Isolation of trans-Diversin

The resin (30 g) was chromatographed on a column (2.5 × 100 cm) of alumina (activity grade II). The column was eluted with hexane, hexane–chloroform in ratios of 9:1, 7:1, 6:1, 5:1, and 4:1, and then with chloroform. The fractions eluted by the hexane–chloroform (5:1) mixture yielded 150 mg of a crystalline substance, $C_{19}H_{20}O_4$, with mp 96-98°C (from aqueous ethanol), R_f 0.41, readily soluble in chloroform, ethyl acetate and acetone.

SUMMARY

1. A new goemetric isomer of diversin has been isolated from the resin of the roots of *Ferula litwinowinanana* K.-Pol. The structure of 7-(3',7'-dimethyl-5'-oxoocta-3'E,6'-dienyloxy)coumarin has been proposed for it.

2. The configuration of diversin has been established as 7-(3',7'-dimenty1-5'-oxoocta-3'Z,6'-dienyloxy)coumarin and its identity with 5'-oxo-$\Delta^{3'}$-aurapten has been demonstrated.

LITERATURE CITED

1. V. Yu. Bagirov, V. I. Sheichenko, N. F. Mir-Babaev, and M. G. Pimenov, Khim. Prir. Soedin., 114 (1984).
2. N. F. Mir-Babaev and S. V. Serkerov, Khim. Prir. Soedin., 110 (1986).
3. F. R. Melek, Ahmed A. Ahmed, J. Gershenzon, and T. Mabry, Phytochemistry, 23, 2573 (1984).
4. J. A. Pople, W. G. Schneider, and J. H. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York (1959), p. 440.
5. W. Herz and P. Kulanthaivel, Phytochemistry, 24, 173 (1985).
6. P. Molnar, J. Szabolcs, and L. Radics, Phytochemistry, 25, 195 (1986).
7. V. V. Kiseleva and M. O. Karryev, Khim. Prir. Soedin., 344 (1975).
8. R. H. Bible, Interpretation of NMR Spectra, Plenum Press, New York (1965), p. 18.
9. F. Bohlmann and M. Grenz, Chem. Ber., 109, 1584 (1976).

TRITERPENE GLYCOSIDES OF *Hedera taurica*

I. STRUCTURE OF TAUROSIDE E FROM THE LEAVES OF *Hedera taurica*

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

UDC 547.918.543.422.25

The structure of tauroside E — the predominating triterpene glycoside from the leaves of Crimean ivy, *Hedera taurica* Carr. has been established by ^1H and ^{13}C NMR spectroscopy using nuclear Overhauser effects. It is 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin.

The high physiological activity of triterpene glycosides from plants of the family Araliaceae is generally known [1]. The aim of the present series of investigations was to study the saponins of *Hedera taurica* Carr. (Crimean ivy), the only representative of this family in the Crimea.

The triterpene glycosides of ivy have been named in order of increasing polarity tarosides A, B, C, D, E, F, G, and H. In the present paper we describe the determination of the structure of tauroside E — one of the predominating saponins of ivy leaves — by ^1H and ^{13}C NMR-spectroscopic methods.

From the results of an analysis of an acid hydrolysate of tauroside E, rhamnose and arabinose were identified as the sugars by paper chromatography, and hederagenin as the aglycon by thin-layer chromatography.

M. V. Frunze Simferopol' State University. Translated from Khimiya Prirodnykh Soedenenii, No. 3, pp. 363-366, May-June, 1987. Original article submitted September 25, 1986; revision submitted December 15, 1986.

0009-3130/87/2303-0299$12.50

TABLE 1. Chemical Shifts of the Signals of the Protons of Tauroside E in the Weak-Field Region of the Spectrum (δ, ppm, O-TMS; C_5D_5N)

Proton	Chemical shift and multiplicity	SSCC, Hz
1′	4,98 d	$J_{1,2}=6,0$
2′	4,44 dd	$J_{2,3}=7,0$
3′		
4′	4,0—4,2 m	
5′e		
23		
5′a	3,59 dd	$J_{4,5a}=2,0$
		$J_{5a,5e}=9,0$
1″	6,12 d	$J_{1,2}=1,4$
2″	4,60 dd	$J_{2,3}=3,3$
3″	4,52 dd	$J_{3,4}=8,8$
4″	4,16 t	$J_{4,5}=8,8$
5″	4,54 dq	$J_{5,6}=6,0$
6″	1,52 d	$J_{6,5}=6,0$
3	3,14 dd	$J_{3,2a}=12,7$
		$J_{3,2e}=4,0$
12	5,33 br.t	
23	3,61 d	$J_{AB}=10,5$

Note. d — Doublet; t — triplet; q — quartet; m — multiplet; br. — broadened; a — axial; e — equatorial.

In the weak-field region of the PMR spectrum (3.0-6.5 ppm) signals from 15 considerably descreened protons were observed (Table 1). In the strong-field region of the spectrum against a background of the methylene hump (the skeletal protons of the hederagenin residue) there were six singlet signals from methyl groups of the hederagenin residue and one three-proton doublet (1.52 ppm) with a spin—spin coupling constant (SSCC) of 6.0 Hz undoubtedly belonging to the protons at C-6" of a rhamnose residue. Thus, the general form of the spectrum corresponds to the monomeric composition rhamnose—arabinose—hederagenin (1:1:1).

The assignment of the lines in the ^1H NMR spectrum was made with the aid of selective homonuclear double resonance and by the observation of nuclear Overhauser effects (NOEs). Two signals in the weak-field region of the spectrum with δ 6.12 and 4.98 ppm have a doublet structure and can belong only to the anomeric protons of sugar residues, while a pseudo-triplet signal with δ 5.33 ppm obviously belongs to the proton at C-12 of the hederagenin residue. An experiment with selective homonuclear double resonance confirmed these assignments: the irradiation of the protons with δ 6.12 and 4.98 ppm gave a response in the difference spectrum in the low-frequency region (suppression of the spin—spin coupling of the protons at C-1' and C-2' and at C-1" and C-2" of the arabinose and rhamnose residues), while irradiation of the proton with δ 5.33 ppm gave a response in the difference spectrum in the region of the methylene hump (decoupling from the C-11 protons of hederagenin). It also followed from the difference spectrum that the proton with δ 3.14 ppm had a spin—spin link only with the skeletal methylene protons of the hederagenin residue, and from the nature of the splitting and the magnitudes of the SSCCs it belonged to the proton at C-3. The assignment of the signal with 3.61 ppm to the protons at C-23 at the hederagenin residue was made similarly.

The successive application of the method of double homonuclear resonance permitted the determination of all the signals belonging to the rhamnose residue. The nature of the splitting of the signals and the values of the SSCCs unambiguously determined the orientation of the protons and could correspond only to an α- or β-rhamnopyranosyl residue.

TABLE 2. Chemical Shifts of the Signals of the ^{13}C Carbon Atoms of Tauroside E

Carbon atom	Chemical shift	Carbon atom	Chemical shift	Carbon atom	Chemical shift	SSSC, $J_{C,H}$, Hz
1	39,1	16	23,9	1′	104,1	162,8
2	26,2	17	46,5	2′	76,0	
3	81,2	18	42,1	3′	74,2	
4	43,6	19	46,7	4′	69,8	
5	47,8	20	31,0	5′	65,1	
6	18,3	21	34,3	1″	101,6	170,2
7	33,0	22	33,3	2″	72,3	
8	39,9	23	64,4	3″	72,5	
9	48,3	24	13,9	4″	74,2	
10	37,0	25	16,1	5″	69,7	
11	23,9	26	17,5	6″	18,5	
12	122,7	27	26,2			
13	144,9	28	179,0			
14	42,3	29	33,3			
15	28,4	30	23,9			

Of the second series of signals, including the signal of an anomeric proton at 4.98 ppm it was possible to determine the position and the nature of the splitting only for that from the proton at C-2', since the signals of the other protons were present in a weakly-resolved region of the spectrum. Here, the greater values of the SSCCs $J_{1,2}$ and $J_{2,3}$ unambiguously show the axial orientation of the H-1', H-2', and H-3' protons, which agrees completely with the α-arabino configuration of the second sugar residue.

Experiments using NOE showed that when the H-1' of the arbinopyranosyl residue was irradiated, additional NOEs were observed for the signal of the proton with δ 3.59 ppm, as well as for those of the H-2' and H-3' protons. It follows from this that this signal must be assigned to the H-5'*a* axial proton (1,3-diaxial interaction). Then the nature of the splitting of the signal of this proton becomes understandable: the larger of the constants (9.0 Hz) undoubtedly is the geminal constant ($J_{5a,5e}$), and the smaller one is the vicinal constant ($J_{4,5a}$). The small value of $J_{4,5a}$ indicates the axial-equatorial arrangement of the H-4' and H-5'*a* protons and, consequently, the axial orientation of the hydroxy group at C-4' thus definitively confirming that this residue is an α-arabinopyranose residue.

In the difference NOE spectrum, on the prior saturation of the H-1" proton of the rhamnopyranose residue enhancements were observed of the signals of the H-2" proton (by 6%) and of the H-2' proton of the arabinonose residue (by 5%). Consequently, the protons at C-1" of the rhamnose residue and at C-2' of the arabinose residue are spatially close, which permits an unambiguous conclusion of the sequence of the linkage of the sugar residues and the type of substitution in them.

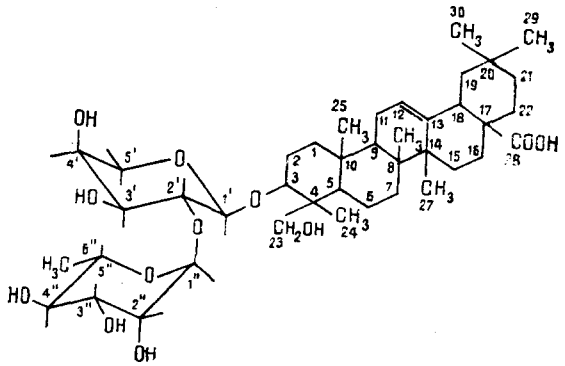
Thus, according to the results of PMR spectroscopy, the carbohydrate moiety of tauroside E consists of rhamnopyranosyl-(1→2)-α-arabinopyranose.

It was possible to assign the majority of signals in the weak-field region of the ^{13}C NMR spectrum by the method of ^{13}C-^{1}H selective heteronuclear double resonance (Table 2). The signals of the hederagenin residue were assigned by comparison with the spectrum of hederagenin obtained under analogous conditions [2].

Since there were no signals in the 79-84 ppm region (apart from that of the C-3 atom of the hederagenin residue) which is characteristic for C-atoms of sugars in the furanose form [3], it was possible to conclude that the sugar residues were present in the pyranose form. This was also confirmed by the values of the SSCCs J_{H_i,H_j}. The downfield shift of the C-3 signal of the hederagenin residue as compared with unsubstituted hederagenin [2] shows that it was the hydroxy group on just this carbon atom that participated in the formation of the glycosidic bond.

The recording of the spectrum of the saponin under conditions retaining the spin–spin coupling of the carbon and hydrogen atoms permitted the SSCC $J_{C,H}$ for the signals of the anomeric carbon atoms to be determined. For C-1" of the rhamnopyranosyl residue the SSCC was 170.2 Hz, which unambiguously determined the axial position of the substituent (oxygen atom at C-1") [4] and, consequently, the α-configuration of the glycosidic bond. For C-1' of the

arabinopyranosyl residue the SSCC, amounting to 162.8 Hz, corresponded to the equatorial position of the oxygen atom at C-1' [4], which, in the light of the $^4C_1$-conformation of an arabinopyranose ring of the L-series (or $^1C_4$ for the D-series) determined the α-configuration of the glycosidic center.



The downfield shift of the C-2' signal of the arabinopyranose residue by 3.8 ppm as compared with unsubstituted methyl α-L-arabinopyranoside (72.2 ppm) [2] confirmed once more the existence of a 1→2-bond between the rhamnose and arabinose residues.

The final confirmation of the structure of tauroside E as 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin followed from the practically complete agreement of the subspectrum of the rhamnopyranose residue in the spectrum of the saponin with that of methyl α-L-rhamnopyranoside [2] and the chemical shifts of the signals of the carbon atoms of the hederagenin and arabinopyranose residues with the spectra of prosapogenins from *Clematis chinenssi* Osbeck [5], where the residues mentioned have a perfectly similar closest environment and type of substitution.

EXPERIMENTAL

The NMR spectra were obtained on a Bruker WM-250 instrument for solutions in pyridine-d_5 at 40°C with the TMS as internal standard. In the ^1H NMR difference spectra the intensity of the signal of the previous saturated proton was taken as 100%, and the NOEs of the enhanced signals were referred to this value.

The comminuted leaves of Crimean ivy as the raw material were extracted with a mixture of isopropanol and acetone (3:1). The combined extractive substances obtained were separated by chromatography on silica gel L with elution by chloroform–methanol–water (9:1:0.5). In addition to glycosides A, B, C, D, and F, the predominating component glycoside E (1% on the crude weight of the leaves) was isolated: mp 235-240°C (chloroform–methanol, 9:1), [α]D +7° (s 3.2; ethanol).

Tauroside E (2 mg) was dissolved in 0.2 ml of dioxane, 0.2 ml of a 2 N aqueous solution of trifluoroacetic acid was added and the mixture was heated in a sealed tube at 100°C for 2 h. Arabinose and rhamnose were identified in the hydrolysate by paper chromatography. The aglycon was identified by the TLC method in comparison with an authentic sample of hederagenin after neutralization of the hydrolysate with 1 N aqueous caustic potash and extraction of the aglycon with chloroform.

SUMMARY

The structure of tauroside E — the predominating triterpene glycoside of Crimean ivy leaves — has been established by ^1H and ^{13}C spectroscopy using nuclear Overhauser effects; it is: 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin.

LITERATURE CITED

1. G. B. Elyakov and Yu. S. Ovodov, Khim. Prir. Soedin., 697 (1972).
2. S. Seo, Y. Tomita, K. Tori, and Y. Yoshimura, J. Am. Chem. Soc., 100, No. 11, 3331 (1978).
3. P. A. J. Gorin and M. Mazurek, Carbohydr. Res., 48, No. 2, 171 (1976).
4. K. Bock, I. Lundt, and C. Pedersen, Tetrahedron Lett., No. 13, 1037 (1973).
5. H. Kizu and T. Tomimori, Chem. Pharm. Bull., 30, No. 3, 859 (1982).