THE STRUCTURE OF PEUCENIDIN

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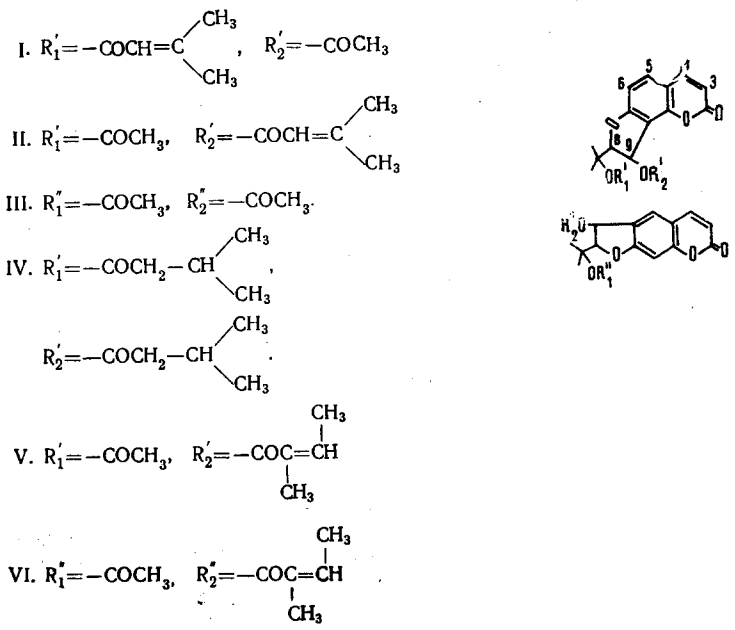
The structure of 9-acetoxy-O-senecionyldihydrooroselol (I), isolated from Ligusticum pyrenaicum Koch. has been established previously [1]. This compound proved to have similar physicochemical properties (Table 1) to those of peucenidin (II) [2, 3]. The NMR spectrum of the latter practically coincided with that of 9-acetoxy-O-senecionyldihydrooroselol (Table 2). However, the mass spectrum of (I) differs somewhat [1] from the mass spectrum of (II) recorded by us. The absence of some fragments with m/e 311 and 271, and others, in the mass spectrum of (I) induced us to study the mass spectra of smyrniorin (III), athamantin (IV), libanotin (V), and smyrnioridin (VI) [4-6] belonging, like peucenidin, to the class of diacyloxydihydrofurocoumarins. As can be seen from Table 3, all the mass spectra of the compounds isomeric with peucenidin contain the same fragments. The absence from the mass spectrum of 9-acetoxy-O-senecionyldihydrooroselol of fragments with m/e 311 and 271, and others shows that incomplete information on the mass spectrum of this compound was given by Bohlmann and Grenz [1].



It is impossible from the NMR spectrum of a compound belonging to the class of diacyloxydihydrofurocoumarins to deduce the position of the acyl residues, and it is necessary to study the NMR spectrum of the intermediate product of methanolysis [1, 6]. The results of a comparison of the mass spectra of (II)-(VI) lead to the same conclusion.

The mass spectra of smyrniorin (III) and athamantin (IV) show that the intensities of the ions with m/e 244, 243 and 229, 227 satisfy the inequalities $I_{244} > I_{243}$ and $I_{229} > I_{227}$. In libanotin (V) and smyrnioridin (VI), these inequalities are reversed. In the mass spectrum of peucenidin (II) the intensities of the ions

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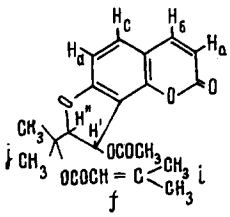
TABLE 1. Main Physicochemical Constants of 9-Acetoxy-O-senecionyldihydrooroselol (I) and Peucenidin (II)

Substance	Empirical formula	M	mp, °C	$[\alpha]_D$, deg	λ_{max}, nm (log ε)
I	$C_{21}H_{22}O_7$	386	123 (ether/petroleum ether)	−45 (t=24°, c 2,25 $CHCl_3$)	244 (3,61); 256 (3,56), 297 (4,00) 318,5 (4,15) (ether)
II	$C_{21}H_{22}O_7$	386	124,5–125,5 (ethanol)	−46 (t=20°, c 1 $CHCl_3$)	246 (3,65); 257 (3,60); 298 (4,03) 318 (4,14) (ether)

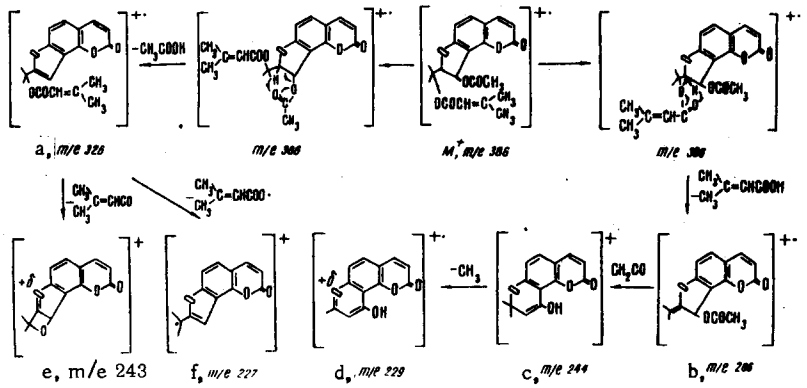
TABLE 2. Values of the Chemical Shifts and Spin–Spin Coupling Constants in the NMR Spectrum of 9-Acetoxy-O-senecionyldihydrooroselol (I) and Peucenidin (II)

Structural formula of (I) and (II)	Chemical shifts, ppm (J, Hz)		
	protons	I	II
	H_a	6,22 (9,5)	6,26 (9,5)
	H_b	7,65 (9,5)	7,65 (9,5)
	H_c	7,45 (8,5)	7,44 (8,5)
	H_d	6,86 (8,5)	6,87 (8,5)
	H'	7,01 (7)	7,04 (7)
	H''	5,19 (7)	5,22 (7)
	H_f	5,62 (1,2)	5,64 (1,2)
	H_k	2,05	2,05
	H_i	2,15; 1,89 (1,2)	2,19; 1,93 (1,2)
	H_j	1,74; 1,66	1,74; 1,68

mentioned satisfy the inequalities observed in the mass spectra of smyrniorin (III) and athamantin (IV). According to the structures of (III) and (IV), and of (V) and (VI), the mutual intensities of the fragments mentioned above do not depend either on the site of addition of the dihydrofuran ring to the coumarin ring [see Table 3, (V) and (VI)] or on the structure of the acyl residues [see Table 3, (III) and (IV)]. The only difference in the structures of (III) and (IV), and of (V) and (VI), leading to differences in their mass spectra is that in (III) and (IV) an acyl residue is attached to a tertiary carbon atom which has a number of atoms not less than that attached to the C_9 carbon atom. Consequently, the distribution of the intensities of the main fragments in the mass spectrum of peucenidin (II), just as in smyrniorin (III) and athamantin (IV), can be explained by the presence on its tertiary carbon atom of an acyl residue having a number of atoms not less than that attached to C_9, i.e., the presence in the isopropyl grouping of the acyl radical of senecionic acid and not of acetic acid.

The formation of the analytically important fragments with m/e 244 and 243, and 229 and 227, permitting the determination of the position of the acyl groups in the diacyloxydihydrofurocoumarins can be represented by the scheme given below.

The intensities of the ions mentioned in dependence on the size and position of the acyl groups in the molecular ion can be obtained from a scheme using peucenidin as an example:



When an acyl radical with a larger or equal number of carbon atoms is present on the tertiary carbon atom, the expulsion of the acid takes place more intensively from the isopropyl group, giving the ion b considerably more intensively than the ion *a*. Although the expulsion of the groups Ac_1 and Ac_1O at the tertiary carbon atom with the formation of the ions e and f takes place readily, the ions c and d arise in larger amounts than the ions e and f. When the acyl radical Ac_2 has a larger number of atoms than Ac_1,

TABLE 3. Main Fragments and Their Intensities in the Regions of High and Moderate Masses in Relation to the Maximum Peaks in the Mass Spectra of Compounds (I)-(VI)

Mass numbers, m/e (relative intensities, %)					
I	II	III	IV	V	VI
386 (10)	386 (6,5)	346 (5)	430 (3,3)	386 (7)	386 (1,3)
326 (0,01)	326 (0,7)	326 (—)	328 (4,2)	326 (1,5)	326 (2,2)
311 (—)	311 (3,1)	311 (—)	313 (2)	311 (6)	311 (3,5)
303 (0,8)	303 (1)	303 (—)	303 (—)	303 (1,5)	303 (—)
286 (3)	286 (5,5)	286 (3,3)	286 (—)	286 (2,3)	286 (1,3)
271 (—)	271 (1,5)	271 (5,5)	271 (—)	271 (1,5)	271 (1)
261 (1)	261 (1,4)	261 (—)	261 (3,3)	261 (2,3)	261 (—)
244 (14)	244 (18)	244 (5)	244 (19)	244 (10)	244 (3,8)
243 (9)	243 (11)	243 (2,3)	243 (11)	243 (14)	243 (4,5)
229 (21)	229 (26)	229 (23)	229 (37)	229 (20)	229 (11)
227 (15)	227 (16)	227 (17)	227 (25)	227 (45)	227 (24)
213 (—)	213 (3,6)	213 (19)	213 (7)	213 (12)	213 (11)
203 (—)	203 (2,4)	198 (6,2)	203 (2,5)	203 (2,3)	203 (0,5)
201 (1,2)	201 (2,2)	191 (14)	201 (—)	201 (2,3)	201 (—)
198 (—)	198 (3,1)	187 (14)	198 (7,6)	198 (19)	198 (4,5)
191 (—)	187 (4)	186 (6)	191 (3,5)	191 (1,9)	191 (1,7)
187 (5)	186 (5,1)	203 (0,5)	187 (9,2)	187 (14)	187 (12)
186 (—)	191 (4,5)	201 (1,5)	186 (6,7)	186 (6)	186 (9,5)
83 (100)	83 (100)	57 (100)	57 (100)	83 (100)	83 (100)
287 (—)	287 (—)	287 (—)	287 (—)	287 (3,5)	287 (—)

the rates of ejection of the acids with the formation of the ions *a* and b become equal, which leads to the opposite pattern of the distribution of the intensities of the ions e, f, and c, d.

Thus, on the basis of the similarity of the main characteristics of peucenidin and 9-acetoxy-O-senecionyldihydrooroselol and also the results of a study of the mass spectra of model compounds of the diacyloxydihydrofurocoumarin series we have arrived at the conclusion that the compounds mentioned above are identical.

EXPERIMENTAL

The NMR spectrum of peucenidin was taken on an HA-100D instrument at a frequency of 100 MHz in $CDCl_3$ with HMDS as internal standard. The chemical shifts for comparison with those given in the literature were recalculated relative to the signal from TMS, taken as 0.

The mass spectra of compounds (II)-(VI) were obtained on an MKh-1303 instrument at an ionizing potential U of 50 V at temperatures of 105°C for (II), 90°C for (III), 83°C for (IV), 126°C for (V), and 90°C for (VI), with an admission system providing for the introduction of the sample into the ion source.

SUMMARY

According to literature information on the physicochemical constants of peucenidin and 9-acetoxy-O-senecionyldihydrooroselol, the results of a comparison of NMR spectra and mass spectra, and also a study of the mass spectra of model compounds, it has been established that these substances are identical.

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