INTERACTION OF TAURINE AND β-ALANYL-L-HISTIDINE (CARNOSINE) WITH THE HYPOCHLORITE ANION (ClO^-)

T. N. Gorshkova, V. E. Formazyuk, V. I. Sergienko, and E. I. Dudina

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One of the known compounds which can neutralize hypochlorite anions in mammals (including man) is the sulfoamino acid taurine [14]. In a previous publication we showed that β-alanyl-L-histidine (carnosine) possesses similar properties [1]. The functions of this dipeptide are still the subject of considerable discussion [5, 7, 8-12]. Nevertheless, this does not rule out the possibility of its use in the treatment of inflammation [8], to accelerate wound healing [9], in radiation damage [7], in the chemotherapy of neoplasms [12], in cataract [1, 6], and in various other diseases. Many investigators associate the diversity of the reactions characteristic of this dipeptide with its ability to interact with active forms of oxygen. The antioxidative properties of carnosine have been established in several studies [3, 7, 13, 14]. We also have shown that carnosine can suppress chemiluminscence in a system consisting of NaClO + H_2O_2 [3]. The writers showed previously that both carnosine and taurine can interact with the hypochlorite anion to form stable chloramine complexes [1]. The aim of this investigation was to make a more detailed comparative study of the reaction of these two substances with ClO^-.

EXPERIMENTAL METHOD

The carnosine used was of Russian origin, and taurine was obtained from "Serva." Solutions were made up in physiological saline buffered with 0.05 M phosphate (pH 7.3).

Interaction of these solutions with sodium hypochlorite was studied on a UV-265 spectrophotometer ("Shimadzu," Japan). Sodium hypochlorite was obtained by electrochemical oxidation of NaCl solution on the EDO-3 apparatus. Its concentration was measured spectrophotometrically as absorption at 292 nm.

EXPERIMENTAL RESULTS

As early as 1 min after mixing of the solutions of taurine or carnosine with sodium hypochlorite, the formation of a new absorption peak at 251.2 nm was recorded, and judging from data in the literature [15] this indicates the formation of a chloramine complex (Fig. 1). Absorption at 292 nm, characteristic of sodium hypochlorite, decreases under these circumstances with an increase in the quantity of taurine or carnosine in the mixture. It will be noted that taurine, if the same solutions of sodium hypochlorite were used, reacted more actively than carnosine (Fig. 2).

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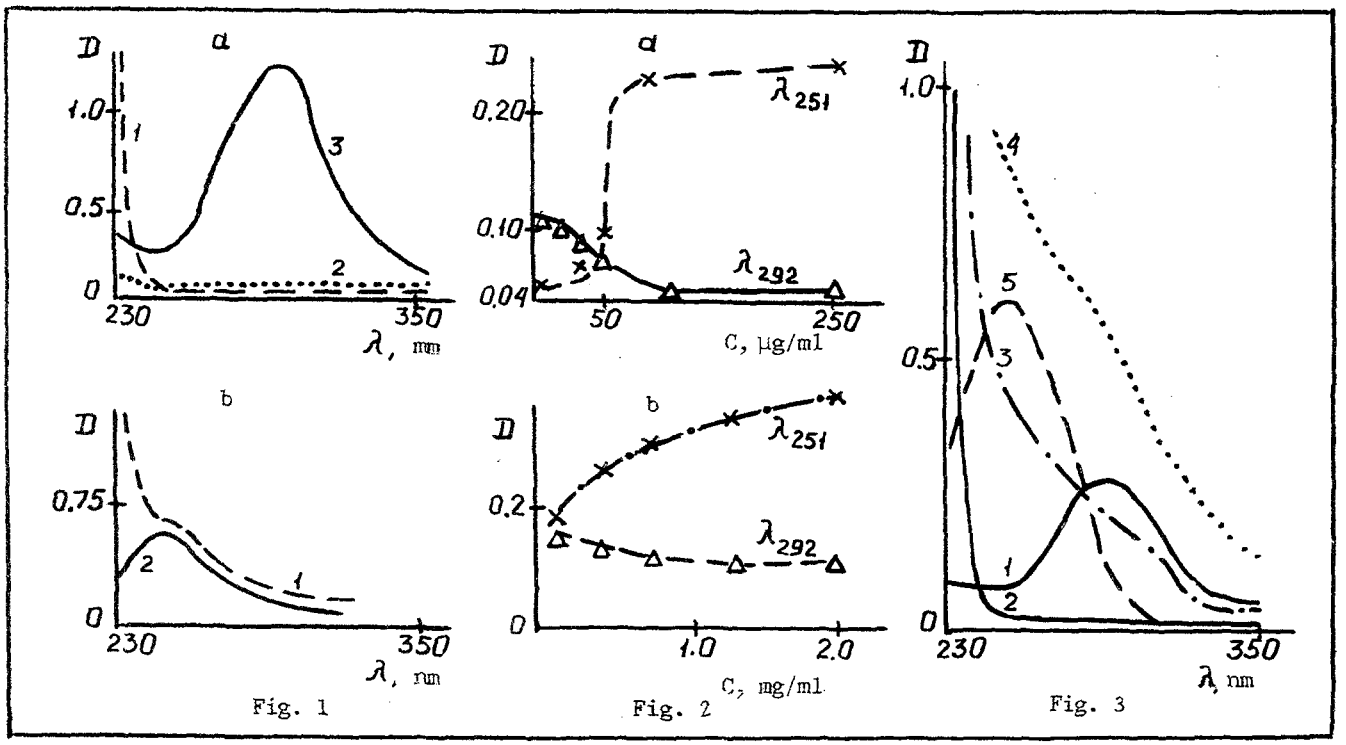

Fig. 1 Fig. 2 Fig. 3

Fig. 1. Absorption spectra of solutions of taurine, carnosine, and sodium hypochlorite: a) without addition of sodium hypochlorite. 1) Carnosine; 2) taurine; 3) sodium hypochlorite (NaClO), b) 10 min after mixing with sodium hypochlorite solution. 1) Carnosine + NaClO; 2) taurine + NaClO. Concentration of taurine and carnosine, each 5 mM, of sodium hypochlorite 4 mM. Ordinate, optical density in relative units. Abscissa, wavelength of absorption, in nm.

Fig. 2. Absorption of solutions of taurine and carnosine at different wavelengths depending on concentration of these amino compounds. Ordinate, optical density in relative units, measured 10 min after mixing of amino compounds with hypochlorite. Abscissa, concentration of taurine (a) or carnosine (b). Sodium hypochlorite concentration 4 nM.

Fig. 3. Stability of taurine and carnosine complexes with hypochlorite: 1) sodium hypochlorite (NaClO); 2) carnosine without any other procedure; 3) carnosine solution after keeping for 2 weeks in light at +33°C; 4) carnosine + NaClO after keeping for 2 weeks; 5) taurine + NaClO after keeping for 2 weeks in light at +33°C. Other explanations and concentrations of substances as in Fig. 1.

The next stage in the work was to compare the stability of the chloramine complexes thus obtained during keeping. In this case we used ratios of concentrations of the oxidizing agent (ClO^-) and the substance to be oxidized so as to ensure the maximal utilization of hypochlorite. It can be concluded from the data in Fig. 3 that the taurine complexes were relatively stable and that the complexes formed with carnosine gradually decomposed. On keeping of the individual solutions of taurine and carnosine in the absence of the oxidizing agent, the sulfoamino acid taurine was found to undergo hardly any decomposition in light, or on elevation of the temperature to +33°C, whereas the solution of the dipeptide carnosine turned appreciably yellow under the same conditions of keeping.

In a recent study by Aruoma and co-workers [5] the absence of any marked reaction of carnosine with the hypochlorite anion was reported. However, these workers used an indirect method of assessing interaction between these compounds: based on the inactivating action of HClO on α-antiperoxidase in the presence of the dipeptide. As our own investigations showed, carnosine, like taurine, interacts with the hypochlorite anion with the formation of a chloramine complex. However, taurine reacts more actively than the dipeptide with the oxidizing agent (Fig. 2), and its chloramine complexes are more stable (Fig. 3). Several times less taurine than carnosine is required to neutralize the same quantity of hypochlorite anions.

The discovery of chloramines as a result of interaction of amino acids or a dipeptide with the Cl^--anion requires a new interpretation of the inhibition of chemiluminescence which we observed previously in the NaClO + H_2O_2 system [3, 4, 13]. Evidently not only carnosine can reduce the quantum yield of luminescence of this reaction (through quenching the luminescence of singlet oxygen), but also its chloramines. For instance, according to our investigations, chloramine complexes can reduce the quantum yield of luminescence by several times.

Russian scientists were the first to discover the anticataract action of taurine (the commercial name of this preparation is "Taufon") and of carnosine ("Sevitin") [1]. Incidentally, both preparations possess an antiinflammatory action. Processes of inflammation accompanied by release of cationic proteins (such as myeloperoxidase, elastase, cathepsin G, defensins, and so on) from neutrophilic granulocytes, can initiate opacity of the lens [1]. It can accordingly be concluded that the anticataract action of Taufon and Sevitin is based on their ability to neutralize one of the products of the reaction catalyzed by myeloperoxidase, namely the hypochlorite anion.

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