REFERENCES

1. V. Ya. Chirva, P. L. Cheban, and G. V. Lazur'evskii, KhPS [Chemistry of Natural Compounds], 4, 140, 1968.
2. P. L. Cheban, V. Ua. Chirva, and G. V. Lazur'evskii, KhPS [Chemistry of Natural Compounds], 5, 129, 1969.

4 February 1969 Institute of Chemistry AS Moldavian SSR

UDC 615.711.5:615.45

THE ISOLATION OF OLITORISIDE FROM THE SEEDS OF CORCHORUS OLITORIUS

M. T. Turakhodzhaev, M.-R. I. Shamsutdinov, and T. T. Shakirov

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 4, pp. 327–328, 1969

The cardiac glycoside olitoriside, which is used in medicine [1], is isolated from the seeds of Corchorus olitorius [2]. We have developed a new method for the isolation of olitoriside. The seeds of Corchorus olitorius, after comminution and defatting by extraction with gasoline, were extracted by steeping in 96% ethanol. The extract was concentrated and was treated twice with acetone to precipitate the sugars.

The acetonic solution was concentrated and was treated with ether to eliminate the residues of fatty and resinous substances. The extractive substances insoluble in ether were precipitated in the form of a viscous dark mass which was separated off and washed with ether.

The viscous mass was dissolved in water and common salt was added, and, to eliminate the monosides and inert substances, the solution was washed with chloroform several times. Then the olitoriside was exhaustively extracted from the aqueous solution with small portions of a mixture of chloroform and isopropanol (1 : 1 by volume). The chloroform-isopropanol extract was concentrated to small volume and filtered through a layer of alumina, and then an equal volume of water was added and the mixture was left in a thermostatted vessel at 36–37° C. As the isopropanol evaporated off, crystals deposited; these were separated off and washed with water.

The crystals obtained were dissolved in boiling acetone, and on cooling the olitoriside deposited.

The crystals of olitoriside that had deposited were recrystallized from aqueous ethanol (1 : 1 by volume). The yield of olitoriside was 0.13% of the weight of the raw material.

REFERENCES

1. M. D. Mashkovskii, in: Medicinal Agents [in Russian], Moscow, part 1, p. 349, 1967.
2. N. K. Abubakirov, V. A. Maslennikova, and M. B. Gorovits, DAN UzSSR, no. 6, 23, 1957.

25 February 1969 Institute of the Chemistry of Plant Substances AS UzSSR

UDC 615.43+615.32

APIGENIN AND ITS GLYCOSIDES FROM GRATIOLA OFFICINALIS

V. I. Litvinenko, L. I. Borodin, and N. V. Kurinnaya

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 4, pp. 328–329, 1969

By one- and two dimensional paper chromatography we have found in the herb drug hedgehyssop, collected in the phase of mass flowering, about ten substances of flavonoid nature. The flavonoids were separated on Kapron, and the individual compounds GF-1, GF-2, GF-3, and GF-4 were isolated.

Apigenin (GF-1), $C_{15}H_{10}O_5$, has mp 346–348° C (aqueous methanol), R_f in 15% acetic acid (system 1) 0.04, and in butan-1-ol–acetic acid–water (4 : 1 : 2) (system 2) 0.92; λ_{max} in ethanol 336, 270 mμ (log ε 4.40, 4.38); λ_{max}

(ethanol + NaAc) 380, 274 mμ; λ_{max} (ethanol + EtONa) 400, 275 mμ; λ_{max} (ethanol + $Zr(NO_3)_2$) 390, 355, 305, 285 mμ; no depression of the melting point with an authentic sample of apigenin.

Cosmosiin (GF-2), $C_{21}H_{20}O_{10}$, mp 254–256° C (aqueous methanol), $[\alpha]_D^{20}$ −80° (c 0.1; methanol); R_f 0.25 (1), 0.66 (2); λ_{max} (in ethanol) 331, 268 mμ (log ε 4.30, 4.25); λ_{max} (ethanol + NaAc) 331, 268 mμ; λ_{max} (ethanol + NaAc) 331, 268 mμ; λ_{max} (ethanol + $Zr(NO_3)_2$) 375, 360, 305, 275 mμ. On acid hydrolysis it was split into apigenin and D-glucose. The percentage content of the aglycone was 59.6% (calculated 62.2%).

One of the forms of saponaretin (GF-3), $C_{21}H_{10}O_{10}$, mp 221–123° C (aqueous methanol), $[\alpha]_D^{20}$ + 26.7° (c 0.135; DMFA); R_f 0.48 (1), 0.74 (2); λ_{max} (in ethanol) 332, 274 mμ (log ε 4.26, 4.28); λ_{max} (ethanol + NaAC) 385, 280 mμ; λ_{max} (ethanol + EtONa) 408, 284 mμ; λ_{max} (ethanol + $Zr(NO_3)_2$) 387, 355, 307, 285 mμ. It did not undergo enzymatic hydrolysis, and on acid hydrolysis (5% HCl in 50% ethanol at 90° C for 2 hr) it formed its isomer GF-4, which is probably one of the forms of vitexin, $C_{21}H_{10}O_{10}$, mp 264–266° C, $[\alpha]_D^{20}$ −15.0° (c 0.1; methanol); R_f 0.20 (1), 0.60 (2); λ_{max} (in ethanol), 332, 272 mμ (log ε 4.30, 4.28); λ_{max} (ethanol + NaAc) 388, 382 mμ; λ_{max} (ethanol + EtONa) 400, 280 mμ; λ_{max} (ethanol + $Zr(NO_3)_2$) 393, 353, 310, 285 mμ. The acid hydrolysis of this substance led to the formation of the initial saponeratin.

On acid hydrolysis according to Kiliani [1], these substances formed apigenin, D-glucose, and a small amount of D-arabinose. The proportions of the aglycone in the glycosides under consideration were 58.9 and 61.5% (calculated 62.2%).

Thus, the herb drug hedgehyssop has been shown to contain apigenin, cosmosiin, and one each of the forms of saponaretin and vitexin.

REFERENCE

1. H. Kiliani, Ber., 63, 866, 1930.

19 February 1969

Khar'kov Chemical and Pharmaceutical Scientific-Research Institute

Zaporozh'e Medicinal Institute

UDC 547.918:582.938

PREGNANE GLYCOSIDES OF CYNANCHUM SIBIRICUM

V. A. Maslennikova, R. N. Tursunova, and N. K. Abubakirov

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 4, pp. 329–330, 1969

From a chloroform extract of the roots of Cynanchum sibiricum Willd. (family Asclepiadaceae) we have obtained a mixture of glycosides consisting of five substances according to thin-layer chromatography on silica gel in the benzene–chloroform–methanol (5 : 5 : 2) system. They all give a positive xanthydrol reaction [1] and, consequently, are glycosides of 2-deoxysugars.

After acid hydrolysis of the mixture of glycosides with 0.1 N H_2SO_4, three chromatographically individual compounds were isolated. Chromatography of the aglycones was carried out on a fixed layer of silica gel in the ethyl acetate–hexane (1 : 1) and benzene–acetone (2 : 1) systems and on paper in the chloroform–ethylene glycol system.

The least polar of the aglycones isolated, which we have called sibirigenin, has the composition $C_{28}H_{42}O_6$ (elementary analysis) mol. wt. 474 (mass spectrometry), mp 208–209° C, $[\alpha]_D^{20}$ +54° (c 0.05, ethanol). The acetate of the substance was obtained with mp 134–135° C, $[\alpha]_D^{16}$ +58.6 ± 2° (c 1.64, methanol).

On being heated with a 5% ethanolic solution of caustic potash, sibirigenin split off an unsaturated acid with the composition $C_7H_{12}O_2$. Desacylsibirigenin, $C_{21}H_{32}O_5$, mp 246–248° C, $[\alpha]_D^{20}$ −8.4° (c 0.024; ethanol), forms an oxime and an acetate with mp 225–227° C, $[\alpha]_D^{20}$ −36.5 ± 2° (c 1.60; methanol). From these results and also from the IR, UV, mass, and NMR spectra, sibirigenin can be classed among the plant pregnanes [2,3].

The second aglycone was obtained in the amorphous state. The genin gave a color reaction with 80% H_2SO_4—red-orange, changing with time to violet— and also one with $SbCl_3$—pink, changing to gray-blue. UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 283 mμ, lg ε 3.86. Absorption maxima of the IR spectrum in KBr: 3450, 1670, 1630, 1600, and 1580 cm^{-1}. On alkaline hydrolysis, the aglycone yielded cinnamic acid $C_9H_8O_2$ and a desacylgenin $C_{21}H_{34}O_6$ (elementary analysis) with