ANOMALOUS EFFECT OF THE ACTION OF THE EHRLICH REAGENT ON STEROID GLYCOSIDES

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The presence of steroid glycosides of the spirostan and furostan series in the butcher's broom Ruscus ponticus growing in Georgia has been established [1]. The spirostan glycosides isolated from this plant (deglucodehamnoruscin, deglucoruscin, and ruscin) give a positive reaction with the Ehrlich reagent. This contradicts the opinion that has grown up that this reagent is characteristic for furostanols and gives a pink coloration with them [2], while it does not react with spirostanols. The mechanism of the reaction is explained by the presence of a center of the covalent binding of the aldehyde group of the reagent with the C-23 atom of the side chain of a furostanol molecule [3].

To answer the question of whether the positive Ehrlich reaction with neoruscogenin glycosides is an exception or is in any way normal for individual groups of spirostanols, we have made a TLC analysis of the interaction of the spirostanol genins and glycosides available to us with the Ehrlich reagent.* After being sprayed with the reagent, the plates were kept in a thermostat at 110-120°C for 3-5 min. The results are presented in Tables 1 and 2. As can be seen from the tables, some spirostanols gave a positive test with the Ehrlich reagent. A further study of the mechanism of this anomalous effect by the isolation and identification of the reaction products may define more closely the possible spectrum of action of the Ehrlich reagent on steroid glycosides.

*A 1% solution of p-dimethylaminobenzaldehyde in 4 N HCl.

TABLE 1. Action of the Ehrlich Reagent on Steroid Sapogenins

Sapogenin	Structure					Coloration	Literature
	C-25	C-5	OH	C=O	double bond		
Tigoenin	R	α	3β	—	—	—	4
Neotigogenin	S	α	3β	—	—	—	4
Smilagenin	R	β	3β	—	—	—	4
Sarsasapogenin	S	β	3β	—	—	—	5
Diosgenin	R	—	3β	—	5	—	6
Chlorogenin	R	α	3β,6α	—	—	—	7
β-Chlorogenin	R	α	3β,6β	—	—	—	8
Gitogenin	R	α	2α,3β	—	—	—	4
Rhodeasapogenin	S	β	1β,3β	—	—	+	9
Strictagenin	S	α	1β,3α[26]	—	5	+	10
Ruscogenin	R	—	1β,3β	—	5	+++	11
(S)-Ruscogenin	S	—	1β,3β	—	5	+++	12,19
Neoruscogenin	—	—	1β,3β	—	5.25[27]	+++	1
Yuccagenin	R	—	2α,3β	—	5	—	4,14
Digitogenin	R	α	2α,3β,15β	—	—	—	13
Alliogenin	R	α(OH)	2α,3β,6β	—	—	—	14
Neoagigenin	S	α	2α,3β,6β	—	—	++	14,15
Agigenin	R	α	2α,3β,6β	—	—	++	15
Neoagigenin benzoate	R	α	2α,3β,6—$OCOC_6H_5$	—	—	++	14
Karatavigenin C	S	—	2α,3β,24S	—	5	++	16
Hecogenin	R	α	3β	12	—	—	4
Neogigenone	R	α	2α,3β		—	++	14
Kammogenin	R	—	2α,3β	12	5	++	4

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TABLE 2. Action of the Ehrlich Reagent on Steroid Glycosides of the Spirostanol Series

Glycoside	Structure	Coloration	Literature
Deltonin	α-*L*-Rha →(2)β-*D*-Glc →(3)(diosgenin); β-*D*-Glc (1→4) β-*D*-Glc	—	6
Yuccaaleoside A	β-*D*-Glc →(2)-*D*-Gal →(3)(smilagenin)	—	17
Yuccaaleoside B	α-*L*-Rha →(4)β-*D*-Glc →(3)β-*D*-Glc →(4)-*D*-Gal →(3)(tigogenin); β-*D*-Glc (1→2) β-*D*-Glc	—	18
Yuccaaleoside C	α-*L*-Rha →(4)β-Glc →(3)β-*D*-Glc →(4)β-*D*-Gal →(3)(tigogenin); β-*D*-Glc (1→2) β-*D*-Glc; β-*D*-Glc →(3) β-*D*-Glc	—	18
Alliospiroside A	α-*L*-Rha →(2)α-*L*-Ara →(1)((25S)-ruscogenin)	+++	12
Alliospiroside B	β-*D*-Gal →(2)α-*L*-Rha →(1)((25S)-ruscogenin)	+++	19
Deglucodesrhamnoruscin	α-*L*-Ara →(1)(neoruscogenin)	+++	1
Deglucoruscin	α-*L*-Rha →(2)α-*L*-Ara →(1)(neoruscogenin)	+++	1
Ruscin	β-*D*-Glc →(3)α-*L*-Rha →(2)α-*L*-Ara →(1)(neoruscogenin)	+++	1
Digitonin	β-*D*-Glc →(3)β-*D*-Gal →(2)β-*D*-Glc →(4)β-*D*-Gal →(3)(digitogenin); β-*D*-Xyl (1→3) β-*D*-Glc	—	20
Eruboside B	β-*D*-Glc →(2)β-*D*-Glc →(4)β-*D*-Gal →(3)(β-chlorogenin); β-*D*-Glc (1→3) β-*D*-Glc	—	21
Karatavioside E	β-*D*-Glc →(2)β-*D*-Glc →(4)β-*D*-Gal →(3)(karatavigenin C); β-*D*-Xyl (1→3) β-*D*-Glc	++	22
Karatavioside F	β-*D*-Glc →(2)β-*D*-Glc →(4)-*D*-Gal →(3)(karatavigenin C) ~(24) β-*D*-Glc; β-*D*-Xyl (1→3) β-*D*-Glc	++	22
Karatavioside A	β-*D*-Glc →(2)β-*D*-Glc →(4)β-*D*-Gal →(3)(yuccagenin); β-*D*-Xyl (1→3) β-*D*-Glc	—	23

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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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