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Study on the Mechanism of Suppression of Lipid Peroxidation by Saccharides

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The mechanism of the suppression of lipid peroxidation by saccharides was investigated. Trehalose effectively inhibited the heat- or radical-induced peroxidation of unsaturated fatty acid (UFA). Several other saccharides, such as sucrose, maltose and neotrehalose, showed negligible effect on the peroxidation, but maltitol's effectiveness was second to that of trehalose. Maltitol inhibited the peroxidation of UFA by its radical-scavenging effect. Thus, among the sugars studied so far, trehalose is a unique antioxidant whose reaction mechanism has not been clarified. We started this study with the hypothesis that trehalose interacts directly with oxidation-sensitive parts of UFA and consequently protects it from the autoxidation. NMR experiments performed, including ^{1}H-^{1}H NOESY measurements, indicated that trehalose selectively interacts with the *cis*-olefine proton pair in the above UFA with 1 : 1 stoichiometry, and the C-3 (C-3´) and C-6´ (C-6) sites of the sugar are responsible for the interaction. Similar interactions were not observed for the mixtures of the UFA and other saccharides. Quantum chemical study indicates that the OH-3 and OH-6 groups of trehalose bind to the olefin double bonds through OH…π and CH…O types of hydrogen bonds, respectively. Furthermore, the activation energies were calculated for the hydrogen abstraction reactions from the activated methylene group of heptadiene by a methyl radical. The activation energy drastically increased to *ca*. 30 kcal mol^{-1} on the complexation with trehalose. These results strongly support the antioxidant mechanism deduced in the previous study and indicate that the formation of unique multiple hydrogen bonds between trehalose and *cis*-olefin bonds is a rather general event, not confined to the case of UFA. This is the first study to elucidate the antioxidant function of trehalose and maltitol.

Key words: trehalose, maltitol, lipid peroxidation, multiple hydrogen bonds interactions,

radical-scavenging effect

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