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CYCLOARTANONE DERIVATIVES FROM *VIGUIERA DENTATA*

FENG GAO, TOM J. MABRY, FERDINAND BOHLMANN* and JASMIN JAKUPOVIC*

Department of Botany, University of Texas at Austin, Austin, TX 78713-7640, U.S.A.; *Institute of Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany

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Key Word Index—*Viguiera dentata*; Compositae; triterpenoids; cycloartanone derivatives.

Abstract—In addition to previously known compounds, three new cycloartanone derivatives were obtained from the aerial parts of *Viguiera dentata* collected in Mexico.

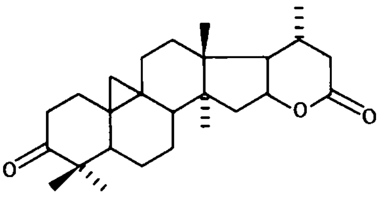
INTRODUCTION

A Bolivian population of *Viguiera dentata* afforded *ent*-kaurenic acid, 9,11-dehydro-*ent*-kaurenic acid and linoleic acid [1]. A collection of *V. dentata* from Mexico yielded manool, *ent*-kaurenic acid, *ent*-kauranol, grandifloric acid, angeloylgrandifloric acid, 15-oxo-*ent*-kaurenic acid, trachylobanic acid, spathulenol and diversifolin [2]. In addition to these known compounds, this Mexican population also produced three new cycloartanone derivatives.

RESULTS AND DISCUSSION

A polar fraction (20% EtOAc–hexane eluate) from silica gel column chromatography afforded as a stable compound cycloartanone lactone (**1**) in a yield of 0.002%. Compound **1**, which was readily soluble in chloroform, but had poor solubility in ether and methanol, gave an intense molecular ion of m/z 398 (100%) in its EIMS in accord with $C_{26}H_{38}O_3$. In its IR spectrum, two carbonyl groups were clearly indicated by absorptions at 1700 (ketone) and 1740 cm^{-1}. The latter data together with the absorption at 1250 cm^{-1} indicated a lactone group. The ^{13}C NMR spectrum of **1** recorded at 67.9 MHz showed twenty-six carbon signals. While two downfield signals appeared at δ174.43 and 216.12 in accord with two carbonyl groups, two significant upfield singlets at δ20.74 and 26.33 were characteristic for a C-9,C-10 cyclopropanyl function typical of cycloartanone-type compounds [3]. In the region of δ60–90, there is only one oxygen-bearing carbon signal (δ80.58, *d*) which together with the carbonyl signal at δ174.43 was in accord with a lactone moiety. In the ^{1}H NMR spectrum of **1**, the cyclopropanyl methylene signals appeared at δ0.59 and 0.85. Signals for H-2, H-16, H-17 and H-20 exhibited similar chemical shifts to the signals for the same protons in **3**, a compound recently isolated from *Balsamorhiza sagittata* [4]. The 16β-configuration could be deduced by comparing coupling constants of H-16α (J = 5, 8, 8 Hz) with published data [4, 5]. The coupling constants of H-17 and H-20 (8 Hz) were not the same as those of **3** due to the lactone ring closure. Inspection of Dreiding models indicated a C-20α methyl (Table 1). All other ^{1}H NMR and ^{13}C NMR data were also in accord with structure **1**.

Compound **2** had a molecular ion of m/z 484 for $C_{31}H_{48}O_4$ and the IR spectrum indicated only one carbonyl group was present (1700 cm^{-1}). Comparison of the ^{1}H NMR spectra of **1** and **2** indicated that in addition



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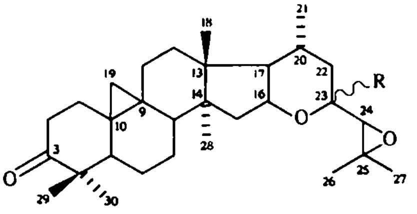

2 **4** **5**

R β-OMe β-OH α-OH

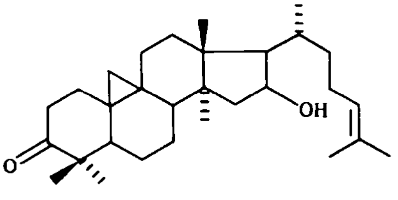

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Table 1. ^{1}H NMR data of compounds 1 and 2 (400 MHz, CDCl$_3$)

H No.	1	2*
1α	1.86 *ddd*	1.86
1β	1.56 *ddd*	1.56
2α	2.30 *ddd*	2.31
2β	2.71 *ddd*	2.71
5	1.16	1.16
6α	1.69 *ddd*	1.69
7α	1.13 *m*	1.12
7β	1.42 *m*	1.42
8	1.69	1.62
11β	1.23 *ddd*	1.18
16	4.73 *ddd*	4.24
17	1.97 *t*	1.64
18†	1.13 *s*	1.04
19α	0.59 *d*	0.58
19β	0.85 *d*	0.83
20	2.07 *ddq*	2.08
21†	1.07 *d*	0.90
22α	2.12 *t*	1.63
22β	2.39 *dd*	1.92
24	—	2.83 *s*
26†	—	1.43 *s*
27†	—	1.33 *s*
28†	1.04 *s*	1.11
29†	1.09 *s*	1.09
30†	0.93 *s*	0.89
OMe†	—	3.30 *s*

J(Hz): 1α,1β = 1α,2β = 2α,2β = 14; 1α,2α = 4; 1β,2α = 2.5; 1β,2β = 6; 5,6α = 6α,7α = 4; 6α,6β = 13; 7α,8 = 13; 7β,8 = 4; 15,15′ = 13.5; 15α,16 = 5; 15β,16 = 8; 16,17 = 8; 17,20 = 8; 19α,19β = 4; 20,21 = 7; 20,22α = 14; 20,22β = 2; 22α,22β = 14.

*Multiplicities are not reported if they are identical with the preceding column.

†Intensity three protons.

Table 2. ^{13}C NMR data of compounds 1 and 2 (67.9 MHz, CDCl$_3$)*

C No.	1	2
1	33.31 *t*	33.34 *t*
2	37.33 *t*	37.39 *t*
3	216.12 *s*	216.35 *s*
4	50.13 *s*	49.66 *s*
5	48.21 *d*	48.34 *d*
6	21.12 *t*	21.28 *t*
7	25.91 *t*	26.03 *t*
8	47.38 *d*	47.40 *d*
9	20.74 *s*	20.73 *s*
10	26.33 *s*	26.37 *s*
11	26.07 *t*	26.27 *t*
12	31.94 *t*	32.98 *t*
13	44.70 *s*	44.53 *s*
14	46.64 *s*	45.88 *s*
15	43.57 *t*	43.03 *t*
16	80.58 *d*	71.17 *d*
17	54.12 *d*	55.94 *d*
18	20.49 *q*	20.19 *q*
19	30.01 *t*	30.15 *t*
20	27.00 *d*	25.06 *d*
21	21.34 *q*	20.47 *q*
22	38.55 *t*	40.65 *t*
23	174.43 *s*	99.80 *s*
24	—	67.46 *d*
25	—	56.90 *s*
26	—	18.74 *q*
27	—	25.62 *q*
28	19.60 *q*	19.46 *q*
29	22.13 *q*	22.13 *q*
30	20.46 *q*	20.74 *q*
OMe	—	50.15 *q*

*Multiplicities were assigned by DEPT spectrum. Chemical shifts were co-related with similar structures [3].

to a methoxy signal, there were three additional singlets in the spectrum of 2 (δ1.33, 3H; 1.43, 3H; 2.83, 1H) for a C-24,25 epoxy system. In the ^{13}C NMR spectrum of 2, an acetal carbon was confirmed (δ99.80, s). All other ^{1}H NMR and ^{13}C NMR data (Table 2) were in accord with structure 2.

From the 17.5% EtOAc–hexane eluate of the silica gel column, we obtained an unstable mixture of 4 and 5, which could only be purified and identified by transforming them into 2. Moreover, periodic acid oxidation of the two compounds gave 1. The EIMS of both 4 and 5 exhibited a molecular ion at *m/z* 470 for $C_{30}H_{46}O_4$. Strong evidence for the presence of a free hydroxyl group in both was indicated by the ion at *m/z* 452 $[M - H_2O]^+$ (11%) and by the IR band at 3440 cm^{-1}. In the ^{1}H NMR spectra of 4 and 5, the only signals significantly different from those found for 2 were those for H-21 (δ0.95, doublet, for 4; δ0.96, *d*, for 5) and H-26 (δ1.51, *s*, for 4; 1.43 for 5) (H-22 was obscured). The fact that 4 and 5 could be easily converted into 2 is not surprising due to the hemi-ketal function at C-23. Similar results have been reported for a compound from *Boswellia treerana* [5].

EXPERIMENTAL

Viguiera dentata (Cav) Spreng was collected in Chiapas, 28.5 km east of Tuxtla Gutierrez, Mexico, by D. Gage and J. Norris on December 29, 1983. The plant was identified by B. L. Turner (Department of Botany, The University of Texas at Austin). A voucher specimen (G.N. 1179) is deposited in the Herbarium of the University of Texas at Austin.

Compound 1. Some of the isolation and purification steps have been reported elsewhere [2]. Compound 1 (40 mg) gave colourless prisms with mp 229–230° (from EtOAc or MeOH). IR ν_{max}^{KBr} cm^{-1}: 1700 (ketone); 1740, 1250 (lactone); 1460; 1390; 1370 (Me); 1190, 1150, 1120, 1080, 1040. EIMS (probe 70 eV), *m/z* (rel. int.): 398 $[M]^+$ (100), 383 $[M - Me]^+$ (81), 260 $[M - C_9H_{14}O]^+$ (82), 245 $[M - 138 - Me]^+$ (40).

Compounds **2**, **4** *and* **5**. From the Sephadex LH-20 column, 268 mg of a mixture of **4** and **5** were obtained as white needles, mp 164–167° (EtOAc). IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1700 (ketone). EIMS (probe 70 eV) *m/z* (rel. int.): 470 $[M]^+$ (3), 452 $[M - H_2O]^+$ (11), 437 $[M - H_2O - Me]^+$ (15), 398 $[M - C_4H_8O]^+$ (21), 383 $[398 - Me]^+$ (48), 260 $[398 - C_9H_{14}O]^+$ (30), 245 $[260 - Me]^+$ (28), $[43]^+$ (100). After the mixture was boiled in MeOH for 10 min the product was eluted through Sephadex LH-20 and compound **2** was obtained. After repeated crystallization from EtOAc and MeOH of the obtained material, 150 mg of white needles were obtained, mp 211–212°. IR ν_{max}^{KBr} cm^{-1}: 1700 (ketone), 1450, 1380, 1110, 1050, 1000, 910. EIMS (probe 70 eV) *m/z* (rel. int.): 484 $[M]^+$ (5), 469 $[M - Me]^+$ (4), 452 $[M - MeOH]^+$ (65), 437 $[452 - Me]^+$ (41), 413 $[M - C_4H_7O]^+$ (100).

Oxidation of **4** *and* **5**. Compounds **4** and **5** (2 mg) were reacted with 10 mg HIO_4 in Et_2O for 30 min. TLC afforded 1.3 mg of **1**, identical with an authentic sample (^1H NMR and TLC).

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SPIROSTANOL GLYCOSIDES FROM *AGAVE CANTALA*

G. PANT*, O. P. SATI, K. MIYAHARA† and T. KAWASAKI†

Department of Chemistry, University of Garhwal, Srinagar (U.P.), 246 174, India; †Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka, 573-01, Japan

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Key Word Index—*Agave cantala*; Agavaceae; saponins; spirostanol glycosides; schistosomiasis; *Biomphalaria glabrata*.

Abstract—Two spirostanol glycosides, cantalasaponins -2 and -4 were isolated from the methanolic extract of the rhizomes of *Agave cantala* and were characterized. The first glycoside was found to be lethal against *Biomphalaria glabrata*, the snail vector of the disease schistosomiasis, at a concentration of 7 ppm.

INTRODUCTION

Agave species are reported to have anticancer [1] and piscicidal [2] properties. Steroidal sapogenins [3] and saponins [4–6] have been reported from the leaves and fruits of *A. cantala*. We have shown that the rhizomes of this plant contain sapogenins [7], a hongguanggenin diglucoside [8] and other steroidal saponins. This paper describes the isolation and characterization of two hecogenin glycosides (**1** and **3**) from the methanolic extract of the rhizomes. Compound **1** was found to be molluscicidal against *Biomphalaria glabrata* at a concentration of 7 ppm.

RESULTS AND DISCUSSION

Repeated column chromatography of the methanolic extract of the rhizomes gave cantalasaponins-2 (**1**), -3 (**2**), -4 (**3**) and -5 (**4**). Compounds **1** and **3** belonged to the 25*R* spirostane series (IR).

FD-mass spectrometry showed that the M_rs of **1** and **3**

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*To whom correspondence should be addressed.