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A New Triterpenoid from *Teucrium Integrifolium*

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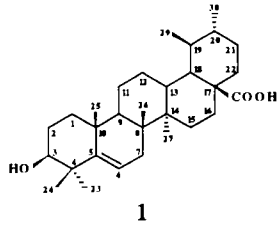
Abstract: A new ursane-type triterpene, 3β-hydroxy-urs-5(6)-en-28-oic acid **1**, was isolated from the aerial parts of *Teucrium integrifolium* and characterized. The structure of this new compound was mainly established by 2D NMR techniques (COSY, HETCOR, HMBC).

Keywords: *Teucrium integrifolium*; labiatae; ursane-type triterpenoid; 3β-hydroxy-urs-5(6)-en-28-oic acid.

In continuation of our studies on biologically active principles from *Teucrium* species[1,2], we have investigated *T. integrifolium* C. Y. Wu *et al*, which was collected in Shibing county, Guizhou province of China and was used for the treatment of sword wounds and to stop bleeding in folk medicine[3]. Analysis of the EtOAc-soluble part of the extract of the aerial parts has led to the isolation of one new triterpenoid **1**, with the known hydrocarbon pentatriacontane. In this paper, we report on the structural elucidation of the new compound **1**.



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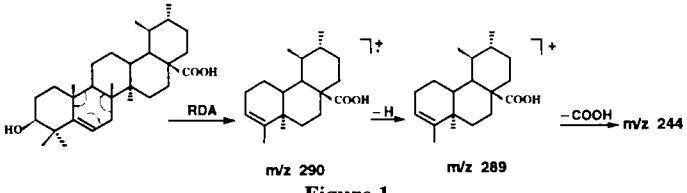

Figure 1.

Compound **1**, mp 315.5-316.5°C, $[\alpha]_D^{18}$ -21.5 (*c* 0.23, C_5H_5N), was shown to have the molecular formula $C_{30}H_{48}O_3$, by EI-and HR-mass spectra[4], implying seven degrees of

unsaturation. Absorption for hydroxyl (3233 cm^{-1}) and carbonyl (1688 cm^{-1}) groups were observed in its IR spectrum. The ^1H NMR[5] spectrum contained the signals for seven skeleton methyl groups, of which five were singlets (δ 0.78, 0.81, 0.92, 1.36, 1.75) and two were doublets (δ 0.85 and 0.91). These data, together with the presence of 30 carbon atom signals in its ^{13}C NMR[6] spectrum suggested that **1** was an ursane-type triterpenoid.

The ^1H NMR spectrum of **1** further revealed a secondary hydroxyl group (δ 3.48, 1H, dd, *J*=12.1, 4.2 Hz), whose chemical shift and splitting pattern were typical of a 3β-equatorial hydroxy in a conventional ursane-type triterpenoid nucleus[7,8], and one olefinic proton which resonated at δ 5.44 (dd, *J*=5.3, 2.7 Hz). Placement of this olefinic function at C-5 and C-6 was established by retro-Diels-Alder fragment ions of **1** in its EI-MS spectrum (**Figure 1**) and 2D NMR techniques. In the ^1H-^1H COSY spectrum of **1**, the signal at δ 3.48 (H-3α) showed correlation with the signals at δ 2.72 (1H, m, H-2α) and at δ 2.04 (1H, m, H-2β); and the olefinic proton (δ 5.44) showed correlations with H-7α (δ 1.53, overlapped) and H-7β (δ 1.57, overlapped) only. Thus, a hydroxyl group and one olefinic bond should be located at the C-3β and C-5(6) positions, respectively. The locations were further confirmed by H-2β and Me-23 correlating to C-3 (δ 78.60, d); and H-1β and H-9α correlating to C-5 (δ 150.77, s) in the HMBC spectrum of **1**.

The stereochemistry of 3β-OH in **1** was supported by an NOESY experiment. Observation of the NOESY correlation between the H-3α with H-1α proton confirmed that the C-3 hydroxyl group has the 3β orientation. Therefore, compound **1** was represented as 3β-hydroxy-urs-5(6)-en-28-oic acid.

The new triterpenoid **1** is also the first natural isolate from the *Teucrium* genus of a triterpenoid possessing an ursane-type skeleton with a double bond in the 5,6-position.

References and Notes

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3. Editorial Board of Flora Guizhouensis, *Flora Guizhounica*, National Publishing House of Sichuan, Chengdu, **1988**, *8*, 310.
4. EI-MS (70eV) m/z (rel. int.): 456 $[M]^+$ (67), 441 $[M-CH_3]^+$ (100), 423 $[M-CH_3-H_2O]^+$ (17), 394 $[M-CH_3-H_2O-CHO]^+$ (10), 379 $[M-CH_3-H_2O-COOH]^+$ (13), 290 (39), 289 (96), 277 (25), 271 (22), 244 (14), 227 (16), 205 (25), 191 (21), 157 (28), 137 (53), 119 (53), 105 (57), 95 (83), 81 (59), 69 (71), 55 (85); HRMS m/z: 456.3601 $[M]^+$, Calc for $C_{30}H_{48}O_3$: 456.3603.
5. ^1H NMR of **1** (400 MHz, C_5D_5N): δ 0.78 (3H, s, 24-H), 0.81 (3H, s, 25-H), 0.85 (3H, d, *J*=6.5 Hz, 29-H), 0.91 (3H, d, *J*=6.5 Hz, 30-H), 0.92 (3H, s, 26-H), 1.36 (3H, s, 27-H), 1.75 (3H, s, 23-H), 1.35 (1H, m, H-1β), 1.53 (1H, overlapped, H-7α), 1.57 (1H, s, overlapped, H-7β), 1.63 (1H, m, H-1α), 1.71 (1H, overlapped, H-9α), 2.04 (1H, m, H-2β), 2.08 (1H, m, H-16β), 2.15 (1H, m, H-19α), 2.68 (1H, m, H-15β), 2.72 (1H, m, H-2α), 3.48 (1H, dd, *J*=12.1, 4.2 Hz, H-3α), 5.44 (1H, dd, *J*=5.3, 2.7 Hz, H-6).
6. ^{13}C NMR of **1** (100 MHz, C_5D_5N): 36.5 (C-1, t), 28.6 (C-2, t), 78.6 (C-3, d), 37.1 (C-4, s), 150.8 (C-5, s), 117.2 (C-6, d), 37.1 (C-7, t), 38.8 (C-8, s), 46.8 (C-9, d), 38.1 (C-10, s), 18.9 (C-11, t), 29.6 (C-12, t), 52.3 (C-13, d), 43.3 (C-14, s), 20.5 (C-15, t), 20.5 (C-16, t), 50.7 (C-17, s), 59.8 (C-18, d), 40.1 (C-19, d), 31.0 (C-20, d), 30.2 (C-21, t), 41.0 (C-22, t), 24.8 (C-23, q), 14.3 (C-24, q), 15.9 (C-25, q), 16.1 (C-26, q), 24.1 (C-27, q), 179.9 (C-28, s), 22.4 (C-29, q), 23.3 (C-30,q).
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