Structure of a New Eudesmane Sesquiterpene Argutinin from *Pluchea arguta* Boiss

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A new eudesmane sesquiterpene, argutinin (I) has been isolated from *Pluchea arguta* Boiss. Its structure has been elucidated by spectroscopic methods.

**Introduction**

*Pluchea arguta* Boiss (Syn. *Conyza odontophylla* Boiss) (Compositae) grows as a common weed in Sind and other parts of Pakistan [1]. Some of the *Pluchea* species are noted for their medicinal properties [2]. A number of compounds have been isolated from the *Pluchea* species [3–5].

In our previous publications we have reported the isolation and structure of several known and new compounds from the whole plant extract [6, 7]. The present communication deals with the isolation and structure elucidation of another new type of eudesmane derivative named as argutinin (I) from this plant.

**Results and Discussion**

The petroleum ether extract from the fresh whole plant of *P. arguta* was chromatographed on a Si gel column as described in experimental. Argutinin (I) was obtained from the CHCl₃–EtOAc (70:30) eluate. Which was subjected to repetitive flash column chromatography with C₆H₆–EtOAc (60:40) affording pure I as colourless gum. The purity of I was checked on TLC, and HPTLC (CHCl₃:MeOH 8.5:1.5) plates as well as on HPLC using Z-Module with RP-18 cartridge and MeOH:H₂O (60:40) as mobile phase.

The pure argutinin (I), colourless gum, showed [α]D²⁰ +102° (c, 1, CHCl₃). Fast atom bombardment mass spectrum showed the molecular ion peak m/z 424, corresponding to the molecular formula C₂₂H₃₂O₈. The peak observed at m/z 408 attributable to the formula C₂₂H₃₂O₇ (M⁺–O). While high resolution mass spectrum exhibited an important fragment at m/z 390.2032 (C₂₂H₂₉O₈, calcd. 390.2042) due to the loss of H₂O from the molecular ion. The peak at m/z 366.2122 (C₂₀H₂₆O₆, calcd. 366.2042) [M⁺–O–(CH₂=CH=O)], and at m/z 348.125 having the composition C₂₀H₂₅O₇. Another fragment appeared at m/z 333.1691 [M⁺–H₂O–(CH₂=CH=O)–CH₃] leading to the formula C₁₉H₂₅O₆. The fragment ion appeared at m/z 233.1162 with the composition C₁₄H₁₇O₃ was due to the loss of epoxyangelate ester side chain from the fragment m/z 333 and at m/z 215.1103 was due to the loss of H₂O molecule from the above fragment having the composition C₁₄H₁₅O₂. The UV (MeOH)

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spectrum of I exhibited the maxima at 227 nm indicating the unsaturation in the molecule. The IR (CHCl₃) spectrum exhibited band at 3540 (OH), 1745 (acetate carbonyl), 1730 (epoxyangelate carbonyl) and 1670 cm⁻¹ (α,β-unsaturation ketone).

The ¹H NMR of argutinin (I) in CDCl₃ (300 MHz) displayed typical signals for epoxyangelate, a quartet for 1H resonating at δ 3.06 with a coupling constant of 6Hz, attributed to H-3', a doublet of 3H at δ 1.32 (J = 6Hz) for 3×H-4', a singlet for sec. methyl at δ 1.59 for 3×H-5'. A singlet for 3H at δ 1.98 indicating the acetate moiety in the molecule. The H-6 olefinic proton was observed at δ 6.84 (d, J = 3Hz), indicating the stereochemistry at C-4. Small differences were also observed in the chemical shift of H-15 and the acetate methyl which appeared at δ 1.33 and δ 1.98 respectively, suggesting the β-orientation of acetate moiety at C-4. A downfield 1H singlet resonated at δ 7.92 indicating the presence of hydroperoxide group in the molecule. The existence of OOH was also confirmed by loss of H₂O₂ from the molecular ion in mass spectrum. The position of hydroperoxide at C-11 was followed from the downfield shift of the corresponding methyl signals at δ 1.48 and δ 1.52 for 3×H-13 and 3×H-12 respectively. The stereochemistry at C-3 was deduced from the coupling J₂,₃ = 3Hz specific for the α-orientation of ester group, which was also suggested by the chemical shift of 3-H at 5.9 (t, J = 3Hz).

2-D NMR measurements determined the multiplicities of the proton signals through 2D-J-resolved spectrum, while the coupling interactions were established by COSY-45 experiment. NOESY spectrum served to show the relative stereochemistry at several points in the molecule. Strong cross peaks were observed between methylene protons of C-9 and 14-methyl protons. The n.O.e. interaction between 13-methyl at δ 1.48 and olefinic proton of C-6 at δ 6.84 could also be observed. The 15-methyl proton at δ 1.33 showed n.O.e. interaction with C-6 olefinic proton at δ 6.84, suggested the α-orientation of 15-methyl at C-4. Similarly the n.O.e. interaction between the C-5' methyl proton and C-3' proton at δ 1.59 and δ 3.06 respectively could also be observed.

The ¹³C NMR spectrum (broad band and DEPT) in CDCl₃ (75.4 MHz) indicated that the presence of hydroperoxy group at C-11 shifted the geminal methyls C-12 and C-13 downfield and also the C-11 also shifted downfield as compare to 4-epi-plucheinol [6]. Presence of an acetate group at C-4 shifts the C-3 signal to high field, but an expected strong deshielding was observed for C-4 (approximately 8 ppm as compare to 4-epi-plucheinol). The complete ¹³C-NMR are given in Table I.

The status of each carbon confirmed through DEPT experiment.

**Experimental**

Optical rotation was measured in CHCl₃ on Polartronic-D polarimeter. UV spectrum scanned on Shimadzu UV 240 spectrophotometer. IR was recorded on JASCO A-302 spectrophotometer. ¹H and ¹³C NMR were scanned on Bruker AM-300 Nuclear Magnetic Resonance spectrometer. The mass spectra were measured on Varian MAT-112 and MAT-312 spectrometer connected to MAT-188 data system and PDP 11/34 computer system. Flash column chromatography was performed on Eyalas Flash Chromatography EF-10 model, using silica gel 60, 230–400 mesh size (E. Merck). HPLC was carried out on Z-Module Radial Compression Separation System millipore (Waters) having RP-18 cartridge, using Constrametric 111 pump (LDC Milton Roy) coupled with UV 1 DEC-100-11 UV dector (JASCO).

**Extraction and isolation:** The fresh plant material of Pluchea arguta Boiss. Collected from Karachi, and identified by a taxonomist of Botany Department, University of Karachi.

The whole plant of P. arguta Boiss (8 kg) was homogenized by Ultra-Turrax homogenizer in hexane and kept at room temperature for about 15 days. The residue obtained after evaporation of hexane

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The status of each carbon confirmed through DEPT experiment.
extract was chromatographed on a large silica gel column and eluted with solvent of increasing polarity in the order, pet-ether pet-ether-CHCl₃, CHCl₃, CHCl₃-EtOAc, EtOAc, EtOAc-MeOH and finally with pure MeOH. The fractions eluted with CHCl₃-EtOAc (70:30) was subjected to repetitive flash column chromatography using C₆H₆-EtOAc (60:40) eluant furnished pure argutinin (1) as colourless gum. The purity of 1 was confirmed on TLC as well as on HPTLC (CHCl₃: MeOH, 8.5:1.5) and by HPLC using Z-Module RP-18 cartridge with MeOH: H₂O (60:40) as mobile phase.

**Argutinin (1)**

Colourless gum [α]D +102° (c, 1, CHCl₃), UV (MeOH) λmax 227 nm. IR (CHCl₃): v max 3540 (OH), 1745 (acetate carbonyl), 1730 (epoxyangelate carbonyl) and 1670 (α,β-unsaturated ketone) cm⁻¹.

1H NMR (CDCl₃, 300 MHz): δ 0.96 (s, 3×H-14), 1.32 (d, J = 6 Hz, 3×H-4'), 1.33 (s, 3×H-15), 1.48 (s, 3×H-13), 1.52 (5, 3×H-12), 1.59 (s, 3×H-5'), 1.98 (s, 3H, OCOCH₃), 2.32 (m, 2×H-9), 2.82 (d, J = 3 Hz, H-5), 3.06 (q, J = 6 Hz, H-3'), 5.90 (t, J = 3 Hz, H-3), 6.84 (d, J = 3 Hz, H-6), 7.92 (br, s, OOH). 13C NMR: See Table I. FABMS: m/z 424 (C₃₂H₃₂O₈) [M⁺]⁺, 408 (C₃₂H₃₂O₇) [M⁺-O]⁺. HRMS: m/z 390.2032 (C₂₂H₃₀O₆, calcd. 390.2042) [M⁺-H₂O]⁺, 366.2122 (C₂₀H₂₆O₆, calcd. 366.2042) [M⁺-O-(CH₂=CH=CH₂)]⁺, 348.1925 (C₂₀H₂₆O₅, calcd. 348.1936) [M⁺-H₂O-(CH₂=CH=CH₂)]⁺, 333.1691 (C₁₉H₂₆O₅, calcd. 333.1701) [M⁺-H₂O-(CH₂=CH=CH₂)-CH₃], 1233.1162 (C₁₄H₁₇O₅, calcd. 1233.1172) [M⁺-H₂O-(CH₂=CH=CH₂)-CH₃-epoxyangelate]⁺, 215.1071 (C₁₄H₁₇O₂, calcd. 215.1071) [M⁺-H₂O-(CH₂=CH=CH₂)-CH₃-epoxyangelate-H₂O]⁺.

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