Istanbul Ecz. Fak. Derg. / J. Fac. Pharm. Istanbul
42(2) 2012 s. 71-76

DITERPENOID ALKALOIDS FROM THE ROOTS OF A PALE-PURPLE FLOWERING *ACONITUM ORIENTALE* SAMPLE GROWING IN TURKEY

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SUMMARY

From the roots of pale purple-flowering *Aconitum orientale* sample, the norditerpenoid alkaloids septentriodine, lappaconitine, finaconitine, ranaconitine, puberanidine and delstaphinine together with the new alkaloid aconitorientaline obtained for the first time from the white-fowering sample, were isolated. All alkaloids isolated from the white-flowering sample were also obtained from the pale purple-flowering *Aconitum orientale* sample.All these results show, although they have different flower colors, both samples belong to *Aconitum orientale* and they are not different species.

ÖZET

Kirli-mor çiçekli *Aconitum orientale* köklerinden norditerpenoid alkaloitler septentriodin, lappakonitin, finakonitin, ranakonitin, puberanidin, delstaphinin ve ilk defa beyaz çiçekli *Aconitum orientale* köklerinden yeni madde olarak izole edilen akonitorientalin izole edilerek tanımlanmışlardır. Beyaz çiçekli *Aconitum orientale* köklerinden elde edilen tüm alkaloitler yeni madde de dahil olmak üzere kirli-mor çiçekli örneğin köklerinden de elde edilmiştir. Tüm bu sonuçlar çiçek renkleri farklı olmalarına karşın her iki örneğin de *Aconitum orientale* türüne ait olduğunu ve bu örneklerin farklı türler olmadığını kanıtlamaktadır.

Key words : *Aconitum orientale,* pale-purple flowering sample, norditerpenoid alkaloids, aconitorientaline

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INTRODUCTION

Aconitum (wolfslayer) species are very toxic plants due to the diterpenoid alkaloid contents. These alkaloids are neurotoxic agents, causing brady-cardy, muscle-system spasms, hypotension, and death by arrest of respiration. *Aconitum* preparations have been used in very diluted forms as cardiotonics, febrifuges, sedatives, and anodynes. Today, *Aconitum* is very popular in homoeopathy and is included in many pharmaka (1-3). In continuation of our investigations on Turkish *Aconitum* species (4- 10), we now report the alkaloids isolated from the roots of a pale purple-flowering *Aconitum orientale* sample.

There are two *Aconitum orientale* samples with either white or pale-purple flowers that grow wild in Turkey. Some authors believe that they are different species (11). To clarify this situation we first investigated the alkaloids from the roots of a white-flowering *Aconitum orientale* sample. From this sample we isolated a new norditerpenoid alkaloid aconitorientaline together with known norditerpenoid alkaloids septentriodine, lappaconitine, finaconitine, ranaconitine, puberanidine, and delstaphisinine (12).

RESULT AND DISCUSSION

Before starting to isolate the compounds, the crude alkaloid extracts from the roots and aerial parts of both samples (white-flowering *Aconitum orientale* sample and pale purple-flowering *Aconitum orientale* sample) were chromatographically compared. The TLC results of the alkaloid extracts of both samples showed that they are very similar to each other.

From the roots of pale purple-flowering *Aconitum orientale* sample, the norditerpenoid alkaloids septentriodine, lappaconitine, finaconitine, ranaconitine, puberanidine and delstaphinine together with the new alkaloid aconitorientaline obtained for the first time from the white-fowering sample, were isolated. All alkaloids isolated from the white-flowering sample were also obtained from the pale purple-flowering *Aconitum orientale* sample.All these results show, although they have different flower colors, both samples belong to *Aconitum orientale* and they are not different species.

EXPERIMENTAL

Plant Material: The roots of pale purple-flowering *Aconitum orientale* MILLER (Ranunculaceae) were collected and identified by one of us (H. Ö.) on Kaçkar Mountains-Ayder Plato, Rize, Turkey at an elevation of 2065 m, in July 2006. A voucher specimen has been deposited with the Herbarium of the Faculty of Science and Literatüre, Süleyman Demirel University (No. Özçelik 12567) Isparta, Turkey.

General: Vacuum liquid chromatography (VLC): Merck Al_2O_3 (EM 1085) and SiO_2 60 G (7731). CC = Column chromatography. Chromatographic separaüons on a chromatotron were carried out on rotors coated with a l mm thick layer of Merck Al_2O_3 60 GF_{254} (1092) or SiO_2 60 PF_{254} (7749). TLC: toluene/AcOEı/Et_2NH 7:4: l or 7:4:2, $CHCl_3$ MeOH/NH_3 • H_2O 5 :3 : l, and toluene/acetone/MeOH/ NH_3-H_2O 49.5:41.5:5.5:1.5. Optical rotations: Perkin-Elmer-24l polaritneter. IR Spectra: Perkin-Elmer-100 FT-IR spectrometer; in $CHCI_3$; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: Varian-Unity-Inova 500 MHz spectrometer: δ in ppm rel. to Me_4Si as internıal Standard, *J* in Hz. MS: Finnigan-MAT-90 spectrometer; in m/z.

Extraction and isolation: Dried and powdered roots (850g) were extracted with 90% EtOH by percolation at r.t., and the extracts obtained were concentrated. The residues were treated with 0.5N H_2SO_4 and extracted with $CHC1_3$. NaOH soln. (5%) was then added to the aq. soln. (cooled in ice) to bring them to pH 10. The solns. were again extracted with $CHC1_3$. The $CHC1_3$ extracts were concentrated yielding the crude alkaloid extract (28.6 g). 10.0 g of this extract was first separated by VLC (neutral Al_2O_3, petroleum ether/$CHCl_3$/MeOH mixtures). VLC Frs. 10 and 11 (petroleum ether/ $CHC1_3$ 50:50: 620 mg) were combined and chromatographed (SiO_2, rotor, petroleum ether/$CHCl_3$/MeOH mixtures): septentriodine (**2***;* 28 mg) and lappaconitine (**3***;* 63 mg). VLC Frs. 12-18 (petroleum ether/$CHCl_3$ 40:60 - 10:90; 902 mg) were combined and chromatographed (SiO_2 rotor, petroleum ether/CHC_3/MeOH mixtures): finaconitine/ranaconitine (90 mg) and puberanidine (**6**: 27 mg). Purification by CC (Sephadex LH-20, $CHC1_3$) gave finaconitine (**4**; 52 mg) and ranaconitine (**5**; 10 mg). VLC Frs. 21-24 ($CHCl_3$/ MeOH 96:4 — 80:20; 782 mg) were combined and chromatographed (SiO_2 rotor, petroleum ether/ $CHCl_3$/MeOH mixtures): delstaphinine (**7**; 25 mg) and aconitorientaline (**1**; 12 mg). Septentriodine (**2**) and lappaconitine (**3**) were purified by prep. TLC(SiO_2, toluene/AcOEt/

Et_2NH 7:4:1). All the known compounds were identified by comparison of their ^1H- and ^{13}C-NMR data and co-TLC behavior with those of authentic samples. The NMR data of the important compound aconitorientaline (**1**) are given in Table 1.

Table 1. *^1H- and ^{13}C-NMR Data* (500 and 125 MHz, resp.; $CDCl_3$) *of Aconitorientaline* (**1**) δ in ppm, *J* in Hz.

	1	
	δ(H)	δ (C)
H–C(l)	3.69 – 3.71 (*m*)	85.4 (*d*)
CH_2(2)	1.72–1.74 (*m*, H_α), 1.65–1.67 (*m*, H_β)	29.9 (*t*)
CH_2(3)	1.74–1.77 (*m*, H_α), 2.43–2.46 (*m*, H_β)	32.0 (*t*)
C(4)	-	39.2 (*s*)
H–C(5)	1.90–1.92 (*m*)	44.5 (*d*)
H–C(6)	4.14 (*dd, J* = 1.6)	81.8 (*d*)
H–C(7)	2.25 (*d*, *J* = l)	41.8 (*d*)
C(8)	-	79.1 (*s*)
H–C(9)	1.79–1.82 (*m*)	46.9 (*d*)
H–C(10)	1.61–1.65 (*m*)	40.0 (*d*)
C(11)	-	48.1 (*s*)
CH_2(12)	2.29–2.31 (*m*, H_a), 1.61–1.65 (*m*, H_b)	29.0 (*t*)
H–C(13)	2.39–2.42 (*m*)	41.5 (*d*)
H–C(14)	3.59 (*t, J* = 5)	82.4 (*d*)
H–C(15)	4,35 (*d, J* = 6)	79.8 (*d*)
H–C(16)	3.75 (*dd*, *J* = 7, 12)	86.4 (*d*)
H–C(17)	2.87 (*s*)	68.3 (*d*)
CH_2(18)	3.52 (*d*, *J* = 10, H_a). 3.32 (*d*, *J* = 10, H_b)	65.8 (*t*)
H–C(19)	3.58 (*s*)	68.9 (*d*)
CH_2(20)	2.58–2.61 (*m*, H_a), 2.44–2.46 (*m*, H_b)	48.2 (*t*)
Me(21)	1.12 (*t*, *J* = 7)	12.2 (*q*)
*Me*O –C(6)	3.20 (*s*)	55.5 (*q*)
*Me*O –C(8)	3.40 (*s*)	57.9 (*q*)
*Me*O –C(14)	3.35 (*s*)	57.0 (*q*)
*Me*O –C(16)	3.32 (*s*)	55.7 (*q*)

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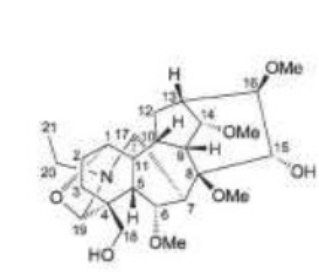
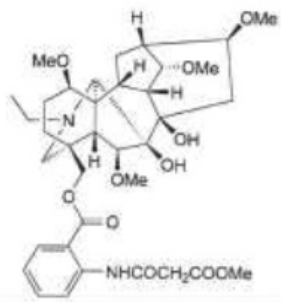
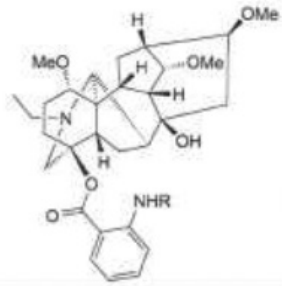


Aconitorientaline (**1**)

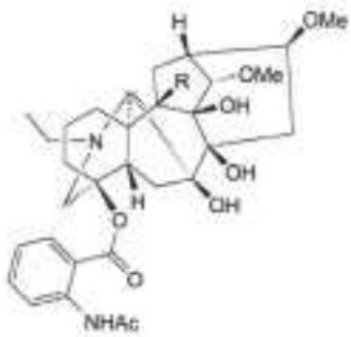


Septentriodine (**2**)

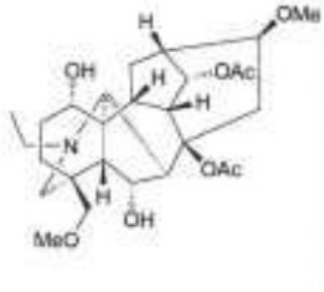


Lappaconitine (**3**) R = Ac

Puberanidine (**6**) R = H



Finaconitine (**4**) R = OH
Ranaconitine (**5**) R = H



Delstaphisinine (**7**)