BRIEF COMMUNICATIONS

CHEMICAL STRUCTURE AND ANTIOXIDANT ACTIVITY AMONG NATURAL COUMARINS

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Continuing investigations of the physicochemical properties of natural coumarins [1], we have studied their antioxidant properties on the sulfite-oxygen model [1-3] with the aim of finding stabilizers for drugs and methods of analyzing them and of establishing a quantitative link between the chemical structure and biological action of natural coumarins [4].

The kinetic parameters of the influence of natural coumarins on the absorption of oxygen by sulfite were measured by the polarographic method from the decrease in the oxygen wave [3].

As a result of the investigations performed it was established that the antioxidant action of natural coumarins depends linearly on the polar influence of a substituent, which was evaluated in our case from the value of $E_{1/2}$ — the half-wave polarographic potential [1]. In view of the fact that $E_{1/2}$ for natural coumarins depends linearly on the energy of the lowest unoccupied orbital [1] and the energy of the long-wave absorption band in the UV and IR region [1], it is possible to evaluate the antioxidant activity of natural coumarins from the above-mentioned parameters of their physicochemical properties, which reflect the chemical structures of the natural coumarins.

Since the energy of electron affinity (EA) is evaluated from the values of $E_{1/2}$ for reduction at a dropping mercury electrode [1, 5], it is also possible to characterize the antioxidant action of natural coumarins from their EA values.

With respect to the efficacy of their antioxidant action, the natural coumarins can be arranged in the sequence esculetin > xanthotoxol > fraxinol > umbelliferone > 4-methylumbelliferone > coumarin > 6-methylcoumarin > xanthotoxin, showing a weakening of antioxidant activity. As for the curve of the integral intensity of the carbonyl group in the IR spectra of natural coumarins [6, 7], in curves of the time of inhibition versus concentration there is a bifurcation or splitting of the main curve when substituents are introduced into the coumarin, psoralen, or angelicin ring.

A characteristic constant of the natural coumarins is the rate of cleavage of the lactone ring, which, as we have shown [1], depends on the π-electron density of the pyrone ring of the coumarin. Therefore, with a rise in the value of $E_{1/2}$ the cleavage of the lactone ring becomes more difficult while the antioxidant or inhibiting action of the natural coumarins rises. Thus, the antioxidant activity of the natural coumarins can be estimated from the values of the rate constants of the cleavage of the lactone ring determined by various physicochemical methods [1, 4, 8].

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