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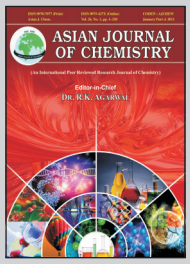

New Steroidal Alkaloid Constituent from *Solanum surrattense*

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A new steroid alkaloid have been isolated from the ethyl acetate soluble fraction of the whole plant of *Solanum surrattense*. The structure was assigned on the basis of 1D (^{1}H-NMR, ^{13}C-NMR, DEPT, NOE) and 2D NMR (HMBC, HMQC, COSY, NOESY) experiments. The isolated steroidal alkaloid was found to be a new addition in the list of natural products.

Keywords: *Solanum surrattense*, Solanaceae, Steroid.

INTRODUCTION

The genus *Solanum* comprises about 3000 species, is widely distributed in the tropical region of Asia, Australia and Polynesian Islands[1]. In Pakistan, it is common in waste places from planes to 1500 M[2]. *Solanum surrattense* is a perennial prickly prostrate herb and have been used in folk medicine for the treatment of bronchial asthma, non specific cough, vomiting, catarrhal fever, rheumatism, diarrhea, blood cancer and controlling of stones in bladders. The plant is bitter, digestive, alterative, astringent, expectorant, aperients and carminative[3-5]. The pharmacological importance of the *S. surrattense* prompted us to investigate the phytochemicals from the ethyl acetate soluble fraction of the whole plant. Our investigation has led to the discovery of a new steroid alkaloid (**1**) and was assigned as 1β,3β-dihydroxy 22αN-spirosol-5-ene. The compound was identified by IR, MS, 1D (^{1}H NMR, ^{13}C NMR, DEPT, NOE) and 2D NMR (HMBC, HMQC, COSY, NOESY) spectroscopic techniques. This is the first report of the natural occurrence of this steroidal alkaloid, following its earlier synthesis[6]. To the best of our knowledge, for this compound we are presenting the physical and spectroscopic data for the first time in literature.

EXPERIMENTAL

Melting points were obtained on Buchi melting point apparatus and uncorrected. Optical rotations were taken on a JASCO DIP 360 polarimeter. The IR spectra were recorded on a FTIR-8900 Shimadzu spectrometer. The 1D and 2D NMR spectra were recorded in pyridine-d_5 at 500 MHz on a Bruker Av 500 spectrometer. The chemical shift values are reported in ppm (δ) units and coupling constant (*J*) are shown in Hz. EIMS, HREIMS and HRFABMS were recorded on a JMS-HX-110 with a data system on JMS-DA 500 mass spectrometer. Aluminium sheets pre-coated with silica gel 60F_{254} (20 × 20 cm, 0.2 mm thick, E-Merck) were used for TLC and silica gel (230-400 mesh) was used for column chromatography. Pre-coated RP-18 gel (E-Merck) glass plates were used for TLC.

The dried (whole plant, 6 kg) *S. surrattense* Burm. f. was collected from Cholistan desert near Bahawalpur, Pakistan and identified by Dr. Muhammad Arshad, Plant Taxonomist, Cholistan Institute of Desert Studies, The Islamia University Bahawalpur, Bahawalpur, Pakistan where a voucher specimen (CIDS/IUB/10) has been deposited.

Extraction and isolation: The shade dried 6 kg crushed plant was chopped and soaked in methanol (3 × 25 L) for thrice and the combined methanolic extracts were concentrated under reduced pressure to give a crude extract (800 g). The crude extract was portioned between *n*-hexane (125 g), EtOAc (85 g) and *n*-ButOH (255 g) extract. The ethyl acetate soluble fraction was applied to silica gel column chromatography and eluted with *n*-hexane-$CHCl_3$ (90: 10, 80: 20, 70: 30, 60: 40, 50: 50, 40: 60, 30: 70, 20: 80, 10: 90, 90: 10), $CHCl_3$ (100 %) and $CHCl_3$-methanol (90:10, 80:20, 70:30), in increasing order of polarity to obtain 14 fractions. The fractions obtained from

TABLE-1
1D (^{1}H, ^{13}C NMR) AND 2D NMR (HMQC, HMBC) DATA OF COMPOUND **1** IN $CHCl_3$ + CH_3OH (1:1)

Position No.	^{1}H[a] (HMQC)	Multiplicity and *J* (Hz)	^{13}C[b]	HMBC[c] (H → C)
1.	3.90	dd, (9.9, 7.1)	75.1	J^2 (C-2, C-10)
				J^3 (C-3, C-19, C-5)
2.	2.43	ddd, (5.0, 9.9, 7.1)	39.6	J^2 (C-1, C-3)
				J^3 (C-4, C-10)
3.	4.10	dt, (7.9, 5.1)	69.9	J^2 (C-2, C-4)
				J^3 (C-1, C-5)
4.	2.65	ddd, (11.5, 8.8, 3.0)	44.7	J^2 (C-3, C-5)
				J^3 (C-2, C-6, C-10)
5.	-	-	140.4	-
6.	5.37	brd (7.1)	122.1	J^2 (C-5, C-7)
				J^3 (C-4, C-8, C-10)
7.	1.85-1.65	m	32.8	J^2 (C-6, C-8)
				J^3 (C-5, C-9, C-14)
8.	1.55-1.65	m	32.0	J^2 (C-7, C-9, C-14)
				J^3 (C-6, C-10, C-11, C-13)
9.	1.00	m	50.8	J^2 (C-8, C-10, C-11)
				J^3 (C-1, C-7, C-5, C-12, C-14, C-19)
10.	-	-	37.5	-
11.	1.55-1.78	m	21.5	J^2 (C-9, C-12)
				J^3 (C-8, C-10, C-13)
12.	1.55-1.78	m	40.4	J^2 (C-11, C-13)
				J^3 (C-9, C-14, C-17, C-18)
13.	-	-	41.3	-
14.	1.15	m	56.9	J^2 (C-8, C-15)
				J^3 (C-16, C-17, C-18)
15.	1.35-2.21	m	33.8	J^2 (C-14, C-16)
				J^3 (C-13 C-17,)
16.	4.24	brd, (8.8, 7.1)	79.9	J^2 (C-15, C-17)
				J^3 (C-13, C-14, C-20, C-22)
17.	1.79	m	62.9	J^2 (C-13, C-16, C-20)
				J^3 (C-14, C-18, C-21, C-22)
18.	0.93	s	17.0	J^2 (C-13)
				J^3 (C-12, C-14, C-17)
19.	1.05	s	19.3	J^2 (C-10)
				J^3 (C-1, C-5, C-9)
20.	2.80	m	42.6	J^2 (C-17, C-21, C-22)
				J^3 (C-13, C-16, C-23)
21.	1.10	d, (6.2)	15.6	J^2 (C-20)
				J^3 (C-17, C-22)
22.	-	-	98.5	-
23.	1.48-1.90	m	34.4	J^2 (C-22, C-24)
				J^3 (C-20, C-25, C-25)
24.	1.34-1.48	m	30.8	J^2 (C-23, C-25)
				J^3 (C-22, C-26, C-27)
25.	1.60	m	31.3	J^2 (C-24, C-26, C-27)
				J^3 (C-23)
26.	2.40 α	dd, (11.5, 6.5)	47.9	J^2 (C-25)
	2.70 β	dd, (11.5, 7.8)		J^3 (C-24, C-27)
27.	0.98	d, (7.2)		J^2 (C-25)
				J^3 (C-24, C-26)

[a] ^{1}H NMR carried out at 500 MHz; [b] ^{13}C NMR carried out at 125 MHz; [c]HMBC, HMQC carried out at 500 MHz.

$CHCl_3$-methanol (80: 20, fraction 13) were combined and re-chromatographed over silica gel column chromatography and eluted with EtOAc-methanol in increasing order of polarity to obtain 5 fractions. Fraction 4 (EtOAc-MeOH, 75:25) was again re-chromatographed over RP-18 PTLC using solvent system $CHCl_3$-methanol (4:6) to obtain **1** (R_f = 0.4) in a 42 mg amount.

1β,3β-Dihydroxy, 22 αN-spirosol-5-ene (1): White amorphous powder, 42 mg, m.p. 300.5-301 °C, $[\alpha]_D^{20}$, -85.5^0 (c 1.0, MeOH), IR (nujol) ν_{max} 3300, 1640, 980 cm^{-1}. EIMS *m/z* 429 (20), 138 (85), 114 (100). HREIMS *m/z* 429.3253 (calcd. for $C_{27}H_{43}NO_3$, 429.3231). HRFABMS $[M+H]^+$ *m/z* 430.3430 (calcd. for $C_{27}H_{44}NO_3$, 430.3469). ^{1}H-NMR ($CHCl_3$ + MeOH, 500 MHz) and ^{13}C-NMR ($CHCl_3$ + MeOH, 125 MHz) Table-1.

RESULTS AND DISCUSSION

The methanolic extract of *S. surrattense* was suspended in H_2O and partitioned successively with *n*-hexane, EtOAc and *n*-BuOH soluble fractions. The ethyl-acetate soluble fraction was dried and subjected to various chromatographic techniques to afford compound **1**.

Compound **1** was isolated as white amorphous powder. The IR spectrum showed strong band at ν_{max} 3300 and 1640 cm^{-1} suggestive for hydroxyl and olefinic moiety in the molecule. The HRFABMS (positive mode, $[M + H]^+$) gave molecular ion peak at *m/z* 430.3430 (calcd. 430.3469) indicated the molecular formula to be $C_{27}H_{44}NO_3$. The ^{1}H-NMR and ^{13}C NMR spectra (Table-1) of **1**, along with various NMR spectroscopic analysis (2D-NMR) showed signals assignable to two tertiary methyls [δ 0.93, 1.05 (3H each, s, H_3-18 and 19)], two secondary methyls [δ 1.10, 0.98 (3H each, both d, *J* = 6.2 and 7.2 Hz respectively, H_3-27 and 21), three methines bearing an oxygen function [δ 3.90 (1H, dd, *J* = 9.9, 7.1 Hz, H-1), 4.10 (1H, dt, *J* = 7.9, 5.1) and 4.24 (1H dt, *J* = 8.8, 7.1 Hz, H-16)] and an olefinic proton [δ 5.37 (1H, brd, *J* = 7.1 Hz, H-6)]. The proton and carbon resonances assignable to **1** were similar to those solasodine[7] except for the signals due to the A-ring moiety. The planner structure in **1** was determined by a detailed HMBC-NMR experiment. Thus long range correlations were observed between the following protons and carbons H-1 and C-2, 3, 10, 9, 5; H-3 and C-1, 2, 4, 5; H-6 and C-4, 7, 8, 10; H-16 and C-17, 22, 14; H-17 and C-13, 16, 18, 20, 21; H_3-18 and C-12, 13, 14, 17; H_3-19 and C-1, 5, 9, 10; H_3-21 and C-17, 20, 22; H_3-27 and C-24, 25, 26. Next the relative stereochemistry of **1** except for the 22-position was characterized by a NOESY experiment which showed correlation between the following proton pairs: H-3 and H-1α, H-4α; H-19 and H-1β, H-4β; H_3 18 and H-8, H-12, H-20; and H-17 and H-14, H-16, H_3-21. The configuration at C-22 position of **1** was characterized by comparison of the 23 methylene carbon signal of **1** in the ^{13}C NMR signals with those of known compounds having a spirosol-5-ene unit[8]. The ^{13}C NMR signal (δ 27.0) of xylosyl-β-solamargine[9], having the 22βN configuration, was shifted upfield relative to that (δ 34.7) of xylosyl-σ-solamargine, having the 22αN configuration, as a result of the strong γ interaction of the 21α methyl group. The C-23 signal of **1** was observed at δ 34.4, so that the C-22 configuration of **1** was determined to be in the aN form. Furthermore, in the NOESY experiment on **1**, no NOE correlation was observed between H_3-21 and H-23. On the bases of these results the configuration of the spiroketal position in **1** was elucidated to be in the 22αN form. These results led to formulate the structure of compound **1** as 1β, 3β, dihydroxy, 22 αN-spirosol-5-ene (Fig. 1).

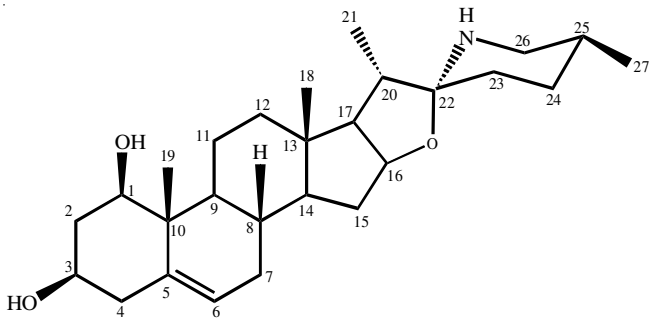

Fig. 1. Structure of compound **1**

REFERENCES

1. D.M.A. Jayaweera, Medicinal Plants, The National Science Council of Sri Lanka, Colombo, Part V, p. 97 (1982).
2. S.R. Baquar, Medicinal and Poisonous Plants of Pakistan, PRINTAS, Karachi, Pakistan, edn 1 (1989).
3. S.K. Bhattacharje, Hand Book of Medicinal Plants, Indian Agriculture Research Institute New Delhi, edn 4, p. 326 (2004).
4. S.G. Joshi, Medicinal Plants, Oxford and IBH Publ. Co. Pvt. Ltd. New Delhi and Calcutta, p. 380 (2000).
5. S.M.H. Jafri, The Flora of Pakistan, The Book Corporation Karachi, edn 1, p. 296 (1966).
6. M. Murayama, Japan Patent, Jpn. Kokai Tokkyo Koho, JP 04230696 A 19920819 (1992).
7. X. Zha, H. Sun, J. Hao and Y. Zhang, *Chem. Biodivers*., **4**, 25 (2007).
8. A.W. Wanyonyi, S.C. Chhabra, G. Mkoji, U. Eilert and W.M. Njue, *Phytochemistry*, **59**, 79 (2002).
9. S. Lorey, A. Porzel and H. Ripperger, *Phytochemistry*, **41**, 1633 (1996).