polarity. The product was crystallized from the two-phase methanol—ethyl acetate—water—petroleum ether (2:2:3:3) system. This gave the individual glycoside with mp 169-170/255-261°C, $[\alpha]_D^{20}$ −20.1 ± 2° (c 1.0; ethanol).

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TRITERPENE GLYCOSIDES OF Hedera taurica

VI. STRUCTURES OF HEDEROSIDES G, H_1, H_2, AND I FROM THE BERRIES OF CRIMEAN IVY

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We have isolated from Crimean ivy berries in addition previously known triterpene glycosides — 3-O-α-L-arabinopyranosyl-28-O-[O-α-L-rhamnopyranosyl-(1 → 4)-O-β-D-glycopyranosyl-(1 → 6)-β-D-glucopyranosyl]hederagenin, 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranosyl]-28-O-[O-α-L-rhamnopyranosyl-(1 → 4)-O-β-D-glucopyranosyl-(1 → 6)-β-D-glycopyranosyl]hederagenin, the new triterpene glycosides hederoside H_2-3-O-[O-β-D-glycopyranosyl-(1 → 2)-β-D-glycopyranosyl-(1 → 2)-β-D-glucopyranosyl]-28-O-[O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl]oleanolic acid- and hederoside I-3-O-[O-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl]-28-O-[O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl]hederagenin. Details of their ^{13}C NMR spectra are given.

We have previously studied the weakly polar triterpene glycosides of the berries of crimean ivy Hedera taurica Carr., family Araliaceae [1-3]. In the present paper we describe the isolation and determination of the structures of glycosides of medium polarity which have been called, in order of increasing polarity, hederosides G, H_1, H_2, and I.

For the isolation of these glycosides, the berries were subjected to boiling with the aim of denaturing the enzymes, and were comminuted and extracted with aqueous ethanol. The extract was evaporated, and the residue was diluted with water and was extracted successively with chloroform to eliminate weakly polar substances and with butanol, into which the triterpeneglycosides of medium polarity passed together with phenolic compounds. The preliminary separation of the glycosides and their freeing from phenolic compounds was carried out by reversed-phase chromatography on silica gel with grafted-on heptyl groups [4]. Under these conditions, free sugars, phenolic compounds, and glicosides I, H, and G, were eluted successively. The latter were additionally purified by chromatography on silica gel.

TLC analysis of the acetates of the glycosides showed that glycosides G and I were individual compounds, while the acetate of glycoside H contained two components — H_1 and H_2. Additional purification of hederosides G and I and the separation of hederosides H_1 and H_2 were achieved by the chromatography of their acetates on silical gel, followed by deacetylation.

The complete acid hydrolysis of the hederosides permittted the identification as their aglycons of hederagenin for glycosides G, H_1, and I. and oleanolic acid for glycoside H_2. The carbohydrate composition of hederosides G and H_1 was represented by arabinose, rhamnose, and glucose, and that of hederoside H_2 and I by glucose.

The alkaline hydrolysis of the hederosides gave progenins the structures of which it was possible to establish by comparing their chromatographic mobilities with glycosides of

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TABLE 1. Chemical Shifts of the Signals of the ^{13}C Atoms of the Aglycon Moieties of Hederosides G (I), H_1 (II), H_2 (III), and I (IV) (δ, ppm, 0 – TMS; C_5D_5N)

C-atom	Chemical shift				C-atom	Chemical shift			
	I	II	III	IV		I	II	III	IV
1	39,0	39,1	39,0	38,9	16	24,0	23,9	23,8	23,9
2	26,2	26,1	26,7	26,1	17	46.4	46,3	46,5	46.4
3	82,2	81,2	89,3	83,2	18	41,8	41,8	41,9	41,8
4	43,6	43,6	39,6	43,5	19	47,2	47,1	47,2	47,2
5	47,7	47,6	56,1	48,3	20	30,9	30,8	30,8	30,8
6	18.4	18,3	18,7	18,4	21	34,1	34,1	34,2	34 2
7	32,7	32,6	33 4	32,7	22	32.9	33.0	32,8	33,0
8	40,1	40,0	40,1	40.1	23	64,5	64,0	28,4	65,5
9	48 3	48,3	48,2	48,4	24	13,8	14,0	16,9	13,6
10	37,1	37,0	37,1	37.0	25	16,4	16,3	15.7	16,2
11	23,5	23,5	23,6	23,5	26	17.7	17,7	17,7	17,7
12	123,1	123.0	123,0	123,0	27	26,2	26,1	26,1	25,9
13	144,3	144,1	144,3	144.3	28	176,7	176,6	176,5	176,6
14	42,3	42,2	42.3	42,3	29	33,3	33,3	33,2	33,2
15	28,4	28,4	28,4	28,4	30	24,0	23,9	23,8	23,8

*The assignment of the signals in (I) between atoms 17 and 19: in (II) between atoms 17 and 19; in (III) between atoms 11 and 16, and 17 and 19; and in (IV) between atoms 11 and 16, and 17 and 19, was made arbitrarily.

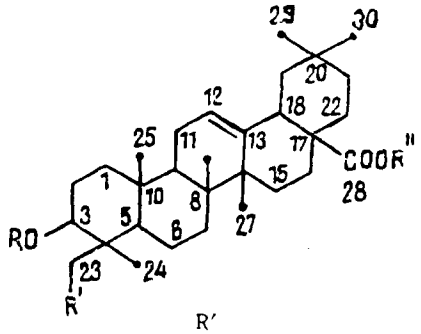
low polarity isolated previously from the ivy berries [1, 3]. Thus, the progenin of hederoside G was identical with hederoside A_3 – i.e., it was 3-O-α-L-arabinopyranosyl-hedergenin; the progenin of hederoside H_1 was identical with hederoside C, consisting of 3-O-[O-α-L-rhamopyranosyl-(L-arabinopyranosyl]hederagenin; and the progenins of hederosides H_2 and 1 were identical with hederosides E_2 and F and were, respectively, 3-O-[O-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl]oleanolic acid and 3-O-[O-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyransyl] hederagenin.

Analysis of the ^{13}C NMR spectra of hederosides G and H_1 (Tables 1 and 2) showed that in the weak-field region there were four signals of anomeric C atoms for glycoside G and five for for glycoside G and five for H_1. In the light of the structures of their progenins, it followed that a trisaccharide fragment was attached to the carboxy group of the aglycon of each glycoside. The assignment of the signals of the carbohydrate residues bound to the C-3 atom of the aglycon in hederosides G and H_1 was made by comparison with literature information for the corresponding progenins [1, 3]. The remaining signals of the carbohydrate moiety at the C-28 atom of the aglycon coincided with literature information for the trisaccharide most frequently found in glycosides of the Araliaceae family: O-α-L-rhamopyranosyl-(1 → 4)-O-β-D-glycopyransyl-(1 → 6)-β-D-glucopyranosyl- [5]. It follows from the facts given that hederoside G is 3-O-α-L-arabinosyl-28-O-[α-L-rhamnopyranosyl-(1 → 4)-O-β-D-glucopyranosyl-(1 → 6)-O-β-D-glycopyranosyl]hederagenin, and hederoside H_1 is 3-O-[O-α-L-rhamnopyranosyl-(1 ← 2)-α-L-arabinopyranosyl]-28-O-α-L-rhamnopyranosyl-(1 → 4)-O-β-D-glycopyranosyl-(1 → 6)-O-β-D-glycopyranosyl]hederagenin. Hederoside G and H_1 are analogs of saponins K_{10} and K_{12} from Hedera rhombea [6], and their complete ^{13}C NMR spectra coincide [6, 7].

Analysis of the ^{13}C NMR spectra of hederosides H_2 and I (Tables 1 and 2) was carried out by deducting the signals of the corresponding progenins [1]. Then the remaining signals of the carbohydrate moiety linked to the carboxy group of the aglycon were assigned, in the light of the results of acid hydrolysis, to the two glucose residues. The subspectrum of this disaccharide coincided completely with that given in the literature for an O-β-D-glycopyranosyl-(1 → 6)-O-β-D-glucopyranosyl- residue [7, 8, 9]. Thus, hederoside H_2 is 3-O-[O-β-D-glucopyranosyl-(1 → 2)-β-D-glycopyranosyl]-28-O-[O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl] oleanolic acid, and hederoside I is 3-O-[O-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl]-28-O-[O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl]hederagenin. Hederosides H_2 and I are new compounds (see on next page.)

TABLE 2. Chemical Shifts of the Signals of the ^{13}C Atoms of the Carbohydrate Moieties of Hederosides G (I), H_1 (II), H_2 (III), and I (IV) (δ, pp,m O – TMS; C_5D_5N)

C-atom	Carbohydrate chain at the C-3 atom of the aglycon				C-atom	Carbohydrate chain at the C-28 atom of the aglycon			
	I	II	III	IV		I	II	III	IV
	Ara-	-Ara-	-Glc-	-Glc-		-Glc-	-Glc-	-Glc-	-Glc-
1	106,7	104,4	105,0	103,7	1	95,8	95,7	95,8	95,7
2	73,1	75,9	83,5	84,0	2	73,9	73,8	74,0	73,9
3	74,7	74,6	78,0	78,0	3	78,6	78,6	78,3	78,2
4	69,6	69,3	72,0	71,4	4	70,8	70,8	71,2	71,1
5	67,0	65,7	78,0	78,0	5	78,1	78,1	78,0	78,0
6			63,0	62,8	6	69,3	69,3	69,8	69,7
			Glc-	-Glc-		-Glc-	-Glc-	-Glc-	-Glc-
1			106,0	105,8	1	104,9	104,9	105,3	105,2
2			76,9	76,6	2	75,3	75,3	75,2	75,1
3			78,3	78,4	3	76,5	76,5	78,7	78,6
4			71,8	71,4	4	78,5	78,4	71,8	71,7
5			78,0	78,2	5	77,2	77,2	78,3	78,2
6			63,0	62,8	6	61,3	61,3	63,0	62,6
		Rha-				Rha-	Rha-		
1		101,7			1	102,9	102,8		
2		72,3			2	72,5	72,5		
3		72,5			3	72,7	72,7		
4		74,1			4	73,9	73,9		
5		69,8			5	70,5	70,4		
6		18,6			6	18,6	18,6		



	R	R′	R″
I	$Ara_p^{1\alpha}\rightarrow$	—OH	$\leftarrow^{\beta1}Glc_p^{6\,\beta1}Glc_p^{4\,\alpha1}Rha_p$
II	$Rha_p^{1\alpha\,2}\rightarrow Ara_p^{1\alpha}\rightarrow$	—OH	$\leftarrow^{\beta1}Glc_p^{6\,\beta1}Glc_p^{4\,\alpha1}Rha_p$
III	$Glc_p^{1\beta\,2}\rightarrow Glc_p^{1?}\rightarrow$	—H	$\leftarrow^{\beta1}Glc_p^{6\,\beta1}Glc_p$
IV	$Glc_p^{1\beta\,2}\rightarrow Glc_p^{1?}\rightarrow$	—OH	$\leftarrow^{\beta1}Glc_p^{6\,\beta1}Glc_p$

EXPERIMENTAL

NMR spectra were obtained on a Bruker WM-250 instrument with a working frequency of 62.9 MHz for ^{13}C atoms at 40°C in pyridine-d_5. Replacement of hydrogen atoms by deuterium atoms was achieved by keeping solutions of the glycosides in a mixture of methanol-d_4 and heavy water for a day. Specific rotations were measured on a SU-4 saccharimeter at λ 589 nm.

TLC monitoring was performed on Silufol plates (Czechslovakia) in the following solvent systems: 1) water-saturated chloroform–methanol (4:1), for glycosides; 2) benzene–acetone (4:1), for glycoside acetates and aglycons; and 3) chloroform–methanol–ammonia (7:3:1), for sugars. The glycosides and aglycons were detected with 10% perchloric acid with the heating of the chromatograms, and the sugars were detected with aniline phthalate. Preparative column chromatography was conducted on silica gel with grafted-on heptyl groups [4] and on silica gel L 100-250 μm (Czechoslovakia).

Isolation of the Glycosides. The ivy berries, collected in March, (2 kg) were treated in boiling water for 15 min and were then ground and extracted with 70% aqueous ethanol. The extract after evaporation to 1/3 of its initial volume was reextracted successively with chloroform and butanol. The combined butanolic extracts were evaporated, giving 50 g of extractive substances. When 10 g of this mixture was separated on silica gel with heptyl groups, elution with water–ethanol (6:4) gave successively 6 g of free sugars and phenolic compounds, 0.5 g of glycoside I, 2.5 g of glycoside H, and 1.0 g of glycoside G. Glycosides

G, H, and I were additionally chromatographed on silica gel L with elution by chloroform–methanol (7:3) that had been saturated with water.

The acetylation of glycosides G, H, and I was effected with acetic anhydride in pyridine (1:1, 20°C, 12 h), followed by evaporation to dryness with the addition of benzene. The purification of the acetates of glycosides G and I and the preparative separation of the components of the acetates of glycoside H–(H_1 and H_2) were performed on silica gel L with elution by solvent system 2. This gave: 0.9 g of the acetate of hederoside G, mp 155-159°C (ethanol); 1.9 g of the acetate of hederoside H_1, mp 158-161°C (ethanol); 0.3 g of the acetate of hederoside H_2, amorphous; and 0.4 g of the acetate of hederoside I, mp 146-148°C (ethanol).

Deacetylation was performed by treating the hederoside acetates with a 0.01 N solution of sodium methanolate in absolute methanol (50°C, 5 h) followed by neutralization with the cation-exchanger KU-2-8 in the H^+-form. This gave: hederoside G (I), $[\alpha]_D^{20}$ + 8° (c, 1.6; pyridine); according to the literature [6]; $[\alpha]_D$ + 10.2 (pyridine); heteroside H_1 (II), $[\alpha]_D^{20}$ - 11° (c, 3.8; pyridine; according to the literature [6]; $[\alpha]_D$–8° (pyridine); hederoside H_2 (III), $[\alpha]_D^{20}$ + 4° (c, 2.2; pyridine); and hederoside I (IV), $[\alpha]_D^{20}$ + 15° (c, 4.1; pyridine).

Acid hydrolysis was performed with 2 N trifluoroacetic acid in water–dioxane (1:1, 100°C, 2 h). With the aid of TLC, in the hydrolysates from (I) and (II) arabinose, rhamnose, glucose and hederagenin were identified; for (III), glucose and oleanolic acid; and for (IV), glucose and hederagenin.

Alkaline hydrolysis was carried out with 10% caustic potash in water–methanol (1:1, 100°C, 2 h). After neutralization with dilute sulfuric acid, the progenins were extracted with chloroform. Compounds (I), (II), (III), and (IV) yielded progenins having chromatographic mobilities identical with those of hederosides A_3, C, E_2, and F [1, 3], respectively.

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