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Short Communication

ALKALOIDS FROM HAEMANTHUS MULTIFLORUS MARTYN

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ABSTRACT

Phytochemical study of the alkaloidal content of Haemanthus multiflorus Martyn grown in Ethiopia, Resulted in the isolation and characterisation of lycorine, in addition to galanthamine and sanguinine, are to be reported for the first time from this species.

INTRODUCTION

Genus Haemanthus (Family Amaryllidaceae) is native to South Africa and has been known for many years to possess several physiological activities. The extracts of different Haemanthus species have been employed by the native Africans for treatment of leprosy ulcers, febrile colds, asthma and cough[1-4].

Reviewing the current literature, it was observed that different Haemanthus species contain alkaloids[5-7].

The alkaloids tazetine and lycorine were isolated from H.albiflos Jacq[5], while coccinine, montanine and manthine were

observed in H.amarylloides Jacq[5]. Coccinine, lycorine, manthidine and montanine were identified in H. coccineus l; montanine from H. montanus baker[5]; natalensine from H.natalensis Hook and H. puniceus L[6]. Galanthamine,haemanthamine, haemultine,hippeastrine, lycorenine and lycorine were isolated from H.katherinae Baker[6]. Haemanthamine, haemanthidine, 6-hydroxy crinamine were isolated from H.natalensis pappe[7]. In addition to kalbretorine, haemanthamine, lycorine and hippadine from H.Kalbreyeri Indian[3].

While recent studies established that certain Haemanthus alkaloids have a marked antitumour activity[3].

The medicinal importance of this genus, as well as, several reports[5-7] on the presence of many alkaloids in different Haemanthus species attracted our attention to re-examine the alkaloids of Haemanthus multiflorus Martyn.

EXPERIMENTAL

All m.p.s. were uncorrected. UV spectra were in methanol using perkin-Elmer 550 Spectrophotometer and IR were in KBr using Perkin-Elmer 298. ^{1}H-NMR spectra were measured at 90& 400 MHz in $CDCl_3$ with TMS as internal standard, chemical shifts were given in p.p.m. and coupling constants in Hz using WH 400 from Bruker, while ^{13}c-NMR was at 100 MHz using WH 400 from Bruker. MS were recorded at 70 ev using direct inlet system with high resolution MS-50, Kratos, A.E.J. Column chromatography was performed on Sephadex L.H. 20 (Merck), TLC was on silica gel G (E. Merck) using $CHCl_3$-MeoH (8:2) and the spots were detected by spraying with modified Dragendorff's reagent.

Plant material:

The bulbs of Haemanthus multiflorus Martyn were collected from Ethiopia in March 1984 during flowering. The powdered bulbs was supplied and identified by Prof. E. Dagne, Faculty of Science, University of Addis Ababa,Ethiopia.

Alkaloids from Haemanthus Multiflorus Martyn.

Isolation Procedure:

The air-dried powdered bulbs (500 g.) were defatted with pet.ether (60-80°C) and then extracted till exhaustion with methanol by maceration and percolation. The concentrated alcoholic extract was acidified with 5% aqueous HCl, shaken with $CHCl_3$ (4x250 ml) and the chloroform was discarded. The aqueous phase was basified with conc. NH_3 and extracted with $CHCl_3$ (4x250 ml).

The combined $CHCl_3$ extract was dehydrated and concentrated under vacuum to yield fraction A (4g).

Fraction A, was digested in MeOH (100 ml), whereby compound 1 separates as a creamy powder (30 mg). The filtrate was concentrated and passed through Sephadex L H. 20 column (4x40 cm) using methanol-acetone (4:1) as eluent. Fractions (50 ml each) were monitored by TLC using solvent system I ($CHCl_3$ - MeOH (8:2). The fractions were combined according to similarity in contents. As a result of this fractionation, compound 2 (R_f, 0.36, syst. 1)and compound 3 (R_f, 0.5, syst. I) were isolated.

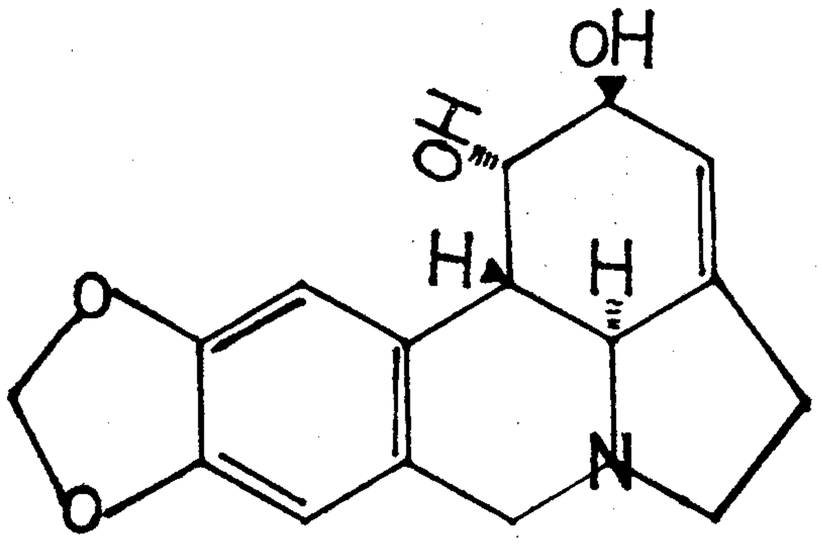
Compound 1 : Colourless needles (EtOH) 30 mg,m.p. 252-54°C, m.p. remained undepressed on admixture with an authentic sample of lycorine, its spectra (UV, IR, NMR and MS), R_f values in different systems, are identical with those of lycorine[8,9].

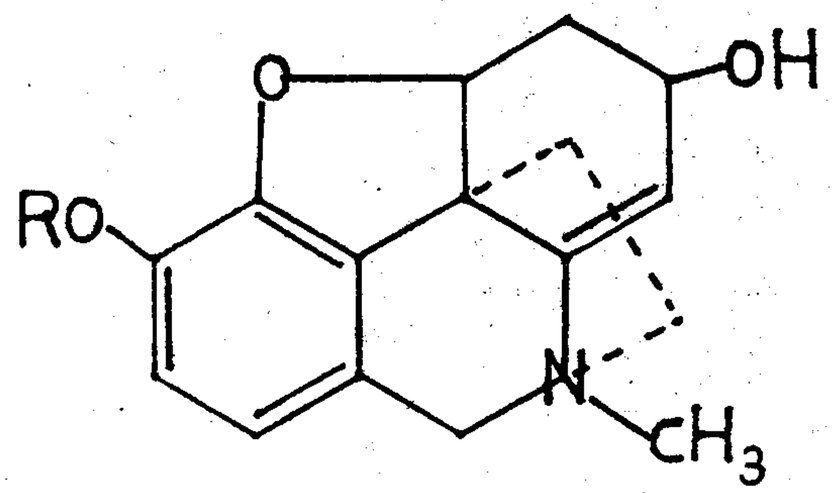
Compound 2 : Colourless crystals (MeOH), 20 mg m.p. 126-128°C, $[\alpha]_D^{20}$ = -118° (C=0.5, EtOH), UV λ_{max}^{MeOH} nm (log E) 203 (4.5), 288 (3.41), IR (KBr)ν(cm^{-1}), 3200 (OH) 1620,1500,1480,1300,1100(O-C). MS m/z (rel.int.)287.1523(9)(calculated for $C_{17}H_{21}NO_3$,287.1521)286(10)($C_{17}H_{20}NO_3$),270 (12)($C_{17}H_{20}NO_2$), 244 (21) ($C_{15}H_{18}NO_2$),216 (22) ($C_{13}H_{14}NO_2$),174 (17) ($C_{11}H_{10}O_2$). ^{1}H-NMR ($CDCl_3$) (Table 1) and ^{13}C-NMR (Table 2). The physical and spectral properties of the compound were indistinguishable from those reported for galanthamine in the literature[10-12].

Compound 3 : Colourless needles (MeOH) 200 mg, m.p. 210-212°C, $[\alpha]_D^{20}$ = -137° (C=1, MeOH), UV λ_{max}^{MeOH} nm (log E) 208(4.47),234 (3.82), 290 (3.4), IR (KBr)ν (cm^{-1}), 3400(OH),2950 (olefinic hydrogen) 1625 (C=C), MS m/z (rel.int),

273.1367(100)(calculated for $C_{16}H_{19}NO_3$, 273.1365), 272 (76) ($C_{16}H_{18}NO_3$), 212 (12)($C_{14}H_{12}O_2$), 202 (26.1)($C_{12}H_{12}NO_2$), 160 (31.7($C_{10}H_8O_2$). ^{1}H-NMR (Table 1), ^{13}C-NMR (Table 2).

The physical and spectral properties of the compound were indistinguishable from those reported for sanguinine in the literature[10-12].





1- Lycorine

2- R = CH_3, Galanthamine

3- R = H, Sanguinine

Alkaloids from Haemanthus Multiflorus Martyn.

Table 1 : ^{1}H-NMR Spectral Data of Alkaloids 2 and 3

Proton	Alkaloid 2*	Alkaloid 3**
H-12	6.65, d, 8.5	6.62, d, 10
H-11	6.62, d, 8.5	6.58,dd, 10,1.5
H-4	6.15-5.95, m	6.15, d, 13
H-3		5.95,dd, 13,6
H-15	4.58,m	4.58,m
H-2	4.2 ,m	4.2 ,m
H-9 B	4.15,d,16	4.12, d, 18
H-9 ∝	3.75,d,16	3.71, d, 18
OCH_3	3.92,S	---
N-CH_3	2.4 ,S	2.4 , S
H-1	4.1, m	2.55, m
H-1`		1.7 , m
H-6	4.1-1,m	2.15, m
H-6`		
H-7		3.1-3.28,m
H-7`		

* Alkaloid 2 : 90 MHz ^{1}H-NMR in $CDCl_3$.

** Alkaloid 3: 400 MHz ^{1}H-NMR in $MeOD_4$.

Table 2 : ^{13}C-NMR* Spectral Data of Alkaloids 2 and 3

Carbon	Alkaloid 2	Alkaloid 3
C-1	30	31.1
C-6	34	35.4
C-5	48.2	51.0
C-7	54.3	54.2
C-9	60.5	61.3
C-2	62.2	62.1
C-15	88.1	88.3
C-12	110.5	116.0
C-11	120.6	121.1
C-10	129.5	124.8
C- 3	126.0**	128.5**
C- 4	126.8**	128.6**
$C-14_a$	132.7	134.0
C-13	144.5	142.9
$O-CH_3$	56.0	---
$N-CH_3$	42.2	43.1

* in MeOH-d_4

** Interchangeable values.

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قلوانيات من الهيمانسس ملتيفلوروس مارتين

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x معهد الكيمياء العضوية والحيوية ـ جامعة بون ـ المانيا الغربية

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