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Diterpene Glycoside from *Acanthopanax koreanum*

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Abstract—From the root bark of *Acanthopanax koreanum* a new diterpene glycoside, mp 212~214°, was isolated. The structure was established as 15(R), 16-dihydroxy-pimar-9(11)-ene-19-oic acid β-D-glucopyranosyl ester (sumogaside) on the basis of spectroscopic methods and chemical transformation.

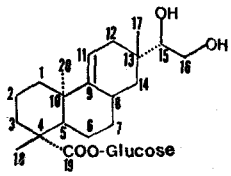
Keywords—*Acanthopanax koreanum* • Araliaceae • diterpene glycoside • sumogaside• ^{13}C-NMR data

Acanthopanax koreanum NAKAI (Araliaceae) grows in Jeju island, Korea indegenously and the root and stem bark of *Acanthopanax* species have been used as a tonic and sedative as well as in the treatment of rheumatism and diabetes[1]. In our earlier investigation of *A. koreanum*, several components, comprising diterpenoids[2], lignans[3], phenylpropanoids, polyacetylenes and fatty acid methyl esters[4], were isolated from the root and stem bark. In continuation of our systematic chemical studies of this plant, we report here a diterpene glycoside from the root bark of *A. koreanum*.

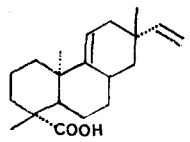
Results and Discussion

The BuOH extracts of the root bark of *A. koreanum* were prepared as described in the Experimental section and were chromatographed on silicagel column to afford compound **1**. Compound **1** had an IR spectrum which showed strong hydroxyl (3,350 cm^{-1}) and carbonyl absorptions(1,750 cm^{-1}). The ^{1}H-NMR spectrum showed signals for one olefinic proton at δ 5.49, complex signals due to the germinal protons of hydroxyl groups at δ 3.70~4.55 and three C-Me singlets at δ 1.09, 1.35 and 1.36. The ^{13}C-NMR spectrum showed 26 carbon peaks and it assumed that compound **1** was a diterpene glycoside. The anomeric carbon of the ester-glucoside of compound **1**(G1-1) was found at a higher field (δ 95.5)[5] and other ester-glucosyl signals (G1-2~6) were somewhat shifted positions owing to esterification effect. The double bond position $\Delta^{9(11)}$ was confirmed by ^{13}C-NMR data (Table I), compared with compound **2** which showed characteristic carbon signal at δ 149.7 and 116.5(C-9 and C-11)[6]. The configuration of C-13 was also confirmed by the chemical shift of C-17 (δ 18-8), which was due to an axial methyl group having γ-gauche effect[7]. The ^{13}C-NMR data provided proof of the stereochemistry at C-15[8,9]: a 15R configuration showed the C-15 carbon resonance at 78.2 ppm, almost identical with the value for compound **1** (79.1 ppm, Table I), but very different from those reported for the 15S epimer (75.5 ppm). The MS spectra showed the base peak at *m/z* 275 (loss of a glucose and -CHO-HCH_2OH), weak peak at *m/z* 336 (aglycon) and retro Diels-Alder fragment[10] of base peak at *m/z* 173. Acetylation of **1** with Ac_2O/pyridine

Table I. ^{13}C-NMR spectral data of compound 1 and compound 2 ((−) pimara-9(11), 15-dien-19-oic acid)[2]



1



2

Carbon No.	1	2
1	42.1	41.9
2	19.2	18.9
3	38.4	38.0
4	44.4	44.2
5	48.2	48.0
6	20.6	20.2
7	28.2	27.7
8	28.3	28.6
9	150.1	149.7
10	38.5	38.4
11	117.0	116.5
12	35.5	37.4
13	34.6	34.8
14	39.7	41.8
15	80.3	150.1
16	62.9	109.1
17	18.8	22.2
18	28.1	28.5
19	176.6	185.0
20	22.8	22.3
Gl -1	95.5	
-2	73.8	
-3	78.7	
-4	70.7	
-5	79.0	
-6	61.8	

gave hexaacetate. The ^{1}H-NMR spectrum showed six acetate peaks at δ 2.00~2.06 and 1,2-diacetoxyethyl group attributed to H-15 and 2H-16 as an ABX system(δ_A=4.23, δ_B=4.29, δ_X=4.86)[11]. From the above all spectral data, we assumed that compound 1 was a 15(R), 16-dihydroxy pimar-9(11)-end 19 oic acid β-D-glucopyranosyl ester, which we named smogaside. This compound was first isolated in nature.

Experimental

General Experimental Procedures-The melting points were uncorrected. IR spectra were recorded on KBr disc (Beckman IR-20A spectrometer). The NMR spectra were obtained in $CDCl_3$, C_6D_5N (Varian FT-80A, Nicolet NT 200 and Nicolet NT 360 spectrometer) using TMS as an internal standard. MS spectra (70eV, Hewlett Packard HP 595B GC/MS system) were taken with a direct inlet.

Plant Material—The root bark (8 kg) of *A. koreanum* was collected from the Hanla Mountain of Jeju-Do in Korea in September 1983. The plant was verified by Dr. Bo Sup Chung, Seoul National University. Vovcher specimens are deposited in our laboratory.

Extraction and Isolation—Air dried root bark was extracted with MeOH (9 l×3). The MeOH extracts were evaporated in vacuo and fractionated with Et_2O and n-BuOH. The n-BuOH extract (75 g) was chromatographed on silica gel column with $CHCl_3$: MeOH(10 : 1→6 : 1). A total of 9 fractions (A-I) were collected. From fraction E (12 g), eluting with $CHCl_3$: MeOH : H_2O(70 : 30 : 4), compound 1 was obtained.

Sumogaside (1)—Compound 1 was a white needle cristal. Mp 212~214°; IR ν_{max}^{KBr} 3,350, 1,750 (C=O)cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_5N) δ 1.09, 1.35, 1.36 (3H×3, s, -CH_3), 5.49 (1H, m, 11-H); ^{13}C-NMR (90MHz, C_6D_5N) see Table I; MS m/z (rel. int.) 336(M^+-glucose, 12.3), 303(18.6), 287(22.7), 275(aglycon -$CHOHCH_2$OH, 100), 257(42.3), 239(40.9), 229(58.2), 173(57.3), 159(65.0). Reaction of compound 1 with Ac_2O/pyridine gave the hexaacetate, amorphous powder. ^{1}H-NMR (80 MHz, $CDCl_3$)

δ: 0.82, 1.25, 1.28 (3H×3, s, $-CH_3$), 2.00~2.06 (3H×6, s, $-COCH_3$), 4.23(1H, dd, J=12.1, 8.2 Hz, H_A-16), 4.29(1H, dd, J=12.1 Hz, 2.0 Hz, H_B-16), 4.86(1H, dd, J=8.2 Hz, 2.0 Hz, H-15); MS m/z (rel. int.) 169(100).

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