lambda_{max}^{95\%\ EtOH}$ nm 228 ($\varepsilon = 40\,000$); $[\alpha]_D^{20}$ −36.73 (*c* 4.6; EtOH); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1760, 1740, 1710, 1600, 1580; MS *m/z* (rel. int.): 491 (1), 369 (15), 331 (15), 271 (5), 247 (5), 211 (1), 105 (100), 47 (17); $C_{43}H_{50}O_{17}$ requires: $[M]^+$ at *m/z* 838.

Dehydration of **2**. The tetra acetyl glycoside (**2**, 20 mg) in dry C_5H_5N (0.5 ml) was treated with $SOCl_2$ (0.1 ml) at 5° for 1 hr. After the usual work up, **3** was obtained, mp 186–187°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1710, 1600, 1580; MS *m/z* (rel. int.): 473 (10), 351 (5), 331 (20), 271 (8), 229 (5), 211 (5), 105 (100), 43 (15); $C_{43}H_{48}O_{16}$ requires: $[M]^+$ at *m/z* 820.

Hydrolysis of **1**. The glycoside **1** (50 mg) was hydrolysed by refluxing it with 18% HCl (3.6 ml) for 4 hr on the steam bath. After cooling, the resulting mixture was extracted with EtOAc. The organic layer was washed with $NaHCO_3$ (10%) and H_2O, dried, and the solvent removed under vacuum. The product obtained, desacetyl mortonol B, showed mp 94–97° from $CHCl_3$–isopropyl ether. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1760, 1720, 1600, 1590; ^1H NMR (80 MHz, $CDCl_3$, TMS as int. standard): δ 1.3 (*s*, 3H), 1.4 (*s*, 3H), 1.55 (*s*, 3H), 1.75 (*s*, 3H), 2.85 (*s*, 1H), 3.75 (*m*, 1H), 5.00 (*dd*, *J* = 6 and 3 Hz, 1H), 5.75 (*d*, *J* = 10 Hz, 1H), 7.15–8.0 (*m*, 10H); MS *m/z*: 508 $[M]^+$, 386, 264, 105 (100%).

Acetylation of desacetyl mortonol B. Desacetyl mortonol B (**4a**) (20 mg) was treated with dry C_5H_5N (0.5 ml) and Ac_2O (0.5 ml). Usual work up gave the acetyl derivative identified as mortonol B by comparison with an authentic sample.

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