ARMIN—A NEW COUMARIN FROM *Artemisia armeniaca*

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From the epigeal part of Artemisia armeniaca Lam. we have isolated a new coumarin with the composition $C_{14}H_{16}O_5$ which we have called armin. IR spectrum (Fig. 1): ν_{max} 3520, 3230 (OH), 1740 (C=O of a δ-lactone), 1625 and 1570 cm^{-1} (C=C in conjugation). In the UV spectrum there are two absorption maxima at 262.5 and 322 nm (log ε 4.0323 and 4.1798, respectively).

Armin forms a diacetate (II) with the composition $C_{18}H_{20}O_7$.

Figure 2 gives the NMR spectrum of armin [1]. The assignment of the signals was made on the basis of the analysis of the spectra of the coumarin itself and of its derivatives [1, 2]. In the NMR spectrum of armin the signals of four protons of the coumarin nucleus are located in the 6.2-7.6 ppm region and therefore there are two substituents in this nucleus. In agreement with literature information, the doublets at 6.24 and 7.60 ppm (J = 9.7 Hz) are the signals of the protons at C_3 and C_4, respectively. It follows from this that both substituents are present in the benzene ring. The other two doublets (at 6.82 and 6.93 ppm) are the signals of the protons of a benzene ring in the ortho position of one another, as is shown by their coupling constant (J = 7 Hz). In this case, three variables of the positions of the substituents are possible: I—at C_7 and C_8; I'—at C_5 and C_6; and I''—at C_5 and C_8. The low value of the chemical shift of the H_4 proton (7.60 ppm) excludes the variants with the substituent at C_5 [3], i.e., armin is a 7,8-disubstituted coumarin.

One of the substituents consists of an isoprene unit connected with the coumarin nucleus through oxygen, as follows from an analysis of the NMR spectrum of armin itself and of its diacetate (II). Thus, the 2 H-triplet at 3.62 ppm is the signal of the proteins of a methylene group to which a hydroxyl is attached; in the NMR spectrum of the diacetate, this signal is shifted downfield by 0.46 ppm. The multiplicity of this signal (triplet) shows the presence of a hydroxymethylene grouping at a methylene group, i.e., the side chain has the fragment CH_2-CH_2OH. The multiplet with an intensity of 2 H at 4.20 ppm in the spectrum of (I) and the doublet at 3.95 ppm in the spectrum of (II) are the signals of the protons of a methylene group attached to oxygen linked to a carbon atom of the benzene nucleus. The doublet in the 1.0-ppm region in the spectrum of (I) and the doublet at 0.98 ppm in the spectrum of (II) are the signals of the protons of a secondary methyl group.

The other substituent is a hydroxy group. In the NMR spectrum of armin diacetate, the signals of the protons of an acetoxy group attached to a benzene ring are present in a weaker field (singlet at 2.36 ppm).

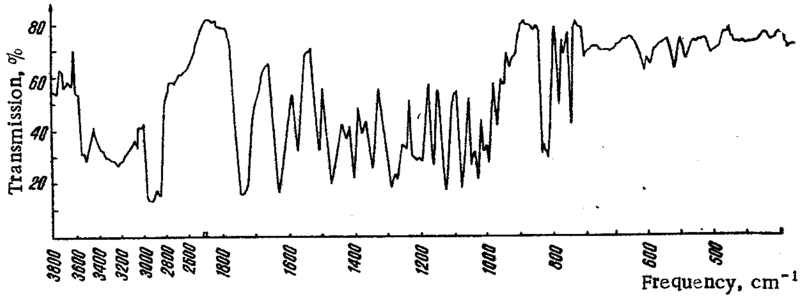

Fig. 1. IR spectrum of armin.

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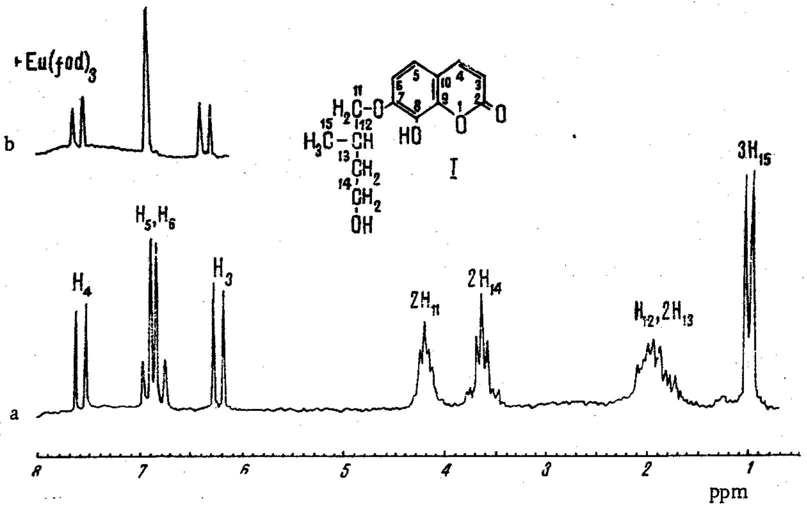


Fig. 2. NMR spectrum of armin without (a) and with (b) the addition of a shift reagent.

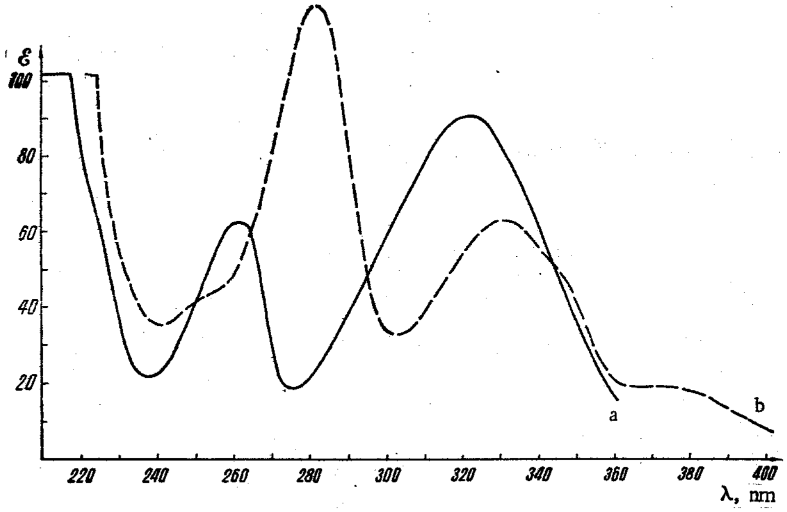


Fig. 3. UV spectrum of armin taken in solution in ethanol (a) and in ethanol with the addition of alkali (b).

The mutual positions of the substituents was shown on the basis of an analysis of the UV spectra of armin taken in solution in ethanol and in ethanol with added alkali (Fig. 3). The UV spectrum of the latter showed a decrease in the intensity of the longwave maximum, which is characteristic for 8-hydroxycoumarins [4, 5], i.e., the hydroxyl in the armin molecule is located at C_8, and the alkoxy group at C_7. Such a position of the substituents is also indicated by the NMR spectrum of armin taken with additions of a chemical shift agent Eu(fod)$_3$. Table 1 gives the values of the shifts $\Delta\delta H$ of the protons of the coumarin nucleus in armin, coumarin, and tavicone [6] relative to the shift of the H_3 proton, which was arbitrarily taken as unity. It follows from this table that the protons of armin show an additional shift in comparison with those of coumarin and tavicone. The large value of the additional shift for one of the protons – H_6 (≈ 0.8 ppm) – shows that this proton is present in the ortho position to the ether grouping and not to the hydroxyl, i.e., the ether grouping is located at C_7 and the phenolic hydroxyl at C_8. The greater shift of the strong-field signal on the addition of the shift reagent permits the signal at 6.82 ppm in the NMR spectrum of armin to be assigned to the H_6 proton. In the NMR spectrum of armin diacetate a downfield shift of the H_5 proton is observed, in complete agreement with its para position to the acetoxy group.

The mass spectra of armin [1] and of its deutero derivative are given in Fig. 4. The presence of the molecular ion in the spectrum of (I) with m/e 264 confirms the empirical formula established for it. The displacement of the molecular ion in the mass spectra of the deutero derivative and the diacetate by 2 and 84 amu,

TABLE 1. Relative Values of ΔEu ($\Delta\delta H_1/\Delta\delta H_3$) in Some Coumarins

Coumarin	Proton					
	1	2	3	4	5	6
Armin	1	0,50	0,40	1,00	—	—
Coumarin	1	0,32	0,23	0,17	0,18	0,33
Tavicone (a 7-O-substituted conmarin)	1	0,31	0,16	0,12	—	0,29

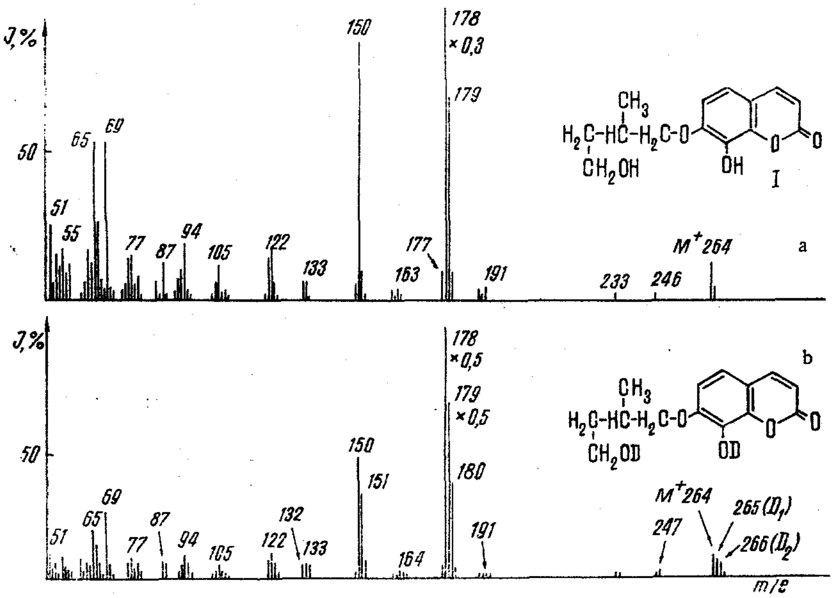


Fig. 4. Mass spectra of armin (a) and of its deutero derivative (b).

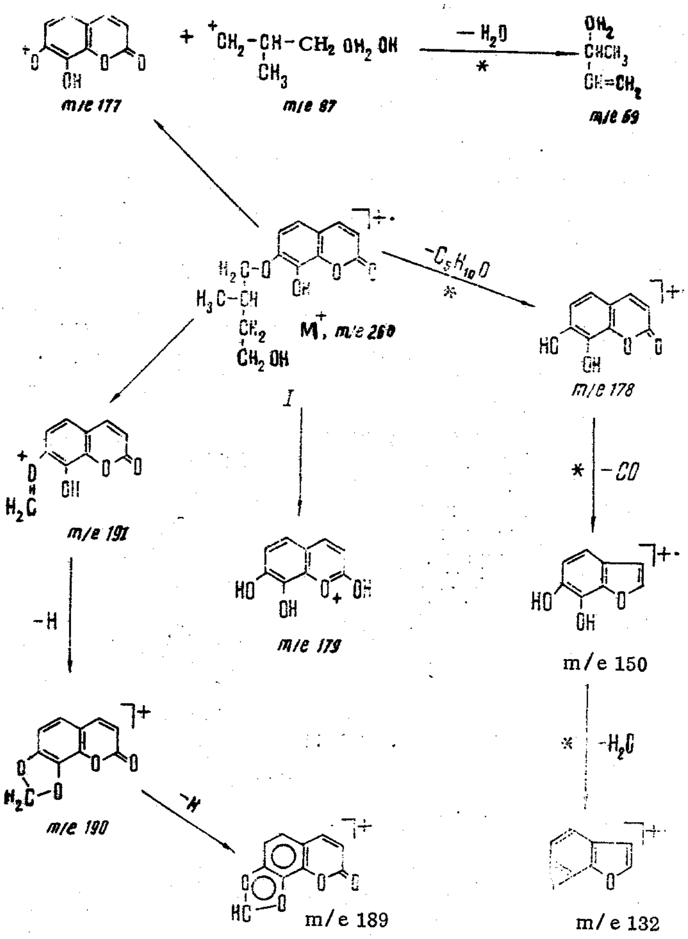
respectively, shows the presence of two hydroxy groups in the armin molecule. The main direction of fragmentation, leading to an ion with m/e 178 (see the Scheme of the decomposition of armin) is characteristic for the fragmentation of ethers of hydroxycoumarins [7, 8] and shows the presence of one of its hydroxy groups in the side chain. The formation of an intense ion $M^+ - CH_2CO$ (m/e 306) in the mass spectrum of (II) is typical for the decomposition of substances containing an acylated hydroxyl of the phenolic type [9, 10]. Consequently, the second hydroxyl in the molecule (I) is attached directly to the coumarin ring. A characteristic feature of the dissociative ionization of (I) in comparison with the decomposition of ethers of 7-hydroxycoumarins studied previously [7, 8] is the low probability of the cleavage of the ether bond with the transfer of two hydrogen atoms to the coumarin ring, which leads to the formation of a fragment of low intensity with m/e 179 (see the Scheme of the decomposition of armin). Furthermore, the ion with m/e 191 formed as a result of a subsidiary direction of the fragmentation of (I) subsequently eliminates two hydrogen atoms. This process can be explained by the formation of a five-membered ring containing the oxygen atoms of both substituents and its subsequent aromatization, which is due to the ortho position of the alkoxy and hydroxy groups in the armin molecule.

EXPERIMENTAL

The IR spectra (mulls in paraffin oil) were taken on a UR-10 spectrometer, the UV spectra (solutions in 96% ethanol) on a Hitachi EPS-3T spectrometer, the NMR spectra on a Varian HA 100D spectrometer using solutions in $CDCl_3$, and the mass spectra on a Varian CH-8 spectrometer.

Isolation of Armin. By water extraction followed by chromatography on KSK silica gel (elution with ether), 1 kg of the epigeal green part of Artemesia armeniaca collected by D. A. Pakaln in July in the Sisian pass in Armenia yielded crystals of armin, $C_{14}H_{16}O_5$, with mp 112-114°C, mol. wt. 264. Yield 0.2%.

Armin Diacetate. A mixture of 0.2 g of armin, 4 ml of pyridine, and 2 ml of acetic anhydride was left at room temperature for 2 h and was then diluted with water and the reaction product was extracted with chloro-



Scheme of the decomposition of armin.

form. The extract was washed with 5% HCl solution and then with water to neutrality, and the solvent was driven off. mp 100–102°C (from ethyl acetate). $C_{18}H_{20}O_7$, mol. wt. 348 (mass spectrometrically). Yield 0.19 g.

IR spectrum, ν_{max} (cm^{-1}): 1730–1750 (C=O of a δ-lactone, $OCOCH_3$), 1620 and 1570 cm^{-1} (C=C in conjugation)

SUMMARY

From the epigeal part of Artemisia armeniaca Lam. we have isolated the new coumarin armin with the composition $C_{14}H_{16}O_5$ and have proposed structure (I) for it.

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