RESEARCH NOTE

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Fomitoside K, a New Lanostane Triterpene Glycoside from the Fruiting Body of *Fomitopsis nigra*

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In an effort to identify the chemical constituents of fruiting bodies of *Fomitopsis pinicola*, a new lanostane triterpene glycoside, designated as fomitoside K, has been isolated from its methanolic extract. Its chemical structure was assigned on the basis of various spectroscopic studies.

KEYWORDS : *Fomitopsis nigra*, Fomitoside K, Lanostane, Triterpene glycoside

Mushrooms produce a large variety of secondary metabolites with unique chemical structures and interesting biological activities. *Fomitopsis*, belonging to Polyporaceae, is known to produce various triterpenoids and triterpene glycosides [1-4]. However, metabolites from *F. nigra* have not yet been reported. In our ongoing effort to identify the chemical constituents of native Korean mushrooms [5-8], a new lanostane triterpene glycoside, designated as fomitoside K (Fig. 1), has been isolated from the methanolic extract of the fruiting body of *F. nigra*. In this paper, the isolation and structural determination of fomitoside K are described.

Following collection of fruiting bodies of *F. nigra* near Odae mountain, Kangwon province, Korea, they were ground and extracted with methanol at room temperature. Concentration of the methanolic extract was performed under reduced pressure, followed by consecutive partitioning of the aqueous resultant between hexane, chloroform and ethyl acetate, and water. Following concentration of the chloroform-soluble portion under reduced pressure, it was subjected to silica gel column chromatography, and stepwise elution with chloroform : methanol (100 : 1~20 : 1, v/v). Chromatography of a fraction containing high levels of triterpene-class compounds was performed on a column of Sephadex LH-20 eluted with chloroform : methanol (1 : 1, v/v), followed by preparative high performance liquid chromatography (HPLC) equipped with a reversed-phase column and elution with 70% aqueous methanol to afford fomitoside K.

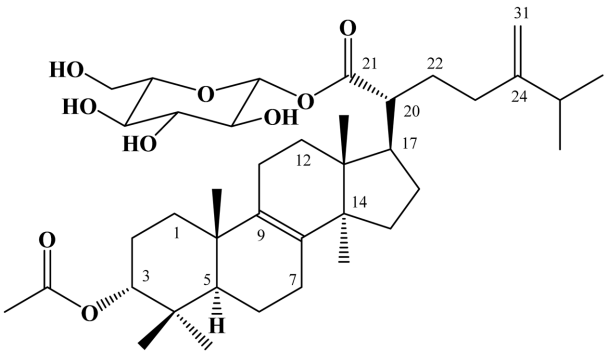

Fig. 1. Structure of fomitoside K.

Fast-atom bombardment (FAB)-mass measurement determined that the molecular weight of fomitoside K was 674 and its molecular formula was established as $C_{39}H_{62}O_9$ by high-resolution FAB-mass measurement (*m/z* 697.4291 $[M+Na]^+$, Δ –0.1 mmu) combined with ^1H and ^{13}C NMR data. This molecular formula requires 9 degrees of unsaturation. ^1H and ^{13}C NMR spectra suggested that this compound was typical of a triterpene glycoside. In the ^1H NMR spectrum, signals from an anomeric proton of sugar at δ 5.48 (d, J = 8.0 Hz), a non-equivalent terminal methylene at δ 4.74 and 4.69, five oxygenated methines at δ 3.3~4.5, an oxygenated methylene at δ 3.81 and 3.70 and six methyls at δ 1.02, 1.01, 1.00, 0.92, 0.90, 0.88 and 0.79

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Table 1. ^{1}H and ^{13}C NMR spectral data of fomitoside K in CD_3OD[a]

No.	δ_C	δ_H	No.	δ_C	δ_H
1	36.6	1.76, 1.24	22	32.5	1.70
2	25.1	1.65	23	32.7	2.08, 1.96
3	82.4	4.44 (dd, J = 9.0, 7.4)[b]	24	156.7	
4	38.9		25	35.0	2.22 (m)
5	52.0	1.15	26	22.3	1.01 (d, J = 6.8)
6	19.2	1.70, 1.54	27	22.4	1.00 (d, J = 6.8)
7	27.4	2.08	28	28.5	0.88 (s)
8	135.5		29	17.0	0.90 (s)
9	135.9		30	24.7	0.92 (s)
10	38.2		31	107.4	4.74 (br s), 4.69 (br s)
11	21.9	2.00	Acyl moiety		
12	29.9	1.59, 1.50	CO	172.9	
13	45.6		CH_3	21.1	2.02
14	50.6		Sugar moiety		
15	31.5	1.65, 1.25	1′	95.7	5.48 (d, J = 8.0)
16	27.9	2.02, 1.39	2′	73.9	3.30~3.45
17	48.3	2.11	3′	78.7	3.30~3.45
18	16.7	0.79 (s)	4′	71.2	3.30~3.45
19	19.6	1.02 (s)	5′	78.4	3.30~3.45
20	48.8	2.39 (m)	6′	62.6	3.81 (br d, J = 10.6)
21	177.3				3.70 (dd, J = 10.6, 4.0)

[a]NMR data were recorded at 400 MHz for proton and at 100 MHz for carbon.
[b]Proton resonance multiplicity and coupling constant (J = Hz) are in parentheses.

suggested that this compound was a triterpene glycoside of the lanostane skeleton. A total of 39 carbon signals were observed in the ^{13}C NMR spectrum, supporting fomitoside K as a triterpene glycoside having two ester carbonyl carbons, four sp^2 carbons, one anomeric carbon, six oxygenated carbons, and 26 other sp^3 carbons. Two-dimensional NMR studies, including ^{1}H-^{1}H COSY, heteronuclear multiple quantum coherence (HMQC), and heteronuclear multiple bond coherence (HMBC) experiments, were performed for further elucidation of structure. As shown in Table 1, the proton-bearing carbons were established by the HMQC spectrum, and, as shown in Fig. 2, the ^{1}H-^{1}H COSY spectrum showed seven partial structures. The partial structures were connected by the HMBC spectrum, which exhibited critical long-range correlations from the oxygenated methine proton at δ 4.44 to the carbonyl carbon at δ 172.9 and from the anomeric proton at δ 5.48 and the methylene protons at δ 1.70 to the carbonyl carbon at δ 177.3. As a result of other long-range correlations, we assigned the lanostane skeleton, as shown in Fig. 2. Based on comparison of its carbon chemical shifts with other triterpene glycosides, the sugar was established as glucose [4]. Therefore, the structure of fomitoside K was determined as a new lanostane triterpene glucoside. Many triterpene glycosides, named fomitosides A~J, have previously been isolated from fruiting bodies of *Fomitopsis pinicola*; fomitoside K was classified as an acetylated form of fomitoside J [4]. Fomitoside K induced apoptosis of human oral squamous carcinoma cells (YD-10B). Details on the biological properties of fomitoside K will be published elsewhere.

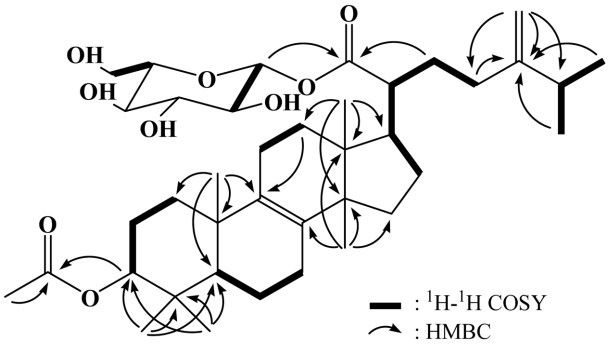

Fig. 2. Two-dimensional NMR correlations for fomitoside K. HMBC, heteronuclear multiple bond coherence.

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