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DITERPENOIDS FROM *RABDOSIA GAPONICA* VAR. *GLAUCOCALYX*

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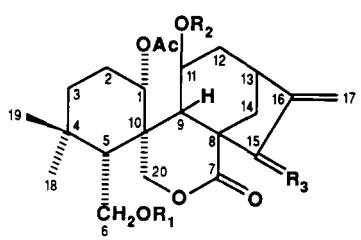
ABSTRACT.—Five diterpenoids have been isolated from the leaves of *Rabdosia japonica* var. *glaucocalyx*. The structure of these diterpenoids were identified as acetylexidonin [**1**], rabdophyllin G [**2**], rabdosinate [**3**], epinodosin, and lasiodonin. It is the first isolation of **1** from a natural source and of these five diterpenoids from this plant species.

As part of our chemical investigation of the genus *Rabdosia* (Labiatae), we report here the isolation and structure elucidation of the diterpenoids acetylexidonin [**1**] (1), rabdophyllin G [**2**] (1), rabdosinate [**3**] (2), epinodosin (1), and lasiodonin (3,4) from *Rabdosia gaponica* var. *glaucocalyx* (Maxim.) Kudo. This is the first isolation of **1** from a natural source, although it was previously obtained from the acetylation of exidonin (1). It is also the first isolation of these five diterpenoids from this plant species (5). The ^{13}C-nmr spectral data of acetylexidonin [**1**] and epinodosin are presented for the first time.

Structures of the five diterpenoids were determined by spectral analysis and those of rabdophyllin G [**2**], rabdosinate [**3**], and epinodosin were confirmed by direct comparison with authentic samples. Acetylexidonin was identified by comparing its spectral data with the previously reported acetylation product of exidonin (1). Acetylation of 11-OH in exidonin changed $\delta_{C\text{-}11}$ from 64.91 to 68.22 ppm. To further confirm this assignment, rabdophyllin G [**2**] was acetylated to give a diacetylated product



1 $R_1=R_2=Ac$, $R_3=O$
2 $R_1=R_2=H$, $R_3=O$
3 $R_1=R_2=Ac$, $R_3=\beta$-OAc,α-H

with tlc, ir, eims, and ^{1}H-nmr spectral data in good agreement with those of **1**.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined with an X-4 Micromelting Point Apparatus and are uncorrected. Uv spectra were recorded with a Hitachi 557 Double Beam Spectrophotometer. Ir spectra were measured with a Perkin-Elmer PE35 Infrared Spectrometer. Mass spectra were obtained with a ZAB-HS Mass Spectrometer using a 70 eV electron impact source. Nmr spectra were measured with Bruker AM400 Ft-nmr Spectrometer. The assignments of ^{13}C-nmr spectral data were made with aid of one-dimensional Distortionless Enhancement Polarization Transfer (DEPT) spectra. All reagents used were of analytical quality (Beijing Chemical Plant). Si gel (200–300 mesh) was used for cc, and tlc Si gel (F_{254}) was used for tlc (Haiyang Chemical Industry Factory, Qingdao).

PLANT MATERIAL.—*R. gaponica* var. *glaucocalyx* was collected by Dr. Jiaming Yue from Guyuan of Ninxia Hui Autonomous Region of China in August 1987. It was identified by Mr. Wenyi Wang (Guyuan Herbs Identification Institute) and Prof. Gualian Zhang of the Biology Department of Lanzhou University, and a voucher specimen is deposited in the Biology Department of Lanzhou University.

EXTRACTION AND ISOLATION.—The air-dried leaves of *R. gaponica* var. *glaucocalyx* (4 kg) were treated with Et_2O at room temperature for 1 week. After removal of Et_2O, 200 g of syrup remained. The syrup was mixed with 200 g Si gel (100 mesh) and extracted with petroleum ether (30–60°) to remove lipids and colored material, then subjected to cc on Si gel and eluted with a gradient of petroleum ether and Me_2CO (6:1, 5:1, 4:1). Five fractions were collected, and 300–400 mg of crude individual compound of the five diterpenoids was obtained from fractions 2–5. Each component was further purified by cc and repeated recrystallization from an appropriate solvent. Finally, acetylexidonin [**1**] (250 mg), rabdophyllin G [**2**] (250 mg), rabdosinate [**3**] (200

mg), epinodosin (310 mg), and lasiodonin (310 mg) were obtained.

ACETYLEXIDONIN [**1**].—White crystals, mp 165–167° (from EtOAc); uv (MeOH) λ max 231 nm (ε 9000); ir ν max (KBr) 1700–1745 (broad), 1644 cm^{-1}; eims *m/z* (%) $[M]^+$ 490 (3), 448 (12), 388 (35), 328 (14); ^{1}H-nmr (C_5D_5N, TMS) δ 1.00, 1.07 (each 3H, s, Me-18, Me-19), 1.26 (1H, dd, *J* = 13.6, 9.3 Hz, H-12β), 1.42 (1H, br td, *J* = 13.8, 4.3 Hz, H-3β), 1.58 (1H, dt, *J* = 14.3, 3.3 Hz, H-3α), 2.02, 2.04, 2.06 (each 3H, s, 3 × OAc), 2.05 (1H, m, H-14β), 2.05 (1H, dd, *J* = 13.0, 4.5 Hz, H-14α), 2.83 (1H, ddd, *J* = 13.6, 9.2, 7.5 Hz, H-12α), 3.03 (1H, d, *J* = 11.6 Hz, H-9β), 3.14 (1H, dd, *J* = 9.2, 4.5 Hz, H-13), 4.14 (1H, dd, *J* = 12.8, 6.0 Hz, H-6a), 4.43 (1H, dd, *J* = 12.8, 3.5 Hz, H-6b), 4.48 and 4.89 (each 1H, ABd, *J* = 12.3 Hz, H-20a, H-20b), 4.63 (1H, dd, *J* = 10.8, 3.8 Hz, H-1β), 4.97 (1H, ddd, *J* = 11.6, 9.3, 7.5 Hz, H-11α), 5.64, 6.16 (each 1H, br s, H-17a, H-17b); ^{13}C nmr (C_5D_5N, TMS) δ 76.47 (d, C-1), 23.76 (t, C-2), 39.99 (t, C-3), 33.90 (s, C-4), 48.99 (d, C-5), 61.48 (t, C-6), 170.17 (s, C-7), 57.41 (s, C-8), 43.26 (d, C-9), 44.02 (s, C-10), 68.22 (d, C-11), 40.10 (t, C-12), 34.24 (d, C-13), 29.58 (t, C-14), 199.61 (s, C-15), 148.97 (s, C-16), 120.56 (t, C-17), 23.90 (q, C-18), 33.60 (q, C-19), 66.71 (t, C-20), 168.76 (s), 168.55 (s), 169.12 (s), 20.96 (q), 21.18 (q), 21.23 (q) 3 × OAc.

RABDOPHYLLIN G [**2**].—White crystals. The identity was confirmed by comparing its mp, uv, ir, eims, ^{1}H-nmr and ^{13}C-nmr spectral data with those of an authentic sample (1).

RABDOSINATE [**3**].—Colorless prisms. Its mp, uv, ir, eims, ^{1}H-nmr and ^{13}C-nmr spectral data were the same as those of an authentic sample (2).

EPINODOSIN.—White crystals. It was identified by direct comparison of its mp, eims, and ^{1}H-nmr spectral data with an authentic sample (1). ^{13}C-nmr (C_5D_5N, TMS) 76.74 (d, C-1), 24.03 (t, C-2), 36.91 (t, C-3), 31.56 (s, C-4), 52.33 (d, C-5), 101.97 (d, C-6), 170.83 (s, C-7), 56.49 (s, C-8), 53.87 (d, C-9), 51.00 (s, C-10), 63.20 (d, C-11), 41.46 (t, C-12), 35.21 (d, C-13), 32.98 (t, C-14), 201.50 (s, C-15), 150.92 (s, C-16), 117.63 (t, C-17), 33.50 (q, C-18), 23.07 (q, C-19), 73.60 (t, C-20).

LASIODONIN.—Colorless flakes. The mp, uv, ir, eims, ^{1}H-nmr and ^{13}C-nmr spectral data were in good agreement with those reported for lasiodonin (3,4). ^{1}H-nmr (C_5D_5N, TMS) δ 1.10, 1.12 (each 3H, s, Me-18, Me-19), 1.35 (1H, dd, *J* = 13.2, 4.2 Hz, H-3β), 1.44 (1H, dt, *J* = 13.2, 3.5 Hz, H-3α), 1.55 (1H, dd, *J* = 5.2, 1.0 Hz, H-5β), 1.66 (1H, dd, *J* = 14.0, 10.4 Hz, H-12β), 1.87 (2H, m, H-2), 1.93 (1H, dd, *J* = 9.7, 1.9 Hz, H-9β), 2.48 (1H, dd, *J* = 12.5, 1.2 Hz, H-14α), 2.52 (1H, dd, *J* = 12.5, 3.7 Hz, H-14β), 3.11 (1H, dd, *J* = 10.0, 3.7 Hz, H-13), 4.15 (1H, dd, *J* = 11.0, 5.2 Hz, changed to doublet after addition of D_2O, *J* = 5.2 Hz, H-6α), 4.22 (1H, br t, *J* = 7.0 Hz, H-1α), 4.40 (1H, dd, *J* = 10.2, 1.9 Hz, H-20a), 4.69 (1H, dd, *J* = 10.2, 1.0 Hz, H-20b), 4.81 (1H, br q, $W_{1/2}$ = 28.3 Hz, H-11β), 5.29, 5.94 (each 1H, s, H-17a and H-17b), 6.64, 6.69 (br, 2 × OH, disappeared after addition of D_2O).

ACETYLATION OF RABDOPHYLLIN G [**2**].—Compound **2** (50 mg) was acetylated (Ac_2O/pyridine) to yield a diacetylated product that showed the same mp, ir, eims, and ^{1}H-nmr spectral data as **1**.

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