

<u>Glycoside</u>	<u>Aglycone</u>	<u>Monosaccharides</u>
Funkioside A	Diosgenin	Glucose
B	(25R)furost-5-en-	Glucose
C	3 β ,22 α ,25-triol Diosgenin	Glucose, galactose
D	Diosgenin	Glucose, galactose
E	Diosgenin	Glucose, galactose, rhamnose
F	Diosgenin	Glucose, galactose, xylose
G	Diosgenin	Glucose, galactose, rhamnose, xylose
H	Diosgenin	Glucose, galactose, rhamnose, xylose
I	(25R)furost-5-en- 3 β ,22 α ,26-triol	Glucose, galactose, rhamnose, xylose

fied as trillin, which has been described previously [7]. When funkioside B was treated with β -glucosidase at room temperature for 12 h, diosgenin was obtained. Since only diosgenin was obtained after the treatment with β -glucosidase, it may be concluded that funkioside B contains only one molecule of glucose in position 26 of the aglycone. Thus funkioside B is 26-(β -D-glucopyranosyloxy)-(25R)furost-5-ene-3 β ,22 α , 25-triol (mp 258-266°C), $[\alpha]_D^{20}$ -135° (c 0.75; methanol).

The study of the structure of the other funkiosides is continuing.

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ISOLATION OF 3,26-BISGLYCOSIDE OF YAMOGENIN FROM

Trigonella foenum-graecum

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The seeds of *T. foenum-graecum* (fenugreek trigonella) contain glycosides of steroid genins [1, 2]. On enzymatic hydrolysis of the total glycosides, diosgenin is obtained [2].

We defatted the comminuted seeds of the plant mentioned with chloroform and then extracted them with methanol. According to TLC on silica gel in the CHCl_3 - CH_3OH -water (61:32:7) system, the extract contained seven glycosides with R_f 0.59, 0.52, 0.46, 0.34, 0.29, 0.18, and 0.14, respectively, these being derivatives of furostan, as was confirmed by a positive reaction with the Ehrlich reagent [3].

By chromatography on silica gel we isolated glycosides B and C with R_f 0.52 and 0.46, respectively. Glycoside B (I) is formed in the process of isolation from glycoside C (II) and is its 22-methyl ether; we have called it trigonelloside C. Furostan glycosides are usually isolated in mixtures with their 22-methyl ethers [4]. By boiling it in methanol, we converted trigonelloside C into (I), $\text{C}_{52}\text{H}_{86}\text{O}_{22} \cdot \text{H}_2\text{O}$, mp 188-190°C (CH_3OH), $[\alpha]_D^{20}$ -92° (c 1;

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CH₃OH). IR spectrum, cm⁻¹: 817, 843, 900, 1640, and 3420. The NMR spectrum of (I) (100 MHz, δ scale, deutero-pyridine, TMS) has singlets at (ppm) 0.82 (18-CH₃), 1.03 (19-CH₃), and 3.23 (22-OCH₃), doublets at 1.00 (J = 4 Hz, 27-CH₃), 1.16 (J = 6 Hz, 21-CH₃), 1.55 (J = 6 Hz, CH₃ of rhamnose attached to C₄ of glucose), 1.69 (J = 6 Hz, CH₃ of rhamnose attached to C₂ of glucose), and 4.77 (J = 7 Hz, the anomeric proton of glucose attached to C₂ of the genin), and multiplets at 2.73 (J = 14 Hz, 2 H at C₄ of the genin), 3.56 (J = 14 Hz, 2 H at C₂ of the genin), 4.87 (anomeric proton of glucose attached to C₃ of the genin), 5.3 (J = 9 Hz, H at C₆ of the genin), 5.73 (J = 4 Hz, anomeric proton of rhamnose attached to C₄ of glucose), 6.27 (J = 4 Hz, anomeric proton of rhamnose attached to C₂ of glucose), and 5.28 (J = 9 Hz, H at C₆). When (I) was treated with water and the aqueous solution was evaporated, we obtained the unexpected chromatographically pure trigonelloside C (II), mp 175-178°C, $[\alpha]_D^{20}$ -48° (c 1; H₂O), the structure of which was confirmed by IR and NMR spectra.

On hydrolysis with 2 NHCl, (I) gave a mixture of diosgenin and yamogenin, as was confirmed by the ratio of the intensities of the absorption bands at 920 and 900 cm⁻¹ in the IR spectrum [6] and by the features of the NMR spectrum (signals at 3.9 and 0.77 ppm) [7]. When (I) was subjected to hydrolysis by β -glycosidase, the glucose residue at C₂ was split out and a spirostan 3-glycoside (III) was formed which coincided in its R_f value with dioscin. Substance (III) has mp 290-294°C (CH₃OH) $[\alpha]_D^{20}$ -104° (c 0.5; CH₃OH). The NMR spectrum of (III) has singlets at (ppm) 0.83 (18-CH₃) and 1.00 (19-CH₃), doublets at 1.13 (J = 6 Hz, 21-CH₃), 1.58 (J = 6 Hz, methyl group of rhamnose attached to C₄ of glucose), and 1.73 (J = 6 Hz, methyl of rhamnose attached to C₂ of glucose), and multiplets at 0.70 (J = 8 Hz, 27-CH₃), 4.87 (anomeric proton of glucose attached to C₃ of the genin), and 5.78 (J = 4 Hz, anomeric proton of rhamnose attached to C₄ of glucose). The peracetate of (III) - (IV) - had mp 140-143°C (CH₃OH) $[\alpha]_D^{20}$ -76.9° (c 0.5; CH₃OH). According to its IR spectrum, (IV) and, therefore, also the native (III), belong to the 25S series [6] and they contain a very small amount, if any, of the 25R epimers. To distinguish it from dioscin, we have called the 25S glycoside (III) yamoscín.

When (I) was heated with 2 NH₂SO₄, the stepwise hydrolysis of the 3-glycosidic bond took place with the formation of 26-(β -D-glucopyranosyloxy)furost-5-ene-3 β ,22-diol (V), mp 195-200°C, $[\alpha]_D^{20}$ -80° (CHCl₃), 3,0-[O-L-rhamnopyranosyl-(1 \rightarrow 4)-D-glucopyranosyl]-(V), mp 200-206°C (decomp.), 3-0-[O-L-rhamnosyl-(1 \rightarrow 2)-D-glucopyranosyl]-(V), mp 175°C (decomp.), and 3-0-(D-glucopyranosyl)-(V), mp 180-189°C (decomp.), the structures of which agreed with their NMR spectra.

From the results of complete and partial acid hydrolysis, and also enzymatic hydrolysis, in trigonelloside C a carbohydrate chain consisting of glucose and two rhamnose residues is attached at C₃ and a glucose residue at C₂.

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