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TRITERPENE GLYCOSIDES OF *Dipsacus azureus*

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Triterpene glycosides – dipsacosides A_4 and B [1, 2] and dipsacobioside [3] – and a triterpenoid – hederagonic acid [4] – have been isolated previously from the roots of the teasel *Dipsacus azureus*.

In the present communication we give the results of a study of a butanol-soluble fraction of a methanolic extract of the roots of this plant. With this aim, a solution of the methanolic extract in water was treated with *n*-butanol (1/3 of the volume of the solution). The treatment was carried out exhaustively, and the process was monitored by TLC in the chloroform–methanol–water (40:17:1) system. The combined butanolic extract was evaporated to dryness, and not less than 14 compounds were detected in the residue by TLC in the chloroform–methanol–water (40:7.5:1) and (40:17:1) systems.

In the chromatographic separation of the butanolic extract on a column of KSK silica gel using the solvent systems chloroform–methanol (25:1), (15:1), and (9:1) successively, compounds (**1**)-(**3**), respectively, were obtained.

Compound (**1**), $C_{30}H_{48}O_4$, mp 330-332°C, $[\alpha]_D^{23}$ +81.5° (*c* 0.97; Py) was identified as hederagenin by its physicochemical constants and the results of a comparison with an authentic sample by TLC in the chloroform–methanol (25:1 and 9:1) systems [5].

Compound (**2**), $C_{35}H_{60}O_6$, mp 289-292°C (from MeOH), $[\alpha]_D^{23}$ –44° (*c* 0.98; Py) coincided in its IR, mass and PMR spectra and the results of acid hydrolysis with β-sitosterol β-*D*-glucopyranoside [6].

Compound (**3**), $C_{35}H_{56}O_8$, mp 277-281°C (from MeOH), $[\alpha]_D^{20}$ +59° (*c* 1.02; $CHCl_3$–MeOH (1:1)).

IR spectrum (KBr, ν, cm^{-1}): 3400 (OH), 2920 (CH_2), 1700 (COOH).

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}): 604 (M^+, 8.4), 472 (9.8), 248 (100), 203 (95).

PMR spectrum (100 Mhz, Py-d_5, δ, ppm, J, Hz, 0 – HMDS): 0.77 (3H, s, CH_3) 0.83, 0.88 (each 6H, s, 4 × CH_3), 1.12 (3H, s, CH_3), 3.13 (1H, br.d, J = 12, H-18), 4.87 (1H, d, J = 6, H-1 of arabinose), 5.35 (1H, br. s, H-12).

On acid hydrolysis (5% H_2SO_4, 75°C, 5 h), compound (**3**) split into hederagenin (aglycon) and arabinose, identified by PC in the *n*-butanol–pyridine–water (6:4:3) system in the presence of a marker. The saponification of glycoside (**3**) with 10% KOH (80°C, 4 h) caused no changes. The physicochemical constants and the spectral characteristics given above showed that the glycoside isolated was hederagenin 3-O-α-*L*-arabinopyranoside. This glycoside has been isolated previously from the plants *Leontice eversmanii* [7], *Koelreuteria paniculata* [5], *Fatsia japonica* [8], and others.

When chloroform–methanol–water (40:12:1) was used as eluent in the same column, we isolated the more polar glycoside (**4**), $C_{47}H_{76}O_{17}$, mp 188-190°C.

IR spectrum (Kbr, ν, cm^{-1}): 3402 (OH), 2945 (CH_2), 1730 (ester bond), 1638, 1460.

PMR spectrum (100 MHz, Py-d_5, δ, ppm, J, Hz, 0 – HMDS): 0.75 (6CH, s, 2 × CH_3), 0.81, 0.88, 0.95, 1.03 (each 3H, s, 4 × CH_3), 1.48 (3H, d, J= 5.0, CH_3 of rhamnose), 3.05 (1H, br. d, J = 10.0, H-18), 4.87 (1H, d, J = 6.5, H_1 of arabinose), 5.3 (1H, br. s, H-12), 6.08 (1H, br. s, H-1 of rhamnose), 6.20 (1H, d, J = 7.0, H-1 of glucose).

The acid hydrolysis of glycoside (**4**) yielded hederagenin. In the hydrolysate, glucose, rhamnose, and arabinose were detected by PC. Saponification of the glycoside with 10% NaOH formed a progenin, $C_{41}H_{66}O_{12}$, mp 235-237°C (from MeOH), $[\alpha]_D^{20*}$ (*c* 1.1; alcohol).

IR spectrum (KBr, ν, cm^{-1}): 3425, 2944, 1705 (COOH), 1453.

*No value given – Translator.

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PMR spectrum (100 MHz, Py-d_5, δ, ppm, J, Hz, 0 – HMDS): 0.80, 0.87 (each 6H, s, 4 × CH_3), 0.91, 1.08 (each 3H, s, 2 × CH_3), 1.45 (3H, d, J = 6, CH_3 of rhamnose), 4.25 (1H, d, J = 6.0, H-1 of arabinose), 5.3 (1H, br. s, H-12), 6.05 (1H, br.s, H-1 of rhamnose).

The carbohydrate component split off from the COOH group of the aglycon proved to be glucose. On acid hydrolysis, as carbohydrates the progenin yielded rhamnose and arabinose.

The characteristics obtained for the progenin agreed with those for dipsacoside A_4 [2]. The IR and PMR spectra of the two compounds were identical.

It follows from the facts given above that compound (**4**) had the structure of the glucopyranosyl ester of hederagenin 3-O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside. A glycoside of this composition has been isolated previously from the plant *Lonicera japonica* [9].

This is the first time that any of the compounds described have been isolated from *Dipsacus azureus*.

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