Studies on the chemical constituents of *Nardostachys jatamansi* DC (Valerianaceae)

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A new sesquiterpene acid, nardin and a new pyranocoumarin have been isolated from the rhizomes of *Nardostachys jatamansi* and characterized as E-2-methyl, 3-(5,9-dimethylbicyclo[4.3.0]-nonen-9-yl)-2-propenoic acid and 2',2'-dimethyl-3'-methoxy-3',4'-dihydropyranocoumarin, respectivel y using spectral studies and chemical correlation. The stereochemistry of nardin has been determined using X-ray crystallographic studies.

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The rhizomes and roots of *Nardostachys jatamansi* DC (locally known as Jatamansi) are used as an antistress agent in traditional medicine and marketed in India as an anti-convulsant Ayurvedic drug, Ayush 56. The occurrence of a number of sesquiterpenes, lignans, neo-lignans and coumarins has been reported1. Previously the authors isolated a new terpenoid ester, nardostachysin 2, the structure and stereochemistry of which was established as 7',8'-di-hydroxy-4'-methylene hexahydrocyclopenta[c]pyran-1'-one-8'-methyl ester of 7,9-guaiadien-14-oic acid using spectral and chemical studies.

**Results and Discussion**

In the present investigation a new sesquiterpene acid, nardin 1 and a new pyranocoumarin 2 have been isolated from this plant, besides several known coumarins. The present communication reports in detail the structure and stereochemistry of nardin 1 and the pyranocoumarin 2.

The hexane extract on column chromatography over silica gel afforded nardin 1, C15H22O2 (M+ 234), [α]D25 -123.8º (EtOH), m.p. 133-34°C, yield 0.01% from the n-hexane eluent. In the infrared spectrum the peak at 1683 cm⁻¹ indicates the presence of an α,β-unsaturated carbonyl group which has been confirmed from the 13C NMR peak at 173.9 ppm. The 1H NMR spectrum of the compound 1 indicates the presence of three methyl groups at δ 1.89 (3H, s, vinylic methyl), 1.63 (3H, s, vinylic methyl) and 0.79 (3H, d, J = 7.0 Hz). A significant peak at 7.19 (1H, d, J = 9.9 Hz) was observed thereby confirming the presence of an olefinic proton.

The 13C NMR spectrum of the compound 1, including DEPT experiment, reveals the presence of 15 carbon atoms of which three methyl carbons appeared at δ 13.5, 12.1 and 12.0 ppm, four methylene carbons were discernible at δ 37.5, 28.8, 25.5 and 24.6 ppm and four quaternary carbons at δ 173.9, 133.3, 131.2 and 125.3 ppm. Considering the spectral properties, the structure of this new compound appeared to be 1.

The structure of nardin 1 was firmly established by X-ray crystallographic analysis (Figure 1. ORTEP diagram). Figure 2 shows the content of the asymmetric unit as a dimer of chatnj-X molecules associated head-to-head through their carboxylic functions. The structure was found to be chiral with tetragonal space group P41212 (solved in P41); cell: a = b = 11.03 and c = 53.5 Å with four molecules in the asymmetric unit. The structure of the compound was thereby established as 1.
Besides nardin 1 several furanocoumarins viz. angelicin, oroselol and pyranocoumarins viz. jatamansin, jatamansinol have been reported from this plant\textsuperscript{3,4}. On chromatographic resolution using 5% ethyl acetate in hexane as eluent colourless crystals of the pyranocoumarin 2, C\textsubscript{15}H\textsubscript{16}O\textsubscript{4} (M\textsuperscript{+} 260), m.p. 81ºC (hexane-methanol mixture) were obtained in 0.004% yield. From the spectral analysis its structure was established as 2',2'-dimethyl-3'-methoxy-3',4'-dihydropyranocoumarin 2. The UV absorption spectrum in ethanol exhibit peaks at \(\lambda_{\text{max}}\text{MeOH} \): 221 (log \(\varepsilon\) 3.01), 249 (log \(\varepsilon\) 2.80), 257 (log \(\varepsilon\) 2.83) and 320 (log \(\varepsilon\) 3.20) nm characteristic of pyranocoumarins. IR spectral band at 1721 cm\textsuperscript{-1} indicates the presence of \(\delta\)-lactone. The \(^1\text{H}\) NMR spectrum of the compound indicate the presence of four aromatic protons at \(\delta\) 6.18 (1H, d, \(J = 9.4\) Hz, H-3), 7.57 (1H, d, \(J = 9.4\) Hz, H-4), 7.25 (1H, d, \(J = 8.4\) Hz, H-5) and 6.80 (1H, d, \(J = 8.5\) Hz, H-6) typical of coumarin moiety. Further, its \(^1\text{H}\) NMR spectrum displayed signals due to two methyls at \(\delta\) 1.82 (3H, s), 1.65 (3H, s) and a methoxyl at 3.9 (3H, s).

**Materials and Methods**

The rhizomes of *N. jatamansi* DC. were collected in June 2003, and were identified by Prof. Nanda Dulal Paria, Department of Botany, Ballygunge Science College, Calcutta University. A voucher specimen (NJ-7) has been deposited at the Centre of
Advanced Studies on Natural Products, Department of Chemistry, Calcutta University.

Air dried powdered rhizomes (2.5 kg) were extracted with *n*-hexane for 48 hr in a Soxhlet apparatus. After removal of the solvent from the extract the residue obtained (134 g) was subjected to column chromatography over silica gel using *n*-hexane, *n*-hexane-ethyl acetate and ethyl acetate-methanol as eluates.

**Experimental Section**

Melting points were determined in an electrically heated chamber and are uncorrected. The specific rotation was measured in a Perkin-Elmer 241 polarimeter in ethanol. The UV (in EtOH) and IR (KBr) spectra were recorded using a Hitachi U-2000, and Perkin-Elmer RX I FT-IR spectrophotometers. The 1H and 13C NMR spectra were run on a Bruker AM-300L spectrometer and mass spectra were recorded on a Finnigan MAT-H-SQ-30 mass spectrometer.

Column chromatographic analysis was carried out using silica gel (60-120, S.D. FINE-CHEM Ltd., India). TLC analysis was carried out using silica gel G (Spectrochem, India). The spots were detected with iodine vapour. Analytical samples were routinely dried in vacuo over P2O5 for 24 hr. Anhydrous sodium sulphate was used for drying the organic solvents.

**Nardin 1**: The hexane fraction afforded the compound 1 as colourless crystals which were crystallized from hexane-methanol mixture, [α]D$_{25}^-123.8$° (c, 0.1042 g/100 mL, EtOH); m.p. 133-34ºC; yield 0.01%; (M+ 234); Anal. Calcd for C$_{15}$H$_{22}$O$_2$: C, 76.92; H, 9.40. Found: C, 76.71; H, 9.34; IR (KBr): 2934, 1683, 1424 and 1299 cm$^{-1}$; UV (EtOH): 224.5 (log ε: 3.04); 1H NMR (300 MHz, CDCl$_3$): δ 7.19 (1H, d, J = 9.9 Hz), 3.55 (1H, m), 2.94 (1H, m), 2.20 (2H, m), 2.17 (1H, m), 1.89 (3H, s), 1.85-1.75 (4H, m), 1.43 (2H, m), 1.63 (3H, s), 0.79, (3H, d, J = 7.0 Hz); 13C NMR (75.5 MHz, CDCl$_3$): δ 173.9 (C-1), 146.3 (C-3), 133.3 (C-2), 131.2 (C-1'), 125.3 (C-9'), 47.5 (C-3'), 37.5 (C-2'), 34.6 (C-6'), 33.1 (C-5'), 28.8 (C-8'), 25.4 (C-4'), 24.6 (C-7'), 13.5 (C-2-Me), 12.1 (C-9'-Me), 12.0 (C-5'-Me).

**Pyranocoumarin 2**: Elution with 5% ethyl acetate in hexane afforded the compound as colourless crystals which were crystallized from hexane-methanol mixture. Yield 0.004%; m.p. 81ºC (M' 260); Anal. Calcd for C$_{15}$H$_{16}$O$_4$: C, 69.23; H, 6.15. Found: C, 69.01; H, 6.11; UV (EtOH): 221 (log ε 3.01), 249 (log ε 2.80), 257 (log ε 2.83) and 320 (log ε 3.20) nm; IR (KBr): 7.57 (1H, d, J = 9.4 Hz), 7.25 (1H, d, J= 8.4 Hz), 6.80 (1H, d, J = 8.4 Hz), 6.18 (1H, d, J = 9.4 Hz), 5.21 (1H, m), 3.9 (3H, s), 3.52 (2H, m), 1.82 (3H, s), 1.65 (3H, s); 13C NMR (75.5 MHz, CDCl$_3$): δ 161.06 (C-2), 160.3 (C-7), 152.97 (C-8a), 143.72 (C-4), 132.4 (C-8), 126.22 (C-5), 121.3 (C-3'), 118.2 (C-2'), 113.06 (C-4a), 113.05 (C-3), 107 (C-6), 56.04 (C-3'-OMe), 25.75 (C-2'-Me), 21.94 (C-4'), 17.91 (C-2'-Me).

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**References**

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