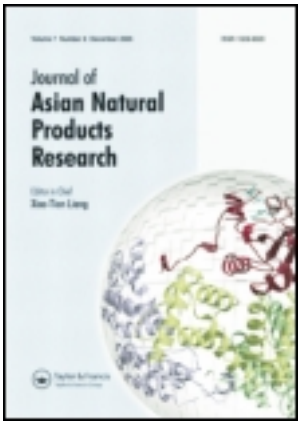

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Alliumonoate: a new cyclopentane derivative from *Allium victorialis*

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NOTE

Alliumonoate: a new cyclopentane derivative from *Allium victorialis*

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Alliumonoate (**1**), a new cyclopentane derivative, has been isolated from the chloroform-soluble fraction of the ethanolic extract of *Allium victorialis*, along with β-amyrin acetate (**2**), β-sitosterol acetate (**3**), 22-cyclohexyl-1-docosanol (**4**), β-amyrin (**5**), β-sitosterol (**6**), and β-sitosterol 3-*O*-β-D-glucopyranoside (**7**), reported for the first time from this species. Their structures were elucidated on the basis of spectral data including mass spectra and 2D NMR experiments.

Keywords: *Allium victorialis*; Alliaceae; cyclopentane derivative; alliumonoate

1. Introduction

The genus *Allium* (Alliaceae) comprises 600 species that are distributed in Asia, Europe, and North western America. In Pakistan, it is represented by 41 species [1]. Various *Allium* species are used for the treatment of different ailments such as cancer, hypertension, heart disease, and disturbance of gastrointestinal tracts [2]. Some of these are also used as indigenous protective drugs against various diseases. For example, *Allium sativum* (garlic) is used to protect against strokes, coronary thrombosis, atherosclerosis, and platelet aggregation [3]. One of the species of the genus *Allium* is *Allium victorialis,* which is a shrub found in Europe, temperate Asia to Japan, and North western America. It grows in northern mountainous regions of Pakistan [1]. Medicinally, it is used as anti-thrombotic [4], anti-scorbutic [1], and carminative in Western Garhwali and to treat profuse menstruation and cold. Its water extracts possess hypolipidimic, anti-lipid, and peroxidative properties on rabbit and mice. The chemotaxonomic and ethanopharmacological importance of the genus *Allium* prompted us to carry out phytochemical studies on *A. victorialis*. As a result, we herein report a new cyclopentane derivative named as alliumonoate (**1**), along with β-amyrin acetate (**2**), β-sitosterol acetate (**3**), 22-cyclohexyl-1-docosanol (**4**), β-amyrin (**5**), β-sitosterol (**6**), and β-sitosterol 3-*O*-β-D-glucopyranoside (**7**), reported for the first time from this species (Figure 1).

2. Results and discussion

The ethanolic extract of *A. victorialis* was suspended in water and successively extracted with *n*-hexane, chloroform, ethyl acetate, and *n*-butanol. The column chromatographic techniques applied to the chloroform-soluble fraction resulted in the isolation of compounds **1**–**7**, respectively.

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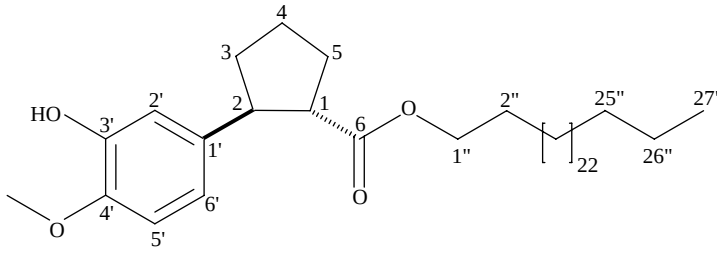

Figure 1. Structure of alliumonoate (**1**).

Alliumonoate (**1**) was obtained as a colorless amorphous solid with $[\alpha]_D^{29} + 68$. It gave violet coloration with $FeCl_3$ for a phenolic function. The IR spectrum showed the presence of hydroxyl group (3415 cm^{-1}), carbonyl (1730 cm^{-1}), and an aromatic moiety (1606–1440 cm^{-1}). The UV spectrum exhibited the absorption maxima at 282, 241, and 217 nm. The HR-EI-MS gave an $[M]^+$ peak at *m/z* 614.5324 consistent with the molecular formula $C_{40}H_{70}O_4$. The broadband and DEPT ^{13}C NMR spectra showed signals of 2 methyl, 29 methylene, 5 methine, and 4 quaternary carbon atoms. The most downfield signal at δ 172.8 was assigned to the ester carbonyl. The signals of a di-substituted cyclopentane moiety were observed at δ 47.4, 44.9, 29.9, 29.7, and 29.3, respectively. It also showed signals of an aromatic moiety at δ 146.5, 144.7, 133.2, 119.6, 114.3, and 109.3. The signals of a long-chain ester moiety included oxymethylene carbon at δ 65.1, a methyl signal at δ 14.1, and 25 methylene carbons resonating in the range of δ 31.9–22.7. An oxymethyl carbon appeared at δ 55.9.

The ^1H NMR spectrum of 1 showed the signals of tri-substituted benzene ring at δ 6.84 (1H, d, $J = 3.0$ Hz), 6.82 (1H, dd, $J = 8.6$, 3.0 Hz), and 6.77 (1H, d, $J = 8.6$ Hz). The methoxyl protons resonated at δ 3.84 (3H, s). The signals of the di-substituted cyclopentane moiety are shown in Table 1. The methine proton at δ 2.92 showed ^1H–^1H COSY correlation to another methine proton at δ 2.61 which could be assigned to C-2 and C-1 on the basis of their HMBC correlations as shown in Figure 2. The signals of long-chain alkyl group were observed at 4.10 (2H, t, $J = 6.7$ Hz), as well as methylene protons in the range of δ 1.51–1.23 (50 H, br) and the terminal methyl protons at δ 0.87 (3H, t, $J = 7.2$ Hz).

The ^1H–^1H COSY and HMBC experiments were used to assign various functionalities. The methoxyl protons at δ 3.84 showed ^3J correlation with C-4′ (δ 146.5), whereas the methylene protons at δ 4.10 (H-1″) showed ^2J correlation with C-2″ (δ 28.6) and ^3J correlations with C-3″ (δ 25.9) and C-6 (δ 172.8). The proton at δ 2.92 (H-2) showed HMBC correlations with C-6 (δ 172.8), C-1′ (δ 133.2), C-2′ (δ 114.3), C-1 (δ 44.9), and C-3 (δ 29.9), whereas the proton at δ 2.61 (H-1) showed correlations with C-6 (δ 172.8), C-1′ (δ 133.2), C-2 (δ 47.4), C-5 (δ 29.7), and C-4 (δ 29.3). The other remaining HMBC correlations are shown in Figure 2.

The relative stereochemistry at C-1 and C-2 was assigned on the basis of their coupling constant. The larger value of coupling constant was in conformity to their pseudo-diaxial configuration, which was further confirmed by non-observance of correlation between H-1 and H-2 in NOESY spectrum. However, H-1 showed correlations with both the aromatic protons H-2′ and H-6′. On the basis of these pieces of evidence, the structure of alliumonoate (**1**) could be assigned as 2-(3-hydroxy-4-methoxyphenyl)-heptacosyl-1-cyclopentane (Figure 1).

Known compounds were identified as β-amyrin acetate (**2**) [5], β-sitosterol

Table 1. ^{1}H ($CDCl_3$, 400 MHz) and ^{13}C ($CDCl_3$, 100 MHz) NMR spectral data of alliumonoate (**1**).

Carbon No.	δ_C	δ_H
1	44.9	2.61 (1H, ddd, $J = 9.5, 7.6, 6.4$ Hz)
2	47.4	2.92 (1H, ddd, $J = 9.5, 7.8, 6.6$ Hz)
3	29.9	2.01–1.85 (2H, m)
4	29.3	2.01–1.85 (2H, m)
5	29.7	2.01–1.85 (2H, m)
6	172.8	–
1′	133.2	–
2′	114.3	6.84 (1H, d, $J = 3.0$ Hz)
3′	144.7	–
4′	146.5	–
5′	109.3	6.77 (1H, d, $J = 8.6$ Hz)
6′	119.6	6.82 (1H, dd, $J = 8.6, 3.0$ Hz)
1″	65.1	4.10 (2H, t, $J = 6.7$ Hz)
2″	28.6	1.51 (2H, m)
3″	25.9	1.23 (2H, br s)
4″	29.4	1.23 (2H, br s)
5″	29.5	1.23 (2H, br s)
6″	29.6	1.23 (2H, br s)
7″	29.8	1.23 (2H, br s)
8″–24″	29.8	1.23 (34H, br s)
25″	31.9	1.23 (2H, br s)
26″	22.9	1.23 (2H, br s)
27″	14.1	0.87 (3H, t, $J = 7.2$ Hz)
OMe	55.9	3.84 (3H, s)

acetate (**3**) [6], 22-cyclohexyl-1-docosanol (**4**) [7], β-amyrin (**5**) [8], β-sitosterol (**6**) [6], and β-sitosterol 3-*O*-β-D-glycopyranoside (**7**) [9], by comparing their physical and spectral data with those reported in the literature.

3. Experimental

3.1 General experimental procedures

Melting points were measured on a Gallenkamp apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-360 polarimeter. UV spectra were recorded on a Hitachi UV-3200 spectrophotometer, whereas the IR spectra were recorded on a Shimadzu FTIR-8900 spectrometer as KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer in deuterated solvents. 2D NMR spectra were recorded on the AM-400 spectrometer. The chemical shifts are in ppm (δ), relative to the tetramethylsilane as an internal standard and scalar coupling are reported in Hz. Mass spectra (EI and HR-EI) were

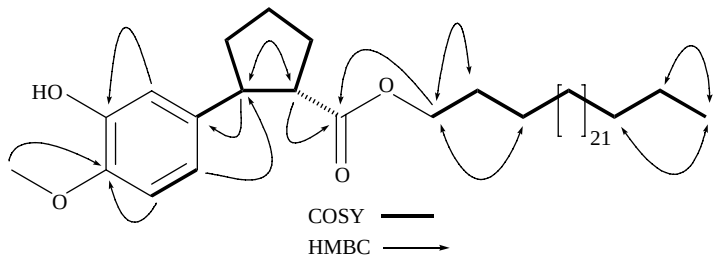

Figure 2. Key ^{1}H–^{1}H COSY and HMBC correlations of alliumonoate (**1**).

obtained in an electron impact mode on Finnigan MAT-112 and MAT-113 spectrometers, and FAB mass spectra were carried out on a Jeol JMS HX 110 spectrometer and ions are given in *m/z* (%). Column chromatography (CC) was carried out on silica gel (70–230 mesh, E. Merck, Darmstadt, Germany), TLC on pre-coated silica gel G-25-UV_{254} plates (E. Merck), and detection at 254 and 366 nm or by spraying ceric sulfate in 10% H_2SO_4 (heating). Melting points were measured on a Gallenkamp apparatus and are uncorrected.

3.2 Plant material

The whole plant material of *A. victorialis* was collected from the northern areas of Pakistan in 2004 and identified by Dr Surriya Khatoon, Plant Taxonomist, Department of Botany, University of Karachi, Karachi, Pakistan, where a voucher specimen has been deposited in the herbarium (Voucher specimen no. 202/KUH).

3.3 Extraction and isolation

The freshly collected whole plant materials of *A. victorialis* (20 kg) were shade dried, ground, and extracted with ethanol (3 × 40 liter, 10 days each) at room temperature (r.t.). The combined ethanolic extract was evaporated under reduced pressure at r.t. to yield a residue (800 g) that was suspended in water (1.0 liter) and successively fractionated into *n*-hexane (80 g), $CHCl_3$ (170 g), EtOAc (220 g), and *n*-BuOH (150 g) parts. The $CHCl_3$-soluble fraction (80 g) was subjected to CC over silica gel and eluted with *n*-hexane, *n*-hexane–$CHCl_3$, $CHCl_3$, and $CHCl_3$–MeOH in increasing order of polarity to obtain 20 sub-fractions. The sub-fraction obtained with *n*-hexane–$CHCl_3$ (6.5:3.5; 2.5 g) was re-chromatographed over silica gel and eluted with *n*-hexane–$CHCl_3$ in increasing order of polarity. The fractions that were obtained with *n*-hexane–$CHCl_3$ (7.0:3.0 and 6.5:3.5; 30 mg) were further purified through preparative TLC using *n*-hexane–$CHCl_3$ (5.0:5.0 and 4.5:5.5) as eluents to afford β-amyrin acetate (**2**) (15 mg) and β-sitosterol acetate (**3**) (12 mg), respectively. The sub-fraction that was obtained with *n*-hexane–$CHCl_3$ (6.0:4.0; 1.7 g) was re-chromatographed over silica gel and eluted with mixture of *n*-hexane–$CHCl_3$. Elution with *n*-hexane–$CHCl_3$ (6.5:3.5) provided 22-cyclohexyl-1-docosanol (**4**) (20 mg). The sub-fraction that was obtained with *n*-hexane–$CHCl_3$ (5.0:5.0; 2 g) was re-chromatographed over silica gel and eluted with *n*-hexane–$CHCl_3$ and $CHCl_3$. The fraction that was obtained with *n*-hexane–$CHCl_3$ (6.0:4.0; 17 mg) afforded a pure compound β-amyrin (**5**) and the fraction obtained with *n*-hexane–$CHCl_3$ (5.5:4.5; 30 mg) was a single compound with trace impurities, which was further re-chromatographed and eluted with same solvent system to afford β-sitosterol (**5**) (27 mg). The sub-fraction that was obtained with *n*-hexane–$CHCl_3$ (4.0:6.0; 35 mg) was re-chromatographed over silica gel and eluted with *n*-hexane–$CHCl_3$ (4.5:5.5) to afford compound **1** (20 mg). The sub-fraction that was obtained with $CHCl_3$–MeOH (9.8:0.2; 3 g) was triturated with acetone and the residue was re-chromatographed over silica gel and eluted with $CHCl_3$–MeOH (9.9:0.1) to afford β-sitosterol 3-*O*-β-D-glucopyranoside (**7**) (50 mg).

3.3.1 Alliumonoate (*1*)

White amorphous solid; $[\alpha]_D^{29} + 68$; UV λ_{max} ($CHCl_3$) nm (log ε): 282 (1.6), 241 (3.0), 217 (1.7); IR ν_{max} (KBr) cm^{-1}: 3415 (OH), 1730 (O—C═O), 1606–1440 (aromatic moiety); ^1H ($CDCl_3$, 400 MHz) and ^{13}C ($CDCl_3$, 100 MHz) NMR spectral data see Table 1; EI-MS *m/z* (rel. int. %): 614 (9), 586 (15), 272 (14), 194 (33), 177 (30), 137 (19), 111 (10), 99 (5), 97 (25), 85 (35), 83 (40), 71 (55), 57 (100), 55 (69); HR-EI-

MS: *m/z* 614.5324 $[M]^+$ (calcd for $C_{40}H_{70}O_4$, 614.5274).

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