TRITERPENE GLYCOSIDES OF Hedera taurica.

IV. STRUCTURE OF HEDEROSIDES A_1, A_2, D_1, AND D_2 FROM THE BERRIES OF CRIMEAN IVY

A. A. Loloiko, V. I. Grishkovets,
A. S. Shashkov, and V. Ya. Chirva

UDC 547.918:543.422

New triterpene glycosides have been isolated from the berries of Crimean ivy Hedera taurica Carr. (family Araliaceae) – hederoside A_1 (methyl ester of 3-O-β-D-glucopyranosylhederagenin) and hederoside D_1 3-O-[O-β-D-glucopyranosyl]-(1→2)-β-D-glucopyranosyl]hederagenin and also the known glycosides 3-O-β-D-glucopyranosyloleanolic acid and 3-O-[O-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin. The structures of these compounds were established on the basis of the results of chemical methods and ^1H and ^{13}C NMR spectroscopy.

In the present paper we describe the establishment of the structures of minor glycosides A_1, A_2, D_1, and D_2 from Hedera taurica berries.

We have described the isolation of hederosides A_1 and A_2 previously [1]. Analysis of the products of the acid hydrolysis of hederoside A_1 (I) showed the presence of glucose in the carbohydrate moiety and hederagenin methyl ester as the aglycon. The ^{13}C NMR spectrum of glycoside A_1 agreed completely with that of the methyl ester 3-O-β-D-glucopyranosylhederagenin obtained previously from hederoside B by treating it with diazomethane [1]. The R_f values of hederoside A_1 acetate and of the acetylated methyl ester of hederoside B also coincided. It is obvious that hederoside A_1 is the previously unisolated natural methyl ester of 3-O-β-D-glucopyranosylhederagenin.

According to the results of acid hydrolysis and PMR spectroscopy, hederoside A_2 (II) contained residues of glucose and oleanolic acid in a ratio of 1:1. The value of the SSCC $J_{1,2}$ corresponded to the β-configuration of the glycosidic bond. The physical constants of this glycoside agreed with those of oleanolic acid 3-O-β-D-glucopyranoside isolated from various plants [2-6].

Acetylation and TLC analysis of the acetate of glycoside D [1] showed that it consisted of two components – D_1 and D_2. By the preparative separation of the acetates on silica gel followed by deacetylation we obtained the glycosides, which have been called hederosides D_1 (III) and D_2 (IV).

The acid hydrolysis of hederoside D_1 showed the presence in it of residues of glucose and of hederagenin methyl ester. The ^{13}C NMR spectra of hederoside D_1 and of the methyl ether of hederoside F [1] were practically identical. The chromatographic mobilities of the acetates of hederoside D_1 and of the methyl ester of hederoside F coincided completely. Thus, hederoside D_1 is the previously unisolated natural methyl ester of 3-O-[O-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl]hederagenin.

On the acid hydrolysis of hederoside D_2, glucose, arabinose, and hederagenin were identified. The chemical shifts of the signals of the C atoms of the aglycon in the ^{13}C NMR spectrum of glycoside D_2 (Table 1) coincided with those given in the literature [7]. It follows from the chemical shifts of the C atoms of the hederagenin residue that the carbohydrate chain was attached at the C-3 atom of the aglycon. The chemical shifts of the C atoms of the carbohydrate moiety (see Table 1) coincided with those for the disaccharide fragment O-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl [8]. Consequently, hederoside D_2 is 3-O-[O-β-D-glucopyranosyl-(1→2)-α-L-arabinosyl]hederagenin. A glycoside of identical structure has been isolated previously from a number of plants [8-11],

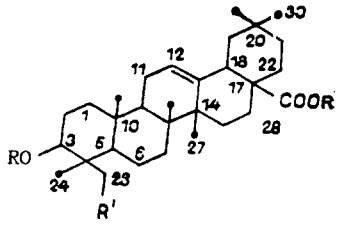
M. V. Frunze Simferopol' State University. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 228-230, March-April, 1990. Original article submitted May 3, 1989.

 0009-3130/90/2602-0184$12.50

TABLE 1. Chemical Shifts of the Signals of the ^{13}C Atoms of Hederosides A_1 (I), D_1 (III), and D_2 (IV) (δ, ppm, 0 – TMS; C_5D_5N)

C atom	Chemical shift			C atom	Chemical shift			C atom	Chemical shift		
	I	III	IV		I	III	IV		I	III	IV
1	38.8	38,7	38,8	16	23,9	23,8	23 7	O-CH_3	51,7	51,5	
2	25,9	25,9	26,0	17	46.1	46,1	46.4				
3	82,3	83,0	82,2	18	41,9	41,9	42,0	1′	105,8	103,7	104,0
4	43.5	43 5	43,5	19	47,0	47,0	46,7	2′	75,8	84,1	81.3
5	47,7	48,1	48,0	20	30,9	30,8	31.0	3′	78,7	77,9	73.7
6	18,3	18.3	18,2	21	34,1	34,0	34,2	4′	71,7	74,4	68,3
7	32,9	32,9	33,0	22	33 2	32,9	33,2	5′	78,3	78,0	64,9
8	39,8	39,8	39.7	23	64,8	65,4	65,0	6′	62,9	62,8	
9	48,1	48 3	48,1	24	13 8	13 5	13,7				
10	37.0	37,0	37,0	25	16,2	16.1	16,0	1″		105,9	106,0
11	23,5	23 5	23,7	26	17.3	17,3	17,5	2″		76 7	76.3
12	122,9	122,9	123,0	27	26 3	26,2	26.2	3″		78,5	78,3
13	144,3	144,2	144,2	28	178 1	178,1	176 5	4″		71,4	71,4
14	42,1	42,0	42,2	29	33 2	33,1	33,2	5″		78,2	78,2
15	28,2	28,2	28,4	30	23,8	23,7	23 7	6″		62,6	62,5

R	R′	R″
I. β-*D*-Glc_p -	—OH	—CH_3
II. β-*D*-Glc_p -	- H	—H
III. β-*D*-Glc_p - (1 → 2)-β-*D*-Glc_p -	—OH	—CH_3
IV. β-*D*-Glc_p (1 → 2)-α-*L*-Ara_p -	—OH	—H



EXPERIMENTAL

NMR spectra were recorded on a Bruker WM-250 instrument using solutions in pyridine-d_5 at 40°C with TMS as internal standard. Specific rotations were measured on a SU-4 polarimeter at λ = 589 nm. The conditions for acid hydrolysis [12] and for deacetylation [1] have been described previously. TLC analysis was conducted on Silufol plates in the solvent systems benzene–acetone (4:1) for the aglycons and the glycoside acetates and butanol–pyridine–25% ammonia (7:3:2) or chloroform–methanol–25% ammonia (7:3:2) for the sugars. To detect the aglycons and glycosides we used 10% perchloric acid, and for the sugars aniline phthalate.

Hederoside A_1 (I), $[\alpha]_D^{20}$ + 40° (c 5.0; pyridine) was obtained by the deacetylation of the acetate of A_1 [1]. Glucose and hederagenin methyl ester were identified in an acid hydrolyzate by the TLC method.

Hederoside A_2 (II), $[\alpha]_D^{20}$ + 52° (c 3.2; methanol), 245-250° (ethanol) was obtained by the deacetylation of the acetate of A_2 [1]. After the acid hydrolysis of (II), glucose and oleanolic acid were identified by TLC analysis. PMR spectrum of (II) (250 MHz, C_5D_5N, δ, ppm: 0 – TMS): 4.94 (d, $J_{1,2}$ = 8.0 Hz, H-1'); 4.09 (t, $J_{2,3}$ = 8.5 Hz, H-2'); 4.14-4.29 (m, H-3', H-4'); 3.69 (m, H-5'); 4.59 (dd, $J_{5,6A}$ = 2.5 Hz, $J_{6A,6B}$ = 12.0 Hz, H-6'A); 4.41 (dd, $J_{5,6B}$ = 5.5 Hz, H-6'B); 3.38 (dd, $J_{3,2a}$ = 12.0 Hz, $J_{3,2e}$ = 4.5 Hz, H-3); 5.47 (br.t, $J_{11,12}$ = 3.8 Hz, H-12); 0.7-1.4 (m, CH_3, CH_2, and CH groups of the aglycon).

Hederoside D [1] was acetylated with acetic anhydride in pyridine (1:1, 20°C, 12 h). TLC analysis showed the presence of two components – the acetates of D_1 with R_f 0.5 and of D_2 with R_f 0.6. Preparative separation of the acetates of D_1 and D_2 was performed on silica gel L 40/100 μ with elution of the benzene–acetone (9:1) solvent system. Deacetylation gave hederoside D_1 (III), $[\alpha]_D^{20}$ + 32° (c 4.0; pyridine) and D_2 (IV), $[\alpha]_D^{20}$ + 40° (c 2.6; pyridine). By TLC analysis residues of glucose and hederagenin methyl ester were identified in (III) and residues of glucose, arabinose, and hederagenin in (IV).

LITERATURE CITED

1. A. A. Loloiko, V. I. Grishkovets, A. S. Shashkov, and V. Ya. Chirva, Khim. Prir. Doedin., 721 (1988).
2. V. Ya. Chirva, P. K. Kintya, and V. N. Mel'nikov, Khim. Prir. Doedin., 297 (1971).

3. T. A. Badalbaeva, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prior. Soedin., 635 (1973).
4. T. Tomimori and H. Kizu, J. Pharm. Soc. Jpn., 99, 92 (1979).
5. L. G. Kretsu and G. V. Lazur'evskii, Khim. Prir. Soedin., 272 (1970).
6. L. P. Vecherko, É. P. Zinkevich, N. I. Libizov, and A. I. Ban'kovskii, The Search for New Biologically Active Substances [in Russian], Moscow (1970), p. 169.
7. H. Kizu and T. Tomimori, Chem. Pharm. Bull., 30, 3340 (1982).
8. B. Domon and K. Hostettman, Helv. Chim. Acta, 66, No. 2, 422 (1983).
9. Z. S. Kemoklidze, G. E. Dekanosidze, O. D. Dzhikiya, M. M. Vugal'ter, and É. P. Kemertelidze, Khim. Prir. Soedin., 788 (1982).
10. R. Higuchi and T. Kawasaki, Chem. Pharm. Bull, 24, 1021 (1976).
11. L. I. Strigina, T. M. Remennikova, A. P. Shchedrin, and G. B. Elyakov, Khim. Prir. Soedin., 303 (1972).
12. A. A. Loloiko, V. I. Grishkovets, A. S. Shashkov, and V. Ya. Chirva, Khim. Prir. Soedin., 379 (1988).

TRITERPENE GLYCOSIDES OF Hedera taurica.

V. STRUCTURE OF HEDEROSIDES C AND E_1 FROM CRIMEAN IVY BERRIES

V. I. Grishkovets, A. A. Loloiko,
A. S. Shashkov, and V. Ya. Chirva

UDC 547.918:543.422

A description is given of the isolation from the berries of Crimean ivy Hedera taurica Carr. (family Araliaceae) and the determination of their structures on the basis of chemical transformations and spectral characteristics of two triterpene glycosides – the known 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin and the new hederoside E_1 which is 3-O-[O-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl]erythrodiol.

Continuing a study of the saponins from the berries of Crimean ivy Hedera taurica Carr. (family Araliaceae) we have established the structures of hederosides C and E_1.

The isolation of hederosides C and E_1 has been described previously [1]. The acid hydrolysis of hederoside C showed the presence in its molecule of residues of hederagenin, arabinose, and rhamnose. Tauroside E, isolated from ivy leaves, has a similar chemical composition [2]. The physical constants and chromatographic mobilities of hederoside C and tauroside E coincided completely. The structure of hederoside C was confirmed by NMR spectroscopy. The ^{13}C NMR spectra of hederoside C and tauroside E were practically identical. Consequently, hederoside C is 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin.

In the products of the acid hydrolysis of hederoside E_1, obtained by the deacetylation of the acetate of E_1 [1], glucose was identified, and an aglycon not agreeing in chromatiographic mobility with hederagenin or oleanolic acid – the predominating aglycons of the triterpene glycosides of Crimean ivy – was detected.

The IR spectrum of hederoside E_1 contained the absorption bands ν_{OH}, ν_{CH}, $\nu_{C=C}$, δ_{CH_3}, and ν_{C-O}, but lacked absorption band $\nu_{C=O}$ that is characteristic for aglycons with a carboxy group.

In an analysis of the PMR spectrum of the acetate of hederoside E_1, doublet signals with δ 4.71 and 4.46 ppm belonging to anomeric protons showed the presence of two sugar residues. In the light of the results of the acid hydrolysis, hederoside E_1 undoubtedly contains two glucose residues. It follows from the values $J_{1,2}$ = 7.7 and 8.0 Hz that both monosaccharide residues have the β-configuration of the anomeric center. By using the method of selective

M. V. Frunze Simferopol' State University. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 230-234, March-April, 1990. Original article submitted June 3, 1989.

 0009-3130/90/2602-0186$12.50