(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.

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19 February 1969

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UDC 547.918:582.938

PREGNANE GLYCOSIDES OF *CYNANCHUM SIBIRICUM*

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

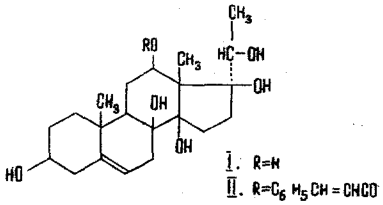
From a chloroform extract of the roots of *Cynanchum sibiricum* Willd. (family Asclepiadaceae) we have obtained a mixture of glycosides consisting of five substances according to thin-layer chromatography on silica gel in the benzene–chloroform–methanol (5 : 5 : 2) system. They all give a positive xanthydrol 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 mp 250° C and $[\alpha]_D^{20}$ +71.5 ± 2° (c 1.15; methanol). From its properties and its IR and mass spectra, the desacylgenin is similar to sarcostin (I) [4]. A direct comparison of it with an authentic sample of the genin kindly provided by H. Mutsuhashi (Hokkaido, Japan), confirmed their identity.



I. R=H

II. R=$C_6H_5CH=CHCO$

Consequently, the genin, sarcostin cinnamate, has the composition $C_{30}H_{40}O_7$ and must be identical with penupogenin [5] the structure of which, taking into account the corrections due to Jaeggi et al. [4], must correspond to formula II.

The most polar compound which we have called sibicoside gives a positive xanthydrol reaction, i.e., it is a glycoside. The acid hydrolysis of sibicoside yielded D-digitoxose, a disaccharide of undetermined structure, and desacylsibirigenin.

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20 March 1969

Institute of the Chemistry of Plant Substances AS UzSSR

UDC 547.944.1

THE STRUCTURE OF ERVINCEINE

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 4, pp. 330–331, 1969

By separating the petroleum ether fraction of the total alkaloids from the epigeal part of Vinca erecta Rgl. et Schmalh. [1] we have isolated a base with mp 99–100° C (methanol), $[\alpha]_D^{12}$ –448° (c 0.9; chloroform), $C_{22}H_{28}N_2O_3$, M^+ 368 (mass spectroscopy), R_f 0.66 in TLC on silica gel [petroleum ether–ether (2 : 1)], hydriodide mp 214–215° C (decomp., methanol).

IR spectrum: NH (3335 cm^{-1}), ester carbonyl group conjugated with a double bond (1672 cm^{-1}) and a 1, 2, 4-trisubstituted benzene ring (805, 863 cm^{-1}).

UV spectrum: λ_{max} (ethanol) 248, 328 mμ (log ε 4.12, 4.26), which is characteristic for α-methyleneindoline alkaloids. The NMR spectrum of ervinceine with signals at δ 8.88 (NH, singlet), 6.14–6.91 (aromatic protons, 3H), 3.69 (singlet, $COOCH_3$), 3.66 (singlet, OCH_3), and 0.53 (triplet, $\overset{|}{\underset{|}{-C-}}C_2H_5$).

The reduction of ervinceine with zinc in methanolic sulfuric acid gave dihydroervinceine, $C_{22}H_{30}N_2O_3$, mp 118–119° C (methanol), $[\alpha]_D^{20}$ +3.3 (c 0.9; chloroform). Its IR spectrum; λ_{max} (ethanol) 249, 305 mμ (log ε 3.78, 3.73) is characteristic of indoline bases. Its mass spectrum has the molecular peak M^+ 370 (16%) and also peaks of ions with m/e 339 $(M-OCH_3)^+$ 10%, 284 $(M-86)^+$ 26% and 124 (100%).

The mass spectrum of ervinceine M + 368 (48%), 125 (16%), 124 (100%) is similar to that of 16-methoxyvincadifformine M + 368 (22%), 125 (10%), 124 (100%) [1], but differs in the intensity of the peaks. Since, according to the IR spectrum, ervinceine is a 1, 2, 4-trisubstituted benzene derivative, the methoxy group may be present in position