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A New Prodelphinine Type Alkaloid From *Aconitum nasutum*

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In a previous study we have isolated five known and a new diterpenoid alkaloids from the aerial parts of *Aconitum nasutum*. In the present paper the structure of a new and rather rare diterpenoid alkaloid aconasutine was determined by using 1D and 2D NMR techniques.

Key words: *Aconitum nasutum*, Ranunculaceae, prodelphinine alkaloid, aconasutine, spectral methods.

Introduction

Due to their high toxicity *Aconitum* species are not included as a part of the folk medicine in Turkey, however they are used as pain relievers under doctor control¹. Four *Aconitum* species naturally grow in Turkey. We have recently studied two of them: *A. orientale* Mill². and *A. nasutum* Fisch. et Reichb³. The latter plant was collected from eastern Turkey, near the Russian border. There is one more study with *A. nasutum*⁴ by a Russian group where a diterpene alkaloid aconosine was isolated but was not found in the Turkish collection of the plant. In our previous study with this species we have isolated five known norditerpenoid alkaloids, talatisamine⁵, lycoctonine⁶, columbidine⁷, 14-Oacetylalatisamine⁵ and anthranoyllycoctonine⁸ together with the new compound 3-hydroxytalatisamine³. In the present study we have obtained and determined the structure of a new prodelphinine type diterpenoid. The new compound was named aconasutine (1).

Experimental

The spectra were recorded with the following instruments: IR with a Perkin- Elmer 1600 FT-IR using $CHCl_3$, 1H and ^{13}C NMR, a Bruker AM 400 MHz, 2D experiments on a 500 MHz Bruker ORX in $CDCl_3$. HREIMS, with a VG ZabSpec.

Plant Material

The above ground parts of *Aconitum nasutum* were collected from Ardahan (Ardanuç pass) near Russian border in August 1984, and identified by Dr. R. Ilarslan (Ankara), a voucher specimen is deposited in the Herbarium of the Faculty of Sciences, University of Ankara, Nr. Ilarslan 1675.

Extraction and Sparation

Powdered plant material (500 g) was extracted with EtOH by percolation, the extract was evaporated to dryness at 35° in vacuo. The residue was treated with 0.5 N H_2SO_4 and extracted in $CHCl_3$. $NaOH$ (5%) was added to the acidic solution to bring it to pH 10. The basic solution was then extracted with $CHCl_3$ to yield 1.5 g crude alkaloidal mixture upon evaporation of $CHCl_3$. The alkaloidal mixture was fractionated in a basic Al_2O_3 column (3x50 cm), eluting with petrol, a gradient of EtOAc were added up to 100%, followed by EtOH. The alkaloidal fractions were further purified on preparative Si gel and Al_2O_3 plates. The yield of aconasutine (1) was 12 mg. Other yields were given in the previous paper³.

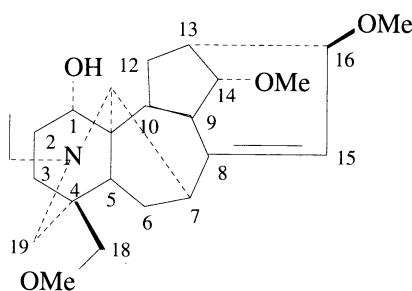


Figure 1.

Aconasutine (1)

IR ν_{max} cm^{-1} : 3450, 2930, 2850, 1610, 1595, 1450, 1380, 1220, 1150, 1080, 1050, 980, 905. 1H NMR spectrum δ : 5.45 (1H, br s, H-15), 3.80 (1H, t, $J=4.5$ Hz, H-14 β), 3.72 (1H, m, H-1 β), 3.41, 3.38, 3.28 (each, 3H, s), 3.23 (1H, m, H-16 α), 1.07 (3H, t, $J=7$ Hz, NCH_2CH_3). Additional 1H NMR signals together with ^{13}C NMR (DEPT) data were given in Table 1. HREIMS, m/z (rel. int.): 403.2719 $[M]^+$ ($C_{24}H_{37}NO_4$) (5), 386 (10), 358 (10), 284 (8), 256 (5), 209 (6), 165 (10), 111 (32), 97 (58), 83 (63), 69 (72), 57 (100).

Results and Discussion

The structure of the new prodelphinine alkaloid aconasutine (1) was decided from 1D and 2D NMR experiments. The presence of a signal at δ 5.45 in its 1H NMR spectrum was indicative of the presence of a double bond at $\Delta^{8(15)}$ as observed in other similar prodelphinine alkaloids^{9,10} ^{13}C NMR (DEPT) spectrum of aconasutine correlated the presence of unsaturation giving the signals at δ 146.5 as a singlet and at δ

116.4 as a doublet. The lack of a methyl singlet ca 0.90-1.10 ppm pointed out the presence of a CH_2OR at C-4 instead of a methyl group. Three methoxyl groups (at δ 3.41, 3.38, 3.28) were assigned to C-14, C-16, C-18 due to following reasons: the typical triplet signal for H-14 β was at δ 3.80, when there is a methoxyl group at that position, the signal appears ca 3.60-3.90 ppm, in case of a hydroxyl group at this position the signal is observed around 4.00-4.40 ppm and instead of a triplet it is usually a double doublet. Due to biogenetic reasons, C-16 generally has a methoxyl group, of which there are only a few exceptions to this rule^{11,12}. The third methoxyl group could be either at C-1 or at C-18. When there is a methoxyl group at C-1 the chemical shifts of C-2 and C-3 show differences at least 5-6 ppm, in case of a hydroxyl group at C-1 these two signals become close together as observed in the present case, ^{13}C NMR signal of C-1 (72.5 ppm) supports this conclusion. On the other hand a hydroxyl group at C-18 causes an upperfield shift (66.0-70.0 ppm) in its ^{13}C NMR, while the presence of a methoxyl group at C-18 causes a downfield shift to 76.0-79.0 ppm as observed in compound 1. COSY experiment showed the relation between the protons at C-1, C-2 and C-3 as well as between C-6 and C-7 protons. The correlation of carbons and protons were observed by HETCOR experiment. NOESY experiment indicated α stereochemistry of C-1 hydroxyl and C-14 methoxyl groups and the β stereochemistry at C-16 and C-18 methoxyl groups compared to H-17 β . Spectral findings showed the suggested structure for aconasutine (1).

Table 1. 1H and ^{13}C -NMR data of Aconasutine

Position	1H	^{13}C
1	3.72 m	72.5 d
2	1.50 m, 1.60 m	29.6 t
3	1.40 m, 1.90 m	31.9 t
4	-	45.4 s
5	1.70 m	48.3 d
6	1.50 m, 1.70 m	29.6 t
7	2.00 m	48.3 d
8	-	146.5 s
9	2.20 m	48.3 d
10	2.15 m	46.4 d
11	-	51.8 s
12	1.50 m, 2.00 m	34.5 t
13	2.30 t (5.0 Hz)	45.6 d
14	3.80 t (4.5 Hz)	81.9 d
15	5.45 s	116.4 d
16	3.23 m	81.9 d
17	2.80 s	77.1 d
18	3.35 d (9.0 Hz)	77.1 t
19	2.25 d (11.0 Hz)	50.4 t
$N - CH_2$	2.50 m	48.3 t
CH_3	1.07 t (7.0 Hz)	13.9 q
14'OMe	3.41 s	58.5 q
16'OMe	3.38 s	56.8 q
18'OMe	3.28 s	59.4 q

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