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Amid derivatives of salicylic acid – effective inhibitors of UV initiated oxidation of organic substrates

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Abstract

The results of the research are presented kinetics of UV initiated oxidation model substrate (methyloleat) in the presence of individual amides: 2-hydroxybenzoic acid N-(4-hydroxybenyl)amide (I); 2hydroxy-3-tretbutyl-5-ethylbenzoic acid N-(4-hydroxy-3,5-di-tret-butylphenyl)amide (II); 2- hydroxybenzoic acid N-[3-(4-hydroxy-3,5-di-tret-butylphenyl)prop-1-yl]amide (III); 2-hydroxy-3-tretbutyl-5-ethylbenzoic acid N-[3-(4-hydroxy-3,5-di-tret-butylphenyl)prop-1-yl]amide (IV) in comparison with reference antioxidants - dibunol and α -tocopherol. It is shown that all amides of salicylic acid I-IV effectively inhibit the process UV initiated oxidation of methyloleat. It is studied a relationship between antioxidant properties of amides salicylic acid I-IV of UV initiated oxidation and features of their structure. It is established that introduction shielding ortho-t-butyl substituents and separation of aromatic fragments by three methylene groups leads to a significant increase of antioxidant activity. It is shown that amide IV in the concentration range $(0.5-2.0) \cdot 10^{-4}$ Mol/L exceeds the efficiency of dibunol by 20%.

Testing the anti-radical activity of amides I-IV estimated by the chemiluminescence method from the constant rate of the reaction with peroxy radicals allowed to establish the range of changes in value $k_7 = 0.52 - 1000$ 6.86.10⁴, mol⁻¹·s⁻¹. It is shown that screening of phenolic OH-groups tret-butyl substituents and reduction of conjugation of electron density in molecules by separating the residue of salicylic acid and phenol by methylene groups leads to a significant decrease in anti-radical activity of antioxidants. Thus, the largest value of k₇ was established for the amide I, which in its structure has two unsubstituted phenolic hydroxyls. The antiradical activity of the shielded analogue (amide II) is 4 times inferior. The mechanism of the inhibitory action of amides of salicylic acid was established, it includes: direct interaction of phenols with free radicals; destruction of hydroperoxides of lipids due to the amide fragment of the molecule; partial absorption of UV radiation, associated with the presence of a salicylic acid residue.

References

- [1] N.M. Emanuel, E.T. Denisov, Z.K. Mayzus. Chain reactions of oxidation of hydrocarbons in the liquid phase. Moscow: Science. 1966. 375p. (russian)
- [2] V.Ya. Shlyapintok. Photochemical transformations and stabilization of polymers. *Moscow: Chemistry*. **1979**. 344p. (russian)
- [3] B.N. Gorbunov, Ya.A. Gurvich, I.P. Maslova. Chemistry and technology of stabilizers of polymeric materials. Moscow: Chemistry. 1981. 368p. (russian)
- [4] M. Diepens, P. Gijsman. Photodegradation of bisphenol a polycarbonate with different types of stabilizers. Polymer Degradation and Stability. 2010. Vol.95. No.5. P.811-817.
- [5] T.G. Denisova, E.T. Denisov. Reactivity of natural phenols in radical reactions. *Kinetics and Catalysis*. 2009. Vol.50. No.3. P.335-343.
- [6] Oxidative stress. Prooxidants and antioxidants. E. B. Menschikova [et al]. Moscow: Firm "Word". 2006. 554p. (russian)
- [7] Phenolic bioantioxidants. N. K. Zenkov [et al]. Novosibirsk. 2003. 328p. (russian)
- [8] Features of inhibitory action of antioxidants of the IBCPhN group. N.M. Storozhok, M.G. Perevozkina. Scientific Bulletin of the Tvumen Medical Academy. 2003. No.1. P.52-59. (russian)
- [9] To the mechanism of action of new sulfur-containing antioxidants. N.M. Storozhok, N.V. Gureeva, A.P. Krysin. Scientific Bulletin of the Tyumen Medical Academy. 2003. No.1. P.18-22. (russian)

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- [10] Synthesis, structure and antioxidant activity of sulfur tetrakispenol G.N. Nugumanova [et al]. Journal of Organic Chemistry. 2010. Vol.80. No.7. P.1175-1184. (russian)
- [11] Synthesis, structure and activity of antioxidants "hybrid structure" based on N-substituted amides of salicylic acid. N.M. Storozhok, N.P. Medianik, A.P. Krysin et al. *Journal of Organic Chemistry.* 2013. Vol.49. No.7. P.1046-1049. (russian)
- [12] Photolysis of sulfosalicylic acid in aqueous solutions over a wide pH range. I. P. Pozdnyakov [et al]. J. *Photochem. Photobiol. A: Chem.* **2006**. Vol.181. No.1. P.37-43.
- [13] Determination of rate constants and inhibition coefficients of phenol antioxidants using a model chain reaction. V.F. Tsepalov [et al]. *Kinetics and Catalysis.* **1977**. Vol.18. No.5. P.1261-1267. (russian)
- [14] Chemiluminescent methods for studying slow chemical processes. V.Ya. Shlyapintokh [et al]. *Moscow: Science*. **1966**. 138p. (russian)
- [15] About the role of the elementary reaction 10 in the kinetics of the oxidation of polyunsaturated lipids.
 N.M. Storozhok, N.V. Gureeva. *Scientific Bulletin of the Tyumen Medical Academy*. 2003. No.1. P.27-35. (russian)
- [16] N.M. Storojok, N.P. Medyanik, S.A. Krekov, and A.P. Krisin. The supramolecular organization *N*-replaced amides of salicylic acid. *Butlerov Communications*. 2011. Vol.24. No.3. P.109-112. ROI-jbc-01/11-24-3-109
- [17] V.L. Antonovsky. Organic peroxy initiators. Moscow: Chemistry. 1972. 448p. (russian)
- [18] Kinetics and mechanism of photochemical reactions of N-substituted amide of salicylic acid. N.P. Medyanik, N.V. Gureeva, N.M. Storozhok. *News of the Tomsk Polytechnic University*. Vol.318. No.3. P.116-120. (russian)
- [19] Photochemistryof *N*-substitutedsalicylicacidamids. I.P. Pozdnyacov, N.M. Storozhok, N.P. Medyanik et al. *Russian Chemical Bulleten, International Edition.* **2015**. Vol.64. No.6. P.1319-1326.