

A New Euphane-Type Triterpene from *Melia Azedarach*

Wei Min ZHAO*, Cheng Qi FAN, Zhi ZHANG

Shanghai Institute of Materia Medica, Academia Sinica, 294 Taiyuan Road, Shanghai 200031

Abstract: A new Euphane-type triterpene, named azedarachic acid, was isolated from the fruits of *Melia azedarach*. Its structure was determined on the basis of NMR and MS experiments.

Keywords: *Melia Azedarach*, triterpene, azedarachic acid.

The family Meliaceae is well known for its limonoid components possessing insect antifeedant activity and those highly oxygenated triterpenes related to tirucallol (euphane type skeleton)^{1,2}. *Melia azedarach* is a plant of the family Meliaceae, distributed widely in China³. In order to find new limonoid with strong insect antifeedant activity and also interesting highly oxygenated triterpenes, we studied systematically the chemical components of *Melia azedarach*. In this paper, we report the structure elucidation of a new triterpene, named azedarachic acid.

Azedarachic acid was obtained as colorless gum, $[\alpha]_D^{22} -127.5$ (CHCl₃, *c* 0.02). FAB-MS exhibited a quasimolecular ion peak at *m/z* 511 [M+Na]⁺. In ¹³C NMR spectrum, thirty carbon signals could be identified, among them there were one carboxylic carbon and seven methyl carbon signals, and no other methyl derived signals could be found. Azedarachic acid was thus suggested to be a triterpenoid. According to MS and ¹³C NMR data, its molecular formulae was deduced to be C₃₀H₄₈O₅.

Analysis of its ¹H NMR and ¹³C NMR spectra further revealed the existence of three hydroxyl groups and two trisubstituted carbon-carbon double bonds in the structure. Two signals at δ_H 1.60 (3H, br s) and 1.67 (3H, br s) suggested allylic position of the two methyls, which was confirmed by their correlation relationship with an olefinic proton at δ 5.09 (m) in ¹H-¹H COSY spectrum. Further analysis of ¹H-¹H COSY and HMQC spectra led to the deduction of the following fragments: C₁-C₂-C₃, C₅-C₆-C₇-C₈-C₉-C₁₁-C₁₂ and C₁₅-C₁₆-C₁₇-C₂₀-C₂₂-C₂₃-C₂₄-C₂₆(C₂₇). In HMBC spectrum of azedarachic acid, a series of ¹H-¹³C long range correlation signals were observed, which enabled the linkage of above fragments and the rest seven methyls and seven quaternary carbons. From biogenetic point of view and results of HMBC experiment, azedarachic acid was also suggested to possess an euphane-type skeleton. The hydroxyl at C₃ should possess β configuration considering the characteristic splitting pattern of H₃ (dd, 11.3, 3.8). Two hydroxyl groups at C₁₂ and C₁₆ were determined to be both in β configuration by analyzing relevant NOE signals in NOESY spectrum. Using NOESY spectrum also

made further assignments of methylene protons in the tetracyclic system. The chemical shifts of ^1H and ^{13}C NMR data of azedarachic acid were listed in **Table 1**.

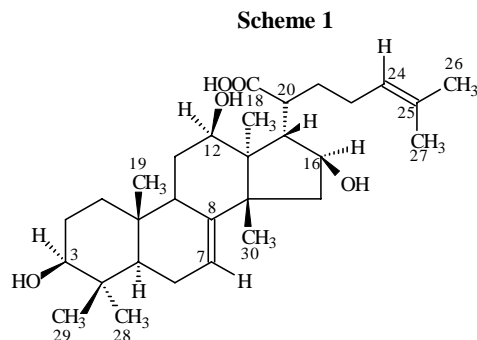


Table 1. ^1H and ^{13}C NMR data of azedarachic acid (CDCl_3).

No.	^1H	^{13}C	No.	^1H	^{13}C
1 α	1.67, m	37.3, t	15 β	2.24, m	
1 β	1.67, m		16	4.16, m	82.4, d
2 α	1.12, m	27.8, t	17	2.49, dd, 12.1, 11.5	53.4, d
2 β	1.63, m		18	0.81, s	20.1, q
3	3.23, dd, 11.3, 3.8	79.2, d	19	0.76, s	13.2, q
4		39.2, s	20	2.37, m	45.7, d
5	1.27, m	51.0, d	21		180.7, s
6 α	2.18, m	24.2, t	22a	1.56, m	29.3, t
6 β	1.98, m		22b	1.98, m	
7	5.32, m	119.5, d	23a	1.64, m	26.2, t
8		142.9, s	23b	2.14, m	
9	2.30, m	48.7, d	24	5.09, m	123.9, d
10		35.5, s	25		132.8, s
11 α	1.47, m	30.3, t	26	1.60, br s	18.1, q
11 β	2.31, m		27	1.67, br s	25.9, q
12	3.98, dd, 9.0, 5.2	72.3, d	28	0.95, s	27.8, q
13		55.1, s	29	0.85, s	14.8, q
14		44.6, s	30	1.32, s	33.9, q
15 α	1.68, m	36.4, t			

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