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 blackness2. 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 sterol3, alkaloid 4, neolignans and lignans5. 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-dimethylbicyclo[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 aldehydey system which is connected to the cyclic system.

Its 13C 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-methylpropanal-3-yl moiety6. All other carbon signals of the compound 1 except side chain were matching with the data of Nardin1 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, [α]D-25 -219° (c 0.102, CHCl3). Its molecular formula was assigned as C21H26N4O4 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
spectrum in methanol showed λ$_{\text{max}}$ 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), C1-H (δ 7.75) with C3-H (δ 6.26), C3-H (δ 6.26) with C5-H (δ 3.74), C3-H (δ 3.74) with C4-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.

Earlier various group have examined this plant and reported the following compounds from the rhizomes. These are pyranocoumarin, eleven unknown aliphatic compounds along with β-sitosterol, nardostachysin, jatamols A and B, spirojatatomol, 9-aristolone-1-α -ol and 1(10)-aristolone-2-one, valeranone, Norseychelanone, α- and β-patchoulenes and patchouli alcohol, seychellene and seychelane, jatamansic acid, nardosinone, β-ionone, 1(10)-aristolone and 9-aristolene, maaliol, β-maaliene and jatamansic acid, nardol, calarenol and β-sitosterol, nardostachone, nardol, jatamansin and jatamansone. Recently, a sesquiterpene unsaturated carboxylic acid, nardin has been isolated from the same plant and its structure has been elucidated and published. Significantly, in the present chemical screening, we isolated nardal with an aldehydic functionality which presumably is the biogenetic precursor of nardin 2.

### 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)

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>$\delta_H$</th>
<th>$\delta_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>9.38 s</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>6.73 dq</td>
<td>7.19 d (9.9)</td>
</tr>
<tr>
<td>1'</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2'</td>
<td>2.02 m &amp; 2.20 m</td>
<td>1.99 m &amp; 2.20 m</td>
</tr>
<tr>
<td>3'</td>
<td>3.73 dd (4.4, 9.7)</td>
<td>3.55 m</td>
</tr>
<tr>
<td>4'</td>
<td>1.82-1.92 br m</td>
<td>1.75-1.85 br m</td>
</tr>
<tr>
<td>5'</td>
<td>1.82-1.92 br m</td>
<td>1.75-1.85 br m</td>
</tr>
<tr>
<td>6'</td>
<td>1.82-1.92 br m</td>
<td>1.75-1.85 br m</td>
</tr>
<tr>
<td>7'</td>
<td>1.43 m</td>
<td>1.43 m</td>
</tr>
<tr>
<td>8'</td>
<td>2.20 m &amp; 2.95 m</td>
<td>2.20 m &amp; 2.94 m</td>
</tr>
<tr>
<td>9'</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Me</td>
<td>1.79 d (1.3)</td>
<td>1.89 s</td>
</tr>
<tr>
<td>5'-Me</td>
<td>0.79 d (7.0)</td>
<td>0.79 d (7.0)</td>
</tr>
<tr>
<td>9'-Me</td>
<td>1.64 s</td>
<td>1.63 s</td>
</tr>
</tbody>
</table>

J values (Hz) are given in parentheses.

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
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 chromatography on silica gel (100-200 mesh). Elution was carried out in hexane (pooled fraction 1) followed by 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; 1H & 13C NMR (Table I).

**Compound 1a**: Pale yellow orange color crystals; m.p. 175-77°C; specific rotation, -219° (c 0.102, CHCl3); Anal. Caled for C21H26N4O4: C, 63.31, H, 12.0 (C-9′-Me), aromatic carbons: 116.6, 123.6, 131.0 (C-1′), 37.4 (C-2′), aromatic protons: 7.95 (1H, d, J = 9.6 Hz, H-3), 7.75 (1H, s, H-1), 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); 13C NMR (CDCl3): 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]+ (C21H26N4O4, 100%).

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

Acknowledgement

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References