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A NEW TERPENOID COUMARIN trans-DIVERSIN FROM *Ferula Litwinowiana*

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The results are presented of investigations into the structure of a new terpenoid coumarin with the composition $C_{19}H_{20}O_4$ with mp 96-98°C (from aqueous ethanol), differing from diversion by the trans position of one bond. On the basis of spectroscopic (IR and ^{1}H NMR) results, the structure of 7-(3',7'-dimethyl-5'-oxoocta-3'E,6'-dienyloxy)coumarin is proposed for this substance.

Continuing a study of the chemical composition of the roots of *Ferula litwinowiana* K.-Pol. [1, 2], by chromatography on a column of alumina we have isolated a crystalline substance with the composition $C_{19}H_{20}O_4$, mp 96-98°C (aqueous ethanol). In the IR spectrum of the substance in the region of characteristic frequencies there are absorption bands at 1730 and 1715 cm^{-1} (CO groups of a δ-lactone and of a conjugated ketone) and at 1680, 1630, 1520 cm^{-1} (double bonds). A direct comparison of the IR spectra of diversin and the coumarin under investigation showed differences characteristic for isomeric compounds. A mixture of the samples being compared gave a depression of the melting point (it melted at 85-87°C).

The NMR spectrum of the substance isolated had the signals characteristic for a 7-substituted coumarin nucleus: doublets at 7.64 ppm (J = 10 Hz, H-4), 6.24 ppm (J = 10 Hz, H-3), and 7.38 ppm (J = 8.5 Hz, H-5), and a quartet at 6.86 ppm (J_1 = 8.5 Hz, J_2 = 2 Hz, H-6).

The H-8 signal, undergoing allyl interaction with H-6, was superposed on one component of the H-6 doublet and therefore appeared in the form of a broadened singlet at 6.80 ppm. In the NMR spectrum, three-proton singlets of vinylmethyl groups at 1.92, 2.20, and 2.26 ppm, two-proton singlets of vinylmethyl groups at 2.57 ppm (J = 7 Hz) and 4.21 ppm (J = 7 Hz) and one-proton broadened singlets of olefinic protons at 6.09 and 6.15 ppm were similar to the signals of the monoterpene moiety of the diversin molecule. However, the singlet of one

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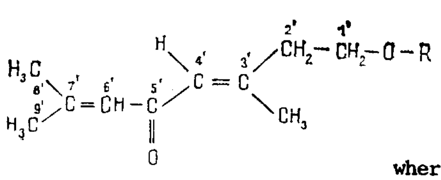
TABLE 1. NMR Spectra of Diversin, 5'-Oxo-$\Delta^{3'}$-aurapten, and the Compound under Investigation

Compound	Chemical shifts at the following atoms (ppm) and multiplicities						
	1'	2'	4'	6'	8'	9'	10'
Diversion	t 4,28 (2 H)	t 3,12 (2 H)	s6,20 (1 H)	s 6,03 (1 H)	s 1,96 (3 H)	s 2,24 (3 H)	s 2,06 (3 H)
5'-Oxo-3'-aurapten	t 4,26 (2 H)	t 3,10 (2 H)	s 6,19 (1 H)	s 6,09 (1 H)	s 1,90 (3 H)	s2,19 (3 H)	s 2,00 (3 H)
Compound under investigation	t 4,21 (2 H)	t 2,57 (2 H)	s6,15 (1 H)	s 6,09 (1 H)	s 1,92 (3 H)	s 2,20 (3 H)	s 2,26 (3 H)

vinylmethyl group was shifted in the downfield direction by 0.20 ppm, while the triplet of one methyl group was shifted in the upfield direction of 0.55 ppm as compared with the analogous signals of diversin. A small diamagnetic shift (by 0.07 ppm) of a second two-proton triplet of a methylene group at 4.21 ppm, of the singlet of an olefinic proton at 6.15 ppm (by 0.05 ppm), of vinylmethyl groups at 1.92 ppm (by 0.04 ppm) and 2.20 ppm (by 0.04 ppm) were observed (Table 1).

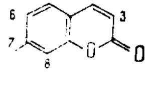
Such NMR-spectroscopic behavior is characteristic for cis and trans isomeric compounds. For example, the signal of the vinylmethyl group of the trans double bond in the NMR spectrum of trans-1,2-secogermacranolide [3] is shifted downfield by 0.18 ppm, that of trans-propenylbenzene [4] by 0.05 ppm, that of N-isobutyldodeca-2E,4E,8Z,10E-tetraenamide [5] by 0.05 ppm, and that of trans-violaxanthin by 0.23 ppm [6] in comparison with the CH_3—C= groups of the corresponding cis compounds. The diamagnetic shift of the singlet of the olefinic proton at 6.15 ppm for the compound under investigation as compared with that of diversin is also due to its trans configuration. The signal of the olefinic proton of trans-1,2-secogermacronanolide and of trans-violaxanthin are shifted similarly as compared with their cis isomers [3, 6]. It is known [3, 4] that the signals of a methylene group vicinal in relation to a trans double bond in the NMR spectrum of a trans compound appear in a comparatively stronger field than the analogous signals of the cis compound. From this point of view, the above-mentioned signal of a methylene group (at 2.57 ppm) of the compound under investigation is located in a stronger field by 0.55 ppm than the signal (triplet at 3.12 ppm) of diversin [2, 7]. As is known [8], the signal of a proton present in the plane of a carbonyl group is shifted to the left (into the region of lower fields), while the signal of a proton located above a carbonyl group is shifted to the right. This apparently also explains the paramagnetic shift of the vinylmethyl group at C-3' and the diamagnetic shift of the olefinic proton at C-4' and of the methylene group of the compound under investigation. Thus, the compound under investigation has the structure of 7-(3',7'-dimethyl-5'-oxoocta-3'E,6'-dienyloxy)coumarin (trans-diversin, I) while to diversin corresponds the structure 7-(3',7'dimethyl-5'-oxoocta-3'Z,6'-dienyloxy)coumarin (cis-diversin, II).

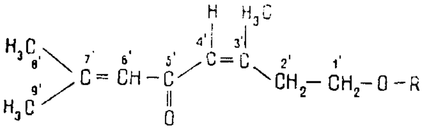
The structure of the trans-diversin (I) coincides with the structure of 5'-oxo-$\Delta^{3'}$-aurapten proposed by Bohlmann and Grenz [9] for a monoterpenoid coumarin isolated from *Macheranthera scanbrella* (Greene) Sbinners. However, a comparison of the NMR spectra of 5'-oxo-$\Delta^{3'}$-aurapten and of cis-diversin (see Table 1) show that they had the same structure.



(I)

where R =





(II)

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrophotometer in paraffin oil, and NMR spectra on a Varian HA-100D spectrometer in $CDCl_3$ with 0 — TMS. Thin-layer chromatography was performed on Silufol UV 254 plates in the hexane—benzene—methanol (5:4:1) system.

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'-dimentyl-5'-oxoocta-3'Z,6'-dienyloxy)coumarin and its identity with 5'-oxo-$\Delta^{3'}$-aurapten has been demonstrated.

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TRITERPENE GLYCOSIDES OF *Hedera taurica*

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

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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 taurosides 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.

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