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^{13}C NMR ANALYSIS OF FUROSTAN GLYCOSIDES FROM Ruscus ponticus

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We have previously [1] reported spirostanol compounds isolated from Ruscus ponticus Wor. Together with them we isolated two furostanol glycosides the physicochemical characteristics and chromatographic behavior of which agreed with those of authentic samples of deglucoruscoside (I) and its 22-O-methyl ether (II) which Bombardelli et al. isolated from Ruscus aculeatus L. [2].

We have now for the first time recorded the ^{13}C NMR spectra of glycosides (I), (II) and have made a complete assignment of them (Table 1). The spectra were taken on a Bruker WP-250 instrument at a resonance frequency of 63 MHz for carbon nuclei with C_5D_5N as solvent and TMS as internal standard, at a temperature of 30°C.

In the assignment of the ^{13}C NMR spectra of the furostanol glycoside isolated, as the initial basis we used results [3] for the 22-O-methyl ether of alliofuroside A, which has an aglycon of similar structure and an analogous carbohydrate moiety. As compared with the latter, in the region of resonance of sp^2-hybridized carbon nuclei two more signals were observed – δ 147.17 (C-25) and δ 110.42 (C-27) for deglucoruscoside, and δ 146.39 (C-25) and δ 110.66 (C-27) for its 22-O-methyl ether.

The glycosylation effect at C-1 (in neoruscogenin C-1 resonates at δ 78.1 [4]) amounted to +5.6 ppm for (I) and +5.9 ppm for (II), which agrees well with the figures given in [3]. The total effect of cleavage of the C_{22}–O bond and glycosylation of neoruscogenin at the C-26 atom (in neoruscogenin the C-26 nucleus resonates at δ 65.1 ppm [4]) amounted to +7.2 and +7.3 ppm for glycosides (I) and (II), respectively, substantially differing from the analogous effect in alliofuroside A (I) (+10.0 ppm) [3]. This fact can be explained only

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TABLE 1. Chemical Shifts of the ^{13}C Nuclei of Deglucoruscoside (I) and Its 22-O-Methyl Ether (II), δ, ppm

Carbon atom	Compound		Carbon atom	Compound	
	I	II		I	II
1	83,71	83,97	L-Rhamnose		
2	37,88	37,51	1	101,50	101,74
3	68,19	68,44	2	72,39	72,66
4	43,69	43,93	3	72,07	72,66
5	139,50	139,73	4	74,17	74,40
6	124,71	124,94	5	69,34	69,57
7	33,11	33,33	6	18,82	19,08
8	31,96	31,89	L-Arabinose		
9	50,50	50,69	1	100,34	100,61
10	42,91	43,14	2	75,30	75,48
11	24,00	24,21	3	75,64	75,91
12	40,42	40,65	4	69,90	70,18
13	40,66	40,75	5	67,12	67,40
14	56,73	56,95	D-Glucose		
15	32,56	32,54	1	103,73	103,90
16	81,22	81,71	2	75,06	75,28
17	63,75	64,34	3	78,22	78,50
18	16,74	16,87	4	71,71	71,94
19	14,97	15,23	5	78,42	78,68
20	40,66	40,89	6	62,76	63,04
21	16,17	16,27			
22	110,82	112,70			
23	37,27	32,19			
24	28,28	28,32			
25	147,17	146,39			
26	72,39	72,25			
27	110,42	110,66			
22-OMe		47,57			

qualitatively – by the presence of a $C_{25}=C_{27}$ double bond, since the influence of the dehydrogenation of the $C_{25}-C_{27}$ bond is difficult to subject to quantitative calculation because of its irregularity.

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