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NEW TRITERPENES FROM *TRICHOCEREUS BRIDGESII*

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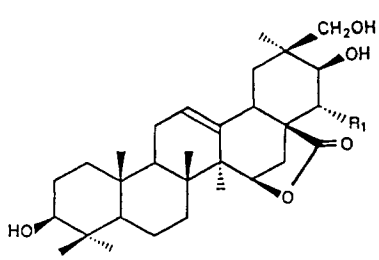
ABSTRACT.—Two known triterpenes, lupeol and lupenone, were isolated from *Hertrichocereus beneckei* as the wax constituents, and two new triterpenes, bridgesigenin A [**1**] and bridgesigenin B [**2**], were isolated from *Trichocereus bridgesii*.

We have been interested in identification and characterization of saponins of cacti, the triterpene sapogenins of which were first studied by Djerassi *et al.* (1) during the period 1953–1956. Only a few reports (2–4) have been recorded since then in this field. In the present paper, we report the occurrence of two known triterpenes, lupeol and lupenone from *Hertrichocereus beneckei* Backbg. [=*Lemaireocereus beneckei* (Ehrbg.)Ber.] (Cactaceae) and two new triterpenes, bridgesigenin A [**1**] and bridgesigenin B [**2**], from *Trichocereus bridgesii* (Salm-Dyck) Britt. et Rose (Cactaceae).

Djerassi *et al.* (1) first studied the constituents of *H. beneckei*, distributed in Mexico, to identify queretaroic acid and oleanolic acid. The stem of this cactus, covered with floury white wax, was washed with $CHCl_3$ to obtain the triterpenes, which were then identified as lupeol and lupenone by ^{13}C-nmr and other physicochemical data in comparison with published data (5,6). Queretaroic acid and oleanolic acid were also isolated from the hydrolyzed mixture of the saponin fraction.



1 R_1=H
2 R_1=OH

Bridgesigenin A [**1**] was isolated (see Experimental) from *T. bridgesii*. The molecular formula of **1** was established by hreims measured on the ion at *m/z* 486 $[M]^+$ (found 486.3337, calcd for $C_{30}H_{46}O_5$, 486.3333). The ^{13}C-nmr spectrum (Table 1) in C_5D_5N contained signals arising from six Me groups and other signal patterns of the A/B ring of the oleanane skeleton as deduced from DEPT experiments. This was also supported by the retro-Diels-Alder fragment ion at *m/z* 207 in the eims. The oleanane skeleton generally possesses seven Me groups, and one of the methyls in bridgesigenin A [**1**] seemed to be oxidized into a carbinol. The 30-hydroxymethyl was assigned by a positive nOe, when H-18 was irradiated at δ 2.92, which showed a cross peak with H-12 by NOESY experiments.

^{1}H-nmr, ^{13}C-nmr, and DEPT experiments of **1** showed the presence of three secondary hydroxyls (δ 78.0, 74.5, and 80.1). The signal of C-3 at δ 78.0 had a long range ^{1}H-^{13}C correlation peak with protons of C-23, while the coupling constant values (J = 5.7, 9.9 Hz) between H-3 and the C-2 methylene protons were indicative of the β configuration of the hydroxyl group at C-3. In comparison with ^{13}C-nmr data of oleanolic acid, the carbon at C-17 was slightly shifted, while the carbon at C-20 was largely shifted to downfield. Accordingly a sec-

TABLE 1. ^{13}C-nmr Chemical Shifts (100 MHz, C_5D_5N) of Oleanolic Acid and Compounds **1** and **2**.

Carbon	Compound		
	Oleanolic acid	**1**	**2**
C-1	38.9	39.4	39.4
C-2	28.2	28.0	28.0
C-3	78.0	78.0	78.0
C-4	39.4	39.4	37.2
C-5	55.8	55.8	55.9
C-6	18.8	18.5	18.5
C-7	33.3	33.8	33.8
C-8	39.8	40.5	40.6
C-9	48.1	48.6	48.7
C-10	37.4	37.4	37.2
C-11	23.3	23.6	23.6
C-12	122.5	127.9	128.1
C-13	144.8	138.2	138.1
C-14	42.0	45.9	46.5
C-15	28.3	80.1	80.2
C-16	23.8	34.6	27.8
C-17	46.7	46.5	52.4
C-18	42.0	41.7	41.6
C-19	46.7	42.5	42.0
C-20	31.0	41.0	41.4
C-21	34.3	74.5	79.6
C-22	33.3	36.7	69.7
C-23	28.7	28.7	28.7
C-24	16.5	16.5	16.5
C-25	15.5	16.3	16.3
C-26	17.5	19.8	19.8
C-27	26.2	25.3	25.4
C-28	180.2	179.5	178.9
C-29	33.3	25.1	25.3
C-30	23.8	63.2	63.8

ondary hydroxyl seemed to be at C-21. The carbon signal at δ 74.5 showed a correlation with the double doublet proton signals at δ 3.97 by ^{1}H-^{13}C COSY experiments, while it correlated with the C-29 methyl protons at δ 1.53 by long range ^{1}H-^{13}C COSY experiments. The coupling constant value (7.8 Hz) between H-21 and H-22 represented the β-hydroxyl at C-21. The doublet of a proton (δ 4.61) attached to the carbon at δ 80.1 correlated with the protons at δ 2.75 and 1.95 by ^{1}H-^{1}H COSY experiments. Long range ^{1}H-^{13}C COSY showed the correlations between C-13 at δ 138.2 and the C-27 Me protons at δ 1.22, and between the latter and C-15 at δ 80.1, the C-16 methylene protons at δ 1.95 and 2.75, and C-16 at δ 34.6. These results revealed that the final secondary hydroxyl is located at C-15. The coupling behavior at H-15 may show that the dihedral angle between this and one of the methylene protons at C-16 is almost 90°. The H-15 signal correlated with the carbonyl carbon at 179.5 by long range ^{1}H-^{13}C COSY experiments. This revealed that bridgesigenin A [**1**] has a five-membered lactone ring. This structure was also supported by the ir absorption spectrum on the carbonyl at 1760 cm^{-1}. On the basis of these results, the structure of **1** was elucidated.

Bridgesigenin B [**2**] was isolated from *T. bridgesii*. The molecular formula of **2** was established by hreims measurement on the ion at *m/z* 502 $[M]^+$ (found 502.3286, calcd for $C_{30}H_{46}O_6$, 502.3282). The ^{13}C-nmr data (Table 1) of **2** was almost overlapped with that of **1** except for the C-16, -17, -21, and -22 signals, while H-21 at δ 3.84 of **2** showed a doublet in contrast to a double doublet in **1**. The proton at δ 4.69 correlated with two protons at δ 2.53 and 2.92 (H-16) by ^{1}H-^{1}H COSY, and this also had a cross peak with the carbon at δ 80.2 by ^{1}H-^{13}C COSY. The latter showed a correlated cross peak with the Me protons at δ 1.27 (C-27) by long range ^{1}H-^{13}C COSY experiments.

On the basis of these results, the configuration of the hydroxyl at C-15 was assigned β. The lactone structure was confirmed by the long range ^{1}H-^{13}C COSY spectrum between the H-15 and C-28 and the ir absorption spectrum at 1760 cm^{-1}. The proton at δ 3.84 was coupled with the proton at δ 4.84, while the latter correlated with the carbon at 69.7 by ^{1}H-^{13}C COSY experiments, and this had a cross peak to the Me protons, δ 1.57, at C-29 by long range ^{1}H-^{13}C COSY. These results led to the assignment of the proton, δ 3.84 at C-21, and δ 4.84 at C-22. Based on the coupling constant (J = 10.0, d) between H-21 and H-22, the configurations of hy-

droxyls at C-21 and C-22 were assigned to be β and α, respectively. Consequently, the structure of bridgesigenin B [**2**] was formulated as shown.

EXPERIMENTAL

PLANT MATERIALS.—Living specimens of *H. beneckei* and *T. bridgeii* were cultivated originally in the Research Institute of Evolutionary Biology (Setagaya-ku, Tokyo, Japan). The plants were also grown by Izu Natural History Park (Itoh, Shizuoka, Japan) and Japan Cactus Planning Co. (Fukushima City, Fukushima, Japan). These cacti were identified by Dr. Norio Kondo and Dr. Hiroshi Yuasa. The specimens are deposited at the Research Institute of Evolutionary Biology, Setagaya-ku, Tokyo, Japan.

INSTRUMENTS.—Mp's were determined with a Yanagimoto MP micro mp apparatus. The ir spectra were measured with a JASCO A-102 ir spectrophotometer. ^{1}H- and ^{13}C-nmr spectra were recorded using a JEOL GSX-400 (^{1}H 400 and ^{13}C 100 MHz) spectrometer in $CDCl_3$, or C_5D_5N with TMS as an internal standard. The chemical shifts are expressed in ppm (Table 1). The $[\alpha]_D$ values were determined with a JASCO DIP-140 digital polarimeter. Cc was carried out on 70–230 mesh Si gel (Merck). Hplc was performed using an SSC-3100-J pump with an Oyo-Bunko Uvilog 7 uv detector. Hrms and eims spectra were obtained using a JEOL JMS-DX 302.

EXTRACTION AND ISOLATION OF BRIDGESIGENINS A [**1**] AND B [**2**].—Dry *T. bridgesii* (141.5 g) was extracted with $CHCl_3$ to remove free triterpenes and then extracted with MeOH. The MeOH extract (21.3 g) was chromatographed on Si gel [$CHCl_3$-MeOH-H_2O (30:12:1)] to give the saponin fraction. The fraction was hydrolyzed with3.5 N HCl at 110° for 2.5 h. The precipitates (980 mg) produced were subjected to cc on Si gel [hexane-Me_2CO (3:1→1:1)] to give two compounds. These were further purified by hplc on a Si gel column (Nucleosil 50-5, 1 × 25 cm), eluting with $CHCl_3$-MeOH (10:1) to give bridgesigenins A [**1**] (53.5 mg) and B [**2**] (9.3 mg). Bridgesigenin A [**1**]: eims *m/z* 486, 453, 279, 207, 189; mp >300°; $[\alpha]^{20}_D$ −31.4° [*c* = 0.082, $CHCl_3$-MeOH (5:3)]; ir ν max, 3300, 2950, 1760, 1660, 1200, 1115. Bridgesigenin B [**2**]: eims *m/z* 502, 484, 464, 207, 189; mp >300°; $[\alpha]^{20}_D$ −29.7° [*c* = 0.176, $CHCl_3$-MeOH (3:1)]; ir ν max 3400, 2925, 1760, 1630, 1100, 1030.

EXTRACTION AND ISOLATION OF LUPENONE AND LUPEOL.—Dry *H. beneckei* (68.7 g) was extracted with $CHCl_3$. The extract (2.5 g) was chromatographed on Si gel [hexane-EtOAc (100:1→0:1)] to give two main compounds. Each compound was purified by hplc using a Si gel column (Nucleosil 50-5, 1 × 25 cm) with solvent system ($CHCl_3$-MeOH (500:1). The compounds were identified by mp, mass, ir, and nmr data as lupenone (80.4 mg) and lupeol (29.2 mg).

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