Journal of Natural Products
Vol. 58, No. 12, pp. 1913-1914, December 1995

A NEW TRITERPENE FROM *RATHBUNIA ALAMOSENSIS*

TAKAOMI TAKIZAWA, KAORU KINOSHITA, KIYOTAKA KOYAMA, KUNIO TAKAHASHI,*

Department of Pharmacognosy and Phytochemistry, Meiji College of Pharmacy, 1-22-1 Yato-cho, Tanashi City, Tokyo 188, Japan

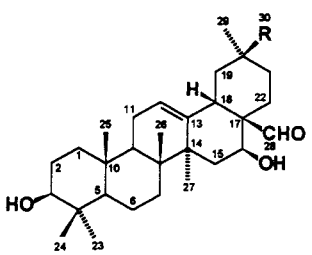
NORIO KONDO, and HIROSHI YUASA

Research Institute of Evolutionary Biology, 4-28, 2-Chome, Kamiyoga, Setagayaku, Tokyo 158, Japan

ABSTRACT.—A new triterpene, alamosenogenin [**1**], was isolated from the hydrolysate of a methanol extract of *Rathbunia alamosensis*, and its structure established by spectral methods.

Several new triterpenes, namely, bridgesigenins A and B, from *Trichocereus bridgesii* (1), pachanol A (which has a new skeleton named pachanane), from *Trichocereus pachanoi* (2), and 16β-hydroxystellatogenin and machaerogenin, from *Stenocereus stellatus* and *Machaerocereus eruca* (3), have been isolated in an ongoing study by our group.

In the present paper, we report the isolation of a new triterpene, alamosenogenin [**1**], and a known triterpene, gummosogenin [**2**] from a hydrolysate of the glycosides of the aerial parts of *Rathbunia alamosensis* (Coult.) Britt. & Rose (Cactaceae). Alamosenogenin [**1**] mp 232–235°, $[\alpha]^{20}D$ +46.2° (c=0.084, $CHCl_3$) exhibited a molecular formula of $C_{30}H_{48}O_4$, established by hrms measured on the molecular ion at m/z 472 $[M]^+$ (found 472.3560, calcd for $C_{30}H_{48}O_4$, 472.3554). The most characteristic eims fragment was observed at m/z 207, representing the retro-Diels-Alder cleavage of ring C of **1**. The ^{13}C-nmr values of the ring-A, -B, and -C carbons of **1** were assigned by comparison with those of gummosogenin [**2**]. Compound **2** possesses seven methyl groups, and one of the methyls in **1** appeared to have been oxidized to a carbinol by analysis of the ^1H-^{13}C COSY nmr spectrum (δ 3.84, 3.91). Five methyl signals at δ 0.89, 0.92, 1.03, 1.23, and 1.37 were assigned to H_3-25, H_3-26, H_3-24, H_3-23, and H_3-27, respectively, by a long-range ^1H-^{13}C COSY nmr experiment. The remaining methyl signal (δ 1.18) was assigned to H_3-29 or H_3-30. In the ^{13}C-nmr spectrum of **1** in C_5D_5N, the signal of C-20 (δ 35.6) was shifted downfield (5.0 ppm) and the signals of C-19 (δ 41.9) and C-21 (δ 28.9) were shifted upfield (4.5 and 4.4 ppm) as compared to analogous signals of gummosogenin [**2**]. The proton at δ 3.21 (H-18) correlated with the aldehyde proton at δ 10.41 (H-28), and this also had a cross-peak with the hydroxy methyl proton (δ 3.84) as indicated by a NOESY nmr experiment. Therefore, the carbinol protons (δ 3.84 and 3.91) were assigned to H_2-30. On the basis of these results, the structure of alamosenogenin was determined as **1**.



1 R=CH_2OH
2 R=Me

Spectroscopic data are also reported from the present investigation for gummosogenin [**2**].

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps were determined on a Yanagimoto micro-melting point apparatus. The ir spectra were measured with a Jasco A-102 ir spectrophotometer. The ^1H- and ^{13}C-nmr spectra were recorded using a JEOL GSX-400 (^1H at 400 and ^{13}C at 100 MHz) spectrometer in C_5D_5N with TMS as internal standard.

Chemical shifts are recorded in ppm. The optical rotations 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 were obtained using a JEOL JMS-DX 302 mass spectrometer.

PLANT MATERIAL.—*Rathbunia alamosensis* was cultivated originally at the Research Institute of Evolutionary Biology, Setagaya-ku, Tokyo, Japan. The plants wre also grown by the Izu National History Park, Itoh, Sizuoka, Japan, and the Japan Cactus Planning Co, Fukushima City, Fukushima, Japan. The aerial parts of *R. alamosensis* were collected in March 1993. The cacti were identified by Drs. Norio Kondo and Hiroshi Yuasa, and the specimens are deposited at the Research Institute of Evolutionary Biology, Setagaya-ku, Tokyo, Japan.

EXTRACTION AND ISOLATION.—Pulverized, dried *R. alamosensis* plant material (91.6 g) was extracted with $CHCl_3$ to remove free triterpenes and then extracted with MeOH. After concentration of the MeOH extract *in vacuo*, approximately 16.6 g of residue remained. This residue (4.39 g) was chromatographed on Si gel [$CHCl_3$-MeOH-H_2O (30:12:1)] to give a saponin fraction (2.43 g). The fraction was hydrolyzed with 1 N HCl at 110° for 2.5 h. The precipitates (526 mg) produced were subjected to cc on Si gel [$CHCl_3$-MeOH (100:1→MeOH only)] to yield two compounds, which were further purified by cc on Si gel ($CHCl_3$-MeOH, 100:1) to afford **1** (13.4 mg) and **2** (145 mg).

Alamosenogenin [**1**].—White powder; mp 232–235°; $[\alpha]^{20}D$ +46.2° (*c*=0.084, $CHCl_3$); ir (KBr) ν max 3425, 2950, 1715, 1460, 1385, 1023 cm^{-1}; ^1H nmr (C_5D_5N, 400 MHz) δ 10.41 (1H, s, H-28), 5.43 (1H, t, *J*=3.6 Hz, H-12), 4.82 (1H, dd, *J*=11.7 and 4.5 Hz, H-16), 3.91 (1H, d, *J*=10.3 Hz, H-30), 3.84 (1H, d, *J*=10.3 Hz, H-30), 3.43 (1H, dd, *J*=10.1 and 5.8 Hz, H-3), 3.21 (1H, dd, *J*=12.9 and 5.8 Hz, H-18), 2.60 (1H, m, H-22), 2.20 (1H, t, *J*=11.7 Hz, H-15), 1.37 (3H, s, H_3-27), 1.23 (3H, s, H_3-23), 1.18 (3H, s, H_3-29), 1.03 (3H, s, H_3-24), 0.92 (3H, s, H_3-26), 0.89 (3H, s, H_3-25); ^{13}C nmr (C_5D_5N, 100 MHz) δ 208.1 (s, C-28), 142.7 (s, C-13), 123.3 (d, C-12), 78.0 (d, C-3), 65.6 (t, C-30), 64.5 (d, C-16), 55.7 (d, C-5), 53.5 (s, C-17), 47.2 (d, C-9), 44.0 (s, C-14), 41.9 (t, C-19), 41.7 (d, C-18), 39.9 (s, C-8), 39.4 (s, C-4), 38.9 (t, C-1), 38.0 (t, C-15), 37.2 (s, C-10), 35.6 (s, C-20), 33.3 (t, C-7), 28.9 (t, C-21), 28.7 (q, C-23), 28.2 (q, C-29), 28.0 (t, C-2), 26.7 (q, C-27), 23.7 (t, C-11), 23.5 (t, C-22), 18.7 (t, C-6), 17.4 (q, C-26), 16.5 (q, C-24), 15.6 (q, C-25); eims *m/z* $[M]^+$ 472, 454, 425, 246, 217, 214, 207, 199, 135; hreims *m/z* $[M]^+$ 472.3560 ($C_{30}H_{48}O_4$ requires 472.3554).

Gummosogenin [**2**].—Colorless needles ($CHCl_3$); mp 251–257°; $[\alpha]^{20}D$ +26.5° (*c*=0.150, $CHCl_3$); ir (KBr) ν max 3550, 2950, 1710, 1390, 1030 cm^{-1}; ^1H nmr (C_5D_5N, 400 MHz) δ 10.35 (1H, s, H-28), 5.41 (1H, t, *J*=3.6 Hz, H-12), 4.70 (1H, dd, *J*=11.9 and 4.4 Hz, H-16), 3.42 (1H, dd, *J*=10.3 and 5.6 Hz, H-3), 3.05 (1H, dd, *J*=13.9 and 4.4 Hz, H-18), 2.52 (1H, m, H-22), 2.14 (1H, t, *J*=12.5 Hz, H-15), 1.31 (3H, s, H_3-27), 1.21 (3H, s, H_3-23), 1.02 (3H, s, H_3-24), 0.94 (3H, s, H_3-30), 0.92 (3H, s, H_3-26), 0.91 (6H, s, H_3-25, H_3-29); ^{13}C nmr (C_5D_5N, 100 MHz) δ 208.1 (s, C-28), 142.7 (s, C-13), 123.2 (d, C-12), 78.0 (d, C-3), 63.9 (d, C-16), 55.7 (d, C-5), 53.4 (s, C-17), 47.2 (d, C-9), 46.4 (t, C-19), 43.9 (s, C-14), 42.1 (d, C-18), 39.9 (s, C-8), 39.4 (s, C-4), 38.9 (t, C-1), 37.9 (t, C-15), 37.2 (s, C-10), 33.3 (t, C-21), 33.3 (t, C-7), 33.0 (q, C-29), 30.6 (s, C-20), 28.7 (q, C-23), 28.1 (t, C-2), 26.6 (q, C-27), 23.8 (t, C-11), 23.7 (q, C-30), 23.5 (t, C-22), 18.7 (t, C-6), 17.3 (q, C-26), 16.5 (q, C-24), 15.6 (q, C-25); eims *m/z* $[M]^+$ 456, 438, 409, 230, 218, 201, 190, 175, 131; hreims *m/z* $[M]^+$, 456.3606 ($C_{30}H_{48}O_3$ requires 456.3605).

ACKNOWLEDGMENTS

This work was supported by a Sasakawa Scientific Research Grant from the Japan Science Society. The authors thank Mr. Toyoji Goto and Toshiaki Katagiri, of the Izu Natural History Park, for the supply of cacti.

LITERATURE CITED

1. K. Kinoshita, K. Koyama, K. Takahashi, N. Kondo, and H. Yuasa, *J. Nat. Prod.*, **55**, 953 (1992).
2. T. Takizawa, K. Kinoshita, K. Koyama, K. Takahashi, N. Kondo, H. Yuasa, and K. Kawai, *J. Nat. Prod.*, **56**, 2183 (1993).
3. K. Koyama, T. Yama, K. Kinosita, K. Takahashi, N. Kondo, and H. Yuasa, *J. Nat. Prod.*, **56**, 2201 (1993).

Received 4 April 1995