POLAROGRAPHIC DETERMINATION OF THE MOLECULAR WEIGHTS OF NATURAL COUMARINS

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Various methods are used to determine the molecular weights of natural coumarins: the spectrophotometric method [1], the mass-spectral method [2], and the classical method of Rast [3]. The most accurate and universal is the spectrophotometric method. The mass-spectral method is technically complex and is unsuitable in some cases, since on electron impact not all coumarins form the molecular ion. The applicability of Rast's classical method is frequently limited by low accuracy and by the poor solubility of coumarin compounds in the eutectic with camphor (particularly for compounds of high molecular weight). However, the spectrophotometric method may also some times give considerable errors when the substances decompose in UV light and when the absorption band is diffuse.

We have proposed a polarographic method for determining the molecular weights of coumarins which is free from the defects described above.

By using the ratio between the molecular weight and the diffusion coefficient, together with Ilkovič's equation [4] we have derived the following equation for determining molecular weights:

$$M_x = \sqrt[5]{10^{16}\frac{I_{st}^4 \cdot M_{st} \cdot C_x^4(\%)}{I_{st}^4 \cdot C_{st}^4\,(\mathrm{mM})}},$$

where M_x is the molecular weight of the coumarin under investigation; I_{st} is the magnitude of the current of a standard coumarin solution, μA; I_x is the magnitude of the current of the coumarin solution under investigation, μA; M_{st} is the molecular weight of the standard coumarin compound; C_{st} is the concentration of the standard coumarin solution, mM; and C_x is the concentration of the coumarin solution under investigation %. We have checked the equation experimentally.

The work was performed on an Lp-55 polarograph. Characteristics of the capillary: 1.80 $mg^{2/3}$ $sec^{1/2}$. Coumarin itself was used as the standard compound.

Method of Determination. About 0.02 g (accurately weighed) of the coumarin compound was dissolved in 70 ml of solvent (water, methanol, ethanol, or mixtures of water and alcohols), and the solution was made up to the mark in a 100-ml flask. To 5 ml of the resulting solution was added 3 ml of the background solution [5% LiCl, 5% $(C_2H_5)_4NI$], and the mixture was placed in an electrolyzer and stirred, and nitrogen was passed through it for 5-10 min. Then polarography was carried out in the range from 1.0 to 2.0 V with cathodic polarization.

We have determined the molecular weights of the following standard compounds by this method: 6-methylcoumarin, xanthotoxin, fraxinol, bergapten, umbelliprenin, peucenidin, osthole, angelicin, isopimpinellin, psoralen, libanotin, visnadin, isopentylcoumarin, fraxinol acetate, and imperatorin. The relative error of the determination was ± 2.5%, and the time of a determination 15-20 min.

The method has been used to determine the molecular weights of a number of coumarins isolated from plants (athamantin, peucenidin, and libanotin). The polarographic results were checked by mass spectroscopy, UV spectroscopy, and the Rast method.

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