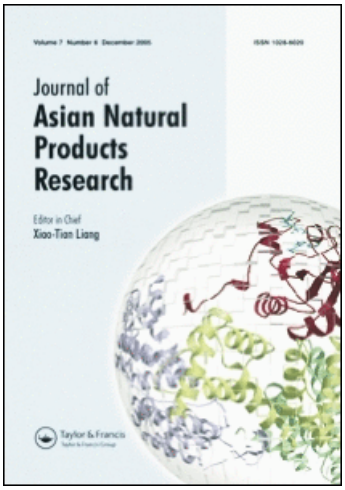

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New triterpenoids from *Arisaema jacquemontii*

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NOTE

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Phytochemical investigation of the roots of *Arisaema jacquemontii* led to the isolation of two new triterpenoids, which were characterized by NMR, IR, and MS spectra as 30-nor-lanost-5-ene-3β-ol (**1**) and 30-norlanost-5-ene-3-one (**2**).

Keywords: *Arisaema jacquemontii*; tetracyclic triterpenoid; anticonvulsant

1. Introduction

Arisaema jacquemontii is a deciduous perennial herb that grows to 1 m. In Kashmir Himalayas, it is considered to be toxic. Toxic symptoms caused by consumption of this plant are described in [1]. *A. jacquemontii* and other plants of the same genus, such as *A. heterophyllum*, *A. peninsulae*, *A. robustum*, *A. consanguineum*, and *A. japonicum*, are frequently used in Chinese herbal medicine as a drug related to anticonvulsants in modern medicine. Its pharmacological effect as an anticonvulsant was reproduced in a modern pharmacological study [1]. Other than anticonvulsant activity, the effects on platelet aggregation were also reported [2]. Despite these interesting biological activities of *A. jacquemontii*, no phytochemical study has yet been reported on this species. Our study on this species has now led to the isolation of two new tetracyclic triterpenoids (Figure 1).

The triterpenoids have a range of unique and potentially usable biological effects and reference to the use of plants with high saponin/triterpenoid content can be found in the first written herbariums. Triterpenoids are also found in a variety of common European plants and fruits [3–7]. Triterpenoids are studied for their anti-inflammatory [8,9], hepatoprotective [10–12], analgesic [13], antimicrobial [14], virostatic [15,16], immunomodulatory [17], and tonic effects. Terpenoids from edible legumes and soybeans also show anti-cancer activity [18].

2. Results and discussion

Compound **1**, obtained as a colorless crystalline solid, in its mass spectrum showed the molecular ion peak at *m/z* 414 with a relatively stronger peak at *m/z* 413 (M^+-1), corresponding to the molecular formula $C_{29}H_{50}O$. The compound gave positive Libermann–Burchard test, showing a violet ring. The IR spectrum revealed the presence of a hydroxyl group by displaying a band at $\nu_{max} = 3427\,cm^{-1}$. The presence of a trisubstituted double bond in the compound was indicated by the IR absorption bands at 1600, 1465, 1063, and 801 cm^{-1}.

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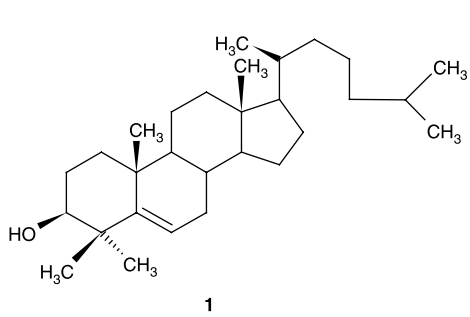

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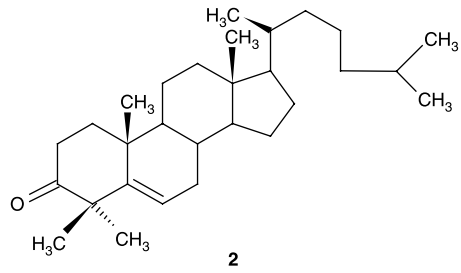

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Figure 1. Structures of compounds **1** and **2**.

The ^{1}H NMR spectrum revealed the presence of seven methyls, four of which appeared as singlets while three methyls gave multiplets at δ 0.68–1.62. The ^{13}C NMR spectrum revealed the presence of methyls at δ_C 11.5–19.9. The ^{1}H NMR spectrum contained a single proton signal at δ 3.65 (dd, $J = 7.1, 2.9$ Hz), attributable to the carbinylic proton carrying the hydroxyl group. A single proton resonance signal at δ 5.35 (d, $J = 5.1$ Hz) indicated the presence of the trisubstituted double bond, which was confirmed by ^{13}C NMR and DEPT 135° spectra which exhibited the vinylic carbon signal at δ_C 121.7 and 140.7. This, together with the molecular formula of the compound, indicated that this triterpenoid was a tetracyclic triterpenoid with one trisubstituted double bond. A comparison of the chemical shift and multiplicity of the vinylic proton signal, together with the ^{13}C NMR signal of the vinylic carbon (δ 121.7 and 140.7), with the literature suggested that the double bond was probably at the C-5 position. Furthermore, the NOE experiment showed no effect on H-20 when 18-Me was irradiated. This result confirmed that the configuration of 21-Me is in β-orientation.

The secondary methyl resonance signal coupled with the mass fragmentation, which indicated the loss of a saturated side chain moiety (C_8H_{17} radical) from the molecular ion to give a daughter ion peak at *m/z* 301, confirmed that the triterpenoid had a side chain similar to that of lanosterol. The daughter ion peak at *m/z* 301 showed a further loss of the acetylenic moiety resulting in the radical ion peak at *m/z* 275. Also, the loss of a molecule of water from the fragment ion at *m/z* 301 resulted in the radical ion peak at *m/z* 283. Furthermore, as a consequence of the fission of the ring C, the fragment ion peak at *m/z* 175 appeared as an abundant ion fragment. The position of the double bond was confirmed by the Retro-Diels-Alder addition fragmentation of the ring B in the molecular ion as well as the daughter ion (*m/z* 283). These resulted in densely populated fragment ion peaks at *m/z* 148 and 135. These observations confirmed that the compound was 30-nor-lanost-5-ene-3β-ol.

The ^{1}H NMR spectra of compounds **1** and **2** were broadly similar, both possessing the same side chain; however, there were significant differences between the compounds. The IR spectrum of compound **2** exhibited a strong band at 1715 cm^{-1}, indicating the presence of the cyclohexanone moiety. The compound does not contain any hydroxyl group, which is evident from its IR spectrum and by its failure to form acetate. The absence of the ^{1}H NMR signal at δ 3.65 and the presence of the ^{13}C NMR signal at δ 211.8 indicated that the hydroxyl group is replaced by the keto functionality.

The proposed structure of compound **2** was confirmed by additional MS and NMR

experimental data. MS gave a molecular ion peak at *m/z* 412 in agreement with the molecular formula $C_{29}H_{48}O$, and the DEPT spectrum showed (by comparison with compound **1**) one carbon signal less for the quaternary carbon (C-3). These observations confirmed that the compound was 30-norlanost-5-ene-3-one.

3. Experimental

3.1 General experimental procedures

Melting points were measured with a Buchi 570 apparatus and are uncorrected. The IR spectra were taken on a Perkin-Elmer Paragon-1000 spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker 200 and 500 MHz spectrometer, using TMS as an internal standard. EI-MS were measured with JOEL-MSD300 and Bruker Esquire 3000 mass spectrometer. Separation and purification was performed by column chromatography on silica gel (60–120 mesh size; E. Merck, Mumbai, India) and TLC on silica gel 60 F_{254} plates (0.25 mm). Detection of spots was done using ceric ammonium sulfate solution.

3.2 Plant material

The roots of the plant *A. jacquemontii* (Araceae) were collected from the hills of Dara in the month of June, and were identified by G.M. Bhat at the Institute of Plant Taxonomy, University of Kashmir, Srinagar, India. A voucher specimen (Collection No. 1307 GM BHAT) is deposited in the herbarium of the institute.

3.3 Extraction and isolation

Two hundred grams of the dried and powdered roots were extracted with chloroform in a Soxhlet apparatus for 36 h. The extract was filtered and air-dried to obtain 10 g of the crude extract. The extract was subjected to column chromatography. The fractions were collected and monitored by TLC. The chloroform–ethyl acetate (4:1) eluates were pooled and the volume was reduced by subjecting them to distillation, which afforded compound **1** (52 mg). The compound was crystallized from methanol.

3.3.1 Compound *1*

A colorless crystalline solid, mp 110°C; $[\alpha]_D^{20}$ + 20.5 (c = 0.50, $CHCl_3$); IR, ν_{max} (KBr, cm^{-1}): 3427, 2937, 2850, 1600, 1465, 1030, 801; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.28 (2H, m, H-1), 1.45 (2H, m, H-2), 3.65 (1H, dd, J = 7.1, 2.9 Hz, H-3), 5.35 (1H, d, J = 5.1 Hz, H-6), 1.09 (2H, m, H-7), 1.61 (1H, m, H-8), 0.90 (1H, m, H-9), 0.85 (2H, m, H-11), 0.91 (2H, m, H-12), 0.95 (1H, m, H-14), 1.29 (2H, m, H-15), 1.32 (2H, m, H-16), 1.59 (1H, m, H-17), 1.00 (3H, s, H-18), 0.68 (3H, s, H-19), 1.35 (1H, m, H-20), 0.97 (3H, d, J = 6.5 Hz, H-21), 1.26 (2H, m, H-22), 2.41 (2H, m, H-23), 1.95 (2H, m, H-24), 2.25 (1H, m, H-25), 1.65 (3H, d, J = 6.9 Hz, H-26), 1.65 (3H, d, J = 6.9 Hz, H-27), 1.30 (3H, s, H-28), 1.50 (3H, s, H-29); ^{13}C NMR (125 MHz, $CDCl_3$) spectral data, see Table 1; MS: *m/z* 414, 413, 301, 283, 275, 203, 175, 148, 135. Elemental analysis: Found: C, 84.25%; H, 11.8%; Calcd for $C_{29}H_{50}O$: C, 84.05%; H, 12.07%.

3.3.2 Compound *2*

A colorless solid, mp 152°C; $[\alpha]_D^{20}$ + 10.5 (c = 0.50, $CHCl_3$); IR, ν_{max} (KBr, cm^{-1}): 2937, 2850, 1715, 1600, 1465, 1030, 801; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27 (2H, m, H-1), 1.42 (2H, m, H-2), 5.35 (1H, d, J = 5.1 Hz, H-6), 1.09 (2H, m, H-7), 1.65 (1H, m, H-8), 0.90 (1H, m, H-9), 0.85 (2H, m, H-11), 0.91 (2H, m, H-12), 0.95 (1H, m, H-14), 1.29 (2H, m, H-15), 1.32 (2H, m, H-16), 1.59 (1H, m, H-17), 1.00 (3H, s, H-18), 0.68 (3H, s, H-19), 1.35 (1H, m, H-20), 0.97 (3H, d, J = 6.5 Hz, H-21), 1.26 (2H, m, H-22), 2.41 (2H, m, H-23), 1.95 (2H, m, H-24), 2.20 (1H, m, H-25), 1.65

Table 1. ^{13}C NMR spectral data of compounds **1** and **2** (125 MHz, in $CDCl_3$).

Carbon no.	**1**	**2**
1	31.9	35.9
2	24.3	29.1
3	71.8	211.8
4	33.2	31.6
5	140.5	140.7
6	121.2	121.7
7	42.3	45.7
8	40.5	45.5
9	42.8	49.8
10	37.9	33.9
11	29.1	26.0
12	30.9	33.9
13	45.5	49.1
14	55.0	55.7
15	40.1	36.1
16	22.2	28.2
17	51.5	56.5
18	15.7	11.7
19	17.5	11.5
20	36.6	31.6
21	16.5	18.5
22	21.1	20.0
23	25.1	28.0
24	34.7	39.7
25	36.2	36.1
26	13.5	19.5
27	15.1	19.1
28	20.1	18.1
29	24.5	28.8

(3H, d, $J = 6.9$ Hz, H-26), 1.65 (3H, d, $J = 6.9$ Hz, H-27), 1.30 (3H, s, H-28), 1.51 (3H, s, H-29); ^{13}C NMR (125 MHz, $CDCl_3$) spectral data, see Table 1; MS: *m/z* 412, 299, 273. Elemental analysis: Found: C, 85.06%; H, 10.95%; Calcd for $C_{29}H_{48}O$: C, 84.46%; H, 11.65%.

3.4 Acetylation of compound 1

To 10 mg of compound **1** in 2 ml pyridine was added acetic anhydride (4 ml) and kept overnight. After the completion of the reaction as revealed by TLC, the reaction mixture was poured into ice-cold water with constant stirring. This was followed by extraction with chloroform. The chloroform layer was washed successively with 10% HCl and distilled water. The chloroform layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated. Further purification was done by repeated crystallization.

*3.4.1 Compound **1-OAc***

A white solid, mp 92°C; IR, ν_{max} (KBr, cm^{-1}): 2930, 2850, 1735, 1600, 1465, 1235; ^1H NMR (200 MHz, $CDCl_3$): δ 1.27 (2H, m, H-1), 1.45 (2H, m, H-2), 4.51 (1H, m, H-3), 5.30 (1H, t, H-6), 1.09 (2H, m, H-7), 1.60 (1H, m, H-8), 0.91 (1H, m, H-9), 0.85 (2H, m, H-11), 0.91 (2H, m, H-12), 0.95 (1H, m, H-14), 1.29 (2H, m, H-15), 1.32 (2H, m, H-16), 1.59 (1H, m, H-17), 1.00 (3H, s, H-18), 0.68 (3H, s, H-19), 1.32 (1H, m, H-20), 0.97 (3H, d, $J = 6.5$ Hz, H-21), 1.26 (2H, m, H-22), 2.41 (2H, m, H-23), 1.95 (2H, m, H-24), 2.25 (1H, m, H-25), 1.65 (3H, d, $J = 6.5$ Hz, H-26), 1.65 (3H, d, $J = 6.5$ Hz, H-27), 1.30 (3H, s, H-28), 1.50 (3H, s, H-29), 2.05 (3H, s, OAc); ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.9 (C-1), 24.3 (C-2), 78.7 (C-3), 31.6 (C-4), 140.7 (C-5), 121.7 (C-6), 42.2 (C-7), 45.5 (C-8), 49.0 (C-9), 33.9 (C-10), 26.0 (C-11), 33.9 (C-12), 45.5 (C-13), 55.7 (C-14), 36.1 (C-15), 28.2 (C-16), 56.5 (C-17), 11.7 (C-18), 11.5 (C-19), 31.6 (C-20), 16.5 (C-21), 21.0 (C-22), 28.0 (C-23), 39.7 (C-24), 36.1 (C-25), 19.5 (C-26), 19.1 (C-27), 18.1 (C-28), 28.8 (C-29); 170.1 (C═O), 25.5 (OAc); MS: *m/z* 456, 343, 283, 175, 148, 135.

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