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TWO PYRROLIZIDINE ALKALOIDS FROM *GYNURA SCANDENS*

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Key Word Index—*Gynura scandens*; Asteraceae; pyrrolizidine alkaloids; gynuramine; acetylgynuramine.

Abstract—Two new pyrrolizidine alkaloids have been isolated from *Gynura scandens* and their structures analysed by spectroscopic methods. The names gynuramine and acetylgynuramine are proposed.

INTRODUCTION

Pyrrolizidine alkaloids are widely distributed in many plant families. Associations of Lepidoptera with *Gynura scandens* made it a likely source of such compounds [1]. These alkaloids are of great pharmaceutical interest, because they are hepatotoxic to man and domestic animals [2–7].

Gynura, a genus not previously examined for alkaloids, is closely related to *Senecio* and also belongs to the tribe Senecioneae, which is a major source of pyrrolizidine alkaloids. These considerations and its use as a medicinal herb in Africa [8, 9] caused me to investigate *G. scandens* with regard to its alkaloid content.

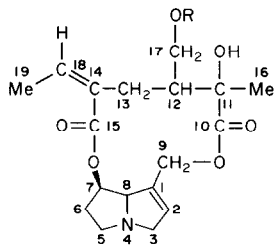
Two new pyrrolizidine alkaloids could be isolated after extraction and purification of plant material. Structural analysis was carried out by IR-, mass-, ^{1}H NMR-, and ^{13}C NMR spectroscopy. For these new alkaloids the names gynuramine and acetylgynuramine are proposed. Gynuramine was identified independently from insect sources [1].

RESULTS AND DISCUSSION

Methanolic extraction of plant material was followed by purification of the residue by distribution between aqueous ammonia and methylene chloride. The two new alkaloids were isolated by low pressure CC from the resulting alkaloid mixture. The IR data of the two substances are very similar. They only differ in showing two carbonyl bands and one hydroxyl band for alkaloid A, and one carbonyl band and two hydroxyl bands for alkaloid B.

The mass spectra proved the molecular formula $C_{20}H_{27}NO_7$ for alkaloid A, and $C_{18}H_{25}NO_6$ for alkaloid B. Typical fragmentations between *m/z* 140 and *m/z* 80 were characteristic of retronecine or its isomeric form. In addition, the other fragmentation shows, that A and B only differ in an acetyl group in alkaloid A. On account of this fact and with regard to the similarity of the IR spectra, alkaloid A must be the acetyl derivative of alkaloid B.

Important information for structure determination can be found from NMR analysis. The ^{1}H NMR spectroscopy data are given in Table 1, and that for ^{13}C NMR spectroscopy in Table 2. All peak-values were



1 R=H

2 R=C(=O)–Me

Table 1. ^1H NMR data of **1** and **2** ($CDCl_3$; TMS)

	1	2
C_{16}–H_3	1.49, *s*, 3H	1.40, *s*, 3H
C_{19}–H_3	1.85, *dd*, 3H	1.83, *dd*, 3H
	$J = 7, J = 2$	$J = 7, J = 2$
C_{21}–H_3	—	2.04, *s*, 3H
C_{12}-H	2.00, *m*, 1H	1.96, *m*, 1H
C_6-H_B	2.12, *m*, 1H	2.09, *m*, 1H
C_6–H_A	2.29, *m*, 1H	2.28, *m*, 1H
C_{13}–H_B	2.37, *d*, 1H	2.31, *d*, 1H
	$J = 6$	$J = 6$
C_{13}–H_A	2.64, *d*, 1H	2.64, *d*, 1H
	$J = 6$	$J = 6$
C_5–H_B	2.47, *t*, 1H	2.47, *t*, 1H
	$J = 6$	$J = 6$
C_5–H_A	2,27, *t*, 1H	3.27, *t*, 1H
	$J = 6$	$J = 6$
C_3–H_B	3.48, *d*, 1H	3.48, *d*, 1H
	$J = 6$	$J = 6$
C_3–H_A	3.90, *d*, 1H	4.02, *d*, 1H
	$J = 6$	$J = 6$
C_9–H_B	4.04, *d*, 1H	4.08, *d*, 1H
	$J = 12$	$J = 12$
C_9–H_A	5.51, *d*, 1H	5.50, *d*, 1H
	$J = 12$	$J = 12$
C_{17}–H_2	3.62/4.05, *d*, 2H	4.16, *d*, 3H
	$J = 5$	$J = 8$
C_8–H	4.29, *m*, 1H	4.31, *m*, 1H
C_7–H	5.03, *m*, 1H	5.08, *m*, 1H
C_{18}–H	5.88, *qd*, 1H	5.77, *qd*, 1H
	$J = 7, J = 2$	$J = 7, J = 2$
C_2–H	6.22, *m*, 1H	6.21, *m*, 1H
C_{17}–OH	3.05, *m*, 1H	—
C_{11}–OH	3.20, *m*, 1H	3.20, *m*, 1H

δ Value in ppm; J in H_2.

Table 2. ^{13}C NMR data of **1** and **2** ($CDCl_3$; TMS)

Carbon No.	1	2	
10	176.8	177.3	C=O
20	—	170.9	C=O
15	167.4	167.2	C=O
18	136.8	136.9	=CH
2	135.6	135.1	=CH
14	132.2	132.2	=C
1	131.3	131.4	=C
8	77.6	77.6	CH
11	78.0	76.2	C
7	75.0	75.1	CH
3	62.9	62.9	CH_2
17	58.5	62.2	CH_2
9	60.7	61.0	CH_2
5	53.1	53.2	CH_2
12	43.9	42.6	CH
13	34.8	34.7	CH_2
6	31.4	34.2	CH_2
16	25.3	25.5	Me
21	—	21.1	Me
19	15.1	15.1	Me

δ Value in ppm.

verified by decoupling experiments and interpretation of the off-resonance and coupled spectra respectively. From these data, alkaloid B possesses a hydroxymethyl group at C-12, whereas in alkaloid A this group must be acetylated. Alkaloid B is thus an isomeric form of the well-known alkaloid retrorsine, which shows this hydroxymethyl group in position 11.

The position of the hydroxymethyl group in alkaloid B is given by the mass spectrum from the ion m/z 264, which is formed from the molecular ion after loss of COO and MeCO.

After interpretation of all data, alkaloid A is thus structure **2**, and alkaloid B structure **1**. I propose the names acetylgynuramine for **2** and gynuramine for **1**.

EXPERIMENTAL

G. scandens O. Hoffm. was collected in Shimba National Reserve, Kwale District, Coast Province, Kenya, East Africa.

The dried and pulverized drug was extracted with MeOH in a Soxhlet apparatus for 1 week. After evaporating to dryness, the resulting residue was resolved in 2.5% HCl and extracted with Et_2O. The aq. phase was basified with NH_3 (25%) and extracted with CH_2Cl_2. The solvent of the organic phase was removed under red. pres. and a solid yellow residue was obtained, which was separated with MeOH–CH_2Cl_2 (9:1) on Si gel 60 by low pressure CC yielding the two new alkaloids. They were recrystallized from Me_2CO.

Gynuramine. Mp: 202–204°; $[\alpha]_D^{20}$: −16° ($CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 3570, 3410 (2 × OH), 3060 (C=C),1735 (satd ester), 1715 (unsatd ester), 1655 (C=C); CIMS ($CHCl_3$), 70 eV, m/z (% rel. int.): 351[M]$^+$ (1.5), 320 [M − CH_2OH]$^+$ (0.4), 307 [M − COO]$^+$ (0.5), 264 [307 − MeCO]$^+$ (0.7), 262[M − $C_3H_5O_3$]$^+$ (2.4), 220 [264 − C_2H_4O]$^+$ (3.1), 138 [220 − C_5H_6O]$^+$ (50.2), 137 [220 − C_6H_7O]$^+$ (31.0), 136 [220 − C_6H_8O]$^+$ (96.9), 121 [138 − OH]$^+$ (55.7), 120 [137 − OH]$^+$ (87.7), 119 [136 − OH]$^+$ (100), 95 [121 − C_2H_2]$^+$ (51.6), 94 [120 − C_2H_2]$^+$ (55.7), 93 [119 − C_2H_2]$^+$ (81.1), 80 [95 − Me]$^+$ (28.6).

Acetylgynuramine. Mp: 153–155°; $[\alpha]_D^{20}$: −33° ($CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 3440(OH), 3080 (C=C), 1740 (Me COO and satd ester), 1720 (unsatd ester), 1630 (C=C); CIMS ($CHCl_3$), 70 eV, m/z (% rel. int.): 393[M]$^+$ (21.2), 365 [M − CO]$^+$ (1.4), 349 [M − COO]$^+$ (5.6), 320 [M − CH_2OCOMe]$^+$ (2.8), 307 [349 − CH_2CO]$^+$ (4.2), 304 [M − CHOHCOO]$^+$ (10.3), 246 [307 − MeCO − H_2O]$^+$ (13.4), 220 [246 − C_2H_2]$^+$ (43.3), 138 (45.9), 137 (25.4), 136 (98.9), 121 (48.2), 120 (87.7), 119 (100), 95 (15.8), 94 (17.3), 93 (22.8) 80 (4.2).

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