Formation of Inclusion Compounds of β-Cyclodextrin with Hydroperoxides

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The degradation of starch by the action of *Bacillus macerans* amylase yields cyclic dextrins composed of six, seven, eight, or more α-D-glucopyranose units linked 1→4 as in amylose. They have void spaces in the molecules and enclose a number of organic compounds in it to form crystalline adducts.[1] We wish to report that various hydroperoxides are also enclosed by β-cyclodextrin (I), a cyclic dextrin with seven glucosyl residues, to form crystalline adducts.

When I (1.00 g) and *t*-butyl hydroperoxide (II) (0.50 g) were dissolved in 50 m*l* of warm water and the solution was cooled in ice water, a white precipitate was formed. On the other hand, no appreciable change occurred when D-glucose, instead of I, was dissolved in the aqueous solution of II. In the former case, the precipitate was separated from the solution by filtration, washed with cold water, dried under vacuum (2 mmHg) at room temperature, and weighed as 0.91 g. mp 215°C (decomp.). The resulting solid (III) contained 0.80 mmol/g of hydroperoxide residue, which was determined by the iodometric method.[2] The content of I in III was determined to be 0.74 mmol/g by the measurement of the optical rotation on the assumption that the specific rotation of I, determined to be +168° in water at room temperature (lit,[3] +162.5°), dose not change by the interaction with II. These results suggest that I and II form an inclusion complex with the mole-ratio of about 1 : 1.

It is interesting that II, which is fairly volatile (bp 4.5—5.0°C/2 mmHg[4]), did not evaporate even at room temperature under 2 mmHg as a result of the formation of the adduct, although at 56°C under 2 mmHg the hydroperoxide content of III decreased to 0.24 mmol/g. This indicates that II is fairly strongly bonded to I. It is considered[5] that the main forces binding the constituents of cyclodextrin complexes are hydrogen bonding, van der Waals forces, and hydrophobic interactions. In the present case, it seems that hydrogen bonding plays a major role, for hydroperoxides are known to have the strong ability of hydrogen bond. This is supported by the fact that no crystalline adduct was formed between I and *t*-butyl alcohol which has less strong ability of hydrogen bonding than II.

Hydroperoxides other than II, such as *n*-butyl, isoamyl, *t*-amyl, *s*-octyl, and cumene hydroperoxides, also formed the crystalline adducts with I. Primary and secondary hydroperoxides, as well as tertiary hydroperoxides, form the inclusion compounds of I with the mole-ratio of about 1 : 1. All the inclusion compounds studied can be dried without loss of hydroperoxides at room temperature under 2 mmHg. In the case of isoamyl, *t*-amyl, and cumene hydroperoxides vacuum drying even at 56°C caused no loss of hydroperoxides. Thus, I serves not only as a precipitant for hydroperoxides but also as a reagent making volatile hydroperoxides non-volatile by means of inclusion.

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