SPECTROPHOTOMETRIC DETERMINATION OF THE MOLECULAR WEIGHTS OF COUMARINS AND FUROCOUMARINS

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The spectrophotometric method is used to determine the molecular weights of various compounds [1, 2]. Two approaches are possible; either a substance having an absorption band in some particular region of the spectrum is added to a substance not absorbing in this region, or the absorption of the substance itself is used as the basis for the determination.

Positions and Intensities of the Long-Wave Bands in the UV Spectra of Coumarins and Furocoumarins and the Results of the Determination of their Molecular Weights by the Spectrophotometric Method

Group number	Compound	λ_{max}	E_{max}	E_{max} mean	M	Mol. wt. Found	Error abs.	Error rel., %
I	Herniarin	324	14345		176.2	183.5	+7.3	+4.1
	Umbelliprenin	325	15015		366.3	366.2	−0.1	—
	Zosimin	325	14844	14935	328.4	330.4	+2.0	+0.6
	Osthole	324	15562		244.3	234.5	−9.8	−4.0
	Suberosin	331	14902		244.3	244.8	+0.5	+0.2
II	Bergapten	311	14075		216.2	226.0	+9.8	+4.5
	Oxypeucedanin	310	14658	14715	286.3	287.4	+1.1	+0.4
	Pranferol [4]	311	14876		288.3	281.7	−6.6	−2.3
III	Isoimperatorin	310	15245		270.3	260.9	−9.4	−3.5
	Xanthotoxin	300	12215	12650	216.2	222.3	+6.1	+2.8
	Imperatorin	300	12907		270.3	263.3	−7.3	−2.7
IV	Isopimpinellin	313	12753		246.2	246.9	+0.7	+0.3
	Phellopterin	313	13005	12790	300.3	295.4	−4.9	−1.6
	Byak-angelicin	313	12616		334.3	339.2	+4.9	+1.5

The second approach is applicable to coumarin derivatives. In the majority of natural coumarins and furocoumarins the chromophoric system remains unchanged and only the aliphatic substituents vary. Consequently, the UV spectra do not fundamentally depend on the size of the side chains or the saturated rings. However, the influence of O-alkyl substituents on the spectrum, which is due to the participation of the unshared pair of electrons of the oxygen atom in conjugation with the aromatic nuclei and depends on the position of the substituent, must be taken into account. Hence, each type of substitution must be characterized by definite features of the absorption.

All the coumarins and furocoumarins investigated can be divided into a number of groups depending on the position of the substituents. We considered four groups: I) coumarins containing O-alkyl substituents in position 7; II) furocoumarins having one O-alkyl substituent in position 5; III) furocoumarins with a substituent in position 8; and IV) furocoumarins with two O-alkyl substituents in positions 5 and 8. As follows from the results that we obtained (table), the position of the longwave maximum is practically constant within each group (suberosin from group I is somewhat of an exception), and the molar absorption coefficient E changes within a range of ±4.5%. If the arithmetic mean of all the values of E within each group is taken and the molecular weights of the compounds are calculated from this, then, as follows from the table, the deviation from the true values does not exceed ±4.5%. Thus, the mean values of the molar absorption coefficients of the longwave band can be used to determine the molecular weights of new coumarin derivatives with an accuracy of ±4.5%.

The assignment of a new compound to one group or another can be carried out on the basis of the position of the maximum of the longwave band in the UV spectrum, chemical data, or data of NMR and IR spectra.

We calculate the molecular weights (M) of the substances investigated from the formula

$$M = \frac{E_\lambda \cdot P \cdot l}{v \cdot D_\lambda},$$

where E_λ is the mean value of the molar absorption coefficient at the maximum of the longwave band (λ, mμ) for the given groups; D_λ is the optical density of a solution of the substance at λ mμ; P is the weight of the sample, mg; v is the

volume of the solution of the substance, ml; and l is the thickness of the cell, cm.

Of course, the four groups mentioned do not exhaust all the possible variants of the substitution of coumarins and furocoumarins. It may be assumed that the condition of constant position of the long-wave maximum and the relative equality of the molar absorption coefficients within a single group will also be satisfied for other types of substituted coumarin derivatives.

The main virtues of the method discussed are its simplicity and the small amount of substance (~1 mg) required for the determination.

Experimental

The determinations were carried out in 96% ethanol in a SF-4A spectrophotometer; 1-cm cells were used. Five to seven independent determinations were carried out for each compound (the mean values are given in the table).

The following procedure for the determination of the molecular weights of coumarins and furocoumarins is recommended: 1 mg of the substance under investigation (accurately weighed on a microanalytical balance) is dissolved in alcohol in a 25-ml measuring flask. To 2 ml of this solution is added 10 ml of alcohol. The resulting solution is examined in a 1-cm cell in the range from 295 to 340 mμ at 2-mμ intervals. When the absorption maximum has been determined, the accurate value of the optical density of the solution is measured at this wavelength. Under these conditions, the formula for calculation has the form

$$M = \frac{E_\lambda \cdot F}{150 \cdot D_\lambda}$$

(symbols as above).

We obtained the compounds studied from G. K. Nikonov, G. A. Kuznetsova, and Yu. A. Dranitsina.

Summary

A spectrophotometric method for the determination of the molecular weights of coumarins and furocoumarins with an accuracy of ±4.5% has been proposed.

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