Aminal IVb (X = I, NR_2 = morpholino) was obtained as crystals with mp 240°C (dec.). Found: C 41.9; H 5.3; N 8.1%. $C_{13}H_{19}IN_2O_3$. Calculated: C 41.3; H 5.1; N 7.4%.

Aminal IVc (X = Br, NR_2 = piperidino) was obtained as crystals with mp 100°C.

Aminal IVd (X = Br, NR_2 = morpholino) was obtained as crystals with mp 220°C (dec.).

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STRUCTURE AND RING-CHAIN TAUTOMERISM OF 2-HYDROXY-5-METHYL-3,4-BENZOCINNAMALDEHYDE

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The previously undescribed 2-hydroxy-5-methyl-3,4-benzocinnamaldehyde was synthesized. A cyclic 2-hydroxy-2H-chromene structure in the crystalline state and in nonpolar solvents was established for it by IR, UV, and PMR spectroscopy. It is shown that transition to a polar solvent leads to the establishment of a tautomeric ring-chain equilibrium, the position of which is determined by the type of solvent.

We have previously shown that transition from 2-hydroxycinnamaldehyde and its imines, which exist exclusively in the benzoid tautomeric form in media with various polarities, to benzo-annelated systems, which are more inclined to undergo quinoidization, has a substantial effect on the structures of vinylogs of o-hydroxy aldehydes and their derivatives [1]. Thus, 2-hydroxy-5,6-benzocinnamaldehyde and its imines in the crystalline state and in solutions in nonpolar solvents have a cyclic 2H-chromene structure, whereas a tautomeric ring-chain equilibrium is realized for them in polar media.

In order to further study prototropic transformations of this type we obtained the previously undescribed 2-hydroxy-5-methyl-3,4-benzocinnamaldehyde (Ia). The synthesis was ac-

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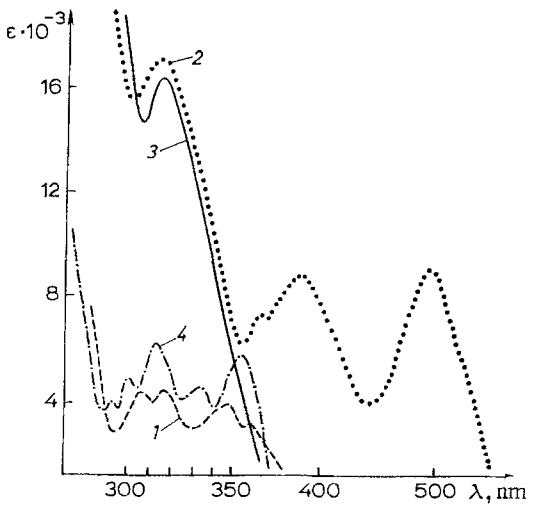
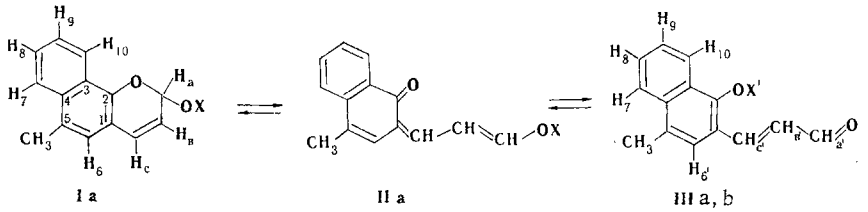


Fig. 1. Electronic absorption spectra of 2-hydroxy-5-methyl-3,4-benzocinnamaldehyde (Ia): 1) in CCl_4; 2) in dimethyl sulfoxide; 3) spectrum of O-acetyl derivative IIIb in CCl_4; 4) spectrum of 2-hydroxy-5,6-benzocinnamaldehyde [1].

complished by the scheme in [2], which was previously used to obtain 2-hydroxy-5,6-benzocinnamaldehyde [1].



I-III a X=H; III b X=COCH$_3$

2-Hydroxy-5-methyl-3,4-benzocinnamaldehyde in the crystalline state and in solutions in nonpolar solvents (CCl_4) exists in the cyclic 2H-chromene form (Ia). The appearance in the IR spectrum of aldehyde Ia of a band of stretching vibrations ($\nu_{C=C}$) of the dihydropyran ring at 1645 cm^{-1} and a band of an associated hydroxy group (ν_{OH}) at 3200-3400 cm^{-1} constitutes evidence in favor of this structure. The electronic absorption spectrum of Ia in CCl_4, like the spectrum of 2-hydroxy-5,6-benzocinnamaldehyde [1], is distinguished by a clearly expressed vibrational structure of two of its long-wave bands at 315 and 355 nm, which are typical for 2H-chromenes [3], and differs considerably from the absorption spectrum of 2-acetoxy-5-methyl-3,4-benzocinnamaldehyde (IIIb) (Fig. 1).

A ring-chain equilibrium of the Ia $\rightleftarrows$ IIa type is established in polar solvents [acetonitrile, ethanol, and dimethyl sulfoxide (DMSO)], as indicated by the appearance in the electronic spectra of Ia of long-wave absorption bands of quinoid tautomeric form IIa at 480-500 nm, the intensity of which increases sharply on passing from acetonitrile to ethanol and subsequently to DMSO.

Signals of protons of two tautomeric forms [the designations of the protons are given in formulas (I-III)] are also recorded in the PMR spectrum of aldehyde Ia (Fig. 2) in acetonitrile. The assignments of the protons are presented in Fig. 2. As in the case of 2-hydroxy-5,6-benzocinnamaldehyde [1], the following complex ABMX system of proton signals corresponds to cyclic 2H-chromene form Ia: an H_a multiplet at 6.03 ppm, which is converted after deuteration to a doublet with J_{ab} = 4 Hz, an H_b quartet centered at 5.90 ppm with J_{ba} = 4 Hz and J_{bc} = 10 Hz, an H_c (M) doublet at 6.75 ppm with J_{cb} = 10 Hz, and a singlet of the proton of the OH (X) group at 4.70 ppm, which vanishes upon deuteration. The doublet at 9.72 ppm with $J_{a'b'}$ = 8 Hz and the quartet at 6.75 ppm with $J_{b'a'}$ = 8 Hz and $J_{b'c'}$ = 16 Hz can be assigned to the $H_{a'}$ and $H_{b'}$ protons of open form IIIa. The same position of the aldovinyl protons is recorded in the PMR spectra of 2-hydroxycinnamaldehyde [4] and O-acetyl derivative IIIb (Fig. 3), which models fixed benzoid structure IIIb. The $J_{b'c'}$ value of 16 Hz and the $J_{a'b'}$ value

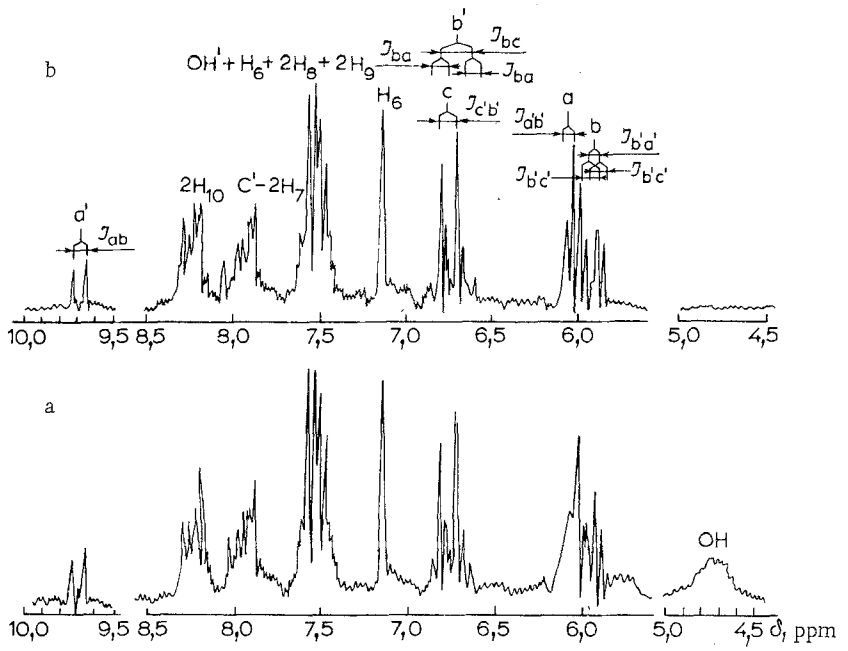


Fig. 2. PMR spectra: a) 2-hydroxy-5-methyl-3,4-benzocinnamaldehyde in acetonitrile; b) spectrum after deuteration.

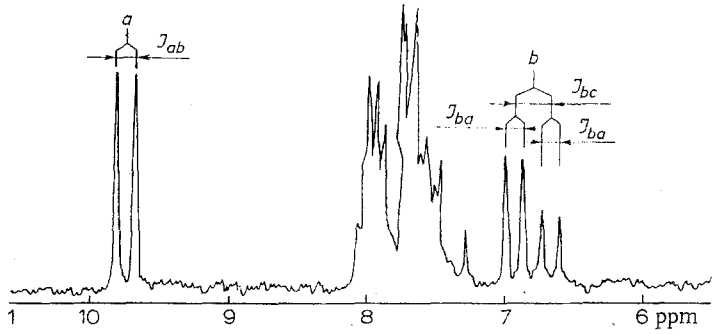


Fig. 3. PMR spectrum of 2-acetoxy-5-methyl-3,4-benzocinnamaldehyde in acetone.

of 8 Hz in the PMR spectrum of 2-acetoxy-5-methyl-3,4-benzocinnamaldehyde (IIIb) (Fig. 3) clearly indicate a trans-transoid structure of the protons of the polyenal chain and, consequently, the E configuration of the double bond.

Equilibrium between the cyclic form of the aldehyde (Ia) and the isomeric structure is established in solution in both DMSO and acetonitrile. However, the indicated structure does not correspond to form IIIa, since an intense band in the long-wave region at 500 nm appears in the electronic absorption spectrum in DMSO (Fig. 1). This band is absent in the spectrum of the O-acetyl derivative and, consequently, can be assigned to quinoid tautomeric form IIa. In the PMR spectrum of Ia in DMSO the signal of the proton of the OH group of cyclic form Ia is shifted to weak field under the influence of the solvent and appears in the form of a doublet at 6.90 ppm with $J_{OH\ a}$ = 8 Hz. The position of the signals of the remaining protons of the tautomeric forms remains unchanged on passing from acetonitrile to DMSO. This is apparently explained by the fact that it is virtually impossible to differentiate tautomeric forms IIa and IIIa by means of the PMR spectra.

Judging from the relative intensities of the multiplets of the protons of the tautomers, the ratio of the forms of aldehyde Ia in the ring-chain equilibrium in acetonitrile can be assumed to be ∿3(Ia):1(IIIa), as compared with 1(Ia):1(IIa) in DMSO.

For comparison, let us note that 2-hydroxy-5,6-benzocinnamaldehyde exists exclusively in the cyclic tautomeric form in acetonitrile and in ethanol and that a ring-chain equilibrium is realized for it only in DMSO [1].

Thus the transition from 5,6- to 3,4-benzo-annelated 2-hydroxycinnamaldehyde promotes lability of the ring-chain transformations; this is apparently associated with an increase in the acidity of the hydroxy proton of 1-hydroxy-2-formylnaphthalene [5]; the systems that we investigated are vinylogs of the latter.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The electronic absorption spectra were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of 10-15% solutions of the compounds were recorded with a Varian XL-100/15 radiospectrometer (100 MHz).

1-Hydroxy-4-methyl-2-formylnaphthalene. This compound was obtained by formylation of 4-methyl-1-naphthol with dichloromethyl butyl ether in dry chloroform in the presence of titanium tetrachloride [6]. The light-yellow crystals had mp 70°C (from hexane) and were obtained in 90% yield. IR spectrum: $\nu_{C=O}$ 1655 cm^{-1}. PMR spectrum (in acetone): 12.60 (OH, s), 9.90 (CHO, s), and 7.0-8.4 ppm (Ar, m). Found: C 77.3; H 5.5%. $C_{12}H_{10}O_2$. Calculated: C 77.4; H 5.4%.

1-Acetoxy-4-methyl-2-formylnaphthalene. This compound was prepared by acylation of 1-hydroxy-4-methyl-2-formylnaphthalene with acetic anhydride in dry pyridine. The fine yellow crystals had mp 114°C (from ethanol) and were obtained in 70% yield. IR spectrum: C=O 1680, 1760 cm^{-1}. Found: C 73.3; H 5.1%. $C_{14}H_{12}O_3$. Calculated: C 73.7; H 5.3%.

1-Acetoxy-4-methyl-2-formylnaphthalene Diethylacetal. This compound was synthesized from 1-acetoxy-4-methyl-2-formylnaphthalene and ethyl orthoformate in the presence of catalytic amounts of phosphoric acid. PMR spectrum (in CCl_4): 1.12 ($2CH_3$, t), 2.26 (CH_3, s), 2.36 (CH_3, s), 3.37 ($2CH_2$, q), 5.67 (CH, s), and 7.27-8.39 ppm (Ar, m). Found: C 71.9%; H 7.3%. $C_{18}H_{22}O_4$. Calculated: C 71.5; H 7.3%.

2-Acetoxy-5-methyl-3,4-benzocinnamaldehyde (Ib). This compound was prepared from 1-acetoxy-4-methyl-2-formylnaphthalene diethylacetal and vinyl ether in the presence of a 10% solution of anhydrous zinc chloride in ethyl acetate. The yellow powder had mp 152°C (from benzene) and was obtained in 63% yield. IR spectrum: $\nu_{C=O}$ 1760, 1680; $\nu_{C=C}$ 1625 cm^{-1}. Electronic spectrum (in CCl_4), λ_{max} ($\varepsilon \cdot 10^{-3}$): 320 nm (16.5). PMR spectrum (in acetone): 9.75 ($H_{a'}$, d, $J_{a'b'}$ = 8 Hz), 6.60 ($H_{b'}$, q, $J_{b'a'}$ = 8 Hz, $J_{b'c'}$ = 16 Hz), and 7.2-8.2 ppm (Ar, $H_{c'}$, $H_{c'}$, m) (the designations of the protons correspond to formula IIIb). Found: C 75.7; H 5.4%. $C_{16}H_{14}O_3$. Calculated: C 75.6%; H 5.5%.

2-Hydroxy-5-methyl-3,4-benzocinnamaldehyde (Ia). This compound was obtained from 2-acetoxy-5-methyl-3,4-benzocinnamaldehyde by treatment with a methanol solution of sodium methoxide. The air-dried product was purified by repeated washing with benzene, chloroform, and petroleum ether. The yellow powder had mp 110°C (dec.) and was obtained in 75% yield. Electronic spectra, λ_{max} ($\varepsilon \cdot 10^{-3}$): in CCl_4 310 (4.2), 320 (4.7), 353 (4.0), and 366 nm (3.8); in acetonitrile 288 (11.7), 319(7.7), 355 (4.9), 375 (3.6), and 490 nm (0.6); in ethanol 293 (13.1), 320 (11.3), 353 (5.0), 392 (4.3), and 480 nm (3.1); in DMSO 318 (16.9), 390 (8.4), and 508 (8.6). PMR spectrum (in DMSO): signals of the protons of the Ia form: 6.04 (H_a, m), 5.90 (H_b, q, J_{ba} = 4, J_{bc} = 10 Hz), 6.70 (H_c, d, J_{cb} = 10 Hz), 6.90 (OH, d, $J_{OH\,a}$ = 8 Hz), and 7.20 (H_6, s); signals of the protons of the IIIa form: 9.70 ($H_{a'}$, d, $J_{a'b'}$ = 8 Hz), 6.70 ($H_{b'}$, m), 8.25 ($2H_{10}$, m), 7.9 ($2H_7$, $H_{c'}$, m), and 7.3-7.7 ppm ($2H_8$, $2H_9$, $H_{b'}$, OH', m). Found: C 79.4; H 5.0%. $C_{14}H_{12}O_2$. Calculated: C 79.6; H 5.2%.

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