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FURTHER DITERPENOID ALKALOIDS FROM *CONSOLIDA STENOCARPA*

F.Meriçli[1], A.H.Meriçli[1], N.Tan[1], H.Özçelik[2] and A.Ulubelen[1]

[1]Faculty of Pharmacy, University of Istanbul, Istanbul, Turkey

[2]Faculty of Sciences and Literature, S. Demirel University, Isparta, Turkey

The aerial parts of *Consolida stenocarpa* were examined in regard to their diterpenoid alkaloids, in addition to the alkaloids isolated before hetisine, hetisinone and ajadelphinine were also isolated and identified.

Key words: *Consolida stenocarpa*, diterpenoid alkaloids.

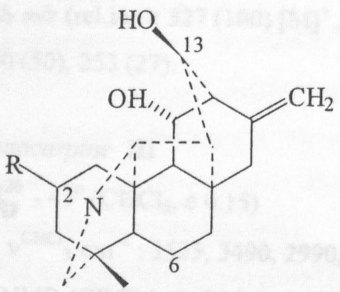
Introduction

The Turkish *Consolida* species are used externally in the treatment of rheumatic pain and sciantica and also used against body lice (**1**). *Consolida* species are important plants due to the diterpenoid alkaloidal contents. In continuation of our studies on the diterpenoid alkaloids we also included *Consolida* species (**2-4**). *Consolida stenocarpa* is an endemic plant growing in Central Turkey (**5**). There is a previous publication about the diterpenoid alkaloids in which a new diterpenoid alkaloid stenocarpine as well as lycoctonine and ajaconine were isolated (**6**).

Results and Discussion

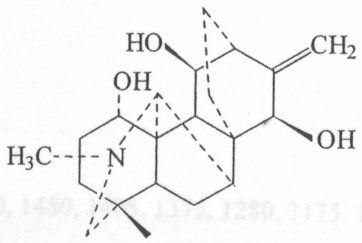
In the present study we have isolated hetisine, hetisinone and ajadelphinine in addition to stenocarpine. Lycoctonine and ajaconine were not obtained in this study.

This results showed that *Consolida stenocarpa* is not a rich source of alkaloids. The alkaloids, isolated were mostly C_{20} diterpenoidal type [hetisine (**I**)(7), hetisinone (**II**)(7) and stenocarpine (**III**)(6)], only ajadelphinine (**IV**)(3) is a C_{19} norditerpenoid alkaloid. The structures of the compounds were established by spectral data (IR, NMR, MS) and by comparing to those of literature values.

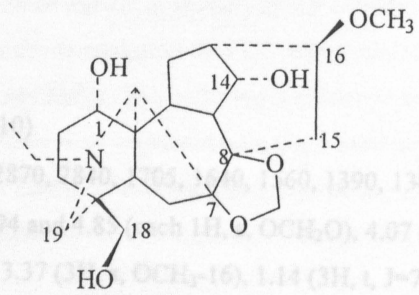


R_1 α OH hetisine (I)

R_1 = O hetisinone (II)



stenocarpine (III)



ajadelphinine (IV)

Hetisine **I**

$[\alpha]_D^{20}$ + 10° ($CHCl_3$, c 0.10)

IR ν^{CHCl_3} cm^{-1} : 3390, 3030, 1653, 1450, 1379, 1365, 1330, 1260, 1220, 1195.

^1H NMR ($CDCl_3$): δ: 4.88 and 4.70 (each 1H, s, H-17), 4.21 (2H, d, J=8.6 Hz, H-13α, 11β), 3.29 (2H, br s, OH), 1.17 (3H, s, H-18).

MS *m/z* (rel.int.): 329 (100) $[M]^+$, 312 (50), 300 (15), 283 (20), 264 (18), 218 (50).

Hetisinone **II**

$[\alpha]_D^{20}$ + 40° ($CHCl_3$, c 0.10)

IR ν^{CHCl_3} cm^{-1} : 3350, 1710, 1645, 1240, 1100, 1055, 890.

^1H NMR ($CDCl_3$): δ: 4.90 and 4.65 (each 1H, s, H-17), 4.15-4.00 (3H, m, H-13, 11, 2), 3.80 (1H, br s, H-20), 0.99 (3H, s, H-18).

MS *m/z* (rel.int.): 327 (100) $[M]^+$, 310 (30), 299 (15), 298 (20), 284 (14), 282 (30), 280 (50), 253 (27).

Stenocarpine **III**

$[\alpha]_D^{20}$ - 43° ($CHCl_3$, c 0.15)

IR ν^{CHCl_3} cm^{-1} : 3525, 3490, 2990, 1650, 1600, 1480, 1405, 1375, 1280, 1175, 1100.

^1H NMR ($CDCl_3$): δ: 5.10 and 4.88 (each 1H, s, H-17), 4.25 (1H, d, J=9.2 Hz, H-11α), 4.20 (1H, br s, H-15α), 4.00 (1H, dd, J=11.6 and 6.6 Hz, H-1β), 2.24 (3H, s, N-$\underline{CH_3}$), 0.61 (3H, s, H-18).

MS *m/z* (rel.int.): 345 (60) $[M]^+$, 344 (30), 328 (45), 327 (100), 316 (20), 298 (19), 286 (30).

Ajadelphinine **IV**

$[\alpha]_D^{20}$ - 18° ($CHCl_3$, c 0.10)

IR ν^{CHCl_3} cm^{-1} : 3400, 2870, 2840, 1705, 1640, 1560, 1390, 1300, 1200, 1160.

^1H NMR ($CDCl_3$): δ: 4.94 and 4.85 (each 1H, s, OCH_2O), 4.07 (1H, t, J=4.5 Hz, H-14), 3.58 (1H, m, H-1), 3.37 (3H, s, OCH_3-16), 1.14 (3H, t, J=7 Hz, N-$CH_2\underline{CH_3}$).

MS *m/z* (rel.int.): 421 (51) $[M]^+$, 405 (53), 404 (100), 391 (76), 376 (50), 363 (38),

The ^{13}C NMR data of **I-IV** were given in Table 1.

Experimental

Plant material

The aerial parts of *Consolida stenocarpa* (Davis & Hossain) Davis (Ranunculaceae), Syn. *Aconitella stenocarpa.* (Hossain and P.H.Davis) Sojak were collected in July 1994 from Davras mountain in Isparta, Turkey at an altitute of 1400 deposited in the Herbarium of the Faculty of Sciences and Literature, S. Demirel University, Isparta, No. Özçelik 6771.

Instruments

The IR spectrum was recorded on a Perkin-Elmer 983 instrument in $CHCl_3$; ^1H and ^{13}C NMR spectra were determined on a Bruker AC-200 L in $CDCl_3$, MS were run on a VG Zabspec spectrometer. Chromatographic sepns. were carried out by VLC and later on a Chromatotron using rotors coated with 1 mm thick layers of neutral Al_2O_3.

Extraction of crude alkaloids

Dried and powdered aerial parts (1200 g) were exhaustively extracted by percolation at room temp., with 95 % EtOH. The extract evaporated in vacuo. This was dissolved in CH_2Cl_2 (500 ml) and extracted with 2 % H_2SO_4 (v/v) (10x 200 ml). The acidic fraction was washed with CH_2Cl_2 (10x 200 ml). The combined acidic fraction was basified at room temperature with NaOH. Extraction CH_2Cl_2 (pH) (15x 250 ml) and evaporation of the combined extract in vacuo yielded a crude mixture of alkaloids (800 mg). The crude alkaloids separated by VLC, using Al_2O_3 and eluting by the addition of PE, EtOAc and EtOH. The collected fractions were separated into three groups and all of the groups were separated on a Chromatotron eluting with PE, followed by EtOAc and finally by MeOH. The yields of compounds were as follows: hetisine (I) (31 mg), hetisinone (II) (23 mg), stenocarpine (III) (22 mg), ajadelphinine (IV) (42 mg).

Table 1. The ^{13}C NMR data of isolated alkaloids

	Compound			
C	I	II	III	IV
1	34.3 t	45.2 t	69.3 d	71.7 d
2	66.8 d	214.5 s	30.0 t	26.8 t
3	39.0 t	49.9 t	38.0 t	28.3 t
4	36.5 s	42.4 s	34.0 s	38.1 s
5	61.4 d	60.4 d	51.0 d	45.3 d
6	64.2 d	65.2 d	22.6 t	32.4 t
7	36.3 t	36.2 t	41.3 d	89.7 s
8	43.6 s	49.6 s	43.6 s	81.7 s
9	55.5 d	60.3 d	53.5 d	45.3 d
10	50.5 s	55.8 s	51.2 s	39.3 d
11	76.5 d	75.8 d	72.3 d	51.3 s
12	51.0 d	50.9 d	46.5 d	26.5 t
13	72.4 d	71.5 d	24.4 t	38.5 d
14	52.0 d	52.0 d	27.1 t	74.6 d
15	34.0 t	33.8 t	77.5 d	33.5 t
16	146.2 s	145.6 s	153.0 s	81.3 d
17	107.7 t	108.2 t	109.2 t	63.6 d
18	29.9 q	27.8 q	25.5 q	67.7 t
19	63.3 t	64.1 t	59.0 t	56.0 t
20	68.0 d	70.1 d	68.9 d	--
OCH_2O	--	--	--	93.8 t
N-$\underline{CH_3}$	--	--	43.4 q	--
N-$\underline{CH_2}$	--	--		50.1 t
$\underline{CH_3}$	--	--		13.7 q
OMe-16	--	--		56.5 q

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