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INFLUENCE OF IONIZING ADDITIVES ON THE UV ABSORPTION SPECTRA OF SOME FUROCOUMARINS

N. V. Chernobrovaya, V. S. Batyuk, and N. F. Komissarenko

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The spectroscopic investigation of substituted hydroxy derivatives of the furocoumarins is known from the literature [1-3]. In our communication we give the results of a study of various hydroxy derivatives of psoralen with additions of sodium ethoxide, borax, and hydrochloric acid (table, p. 244). The use of these additives permits furocoumarins with three hydroxy groups to be distinguished from their substituted derivatives and 5-hydroxyfurocoumarins to be distinguished from 8-hydroxyfurocoumarins.

In all the substances studied (see table), with the exception of 5,8-dihydroxypsoralen and psoralen itself, four main absorption bands of greater or smaller intensity according to the structure of the substance are observed: 298-330 mμ (band I), 268-273 mμ (band II), 247-251 mμ (band III), and 218-225 mμ (band IV). The UV spectrum of 5,8-dihydroxypsoralen has bands in the 308 mμ (band I), 254 mμ (band II), and 222 mμ (band III) regions; in psoralen there are bands at 332 mμ (band I), 287 mμ (band II), and 245 mμ (band III).

5-Hydroxypsoralen and 5-hydroxy-8-methoxypsoralen are distinguished from 8-hydroxypsoralen and 8-hydroxy-5-methoxypsoralen by the presence of an absorption band in the 289-295 mμ region.

In the case of 5-hydroxypsoralen, 5-hydroxy-8-methoxypsoralen, 8-hydroxypsoralen, 5-methoxy-8-hydroxypsoralen, and 5,8-dihydroxypsoralen, sodium ethoxide causes a bathochromic shift of band IV by 10 mμ. Instead of bands II and III, a band appears with a peak at 286 mμ. Band I undergoes a bathochromic shift of 7 mμ. In psoralen and 5,8-dimethoxypsoralen, no shifts are found with this additive. This characteristic of furocoumarins can be used to detect free hydroxy groups in their molecules from the bathochromic shifts of the main bands (see table).

The UV spectra of 8-hydroxypsoralen, 5-hydroxypsoralen, 8-hydroxy-5-methoxypsoralen, and 5,8-dihydroxypsoralen have also been recorded with the addition of borax.

In the UV spectra of the furocoumarins hydroxylated at position 5 or 8 studied, bathochromic shifts of all the bands were found. In the UV spectra of substances not hydroxylated or esterified in these positions, no bathochromic shifts were found. An exception was 5,8-dihydroxypsoralen, in which, unlike the other hydroxysubstituted derivatives, the addition of borax led to the appearance of an absorption band at 360 mμ. The other bands of this substance did not change.

On the addition of hydrochloric acid to the initial solution, the band at 288 mμ disappeared from the spectra of 5-hydroxypsoralen and 5-hydroxy-8-methoxypsoralen. However, no similar changes were found in the spectra of 8-hydroxypsoralen and 8-hydroxy-5-methoxypsoralen. Their spectra were similar to the spectra of the substances without additives. This characteristic may be used to distinguish 5-hydroxyfurocoumarins from 8-hydroxyfurocoumarins.

Conclusions

In the study of the UV spectra of furocoumarins, ionizing additives can be used to determine their structure.

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Substance	λ mμ	log ε	λ mμ	log ε	λ mμ	log ε	λ mμ	log ε	λ mμ	log ε	λ mμ	log ε	λ mμ	log ε
Psoralen	240*	4.32	243	4.35	288	4.02	330	3.72	—	—	—	—	—	—
Psoralen + HCl	240*	4.36	246	4.39	288	4.03	330	3.87	—	—	—	—	—	—
Psoralen + Na ethoxide	240*	4.31	245	4.33	288	3.96	330	3. 8	—	—	—	—	—	—
Psoralen + Borax	240*	4.41	246	4.43	288	4.09	330	4.86	—	—	—	—	—	—
5,8-dihydroxypsoralen	222	4.34	255	4.32	308	3.97	—	—	—	—	—	—	—	—
5,8-dihydroxypsoralen + HCl	221	4.41	254	4.38	308	4.04	—	—	—	—	—	—	—	—
5,8-dihydroxypsoralen + Na ethoxide	230	4.34	275	4.28	325	3.93	—	—	—	—	—	—	—	—
5,8-dihydroxypsoralen + Borax	217	5.20	257	3.59	310	3.94	360	4.18	—	—	—	—	—	—
5-Hydroxypsoralen	221	4.12	232*	4.00	248	3.93	260*	3.92	268	3.98	288	3.85	315	3.85
5-Hydroxypsoralen + HCl	219	4.17	242*	4.03	248	4.04	260*	3.99	267	4.05	312	3.86	—	—
5-Hydroxypsoralen + Na ethoxide	232	4.10	250*	3.63	260*	3.65	287	4.03	322	3.67	—	—	—	—
5-Hydroxypsoralen + Borax	233	4.16	250*	3.73	260*	3.75	287	4.10	323	3.78	—	—	—	—
5-Hydroxy-8-methoxypsoralen	225	3.69	247*	3.32	277	3.54	295	3.45	318	3.34	—	—	—	—
5-Hydroxy-8-methoxypsoralen + HCl	223	4.72	247	4.45	274	4.60	315	4.39	—	—	—	—	—	—
5-Hydroxy-8-methoxypsoralen + Na ethoxide	232	4.70	293	4.68	325	4.26	—	—	—	—	—	—	—	—
8-hydroxypsoralen	218	4.32	242*	4.11	250	4.15	262	4.09	268	4.10	307	—	—	—
8-hydroxypsoralen + HCl	218	4.36	242	4.17	248	4.20	260*	4.16	267	4.17	308	3.95	—	—
8-hydroxypsoralen + Na ethoxide	228	4.33	282	4.20	327	3.86	—	—	—	—	—	3.99	—	—
8-hydroxypsoralen + Borax	228	4.38	282	4.25	327	3.97	—	—	—	—	—	—	—	—
8-Hydroxy-5-methoxypsoralen	222	4.43	241	4.09	248	4.04	273	4.31	317	4.35	—	—	—	—
8-Hydroxy-5-methoxypsoralen + HCl	222	4.50	241*	4.18	248*	4.15	273	4.38	317	4.13	—	—	—	—
8-Hydroxy-5-methoxypsoralen + Na ethoxide	227	4.45	290	4.35	325	3.93	—	—	—	—	—	—	—	—
8-Hydroxy-5-methoxypsoralen + Borax	228	4.47	287	4.35	328	4.01	—	—	—	—	—	—	—	—
5,8-Dimethoxypsoralen	223	4.41	242	4.16	250	4.16	272	4.25	314	4.06	—	—	—	—
5,8-Dimethoxypsoralen + HCl	223	4.53	242	4.34	250	4.34	270	4.38	314	4.21	—	—	—	—
5,8-Dimethoxypsoralen + Na ethoxide	220	4.48	242	4.25	249	4.24	270	4.31	314	4.12	—	—	—	—

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