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GLYCOSIDES OF THE BULBS OF *Lilium regale*

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It is known [1] that the bulbs of *Lilium regale* W. contain acylated glycerol glycosides — regalosides A and B. In the present paper we report the presence in this material of a series of glycosides of steroid nature and give information on their isolation and proofs of their structures.

By TLC in an ethanolic extract of fresh bulbs of *Lilium regale* we have detected, together with regalosides, at least 15 steroid glycosides giving a positive reaction with the Sannié reagent [2] and called, in order of increasing polarity, lilioglycosides A-T.

By repeated column chromatography of the above extract it was possible to individualize compounds A, D, G, K, N, and R. The IR spectra of lilioglycosides A, D and G contained the absorption bands 900 > 920 cm^{-1}, characteristic for a spiroketal chain of the (25R) series, showing the spirostanol nature of these glycosides [3]. The more polar lilioglycosides were stained pink by the Ehrlich reagent, which is characteristic for furostanols [4], as also was a broad absorption band at 900 cm^{-1} in the IR spectra [5].

On analyzing the products of complete acid hydrolysis of each lilioglycoside, from its physicochemical constants we identified diosgenin as the aglycon (mp 207.5°C, $[\alpha]_D^{20}$ −128° (Py); lit.: mp 208°C, $[\alpha]_D^{20}$ −129° (Py) [6].

In view of the furostan nature of compounds K, N, and R, it may be assumed that their aglycon is (25R)-furost-5-en-3β,22α,26-triol.

TABLE 1. ^{13}C NMR Spectra of the Lilioglycosides (C_5D_5N) [13]

C	Lilioglycoside			C	Lilioglycoside		
	A	D	G		A	D	G
Aglycon				Glc-1			
1	37.6	37.6	37.6	1	109.8	101.0	100.0
2	30.2	30.2	30.2	2	75.4	79.8	78.7
3	78.5	78.5	78.5	3	78.4	78.0	83.9
4	39.3	39.3	38.8	4	71.8	72.3	69.5
5	140.9	140.9	149.9	5	78.1	78.0	77.8
6	121.9	121.9	121.9	6	62.9	62.9	62.5
7	32.4	32.4	32.4	Rha-1			
8	31.8	31.8	31.8	1	–	101.0	100.0
9	50.3	50.3	50.3	2	–	72.5	72.8
10	37.2	37.2	37.2	3	–	77.9	72.5
11	21.2	21.2	21.2	4	–	74.2	74.1
12	39.9	39.9	39.9	5	–	69.2	69.7
13	40.5	40.5	40.5	6	–	18.8	18.7
14	56.7	56.7	56.7	Glc-2			
15	31.9	31.9	31.8	1	–	–	104.6
16	81.8	81.8	81.2	2	–	–	75.0
17	62.9	62.9	62.9	3	–	–	77.1
18	16.4	16.4	16.4	4	–	–	72.8
19	19.6	19.5	19.5	5	–	–	77.8
20	42.0	42.0	42.0	6	–	–	18.7
21	15.1	15.1	15.1				
22	109.9	109.9	109.9				
23	32.3	32.3	31.8				
24	29.3	29.3	29.3				
25	30.6	30.6	30.6				
26	66.9	66.9	66.9				
27	17.4	17.4	17.4				

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The structures of the spirostanol lilioglycosides were established with the aid of ^{13}C NMR spectroscopy (Table 1). The structures of the furostanol lilioglycosides were determined by making use of complete and stepwise hydrolysis and by methylation followed by the methanolysis of the permethylates. Taking into account the results of physicochemical analysis, it was shown with the aid of IR and UV spectroscopy and GLC, together with melting points and specific rotations that the liliogycosides corresponded to the following structures:

lilioglycoside A: (25R)-spirost-5-en-3β-ol 3-O-β-*D*-glucopyranoside (mp 275.5°C, $[\alpha]_D^{20}$ −103° (dioxane) [7]);

lilioglycoside D: (25R)-spirost-5-en-3β-ol 3-O-[O-*L*-rhamnopyranosyl-(1→2)-*D*-glucopyranoside] (mp 237-238°C, $[\alpha]_D^{20}$ −99° (Py) [8]);

lilioglycoside G: (25R)-spirost-5-en-3β-ol 3-O-{[O-*L*-rhamnopyranosyl-(1→2)][O-*D*-glucopyranosyl-(1→3)]-β-*D*-glucopyranoside} (mp 290-292°C, $[\alpha]_D^{20}$ −88° (Py) [9]);

lilioglycoside K: (25R)-furost-5-en-3β,22α,26-triol 3,26-di-O-β-*D*-glucopyranoside (mp 258-266°C, $[\alpha]_D^{20}$ −134° (MeOH) [10];

lilioglycoside N: (25R)-furost-5-en-3β,22α,26-triol 3-O-[O-*L*-rhamnopyranosyl-(1→2)-*D*-glucopyranoside] 26-O-β-*D*-glucopyranoside (mp 193-196°C, $[\alpha]_D^{20}$ −70.4° (Py) [11];

lilioglycoside R: (25R)-furost-5-en-3β,22α,26-triol 3-O-{[O-*L*-rhamnopyranosyl-(1→2)][O-*D*-glucopyranosyl-(1→3)]-β-*D*-glucopyranoside} 26-O-β-*D*-glucopyranoside (mp 193-196°C, $[\alpha]_D^{20}$ −70.4° (Py) [12]).

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