Pergamon

PII: S0031-9422(96)00338-X

Phytochemistry, Vol. 43, No. 4, pp. 913–915, 1996

3-AMINOSPIROSOLANE ALKALOIDS FROM *SOLANUM ARBOREUM*

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(*Received in revised form* 3 *April* 1996)

Key Word Index—*Solanum arboreum*; Solanaceae; steroidal alkaloids; 3-aminospirosolanes.

Abstract—Two new 3-aminospirosolane steroidal alkaloids, (22*S*,25*S*)-3α-amino-5α-spirosolane and (22*S*,25*S*)-3β-aminospirosol-5-ene, along with the known soladunalinidine were isolated from the alkaloid fraction of a methanol extract of *Solanum arboreum*. Their structures were determined by a combination of 1D and 2D NMR techniques and mass spectrometry. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Steroidal alkaloids isolated from the Solanaceae possess almost exclusively the 3-hydroxyl substituent or its glycosylated derivative [1, 2]. By contrast, 3-amino steroidal alkaloids are rare in the family. In particular, there had been only one report [3] of a 3-aminospirosolane, soladunalinidine (**1**), before we isolated compounds **2–5** from *Solanum triste* Jacq. [4, 5]. Our continuing interest in *Solanum* species from Trinidad led us to investigate *S. arboreum* Kunth ex Dunal, and we now report the isolation of two further related 3-aminospirosolanes, **6** and **7**, from this plant.

RESULTS AND DISCUSSION

The crude alkaloid fraction from a methanolic extract of the leaves and stems of *S. arboreum*, after silica gel column chromatography followed by preparative TLC, yielded the new compounds **6** and **7** as well as the known **1**. Compound **6** was an amorphous solid whose IR spectrum showed a peak at 3415 cm^{-1} (NH/OH). Its EI mass spectrum had fragment ions at *m/z* 138, 114 and 56 which are characteristic of 3-aminospirosolanes [6] while the $[M]^+$ in the HR EI mass spectrum (414.3615) was consistent with the molecular formula $C_{27}H_{46}N_2O$ for **6**. The ^1H and ^{13}C NMR spectra (Table 1) confirmed that **6** possessed the (22*S*,25*S*)-3α-amino-5α-spirosolane structure [1–4, 7, 8]. The stereochemistry at C-3 was determined from the H-3 (δ 3.18, $W_{1/2}$ = 17 Hz) and C-3 (δ 45.70) signals [3, 4].

The ^1H and ^{13}C NMR data for **7** indicated the unsaturated (22*S*,25*S*)-3β-aminospirosol-5-ene structure [1–4, 7, 8]. The β-orientation of the amino group followed from a consideration of the H-3 (δ 2.60, $W_{1/2}$ = 25 Hz) and C-3 (δ 51.92) signals [3, 4]. The HR mass spectrum had an $[M]^+$ peak as well as fragment ions which agreed with the structure proposed for **7**.

The spectral data (IR, EI mass spectra, ^1H and ^{13}C NMR) of the most polar compound led to the structure shown for **1**, and the data agreed very closely with those previously reported [3]. The complete assignment of the ^1H and ^{13}C chemical shifts of all three compounds (Table 1) was achieved with the aid of ^1H–^1H COSY, HMQC, HMBC and NOESY experiments.

EXPERIMENTAL

General. Mps: uncorr.; TLC and prep. TLC on silica gel 60 PF254 and 366, 0.25 and 1 mm layers, respectively; CC with silica gel 60, 70–230 mesh; EIMS (probe) 70 eV; NMR: ^1H, COSY, HMQC (optimized for $^1J_{H-C}$ = 140 Hz), HMBC (optimized for $^nJ_{H-C}$ = 8 Hz) and NOESY spectra at 500 MHz, ^{13}C at 100 MHz in $CDCl_3$ with TMS as int. standard.

Plant material. Aerial parts of *S. arboreum* were collected in May 1993 at the base of the Maracas Waterfall, Maracas, St Joseph, Trinidad. The plant material was identified by W. Johnson of the National Herbarium of Trinidad and Tobago where a voucher specimen is deposited. The aerial parts were sun dried (*ca* 30°) for week.

Extraction and isolation. The dried milled plant material (1.3 kg) was exhaustively extracted by percolation with MeOH (15 l) at room temp. Evapn of the solvent under red. pres. gave 200 g crude extract which was treated with 600 ml 10% HOAc. The resulting soln was extracted with EtOAc (3 × 200 ml) and the remaining aq. phase then basified to pH 9 by addition of 2 M aq. NH_3. The ppt. obtained was filtered off and dried to yield 17.7 g crude alkaloid extract. Silica gel CC of this extract (14.3 g), eluting with $CHCl_3$–MeOH–aq. NH_3 mixts of increasing polarity, resulted in 5 combined frs. Repeated silica gel prep. TLC ($CHCl_3$–MeOH–aq.

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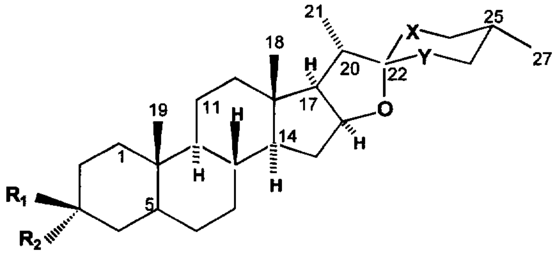

1	R_1=NH_2	R_2=H	5α-H	X=CH_2	Y=NH
2	R_1=NH_2	R_2=H	Δ^5	X=NH	Y=CH_2
3	R_1=NH_2	R_2=H	5α-H	X=NH	Y=CH_2
4	R_1=H	R_2=NH_2	Δ^5	X= CH_2	Y=NH
5	R_1=H	R_2=NH_2	Δ^5	X=NH	Y=CH_2
6	R_1=H	R_2=NH_2	5α-H	X=CH_2	Y=NH
7	R_1=NH_2	R_2=H	Δ^5	X=CH_2	Y=NH

NH_3, 1:4:satd) on fr. III yielded **6** (11 mg, 0.0009%), **7** (5 mg, 0.0004%) and **1** (10 mg, 0.0008%).

Compound **6**. Amorphous solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3415. EIMS *m/z* (rel. int.): 414 $[M]^+$ (41), 138 $[C_9H_{16}N]^+$ (100), 114 $[C_6H_{12}NO]^+$ (53), 56 $[C_3H_6N]^+$ (42). HR EIMS *m/z*: 414.3615 $[M]^+$ ($C_{27}H_{46}N_2O$ requires 414.3610). ^1H and ^{13}C NMR: Table 1.

Table 1. ^1H and ^{13}C NMR spectral data for compounds **1**, **6** and **7** in $CDCl_3$ at 500 MHz

	1		**6**		**7**	
C	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	37.7	0.95, 1.65	32.1	1.22, 1.44	38.1	1.09, 1.84
2	32.7	1.22, 1.67	29.1	1.43, 1.73	32.6	1.33, 1.71
3	51.1	2.64	45.7	3.18	51.9	2.60
4	39.4	1.10, 1.41	36.3	1.18, 1.54	43.3	2.06, 2.16
5	45.6	1.09	39.2	1.45	141.8	-
6	28.7	1.25, 1.25	28.6	1.19, 1.19	120.2	5.31
7	32.4	0.87, 1.66	32.3	0.92, 1.68	32.1	1.54, 2.00
8	35.1	1.53	35.1	1.54	31.4	1.65
9	54.5	0.64	54.6	0.76	50.2	0.97
10	35.7	—	36.5	—	36.7	—
11	21.0	1.27, 1.51	20.6	1.26, 1.52	20.8	1.46, 1.53
12	40.3	1.11, 1.70	40.3	1.12, 1.72	39.9	1.17, 1.74
13	40.9	—	40.9	—	40.6	—
14	55.8	1.05	55.9	1.05	56.0	1.07
15	32.6	1.22, 2.00	32.7	1.24, 2.00	32.7	1.28, 2.00
16	78.5	4.12	78.6	4.12	78.5	4.14
17	62.0	1.58	62.0	1.61	61.8	1.62
18	17.0	0.81	16.4	0.82	16.7	0.85
19	12.4	0.80	11.4	0.80	19.5	1.02
20	43.0	1.63	43.1	1.64	43.0	1.65
21	15.9	0.95	15.9	0.96	15.9	0.98
22	99.0	—	99.1	—	99.0	—
23	26.7	1.35, 1.66	26.7	1.36, 1.67	26.6	1.36, 1.68
24	28.6	1.36, 1.53	28.6	1.36, 1.55	28.5	1.37, 1.55
25	31.1	1.59	31.1	1.60	31.1	1.60
26	50.2	2.72, 2.74	50.3	2.72, 2.74	50.2	2.72, 2.74
27	19.4	0.85	19.4	0.86	19.4	0.86

Compound **7**. Amorphous solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3445, 1640. EIMS *m/z* (rel. int.): 412 $[M]^+$ (27), 138 $[C_9H_{16}N]^+$ (100), 114 $[C_6H_{12}NO]^+$ (51), 56 $[C_3H_6N]^+$ (71). HR EIMS *m/z*: 412.3452 $[M]^+$ ($C_{27}H_{44}N_2O$ requires 412.3454). ^1H and ^{13}C NMR: Table 1.

Compound **1**. Amorphous solid, $[\alpha]_D^{22}$ +13.3° (MeOH; *c* 1.5) [lit. [3] $[\alpha]_D^{35}$ +1.3° ($CHCl_3$; *c* 0.46); lit. [9] $[\alpha]_D^{22}$ +3.7° ($CHCl_3$; *c* 0.25) for synthetic **1**]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425. EIMS *m/z* (rel. int.): 414 $[M]^+$ (14), 138 $[C_9H_{16}N]^+$ (100), 114 $[C_6H_{12}NO]^+$ (58), 56 $[C_3H_6N]^+$ (26). HR EIMS *m/z*: 414.3612 $[M]^+$ (calc. for $C_{27}H_{46}N_2O$, 414.3610). Full ^1H and ^{13}C NMR data: Table 1.

Acknowledgements—We thank Mr W. Johnson of the National Herbarium of Trinidad and Tobago for assistance in the collection and identification of the plant material. Financial assistance from the U.W.I., the CIDA Canada/U.W.I. Institutional Strengthening Project (Grant SD-13) and the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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