2,3-di-O-methylrhamnopyranose and 2,4-dimethylglucopyranose. The oligosaccharide was found to contain 2,3,4,6-tetra-O-methylglucose, 2,3-di-O-methylrhamnose, and 3,4-dimethylarabitol. Thus, the carbohydrate chain attached by the acyl glycosidic bond has the structure D-G_p1-4L-Rha_p1-2L-Ara_p1-.

When the saponin was heated with 0.12 N HCl (14 hr), a group of mono-, di-, and tetraglycosides of echinocystic acid was obtained.

The acid hydrolysis of the monoglycosoide showed that a glucose residue is directly attached to the aglycone.

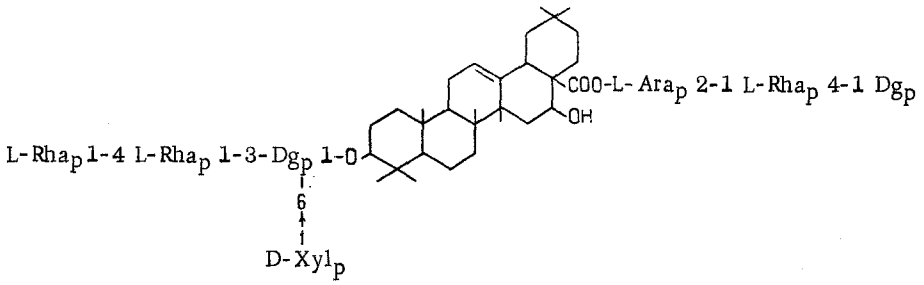
The diglycoside contained glucose and xylose. When the diglycoside was subjected to periodate oxidation, both sugars were decomposed, which excludes the possibility of a 1→3 bond between them. It was shown by methylation that the xylose residue is attached to the OH group of glucose in position 6.

When the tetraglycoside was hydrolyzed, glucose, xylose, and rhamnose were identified. Among the methylation products the same monosaccharides were found as in the lithium aluminum hydride decomposition of methylated helianthoside C.

Thus, the structure of the carbohydrate chain attached to the hydroxy group of echinocystic acid is expressed by the formula

$$\begin{array}{l} LRha_p1 \rightarrow 4LRha_p1 \rightarrow 3D\ Gl_p \\ \qquad\qquad\qquad\qquad\qquad\quad \uparrow 6 \\ \qquad\qquad\qquad\qquad\qquad\quad D\ Xy_p \end{array}$$

Apparently, by analogy with other triterpene glycosides [3,4], this carbohydrate fragment is attached to the hydroxyl at C_3 of the aglycone and, therefore, the most probable structure of helianthoside C is expressed by the following formula:



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ISOLATION OF ALKALOIDS FROM THERMOPSIS ALTERNIFLORA

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This paper reports a method for the qualitative monitoring of the production of the alkaloids of Th. alterniflora [1] using thin-layer chromatography. For this purpose, alumina or grade KSK silica gel mixed with gypsum (9 : 1) were used. The mixture (layer thickness 25 μ) was deposited using the equipment described by Stahl [2], dried at 60-70° C for 4 hr, and chromatographed in chambers (D = 100 mm, H = 250 mm). The alkaloids were deposited in 8-12 γ portions to a total of 20-30 γ. The spots were revealed with Dragendorff's reagent. Several systems of solvents were investigated (table).

In the extraction of the alkaloids from the plant with water (time of steeping with one portion of solvent 24 hr, extractants used at the rate of 1 kg of plant to 4 l) it was found that the fourth extract no longer contained cytisine and

the sixth no longer contained pachycarpine, while the other alkaloids (N-methylcytisine, thermopsine, etc.) continued to be extracted. At the stage of the adsorption of the alkaloids by KU-2 ion-exchange resin, after "breakthrough", with a qualitative analysis of the solution issuing from the column every hour, almost all the main alkaloids present in the extract were detected, but the investigation of this process is continuing. At the stage of the desorption of the alkaloids from the sorbent by alkaline methanol, the qualitative composition of the alkaloids in the eluates taken every hour was again checked. In this case, the cytisine was extracted far more rapidly, i.e., it could no longer be detected by the method used even in the seventh sample of eluate. Analysis of the subsequent sample showed that the remaining alkaloids and small traces of pachycarpine were continuing to pass into the eluting solution.

No.	System	Cytisine	N-Methyl-cytisine	Thermopsine	Pachycarpine	
		R_f				
1	Benzene–methanol (1 : 1)	0.24	0.57	0.66	0.12	*
2	Ethanol–chloroform (1 : 5)	0.23	0.46	0.65	0.13	
3	Acetone–ethanol (1 : 2)	0.18	0.37	0.59	0.05	
4	Isopropanol–chloroform (5 : 2)	0.14	0.27	0.61	0.06	
5	Benzene–methanol (8 : 1)	0.38	0.61	0.80	0.21	**
6	Acetone–water–ethyl acetate–benzene (6 : 1 : 2 : 2)	0.22	0.54	0.71	0.50	
7	Ethyl acetate–benzene–methanol (4 : 5 : 1)	0.31	0.81	0.90	0.41	
8	Cyclohexane–ethanol (5 : 1)	0.10	0.25	0.40	0.42	

*Silica gel-gypsum (9 : 1). **Alumina-gypsum (9 : 1)

Thus, the use of thin layer chromatography for the qualitative monitoring of the stages of the industrial process for the production of alkaloids from Th. alterniflora permits the optimum conditions for the performance of the industrial operations to be selected.

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ALKALOIDS OF HAPLOPHYLLUM DUBIUM ACCOMPANYING FOLIOSIDINE

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From the epigeal part of H. dubium collected at the end of August 1967, in the flowering stage in the Surkhan Dar'ya region of the Uzbek SSR we have isolated by chloroform extraction 0.75% of total alkaloids (of the weight of the dry plant), and by their separation we have obtained eight alkaloids.

By chromatography on alumina of the nonphenolic fraction we obtained dubamine, haploperine, foliosine [1], foliosidine, and dubinidine, and from the phenolic fraction we obtained haplopine [2], robustine [3], and folifidine [4].

The phenolic alkaloids, and also foliosidine, were obtained from the epigeal part of H. dubium for the first time.

Technical foliosidine [5] was heated in water (1 : 20) at 60–70° C and the solution was separated from the resinous residue and filtered hot. On cooling, a mixture of foliosidine and skimmianine deposited. On repeated crystallization, the sparingly soluble skimmianine was separated from the foliosidine.

The yield of pure foliosidine amounted to 35% and that of skimmianine 45% of the technical product.

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