

that the presence of bromine atoms in the chain of a fatty acid leads to the magnetic non-equivalence of the  $^{13}\text{C}$  nuclei of the methylene groups present at a distance of three carbon-carbon bonds from the nucleus to which the halogen is directly attached. A dependence has been found of the shift parameter of the carbon nuclei in a fatty acid chain on the relative arrangement of the bromine atoms.

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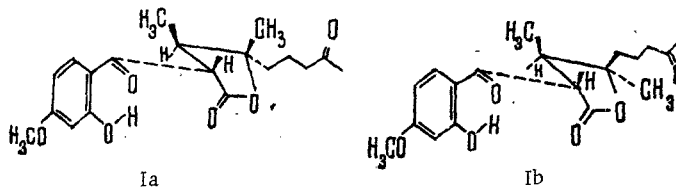
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#### THE STRUCTURE OF THE LACTONES $\alpha$ - AND $\beta$ -REOLONES

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From the resin of the roots of *Ferula pseudooreoselinum* (Rgl. et Schmalh) K. Pol. two stereoisomeric substances  $\text{C}_{19}\text{H}_{24}\text{O}_4$ , mol. wt. 348,  $[\alpha]_D^{22} 0$ , mp 107 and 138°C have been isolated, and they have been called  $\alpha$ - and  $\beta$ -reolones, respectively [1]. On the basis of spectral and chemical characteristics, formulas (Ia) and (Ib), differing by the orientation of the constituent at  $\text{C}_4$ , have been proposed for them



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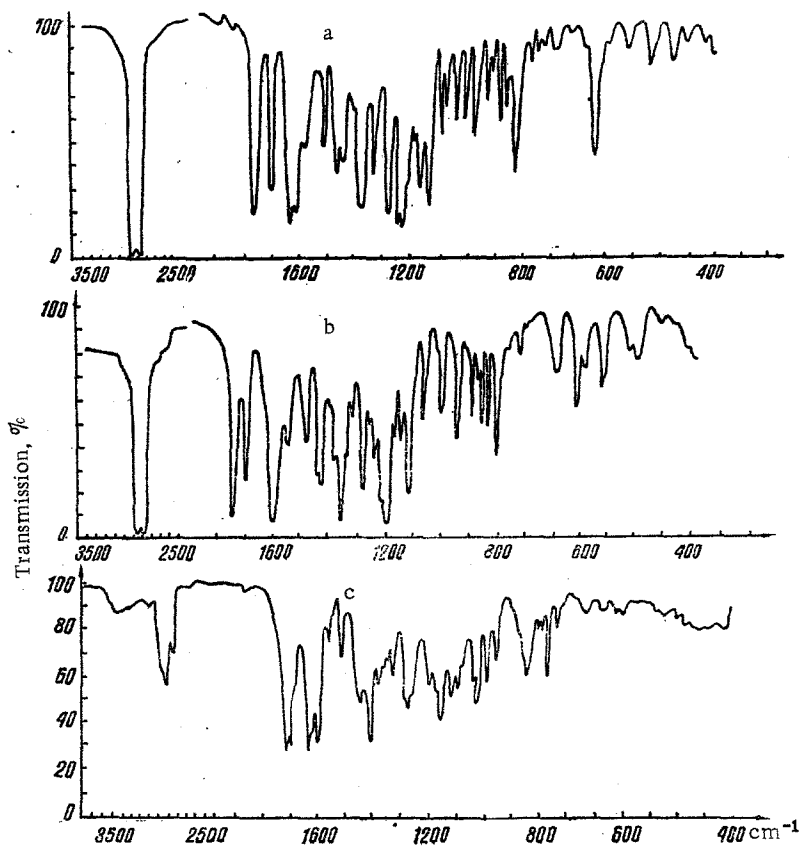
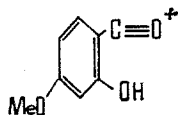


Fig. 1. IR spectra of  $\alpha$ -reolone (a) and  $\beta$ -reolone (b) (paraffin oil) and of the 7'-methoxy-4'-oxodihydrocoumarin derivative of  $\alpha$ -reolone (c).

The closeness of the structures of these substances can be judged from the identity of their UV spectra, the similarity of the IR spectra in  $\text{CHCl}_3$ , the small differences in the ratios of the intensities of the peaks in their mass spectra, the similarity of the chemical shifts of the protons in their PMR spectra with the exception of those with respect to the spatial position of which (Ia) and (Ib) differ, and the closeness of the chromatographic patterns of the mixtures of products obtained from identical reactions.

The following facts are in favor of an o-hydroxy-p-methoxy aromatic fragment conjugated with the keto group. In the UV spectra of (Ia) and (Ib) there are strong absorption bands shifted in the long-wave direction that are characteristic for such a system. In their IR spectra (Fig. 1a, b) there are the absorption bands of an aromatic nucleus ( $1580, 1518 \text{ cm}^{-1}$ ) and of a keto group conjugated with it ( $1630 \text{ cm}^{-1}$ , lowered because of the formation of an intramolecular H bond with the o-hydroxy group); the absorption band of the phenolic hydroxyl itself is indistinct, and almost invisible. In the PMR spectra of (Ia) and (Ib) this is represented by a one-proton singlet at 12.3 ppm in the weak field because of the H bond with the keto group. The protons of the methoxy group and of H-3', H-5', and H-6' of the aromatic ring are represented by signals at 3.82 (s, 3 H), 6.45 (s, 1 H), 6.50 (q, 1 H,  $J_{5',6'} = 9 \text{ Hz}$ ,  $J_{5',3'} = 3 \text{ Hz}$ ), and 7.70 (d, 1 H,  $J_{6',5'} = 9 \text{ Hz}$ ), respectively (see Fig. 2a). In the mass spectra of (Ia) and (Ib) the strongest peak in each case is that with m/e 151 (50% and 46%), corresponding to the fragment



The alkaline hydrolysis of (Ia) and (Ib) formed, with numerous other reaction products, 4-O-methyl-1- $\beta$ -resorcylic acid (II) (Scheme of transformations), which was identified by its spectral characteristics and by the melting point of the acid itself and of its methyl ester [3]. However, (II) was not obtained by the acid hydrolysis of (Ia) and (Ib) nor by the

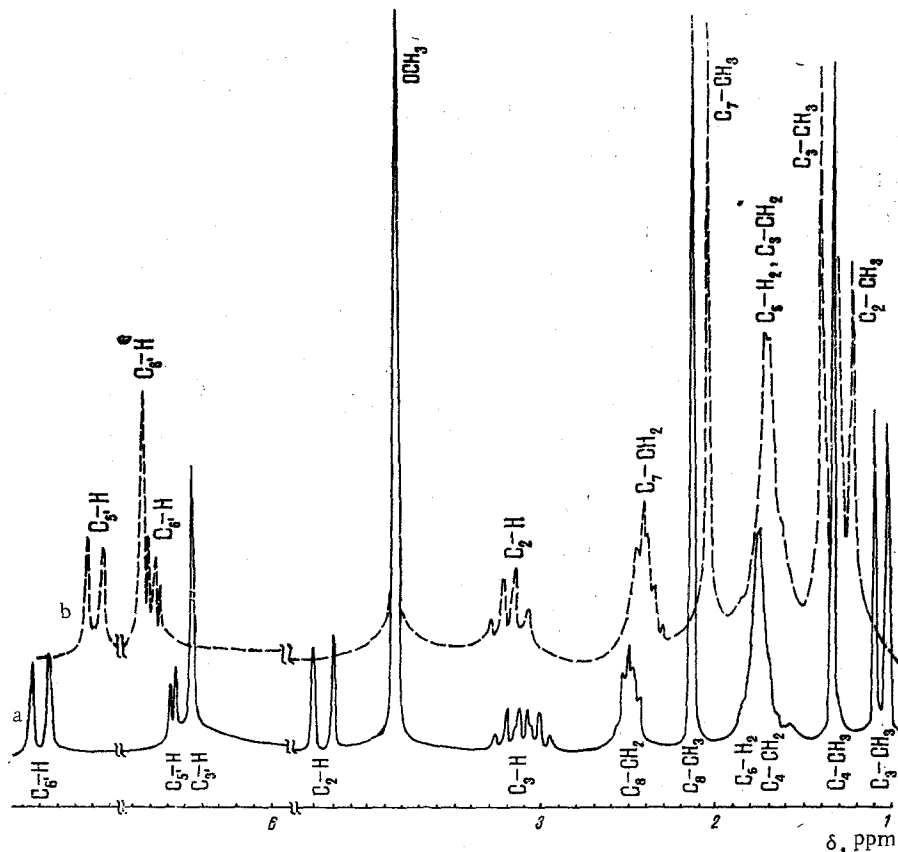
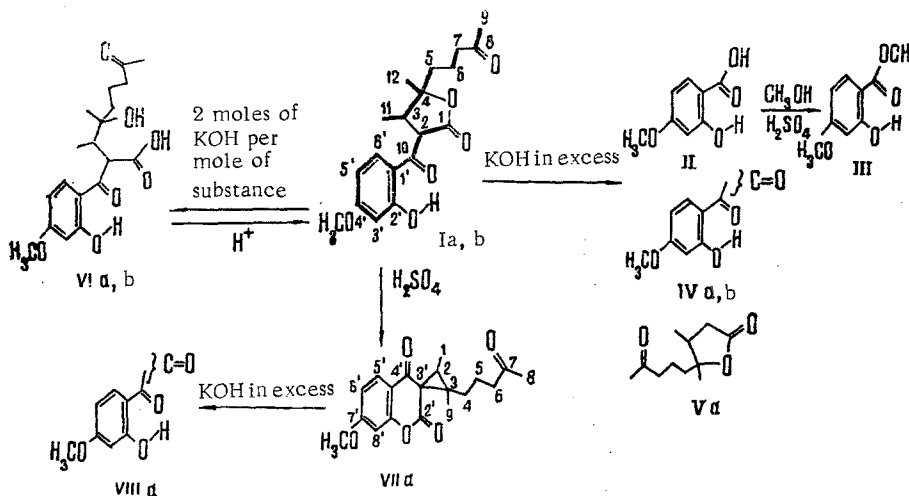


Fig. 2. PMR spectra of  $\alpha$ -reolone (a) ( $\text{CDCl}_3$ ) and of the 7'-methoxy-4'-oxodihydrocoumarin derivative of  $\alpha$ -reolone (b) ( $\text{CCl}_4$ ).



Scheme of the Transformations of  $\alpha$ - and  $\beta$ -Reolones

alkaline or acid hydrolysis of the hydrogenation products of (Ia) and (Ib); this once again confirms the assumption that a keto group, and not a ester group, participates in conjugation with the aromatic nucleus.

The structure of the lactone-containing part of the molecule was determined in the following way. The IR spectra of (Ia) and (Ib) (see Fig. 1a, b) show an absorption band at  $1765\text{ cm}^{-1}$  characteristic for a five-membered lactone ring which disappears in the IR spectra of the hydroxy acids (VIa) and (VIb) obtained in an alkaline medium from (Ia) and (Ib) as the result of the opening of the ring. In an acid medium, the hydroxy acids are reconverted into the initial compound. It follows from the PMR spectra of (Ia) (Fig. 2a) and (Ib) in

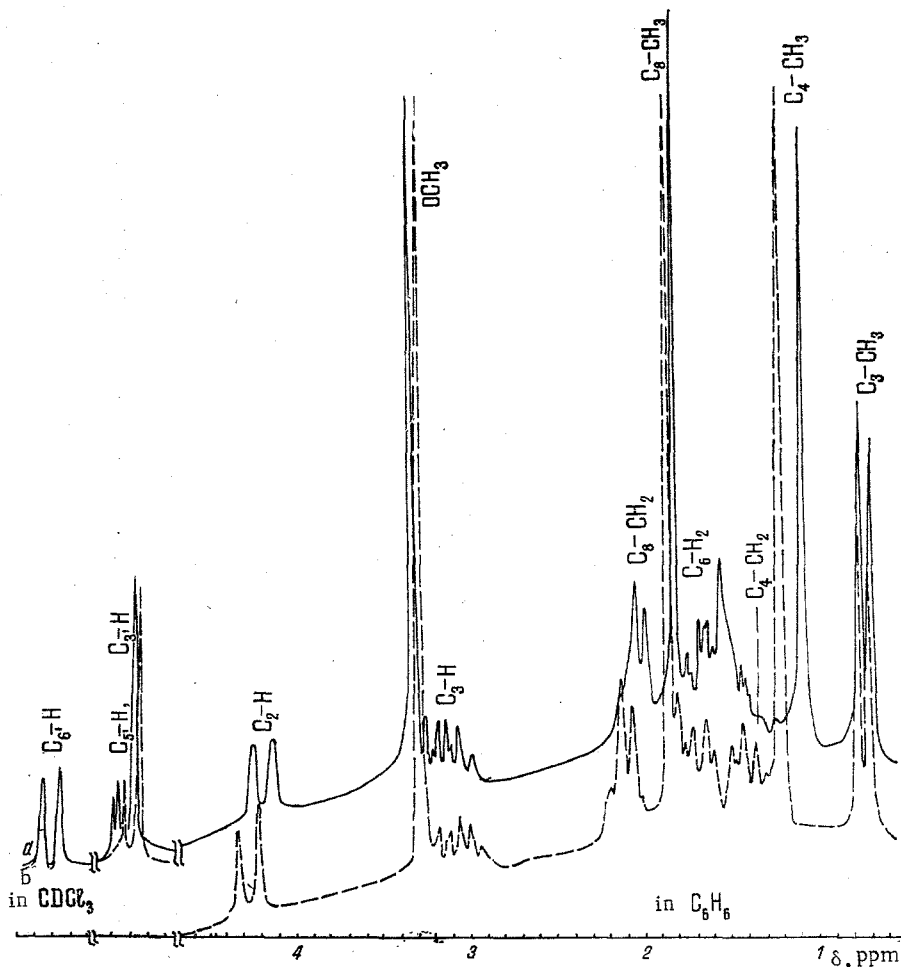


Fig. 3. NMR spectrum of  $\alpha$ -reolone (a) and  $\beta$ -reolone (b) in  $C_6H_6$ .

$CDCl_3$  that the substituted  $\gamma$ -lactone ring contains, judging from the spin-spin coupling constant, two vicinal trans-diaxial methine protons  $C_2-H$  giving signal at 4.3 ppm (d, 1 H,  $J_{2,3} = 12$  Hz) and  $C_3-H$  giving a signal at 3.14 ppm (octet, 1 H,  $J_{3,2} = 12$  Hz,  $J_{3,11} = 7$  Hz), these resonances being in the weak field because of the inclusion of the first proton in a  $\beta$ -keto lactone group and the adjacent position of the other proton, the signal of which is split because of coupling with the geminal  $CH_3$  group the signal of which is located at 1.07 ppm (d, 3 H,  $J_{11,3} = 7$  Hz).

Judging from the chemical shifts, in the spectra of (Ia) and (Ib) there are signals of tertiary methyl groups adjacent to the  $C_4$  carbons bearing the ester oxygen at 1.35 ppm (s, 3 H) and 1.53 ppm (s, 3 H), respectively, and of methylene groups at 1.77 ppm (broadened signal, 2 H + 2 H) and 1.65 ppm (broadened signal, 2 H), respectively. A comparison of the chemical shifts of the methyl and methylene groups at  $C_4$  in (Ia) and (Ib) shows their different orientations. In (Ia) the signal of the  $CH_3-C_4$  group is located at 18 Hz more up-field than the signal of the corresponding group in (Ib), i.e., the tertiary methyl group in the cis position with respect to the adjacent screening equatorial  $CH_3$ , and is axial. In (Ib) the protons of the  $-CH_2-C_4$  group resonate in a stronger field by 12 Hz than the corresponding protons in (Ia), i.e., in (Ib) the side chain is present in the cis-axial position to the vicinal methyl.

The structure of the side chain follows from the following facts. In the mass spectra of (Ia) and (Ib) there is a peak with  $m/e$  265 (0.8 and 1.6%, respectively) appearing as the result of the elimination of the side chain of the  $\gamma$ -lactone ring  $-C_5H_5O$ . This transition  $348^+ \rightarrow 263^+ + 85$  is confirmed by the presence of a metastable peak with  $m/e$  199; peaks with  $m/e$  305 (0.2 and 1%) formed as a result of the transition  $348^+ \rightarrow 305^+ + 43$  (metastable  $-m/e$  267.5) and  $m/e$  43 (22 and 3%) owe their appearance to the presence of an acetyl group in the side chain. In the PMR spectra of (Ia) and (Ib), the acetyl group is represented by a sig-

nal at 2.17 ppm (s, 3 H). The signals of the three neighboring methylene groups are separated more clearly in the spectrum of  $\beta$ -reolone in benzene (Fig. 3): 2.12 (t, 2 H,  $J_{7,6} = 7$  Hz) ( $-\text{CH}_2-\text{C}=\text{O}$ ); 1.42 (t, 2 H,  $J_{5,6} = 7$  Hz) ( $-\text{CH}_2-\text{C}_4-\text{O}-$ ); 1.72 (multiplet, 2 H,  $W_{1/2} \approx 28$  Hz) ( $-\text{C}_6-\text{H}_2$ ) (part of the signal overlaps the signal of the acetyl methyl).

The presence of a  $\beta$ -keto lactone group in compounds (Ia) and (Ib) was shown by the transformations [4] in an alkaline medium that are typical for such a case. The decomposition of the (Ia) and (Ib) at the  $\text{C}_2-\text{C}_{10}$  bonds forms the previously-mentioned 4-O-methyl-1- $\beta$ -resorcylic acid (II) and the keto lactone (Va), the IR spectrum of which has the absorption bands characteristic for a  $\gamma$ -lactone ring and a keto group in a side chain (1765 and  $1715\text{ cm}^{-1}$ ), while there is no hydroxy group in the compound. On decomposition at the  $\text{C}_1-\text{C}_2$  bond, the decarboxylation of (Ia) and (Ib) takes place. In the IR spectra of the neutral fraction of the products of the alkaline hydrolysis of (Ia) and (Ib), which consist of a complex mixture, there is no absorption band of a  $\gamma$ -lactone ring. The spectrum of the mixture is determined by the presence of fragment (IV) and is very similar to the spectrum of 2-hydroxy-4-methoxyacetophenone [5]. An addition to the spectrum of the mixture is the absorption band of a keto group of the side chain of the  $\gamma$ -lactone ring of reolone at  $1715\text{ cm}^{-1}$ .

In an acid medium, in addition to numerous other products, (Ia) forms an oily substance (VIIa) the IR spectrum of which (Fig. 1c) lacks the absorption band of OH and  $\gamma$ -lactone groups; in place of the latter an absorption band at  $1722\text{ cm}^{-1}$  characteristic for coumarin derivatives has appeared. The PMR spectrum of (VIIa) (Fig. 2b) lacks the signals of the protons of a phenolic hydroxyl and of the labile methine proton at C-3'. Because of the elimination of the latter there is a change in the splitting of the signal of the C-2 methine proton at 3.18 ppm (q, 1 H,  $J_{2,1} = 7$  Hz) which now interacts only with the protons of the geminal methyl group. Judging from the mass spectrum, the molecular weight has fallen by 18 units as the result of the loss of water. All this can be explained in the following way. In an acid medium the intramolecular hydrogen bond present in the molecule of each reolone is weakened, and the phenolic hydroxyl proves to be capable of forming a  $\delta$ -lactone ring with the carboxy group which previously formed a  $\gamma$ -lactone ring with the  $\text{C}_4-\text{OH}$  group. The process proves to be irreversible because of the formation of a cyclopropane ring as a result of the dehydration of the liberated  $\text{C}_4-\text{OH}$  alcoholic hydroxyl with the labile methine proton of the  $\beta$ -keto carboxy group. From the considerations given, formula (7a) followed from the product of the acid treatment of the (Ia). The spectral characteristics do not contradict this structure of a 7'-methoxy-4'-ketodihydrocoumarin derivative at the 3' carbon atom. Judging from the PMR spectrum in the 1.6-2.7 ppm region, the structure of the open chain of the molecule has not changed. The methine proton [3.18 ppm (q, 1 H,  $J_{2,1} = 7$  Hz)] and the protons of the secondary and tertiary methyl groups, with close values of the chemical shifts [1.23 ppm (d, 3 H,  $J_{1,2} = 7$  Hz) and 1.37 (s, 3 H)], now adjacent to a cyclopropane ring, are considerably descreened because of their immediate propinquity to a  $\beta$ -oxo lactone group. Thanks to this, the  $\text{C}_3'-\text{C}_4'$  bond has some of the nature of a double bond and the absorption frequency of the lactone carbonyl approximates to that usually observed in coumarin derivatives. Compound (VIIa) readily changes under the action of light. The violet spot on an  $\text{Al}_2\text{O}_3$  plate, which is dark at first, begins to fluoresce brightly under UV irradiation after a few seconds. A decarboxylation reaction is also characteristic for compound (VIIa). 4-O-Methyl-1- $\beta$ -resorcylic acid is formed in small amount on alkaline hydrolysis.

On the basis of the facts given above, the spatial isomers  $\alpha$ - and  $\beta$ -reolones have the structure of 3,4-dimethyl-2-(4'-O-methyl-1'- $\beta$ -resorcyloyl)-8-oxononan-1,4-olide. They can be represented as compounds including phenylpropanoid and isoprene chains and two acetate residues (one reduced).

#### EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument, the UV spectra on a SF-16 spectrophotometer in ethanol, the PMR spectra on a Varian H-100D/15 spectrometer ( $\delta$  scale, ppm; s) singlet; d) doublet; t) triplet; q) quartet); and the mass spectra on an MKh-1303 instrument with direct introduction at an ionizing voltage of 40 V, the intensities of the peaks being given as percentages of their sum; the specific rotations were determined on a EPL automatic polarimeter.

Isolation of  $\alpha$ - and  $\beta$ -Reolones. Dried comminuted roots of *Ferula pseudooreoselinum* (Rgl. et Schmalh) K. Pol. collected in the valley of the R. Ugam in the Tashkent region by an expedition under the direction of L. P. Markov, were extracted three times with a four-fold amount of acetone. The solvent was distilled off and the residue was dissolved in diethyl ether. The small flocculant precipitate (reoselin with impurities) was separated off [6]. The ethereal solution was treated with 3% aqueous KOH in order to separate the resin into neutral and phenolic/acidic fractions. On prolonged standing, the latter deposited a precipitate from which, by repeated recrystallization from ethanol, aqueous ethanol, and diethyl ether,  $\alpha$ - and  $\beta$ -reolones were obtained.

$\alpha$ -Reolone (Ia):  $C_{19}H_{24}O_6$ , mol. wt. 348,  $[\alpha]_D^{22} 0$  (c 1.5; chloroform), mp 107°C (from aqueous ethanol);  $R_f$  0.23 [Silufol; hexane-benzene-methanol (5:4:1)]; UV spectrum,  $\lambda_{max}$ , nm (log  $\epsilon$ ): 322, 283, 239 sh, 232, 219, 214 (3.756, 4.064, 3.620, 3.798, 3.953, and 4.043, respectively). IR spectrum,  $\nu_{max}$ ,  $cm^{-1}$ :  $CHCl_3$  1765 s (C=O of a  $\gamma$ -lactone), 1713 s (C=O in a side chain), 1630 v.s (Ar-C=O, participating in a H bond with an o-hydroxy group), 1580 m and 1520 w (Ar), 1470 m, 1450 m, 1375 s, 1333 m, 1280 s (Ar-O-), 1160 s (C-O- of a  $\gamma$ -lactone), 1130 s, 1083 w, 1055 w, 1040 w, 1000 w, 970 m, 910 w (s, strong; m, medium; w, weak; sh, shoulder).

$\beta$ -Reolone (Ib):  $C_{19}H_{24}O_6$ , mol. wt. 348  $[\alpha]_D^{22} 0$  (c 1.2; chloroform), mp 138°C (from aqueous ethanol);  $R_f$  0.23 [Silufol, hexane-benzene-methanol (5:4:1)]; UV spectrum,  $\lambda_{max}$ , nm (log  $\epsilon$ ): 322, 283, 239 sh, 232, 219, 214 (3.764, 4.070, 3.634, 3.804, 3.962, and 4.050, respectively). IR spectrum,  $\nu_{max}$ ,  $cm^{-1}$  ( $CHCl_3$ ): 1765 s, 1713 s, 1630 v.s, 1580 m, 1520 m, 1470 m, 1450 m, 1375 s, 1338 m, 1285 s, 1170 m, 1130 s, 1080 m, 1035 w, 970 m, 910 w, 875 w.

Alkaline Treatment of  $\alpha$ -Reolone (Ia). 4-O-Methyl-1- $\beta$ -resorcylic Acid (II). A solution of 0.5 g of (Ia) in 50 ml of ethanol was treated with 5 ml of a 5% aqueous solution of KOH. After being heated for 1 h, the resulting solution was diluted with water, the ethanol was evaporated off, and the residue was cooled, acidified with dilute  $H_2SO_4$ , and extracted with diethyl ether. The ethereal solution was shaken with 0.5% sodium carbonate solution. The precipitate that deposited from the sodium carbonate solution after acidification was filtered off and recrystallized several times from aqueous ethanol to give acicular crystals of 4-O-methyl-1- $\beta$ -resorcylic acid (II) with mp 157°C [3], composition  $C_8H_8O_4$ ,  $R_f$  0.16 [Silufol; petroleum ether-benzene-methanol (5:4:1)]. UV spectrum,  $\lambda_{max}$ , nm (log  $\epsilon$ ): 292, 248 (4.1, 4.41). IR spectrum,  $\nu_{max}$ ,  $cm^{-1}$  (paraffin oil): 3200-2600 (phenolic and carboxylic OH's), 2835 ( $OCH_3$ ), 1655 (COOH), 1620, 1580, 1505 (Ar), 1260 (Ar-O).

Methyl 4-O-Methyl-1- $\beta$ -resorcylic Acid (III). A solution of 50 mg of (II) in 5 ml of 6%  $H_2SO_4$  in methanol was heated for 1 h and was then diluted with water. The precipitate that deposited was filtered off and, after two crystallizations from petroleum ether, colorless plates of (III) with mp 48°C [3] were obtained.

Products of the Decarboxylation of (IVa). The neutral fraction of the products of alkaline hydrolysis consisted of a complex mixture containing products of the decarboxylation and further transformation of  $\alpha$ -reolone. IR spectrum of the mixture,  $\nu_{max}$ ,  $cm^{-1}$ : 3500 (alcoholic OH), 2600-3200 (indistinct, phenolic OH), 1710 (C=O in a side chain), 1630 v.s (Ar-C=O participating in a H bond with o-hydroxy group), 1585, 1510, 845, 810 (Ar), 1285, 1215 (Ar-O and Ar-O-C-).

The Keto Lactone (Va). After chromatography on a column of  $Al_2O_3$  (activity grade III,  $CHCl_3$ ) of the neutral fraction of the products of alkaline hydrolysis of (Ia) an oily substance (VIa) was obtained with  $R_f$  0.43 ( $Al_2O_3$ , activity grade III;  $CHCl_3$ ), the spot of which did not show up in UV light. UV spectrum,  $\lambda_{max}$ , nm (log  $\epsilon$ ): 281, 218 (1.23, 1.90). IR spectrum,  $\nu_{max}$ ,  $cm^{-1}$ : 1760 (C=O of a  $\gamma$ -lactone ring), 1715 (C=O in a side chain), 1270 m, 1170 m, 960 m, 930 m, no absorption band of an OH group.

The alkaline treatment of  $\beta$ -reolone (200 mg) was performed similarly. This gave 4-O-methyl-1- $\beta$ -resorcylic acid and a mixture of decarboxylation products.

Preparation of the Hydroxy Acid (VIa) from  $\alpha$ -Reolone. A solution of 0.2 g of (Ia) in 10 ml of ethanol was treated with 70 mg of KOH in 1 ml of water (calculated at 2 moles of alkali per mole of substance). On standing at room temperature for a week, the yellowish greenish solution became lighter; it was diluted with water and, after the ethanol had been distilled off it was acidified and the reaction products were extracted with chloroform. The chloroform extract was shaken with 0.5% sodium carbonate solution, and the sodium carbonate

solution was acidified and extracted with chloroform; the solid extract obtained after the evaporation of the  $\text{CHCl}_3$  was recrystallized several times from diethyl ether to give colorless crystals of the hydroxy acid (VIa) with mp  $142^\circ\text{C}$ . IR spectrum,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$  (petroleum jelly): 3220 and 2450 (alcoholic, phenolic, and carboxylic OH's), 1715 (C=O in a side chain), 1650 (C=O of a carboxy group), 1610 v.s (Ar-C=O), 1580 and 1510 m (Ar), 1285 s, 1235 s, 1195 s, 1175 s, 1115 s, 1040 s, 1025 s, 960 (C=O stretching and O-H deformation vibrations of carboxy, hydroxy, methoxy, and phenol groups).

Re-formation of the Initial  $\alpha$ -Reolone from the Hydroxy Acid (VIa). A solution of 30 mg of (VIa) in 2 ml of ethanol was treated with 2 ml of 1%  $\text{H}_2\text{SO}_4$  and, after a day, the mixture was diluted with water. The precipitate formed was extracted with chloroform. After crystallization from ethanol,  $\alpha$ -reolone, identified by its melting point and IR spectrum, was obtained.

Production of the Hydroxy Acid (VIb) from  $\beta$ -Reolone. A solution of 0.2 g of (Ib) in 10 ml of methanol was treated with 70 mg of KOH in 1 ml of  $\text{H}_2\text{O}$  and the mixture was heated until it had become lighter in color (0.5 h). After the treatment described for (VIa), the hydroxy acid (VIb) was obtained with mp  $144^\circ\text{C}$ . IR spectrum,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$  (petroleum jelly): 3330, 2620, 1705 s, 1675 s, 1615 v.s, 1575 m, 1515 m, 1265 m, 1233 m, 1200 s, 1165 s, 1112 s, 1090 s, 1030 s, 960 m.

Re-formation of the Initial  $\beta$ -Reolone from the Hydroxy Acid (VIb). When (VIb) was treated in the same way as (VIa),  $\beta$ -reolone, identified by its melting point and IR spectrum, was obtained. Compounds (VIa) and (VIb) were also reconverted into the initial lactones on heating.

Acid Hydrolysis of  $\alpha$ -Reolone. A solution of 1 g of (Ia) in 20 ml of 2%  $\text{H}_2\text{SO}_4$  in ethanol was heated in the water bath for 2 h and was then diluted with water; the ethanol was evaporated off, the reaction products were extracted with chloroform, and the extract was chromatographed on inactive  $\text{Al}_2\text{O}_3$  (chloroform). The main reaction product (VIIa) was a viscous colorless oil with  $R_f$  0.24 [Silufol, ethyl acetate-benzene-petroleum ether (1:1:1)], with a dark violet color in UV light; mol. wt. 330;  $[\alpha]_D^{22} -8^\circ$  (c 0.7; chloroform). UV spectrum,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ): 334 sh, 319, 306 sh, 289 sh, 278 sh, 244 sh, 228, 214 sh (3.992, 4.043, 3.950, 3.774, 3.600, 3.852, 3.920, and 3.854, respectively). IR spectrum,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1722 (C=O of a  $\delta$ -lactone), 1710 (C=O in a side chain), 1640 (Ar-C=O), 1615, 1570, and 1520 (Ar).

Alkaline Treatment of (VIIa). A solution of 125 mg of (VIIa) in 15 ml of methanol was treated with 1 ml of a 5% aqueous solution of KOH and, after being heated on the boiling water bath for half an hour, the mixture was worked up as described for (Ia). IR spectrum of the mixture of products of the neutral fraction;  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ : 3500, 1715 s (C=O in a side chain), 1630 v.s (Ar-C=O), 1585 sh, 1515 m, 1465 m, 1450 m, 1380 s, 1280 s. The acidic ( $\approx 5\%$ ) fraction of the reaction products contained several compounds; one of the spots with  $R_f$  0.25 [Silufol; petroleum ether-benzene-methanol (5:4:2)] and with a blue-violet fluorescence in UV light coincided with that for 4-O-methyl-1- $\beta$ -resorcylic acid.

#### SUMMARY

1. Structures have been proposed for  $\alpha$ - and  $\beta$ -reolones (Ia and Ib), two spatial isomers isolated by us previously, as 3,4-dimethyl-2-(4'-O-methyl-1'- $\beta$ -resorcyloyl)-8-oxononan-1,4-olides with the trans-diaxial position of the methine protons in the lactone ring, and with the equatorial orientation of the open chain at  $C_4$  in  $\alpha$ -reolone and the axial orientation in  $\beta$ -reolone.

2. The possibility has been found of converting  $\alpha$ -reolone in an acid medium into a 7'-methoxy-4'-oxodihydrocoumarin derivative at the 3'-carbon atom.

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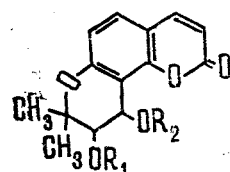
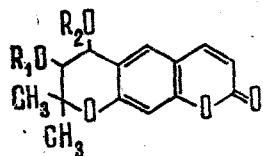
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MASS-SPECTROMETRIC DISTINCTION OF LINEAR AND ANGULAR  
 3',4'-DIHYDROXY-SUBSTITUTED DIHYDROPYRANOCOUMARINS  
 AND THEIR DERIVATIVES

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The mass-spectral behavior of angular 3',4'-dihydroxy- and 3',4'-diacyloxy-2',2'-dimethyldihydropyranocoumarins has been studied previously [1]. In the present paper we consider the dissociative ionization of a number of linear compounds of this class: isokhellactone (I), methylisokhellactone (II), and products of the partial hydrolysis and methanolysis of andelin (III, IV), and their deuterium analogs (V-VII) in order to establish the differences in the mass spectra of these compounds from the mass spectra of angular representatives of 3',4'-substituted dihydropyranocoumarins isomeric with or having a similar structure to them (VIII-X). The mass spectra of the latter were taken under conditions identical to those for the mass spectra of (I-VII). Substances (I-IV) are the products of the complete or partial hydrolysis and methanolysis of andelin [2] and their deuterium analogs were obtained synthetically.



- I.  $R_1=R_2=-H$ ; II.  $R_1=-H$ ,  $R_2=-CH_3$ ;  
 III.  $R_1=-COCH=C \begin{matrix} CH_3 \\ CH_3 \end{matrix}$ ,  $R_2=-H$ ;  
 IV.  $R_1=-COCH=C \begin{matrix} CH_3 \\ CH_3 \end{matrix}$ ,  $R_2=-CH_3$ ;  
 V.  $R_1=R_2=-D$ ; VI.  $R_2=-CH_3$ ;  
 VII.  $R_1=-COCH=C \begin{matrix} CH_3 \\ CH_3 \end{matrix}$ ,  $R_2=-D$ ;  
 VIII.  $R_1=R_2=-H$ ; IX.  $R_1=-H$ ,  $R_2=CH_3$ .  
 X.  $R_1=-COCH=C \begin{matrix} CH_3 \\ CH_3 \end{matrix}$ ,  $R_2=-CH_3$ .

The results of a comparison of the mass spectra of compounds (I and VIII) and (II and IX) (Figs. 1 and 2) show that they differ by the relative intensities of a number of fragments. As follows from the mass spectra of the deuterium analogs (V and VI), this fact is due not to differences in the mechanism of the behavior of these fragments but to the different decomposition stabilities of the linear and angular isomers of this class of substances. In the case of isokhellactone (I) and khellactone (VIII), such a difference is connected with a subsidiary direction of their dissociative ionization as a result of which the elimination of a molecule of  $H_2O$  takes place with the subsequent ejection of a  $CH_3$  radical (Scheme 1). For the linear isomer (I), the ratio  $I_{M^+}/I_{(M-H_2O)^+}$  is approximately 2.5 times lower than for the angular isomer (VIII) (1.6 and 4.0 units, respectively), while, conversely, the ratio  $I_{(M-H_2O)^+}/I_{(M-OH)^+}$  is twice as great (3.5 and 1.7 units, respectively). The mass spectra of the isomers (I) and (VIII) also differ by the mutual intensities of the ions with  $m/e$  229 and 228, 176 and 175, and 175 and 162.

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