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IRIDOIDS FROM *Catalpa bignonioides*

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Continuing a study of the iridoids of plants growing in Uzbekistan, we have investigated the pods of *Catalpa bignonioides* (fam. Binoniaceae) gathered in Tashkent.

The air-dry comminuted raw material (3.0 kg) was extracted at room temperature with methanol (5 × 10 liters). The extract was concentrated, the residue was diluted with water, and the resulting precipitate was removed. The aqueous solution was extracted successively with chloroform and butanol. After the butanol had been distilled off, the dry residue consisted of the total iridoids (320 g). Of this material, 30 g was chromatographed on a column of silica gel (chloroform–methanol–water (70:23:4) system), which gave compounds (**1**), (**4**), and (**5**) and a mixture of (**2**) and (**3**). After this mixture had been rechromatographed under the same conditions, compounds (**2**) and (**3**) were also isolated in the individual state.

Substance (**1**), $C_{22}H_{26}O_{11}$, mp 170-171°C (from methanol), $[\alpha]_D^{22}$ — 184.2 ± 2° (*c* 0.56; methanol). $[MH]^+$ 467 (70%).

^{13}C NMR (100 MHz, CD_3OD, 0-HMDS, δ, ppm): 93.12 (C-1, d), 141.30 (C-3, d), 101.86 (C-4, d), 36.75 (C-5, d), 80.34 (C-6, d), 58.31 (C-7, d), 66.00 (C-8, s), 41.95 (C-9, d), 58.68 (C-10, t), 98.05 (C-1′, d), 73.55 (C-2′, d), 77.58 (C-3′, d), 70.41 (C-4′, d), 76.54 (C-5′, d), 61.52 (C-6′, t), 129.42 (C-1″, s), 129.42 (C-2″, d), 128.97 (C-3″, d), 133.83 (C-4″, d), 128.97 (C-5′, d), 129.42 (C-6″, d), 165.95 (C=O, s).

Substance (**1**) was identified from its UV, IR, and PMR spectra as veronicoside [1].

Substance (**2**), $C_{25}H_{30}O_{13}$, mp 138-140°C (from methanol), $[\alpha]_D^{22}$ — 180 ± 2° (*c* 0.75; methanol).

Substance (**3**), $C_{24}H_{28}O_{12}$, mp 248-250°C (from methanol), $[\alpha]_D^{22}$ — 214.0 ± 2° (*c* 0.68; methanol).

^{13}C NMR (100 MHz, CD_3OD, 0-HMDS, δ, ppm): 95.09 C-1, d), 142.30 (C-3, d), 102.93 (C-4, d), 36.75 (C-5, d), 81.24 (C-6, d), 60.28 (C-7, d), 66.85 (C-8, s), 43.17 (C-9, d), 61.32 (C-10, t), 99.72 (C-1′, d), 74.84 (C-2′, d), 78.58 (C-3′, d), 71.71 (C-4′, d), 77.68 (C-5′, d), 62.89 (C-6′, t), 127.06 (C-1″, s), 131.32 (C-2″, d), 116.90 (C-3″, d), 161.42 (C-4″, s), 115.93 (C-5″, d), 131.32 (C-6″, d), 147.22 (C(α), d), 114.58 (C(β), d), 168.96 (C=O, s).

A comparison of the above-given constants and spectral characteristics with literature figures [1-4] showed that substances (**2**) and (**3**) were identical with minecoside and specioside, respectively.

Substance (**4**), $C_{22}H_{26}O_{12}$, mp 210-212°C (from water), $[\alpha]_D^{20}$ — 165.0 ± 2° (*c* 0.71; water), $[MH]^+$ 483.

^{13}C NMR (100 MHz, CD_3OD, 0-HMDS, δ, ppm): 95.16 (C-1, d), 142.37 (C-3, d), 103.0 (C-4, d), 36.75 (C-5, d), 81.42 (C-6, d), 60.35 (C-7, d), 66.85 (C-8, s), 43.17 (C-9, d), 62.25 (C-10, t), 99.79 (C-1′, t), 74.77 (C-2′, d), 78.50 (C-3′, d), 71.71 (C-4′, d), 77.68 (C-5′, d), 62.82 (C-6′, t), 121.01 (C-1″, d), 133.03 (C-2″, d), 116.67 (C-3″, d), 164.85 (C-4″, s), 116.67 (C-5″, d), 133.03 (C-6″, t), 168.06 (C=O, s).

The acetylation of substance (**4**) with acetic anhydride in pyridine under the usual conditions led to a hexaacetate, $C_{34}H_{38}O_{18}$, mp 136-138°C (from methanol), $[\alpha]_D^{22}$ — 85.0 ± 2° (*c* 0.52; methanol).

^{13}C NMR ($CDCl_3$): 94.3 (C-1), 141.3 (C-3), 102.2 (C-4), 35.4 (C-5), 80.3 (C-6), 58.9 (C-7), 62.4 (C-8), 41.8 (C-9), 61.3 (C-10), 96.8 (C-1′), 70.9 (C-2′), 72.9 (C-3′), 68.4 (C-4′), 72.6 (C-5′), 62.8 (C-6′), 127.1 (C-1″), 132.0 (C-2″), 122.3 (C-3″), 155.7 (C-4″), 122.3 (C-5″), 132.0 (C-6″), 165.9 (C=O), 169.0-170.9 (C=O), 20.5 (CH_3Ac).

Substance (**5**), $C_{15}H_{22}O_{10}$, mp. 205-207°C (from methanol), $[\alpha]_D^{22}$ — 100.0 ± 2° (*c* 0.70; ethanol), $[MH]^+$ 363.

From their physicochemical constants and spectral characteristics, substance (**4**) and its hexaacetyl derivative were identified as catalposide and its acetate [2, 5, 6], and substance (**5**) as catalpol [7-9].

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