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# FLAVONOIDS FROM *Stachys annua* GROWING IN AZERBAIJAN

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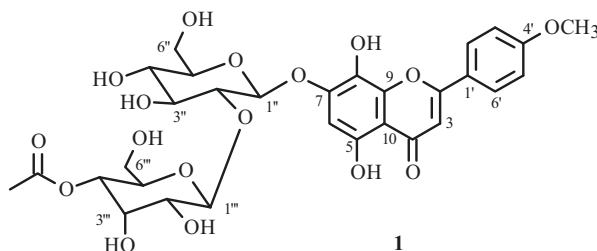
The new acylated flavonoid bioside 4'-*O*-methylisoscuteallarein-7-*O*-[4'''-*O*-acetyl]allopyranosyl-(1→2)-glucopyranoside (**1**) was isolated from the aerial parts of *Stachys annua* L. (Lamiaceae). Subterranean organs yielded for the first time 4'-*O*-methylisoscuteallarein (**2**) and 4'-*O*-methylisoscuteallarein-7-*O*-[6''-*O*-acetyl]allopyranosyl-(1→2)-glucopyranoside (**3**). Chemical structures of the isolated compounds were elucidated using NMR spectroscopy.

**Keywords:** *Stachys annua*, Lamiaceae, new acylated bioside, annuoside.

In continuation of the search for potential new sources of biologically active compounds [1], we studied the aerial and subterranean organs of *Stachys annua* L. from the flora of Azerbaijan.

Previously, several *Stachys* species including *S. annua* from Ukraine, Azerbaijan, and European countries were incompletely studied [2]. Earlier, we isolated from the aerial parts of *S. annua*  $\beta$ -sitosterol, ursolic acid, and 4'-*O*-methylisoscuteallarein-7-*O*-[6'''-*O*-acetyl]allopyranosyl-(1→2)-glucopyranoside [3].

Herein, data are presented for the new acylated bioside 4'-*O*-methylisoscuteallarein-7-*O*-[4'''-*O*-acetyl]allopyranosyl-(1→2)-glucopyranoside (annuoside, **1**) from the aerial part and 4'-*O*-methylisoscuteallarein (**2**) and 4'-*O*-methylisoscuteallarein-7-*O*-[6'''-*O*-acetyl]allopyranosyl-(1→2)-glucopyranoside (**3**) from the subterranean organs of *S. annua*.



Acid hydrolysis of **1** produced the aglycon, acetic acid, D-glucose, and D-allose.

PMR spectra showed resonances for aromatic-ring protons at  $\delta$  8.2–6.0 ppm. Correlations were observed in the COSY spectrum between H-1''–H-2''–H-3''–H-4''–H-5'' and H-1'''–H-2'''–H-3'''–H-4'''–H-5''' and corresponded to ring protons of the two sugars.

Resonances for anomeric protons could be seen in the HMBC spectrum. A correlation between H-1'' ( $\delta$  5.17 ppm) and C-7 ( $\delta$  151.0) confirmed that the first sugar was bonded to C-7. Two correlations between H-2'' ( $\delta$  3.63) and C-1''' ( $\delta$  101.4) in addition to H-1''' ( $\delta$  4.97) and C-2'' ( $\delta$  81.7) confirmed that the second sugar was bonded to the first at C-2''. The HMBC spectrum established that the OCH<sub>3</sub> group ( $\delta$  3.87) was situated on C-4' ( $\delta$  162.3); the CH<sub>3</sub> ( $\delta$  1.99), to –COO ( $\delta$  169.4); the methyl ester –COOCH<sub>3</sub>, to C-4''' ( $\delta$  4.53).

The aglycon had the formula  $C_{16}H_{12}O_6$ , mp 272–274°C (EtOH), and  $R_f$  0.81. The physicochemical and chemical properties and chromatographic and spectroscopic data for the aglycon of annuoside identified it as 4'-*O*-methylisoscuteallarein.

## EXPERIMENTAL

**General Comments.** Chromatography used Filtrak FN5 paper and solvent system *n*-BuOH–HOAc–H<sub>2</sub>O (4:1:5, 1). UV spectra were recorded on an Agilent Technologies Cary 60 UV-Vis instrument; NMR spectra, on a Bruker AM-600 spectrometer; melting points, on a CMP 20 apparatus.

**Isolation of Glavonoids from the Aerial Part of *S. Annua*.** Raw material was collected in June 2015 in the vicinity of Shamakhi, Republic of Azerbaijan. Air-dried and ground aerial plant parts (1.0 kg) were extracted (3×) with EtOH (80%) at room temperature. The extracts were combined and evaporated *in vacuo* to a watery residue that was worked up sequentially with hexane, CHCl<sub>3</sub>, and EtOAc.

Recrystallization from aqueous EtOH of the EtOAc extract afforded 4'-*O*-methylisoscuteallarein-7-*O*-(6'''-*O*-acetyl)allopyranosyl-(1→2)-glucopyranoside [3] and compound **1**, which was called annuoside [3].

**Annuoside (1)**, C<sub>30</sub>H<sub>34</sub>O<sub>17</sub>, greenish-yellow crystals; soluble in aqueous EtOH, DMF, and Py; poorly soluble in EtOH and H<sub>2</sub>O; insoluble in CHCl<sub>3</sub> and EtOAc; mp 176–178°C (H<sub>2</sub>O),  $R_f$  0.59. <sup>1</sup>H NMR spectrum (600 MHz, DMSO-*d*<sub>6</sub>, δ, ppm, J/Hz): 8.11 (2H, d, J = 8.8, H-2', 6'), 7.14 (2H, d, J = 8.8, H-3', 5'), 6.92 (1H, s, H-3), 6.64 (1H, s, H-6), 5.17 (1H, d, J = 7.7, H-1''), 4.97 (1H, d, J = 7.7, H-1'''), 4.53 (1H, dd, J = 10.2, 2.5, H-4'''), 4.09 (1H, br.t, J = 2.8, H-3'''), 3.87 (3H, s, OCH<sub>3</sub>), 3.86 (1H, m, H-5'''), 3.73 (1H, m, H-6''), 3.63 (1H, dd, J = 9.0, 7.7, H-2''), 3.51 (1H, m, H-3''), 3.48 (1H, m, H-6''), 3.46 (1H, m, H-5''), 3.27 (1H, m, H-6'''), 3.25 (1H, m, H-4''), 3.22 (1H, m, H-2'''), 3.23 (1H, m, H-6'''), 1.99 (s, OAc). <sup>13</sup>C NMR spectrum (150 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 163.5 (C-2), 103.4 (C-3), 182.2 (C-4), 152.3 (C-5), 98.1 (C-6), 151.0 (C-7), 126.8 (C-8), 144.1 (C-9), 104.8 (C-10), 122.8 (C-1'), 128.3 (C-2', 6'), 114.4 (C-3', 5'), 162.3 (C-4'), 55.4 (OCH<sub>3</sub>), 98.9 (C-1''), 81.7 (C-2''), 75.4 (C-3''), 69.0 (C-4''), 76.7 (C-5''), 60.3 (C-6''), 101.4 (C-1'''), 70.9 (C-2'''), 67.6 (C-3'''), 69.0 (C-4'''), 71.6 (C-5'''), 59.6 (C-6'''), 20.8, 169.4 (OAc) [3].

**Isolation of Flavonoids from Subterranean Organs of *S. Annua* L.** Ground and air-dried subterranean organs (0.8 kg) were extracted (3×) with EtOH (80%) at room temperature. The combined extracts were evaporated *in vacuo* to an aqueous residue that was worked up sequentially with hexane, CHCl<sub>3</sub>, hexane–EtOAc, and EtOAc.

Recrystallization of the hexane–EtOAc extract from aqueous EtOH produced **2** (4'-methoxyisoscuteallarein), C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>, mp 270–272°C,  $R_f$  0.81. Alkaline hydrolysis of **2** formed 4-methoxybenzoic acid [4].

Recrystallization of the EtOAc extract from EtOH produced **3**, acid hydrolysis (5% H<sub>2</sub>SO<sub>4</sub>, 5 h) of which cleaved **3** into the aglycon, AcOH, D-glucose, and D-allose. Aglycon, C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>, mp 270–272°C (EtOH),  $R_f$  0.81. Compound **3** was isolated earlier from the subterranean organs of *S. annua* [5].

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