SPECTRAL-LUMINESCENT PROPERTIES OF NATURAL COUMARIN DERIVATIVES AND THEIR USE FOR GROUP IDENTIFICATION

V. P. Georgievskii and A. I. Rybachenko

UDC: 535.372

Natural hydroxycoumarins and their derivatives possess an intensive fluorescence depending on the type and position of substituents. From the wavelengths of the fluorescence maxima and the sizes of the Stokes shifts it is possible to identify the groups to which coumarins belong — hydroxycoumarins, furocoumarins, and angular dihydrofuro- and dihydropyranocoumarins.

It is known that in the series of simple natural coumarins and their glycosides the most pronounced fluorescence is possessed by 7-hydroxycoumarin and its derivatives. The presence of intense fluorescence in a series of linear and angular furocoumarins and angular dihydrofuro- and dihydropyranocoumarins has also been established [1, 2]. At the same time, the literature information on the luminescence of the compounds mentioned is contradictory and nonsystematic. The aim of our work was to supply this deficiency and to find spectroluminescent characteristics suitable for the qualitative and quantitative analysis of coumarin derivatives.

The wavelengths of the absorption and fluorescence maxima and the Stokes shifts are given in Table 1. Typical spectral curves of some compounds are shown in Fig. 1.

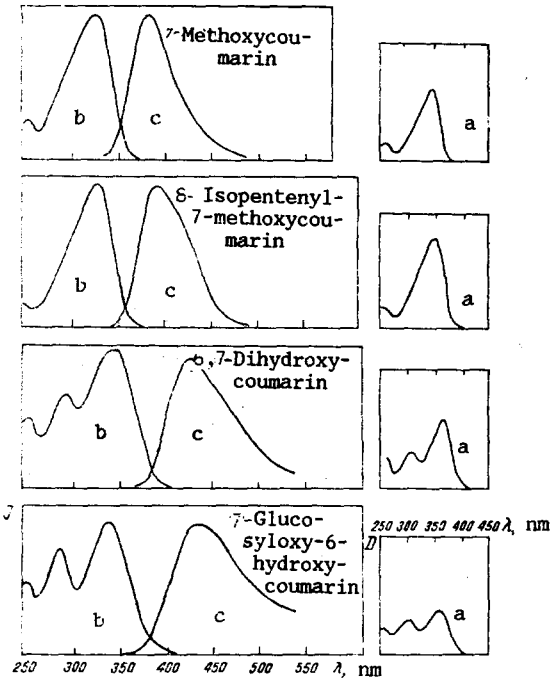
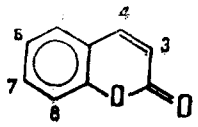
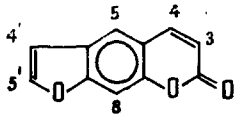
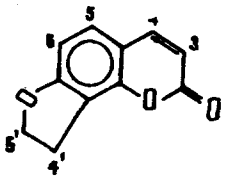
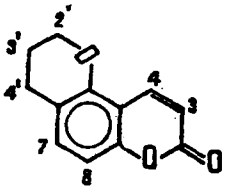


Fig. 1. Spectra of coumarin derivatives in ethanol: a) absorption; b) excitation of fluorescence; c) fluorescence.

All-Union Scientific-Research Institute of Drug Chemistry and Technology, Khar'kov.
Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 766-769, November-December, 1985. Original article submitted December 20, 1984.

0009-3130/85/2106-0725$09.50

TABLE 1. Maxima of the Absorption (long-wave part) and Fluorescence Bands and Stokes Shifts, nm

Compound	λ_{max}		Stokes shift, $\Delta\lambda$
	absorption	flourescence	
Simple coumarins			
			
1. 7-Hydroxycoumarin	324	454	130
2. 5-Methyl-7-hydroxycoumarin	333	460	127
3. 3-Carboxy-7-hydroxycoumarin	396	456	60
4. 3-Ethoxycarbonyl-7-hydroxycoumarin	398	456	58
5. 6-Methoxy-7-hydroxycoumarin	347	427	80
6. 4-Methyl-7-hydroxycoumarin	325	448	113
7. 3,4-Dimethyl-7-hydroxycoumarin	325	458	133
8. 8-Glucosyloxy-7-hydroxycoumarin	314	430	96
9. 4'4'-Dimethylcyclohexanyl-6-methyl-7-hydroxycoumarin	338	394	56
10. 6-(3,7-Dimethylocta-2,6-dienyl)-7-hydroxycoumarin	338	400	62
11. 6-Glucosyloxyl-7-hydroxycoumarin	391	458	67
12. 7-Methoxycoumarin	319	385	66
13. 5-Geranyloxy-7-methoxycoumarin	335	420	85
14. 6,7-Dimethoxycoumarin	343	420	77
15. 6,7-Dihydroxycoumarin	357	440	83
16. 4-Methyl-6,7-dihydroxycoumarin	360	440	80
17. 5-Methyl-6,7-dihydroxycoumarin	357	437	80
18. 7-Glucosyloxy-6-hydroxycoumarin	345	440	95
19. 7,8-Dihydroxycoumarin	327	434	107
20. 8-Isopentenyl-7-methoxycoumarin	320	394	74
21. 5,7-Dimethoxycoumarin	328	514	196
Linear furocoumarins			
			
Furo[2',3': 6,7]coumarin (psoralen)			
22. 8-Isopentenoyloxypsoralen	312	460	148
23. 5,8-Dimethoxypsoralen	318	514	202
24. 5-(2,3-Dihydroxy-3-methylbutoxy)-psoralen	310	474	164
25. 5,6-Dimethoxypsoralen	306	510	204
Angular dihydrofurocoumarins			
			
4',5'Dihydrofuro[2',3': 7,8]coumarin (dihydroangelicin)			
26. 4')-2'-Acetoxyisopropyl)-5'-tigloyoxy-4'-5'-dihydroangelicin	327	384	67
27. 4'-Acetoxy-5'-senecioyloxypropyl-4',5'-dihydroangelicin	326	383	57
Angular dihydropyranocoumarins			
			
4,5,-Dihydropyrano[2',3':5,6]coumarin (dihydroseselin)			
28. 4'-Acetoxy-5'-α-methylbutyryloxy-4',5'-dihydroseselin	326	386	60

As can be seen, all the fluorescence spectra of the simple coumarins and of the furo- and pyranocoumarins consist of broad structureless bands. The maxima of the fluorescence of the simple coumarins lie between 385 and 514 nm, those of the linear and angular coumarins between 420 and 514 nm, and those of the angular dihydrofuro- and dihydropyranocoumarins between 383 and 386 nm.

On the introduction of OH groups into the 7-hydroxycoumarin molecule at positions 6 and 8, a small hypsochromic shift of the fluorescence maxima is observed (compounds 15 and 19). The methylation of the 7-hydroxy group, glycosylation, and the introduction of radicals with unsaturated bonds (compounds 9 and 10) also lead to hypsochromic shifts of the fluorescence maximum. A "blue shift" from 454 to 385 nm for methylated umbelliferone is evidence in favor of the hypothesis that the maximum influence on fluorescence is exerted by a 7-hydroxy group, which possesses greater acidic properties, especially in methanol [3], than 6- and 8-hydroxy groups. Furthermore, the intensity of fluorescence of 7-methoxycoumarin is not much more than half the intensity of the fluorescence of 7-hydroxycoumarin, which also indicates the importance of the influence of 7-hydroxy group on the formation of the emission properties of the coumarins.

Angular and linear furocoumarins possess fluorescence with longer-wave maxima; linear furocoumarins with two methoxy groups in positions 5 and 8 and angular furocoumarins with methoxy groups in positions 5 and 6 are characterized by the greatest shift in the values of λ_{max}.

As was expected, the hydrogenation of the furan and pyran rings led to a hypsochromic shift of the fluorescence spectra.

The measurement of the Stokes shifts showed that for derivatives of 7-hydroxycoumarins with no additional hydroxy groups these shifts amounted to 113-133 nm (for compounds with free 7-hydroxy groups in the absence of substituents with unsaturated bonds or electron-accepting substituents; for the 5,7-dihydroxy derivatives this magnitude reaches 196 nm, for the 7,8-dihydroxy derivative 107 nm, and for the 5,6-dihydroxy derivatives 80 nm. Glycosylation at the 7-hydroxy group of the 7,8-dihydroxycoumarins and the 6,7-dihydroxycoumarins lowers the magnitude of the Stokes shift to 95-96 nm, and the glycosylation of the 6,7-dihydroxy compounds at the 6-hydroxy group lowers it to 67 nm. This difference in the values of $\delta\lambda_S$ is a distinguishing feature for glycosides of 6,7-dihydroxycoumarin.

A $\Delta\lambda_S$ value of 148 nm is characteristic for 8-hydroxypsoralen derivatives and one of 202-204 nm for a 5,8-dihydroxypsoralen or a 5,6-dihydroxyisopsoralen.

The angular dihydrofurano- and dihydropyranocoumarins have $\Delta\lambda_S$ values of 57-60 nm.

Thus, from the magnitude of the Stokes shifts and the maxima of the fluorescence spectra it is possible to identify the following groups of coumarin derivatives:

1) 7-hydroxycoumarin and its derivatives without substituents having unsaturated bonds or electron-accepting substituents have $\Delta\lambda_S$ values of 113-133 nm at λ_{max} = 448-460 nm;

2) 7-hydroxycoumarin derivatives having radicals with unsaturated double bonds or electron-accepting substituents have $\Delta\lambda_S$ values of 56-62 nm at λ_{max} = 394-456 nm;

3) derivatives of 7-methoxycoumarin and 6,7- and 7,8-disubstituted derivatives of coumarin have $\Delta\lambda_S$ values of 66-85 nm at λ_{max} = 385-420 nm;

derivatives of:

6,7-dihydroxycoumarin have $\Delta\lambda_S$ = 88-83 nm at λ_{max} = 440 nm;

6,7-dihydroxycoumarin have $\Delta\lambda_S$ = 107 nm at λ_{max} = 434 nm;

5,7-dihydroxycoumarin have $\Delta\lambda_S$ = 196 nm at λ_{max} = 514 nm;

4) dihydroxycoumarins glycosylated at a 7-hydroxy group have $\Delta\lambda_S$ = 95-96 nm at λ_{max} = 410-440 nm;

5) dihydroxycoumarins glycosylated at a 6-hydroxy group have $\Delta\lambda_S$ = 67 nm at λ_{max} = 458 nm

6) linear derivatives of:

8-hydroxypsoralen have $\Delta\lambda_S$ = 148 nm at λ_{max} = 460 nm;

5-hydroxypsoralen have $\Delta\lambda_S$ = 164 nm at λ_{max} = 474 nm;

5,8-dihydroxypsoralen have $\Delta\lambda_S$ = 202 nm at λ_{max} = 514 nm;

7) angular furocoumarin derivatives:

5,6-dihydroxyisopsoralen has $\Delta\lambda_S$ = 204 nm at λ_{max} = 510 nm;

8) angular dihydrofurano- and dihydropyranocoumarins have $\Delta\lambda_S$ = 57-60 nm at λ_{max} = 383-386 nm.

EXPERIMENTAL

The investigation was carried out with chromatographically pure natural compounds.* Absorption spectra were recorded on a Specord UV-VIS spectrophotometer and fluoresence spectra on a Hitachi MPF-4 spectrofluorimeter with a correction for the spectral sensitivity of the instrument. As an additional test for the purity of the compounds the pure excitation fluorescence spectra were obtained on the latter instrument and these were compared with the absorption spectra [4]. Ethanol purified by a standard method [5] was used as solvent.

SUMMARY

1. The absorption and fluorescence spectra and the Stokes shifts of 28 natural coumarins in ethanol have been measured.

2. It is proposed to perform the identification of natural coumarin derivatives from the values of the fluorescence maxima and the magnitudes of the Stokes shifts.

LITERATURE CITED

1. D. W. Fink and W. R. Kochler, Anal. Chem., 42, No. 9, 990 (1970).
2. G. F. Fedorin and V. P. Georgievskii, Zh. Prikl. Spektrosk., 20, No. 1, 165 (1974).
3. G. J. Yakaban, R. J. Juneau, and S. G. Schulman, J. Pharm. Sci., 61, No. 5, 749 (1972).
4. C. Parker, The Photoluminescence of Solutions, Elsevier, Amsterdam (1968).
5. A. J. Gordon and R. A. Ford, The Chemist's Companion, Wiley-Interscience, New York (1962).

*Samples of the compounds were provided by Professors A. P. Prokopenko and N. F. Komissarenko and by G. A. Zhukov (All-Union Scientific-Research Institute of Drug Chemistry and Technology).