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Note

Nardal, a new sesquiterpene aldehyde from the plant, *Nardostachys jatamansi* DC

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A new bicyclic sesquiterpene aldehyde has been isolated along with nardin **2** from the hexane extract of the rhizomes of the plant, *Nardostachys jatamansi* DC. The structure of bicyclic sesquiterpene aldehyde has been established as *E*-2-methyl, 3-(5,9-dimethylbicyclo[4,3,0]-non-9(1)-en-3-yl)-2-propenal based on the spectral data of its 2,4-DNP derivative and its comparison with known compound isolated from the same plant.

Keywords: Nardal, sesquiterpene aldehyde, *Nardostachys jatamansi*

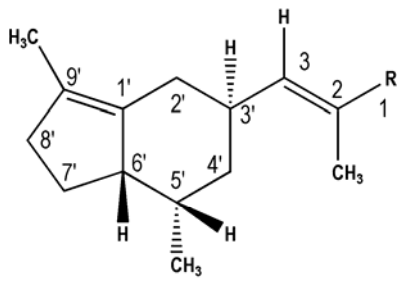
The rhizomes and roots of *Nardostachys jatamansi* DC are used as anti-stress agents in traditional medicine and marketed in India as an anticonvulsant Ayurvedic drug, Ayush 56 (ref.1). The rhizome is used as an aromatic adjunct in the preparation of medicinal oils, to promote growth of hair and also imparts blackness[2]. In continuation of our interest on the isolation of bioactive compounds for cosmetics use, we have undertaken chemical examination of the rhizomes of *Nardostachys jatamansi*. Previous reports on this plant occurring in different regions of India yielded, terpenoids and sterol[3], alkaloid[4], neolignans and lignans[5]. The present paper describes the isolation of a new bicyclic sesquiterpene aldehyde, nardal **1** along with nardin **2**. The new compound **1** has been characterized as *E*-2-methyl, 3-(5,9-dimethyl-bicyclo[4,3,0]-non-9(1)-en-3-yl)-2-propenal through its 2,4-DNP derivative spectroscopic data.

Results and Discussion

Compound **1** was obtained as a colorless and odorless oil. It was readily recognized as sesquiterpene aldehyde by its preliminary spectral data. The Proton NMR spectrum (**Table I**) clearly showed an aldehydic proton at δ 9.38 (1H, s). It further showed one secondary methyl at δ 0.79 as doublet (J = 7.0Hz) and two double bonded methyls at δ 1.64 (s) and 1.79 (d, J = 1.3 Hz). In the olefinic region the spectrum showed only one proton at δ 6.73 as double quartet and this might be due to be the β-proton of an α, β-unsaturated aldehydic system which is connected to the cyclic system.

Its ^{13}C NMR spectrum (**Table I**) showed 15 carbon signals. Out of these, four peaks at δ 155.9, 137.4, 132.5 and 131.9 correspond to two double bonds. The spectrum also showed an aldehydic carbonyl signal at δ 195.8 and a double bonded methyl carbon at δ 9.2 which is connected to the α carbon of the α, β-unsaturated aldehyde group. By scanning the literature, the proton and carbon data of isopropenyl aldehyde (side chain) group is found exactly matching with the reported data of *E*-2-methylpropenal-3-yl moiety[6]. All other carbon signals of the compound **1** except side chain were matching with the data of Nardin[1] reported from the same species recently. So, the structure of the compound **1** basic skeleton is similar to that of the known compound except in the side chain, i.e., isopropenyl aldehyde instead of isopropenyl carboxylic acid.

As compound **1** was found to be unstable, it was derivatized with 2,4-DNP and the product was re-crystallized with methanol to get pale yellow orange colored crystals **1a** from methanol, m.p. 175-77°C, $[\alpha]_D^{25}$ -219° (c 0.102, $CHCl_3$). Its molecular formula was assigned as $C_{21}H_{26}N_4O_4$ based on FAB mass (M+ positive mode, 399) and supported by elemental analysis data. Its IR spectrum showed the presence of amine absorption (3268 cm^{-1}) and olefinic absorption (1613 cm^{-1}) along with other peaks at 2916, 1514, 1321, 1132, 1081 and 953cm^{-1}. Its UV absorption



1 R= CHO
1a R= CH=N-NH-$C_6H_3(NO_2)_2$
2 R= COOH

Table I — Comparison of ^{1}H and ^{13}C NMR spectral data of compounds **1** and **2** in $CDCl_3$ (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR)

	δ_H		δ_C	
	1	**2**	**1**	**2**
Carbon No.				
1	9.38 s	-	195.8	173.9
2	-	-	137.4	133.3
3	6.73 dq	7.19 d (9.9)	155.9	146.3
1'	-	-	132.4	131.2
2'	2.02 m & 2.20 m	1.99 m & 2.20 m	37.4	37.5
3'	3.73 dd (4.4, 9.7)	3.55 m	47.5	47.5
4'	1.82-1.92 br m	1.75-1.85 br m	25.4	25.4
5'	1.82-1.92 br m	1.75-1.85 br m	32.9	33.1
6'	1.82-1.92 br m	1.75-1.85 br m	34.6	34.6
7'	1.43 m	1.43 m	24.5	24.6
8'	2.20 m & 2.95 m	2.20 m & 2.94 m	28.8	28.8
9'	-	-	131.9	125.3
2-Me	1.79 d (1.3)	1.89 s	9.2	13.5
5'-Me	0.79 d (7.0)	0.79 d (7.0)	12.0	12.0
9'-Me	1.64 s	1.63 s	13.5	12.1

J values (Hz) are given in parentheses

spectrum in methanol showed λ_{max} at 369 nm indicating conjugation in the molecule.

The proton spectrum of **1a** showed disappearance of an aldehyde proton signal at δ 9.38 and an appearance of five other peaks. Out of the five, three aromatic protons appeared at [δ 7.95 (1H, d, J = 9.6 Hz), 8.29 (1H, dd, J = 2.5, 9.6 Hz) and 9.11 (1H, d, J = 2.5 Hz)], one secondary amine proton appeared at δ 11.12 (1H, s) and an imine proton appeared at δ 7.75 as singlet. All other signals were exactly matching with the original compound. Its carbon spectrum showed 21 signals including eleven olefinic carbons and ten other carbons. The 2D NMR NOESY spectrum showed the following spatial connectivities: N-H (δ 11.12) with C_1-H (δ 7.75), C_1-H (δ7.75) with C_3-H (δ 6.26), C_3-H (δ 6.26) with $C_{3'}$-H (δ 3.74), $C_{3'}$-H (δ 3.74) with $C_{4'}$-H (δ 1.82). Based on the above data it has been established that the structure of the unstable molecule from *N. jatamansi* is as depicted in **1**.

Nardin **2** was isolated from later fractions eluted with the same ratio of hexane-ethyl acetate and confirmed by co-comparison with an authentic sample and mmp[1].

Earlier various group have examined this plant and reported the following compounds from the rhizomes. These are pyranocoumarin[1], eleven unknown aliphatic compounds along with β-sitosterol[7], mono and sesquiterpenes[8], nardostachysin[9], jatamols A and B[10], spirojatatomol[11], 9-aristolen-1-α -ol and 1(10)-artistolen-2-one [12], valeranone[13], Norseychelanone, α- and β-patchoulenes and patchouli alcohol[14], seychellene and seychelane[15], jatamansic acid[16], nardosinone, β-ionine, 1(10)-aristolen-2-one and 1,8,9,10-dehydroaristolan-2-one[17], nardosinone, 1(10)-aristolene and 9-aristolene, maaliol, β-maaliene and jatamansic acid[18], nardol, calarenol and β-sitosterol[19], nardostachone[19,20], nardol[19,21], jatamansin[22] and jatamansone[23]. Recently, a sesquiterpene unsaturated carboxylic acid, nardin **2** has been isolated from the same plant and its structure has been elucidated and published[1]. Significantly, in the present chemical screening, we isolated nardal **1** with an aldehydic functionality which presumably is the biogenetic precursor of nardin **2**.

Experimental Section

Melting points reported are uncorrected. The 400 MHz NMR spectra were recorded on a Bruker AMX 400 in $CDCl_3$ with TMS as an internal standard. The ^{13}C NMR spectra were recorded at 100 MHz. IR spectra were recorded on a Shimadzu IR Prestige 21; elemental analysis was performed on Elementar Vario

EL III; FAB mass spectrum on a Jeol SX 102/DA-6000 mass spectrometer; Optical Rotation: Rudolf Autopol III. TLC was performed on precoated silica gel 60 F_{254} plates (Merck) and the spots were visualized by exposure to iodine vapour or spraying with 5% sulphuric acid in methanol followed by heating the plate at 110°C for 10 min.

Plant material. Rhizomes of *Nardostachys jatamansi* DC were collected from Bazar in November, 2005 and a voucher specimen was deposited in M/s.Cavinkare Research Centre, Chennai.

Extraction and Isolation. Air-Dried and finely powdered rhizomes (2 Kg) were extracted with hexane. The hexane extract (9.4g) was subjected to column chromato-graphy on silica gel (100-200 mesh). Elution was carried out in hexane (pooled fraction 1) followed by hexane: chloroform mixture (3:1 and 1:1, pooled fraction 2 and 3 respectively). Pooled fraction 2 and.3 were combined and re-chromatographed over silica gel using hexane: chloroform (3:1) and afforded compounds **1** and **2.** Compound **1** (0.621g) obtained as a colourless and odorless oil and compound **2** (0.537g) was obtained as colourless crystals from hexane: diethyl ether

Compound **1**: Colorless oil; ^{1}H & ^{13}C NMR (**Table I)**.

Compound **1a:** Pale yellow orange color crystals; m.p. 175-77°C; specific rotation, -219° (c 0.102, $CHCl_3$); Anal. Calcd for $C_{21}H_{26}N_4O_4$: C, 63.31, H, 6.53, N, 14.07. Found: C, 63.74, H, 6.87, N, 13.28. IR: 3268 (amine), 1613 cm^{-1} (aromatic); UV(nm): 369; ^{1}H NMR ($CDCl_3$): δ 0.79 (3H, d, *J* = 7.0 Hz, H-5'), 1.43 (1H, m, H-7'), 1.67 (3H, s, Me-9), 2.0 (3H, d, J = 0.9 Hz, Me-2), 1.82-1.92 (4H, m, H-4'-6'), 2.02 (1H, m, H-2'), 2.20 (2H, m, H-2' and 8'), 2.90 (1H, t, H-8'), 3.74 (1H, dd, *J* = 4.4, 9.7 Hz, H-3'), 6.26 (1H, d, *J* = 9.6 Hz, H-3), 7.75 (1H, s, H-1), Aromatic protons: 7.95 (1H, d, *J* = 9.6 Hz, 8.29, 1H, dd, *J* = 2.5, 9.6 Hz, 9.1(1H, d, *J* = 2.6 Hz), amine proton, 11.12 (1H, s); ^{13}C NMR ($CDCl_3$): δ 144.5 (C-1), 133.4 (C-2), 153.7 (C-3), 131.1 (C-1'), 37.4 (C-2'), 47.4 (C-3'), 25.7 (C-4'), 33.0 (C-5'), 34.3 (C-6'), 24.5 (C-7'), 28.7 (C-8'), 131.0 (C-9'), 13.5 (C-2-Me), 11.4 (C-5'-Me), 12.0 (C-9'-Me), aromatic carbons: 116.6, 123.6, 128.8, 129.9, 133.4, 144.9; FAB MS m/z (rel. int.): 399$[M+ Na]^+$ ($C_{21}H_{26}N_4O_4$, 100%).

Compound **2**: Colorless crystals, m.p. 133-34°C, ^{1}H and ^{13}C NMR (**Table I).**

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