STERIODS OF THE SPIROSTAN AND FUROSTAN SERIES FROM PLANTS OF THE GENUS Allium

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In this review steroids of the spirostan and furostan series produced by the genus Allium are considered. A description is given of 26 genins (25 of the spirostan and one of the 22,25-epoxyfurostan series) and of 40 glycosides (29 of the spirostan series, 10 of the furostan series and one of the 22,25-epoxyfurostan series).

Steroids of the spirostan and furostan series (sapogenins and glycosides) are attracting the attention of research workers not only as an economically important raw material convertible into various steroid hormonal drugs [1-3], but, recently, also as biologically active material having independent value [4].

Plants of the genus Allium family (Liliaceae) are promising from among the domestic flora in connection with the search for saponin-bearing species. This genus is fairly widely distributed over the terrestrial globe: In the world flora more than 1000 species are known [5] of which 228 grow in our country [6].

The present paper gives information on the steroid sapogenins and their glycosides produced by various species of the genus Allium.

Of the various analytical expedients permitting the presence of steroid saponins (sapogenins) in a plant raw material can be judged, the most reliable is the analysis of plant extracts with the aid of TLC [2, 7]. The detecting reagents used are sulfuric acid, iodine vapor, antimony trichloride, a mixture of chlorosulfonic and acetic acids, and anisaldehyde, but the most frequently used is vanillin/phosphoric acid [8], which colors spirostan genins and their glycosides yellow, and glycosides of the furostan series green. The Ehrlich reagent [9] is also used to detect glycosides of the furostan series; with it, the compounds sought acquire a bright red coloration. However, it must be borne in mind that the presence of oxygen-containing substituents in rings E and F changes the color of the products of color reactions unpredictably [2].

At the present time, instrumental methods of analysis are permitting the identification of genins and glycosides with the use of micro amounts of the samples being analyzed [10].

The isolation of genins and glycosides from plant raw material, although it consists of a number of standard operations (extraction with ethanol or methanol, chromatographic separation on silica gel or alumina, etc.), nevertheless naturally has its own characteristic features determined by the specific nature of the raw material being treated with each concrete case [1, 2, 4, 7].

The main products of biosynthesis are, most probably, the glycosides, which are detected in the epigeal organs, the flower heads, and the seeds of plants of the genus Allium. The leaves and flower-bearing shoots, in their majority, contain only trace amounts of glycosides and sapogenins. To isolate the sapogenins, the purified plant extracts are subjected to hydrolysis, or the whole of the plant material is subjected to acid treatment [11, 12], which, in our opinion, is less rational. According to the authors' observations, one may expect a greater accumulation of free sapogenins in the epigeal parts and of glycosides in the reproductive organs of alliums.

Methods of demonstrating the structures of the compounds under discussion have been considered in detail in the literature [1, 2, 4, 7]. We may note only that the main emphasis is

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TABLE 1. Plants of the Genus Allium Producing Steroids of the Spirostan and Furostan Series (genins and glycosides)

Name of plant	Genins	Glycosides
1. A. affine Ldb.	1,4,13	
2. A. albanum A. Crossh.	13	
3. A. albidum Fisch.	1,2,4	
4. A. angulosum L.	1	
5. A. cepa L.	1,5,9	27, 28 34, 35, 40, 41, 52, 56*
6. A. cernuum Roth.	1	
7. A. erubescens C. Koch.	16	37
8. A. fuscoviolaceum L.	1	
9. A. giganteum Rgl.	1,3,16,17,18,19,20,22	42, 44
10. A. gramineum C. Koch.	1,16,17	37
11. A. grayi Rgl.	13,14,15	
12. A. karataviense Rgl.	1, 3, 8, 20, 24, 25	32, 33, 38, 39, 44, 46, 51
13. A. leucanthum C. Koch.	1	
14. A. norcissiflorum Wells.	1	26, 47, 48, 49, 50
15. A. nutans L.	1	
16. A. porrum L.		42
17. A. rubellum M. B.	1, 13	
18. A. stipitatum Rgl.	1, 3, 10, 12, 20, 25a*	62*
19. A. suvorovii Rgl.		
20. A. tricoccum Rgl.	13	
21. A. turcomanicum Rgl.	3, 11, 18, 20, 21, 23	43, 45, 53
22. A. vineale L.	1, 6, 7	29,30,31,36,54,55*57*—59*
23. A. waldsteinii Don.	1, 16	
24. A. wallichii Kunth.	1, 13	
25. A. ampeloprasum L.		60*, 61*, 63*, 64*
26. A. sativum L.		65*

placed on instrumental methods of analysis, and here particularly wide use is made of IR spectroscopy [13-16], mass spectrometry [17-20], and ^1H and ^{13}C NMR spectroscopies [21-25].

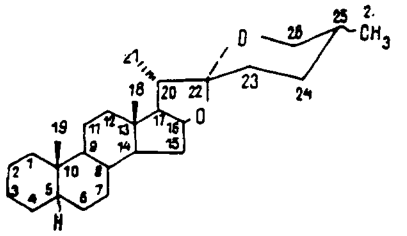
Earlier screening studies in the search for saponin-bearing plants, although based on such comparatively uninformative tests as the determination of hemolytic and foam-forming indices, nevertheless permitted the revelation of the wide distribution of saponin-containing species among representatives of the genus Allium. Thus, Chetverikova et al. [11] analyzed 32 species of Allium and detected the presence of saponins in 12 of them. Similar information is given in [26, 27]. Of the 38 Allium species known in Georgia, 29 have been investigated by the TLC method. In this case, as well, a high percentage of saponin-bearing plants was confirmed; they included 22 species [28].

The presence of sapogenins in alliums was first shown by Marker et al. as early as 1943 [29]. They isolated tigogenin (13) from Allium tricoccum. At the present time, from the 26 Allium species that have been investigated chemically, 26 genins have been isolated (Tables 1 and 2). The most widespread genin is diosgenin (1), which has been found in 18 Allium species. Great attention is being devoted to the search for a raw material rich in diosgenin even now in connection with its use as the starting material for the synthesis of steroid hormonal drugs [3]. In this connection, A. fuscoviolaceum [30] and A. nutans [31-34], which contain 2.1 and 2.3% of diosgenin, respectively, are of interest. The methods of photocolorimetry [35], GLC [36], and others [2] are used for the quantitative determination of diosgenin in plant material. It has been noted that the amount of diosgenin in the inflorescences of alliums is far higher than in the hypogeal organs [32, 34, 37].

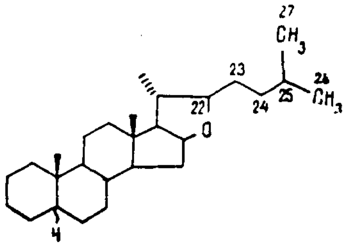
For the case of A. nutans it has been shown that the preliminary autofermentation of the inflorescences and hypogeal organs of the plant, which favors the conversion of furostan glycosides into spirostan glycosides, leads to an increase in the yield of diosgenin after acid hydrolysis by 20-70% [34].

The presence of genins having two and more hydroxy groups is characteristic for the bulk of the alliums (Table 2); some of them predominate in the quantitative respect. Thus, β-chlorogenin (16) has proved to be the main genin of A. waldsteinii growing in Georgia [38]. Yuccagenin (3) has been shown to be present in all the Central Asian species of Allium studied — A. giganteum, A. karataviense, A. turcomanicum, A. stipitatum, and A. suvorovii. All the species of Allium mentioned have been found to contain products of the further oxidation of yuccagenin having three [karatavigenin C (8), anzurogenin B (10), agigenin (17), and gantogenin (19)], four [anzurogenin A (12), alliogenin (20), and neoalliogenin (21)], and five

TABLE 2. Steroid Sapogenins Isolated from Plants of the Genus <u>Allium</u>



1) Spirostan



2) Furostan

Composition and trivial name	Rational name	mp, °C	$[\alpha]_D^a$ deg	Source, plant organ, literature
1	2	3	4	5
$C_{27}H_{42}O_3$				
1. Diosgenin	(25R)-Spirost-5-en-3β-ol	208	-129^b	1^i (inflorescences) [37]; 3 [54]; 4 (inflorescences, hypogeal part) [55]; 5 (seeds) [43]; 6 (inflorescences, hypogeal part) [31]; 8 (epigeal part) [30]; 9 (bulb skins) [56]; 10 (inflorescences) [57]; 12 (bulbs) [58]; 13 (inflorescences) [37]; 14 (bulbs) [59]; 15 (inflorescences, hypogeal part) [31]; 17 (inflorescences) [37]; 18, 19 (fruit) [60]; 22 (bulbs) [25]; 23 (epigeal part) [38]; 24 (bulbs) [61]
$C_{27}H_{42}O_4$				
2. Hecogenin	(25R)-3β-Hydroxy-5α-spirostan-12-one	268	+10	3 [62]
3. Yuccagenin	(25R)-Spirost-5-ene-2α,3β-diol	248	−122	9 (bulb skins) [55]; 12 (bulbs) [58]; 18, 19 (fruit) [60]; 21 (epigeal part) [63]
4. Ruscogenin	(25R)-Spirost-5-ene-1β,3β-diol	205-210	−127	1 (inflorescences) [37]; 3 [64]
5. (25S)-Ruscogenin	(25S)-Spirost-5-ene-1β,3β-diol	190-192	−105.6	5 (fruit) [40]
6. Isonuatigenin	(25S)-Spirost-5-ene-3β,25-diol	215-218	−140	22 (bulbs) [25]
7. Nuatigenin	(20S,22S,25S)-22,25-Epoxyfurost-5-ene-3β,26-diol	210-214	−93	22 (bulbs) [25]

TABLE 2 (continued)

1	2	3	4	5
$C_{27}H_{42}O_5$				
8. Karatavigenin C	(24S,25S)-Spirost-5-ene-2α,3b,24-triol	309-311	−95.9	12 (inflorescences) [65]
9. Cepagenin	(24S,25R)-Spirost-5-ene-1β,3β,24-triol	268-270	−82.6	5 (fruit) [42]
10. Anzurogenin B	(25R)-2α,5α-Epoxyspirostan-3β,6β-diol	210-212	−32.9	18, 19 (fruit) [66]
11. Neoagigenone	(25S)-2α,3β-Dihydroxy-5α-spirostan-6-one	236-238	−97.5[b]	21 (epigeal part) [63]
$C_{27}H_{42}O_6$				
12. Anzurogenin A	(25R)-2α,3β,5-Trihydroxy-5β-spirostan-6-one	235-236	−81.8	18, 19 (fruit) [60]
$C_{27}H_{44}O_3$				
13. Tigogenin	(25R)-5α-Spirostan-3β-ol	205-208	−67[c]	1 (inflorescences) [37]; 2, 17 (inflorescences) [37, 67]; 11 (whole plant) [68]; 20 [29]; 24 (bulbs) [61]
14. Smilagenin	(25R)-5β-Spirostan-3β-ol	187-188	−66	11 (whole plant) [68]
$C_{27}H_{44}O_4$				
15. Gitogenin	(25R)-5α-Spirostan-2α,3β-diol	264-267	−78	11 (whole plant) [68]
16. β-Chlorogenin	(25R)-5β-Spirostan-3β,6β-diol	249-251	−78	7 (inflorescences) [69]; 9 (inflorescences, bulb skins) [55, 70]; 10 (inflorescences) [57]; 23 (epigeal part) [38]
$C_{27}H_{44}O_5$				
17. Agigenin	(25R)-5α-Spirostan-2α,3β, 6β-triol	265-267	−17.2[b]	9 (bulb skins, inflorescences) [55, 70]; 10 (inflorescences) [57]
18. Neoagigenin	(25S)-5α-Spirostan-2α,3β,6β-triol	269-271	−76[b]	9 (bulb skins) [70, 71]; 21 (epigeal part, bulb skins) [63, 72]
19. Gantogenin	(25R)-5α-Spirostan-2α,3β,6α-triol	265-268	−49.1[b]	9 (bulb skins) [73]
$C_{27}H_{44}O_6$				
20. Alliogenin	(25R)-5α-Spirostan-2α,3β,5,6β-tetraol	321-325	−7.14	9 (bulbs) [74]; 12 (bulbs) [58]; 18, 19 (fruit) [60]; 21 (bulb skins) [63]

TABLE 2 (continued)

1	2	3	4	5
21. Neoalliogenin	(25S)-5α-Spirostan-2α,3β,5,6β-tetraol	315-317	−61.9	21 (bulb skins) [72]
$C_{27}H_{48}O_2$ 22. Luvigenin	(25R)-4-Methyl-19-norspirost-1,3,5(10)-triene	181-182	−31.9	9 (bulb skins) [55]
$C_{34}H_{48}O_6$ 23. Neoagenin-6-O-benzoate	(25S)-5α-Spirostan-2α,3β,6β-triol 6-O-benzoate	138-140	-63.7^b	21 (epigeal part) [63]
$C_{34}H_{48}O_7$ 24. Karatavigenin B	(25R)-5α-Spirostan-2α,3β,5,6β-tetraol 2-O-benzoate	301-303	−84.7	12 (bulbs) [75]
25. Karatavigenin A	(25R)-5α-Spirostan-2α,3β,5,6β-tetraol 3-O-benzoate	277-281	−96.8	12 (bulbs) [58]
$C_{27}H_{42}O_7$ 25a.* Anzurogenin C	(24S,25S)-2α,3β,-5,24-Tetrahydroxy-5β-spirostan-6-one	255-257	−143	18, 19 (fruit) [88]

For notes to the Table, see after Table 3.

[anzurogenin C (25a*)] oxygen functions. It must be mentioned that another dihydroxysapogenin [(25S)-ruscogenin (5)] and the product of its hydroxylation at C-24 [cepagenin (9)] have been isolated from *Allium cepa* cultivated in Central Asia.

We may also mention that esters of genins of the spirostan series (23-25) have been isolated only from Central Asian alliums. It is also striking, in our view, that wild-growing Central Asian alliums have proved a rich source of new sapogenins: 14 previously undescribed substances (8-12, 17-21, 23-25, and 25a*) have been isolated from them.

Of the 25 genins listed in Table 2, 14 (1, 3, 5-9, 16-18, 20, 23, 24, and 25a*) are known in the form of glycosides (Table 3).

Plants of the genus *Allium* have yielded 29 glycosides of the spirostan series and 11 furostan glycosides. The carbohydrate chains of these compounds include D-glucose, D-xylose, D-galactose, L-rhamnose, and L-arabinose.

Characteristic for the majority of spirostan glycosides is the attachment of the sugar chains to the hydroxyl at C-3 of the aglycon (see Table 3). In addition to this, glycosides of (25S)-ruscogenin [alliospirosides A (34) and B (35)] and of cepagenin [alliospirosides C (40) and D (41)] bearing carbohydrate components at C-1 of the aglycon have been isolated from *Allium cepa*. A spirostan glycoside — karatavioside F (39), the carbohydrate moiety of which is represented by two chains, at C-3 and C-24 — has been isolated from *A. karataviense*.

A component of many natural glycosides is lycotetraose. This sugar chain consists of a tetrasaccharide [39]. Lycotetraoside includes D-xylose, D-glucose, and D-galactose residues in a ratio of 1:2:1 and has the structure

TABLE 3. Steroid Glycosides of the Spirostan and Furostan Series Isolated from Plants of the Genus Allium

Name, composition	Structure of the carbohydrate component	mp, °C	$[\alpha]_D$, deg	Source, plant organ, literature
1	2	3	4	5
	Glycosides of the spirostan series[d] Diosgenin glycosides			
26. Trillin $C_{33}H_{52}O_8$	$\beta\text{-}D\text{-Glc}\xrightarrow{3}(\text{Ag})$	275	—103[c]	14 (bulbs) [59]
27. Ceposide A $C_{38}H_{60}O_{11}$	$\alpha\text{-}L\text{-Rha}\xrightarrow{2}\alpha\text{-}L\text{-Ara}\xrightarrow{3}(\text{Ag})$	h	h	5 (seeds) [43]
28. Ceposide B $C_{44}H_{70}O_{16}$	$\beta\text{-}D\text{-Gal}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{2}\alpha\text{-}L\text{-Ara}\xrightarrow{3}(\text{Ag})$	h	h	5 (seeds) [43]
29. Ophiopogonin C $C_{39}H_{62}O_{12}$	$\alpha\text{-}L\text{-Rha}\xrightarrow{2}\beta\text{-}D\text{-Glc}\xrightarrow{3}(\text{Ag})$	238— 240	—99	22 (bulbs) [25]
30. Deltonin $C_{45}H_{72}O_{17}$	$\alpha\text{-}L\text{-Rha}\xrightarrow{2}\underset{\substack{\uparrow 4\\ \beta\text{-}D\text{-Glc}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{3}(\text{Ag})$	290— 292	—98,7	22 (bulbs) [25]
31. g $C_{45}H_{72}O_{17}$	$\beta\text{-}D\text{-Glc}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{4}\beta\text{-}D\text{-Glc}\xrightarrow{3}(\text{Ag})$		h	22 (bulbs) [25]
	Yuccagenin glycosides			
32. Karatavioside A $C_{50}H_{80}O_{23}$	$\beta\text{-}D\text{-Glc}\xrightarrow{2}\underset{\substack{\uparrow 3\\ \beta\text{-}D\text{-Xyl}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}(\text{Ag})$	283— 285	—72,9[e]	12 (inflorescences) [76]
33. Karatavioside B $C_{56}H_{88}O_{27}$	$\text{HOOC—CH}_2\text{—}\overset{\text{OH}}{\overset{\vert}{\text{C}}}(\text{CH}_3)\text{—CH}_2\text{—}\overset{\text{O}}{\overset{\Vert}{\text{C}}}\xrightarrow{4}\beta\text{-}D\text{-Xyl}\xrightarrow{3}\underset{\substack{\uparrow 2\\ \beta\text{-}D\text{-Glc}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}(\text{Ag})$	224— 227	—75[f]	12 (inflorescences) [85]

TABLE 3 (continued)

1	2	3	4	5
	(25S)-Ruscogenin glycosides			
34. Alliospiroside A $C_{38}H_{60}O_{12}$	α-*L*-Rha $\xrightarrow{2}$ α-*L*-Ara $\xrightarrow{1}$ (Ag)	186— 189	—101,8	5 (collective fruit) [40]
35. Alliospiroside B $C_{39}H_{62}O_{13}$	α-*L*-Rha $\xrightarrow{2}$ β-*D*-Gal $\xrightarrow{1}$ (Ag)	200— 202	—110,9	5 (collective fruit) [41]
	Isonuatigenin glycoside			
36. g $C_{39}H_{62}O_{13}$	α-*L*-Rha $\xrightarrow{2}$ β-*D*-Glc $\xrightarrow{3}$ (Ag)	h	h	22 (bulbs) [25]
	β -Chlorogenin glycoside			
37. Eruboside B $C_{51}H_{84}O_{24}$	β-*D*-Glc $\xrightarrow{2}$ β-*D*-Glc $\xrightarrow{4}$ β-*D*-Gal $\xrightarrow{3}$ (Ag) ↑3 (on the second Glc) β-*D*-Glc	274— 280	—71,8^{e}	7 (inflorescences) [69]; 10 (inflorescences) [57]
	Karatavigenin C glycosides			
38. Karatavioside E $C_{50}H_{80}O_{24}$	β-*D*-Xyl $\xrightarrow{3}$ β-*D*-Glc $\xrightarrow{4}$ β-*D*-Gal $\xrightarrow{3}$ (Ag) ↑2 β-*D*-Glc	271— 275	—82,5	12 (inflorescences) [77]
39. Karatavioside F $C_{56}H_{90}O_{29}$	β-*D*-Xyl $\xrightarrow{3}$ β-*D*-Glc $\xrightarrow{4}$ β-*D*-Gal $\xrightarrow{3}$ (Ag) ↑2 ↑24 β-*D*-Glc β-*D*-Glc	252— 254	—73,2	12 (inflorescences) [77]
	Cepagenin glycosides			
40. Alliospiroside C $C_{38}H_{60}O_{13}$	α-*L*-Rha $\xrightarrow{2}$ α-*L*-Ara $\xrightarrow{1}$ (Ag)	223— 225	—105,7	5 (collective fruit) [42]

TABLE 3 (continued)

1	2	3	4	5
41. Alliospiroside D $C_{39}H_{62}O_{14}$	$\alpha\text{-}L\text{-Rha}\xrightarrow{2}\beta\text{-}D\text{-Gal}\xrightarrow{1}(\text{Ag})$	242— 213	—89,9	5 (collective fruit) [42]
	Agigenin glycoside			
42. Aginoside $C_{50}H_{82}O_{24}$	$\beta\text{-}D\text{-Glc}\xrightarrow{2}\underset{\substack{\uparrow 3\\ \beta\text{-}D\text{-Xyl}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}(\text{Ag})$	272— 276	—66,7^e	9 (bulb skins) [78]; 16 (inflorescences) [45]
	Neoagigenin glycoside			
43. Turoside A $C_{50}H_{82}O_{24}$	$\beta\text{-}D\text{-Glc}\xrightarrow{2}\underset{\substack{\uparrow 3\\ \beta\text{-}D\text{-Xyl}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}(\text{Ag})$	279 — 284	—60,9^e	21 (bulbs) [79]
	Alliogenin glycoside			
44. Alliogenin glucopyranoside $C_{33}H_{64}O_{11}$	$\beta\text{-}D\text{-Glc}\xrightarrow{3}(\text{Ag})$	263 — 265	—76,2	9 (bulbs) [74]; 12 (bulbs) [58]
	Neoagigenin 6-0-benzoate glycoside			
45. Turoside A 6-0-benzoate $C_{57}H_{86}O_{25}$	$\beta\text{-}D\text{-Glc}\xrightarrow{2}\underset{\substack{\uparrow 3\\ \beta\text{-}D\text{-Xyl}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}\underset{\substack{\uparrow\\ O=C-C_6H_5}}{(\text{Ag})}$	242 — 245	—108,7^e	21 (bulbs) [80]
	Karatavigenin B glycoside			
46. Karatavigenin B glucopyranoside $C_{40}H_{68}O_{12}$	$\beta\text{-}D\text{-Glc}\xrightarrow{3}(\text{Ag})$	294— 296	—98,1	12 (bulbs) [75]
	Glycosides of the furostan series^d (25R)-Furost-5-ene-3 β,22R,26-triol glycosides			
47. Alliumoside B $C_{51}H_{84}O_{24}$	$\beta\text{-}D\text{-Glc}\xrightarrow{3}\beta\text{-}D\text{-Glc}\xrightarrow{6}\beta\text{-}D\text{-Glc}\xrightarrow{3}(\text{Ag})\xleftarrow{26}\beta\text{-}D\text{-Glc}$	270— 272	—70^c	14 (bulbs) [59]

TABLE 3 (continued)

1	2	3	4	5
48. Alliumoside C $C_{63}H_{104}O_{31}$	$\alpha\text{-}L\text{-Rha}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{6}\beta\text{-}D\text{-Gal}\xrightarrow{6}\beta\text{-}D\text{-Glc}\xrightarrow{3}(\text{Ag})\xleftarrow{26}\beta\text{-}D\text{-Glc}$	290— 291	-66^{c}	14 (bulbs) [81]
49. Alliumoside D $C_{63}H_{114}O_{32}$	$\alpha\text{-}L\text{-Rha}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{6}\beta\text{-}D\text{-Glc}\xrightarrow{2}\underset{\substack{\uparrow 3\\ \beta\text{-}D\text{-Glc}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{3}(\text{Ag})\xleftarrow{26}\beta\text{-}D\text{-Glc}$	268— 269	-88^{c}	14 (bulbs) [82]
50. Alliumoside E $C_{69}H_{11}O_{37}$	$\beta\text{-}D\text{-Glc}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{6}\beta\text{-}D\text{-Glc}\xrightarrow{2}\underset{\substack{\uparrow 3\\ \beta\text{-}D\text{-Glc}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{3}(\text{Ag})\xleftarrow{26}\beta\text{-}D\text{-Glc}$	286 — 288	-33^{c}	14 (bulbs) [82]
	(25R)-Furost-5-ene-2α,3β, 22R, 26-tetraol glycoside			
51. Karatavioside C $C_{56}H_{92}O_{29}$	$\beta\text{-}D\text{-Glc}\xrightarrow{2}\underset{\substack{\uparrow 3\\ \beta\text{-}D\text{-Xyl}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}\underset{\substack{\uparrow 26\\ \beta\text{-}D\text{-Glc}}}{(\text{Ag})}$	241 - 245	—54,4	12 (inflorescences)[83]
	(25S)-Furost-5-ene-1β, 3β, 22R, 26-tetraol glycoside			
52. Alliofuroside A $C_{44}H_{72}O_{18}$	$\alpha\text{-}L\text{-Rha}\xrightarrow{2}\alpha\text{-}L\text{-Ara}\xrightarrow{1}(\text{Ag})\xleftarrow{26}\beta\text{-}D\text{-Glc}$	164— 166	—53,7	5 (collective fruit) [40]
	(25S), 5α-Furostan-2α,3β,6β,22R,26-pentaol glycoside			
53. Turoside C $C_{62}H_{104}O_{35}$	$\beta\text{-}D\text{-Glc}\xrightarrow{2}\beta\text{-}D\text{-Glc}\xrightarrow{2}\underset{\substack{\uparrow 3\\ \beta\text{-}D\text{-Xyl}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}(\text{Ag})\xleftarrow{26}\beta\text{-}D\text{-Glc}$	192— 196	$-69{,}5^{e}$	21 (bulbs) [84]
	Nuatigenin glycoside			
54. ^{g} $C_{39}H_{62}O_{13}$	$\alpha\text{-}L\text{-Rha}\xrightarrow{2}\beta\text{-}D\text{-Glc}\xrightarrow{3}(\text{Ag})$	h	h	22 (bulbs) [25]

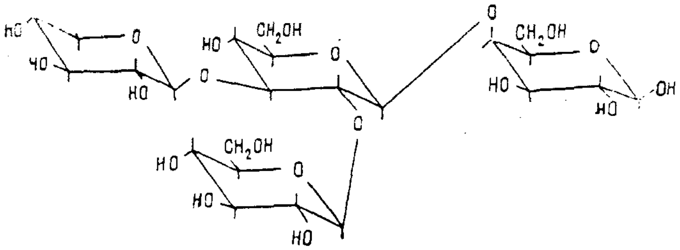
TABLE 3 (continued)

1	2	3	4	5
	Glycosides of the spirostan series Diosgenin glycosides			
55.* g $C_{51}H_{82}O_{21}$	$\beta\text{-}D\text{-Glc}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{4}\underset{\substack{\uparrow 2\\ \alpha\text{-}L\text{-Rha}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{3}(\text{Ag})$	h	−62,9	22 (whole plant) [86]
56.* Ceposide D $C_{56}H_{90}O_{26}$	$\beta\text{-}D\text{-Glc}\xrightarrow{3}\underset{\substack{\uparrow 2\\ \beta\text{-}D\text{-Glc}}}{\beta\text{-}D\text{-Gal}}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{2}\alpha\text{-}L\text{-Ara}\xrightarrow{3}(\text{Ag})$	197—198	$-68,1^{c}$	5 (seeds) [90]
57.* g $C_{57}H_{92}O_{27}$	$\beta\text{-}D\text{-Glc}\xrightarrow{6}\underset{\substack{\uparrow 4\\ \beta\text{-}D\text{-Glc}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\underset{\substack{\uparrow 2\\ \alpha\text{-}L\text{-Rha}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{3}(\text{Ag})$	h	−62,2	22 (whole plant)
58.* g $C_{57}H_{92}O_{26}$	$\beta\text{-}D\text{-Glc}\xrightarrow{6}\beta\text{-}D\text{-Glc}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{4}\underset{\substack{\uparrow 2\\ \alpha\text{-}L\text{-Rha}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{3}(\text{Ag})$	h	−65,0	22 (whole plant) [86]
59.* g $C_{63}H_{102}O_{31}$	$\beta\text{-}D\text{-Glc}\xrightarrow{6}\underset{\substack{\uparrow 4\\ \beta\text{-}D\text{-Glc}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\alpha\text{-}L\text{-Rha}\xrightarrow{4}\underset{\substack{\uparrow 2\\ \alpha\text{-}L\text{-Rha}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{3}(\text{Ag})$	h	−63,6	22 (whole plant) [86]
	agigenin glycosides			
60.* g $C_{39}H_{64}O_{15}$	$\beta\text{-}D\text{-Glc}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}(\text{Ag})$	249—251	−48,3	25 (bulbs) [87]
61.* Ampeloside Bs_1 $C_{45}H_{74}O_{20}$	$\beta\text{-}D\text{-Glc}\xrightarrow{3}\beta\text{-}D\text{-Glc}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}(\text{Ag})$	300	−52,5	25 (bulbs) [87]

TABLE 3 (continued)

1	2	3	4	5
	anzurogen C glycosides			
62. * Anzuroside $C_{33}H_{52}O_{12}$	$\beta\text{-}D\text{-Glc}\xrightarrow{24}(\text{Ag})$	242—244	−62,0	18, 19 (collective fruit) [88]
	Glycosides of the furostan series (25R)-5α-Furostan-2α,3β,22R,26-pentaol glycosides			
63.* Ampeloside B_{f_2} $C_{45}H_{76}O_{21}$	$\beta\text{-}D\text{-Glc}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}(\text{Ag})\xleftarrow{26}\beta\text{-}D\text{-Glc}$	h	−40,7	25 (bulbs) [87]
64.* Ampeloside B_{f_1} $C_{51}H_{86}O_{25}$	$\beta\text{-}D\text{-Glc}\xrightarrow{3}\beta\text{-}D\text{-Glc}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}\underset{\substack{\uparrow 26\\ \beta\text{-}D\text{-Glc}}}{(\text{Ag})}$	h	−25,1	25 (bulbs) [87]
	(25R)-5α -Furostan-3β,6β,22R,26-tetraol glycosides			
65.* g $C_{57}H_{96}O_{30}$	$\beta\text{-}D\text{-Glc}\xrightarrow{2}\underset{\substack{\uparrow 3\\ \beta\text{-}D\text{-Glc}}}{\beta\text{-}D\text{-Glc}}\xrightarrow{4}\beta\text{-}D\text{-Gal}\xrightarrow{3}(\text{Ag})\xleftarrow{26}\beta\text{-}D\text{-Glc}$	h	−36,5	26 (bulbs) [89]

Remarks. [a]If the solvent is not specially mentioned, the specific rotation was determined in pyridine; [b]in chloroform; [c]in methanol; [d]in all the glycosides given, the monosaccharides are present in the pyranose form; [e]in chloroform—methanol; [f]in dimethyl sulfoxide; [g]the authors do not give a trivial name; [h]the authors do not give physicochemical constants; [i]the figure denotes the serial number of the name of the plant shown in Table 1.
The symbol * indicates compounds the structures of which were published in 1988-1989.



Glycosides bearing lycotetraose as the carbohydrate component isolated from Allium plants have been detected only in Central Asian species of Allium: A. karataviense, A. turcomanicum, and A. giganteum (Table 3).

An interesting fact is the detection of glycosides in garden onion (A. cepa). Glycosides have been isolated from the collective fruit [40-42] and from the seeds [43]; the bulbs, the leaves, and flowering-bearing shoots do not contain saponins.

Two esterified glycosides have been isolated from plants of the genus Allium, their acyl group being represented by a benzoic acid residue and being localized in the genin part of the molecule. These are turoside A 6-O-benzoate (45), and karatavigenin B glucopyranoside (46). In addition, A. karataviense has yielded a glycoside bearing an acyl group (β-hydroxy-β-methylglutaric acid) in the carbohydrate moiety of the molecule – karatavioside B (33).

At the present time, more than 80 glycosides of the furostan series are known [2]. These compounds have an opened ring F and a D-glucose residue at C-26. An exception is afromontoside, side, isolated from flowers of Dracaena afromontana [44], in this glycoside, the sugar residue at C-26 is L-rhamnose. Among alliums, have been found seven glycosides of the furostan series and one of the 22,25-epoxyfurostan series, these being present both in the bulbs (A. narcissiflorum, A. turcomanicum, and A. vineale) and in the flower heads (A. karataviense, A. cepa).

The role of the steroid saponins in plants has not been definitely elucidated. It is assumed that, thanks to their fungicidal activity [1, 4], they fulfill protective functions, suppressing the vital activity of lower organisms. It has recently been shown that spirostan glycosides may be toxic for insects. The tetraoside aginoside (42) has proved to be highly toxic for the larvae of the leek moth (Acrolepia assectella), interfering with the cholesterol balance in this insect [45]. A stimulating action of certain steroid glycosides on the fertility of tomato [4] and maize [46] pollens has been reported.

There is information in the literature on the antitumoral [4, 47, 48], hypocholesteremic [4, 49, 50], contraceptive [51], and other types of biological activity of steroids of the spirostan and furostan series [4].

Alliums are widely used in folk medicine of various countries [52]. They are used in diseases of organs of the digestive system, and also as antiseptic, antipyretic, and wound-healing agents [53].

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TRITERPENOIDS OF PLANTS OF THE GENUS Abies HILL

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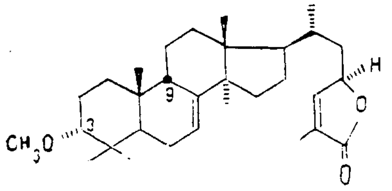
A review is given for the first time of the results of investigations of Soviet and foreign authors on the isolation of triterpenoids from the bark, needles, oleoresin, and seeds of various species of *Abies* (fir) and the determination of their structures and properties. Features of the PMR, mass, UV, and CD spectra of the compounds under consideration are discussed specially and information is given on their classification, distribution in firs, and biological activities.

In recent years, investigations connected with the study of the composition of the extractive substances of coniferous plants of the genus *Abies* Hill (fir) have been developed intensively. In a review published in 1972, Norin [1] reported that the bark of three species of fir contained "a triterpenoid of a unique type" – abieslactone (I). This compound has the well-known lanostane carbon skeleton, and its uniqueness consists in the β-configuration of the hydrogen atom at C-9 and the α-configuration of the oxygen-containing substituent at C-3. Triterpenoids have also been found in other conifers of the Pinaceae family, but they belong to different structural types (for example, serratane derivatives from the bark of species of *Pinus* [2] and *Picea* [3]) or are assigned to widely distributed triterpenols or 4,4-dimethylsterols [4-6]. The closest to abieslactone are the lanost-9(11)-enetriol (II) and the methoxydiol (III), which have been detected in the bark of *Pinus monticola* Dougl. [7].



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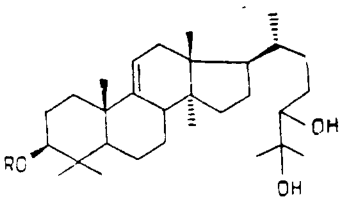

II R = H
III R = CH$_3$

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