Two New *ent*-Kauranoids from *Isodon excisa*

Yan-Hong Wang and Yao-Zu Chen

State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, 730000, China

Dong-Sa Kim

The Botanical Institute Academy of Science DPRK, Pyongyang, D. P. R., Korea

Han-Dong Sun*

Laboratory of Phytochemistry, Kunming Institute of Botany, Academia Sinica, Kunming, 650204, China

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Two new *ent*-kaurane diterpenoids, excisanins F (**1**) and G (**2**), were isolated from the leaves of *Isodon excisa*. Their structures were elucidated based on spectral analysis.

In a previous paper, we have reported on five diterpenoids, excisanins A−E,[1−3] isolated from *Isodon excisa* (Maxim.) Hara, a perennial herb of the Labiatae family, which is distributed in the northeast area of the People's Republic of China and northern Korea and is used as an antiinflammatory and antibacterial agent in local folk medicine. A continuation of our study on this plant, collected from a different district of northern Korea, led to the isolation of two new diterpenoids, excisanins F (**1**) and G (**2**), which is reported in this paper.

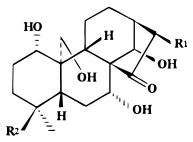
Excisanin F (**1**), $C_{20}H_{28}O_6$ ($[M]^+$ *m/z* 364), showed the presence of one methyl carbon, six methylenes, six methines, three quaternary carbons, two olefinic carbons, one ketonic carbon, and one aldonic carbon in the ^{13}C-NMR and DEPT spectra (see Table 1). It had a five-membered ring with a ketone conjugated with an *exo*-methylene group from the following spectral data: UV (MeOH) λ_{max} 232 nm (log ϵ 3.71); IR (KBr) ν_{max} 1732 and 1648 cm^{-1}; ^{1}H NMR δ 6.31 and 5.69 (each 1H, s); ^{13}C NMR δ 150.7 (s), 115.9 (t) (*exo*-methylene), 209.0 (s) (ketone).[4] In addition, the presence of one methyl signal at δ 15.0 (q, C-19), an aldonic signal at δ 205.7 (d, C-18), a methylene signal at δ 62.2 (t, C-20) in the ^{13}C-NMR spectrum of **1** suggested that this compound has an 18,20-dioxy-*ent*-kaur-16-en-15-one as the basic skeleton.[1,5]

Excisanin F was found to have three secondary hydroxy groups, one primary hydroxy group, and one aldo group based on the following spectroscopic data: IR (KBr) ν_{max} 3243, 2872, 2718, 1723, and 1068 cm^{-1}; ^{1}H NMR δ 3.80 (1H, dd, J = 4.6, 10.3 Hz), 4.94 (1H, dd, J = 4.4, 12.1 Hz), 5.39 (1H, br s), 4.65, and 4.46 (each 1H, d, J = 12.1 Hz), and 9.30 (1H, s); ^{13}C NMR δ 80.5, 74.2, and 76.7 (each CH). The locations of five functional oxygen groups were deduced as follows. Excisanin F differs from the known compound kamebakaurin (**3**)[1] by the addition of one aldo group (see Table 1). The singlet at δ 9.30 was assigned to the proton of 18-CHO, which was deduced because of the upfield shifts of C-3 (δ 32.7), C-5 (44.8), and C-19 (15.0) due to a γ-gauche shielding shift effect between 18-CHO and C-3, C-5, C-19, respectively.[5] Thus, excisanin F was elucidated as 1α,7α,14β,20-tetrahydroxy-18-formyl-*ent*-kaur-16-en-15-one.

Table 1. ^{13}C-NMR Spectral Data of Compounds 1−**2** in C_5D_5N

carbon	1	2	carbon	1	2
1	80.5 d	81.2 d	11	21.5 t	21.7 t
2	30.2 t	30.3 t	12	31.6 t	24.6 t
3	32.7 t	39.0 t	13	47.9 d	42.0 d
4	47.1 s	33.3 s	14	76.7 d	76.7 d
5	44.8 d	52.4 d	15	209.0 s	221.4 s
6	29.4 t	30.5 t	16	150.7 s	53.4 d
7	74.2 d	75.2 d	17	115.9 t	58.6 t
8	62.1 s	62.0 s	18	205.7 d	32.6 q
9	56.6 d	57.0 d	19	15.0 q	22.2 q
10	49.4 s	47.6 s	20	62.2 t	61.9 t

Excisanin G (**2**)had a molecular formula determined as $C_{20}H_{32}O_6$ ($[M + 1]^+$ *m/z* 369) on the basis of mass and NMR spectra. The NMR spectra (experiment and Table 1) of **2**, compared with that of kamebakaurin (**3**), differed only in the D-ring signals: the *exo*-methylene protons at C-17 in **3** were replaced by a hydroxy group in **2**, which was judged from the presence of the signals at δ 3.29 and 3.23 (each 1H, m) and δ 53.4 (CH) and 58.6 (CH_2), which replaced the signals at δ 6.34 and 5.69 (each 1H, br s), and at δ 150.9 (C) and 115.3 (CH_2), respectively. Consequently, the structure of **2** was elucidated as 1α,7α,14β,17,20-pentahydroxy-*ent*-kauran-15-one.



1 R_1 = exo-methylene R_2 = CHO
2 R_1 = CH_2OH R_2 = CH_3
3 R_1 = exo-methylene R_2 = CH_3

Experimental Section

General Experimental Procedures. Melting points were determined on a Kolfer apparatus. ^{1}H-NMR, ^{13}C-NMR and DEPT spectra were recorded on a Bruker AM-400 NMR spectrometer with TMS as internal standard and C_5D_5N as solvent. UV spectra in MeOH were determined on a UV-240 spectrophotometer. IR spectra with KBr plates were determined on a FT-170SX spectrometer. Mass spectra were obtained on VG ZAB-HS mass spectrometer.

* To whom correspondence should be addressed. Phone: (0871)-5150660. FAX: (0871)-5150227.

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Plant Material. The leaves of *Isodon excisa* were collected near Pyongyang, Democratic People's Republic of Korea, on August 1993, and identified by Prof. H.-W. Li. A voucher specimen is deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany, Academia Sinica, Kunming, People's Republic of China.

Extraction and Isolation. Dried and powdered leaves (5 kg) were extracted with MeOH three times, and the solvent was evaporated, yielding the residue (390 g), which was dissolved in EtOH−H_2O (9:1) and partitioned with petroleum ether. The layer of EtOH was evaporated and partitioned with EtOAc. From the EtOAc solution, the residue (122 g) was obtained and subjected to column chromatography (Si gel) eluting with petroleum ether−Me_2CO (9:1−6:4). The fractions (7:3 and 6:4 parts) were further purified by Si gel column chromatography, yielding excisanins F (**1**, 32 mg) and G (**2**, 25 mg).

Excisanin F (1): powders, $[\alpha]^{20}_D$ +27.3° (*c* 0.55, MeOH); UV (MeOH) λ_{max} (log ϵ) 232 (3.71) nm; IR (KBr) ν_{max} 3243, 2872, 2718, 1723, 1648, 1549, 1456, 1068 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 3.80 (1H, dd, J = 4.6, 10.3 Hz, H-1β), 4.94 (1H, dd, J = 4.4, 12.1 Hz, H-7β), 3.31 (1H, m, H-13α), 5.39 (1H, br s, H-14α), 6.31 and 5.69 (each 1H, s, Ha and Hb-17), 9.30 (1H, s, CHO-18), 4.65 and 4.46 (each 1H, d, J = 12.1 Hz, Ha and Hb-20); ^{13}C NMR, see Table 1; EIMS *m/z* 364 ($[M]^+$, 9), 346 (11), 328 (15), 310 (26), 299 (86), 281 (100), 235 (29).

Excisanin G (2): colorless needles, mp 214−216 °C; $[\alpha]^{20}_D$ −100.8° (*c* 0.51, MeOH); IR (KBr) ν_{max} 3525, 3275, 1730, 1255, 1245 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 3.64 (1H, dd, J = 4.1, 10.1 Hz, H-1β), 4.71 (1H, dd, J = 4.7, 11.1 Hz, H-7β), 3.22 (1H, m, H-13α), 5.78 (1H, br s, H-14α), 2.90 (1H, m, H-16), 3.29 and 3.23 (each 1H, m, Ha and Hb-17), 0.78 and 0.84 (each 3H, s, Me-18 and Me-19), 4.74 and 4.68 (each 1H, d, J = 11.9 Hz, Ha and Hb-20); ^{13}C NMR see Table 1; FABMS *m/z* 369 ($[M + 1]^+$ 33), 333 (27), 315 (37), 297 (27), 253 (49).

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References and Notes

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