

22-METHYL ETHER OF PROTODIOSCIN FROM THE SEEDS
OF *Trigonella coerulea*

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Continuing an investigation of blue-white trigonella, we have isolated from a methanolic extract of the seeds 26-(β -D-glucopyranosyloxy)-22 α -methoxy-3 β -[α -L-rhamnopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosyloxy]-(25R)-furost-5-ene (I); mp 186-189°C (MeOH). According to the literature: mp 187-191°C [2]. The structure of (I) was found by the results of complete and partial hydrolyses.

The enzymatic hydrolysis of (I) with β -glucosidase led to dioscin (II), mp 295-298°C (MeOH), identical with an authentic sample in chromatographic behavior and IR and NMR spectra. D-Glucose was identified in the hydrolyzate.

The stepwise hydrolysis of (I) (2 N H₂SO₄, boiling for 20 min) gave 26-O- β -D-glucopyranosylfurost-5-ene-3 β , 22 α , 26-triol (III), mp 200-208°C (according to the literature: mp 182°C (decomp.) [3]; 3-O- β -D-glucopyranosyl-(III), mp 199-208°C; 3-O-[α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosyl]-(III), mp 249-256°C (decomp.) (according to the literature: mp 261-271°C (decomp.) [5]; and 3-O-([α -L-rhamnopyranosyl-(1 \rightarrow 2)] [β -D-glucopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl)-(III), mp 238-246°C (decomp.) (according to the literature: mp 249-251°C [2]); and very small amounts of spirostan glycosides and diosgenin.

The structures of the carbohydrate chains of the products of stepwise hydrolysis were confirmed by NMR spectroscopy [3]. The configurations of the glycosidic centers were determined by means of Klyne's rule [4].

Acid hydrolysis (2 N HCl, 100°C, 2 h) gave diosgenin, m.p. 202-206°C (acetone), [α]_D-118°C (c 0.5; CHCl₃).

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