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CARDENOLIDE-CONTAINING PLANTS OF THE FAMILY CRUCIFERAE

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Plants of the family Cruciferae L. (Brassicaceae), which are widely distributed in the countries of the CIS, are important sources for obtaining new cardiac glycosides. Up to the present time, about 40 species of this family have been studied chemically. From them, 75 glycosides and aglycons, including 50 new, previously unknown, compounds have been isolated. From the glycosides, 10 monosaccharides have likewise been isolated, three of which are new. In this way, a considerable contribution has been made to the chemistry of the cardenolide glycosides.

Plants with a high content of cardiac glycosides — from 2 to 4% and, in individual species, 5% and more — have been found. These include *Erysimum canescens, E. contractum, E. crepidifolium, E. silvestris, E. badghysi, E. gypsacum, and Cheiranthus allioni (E. asperum)*. These plants are important for the national economy of the countries of the CIS, where they are readily introduced, and some have already been introduced into cultivation and are being used for obtaining drugs. The bibliography amounts to 90 items, mainly for 1960-1992. The number of botanical families containing such valuable natural compounds as the cardiac glycosides (cardenolides and bufadienolides) is small — 16. The majority of them are found on the African continent.

The cardenolide families also include the enormous family of the Cruciferae (Brassicaceae) including 128 genera and 740 species [1] growing on the territories of the countries of the CIS. Cardiac glycosides have been detected in three genera — *Erysimum* L., *Cheiranthus* L., and *Syrenia* Andrz. This family is of particular interest for the following reasons. In the first place cardenolide-bearing species of Cruciferae are widely distributed in the Ukraine, Russia, Uzbekistan, and other countries of the CIS and are readily susceptible to cultivation under the climatic condidtions of these countries. In the second place, it is just in this family that plants have been found with the highest level of cardiac glycosides. These facts are of particular importance from the point of view of providing independent governments with their own raw materials resources.

With the aim of the greatest economy in the presentation of the material, we give information on the qualitative and quantitative compositions of the cardenolides of the plants studied, their distribution, and their use.

The reader can readily deduce the chemical structural formulas of the glycosides from the structural formulas of the aglycons and the monosaccharides that are given and the names of the glycosides — chemical and trivial (**1-71**) — while the structures of the monosaccharides (**72-81**) include an indication of the hemiacetal hydroxyls in the configuration which they assume in the glycosides. The conformational formulas of the sugars in the form in which they are present in the glycosides are also given. All the monosaccharide units exist in the pyranose form. New compounds are marked with asterisks.

GENUS *Erysimum* L.

A large genus from the Mediterranean Sea area, includes annual and biennial species in the north and perennial species in the south of the area. Of the 130 species of the genus, more than 60 are found on the territory of the countries of the CIS [1]. They have been used in medical practice since early antiquity. The name of the species was given by Linnaeus and derived from the Greek "eruomai," which means "rescue," "assist," "heal" [2]. Pharmacological investigations of them

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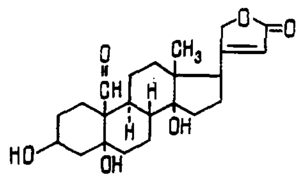
TABLE 1. Strophanthidin and Its Glycosides



1. Strophanthidin $C_{23}H_{32}O_6$, mp 144-145/230-233°
[α]D + 44.0° [3, 10]

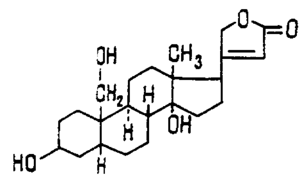
Number	Glycoside	Molecular formula	mp, °C	$[\alpha]_D$, deg	Carbohydrate component	Literature
1	2	3	4	5	6	7
2	Erysimin*	$C_{29}H_{42}O_9$	176—178	+27.0	β-D-Digitoxose	[4, 22, 29]
3	Erysimoside*	$C_{35}H_{52}O_{14}$	170—176	+18.6	β-D-Digitoxose-(4←1)-β-D-glucose	[6, 7, 8]
4	Glucoerysimoside*	$C_{41}H_{62}O_{19}$	203—206	+11.6	β-D-Digitoxose-4←1)-β-D-glucose-(4←1)-β-D-glucose	[72]
5	Glucostrophanthidin	$C_{29}H_{42}O_{11}$	170—173/ 234—235	+18.8	β-D-Glucose	[72]
6	Deglucocheirotoxin*	$C_{29}H_{42}O_{10}$	188—192	+1.4	β-D-Gulomethylose	[7b, 9, 71]
7	Cheirotoxin*	$C_{35}H_{52}O_{15}$	210—211	—15.8	β-D-Gulomethylose-(4←1)-β-D-glucose	[7b, 9, 13,74,82]
8	Glucostrophalloside*	$C_{35}H_{52}O_{15}$	189—192	+3.3	β-D-Allomethylose-(4←1)-β-D-glucose	[50]
9	Corchoroside A	$C_{29}H_{42}O_9$	167—169/ 188—190	+11.0	β-D-Bovinose	[34]
10	Strophalloside	$C_{29}H_{42}O_{10}$	163—165/ 177—181	+5.0	β-D-Allomethylose	[50]
11	Erychroside*	$C_{34}H_{50}O_{13}$	242—248	+17.1	β-D-Digitoxose-(4←1)-β-xylose	[30]
12	Erythriside*	$C_{40}H_{60}O_{18}$	194—197	+5.0	β-D-Digitoxose-(4←1)-β-D-xylose-(4←1)-β-D-glucose	[35]
13	Perofskoside*	$C_{29}H_{42}O_{10}$	Amorph.	+25.5	2-Deoxy-β-D-glucose	[39,40]
14	Cabuloside*	$C_{29}H_{42}O_{10}$	Amorph.		2-Deoxy-β-D-gulose	[39, 40]
15	Eryperoside*	$C_{35}H_{52}O_{14}$	178—180	+43.9	β-D-Digitoxose-(4←1)-α-D-glucose (provisional)	[39, 40]
16	Erycorchoside*	$C_{35}H_{52}O_{14}$	238—240	+30.3	β-D-Bovinose-(4←1)-α-D-glucose (provisional)	[39, 40]
17	Erycanoside*	$C_{35}H_{52}O_{15}$	249—253	+50.4	Acetyl-β-D-digitoxose-(4←1)-α-D-glucose	[19,60]
18	Sinapoylerysimoside*	$C_{48}H_{62}O_{18}$		+33.6	β-D-Digitoxose-(4←1)-(6-O-sinapoyl)-β-D-glucose.	[66]

have been carried out fairly intensively by R. Yaretskii, M. Vilke, V. V. Reverdatto, M. N. Varlakov, A. I. Mazina, N. V. Vershinin, E. M. Dumenova, and others, beginning from the 1930s-1940s and have determined chemical investigations for about 20 years. These early investigations have been well presented in a review [1] and a monograph [2] and therefore we believe we need not repeat them in the present paper.

***Erysimum canescens* Roth. syn. *E. diffusum* Ehrh.** — hoary erysimum — native to the flora of Eurasia, cultivated in the Ukraine. Biennial herbaceous plant. With respect to its content of cardiac glycosides it is not inferior to *Strophanthus* and is considerably superior to other plants.

The chemical study of the plant was begun by V. F. Feofilaktov and M. V. Tsarev at the Moscow Institute VILAR [All-Union Scientific-Research Institute of Medicinal and Aromatic Plants], who isolated erysimolactone (strophanthidin (**1**)) [3]. In this Institute, later, in 1954, the glycoside erysimin* (**2**) was isolated [4], although its structure remained unknown until 1957, when Swiss workers [22] isolated the same glycoside from another *Erysimum* species and established its structure

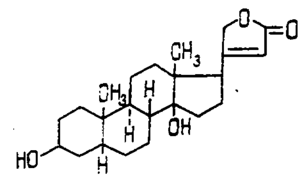
TABLE 2. Cannogenol and Its Glycosides



19. Cannogenol, $C_{23}H_{34}O_5$, mp 236-239°C, $[\alpha]_D$ +29.2° [33]

1	2	3	4	5	6	7
20	Deglucoery-cordin*	C29H44O9	162—164	—21.1	β-D-Gluomethylose	[33 68]
21	Erycordin*	C35H54O14	200—203	—25.3	β-D-Gulomethylose-(4←1)-β-D-glucose	[33]
22	Glucoery-cordin	C41H64O19	131—135	—22.5	β-D-Gulomethylose-(4←1)-β-D-glucose-(4←1)-β-D-glucose	[80]
23	Glucocan-nogenol	C29H44O10	225—229	+7.0	β-D-Glucose.	[74]

TABLE 3. Digitoxigenin and Its Glycosides



24. Digitoxygenin, $C_{23}H_{34}O_4$, mp 253-256°C, [α]D+18.5° [68]

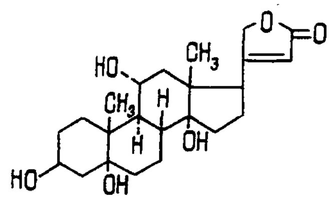
1	2	3	4	5	6	7
25	Glucodigi-fucoside	C35H54O13	188—192	—5.6	β-D-Fucose-(4←1)-β-D-glucose	[31, 68]
26	Evomonoside	C29H44O8	239—242	—28.9	α-Rhamnose	[68]
27	Evobioside	C35H54O13	267—271	—24.3	α-L-Rhamnose-(4←1)-β-D-glucose	[68]
28	Digitoxi-genin gulo-methyloside	C29H44O8	150—152	—22.0	β-D-Gulomethylose	[78]
29	Digifucocel-lobioside	C41H64O18	238—242	—1.4	β-D-Fucose-(4←1)-β-D-glucose-(4←1)-β-D-glucose	[78]
30	Glucodigigulo-methyloside*	C35H54O13	197—199	—34.3	β-D-Gulomethylose-(4←1)-β-D-glucose	[78]
30A	Er. 10*	C35H54O13	267—270	—5.8	β-D-Allomethylose-(4←1)-β-D-glucose	[47]

as a 3β-O-β-D-digitoxopyranoside and called it helveticoside. Later, the identity of these glycosides was recognized and was confirmed in a number of other investigations. However, the name "erysimin" has been retained by many authors, as also in our monograph-handbook [5], as having priority.

The following were isolated subsequently from hoary erysimum: erysimoside* (**3**) [6-8], deglucocheirotoxin (**6**) [7b, 9], cheirotoxin (**7**) [7b, 9], strophanthidin (**1**) [10], nigrescigenin (**65**) [10], glucostrophalloside (**8**) [10], canescein* (**66**) [7b, 10, 11], glucocanescein* (**67**) [7b, 9], diffugenin* (**61**) [12], and erycanoside (**17**) [19]. The chemical structures of canescein, glucocanescein*, and cheirotoxin were additionally investigated by I. F. Makarevich [11, 13] and given in corrected form.

The presence in *E. canescens* of erycordin (**21**) and erysimosol (**40**), as well, has been shown with the aid of paper chromatography. Hoary erysimum forms several geographic races and varieties the characteristics of which have still been studied inadequately [2].

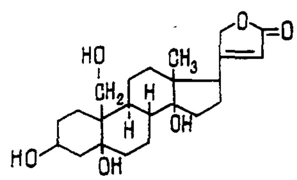
TABLE 4. Bipindogenin



31. Bipindogenin, $C_{23}H_{34}O_6$, mp 260-262°C, $[\alpha]_D$ +30.0° [70]

1	2	3	4	5	6	7
32	Bipindogulo-methyloside*	C29H44O10	150—154/ 168—170	—16.0	β-D-Culomethylose	[78]
33	Alliside*	C29H44O10	180—183	—47.7	α-L-Glucomethylose	[70]
34	Glucolokund joside	C35H54O15		—8.0	α-L-Rhamnose-(4←1)-β-D-glucose	[41]
35	Glucoal-liside	C35H54O15	203—206	—47.1	α-L-Glucomethylose-(4←1)-β-D-glucose	[73]
36	Glucobip-indogulo-methyloside*	C35H54O15	192—195	—31.0	β-D-Gulomethylose-(4←1)-β-D-glucose	[77]
37	Lokundjoside	C29H44O10	184—187/ 277—279	—12.1	α-L-Rhamnose	[17, 38]

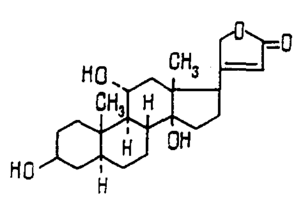
TABLE 5. Strophanthidol and Its Glycosides



38. Strophanthidol, $C_{23}H_{34}O_6$, mp 140-142°C, $[\alpha]_D$ +36.0° [36, 71]

1	2	3	4	5	6	7
39	Helveticosol*	C29H44O9	147—151/ 166—171	+27.1	β-D-Digitoxose	[36, 71]
40	Eryisimosol*	C35H54O14	173—176	+21.6	β-D-Digitoxose-(4←1)-β-D-glucose	[36, 71]
41	Glucoerys-imosol	C41H64O19	260—262	+15.8	β-D-Digitoxose-(4←1)-β-D-glucose-(4←1)-β-D-glucose	[72]
42	Erychrosol*	C34H52O13	228—232	+18.7	β-D-Digitoxose-(4←1)-β-D-xylose.	[32]

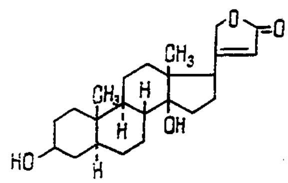
TABLE 6. Alliotoxigenin and Its Glycosides



43. Alliotoxigenin,* $C_{23}H_{34}O_5$, mp 295-301°, $[\alpha]_D$ +25.8° [69]

1	2	3	4	5	6	7
44	Alliotoxin*	C29H44O9	262—272	—40.0	α-L-Rhamnose	[69]

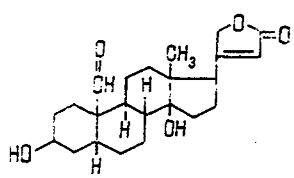
TABLE 7. Uzarigenin and Its Glycosides



45. Uzarigenin, $C_{23}H_{34}O_5$, mp 240–256°C, $[\alpha]_D$ +14° [73, 75]

1	2	3	4	5	6	7
46	Cheiroside A*	C35H54O13	295—297	—23.7	β-D-Fucose-(4←1)-β-D-glucose	[73]
47	Deglucouzarin	C29H44O9	269—273/277—279	—17.1	β-D-Glucose	[75]
48	Neouzarin	C35H54O14	268—277/292—300	—18.7	β-D-Glucose-(4←1)-β-D-glucose	[75]
48A	Er. 9*	C29H44O8	250—254/278—280	—12.4	β-D-Gulomethylose	[43,47]
48Б	Deglucocheiroside A*	C29H44O8	239—244	—12.9	β-D-Fucose	[82]

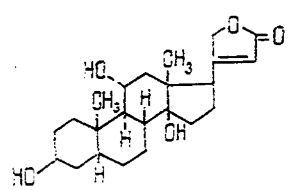
TABLE 8. Cannogenin and Its Glycosides



49. Cannogenin, $C_{23}H_{32}O_5$, mp 145/185/200-210°C, $[\alpha]_D$ −15.0° [71]

1	2	3	4	5	6	7
50	Cheiranthoside*	C29H42O9	154—156	—41.3	β-D-Gulomethylose	[71]
50A	Glucocheiranthoside	C35H52O14		—44.4	β-D-Gulomethylose-(4←1)-β-D-glucose.	[90]

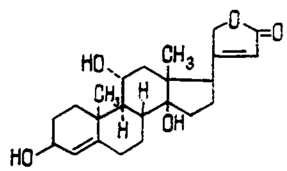
TABLE 9. Sarmentogenin and Its Glycosides



51. Sarmentogenin, $C_{23}H_{34}O_5$, mp 265-267/278-282°C, $[\alpha]_D$ +21.5° [76]

1	2	3	4	5	6	7
52	Sarmentogulomethyloside*	C29H44O9	307—309	—33.5	β-D-Gulomethylose	[76]
53	Gulosarmentoglucoside*	C35H54O14	204—207	—23.9	β-D-Gulomethylose-(4←1)-β-D-glucose.	[76]

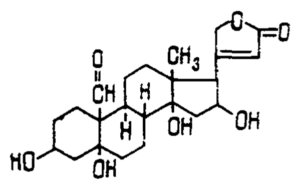
TABLE 10. 4-Dehydrosarmentogenin and Its Glycosides



54. 4-Dehydrosarmentogenin,* $C_{23}H_{32}O_5$, mp 296-302°C, $[\alpha]_D$ +26.2° [79]

1	2	3	4	5	6	7
55	Ch-30*	C29H42O9	268—275	—38.2	α-L-Rhamnose	[79]
56	Ch-31*	C35H52O14		—44.1	α-L-Rhamnose-(4←1)-β-D-glucose.	[79]

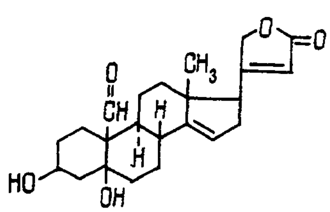
TABLE 11. Strophadogenin and Its Glycosides



57. Strophadogenin, $C_{23}H_{32}O_7$, mp 233-237/240-242°C, $[\alpha]_D$ +50.7° [37]

1	2	3	4	5	6	7
58	Erygypsoside*	C29H42O10	168—170		β-D-Digitoxose	[37]
59	Gypsobioside*	C34H50O14	238—240	+28.9	β-D-Digitoxose-(4←1)-β-D-xylose	[37]
60	Gypsotrioside*	C40H60O19	165—172		β-D-Digitoxose-(4←1)-β-D-xylose-(4←1)-β-D-glucose	[37]

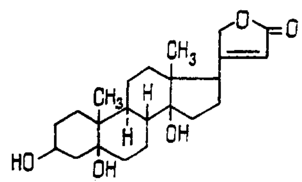
TABLE 12. Diffugenin



61. Diffugenin,* $C_{23}H_{30}O_5$, mp 186-188°C, $[\alpha]_D$ + 5.4°
(its native nature requires confirmation) [12]

A number of authors have made analytical investigations on the quantitative levels of the glycosides. It has been established that the total amount of cardiac glycosides in the leaves is 1.76% [15], in the flowers 2.35% [15], in the seeds 2.5-4% [16], 4.99% [17], 5.92% [18], or 6.2% [7a]. The amount of erysimoside in the seeds is, according to different authors, 2.9% [17] and 2.5-4% [16]. The numerical results given, with all their scatter, show a high content of glycosides and the great practical value of this species of erysimum. The differences in the quantitative levels found can be explained by many factors, one of which is the possibility of the existence of different races and varieties. It is assumed that the highest content of glycosides is present in the so-called Minsk form of *E. canescens*.

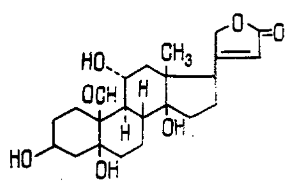
TABLE 13. Periplogenin and Its Glycosides



62. Periplogenin, $C_{23}H_{34}O_5$, mp 135-140/233-235°C, $[\alpha]_D$ +31.5° [43-45]

1	2	3	4	5	6	7
63	Periplorhamno-side	C29H44O9	170—174	—20.0	α-L-Rhamnose	[43, 44]
64	Glucoperiplor-hamnoside	C35H54O14	202—204	—1.6	α-L-Rhamnose-(4←1)-β-D-glucose.	[43, 44]

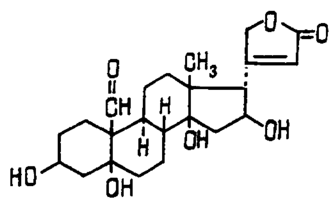
TABLE 14. Nigrescigenin and Its Glycosides



65. Nigrescigenin, $C_{23}H_{32}O_7$, mp 150/220-230°C, $[\alpha]_D$ +16.5° and +24.8° [7b, 10, 11]

1	2	3	4	5	6	7
66	Canescein*	C29H42O11	193—195	—23.4	β-D-Gulomethylose	[76, 9, 10, 11]
67	Glucocanescein*	C35H52O16	248—250		β-D-Gulomethylose-(4←1)-β-D-glucose	[76, 9, 10, 11]
68	Nigrescigenin digitoxoside*	C29H42O10	141—145	+16.1	β-D-Digotoxose	[52]
69	Nigrescigenin digilanidobio-side*	C35H52O15	169—174	—2.6	β-D-Digitoxose-(4←1)-β-D-glucose	[53]

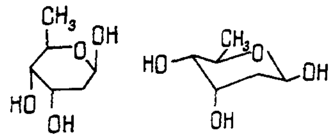
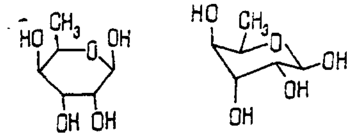
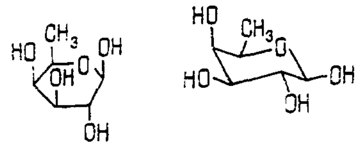
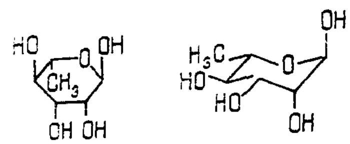
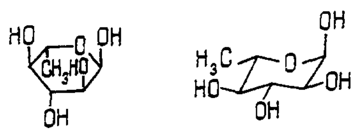
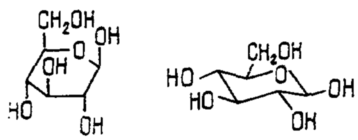
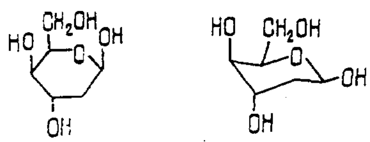
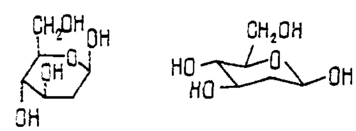
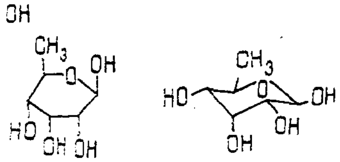
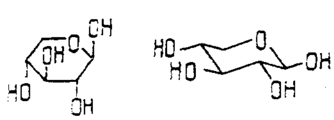
TABLE 15. 17βH-Strophadogenin and Its Glycosides



70. 17βH-Strophadogenin,* $C_{23}H_{32}O_7$ [37]

1	2	3	4	5	6	7
71	17βH-Gypsobio-side*	C34H50O14	272—274		β-D-Digitoxose-(4←1)-β-D-xylose.	[37]

TABLE 16. Monosaccharides Isolated from Glycosides

72		β-D-Digitoxose
73		β-D-Gulomethylose
74		β-D-Fucose
75		α-L-Rhamnos
76		α-L-Glucomethylose * [70,73]
77		β-D-Glucose
78		2-Deoxy-β-D-gulose* [39,40]
79		2-Deoxy-β-D-glucose* [39,40]
80		β-D-Allomethylose
81		β-D-Xylose

Medicinal preparations with the same name, authorized for use in medical practice, have been created from two individual glycosides — erysimin (**2**) and erysimoside (**3**) [2, 21, 63]. The multicomponent medicinal preparation kardiovalen, a component part of which is the juice from the leaves of hoary erysimum, is also used for the treatment of cardiovascular insufficiency. In addition, hoary erysimum is an excellent raw material for the production of the aglycon strophanthidin, since the main glycosides of this plant — erysimoside, glucoerysimoside, and erysimin — are strophanthidin derivatives and are readily-hydrolyzed glycosides containing the 2-deoxysugar D-digitoxose, which permits the aglycon to be isolated in high yield [10, 64]. It is assumed that new biologically active compounds intended for use in medical practice will be synthesized from strophanthidin; see, for example [23-27, 64].

***Erysimum cheiranthoides* L.** — treacle erysimum. As a weed, annual or perennial, this is found from the Atlantic to the Pacific oceans. It has long attracted the attention of researchers. In the leaves of this plant 12 cardenolides have been found [28], and in the seeds 14 [36]. Of them, 12 have been isolated in the individual crystalline state, including five new ones. Their chemical structures have been established. They are the following compounds: erysimin **(2)** [28, 29], strophanthidin **(1)** [28], erysimoside **(3)** [34, 36], erychroside* **(11)** [30], glucodigifucoside **(25)** [31], erychrosol* **(42)** [32], erycordin* **(21)** [33], deglucoerycordin* **(20)** [33], corchoroside A **(9)** [34], erythriside **(12)** [35], helveticosol **(39)** [36], and erysimosol **(40)** [36]. Erychroside **(11)** was the first cardiac glycoside found to contain a pentose residue [30].

The new glycoside erychroside **(11)** [30] has successfully undergone pharmacological and clinical trials and its introduction as a drug for the treatment of cardiac insufficiency is planned.

***Erysimum gypsaceum* Botsch. et Vved.** Central Asian desert plant [1]. Seven glycosides have been isolated from this plant [37], including erysimin **(2)**, erysimoside **(3)**, and erychroside **(11)**, and the new glycosides gypsobioside* **(59)**, gypsotrioside* **(60)**, 17β-H-gypsobioside* **(71)**, and erygypsoside* **(58)**. It has been established [37] that the level of erychroside **(11)** in the flowers is 0.16% and in the leaves 0.08%, and the total cardenolide glycoside content is 0.44% in the flowers and 1.28% in the seeds, this 1.28% including 0.46% of erysimoside **(3)** [17].

***Erysimum Perofskianum* Fisch. et Mey** – Afghan erysimum. Its homeland is Baluchistan and Afghanistan. Annual-biennial plant. It is frequently cultivated in gardens as a decorative plant under the name of *E. compactum aureum* Hort. [39].

With the aid of paper chromatography, the presence of 13 cardenolides in the seeds has been established [39]. Seven of them have been isolated in the individual state. They include erysimin **(2)** [39], corchoroside A **(9)** [39], erysimoside **(3)** [39], and the new glycosides cabuloside* **(14)** [39, 40], perofskoside* **(13)** [39, 40], eryperoside E* **(15)** [39, 40], and erycorchoside* **(16)** [39, 40]. The structures of the new glycosides have been given provisionally.

By a chromatographic comparison with standard substances, the following have also been detected in this plant [14]: erycordin **(21)** deglucoerycordin **(20)**, and helveticosol **(39)**. The total content of cardiac glycosides in the leaves is 0.34%, in the flowers 0.7%, and in the stems 0.15% [17]. It is striking that the glycosides isolated contain one and the same aglycon – strophanthidin – with which readily hydrolyzable 2-deoxysugars are linked (see the structural formulas). It follows from this that Afghan erysimum may prove to be a convenient raw material source for the production of strophidin.

***Erysimum cuspidatum* (M.B.) DC**, is a biennial herbaceous plant growing in the Crimea, the lower Don, north Caucasus, and west and east Transcaucasia.

By chromatographic comparison with authentic samples, the following have been determined in the herbage of *E. cuspidatum*: erysimoside **(3)**, erysimin **(2)**, erycordin **(21)**, erysimosol **(40)**, erychroside **(11)**, deglucoerycordin **(20)**, helveticosol **(39)**, and strophanthidin **(1)** [14]. The seeds contain 0.66% of erysimoside **(3)** and 0.06% of erysimin **(2)** [17]. Erysimin **(2)**, deglucocheirotoxin **(6)**, lokundjoside **(37)**, erysimoside **(3)**, cheirotoxin **(7)**, and glucoerysimoside **(4)** and the new glycoside glucolokundjoside* **(34)** have been isolated from it in the individual state [41].

***Erysimum suffruticosum* Spreng.** The following have been isolated from the seeds of this plant [11, 42], which contain not less than 12 cardenolides [42]: erysimin **(2)**, canescein **(66)**, digitoxigenin **(24)** deglucoerycordin **(20)**, strophanthidin **(1)**, deglucocheirotoxin **(6)**, and the new cardiac glycoside bipindogulomethyloside* **(32)** [42].

Also detected in the herbage of *E. suffruticosum* by chromatographic comparison with authentic samples are erysimoside **(3)**, erycordin **(21)**, erysimosol **(40)**, and glucodigifucoside **(25)** [14].

The total amount of cardiac glycosides in the flowers is 0.15% and in the leaves 0.08% [17].

***Erysimum repandum* L.** – spreading erysimum. Species of eastern Mediterranean origin. It also grows in Asia Minor, Transcaucasia, Iran, Kashmir, and the Balkans. The seeds of this plant have yielded [43-45] periplogenin **(62)**, strophanthidin **(1)**, periplorhamnoside **(63)**, glucoperiplorhamnoside **(64)**, and glucostrophalloside **(8)**. The isolation of erysimin **(2)**, erysimoside **(3)** and cheirotoxin **(7)** was reported somewhat earlier [46], although these results have not been not been fully confirmed in later studies [43, 44]. Two glycosides out of those isolated proved to be new; these are Er. 9* **(48A)** [43, 47], and Er. 10* **(30A)** [47]. The main glycosides of *E. repandum* are glucostrophalloside **(8)** and glucoperiplorhamnoside **(64)** [43]. Attention is attracted [43] to the anomalous nature of this species, since it almost completely lacks such typical glycosides for the genus *Erysimum* as erysimin **(2)** and erysimoside **(3)**. Cheirotoxin was also completely absent [43]. The hypothesis has been expressed that as the plant ripens, erysimin and erysimoside are possibly converted into strophalloside **(10)** and glucostrophalloside **(8)** by hydroxylation at C-2′.

The total amount of cardiac glycosides in the seeds is 0.45%, in the flowers 0.05%, and in the leaves 0.02% [17].

***Erysimum pulchellum* (Willd) J. Gay**. This grows in the Alpine zone of the mountains of southern Transcaucasia and in Asia Minor. Erysimoside (**3**), erysimin (**2**), bipindogulomethyloside (**32**), erycordin (**21**), strophanthidin (**1**), and glucostrophanthidin (**5**) have been obtained from the herbage of this plant. Its erysimoside content is 0.055%, bipindogulomethyloside 0.08%, and erysimin 0.006% [48].

***Erysimum Marshallum* Andrz.** This has a broad area of distribution: Central Europe, the upper and middle parts of the Dnepr, the Black Sea coast, Siberia (apart from the tundra), the Far East, Central Asia, and Mongolia.

It has been established [14] that the epigeal part of the plant contains no fewer than 14 cardenolides, and the seeds no fewer than 17. The seeds of this plant have yielded erysimoside (**3**), erysimin (**2**), strophanthidin (**1**), and corchoroside A (**9**). By chromatographic comparison with authentic specimens, erycordin (**21**), erysimosol (**40**), glucodigifucoside (**25**), deglucoerycordin (**20**), and helveticosol (**39**) have been detected in the herbage, as well as the glycosides mentioned above [14].

The total level of cardiac glycosides in the seeds is 0.98% [49], in the leaves 0.16% [17], and in the flowers 0.26% [17]. There is a report on the presence in this plant of a sinapoylglucoerysimoside [65], but this has not been isolated in the pure form and its precise structure has not been established.

***Erysimum crepidifolium* Rchd**. This is cultivated in the botanical gardens of Western Europe and the Ukraine. The seeds, which contain not less than seven cardenolides [17], have yielded [50] erysimin (**2**), erysimoside (**3**), erycordin (**21**), and a new glycoside which has been called glucostrophalloside* (**8**). The isolation and a detailed investigation of erysimin was carried out even earlier [22]. The total glycoside content of the seeds is, according to some results, 1% [17] and according to others about 3.5% [15, 61]. Erysimin (**2**), erysimoside (**3**), and erycordin (**21**) have been detected in the herbage of *E. crepidifolium* with the aid of paper chromatography [14]. Erysimin and erysimoside have been reported in all the organs of the plant [59].

***Erysimum altaicum* C.A.M.** grows in the steppes and on the southern slopes of the mountains of Western and Eastern Siberia, in Central Asia, and in northern Mongolia. The presence in the epigeal part of the plant of not less than eight cardenolides has been established chromatographically [17]. The total content of cardiac glycosides in the epigeal part is 0.25% [17]. Erysimin (**2**), erysimoside (**3**), deglucocheirotoxin (**5**), and two unidentified glycosides have been isolated in the individual state [58].

***Erysimum contractum* Somm. et Lew.** This grows in Western Transcaucasia on rocks in the mountain region and, more rarely, in the forest zone. It has been established that the seeds contain not less than 13 cardenolides [52]. Strophanthidin (**1**), erysimin (**2**), erysimoside (**3**), and erycordin (**21**) [52, 53] and two new glycosides – nigrescigenin digitoxoside* (**68**) [52] and nigrescigenin digilanidobioside* (**69**) [53] have been isolated in the individual state.

The total glycoside content in the seeds is 3.2%, which indicates the promising practical nature of this species of erysimum. The content of erysimoside (**3**) is 1.26%, of erysimin (**2**), 0.22%, and of nigrescigenin digilanidobioside* (**69**) 0.45% [52].

***Erysimum Czernjajevii* N. Busch.** This grows on dry rocky slopes and on the steppes of Western Siberia and Central Asia. The seeds contain not less than four cardenolides [54]. Erysimin (**2**) and erysimoside (**3**) have been isolated in the individual state [54]. In the seeds these glycosides amount to 0.25-0.3% and 0.85-0.9%, respectively [54].

***Erysimum helveticum* (Jacquin) A.P.DC**. Erysimin (**2**) has been isolated from the seeds and has been studied, with an unambiguous determination of its chemical structure. In the relevant paper [22] it was actually called helveticoside.

The total amount of glycosides in the leaves is 0.16% and in the flowers 0.41% [15].

***Erysimum ferganicum* Botsch. et Vved.** The epigeal part of the plant contains not less than seven cardenolides [14], of which the following have been determined by chromatographic analysis: erysimin (**2**), erysimoside (**3**), erycordin (**51**), strophanthidin (**1**), canescein (**66**), and helveticosol (**39**) [14]. The seeds of this plant contain a more complex mixture of cardenolides – not less than 11 [14].

***Erysimum croceum* M. Pop.** Distributed in Central Asia as an endemic species, growing in the conifer zone of the Tien Shan at a height of 1500-1800 m. The epigeal part and the seeds contains not less than 10 cardenolides [14]. By a chromatographic comparison with authentic samples, the following glycosides were found in the herbage: erysimin (**2**), erysimoside (**3**), erycordin (**21**), erysimosol (**40**), canescein (**66**), erychroside (**11**), and strophanthidin (**1**) [14]. The total amount of cardiac glycosides in the flowers is 0.37%, in the leaves 0.17%, and in the seeds 0.83%, including 0.32% of erysimoside [17].

***Erysimum leptophyllum* (M.B.) Andrz.** grows in dry rocky places on hills and mountain slopes (400-1200 m) in the Caucasus and in Eastern and Western Transcaucasia.

The epigeal part contains not less than eight cardenolides, and the seeds not less than 10 [14]. The following have been detected in the herbage by chromatographic comparison with authentic samples: erysimoside (**3**), erycordin (**21**), erysimin (**2**), and glucodigifucoside (**25**); and in the seeds: erycordin (**21**), erysimoside (**3**), and canescein (**66**) [14].

***Erysimum pannonicum* Crantz.** Distributed on the Atlantic coast of Europe, in the central part of Europe, Spain, the Balkans, the central part of the Dnepr, and the Black Sea region. The epigeal part contains not less than seven cardenolides, and the seeds not less than 10 [14]. Erysimoside (**3**), erycordin (**21**), erysimin (**2**), canescein (**66**), and helveticosol (**39**) have been detected in the herbage by chromatographic comparison with authentic samples [14]. The total amount of cardiac glycosides in the flowers is 0.16%, and in the leaves 0.04% [17].

***Erysimum persicum* Boiss.** Distributed in Iran and Southern Transcaucasia. The epigeal part contains not less than 13 cardenolides, and the seeds not less than 8 [14]. Erysimoside (**3**), erycordin (**21**), erysimin (**2**), erysimosol (**40**), and canescein (**66**) have been detected in the herbage with the aid of chromatography [14].

***Erysium aureum* M. B.** Grows in woods and shady places along streams. Endemic to the Caucasus. Not less than 13 cardenolides have been detected in the herbage with the aid of paper chromatography [14], and erysimoside (**3**), erycordin (**21**), erysimin (**2**), erychroside (**11**), deglucoerycordin (**20**), and helveticosol (**39**) have been identified [14].

***Erysimum Pallasi* (Pursch) Fernald.** Grows in rocky places, on gravels, and on sandy slopes in the Arctic, including the American Arctic, in the Far East, Kamchatka, and Northern Sakhalin. Not less than eight cardenolides have been detected in the herbage by paper chromatography, including: erysimoside (**3**), erysimin (**2**), erycordin (**21**), and strophanthidin (**1**) [14].

***Erysimum nuratense* M. Pop.** Erysimoside (**3**) and erysimin (**2**) have been detected chromatographically in the epigeal part of the plant [17].

***Erysimum violascens* M. Pop.** Endemic, growing in the Syrdar'ya region and on the rocky slopes of the mountains of Central Asia. The leaves of this plant have yielded erysimoside (**3**), erysimim (**2**), and gypsobioside (**59**) [17]. The total glycoside content in the flowers is 0.5% including 0.21% of erysimoside; the leaves contain 0.08% of glycosides [17].

***Erysimum linifoliun* (Pers.) Yag.** Flaxleaf erysimum. The total content of glycosides in the leaves is 0.26%, and in the seeds 0.98%, including 0.67% of erysimoside (**3**) [17].

***Erysimum silvestris* Scop.** Belongs among the most promising raw materials sources for obtaining cardiac glycosides. In the seeds of this plant the total glycoside content is 4.3%, including 2.42% of erysimoside (**3**) [17]. In the flowers and leaves the total glycoside contents are 0.14 and 0.11%, respectively [17].

***Erysimum sylvaticum* M. B.** Grows in woody thickets and undergrowth in Eastern Europe and in the central part of the Dnepr, the lower Don, and the Black Sea region. The amount of glycosides in the flowers is 0.2% [17].

***Erysimum Badghysi* (Korsch) Lipsky.** Endemic, found on the dry sandy-rocky slopes of mountainous Turkmenistan, and also the sand-dune steppes of this region. The total amount of cardiac glycosides in the flowers is 0.29% [17], in the leaves 0.36%, and in the seeds 1.6% [55].

***Erysimum clausioides* Botsch. et Vved.** The amount of glycosides in the flowers is 0.12% and in the leaves 0.06% [17].

***Erysium hieracifolium* L.** By means of paper chromatography 14 cardenolides have been detected, including: erysimoside (**3**), erycordin (**21**), erysimin (**2**), erychroside (**11**), glucodigifucoside (**25**), and strophanthidin (**1**), [14].

***Erysimum humillimum* (Ldb.) N. Busch.** Grows at the height of the Alpine zone of the mountains of Western Siberia, Central Asia, and the Tien Shan. The total content of cardiac glycosides in the flowers is 0.29% and in the leaves 0.2% [17].

***Erysimum pienicum* (Zap.)** Strophanthidin (**1**), corchoroside A (**9**), and erysimoside (**3**) have been isolated from the seeds [56]. Digitoxigenin (**24**), deglucoerycordin (**20**), and erychroside (**11**) have been determined with the aid of paper chromatography. According to these authors, the main glycosides in the autofermented raw material are erysimin and corchoroside A.

***Erysimum carniolicum* Doll.** Strophanthidin (**1**) and erysimin (**2**) have been determined in the seeds by TLC [57].

***Erysimum transsilvanicum* Schur.** The total cardiac glycosides have been obtained from the leaves and have been hydrolyzed with acid: as a result, pure strophanthidin (**1**) was isolated [62]

GENUS *Cheiranthus* (L.) R. Br. – WALLFLOWER

The genus includes 12 species the homeland of which is the Eastern Mediterranean and Western Asia [1].

***Cheiranthus Allioni* hort.**† This is the only cardenolide-bearing species in its genus. The plant is distinguished by containing an unusually large set of glycosides, aglycons and sugars with diverse chemical structures and a wealth of isomeric compounds and genetically related compounds.

One of us has published in this journal ("Khimiya Prirodnikh Soedinenii" [Chemistry of Natural Compounds]) 14 papers [68-80, 87] devoted to the investigation of the glycosides of *Ch. Allioni*.

The glycosidic composition of the plant is complex, consisting of not less than 40 cardenolides of which 35 have been isolated in the individual states and their chemical structures have been determined. Half of these substances proved to be new The latest cardenolides of this wallflower are: strophanthidin (**1**) [68], erysimum (**2**) [68], erysimoside (**3**) [68], glucostrophanthidin (**5**) [72], deglucocheirotoxin (**6**) [71], cheirotoxin (**7**) [74], glucoerysimoside (**4**) [72], erycordin (**21**) [68], deglucoerycordin (**20**) [68], glucoerycordin* (**22**) [80], glucocannogenol* (**23**) [74], digitoxigenin (**24**) [68], glucodigifucoside (**25**) [68], evomonoside (**26**) [68], evobioside (**27**) [68], digitoxigenin gulomethyloside (**28**) [78], digifucocellobioside (**29**) [78], glucodigigulomethyloside* (**30**) [78], bipindogulomethyloside* (**32**) [78], alliside* (**33**) [70], glucoalliside* (**35**) [73], glucobipindogulomethyloside* (**36**) [77], helveticosol (**39**) [71], erysimosol (**40**) [71], glucoerysimosol* (**41**) [72], alliotoxin* (**44**) [69], cheiroside A (**46**) [73], deglucouzarin (**47**) [75], neouzarin* (**48**) [75], cheiranthoside* (**50**) [71], glucocheiranthoside* (**50A**) [90], sarmentogulomethyloside* (**52**) [76], gulosarmentoglucoside* (**53**) [76], Ch.-30* (**55**) [79], and Ch.-31* (**56**) [79].

In the process of establishing the chemical structures of the glucosides isolated, a number of new aglycons and mono- and oligosaccharides were obtained. The cardiac glycosides isolated in the individual state were derivatives of 10 aglycons – digitoxigenin (**24**), uzarigenin (**45**), sarmentogenin (**51**), alliotoxigenin* (**43**), cannogenol (**19**), cannogenin (**49**), strophanthidin (**1**), strophanthidol (**38**), bipindogenin (**31**, and 4-dehydrosarmentogenin* (**54**) – and six monosaccharides – D-digitoxose (**72**), D-gulomethylose (**73**), D-fucose (**74**), L-glucomethylose* (**76**), L-rhamnose (**75**), and D-glucose (**77**). The presence of such a number of cardiac aglycons and monosaccharides in one plant is a phenomenon that is unusual in itself. At least, no other such plant has yet been found.

There are cardenolides of two types – the 5α- and the 5β-series. The componds of the 5β-series predominate numerically.

The main glycosides of the plant are: erysimoside (**3**), cheirotoxin (**7**), glucoerysimoside (**4**), erycordin (**21**), glucodigifucoside (**25**), digifucocellobioside (**29**), glucoalliside* (**35**) [73], glucobipindogulomethyloside* (**6**), cheiroside A (**460**, and neouzarin* (**48**) [87].

On the basis of chemotaxonomic characteristics, *Cheiranthus allioni* [also known as *Erysimum asperum*, "plains erysimum"] has been unambiguously assigned to the genus *Cheiranthus*. This conclusion is timely, since among botanists there has been no established opinion both in relation to the name of the plant and its assignment either to the genus *Cheiranthus* or to *Erysimum* [81].

Cheiranthus Allioni is undoubtedly one of the sources of cardiac glycosides that is promising in the practical respect.

***Cheiranthus cheiri* L. – Common Wallflower.** Biennial or perennial plant in garden and room cultivation [1]. From the seeds of this plant, Swiss researchers have isolated the new biosides cheirotoxin* (**7**) and cheiroside A* (**46**) [82-84]. The enzymatic hydrolysis of these glycosides gave the monosides deglucocheirotoxin* (**6**) and deglucocheiroside A* (**48B**) [82]. It may be assumed that these monosides are also present in the native state in the plant. Later, Kharkov workers [85, 86] continued a study of the cardenolides of common wallflower. From seeds grown by the Moscow Flower-Growing Association they isolated eight cardiac glycosides [85, 86] including, again, cheirotoxin (**7**) and cheiroside A (**46**), and also erycordin (**21**), glucoalliside (**35**), glucobipindogulomethyloside (**36**), alliside (**33**), erysimoside (**3**), and glucoerysimoside (**4**). In addition, with the aid of paper chromatography [85], they detected neouzarin (**48**) and digifucocellobioside (**29**). These facts, and also a direct chromatographic comparison [85] showed a considerably similarity of the cardenolide compositions of *Ch. cheiri* and *Ch. Allioni*.

GENUS *Syrenia* Andrz

In the flora of the CIS, this genus is represented by five species, which grow in the steppe and desert zones [1].

†Formerly known as *Erysimum asperum* ("plains erysimum"): see below, and Khim. Prir. Soedin., No. 3-4, 305-312 (1992).

Syrenia ukrainica **Klok (*S. angustifolia* auct).** Annual or perennial plant. The area of distribution is between the Dnestr and the Volga [1]. The glycoside syreniatoxin (= erysimin) (**2**) has been isolated from the herbage of the plant [88]. Strophanthidin (**1**) and erysimin (**3**), in addition, have been isolated from the seeds [89]. The total amount of cardiac glycosides in the seeds is 0.48% [17].

Syrenia siliculosa **(M.B.) Andrz.** Distributed in the Black Sea region, the Northern Caucasus, Western Siberia, and in desert regions of Central Asia and Kazakhstan. Erysimin (**2**), corchoroside A (**9**), cabuloside (**14**), and erysimoside (**3**) have been isolated from the seeds [89]. The total amount of cardiac glycosides in the seeds is 0.88%, including 0.39% of erysimoside (**3**) [17], and in the flowers it is 0.11% [17] and in the leaves 0.17% [17].

Syrenia dolichostylos **Klok**. Erysimim (**2**) and erysimoside (**3**) have been isolated from the seeds, flowers, and leaves, and erychroside (**11**) from the leaves, as well [89].

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