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A new lanostane triterpenic ether from *Adiantum venustum*

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A new lanostane triterpenic ether, lanost-20(22)-en-3,19-ether, named adiantulanostene ether was isolated from *Adiantum venustum*. Its structure was elucidated on the basis of full spectral data analyses and chemical means.

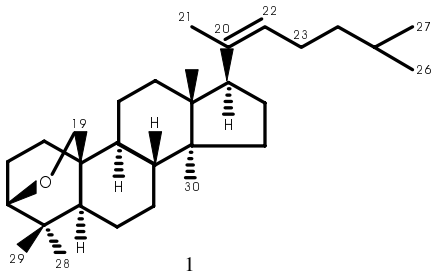
1. Introduction

The medicinal importance of the genus Adiantum [1–3] has attracted our attention to carry out chemical investigations of the aerial parts of *Adiantum venustum* (Adiantaceae). *A. venustum*, commonly known as 'Hansraj', is a little fern and found in moist areas in north east Himalayas, Kashmir and Shimla. The plant is used in the treatment of biliousness, inflammatory diseases of the chest, tumors, opthalmia, cold and headache [4]. Earlier investigation of this fern led to the isolation of adiantone, 3-filicene, kaempferol, hakonanol, ketone, fern-9(11)-en-25-oic acid and tirucallane triterpene [5–7]. In the present communication, we report the isolation and structural determination of a new lanostane-type triterpene, which has been named as adiantulanostane ether from the aerial parts of *A. venustum*.

2. Investigations, results and discussion

Compound **1**, responded positively to the Liebermann Burchard test and showed IR absorption at 1635 cm^{-1} (C=C). It had a molecular ion peak at 426 corresponding to a molecular formula $C_{30}H_{50}O$ indicating six degrees of unsaturation. The MS of **1** showed diagnostically important peaks at m/z 411 $[M-Me]^+$, 395 $[M\text{-}2\times Me]^+$, 380 $[395\text{-}Me]^+$, 365 $[385\text{-}Me]^+$, 111 $[C_8H_{15}$, side chain$]^+$, 138$[C_{5,6}-C_{9,10}$ fission$]^+$, 152, 274$[C_{6,7}-C_{9,10}$ fission$]^+$ 166, 260 $[C_{7,8}-C_{9,10}$ fission$]^+$, 192, 234$[C_{8,14}-C_{9,11}$ fission$]^+$, 206, 220$[C_{8,14}-C_{11,12}/C_{8,14}-C_{12,13}$ fission$]^+$, 177$[M-138$-side chain$]^+$, 163[274-side chain]$^+$, 123[234-side chain]$^+$, 109[220-side chain]$^+$ and 95 [206-side chain]$^+$ which supported saturated nature of the carbocyclic framework and the presence of unsaturated C_9-side chain in the molecule.

The ^{1}H NMR spectrum of 1 displayed a one-proton olefinic singlet at δ 5.16 assigned to H-22, a carbinol proton appeared as a broad singlet at δ 3.46, ascribed to H-3 and an oxygen substituted methylene (CH_2-19) group resonating at δ 3.82 (d, J = 11.72 Hz) and δ 3.90 (d, J = 11.72 Hz). Four broad singlets at δ 0.79, 1.04, 0.92 and 0.89 integrating for three protons each, were attributed to C-18, C-28, C-29 and C-30 methyl groups, respectively (Table 1). Two three-proton doublets at δ 0.80 (J = 6.89 Hz) and 0.86 (J = 0.59Hz) were associated with C-26 and C-27 secondary methyl group, respectively. A three-proton singlet at δ 1.56 was accounted for C-21 vinylic methyl function.



1

The ^{13}C NMR spectrum (Table 2) showed the presence of 30 carbon atoms. The values were compared with the lanostane-type triterpenoids [8–10]. The oxygen substituted C-3 methine and C-19 methylene groups resonated at δ 64.88 and 64.75, respectively. The methyl signals appeared at δ 15.74 (Me-18), 17.99 (Me-21), 16.30 (Me-

Table 1: ^{1}H NMR chemical shifts (δ ppm) of 1

Position	1 ^{1}H NMR	
	α	β
1	1.61m	1.61m
2	1.41m	1.05m
3	3.46 brs	–
4	–	–
5	1.35dd (6.13, 12.45)	–
6	1.20m	1.33m
7	1.98 m	1.98 m
8	–	0.97 m
9	1.45m	–
10	–	–
11	1.78 m	1.54 m
12	1.31 dddd (11.73, 11.72, 6.59, 12.46)	1.19dddd (4.39, 5.86, 2.93, 10.26)
13	–	–
14	–	–
15	1.06ddd (3.67, 2.19, 5.6)	1.43m
16	1.25 m	1.80 m
17	1.53 dd (5.87,11.72)	–
18	0.79 s	–
19	3.82 d (11.72)	3.90 d (11.72)
20	–	–
21	1.56 s	–
22	5.16 brs	–
23	1.98 m	1.80 m
24	1.45 m	1.45 m
25	1.35 m	–
26	0.80d (6.59)	–
27	0.86 d (6.59)	–
28	1.04 s	–
29	0.92 s	–
30	0.89 s	–

Table 2: ^{13}C NMR chemical shifts (δ ppm) of 1 in $CDCl_3$

Position	^{13}C NMR	DEPT
1	35.83	CH_2
2	29.60	CH_2
3	64.88	CH
4	38.68	C
5	58.34	CH
6	19.90	CH_2
7	28.32	CH_2
8	60.08	CH
9	50.23	CH
10	39.71	C
11	20.38	CH_2
12	29.26	CH_2
13	42.47	C
14	42.72	C
15	29.57	CH_2
16	39.17	CH_2
17	51.62	CH
18	15.74	CH_3
19	64.75	CH_2
20	144.00	C
21	17.99	CH_3
22	120.68	CH
23	17.93	CH_2
24	78.39	CH_2
25	30.75	CH
26	16.30	CH_3
27	22.88	CH_3
28	21.94	CH_3
29	15.74	CH_3
30	15.46	CH_3

26), 22.88 (Me-27), 21.94 (Me-28), 15.74 (Me-29) and 15.46 (Me-30). The degree of protonation of each carbon atom was determined by ^{13}C DEPT NMR spectra. The spectra revealed the presence of seven methyl, eleven methylene, seven methine and five quaternary carbons. The 2D long range ^{1}H-^{13}C COSY spectrum of **1** showed correlation for signals of H-6 (with C-5 and C-7), Me-23 (with C-3, C-4, C-5 and C-24), Me-24 (with C-3, C-4, C-5 and C-23), Me-18 (with C-12, C-13 and C-17) and Me-30 (with C-8, C-13, C-14 and C-15), respectively. On biogenetic grounds and by ^{1}H-^{1}H correlated NMR spectroscopy, the secondary carbinylic carbon was assigned to C-3. The carbinylic proton at δ 3.46 showed cross-peaks with H-1. The cross correlations between signals H-22 and H-23, H-5 and H-6 as well as H-11 and H-12 were also observed. Compound **1** resisted to react with normal reagents such as acetic anhydride-pyridine and oxidising reagents. On the basis of these evidences, adiantulanostene ether A (**1**) was identified as lanost-20 (22)-en-3,19-ether.

Compound **2**, m.p. 204–205 °C, responded positively to the Liebermann Burchard test and showed IR absorption band at 1605 cm^{-1} (C=C). It also had a molecular ion peak at m/z 426 corresponding to a molecular formula $C_{30}H_{50}O$. The ^{1}H NMR spectrum of **2** was similar to that of **1** except that the signals of the vinylic methyl groups in **2** appeared at δ 1.56 (Me-26) and 1.57 (Me-27) and C-21 oxymethylene signals resonated at δ 3.80 (1 H, d, J = 11.72Hz, H-21a) and δ 3.88 (1 H, d, J = 10.99Hz, H-21b) (Table1). Comparison of ^{13}C NMR, (Table 2), EIMS and COSY spectra of **2** with that of **1** indicated that the two compounds differed only in the position of double bond and ether linkage that **2** was an isomer of **1**. Therefore, the structure of **2** is lanost-24(25)-en-21,23-ether.

3. Experimental

3.1. Equipment

Mps: uncorr. IR: Hitachi 260–30, KBr; ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR: JEOL A-600, $CDCI_3$ with TMS as int. standard; MS: Hitachi M-80; CC: silica gel (E. Merck, 60–120 mesh).

3.2. Thin layer chromatography

Silica gel 60 F254 pre-coated plates. The spots were visualised by exposure to Iodine vapour and by spraying with vanillin-H_2SO_4 reagent.

3.3. Plant material

The aerial parts of *A. venustum* were procured from Herba Indica, Chandigarh, and identified in the Botany Department by Dr. M.P. Sharma. A voucher specimen is preserved in our laboratory.

3.4. Isolation of the constituents

Air-dried and coarsely powdered aerial parts (3 kg) were exhaustively extracted (Soxhlet) with EtOH (95%) and the combined extracts concentrated to dryness under reduced pressure. The residue (200 g) was sequentially refluxed with solvents of increasing polarity viz. petroleum ether, C_6H_6, EtOAc and MeOH. Petroleum ether and C_6H_6 fractions were found to be identical on TLC and, therefore, mixed together, concentrated and chromatographed over silica gel column. Elution was carried out with petroleum ether and petroleum ether containing increasing amounts of $CHCl_3$. The petroleum ether-$CHCl_3$ (1 : 1) fraction gave green solid which was washed thoroughly with C_6H_6. The white solid obtained was found to be single entity on TLC but had no sharp m.p. The solid was dissolved in $CHCl_3$ and precipitated with MeOH. The ppt. obtained was crystallised from petroleum ether-$CHCl_3$ to get compound **1** as white needles. The mother liquor gave a white solid on concentration which was crystallised from $CHCl_3$–MeOH to furnish white fibers of **2**.

Adiantulanostene ether A (**1**). M.p. 192–194 °C. IR ν_{max} cm^{-1} 2950; 2870, 1635, 1460, 1390, 1260, 1220, 1170, 1110, 1100, 1045, 805. EIMS m/z (ret. Int.): 426 $[M]^+$ ($C_{30}H_{50}$ O) (41.3), 411(20.6), 395 (36.4), 380 (8.2), 365 (4.2), 302 (9.0), 274 (7.5), 260 (6.3), 243 (6.5), 220 (12.1), 206 (31.3), 192 (30.2),177 (46.0),166 (6.6), 163 (10.6), 152 (13.6), 149 (8.7), 138 (33.1), 125 (35.5), 123 (58.2), 111 (12.1), 109 (32.3), 95 (100), 83 (27.5), 69 (81.3), 55 (63.1). ^{1}H NMR (Table 1) ^{13}C NMR (Table 2).

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