TRITERPENE GLYCOSIDES OF PLANTS OF THE FAMILY CARYOPHYLLACEAE

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In this review, tables of 25 glycosides are given and the previously unknown structures of 11 of them are established. Characteristic features of the glycosides of the family Caryophyllaceae are considered. Methods are shown for isolating the glycosides and, using acanthophylloside B – a compound having carbohydrate chains of complex structure – as example, methods of determining their structures are demonstrated.

Plants of the family Caryophyllaceae include more than 80 genera and 2000 species and are widely distributed in all the climatic zones of the terrestrial globe. In the USSR, 40 genera including 630 species have been recorded, most of them occurring in the steppe, desert, and mountain regions, including the territory of Central Asia [1].

An important feature of a number of the plants of this family is their capacity on being shaken with water for producing a voluminous stable foam, which is connected with the presence of saponins in them. Saponins are present in all the organs of such a plant but accumulate mainly in the roots. Many plants of the family Caryophyllaceae have been used by the population from ancient times for obtaining saponins. There is every reason to consider that the first acquaintanceship of humanity with saponins was due to such plants as *Gypsophila paniculata* (baby's breath), *Acanthophyllum gypsophiloides* (Turkestan soap root), and *Saponaria officinalis* (bouncing Bet or soapwort). The possibility of using the foam-forming properties of saponin-bearing plants as soap substitutes (which is particularly important for the washing and bleaching of woolen and silken fabrics where ordinary alkaline soap is unsuitable), in the production of shampoos, sparkling beverages, and halvah, and in the enrichment of ores by the flotation method has been the reason for the increasing demand for this type of raw material.

As the result of harvesting for many years, stocks of wild saponin-bearing plants have been practically exhausted, and the necessity has risen for introducing them into cultivation and, consequently, so has the demand for the standardization of the raw material. In this respect, of course, chemical methods are the most objective.

The chemical study of saponin-bearing plants of the family Caryophyllaceae has been carried out with inadequate intensity. Only 27 species have been studied in more or less detail, and from these 36 triterpene glycosides have been isolated. The structures of 25 of the compounds have been established, and for another 11 only the nature of the aglycone and the monosaccharide composition have been shown. This can be explained both by the complexity of the study of saponins, the possibility of separating which into their individual components has appeared only in the last 20 years together with the development of chromatographic methods, and also by the additional difficulties arising just in the study of the glycosides of plants of the Caryophyllaceae family.

The time has obviously come to introduce clarity into the use of the terms "saponins" and "glycosides." As is well known, initially the saponins (sapo – Latin for soap) was the name given to all substances of plant origin with surface-active and, in particular, with pronounced foam-forming properties. After the chemical nature of the aglycone moiety had become known, they began to be subdivided into steroid saponins, triterpene saponins, and steroid glycoalkaloids. When it became clear that the saponins were based on glycosides, the terms "steroid" and "triterpene glycosides" appeared, and these are not infrequently used as synonyms for the corresponding saponins.

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TABLE 1. Glycosides of Established Structure from Plants of the Family Caryophyllaceae

Glycoside	Aglycone	Structure of the carbohydrate chains	Literature
		Acanthophyllum gypsophiloides Regel (roots)	
Acanthophylloside B $C_{86}H_{136}O_{48}$, mp 240–242°, $[\alpha]_D^{20}$+40.3° (water)	Gypsogenin, mp 286–286°, $[\alpha]_D^{20}$+96.8° (methanol)	C_3-*D*-GlcUA|4←1-*L*-Ara-4←1-*D*-Gal; 2←1-*D*-Gal C_{28}-*D*-Fuc|4←1-*L*-Rha-4←1-*D*-Xyl-3←1-*D*-Xyl-3; 2←1-*D*-Chi; ↑1 *D*-Xyl	24, 39–41
Acanthophylloside C $C_{92}H_{146}O_{53}$, mp 241–246°, $[\alpha]_D^{20}$–10.9° (water)	"	C_3-*D*-GlcUA|6←1-*D*-Glc; 4←1-*L*-Ara-4←1-*D*-Gal; 2←1-*D*-Gal C_{28}-*D*-Fuc|4←1-*L*-Rha-4←1-*D*-Xyl-3←1-*D*-Xyl-3; 2←1-*D*-Chi; ↑1 *D*-Xyl	24, 39–41
Acanthophylloside D $C_{86}H_{136}O_{49}$, mp 235–237°, $[\alpha]_D^{20}$–13° (water)	Quillaic acid, mp 258–265° $[\alpha]_D^{20}$+65° (methanol)	C_3-*D*-GlcUA|4←1-*L*-Ara-4←1-*D*-Gal; 2←1-*D*-Gal C_{28}-*D*-Fuc|4←1-*L*-Rha-4←1-*D*-Xyl-3←1-*D*-Xyl-3; ↓1 *D*-Xyl	21
		Acanthophyllum paniculatum Regel (roots)	
Paniculatoside C $C_{54}H_{86}O_{25}$, mp 220–230°, $[\alpha]_D^{20}$+5.3° (methanol)	Gypsogenic acid mp 350°, $[\alpha]_D^{20}$+97.6° (dioxane)	C_{28}-*D*-Glc|6←1-*D*-Glc-6←1-*D*-Glc; 4←1-*D*-Glc	16
		Agrostemma githago L. (seeds)	
Gigathoside $C_{54}H_{86}O_{21}$, mp 228°. $[\alpha]_D^{20}$–20.8° (pyridine)	Gypsogenin	C_3-*D*-Fuc-2←1-*L*-Rha|3←1-*D*-Glc; 4←1-*D*-Xyl	20
		Dianthus deltoides L. (whole plant)	
Dianthoside A $C_{36}H_{56}O_{10}$, mp 220–225°, $[\alpha]_D^{20}$+37° (pyridine)	Gypsogenic acid	C_3-*D*-Glc	14
Dianthoside B $C_{42}H_{66}O_{15}$, mp 229–234°, $[\alpha]_D^{20}$–18° (pyridine)	"	C_3-*D*-Glc-6←1-*D*-Glc	14,15
Dianthoside C $C_{81}H_{128}O_{44}$, mp 270–275°, $[\alpha]_D^{20}$+28° (pyridine)	Gypsogenin	C_3-*D*-GlcUA-3←1-*D*-Xyl-3←1-*D*-Gal C_{28}-*D*-Fuc|3←1-*L*-Rha-2←1-*L*-Ara; 4←1-*D*-Xyl|3←1-*D*-Gal; 2←1-*L*-Rha	14,15
		Gypsophila acutifolia Fisch. (roots)	
Acutifolioside $C_{88}H_{146}O_{53}$, mp 232–234°, $[\alpha]_D^{20}$+43° (water)	Gypsogenin	C_3-*D*-GlcUA|3←1-*L*-Ara; 4←1-*D*-Gal C_{28}-*D*-Fuc|3←1-*D*-Xyl|2←1-*D*-Gal; 3←1-*D*-Gal; 4←1-*D*-Glc-4←1-*D*-Gal; 4←1-*L*-Rha	42,43

(continued)

TABLE 1. (continued)

Glycoside	Aglycone	Structure of the carbohydrate chains	Literature
Gypsophila pacifica Kom. (roots) **Gypsophila paniculata L.** (roots)			
Gypsoside $C_{80}H_{128}O_{44}$, mp 200–212°, $[\alpha]_D^{20}$ +35° (water)	Gypsogenin	C_3-*D*-GlcUA | 4←1-*D*-Glc-4←1-*D*-Gal; 3←1-*L*-Ara C_{28}-*L*-Rha | 4←1-*D*-Fuc-3←1-*D*-Xyl; 2←1-*D*-Xyl-3←1-*D*-Xyl	29, 44–46
Gypsophila patrinii Ser. (roots)			
Philoside A $C_{82}H_{130}O_{45}$, mp 258–262°; $[\alpha]_D^{20}$ –4.9° (pyridine)	Gypsogenin	C_3-*D*-GlcUA | 2←1-*D*-Xyl; 3←1-*D*-Gal-2←1-*D*-Xyl; 4←1-*D*-Gal C_{28}-*D*-Fuc-2←1-*D*-Glc | 4←1-*L*-Rha; 6←1-*L*-Rha	47, 48
Philoside B $C_{80}H_{126}O_{44}$, mp 232–235°, $[\alpha]_D^{20}$ ±0° (aqueous pyridine)	"	C_3-*D*-GlcUA | 2←1-*D*-Xyl; 3←1-*D*-Gal-2←1-*D*-Xyl-2←1-*L*-Ara; 4←1-*D*-Gal C_{28}-*D*-Fuc-2←1-*L*-Ara-4←1-*L*-Rha	47–49
Gypsophila trichotoma Wend. (flowers, leaves)			
Trichoside A $C_{18}H_{74}O_{20}$, mp 310–312°, $[\alpha]_D^{20}$ +1.8° (aqueous methanol)	Gypsogenin	C_3-*D*-GlcUA-3←1-*D*-Glc C_{28}-*D*-Gal	50, 51
Trichoside B $C_{54}H_{84}O_{25}$, mp 228–230°, $[\alpha]_D^{20}$ +12.3° (aqueous metha	Gypsogenin	C_3-O-*D*-GlcUA-3←1-*D*-Glc C_{28}-*D*-Gal-4←1-*D*-Glc	50–52
Trichoside C $C_{60}H_{94}O_{28}$, mp 245–247° $[\alpha]_D^{20}$ +11.0° (aqueous methanol)	"	C_3-*D*-GlcUA-3←1-*D*-Glc C_{28}-*D*-Fuc-4←1-*L*-Rha-4←1-*D*-Gal	50, 53
Trichoside D $C_{81}H_{128}O_{45}$, mp 231–235°, $[\alpha]_D^{20}$ ± 0° (aqueous methanol)	"	C_3-*D*-GlcUA | 3←1-*D*-Xyl-4←1-*D*-Gal; 4←1-*L*-Ara C_{28}-*D*-Fuc | 2-*L*-Rha, *D*-Glc; 4-*D*-Gal, *D*-Xyl	32, 50
Herniaria glabra L. (whole plant)			
Glabroside B $C_{42}H_{66}O_{16}$, mp 240–245°, $[\alpha]_D^{20}$ +20° (pyridine)	Medicagenic acid, mp 349–350°, $[\alpha]_D^{20}$ +111° (ethanol	C_{28}-*D*-Glc-6←1-*D*-Glc	17
Glabroside C $C_{48}H_{76}O_{19}$, mp 254–257°. $[\alpha]_D^{20}$ +23° (pyridine)	"	C_{28}-*L*-Rha | 4←1-*D*-Glc; 2←1-*D*-Fuc	17
Saponaria officinalis L. (roots)			
Saponoside A* $C_{54}H_{84}O_{25}$, mp 132–134°. $[\alpha]_D^{20}$ +35° (methanol)	Gypsogenin	C_3-*D*-GlcUA C_{28}-*D*-Glc | 6←1-*D*-Glc; 3←1-*D*-Glc	54–56
Saponoside D $C_{87}H_{138}O_{49}$, mp 241–244°, $[\alpha]_D^{20}$ +40° (water)	Gypsogenin	C_3-*D*-GlcUA | 3←1-*D*-Xyl | 2←1-*D*-Gal; 4←1-*L*-Ara; 4←1-*L*-Rha C_{28}-*D*-Fuc | 3←1-*D*-Xyl | 2←1-*D*-Glc; 4←1-*D*-Gal; 4←1-*L*-Rha	30, 54, 57, 58

(continued)

TABLE 1. (continued)

Glycoside	Aglycone	Structure of the carbohydrate chains	Literature
Saponaroside $C_{35}H_{54}O_9$, mp 220–222°, $[\alpha]_D^{20}$ −9,0° (pyridine)	Gypsogenic acid	C_3-*D*-Xyl	12,13
Silene nutans L. (roots)			
Nutanoside $C_{82}H_{130}O_{46}$, mp 233–235° $[\alpha]_D^{20}$ +11° (aqueous pyridine)	Gypsogenin	C_3-*D*-GlcUA-3←1-*D*-Gal | 6←1-*L*-Ara, 4←1-*D*-Xyl; C_{28}-*L*-Rha | 4←1-*D*-Glc, 3←1-*D*-Gal-2←1-*D*-Fuc-4←1--*D*-Glc	59,60
Vaccaria segetalis (Neck.) Garcke (seeds)			
Vacsegoside B $C_{70}H_{110}O_{36}$, mp 250–251°, $[\alpha]_D^{25}$ +23,9° (water)	Gypsogenic acid	C_3-*D*-GlcUA | 6←1-*L*-Ara, 3←1-*D*-Gal, 2←1-*D*-Gal; C_{28}-*D*-Fuc-3←1-*L*-Rha-4←1-*D*-Xyl	31,61
Vacsegoside C $C_{87}H_{138}O_{49}$, mp 242–245°, $[\alpha]_D^{25}$ +8,2° (water)		C_3-*D*-GlcUA | 6←1-*L*-Ara, 4←1-*D*-Xyl, 3←1-*D*-Gal, 2←1-*D*-Gal; C_{28}-*D*-Fuc | 3←1-*L*-Rha-4←1-*D*-Xyl-3←1-*L*-Rha, 4←1-*D*-Glc	61,62
Viscaria viscosa Bernh. (roots)			
Viscoside $C_{75}H_{118}O_{40}$, mp 258–262°, $[\alpha]_D^{20}$ +3,9° (pyridine)	Gypsogenin	C_3-*D*-GlcUA | 4←1-*D*-Gal, 3←1-*D*-Gal-2←1-*D*-Xyl, 2←1-*D*-Xyl; C_{28}-*D*-Fuc-2←1-*L*-Rha-2←1-*D*-Glc	63,64

*Also isolated from the roots of *Dianthus inacothus* L.

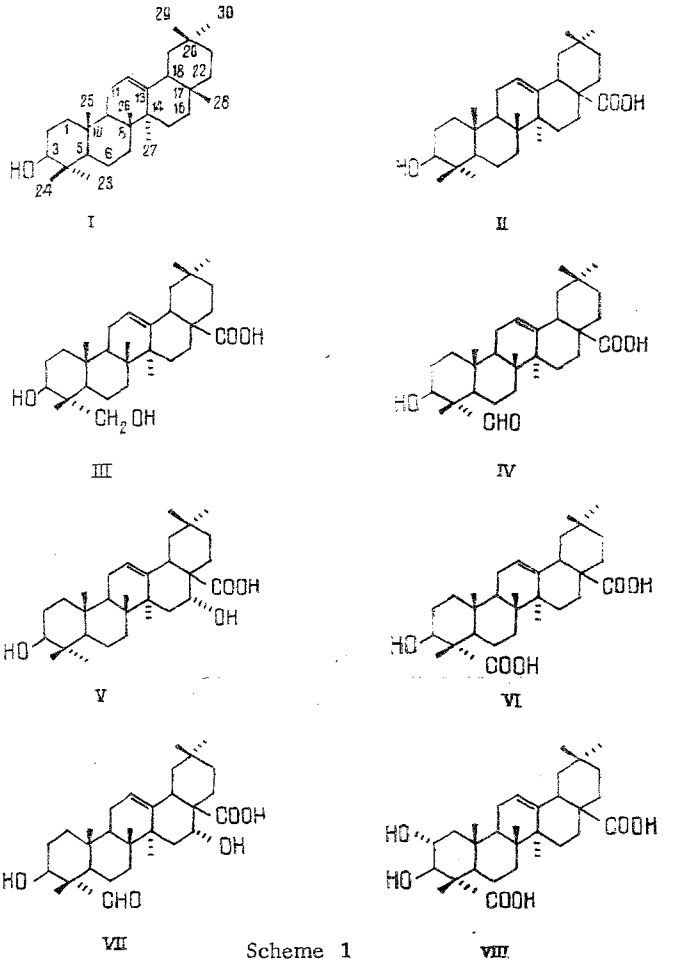
In our view, these are far from adequate concepts. On investigating the structures of individual triterpene glycosides, we elucidate only the primary structure — the nature of the aglycone, the composition and sequence of the monosaccharides, the degree of branching of the carbohydrate chains, the positions of their attachment to the aglycone, the dimensions of the oxide rings in the monosaccharides, and the anomerism of the glycosidic centers. But long and branched carbohydrate chains may also have a "secondary structure" — a particular three-dimensional configuration depending both on the structure of the glycoside itself and the spatial positions of the individual elements of the structure and on the presence of other compounds, primarily oligo- and polysaccharides, in the products isolated. If we also take into account the possibility of the presence of inorganic substances, the nature of the bond of which with the saponins has not yet been established, it is obvious that the term "saponins" can be used only for the total plant extracts, or sometimes, those having undergone rough purification or enrichment. The term "triterpene glycosides," on the other hand, should be used only for individual compounds with definite molecular weights. This type of delimitation is justified by the difference not only in the physicochemical propoerties but also in the biological activities of combined preparations and of individual glycosides.

For the same reason, obviously, it is undesirable to connect the names of individual glycosides with the term "saponin," as has been done, for example, for the soyasaponins, saikosaponins, etc.

The pharmacological action of the triterpene glycosides of the Caryophyllaceae has so far been studied only from case to case, superficially, and insufficiently broadly [2-8], although some interesting preparations have been proposed [3, 4]. At the same time, there is every reason to assume that with a deeper systematic study of their biological activity possibilities for their expanded medical use will also be found.

Aglycones and Monosaccharide Composition

The aglycones of all the triterpene glycosides of plants of the family Caryophyllaceae studied up to the present time are based on the β-amyrin skeleton (I, Scheme 1). The simplest aglycone of this series — oleanolic acid (II) — has been found only in the glycosides of *Spergularia arbuscula* [9]. In all the other plants studied, glycosides have been found with aglycones having a high degree of oxidation and with additional oxygen-containing functional groups (III-VII, Scheme 1).



Scheme 1

(I) — β-amyrin; (II) — oleanolic acid; (III) — hederagenin; (IV) — gypsogenin; (V) — echinocystic acid; (VI) — gypsogenic acid; (VII) — quillaic acid; (VIII) — medicagenic acid

The overwhelming majority of the glycosides contain gypsogenin (IV) as aglycone, and until recently this was considered as a characteristic feature of the glycosides of plants of this family. However, in recent years glycosides of hederagenin (III) [10], of echinocystic acid (V) [9], of gypsogenic acid (VI) [11-16], of quillaic acid (VII) [18-21], and of medicagenic acid (VIII) [17] have been found in the Caryophyllaceae. It is quite likely that when new plant material are studied still other aglycones will be detected.

TABLE 2. Glycosides of Undetermined Structure

Glycoside	Aglycone	Monosaccharides	Literature
Acanthophyllum adenophorum Freyn (roots)			
Glycoside with mp. 212—218°, $[\alpha]_D^{20}$ +19,7° (water—ethanol 1:1)	Gypsogenin	*D*-GlcUA, *D*-Glc, *D*-Gal, *D*-Fuc, *L*-Rha, *D*-Xyl, *L*-Ara	33
Arenaria graminifolia Schrad. (roots)			
Arenarioside A mp 255—260°, $[\alpha]_D^{20}$ —11° (pyridine)	Gypsogenin	*D*-GlcUA, *D*-Gal, 2*L*-Rha, 2*D*-Xyl	65
Arenarioside B mp 248—252°, $[\alpha]_D^{20}$ —26° (pyridine)	"	*D*-GlcUA, *D*-Glc, *D*-Gal, *L*-Rha, 2*D*-Xyl	65
Coronaria flos-cuculi L. (whole plant)			
Coronoside A $C_{63}H_{98}O_{30}$, mp 251—253°, $[\alpha]_D$ ±0° (pyridine)	Gypsogenin	*D*-GlcUA, 3D-Xyl, 2*L*-Rha	10
Coronoside B $C_{69}H_{112}O_{40}$, mp 255—258° $[\alpha]_D^{20}$ +18° (pyridine)	Hederagenin	2 *D*-Gal, 2*L*-Rha, 3*D*-Xyl	10
Dianthus superbus L.			
Glycosides A, B, C, and D	Gypsogenic acid	*D*-Glc	11
Gypsophila vicolor Freyn (roots)			
(aqueous ethanol) mp 218–222°, $[\alpha]_D^{20}$ +21° (aqueous ethanol)	Gypsogenin	*D*-GlcUA, *D*-Glc, *D*-Gal, *D*-Fuc, *L*-Rha, *D*-Xyl, *L*-Ara	34
Gypsophila capitata M. B. (roots)			
Glycoside A $C_{90}H_{136}O_{44}$, mp 199—206°, $[\alpha]_D$ +33,5° (50% aqueous methanol)	"	*D*-GlcUA, *D*-Gal, *D*-Glc, *D*-Fuc, *L*-Rha, *D*-Xyl, *L*-Ara	35
Silene latifolia (Mill.) Rendle et Britt (roots)			
Silenoside, mp 220—230°	"	*D*-GlcUA, 3*D*-Glc, *D*-Fuc, 2*L*-Rha, 3*D*-Xyl, *L*-Ara	66
Spergularia marginata DC			
Spergulasaponin mp 275.5-277°	Genin $C_{30}H_{48-50}O_5$	*D*-Glc, 4*D*-Ara, *L*-Rha, 2*D*-Xyl	67,68

(continued)

TABLE 2. (continued)

Glycosid	Aglycone	Monosaccharides	Literature
	Spergularia arbuscula		
Espergularin mp 235—238°, $[\alpha]_D^{21}$ −23,8° (ethanol)	Oleanolic acid, mp 306—308.5°, $[\alpha]_D^{9}$ +78,6° (chloroform) Echinocystic acid, mp 306—310°, $[\alpha]_D^{20}$ +40,7° (ethanol)	*D*-Gal, *L*-Rha, *D*-Xyl	69,70

The monosaccharides of the carbohydrate chains include, in addition to L-ribose, found in the glycosides of *Clematis vitalba*, family Ranunculaceae [22], practically the whole set of sugars found in the triterpene glycosides from plants of other families: D-glucuronic acid, D-glucose, D-galactose, D-fucose, L-rhamnose, D-quinovose, D-xylose, and L-arabinose.

D-Quinovose had been found previously only in the triterpene glycosides of cinchona [23]. It has recently been detected also in the glycosides of Caryophyllaceae — acanthophyllosides B, C, and D [21, 24]. It must be mentioned that it has been possible to detect D-quinovose only with the aid of the gas—liquid chromatography (GLC) of silyl derivatives of the monosaccharides. In many of the systems of paper chromatography (PC) and thin-layer chromatography (TLC) used, D-quinovose migrates together with L—rhamnose [25-27], and the 2,3,4-tri-O-methylquinovose formed as the result of methylation migrates together with the corresponding derivative of L-rhamnose. In the analysis of monosaccharides with the aid of the GLC of the acetates of the corresponding aldononitriles, the retention time of the D-quinovose derivative coincides with the retention time of the D-fucose derivative [28]. These properties of D-quinovose make its detection extremely difficult without the use of special methods and, in particular, the GLC of the silyl derivatives, especially where L-rhamnose is present simultaneously.

Thus, for example, D-quonovose was found in gypsoside [29], saponoside D [30], vacsegoside B [31], and trichoside D [32] only after their structures had been established. It was possible to detect this comparatively rarely found methylpentose only with the aid of the GLC of the silyl derivatives [24]. The structures of the glycosides mentioned must apparently be demonstrated anew.

Errors of a different type have also been postulated. Thus, after the establishment of the structure of gypsoside [29], now, as has been found, requiring corrections, individual publications appeared [33-35] in which on the basis of the identity of the aglycone and the monosaccharide composition, alone, considerations were expressed on the similarity of the structures of the glycosides isolated with gypsoside. In a number of other papers [36-38], the question of identity with gypsoside was answered only by comparing R_f values on PC. It appeared as if gypsoside was a taxonomic characteristic of plants of the family Caryophyllaceae.

Table 1 gives 25 individual glycosides of established structure, and Table 2 gives compounds for which only the nature of the aglycone and the monosaccharide composition have been determined.

As can be seen from these Tables, as a rule, almost all the glycosides containing in their carbohydrate chains nine or more sugar units include the whole of the above-litested set of monosaccharides.

The carbohydrate chains in the glycosides are usually present both at the hydroxy group at C-3 of the aglycone and at the carboxy group at C-17, i.e., in Tschesche's terminology they are bisdesmosides [7]. Only four glycosides have a sugar chain solely at C-3 of the aglycone. The presence of only an acyloside carbohydrate chain, i.e., one attached to the

COOH group of the aglycone, in the triterpene glycosides is rare. Three such glycosides are known – glabrosides B and C [17], and paniculatoside C [16].

On the whole, though, a characteristic feature of the glycosides of the family Caryophyllaceae is that they are highly polar compounds of complex structure. The complexity of the molecular structure of the main glycosides is mostly due to the structure of the branched carbohydrate chains. Comparatively simple glycosides with short unbranched chains are usually minor components present in small amount in the total glycosides and they are apparently intermediate products of biosynthesis.

As a rule, a considerable proportion of the Caryophyllacea glycosides each has 2-3 centers of branching both in the O-glycosidic and in the acylosidic chain. Not infrequently, several branches "grow out" from a single sugar molecule (acutifolioside, vacsegosides B and C, philosides A and B, acanthophylloside C, viscoside), all the hydroxyls and even a carboxy group which may be substituted by carbohydrate residues [24, 31, 43, 48, 49, 62, 64]. In spatial projection, such a molecule with a high molecular weight more frequently resembles a globular formation than a linear one. Several other characteristic features can also be recognized in the structure of the carbohydrate chains of the group of glycosides under consideration. Thus, all gypsogenin glycosides, with the exception of githagoside from *Agrostemma githago* [20], contain D-glucuronic acid, which is always bound directly to the aglycone through the hydroxyl at C-3. As is well known, glucuronosidic bonds are cleaved with greater difficulty than glycosidic bonds of other monosaccharides, which is responsible for the difficult hydrolyzability of compounds of this type. As a rule, in addition to the free aglycone, a gypsogenin glucronoside – vaccaroside, which was first detected in an investigation of the glycosides of *Vaccaria segetalis* [73] – is always found in the hydrolysis products.

Another sugar not found very frequently among plant triterpene glycosides but typical for the complex glycosides of the Caryophyllacea is D-fucose. This monosaccharide is largely found in the acyloside chain and directly attached to the carboxy group of the aglycone. Exceptions from this rule are nutanoside [60], glabroside C [17], and gypsoside [29], where L-rhamnose is attached directly to the carboxy and D-fucose follows this. Furthermore, in githagoside [20], D-fucose is present in the O-glycosidic chain and is attached to the aglycone through the hydroxyl at C-3.

Several properties of the glycosides described are explained by the multicomponent nature and complexity of the sugar chains: a good solubility in water combined with low solubility or absence of solubility in organic solvents, and their low capacity for crystallization. All this complicates the separation of complex mixtures and the preparation of individual compounds.

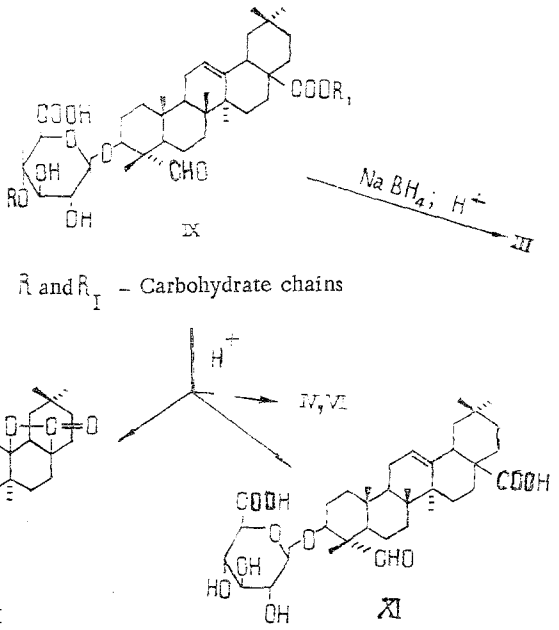
Not infrequently, purification processes are also complicated by the lability of the aglycone. Earlier, attempts were made to explain the lability of gypsogenin glycosides by the formation of an acylal bond between the hydrate form of the aldehyde group of the sapogenin and the carboxy group of the glucuronic acid usually attached to the aglycone at the C-3 hydroxy [45]. However, an interaction of this type is excluded for such compounds as acanthophylloside C [40] and vacsegosides B and C [31, 62], since in them the carboxy group of the glucuronic acid is substituted by a sugar residue.

Because of the lability of gypsogenin, the acid hydrolysis of glycosides frequently forms not an individual aglycone but several substances among which, in addition to gypsogenin (VI, Scheme 2) and vaccaroside (XI), gypsogenin lactone (X), and gypsogenic acid (VI) have also been identified [44, 74]. (see Scheme 2 on following page)

One of the main reasons for the lability of gypsogenin is the presence of an aldehyde group in it. In order to eliminate this difficulty, i.e., to exclude the appearance of artefacts and to facilitate work with complex mixtures, it has been proposed to convert gypsogenin glycosides into the more stable glycosides of hederagenin (III) by reduction with sodium tetrahydroborate [50].

Isolation and Proof of Structure

The methods for isolating and separating the triterpene glycosides from plants of the family Caryophyllaceae vary according to the physicochemical properties of the particular compound but also have much in common.



Scheme 2

Extraction is largely carried out with methanol [50, 61], either cold or hot, and sometimes with aqueous methanol [59, 63, 10]. Not infrequently the plant material is treated with petroleum ether [31, 54] or with chloroform [14, 17, 10] before extraction. This is done not only for defatting purposes but also to break down the complexes of the triterpene glycosides with sterols. In some cases, it has been possible to isolate individual glycosides by chromatography on silica gel of the dry methanolic extract directly [16, 54, 59]. Saponoside A, nutanoside, and paniculatoside C have been obtained in this way.

Sometimes a methanolic extract was subjected to additional purification by reprecipitation with acetone [44] or with ether [50] but in the majority of cases the extract is transferred into water and is then re-extracted with ethyl acetate [12;15] or with butanol [17, 63, 10], and sometimes with both successively [10]. The aqueous residue may contain heavy polar glycosides insoluble in butanol, and it is purified with the aid of Sephadexes and then the glycosides are separated chromatographically [14, 15, 17]. In individual cases, use has been made of ion-exchange resins to purify the extracts and to isolate the glycosides [12-14].

At the present time, as a rule, chromatographic separation is carried out on columns of silica gel-cellulose powder is also used occasionally [74]. The systems of solvents used for preparative chromatography always included water. In early investigations, binary systems based on butanol were frequently used: butanol saturated with water [12, 17] or with ammonia [17]. Ternary systems of the following types have also been widely used: butanol–acetic acid–water (4:1:5; 5:1:1) [50, 65]; butanol–ethanol–water (10:2:5) [54]; butanol–ethanol–25% ammonia (7:2:5; 10:2:5; 15:2:5) [30, 52, 60]; and butanol–methanol–water (5:3:2; 5:2:1) [10, 48, 63]. In individual cases the acetic acid-methanol-water (1:4:4) and ethyl acetate; methanol-water (10:1:1; 10:2:3) systems have been used [48, 49, 64]. Today, an effective "universal" system of the chloroform–methanol–water (65:35:8) type is being used more and more widely [21, 61].

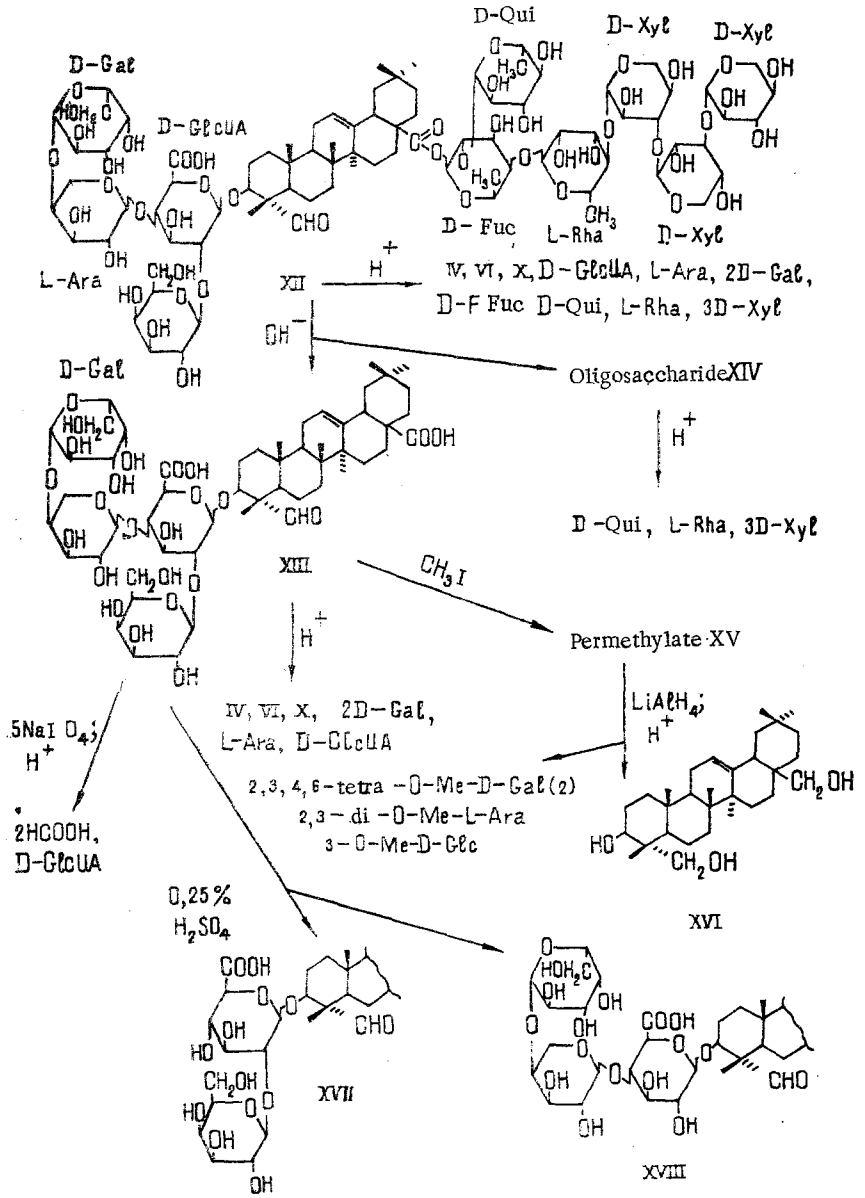
The individual triterpene glycosides isolated form white or cream-colored powders, rarely in the form of crystals, with unsharp melting points. As a rule, the melting points are above 200°C and are, in essence, decomposition points.

Since all the glycosides of Caryophyllacea that have been described contain known aglycones, the determination of the structures of such glycosides has amounted to identifying the sapogenins and establishing the positions and structures of the carbohydrate chains. The complexity of the structures of the latter demand the involvement of almost all modern methods of carbohydrate chemistry. As an illustration, let us consider the proof of the structure of acanthophylloside B, isolated from *Acanthophyllum gypsophiloides* Rgl. [24, 40, 41, 73].

The aglycone of acanthophylloside B is gypsogenin (IV), but the acid hydrolysis of the glycoside formed, together with gypsogenin, a series of artifacts, among which gypsogenin

lactone (X), gypsogenic acid (VI), and gypsogenin 3-O-β-D-glucuronoside (XI) were identified. To confirm the purity and individuality of acanthophylloside B it was reduced with sodium tetrahydraborate and was then hydrolyzed. As a result of this procedure, only hederagenin (III) (Scheme 2) was identified.

Analysis of the hydrolysate by PC and TLC, and also GLC of the trimethylsilyl ethers of the methyl glycosides showed that the carbohydrate moiety of the glycoside contains residues of D-glucuronic acid, D-galactose, D-fucose, L-rhamnose, D-quinovose, D-xylose, and L-arabinose in a ratio of 1:2:1:1:1:3:1. Consequently, acanthophylloside B is a gypsogenin decaoside (Scheme 3).



Scheme 3.

Alkaline saponification of acanthopylloside B led to its cleavage into a gypsogenin tetraoside (XIII) and an oligosaccharide (XIV), which is the acyloside component of the glycoside. It follows from this that the acanthophylloside is a bisdesmoside with O-glycosidic (at the C-3 hydroxyl) and acyl-glycosidic (at the C-17 carboxyl) carbohydrate chains.

The gypsogenin tetraoside (XII) includes residues of D-glucuronic acid, of L-arabinose, and of two galactose molecules. The periodate oxidation of compound (XIII) consumed 5 moles of periodate. As a result of the reaction, 2 moles of formic acid were liberated and the D-glucuronic acid residue remained unchanged. The conclusion suggests itself that the chain is branched and the D-glucuronic acid forms the center of branching.

The Hakomori methylation [75] of the gypsogenin tetraoside (XIII) and hydrolysis of the permethylate (XV) led to the formation of 2,3,4,6-tetra-O-methyl-D-galactose, 2,3-di-O-methyl-L-arabinose, and 3-O-methyl-D-glucuronic acid. The same results were obtained when the lithium-tetrahydroaluminate-reduced permethylate (XV) was hydrolyzed, except for the fact that instead of 3-O-methyl-D-glucuronic acid, 4-O-methyl-D-glucose was detected. Under these conditions, gypsogenin is reduced to 23-hydroxyerythrodiol (XVI)

Two new glycosides were isolated from the products of the stepwise hydrolysis of the gypsogenin tetraoside (XIII) with 0.25% sulfuric acid — the bioside (XVII) and the trioside (XVIII). In an analysis of a hydrolysate of the permethylate of the bioside (XVII), 2,3,4,-6-tetra-O-methyl-D-galactose and 3,4-di-O-methyl-D-glucuronic acid were isolated. After permethylation and hydrolysis of the trioside (XVIII), 2,3,4,6-tetra-O-methyl-D-galactose, 2,3-di-O-methyl-L-arabinose, and 2,3-di-O-methyl-D-glucuronic acid were found. From this the conclusion follows that the bioside and trioside have structures (XVII) and (XVIII), respectively, and the gypsogenin tetraoside the structure (XIII). This series of experiments determines the structure of the O-glycosidic carbohydrate chain of acanthophylloside B (XII) (Scheme 3).

The acyloside chain of acanthophylloside B (XII) includes residues of D-fucose, of L-rhamnose, of D-quinovose, and of thee D-xylose molecules, while in the oligosaccharide (XIV) formed in the alkaline saponification of glycoside B there is no D-fucose. This shows its direct linkage to the carboxy group of the aglycone and its subsequent destruction on alkaline treatment.

When 1 mole of acanthophylloside B was oxidized with sodium periodate, 10 moles of the oxidizing agent are consumed and 4 moles of formic acid were liberated. Mentally deducting the 5 moles of reagent necessary, as shown above, for the oxidation of the O-glycosidic chain — which liberates 2 moles of formic acid — we come to the conclusion that 5 moles of periodate were also consumed in the degradation of the acyloside chain. As a result of the reaction, again 2 moles of formic acid were formed. Of the residual (unoxidized) sugars, D-fucose and D-xylose were detected in addition to D-glucuronic acid. Consequently, the acyloside chain contains two terminal sugars and is branched. One of the residual sugars is the center of branching and the other is substituted at the C-3 hydroxyl.

As the result of the exhaustive methylation of acanthophylloside B (XII) by Hakomori's and hydrolysis of the permethylate (XIX) (Scheme 4) 2,3,4,6-tetra-O-methyl-D-galactose (2 molecules), 2,3-di-O-methyl-L-arabinose, 3-O-methyl-D-glucuronic acid, 3-O-methyl-D-fucose, 2,3-di-O-methyl-L-rhamnose, 2,4-di-O-methyl-D-xylose (2 molecules), 2,3,4-tri-O-methyl-D-quinovose, and 2,3,4-tri-O-methyl-D-xylose were identified.

On excluding the methyl ethers of galactose, arabinose, and gluconic acid, which are components of the O-glycosidic chain (Scheme 3), the remaining methylated sugars must belong to the O-acylosidic part of the molecule.

The difficulties in the identification of D-quinovose which were metnioned above required in this case the preparative isolation of the trimethyl derivative of this sugar and its demethylation [76] to the free sugar.

In a study of the products of the methylation of the glycoside (XII), in addition to the permethylate (XIX) the authors succeeded in isolating another compound. It was obtained in the crystalline form and proved to be the methyl glycoside of the methylated oligosaccharide (XX) (Scheme 4), split off from the carboxy group of gypsogenin in the methylation process [41]. No such phenomenon has been detected previously in the methylation of the triterpene glycosides. Consequently, in subsequent investigations it was obviously necessary to take into account the possibility of the splitting off of the whole of the acyloside chain in the form of a large portion of the molecule during the Hakomori reaction.

In the hydrolysis of the methylated oligosaccharide (XX) with 0.2% hydrochloric acid, the terminal 2,3,4-tri-O-methyl-D-xylose was split off, and then 2,4-di-O-methyl-D-xylose. This indicates the presence in the acyloside chain of a section consisting of xyloses bound to one another by a 1→3 bond.

The permethylate (XIX) of acanthophylloside B was cleaved by lithium tetrahydroaluminate. This gave two compounds: a methylated glycoside of 23-hydroxyerythrodiol (XX) and the reduced oligosaccharide (XXII) (Scheme 4). 2,3,4,6-Tetra-O-methyl-D-galactose (2 molecules), 2,3-di-O-methyl-L-arabinose, and 3-O-methyl-D-glucose were detected in the products of the hydrolysis of the glycoside (XXI).

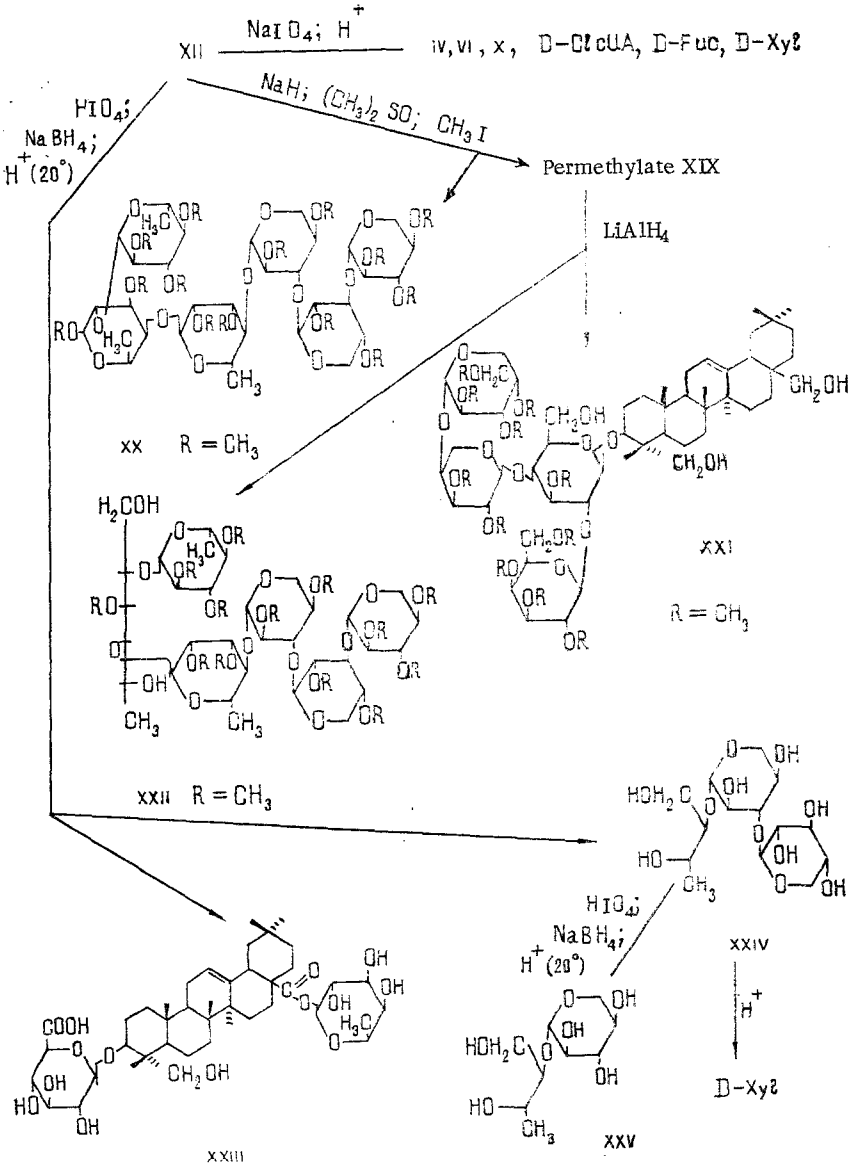
The oligosaccharide (XXII) was decomposed into 3-O-methyl-D-fucitol, 2,3-di-O-methyl-L-rhamnose, 2,4-di-O-methyl-D-xylose (2 molecules), 2,3,4-tri-O-methyl-D-xylose, and 2,3,4-tri-O-methyl-D-quinovose.

It follows from the results obtained that the acylosidic carbohydrate chain of acanthophylloside B is branched. The center of branching is a D-fucose residue directly attached to the carboxy group of the aglycone. The terminal sugars are D-quinovose and D-xylose, the latter attached to another molecule of D-xylose occupying the middle position.

For a further study of the structure of the carbohydrate chain use was made of twofold Smith degradation [77]. Acanthophylloside B was oxidized with periodic acid, reduced with sodium tetrahydroborate, and subjected to mild acid hydrolysis [41]. The glycoside (XXIII) and the polyol (XXIV) (Scheme 4) were detected in the reaction products.

Analysis of the glycoside (XXIII) showed that it was hederagenin bioside in which D-glucuronic acid was attached to the aglycone at the C-3 hydroxyl and fucose was attached to the carboxy group. Only D-xylose was found in a hydrolysate of the polyol (XXIV).

The polyol (XXIV) was subjected to a second degradation, giving a new polyol (XXV) which also contained D-xylose. When the polyol (XXIV) was methylated and the product was subjected to hydrolysis, 2,3,4-tri-O-methyl-D-xylose was identified.



Scheme 4

These facts clearly show the presence in the acyloside chain of a linear tetrasaccharide consisting of L-rhamnose with, attached to its C-4 hydroxyl, an oligosaccharide consisting of three D-xylose residues. The latter are connected to one another by 1→3 bonds [41].

Taking into account all the above experimental facts, we come to the conclusion that the acyloside carbohydrate moiety of acanthophylloside B consists of a branched chain. In it, the above-described tetrasaccharide is attached to the C-2 hydroxyl and D-quinovose to the C-4 hydroxyl of a D-fucose residue. In sum, acanthophylloside B has the structure (XII) (Scheme 3). The configurations of the glycosidic bonds were determined from molecular rotation differences or, where this was not possible, they were taken in accordance with Klyne's rule [78].

As shown in Table 1, *Acanthophyllum gypsophiloides* has yielded, in addition to acanthophylloside B, two other glycosides having the same complex structure of the carbohydrate chains: acanthophyllosides C and D.

Acanthophylloside C is a gypsogenin undecaoside and differs from glycoside B by the presence in the carbohydrate chain of an additional sugar — D-glucose — attached to the carboxy group of the D-glucuronic acid.

Acanthophylloside D differs from the two preceding ones by the fact that it contains as the aglycone quillaic acid, which is rarely found in natural materials. The structure of the carbohydrate chains in this glycoside is similar to their structure in acanthophylloside B.

Compounds of gypsogenin with two branched sugar chains containing up 10-11 monosaccharide units probably have the most complex structures among the triterpene glycosides now known. As the example given above shows, in the proof of their structures it is extremely important to accurately establish the localization of the carbohydrate components and where possible to perform stepwise hydrolysis. This method is the most reliable in the elucidation of the structures of any glycosides, including oligosaccharides. It is desirable to plan experiments overlapping one another in order to approach the elucidation of the structures of the individual fragments from two or more directions. Then the possibility of errors is decreased. Frequently, logical structures not based on reliable experimental material may lead to errors and they must be treated with great caution. In the chemistry of the glycosides of the gypsogenin series there are still few fully perfect investigations. It is not excluded that the structures of individual compounds (Table 1) work upon which has been performed with other possibilities of experimental technique will have a different form as a result of re-investigations.

LITERATURE CITED

1. Flora of the USSR [in Russian], Moscow–Leningrad, Vol. 6 (1936), p. 802.
2. Z. Shukhbakhtova, Kh. U. Aliev, and M. B. Sultanov, Dokl. Akad. Nauk Uzbek. SSR, No. 4, 37 (1977).
3. A. I. Yatsyno and A. D. Turova, Medicinal Plants. Pharmacology and Chemotherapy [in Russian], Proceedings of the All-Union Institute of Medicinal Plants, Moscow, Vol. 14 (1971), p. 185.
4. A. D. Turova and A. S. Gladkikh, Farmakol. Toksikol., 27, 242 (1964)
5. Kh. U. Aliev and E. D. Bazhenova, in: The Pharmacology of Natural Compounds [in Russian], Tashkent (1978), p. 93.
6. E. D. Bazhenova, Kh. U. Aliev, and M. B. Sultanov, in: The Pharmacology of Natural Compounds [in Russian], Tashkent (1979), p. 85.
7. Kh. Abdullaev, in: The Pharmacology of Natural Compounds [in Russian], Tashkent (1978), p. 103.
8. A. Abd Elbary and Samia A. Nour, Pharmazie, 34, 560 (1979).
9. S. K. Agarwal and R. P. Rastogi, Phytochemistry, 13, 2623 (1974).
10. W. G. Bucharov [V. G. Bukharov], V. J. Chirva [V. Ya. Chirva], and I. L. Bucharova [Bukharova], Pharmazie, 29, 540 (1974).
11. M. Shimizu and T. Takemoto, J. Pharm. Soc. Jpn., 87, 250 (1967).
12. V. G. Bukharov and S. P. Shcherbak, Izv. Akad. Nauk SSSR, Ser. Khim., 137 (1969).
13. V. G. Bukharov and S. P. Shcherbak, Khim. Prir. Soedin., 389 (1969).
14. V. G. Bukharov, S. P. Shcherbak, and A. P. Beshchekova, Khim. Prir. Soedin., 33 (1971).
15. V. G. Bukharov and S. P. Shcherbak, Khim. Prir. Soedin., 420 (1971).
16. Zh. M. Putieva, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 104 (1974).
17. V. G. Bukharov and S. P. Shcherbak, Khim. Prir. Soedin., 307 (1970).

18. T. Kubota, H. Kitatani, and H. Hinoh, Tetrahedron. Lett., 771 (1969).
19. Th. Kartnig and O. Wegschaider, Planta Med., 21, 144 (1972): Chem. Abstr., 76, 138114 (1972).
20. R. Tschesche and H. Schulze, Chem. Ber., 107, 2710 (1974).
21. Zh. M. Putieva, T. T. Gorovits, E. S. Kondratenko, and N. K. Abubakirov, Chim. Prir. Soedin., 176 (1979).
22. V. Ya. Chirva, P. K. Kintya, and V. N. Mel'nikov, Khim. Prir. Soedin., 297 (1971).
23. R. Tschesche, J. Duphorn, and G. Snatzke, Ann. Chem., 667, 151 (1963).
24. Zh. M. Putieva, L. G. Mzhel'skaya, T. T. Gorovits, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 806 (1977).
25. S. Singh and B. E. Stacey, Analyst, 97, 977 (1972).
26. H. Kaufman, P. Muhlardt, and T. Reichstein, Helv. Chim. Acta, 50, 2287 (1967).
27. H. Ripperger and K. Schriber, Chem. Ber., 101, 2450 (1968).
28. T. T. Gorovits and N. K. Abubakirov, Khim. Prir. Soedin., 241 (1975).
29. N. K. Kochetkov, A. J. [Ya.] Khorlin, and Ju. [Yu.] S. Ovodov, Tetrahedron Lett., 477 (1963).
30. V. Ya. Chirva and P. K. Kintya, Khim. Prir. Soedin., 214 (1970).
31. R. T. Baeva, M. O. Karryev, and N. K. Abubakirov, Khim. Prir. Soedin., 804 (1974).
32. V. N. Luchanskaya, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 69 (1972).
33. K. Amanmuradov and T. N. Tanyurcheva, Khim. Prir. Soedin., 326 (1969).
34. K. Amanmuradov and M. V. Gronovich, Khim. Prir. Soedin., 449 (1969).
35. G. B. Iskenderov, R. K. Aliev, and N. I. Libizov, Farmatsiya, 16, 29 (1967).
36. D. Kh. Yukhananov, I. N. Sokol'skii, E. P. Zinkevich, and V. B. Kubaev, Rast. Resur., 7, No. 3, 386 (1971).
37. D. Kh. Yukhananov, L. S. Bondarchuk, and L. A. Sapunova, Khim.-Farm. Zh., No. 11, 49 (1971).
38. D. Kh. Yukhananov and L. A. Sapunova, Rast. Resur., 12, No. 2, 244 (1976).
39. Zh. M. Putieva, L. G. Mzhel'skaya, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 486 (1970).
40. Zh. M. Putieva, L. G. Mzhel'skaya, T. T. Gorovits, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 177 (1975).
41. Zh. M. Putieva, L. G. Mzhel'skaya, T. T. Gorovits, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 728 (1975).
42. V. Ya. Chirva, P. K. Kintya, and P. L. Cheban, Khim. Prir. Soedin., 487 (1970).
43. V. Ya. Chirva, P. K. Kintya, V. N. Mel'nikov, and V. N. Paukov, Khim. Prir. Soedin., 330 (1974).
44. A. Ya. Khorlin, Yu. S. Ovodov, and N. K. Kochetkov, Zh. Obshch. Khim., 32, No. 3, 782 (1962).
45. A. Ya. Khorlin, Yu. S. Ovodov, and R. G. Ovodova, Izv. Akad. Nauk SSSR, Ser. Khim., 1521 (1963).
46. N. K. Kochetkov, A. Ya. Khorlin, and Yu. S. Ovodov, Izv. Akad. Nauk SSSR, Ser. Khim., 83, 90, 2436 (1964).
47. V. G. Bukharov and S. P. Shcherbak, Khim. Prir. Soedin., 291 (1966).
48. V. G. Bukharov, V. V. Karlin, I. L. Bukharova, and L. N. Surkova, Khim. Prir. Soedin., 598 (1974).
49. V. G. Bukharov, V. V. Karlin, I. L. Bukharova, and L. N. Surkova, Khim. Prir. Soedin., 603 (1974).
50. V. N. Luchanskaya, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 434 (1970).
51. V. N. Luchanskaya, E. S. Kondratenko, T. T. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 151 (1971).
52. V. N. Luchanskaya, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 431 (1971).
53. V. N. Luchanskaya, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 608 (1971).
54. V. Ya. Chirva, P. K. Kintya, and G. V. Lazur'evskii, Khim. Prir. Soedin., 59 (1969).
55. V. Ya. Chirva and P. K. Kintya, Khim. Prir. Soedin., 188 (1969).
56. V. Ya. Chirva and P. K. Kintya, Khim. Prir. Soedin., 532 (1971).
57. G. V. Lazur'evskii, P. K. Kintya, and V. Ya. Chirva, Dokl. Akad. Nauk SSSR, 188, 1060 (1969).

58. V. Ya. Chirva, P. K. Kintya, and G. V. Lazur'evskii, Khim. Prir. Soedin., 494 (1969)
59. V. G. Bukharov and L. N. Karneeva, Khim. Prir. Soedin., 205 (1971).
60. V. G. Bukharov and L. N. Karneeva, Khim. Prir. Soedin., 412 (1971).
61. R. T. Baeva, M. O. Karryev, K. Amanmuradov, and N. K. Abubakirov, Khim. Prir. Soedin., 258 (1974).
62. R. T. Baeva, M. O. Karryev, and N. K. Abubakirov, Khim. Prir. Soedin., 658 (1975).
63. V. G. Bukharov and I. L. Bukharova, Khim. Prir. Soedin., 534 (1974).
64. W. G. Bucharov [V. G. Bukharov], W. J. Tschirva [V. Ya. Chirva], and I. L. Bucharova [Bukharova], Pharmazie, 30, 394 (1975).
65. V. G. Bukharov and S. P. Shcherbak, Khim. Prir. Soedin., 123 (1973).
66. E. T. Tegisbaev, T. K. Chumbalov, and N. K. Abubakirov, Rast. Resur., 1, No. 1, 102 (1965).
67. R. Paris and P. Lys, Ann. Pharm. Fr , 12, 171 (1954); Chem. Abstr., 48, 10848 (1954).
68. R. Bouche, J. Pharm. Belg., 10, 169 (1955); Pharm. Tijdschr. Belg., 32, 97 (1955); Chem. Abstr., 50, 11288 (1956).
69. H. H. Appel, E. Lobos, and K. H. Overton, Scientia 30, 123 (1964); Chem. Abstr., 62, 10484 (1965).
70. H. H. Appel and A. Haleby, Scientia, 32, 17 (1965); Chem. Abstr. 66, 38202 (1967).
71. R. Tschesche and G. Wulff, Fortschr. Chem. Org. Naturstoffe, 30, 461 (1973).
72. K. Amanmutadov and N. K. Abubakirov, Zh. Obshch. Khim., 34, 1661 (1964).
73. Zh. M. Putieva, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 236 (1979).
74. Zh. M. Putieva, Author's Abstract of Candidate's Dissertation, Tashkent (1980).
75. S. Hakomori, J. Biochem. (Tokyo), 55, 205 (1964).
76. L. Hough and R. S. Theobald, in: Methods in Carbohydrate Chemistry, Academic Press, New York, Vol. 1, R. L. Whistler and M. L. Wolfram, eds. (1962), pp. 94-98.
77. I. J. Goldstein, A. V. Hay, B. A. Lewis, and F. Smith, in: Methods in Carbohydrate Chemistry, Academic Press, New York, Vol. 5, R. L. Whistler, ed. (1965), pp. 361-370.
78. W. Klyne, Biochem. J., 47, xli (1950).

POLYSACCHARIDES OF *Ungernia*.

VII. PARTIAL HYDROLYSIS OF THE MANNAN OF THE BULBS OF *U. vvedenskyi*

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UDC 547.917

4-O-β-D-Manopyranosyl-D-mannose, O-β-D-mannopyranosyl-(1→4)-O-β-D-mannopyranosyl-(1→4)-D-mannose, and O-β-D-mannopyranosyl-(1→4)-O-β-D-mannopyranosyl-(1→4)-O-β-D-mannopyranosyl-(1→4)-D-mannose have been isolated from the products of the partial hydrolysis of ungeromannan-V, obtained from the bulbs of *Ungernia vvedenskyi*, and have been identified. This set of oligosaccharides confirms the regular structure of the carbohydrate chain of ungeromannan-V, which consists of a linear sequence of β-1→4-bound D-mannose residues.

Information on the structure of ungermannan-V obtained on the basis of chromium trioxide and sodium periodate oxidation and methylation has been reported previously [1]. It was established that the monosaccharide residues in it are linked by β-1→4 glycosidic bonds.

For an additional confirmation of the results of methylation, we have studied the structure of ungermannan-V with the aid of ^{13}C NMR spectra and partial hydrolysis. The partial hydrolysis of deacetylated ungermannan-V [1] with formic acid yielded a mixture of mono- and oligosaccharides which was separated by preparative PC. Three chromatographically individual oligosaccharides (I-III) were isolated. Their structures were established from the results of acid hydrolysis, periodate oxidation, methylation, and mass spectrometry.

*Deceased.

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