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NOTE

X-Ray Structure Analysis of Nardin

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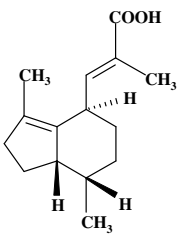
Structural determination of nardin, a novel sesquiterpene acid, is reported. The crystal structure of this compound is determined by single crystal X-ray studies. X-ray crystallography revealed the presence of two conformers arising from the intermolecular hydrogen bond of the O–H···O type. The crystal of the compound belongs to the tetragonal crystal system and space group is $P4_12_12$ (or $P4_32_12$). Crystal data are as follows: a = 11.030 (3) Å, b = 11.030 (3) Å, c = 43.350 (5) Å; V = 5274 Å^3; Z = 16. The final R factors are R = 0.065 (for all 2399 accepted reflections), R = 0.064 (for 2355 observed reflections).

Key Words: *Nardostachys jatamansi*, Valerianaceae, Nardin, X-ray crystallography.

Nardostachys jatamansi DC (Valerianaceae), popularly known as 'Jatamansi', is a medicinal herb, growing in the Alpine Himalayas. It has been recommended in the Indian system of medicine as a sedative and an antistress remedy[1]. The rhizomes are used in Ayurvedic formulations as an anti-convulsant[2]. The plant is a rich source of sesquiterpenes, coumarins, lignans and neolignans. In continuation of our work with this plant[3], a new sesquiterpene acid, nardin, has been isolated from the rhizomes. This communication reports the isolation and crystal structure of nardin (**1**).

Air dried powdered rhizomes (2.5 kg) were extracted with *n*-hexane for 48 h 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. The hexane fraction afforded nardin (**1**) in 0.01 % yield. The compound on crystallization gave crystals as colourless small plates, *ca.* 15 to 20 μ thick, m.p. 134 °C, $[\alpha]_D^{25}$ -123.8° (C, 0.1042 g/100 mL, EtOH). Anal. found (%): C 76.87, H 9.34 Calcd. (%): C 76.92, H 9.40 for $C_{15}H_{22}O_2$.



(**1**)

Details of crystal data collection and refinement parameters for nardin (**1**) are listed in Table-1. Data were recorded with a MARRESEARCH Image Plate detector (345 mm)[4]. Data consisted of 100 frames, 4º rotation each (more than 360°). They were processed using the DENZO/SCALEPACK computer programs[5]. The structure was solved by direct methods and refined with the SHELX 97 suite of programs[6]. Coordinates have been deposited with the Cambridge Centre with reference CCDC-212288.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT OF NARDIN (**1**)

Parameter	Nardin (**1**)
Formula	$C_{15}H_{22}O_2$
Molecular weight	234
Temperature	123 K
Wavelength	0.976 Å
Crystal system	Tetragonal
Space group	$P4_12_12$ (or $P4_32_12$)
Unit cell dimensions	
a (Å)	11.030 (1)
b (Å)	11.030 (1)
c (Å)	43.350 (1)
V, (Å^3)	5274.0 (7)
Z	16
Final R factors	R = 0.065 (for all 2399 all reflections) R = 0.064 (for 2335 observed reflections)

Supplementary material: CCDC 212288 contains the supplementary crystallographic data for (**1**). This can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

TABLE-2
DISTANCES (Å FOR NON-HYDROGEN ATOMS WITH e.s.d.'s GIVEN IN PARENTHESES

Molecule A						Molecule B					
C1-O2	1.232(6)	C1-O1	1.305(7)	C1-C2	1.490(8)	C1'-O2'	1.240(6)	C1'-O1'	1.311(7)	C1'-C2'	1.472(8)
C2-C3	1.324(7)	C2-C21	1.500(8)	C3-C-4	1.491(7)	C2'-C3'	1.330(7)	C2'-C21'	1.500(8)	C3'-C4'	1.492(8)
C4-C5	1.522(7)	C4-C13	1.557(7)	C5-C6	1.302(7)	C4'-C5'	1.506(7)	C4'-C13'	1.552(7)	C5'-C6'	1.331(7)
C5-C9	1.498(7)	C6-C61	1.492(8)	C6-C7	1.508(7)	C5'-C9'	1.507(7)	C6'-C61'	1.497(8)	C6'-C7'	1.512(8)
C7-C8	1.537(8)	C8-C9	1.546(7)	C9-C10	1.541(7)	C7'-C8'	1.533(7)	C8'-C9'	1.554(7)	C9'-C10'	1.536(7)
C10-C11	1.520(8)	C10-C12	1.533(7)	C12-C13	1.502(8)	C10'-C11'	1.512(7)	C10'-C12'	1.533(7)	C12'-C13'	1.517(8)

TABLE-3
BOND ANGLES (°) FOR NON-HYDROGEN ATOMS WITH e.s.d.'s GIVEN IN PARENTHESES

Molecule A				Molecule B			
O2-C1-O1	123.9(5)	O2-C1-C2	121.4(5)	O2'-C1'-O1'	122.4(5)	O2'-C1'-C2'	120.6(6)
O1-C1-C2	114.7(5)	C3-C2-C1	119.6(5)	O1'-C1'-C2'	117.0(5)	C3'-C2'-C1'	119.1(5)
C3-C2-C21	125.9(5)	C1-C2-C21	114.5(5)	C3'-C2'-C21'	124.8(5)	C1'-C2'-C21'	116.2(5)
C2-C3-C4	129.1(5)	C3-C4-C5	109.6(4)	C2'-C3'-C4'	127.7(5)	C3'-C4'-C5'	110.1(4)
C3-C4-C13	112.1(4)	C5-C4-C13	109.5(4)	C3'-C4'-C13'	110.4(4)	C5'-C4'-C13'	108.7(4)
C6-C5-C9	113.5(4)	C6-C5-C4	127.4(5)	C6'-C5'-C4'	127.8(5)	C6'-C5'-C9'	112.9(4)
C9-C5-C4	119.1(4)	C5-C6-C61	128.9(5)	C4'-C5'-C9'	119.0(4)	C5'-C6'-C61'	128.4(5)
C5-C6-C7	111.1(5)	C61-C6-C7	119.9(4)	C5'-C6'-C7'	110.9(4)	C61'-C6'-C7'	120.6(4)
C6-C7-C8	105.2(4)	C7-C8-C9	105.9(4)	C6'-C7'-C8'	104.9(4)	C7'-C8'-C9'	105.4(4)
C5-C9-C10	112.3(4)	C5-C9-C8	104.0(4)	C5'-C9'-C10'	111.8(4)	C5'-C9'-C8'	103.5(4)
C10-C9-C8	116.7(4)	C11-C10-C12	111.6(4)	C10'-C9'-C8'	116.9(4)	C11'-C10'-C12'	111.2(4)
C11-C10-C9	113.2(4)	C12-C10-C9	107.4(4)	C11'-C10'-C9'	113.9(4)	C12'-C10'-C9'	107.9(4)
C13-C12-C10	113.1(4)	C12-C13-C4	114.2(4)	C13'-C12'-C10'	111.7(4)	C12'-C13'-C4'	112.1(4)

The ORTEP drawing of one monomer of the asymmetric unit is shown in Fig. 1 with thermal ellipsoids drawn at the 50 % probability level. Fig. 2 showed the content of the asymmetric unit as a dimer of nardin (**1**) molecules associated head-to-head through their carboxylic functions. It contains six/five fused bicyclic ring system. The six membered ring is in a classic chair conformation whereas the five membered ring is in a boat-type conformation. From the ORTEP view it can be seen that the carboxylic group and the bicyclic system are present in *trans* manner. No attempt was made to determine absolute configuration on the basis of the diffraction data.

The atomic coordinates and anisotropic displacement parameters, bond distances and angles with estimated standard deviations are given in Tables 2 and 3, respectively.

No anomalies are observed in the values of the bond angles (Table-3) and distances (Table-2). The mean-square deviations in the values of the bond distances and angles are not more than 0.007 Å and 0.4°, respectively. An analysis of intermolecular contacts has shown that the carboxyl group (O1-H) and the carboxyl group (O2') form an intermolecular H-bond

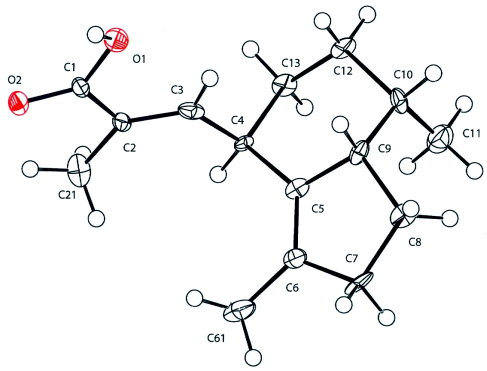


Fig. 1. View of the nardin (**1**) (ORTEP with ellipsoids at the 50 % probability level)

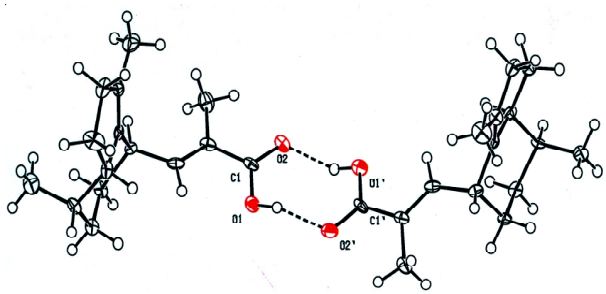


Fig. 2. Asymmetric unit as a dimer of Nardin (1) molecules, associated head-to-head through their carboxylic functions

of the O–H···O type, due to which the molecules transformed by 2_1 screw axes (x; ¼; 0) form an infinite chain directed along the axis[7].

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