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Recognition of Tetralin Hydroperoxide by Cyclodextrins

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The recognition ability of α-, β- and γ-cyclodextrins (CDs) to tetralin hydroperoxide is discussed. CDs formed inclusion complexes more predominantly with tetralin hydroperoxide than with tetralin. The most noticeable specificity was found when β-CD was used as a host. Inclusion complexes of CDs with tetralin were also prepared and their molar ratios were determined.

Organic substrates such as oils, plastics and rubbers deteriorate by the action of atmospheric oxygen. These oxidative deterioration, called autoxidation, proceeds through radical chain reactions supported by peroxyl radicals to produce hydroperoxides in the substrates. The hydroperoxides are readily decomposed to peroxyl radicals, and initiate the radical chain reaction of autoxidation.[1,2] Recently, free radicals and reactive oxygen intermediates, such as lipid hydroperoxides, are suggested as a major cause of aging and various diseases.[3,4] The hydroperoxides do not only accelerate oxidative deterioration of organic substrates, but also injure the biological system.

Cyclodextrin (CD), which is a cyclic oligomer composed of α-(1,4)-linkages of six or more members of glucose units, has the ability to form inclusion complexes with various compounds.[5] β-CD is known to form a crystalline adduct with *t*-butyl hydroperoxide, but not with *t*-butyl alcohol.[6] This substrate specificity may be due to their hydrogen bonding between the hydroperoxyl group of *t*-butyl hydroperoxide and the hydroxyl groups of CD. From these facts, it appears feasible to remove the tetralin hydroperoxide from the autoxidized tetralin by means of the selective inclusion with CD. Tetralin is oxidized readily by atmospheric oxygen to form tetralin hydroperoxides as shown in Fig. 1.[7]

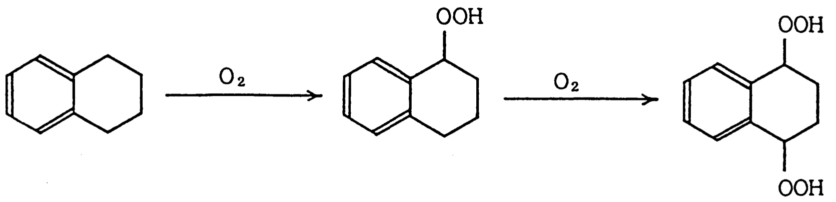

Fig. 1. Autoxidation of tetralin.

Selective inclusion of tetralin hydroperoxide by CD was discussed. A 1.0×10^{-1} mol·dm^{-3} α-CD aqueous solution, a 1.0×10^{-2} mol·dm^{-3} β-CD solution or a 1.0×10^{-2} mol·dm^{-3} γ-CD solution were added to 0.66 g (5.0×10^{-3} mol) autoxidized tetralin having initial peroxide values (POV)[8] of 20.6, 45.4 and 135.4, respectively, and stirred at 25 ℃ for 1 h. The molar ratio of CD to tetralin was 0.01, 0.05, 0.10 and 0.20. The resulting white precipitate of the inclusion complex of CD was then filtered off and washed with hexane. The organic layer of the combined filtrates was separated and the solvent was evaporated in vacuo to obtain the treated tetralin. The POV of the treated tetralin was determined and compared with the initial POV.

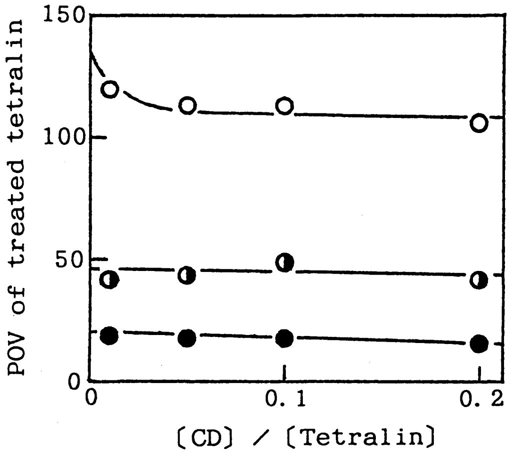

Fig. 2. Selective inclusion of tetralin hydroperoxide by α-CD.

Figures 2, 3, and 4 show the POV of tetralin after treatment with each CD.

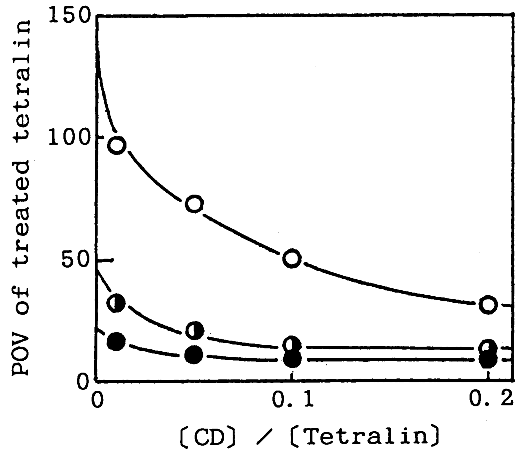

Fig. 3. Selective inclusion of tetralin hydroperoxide by β-CD.

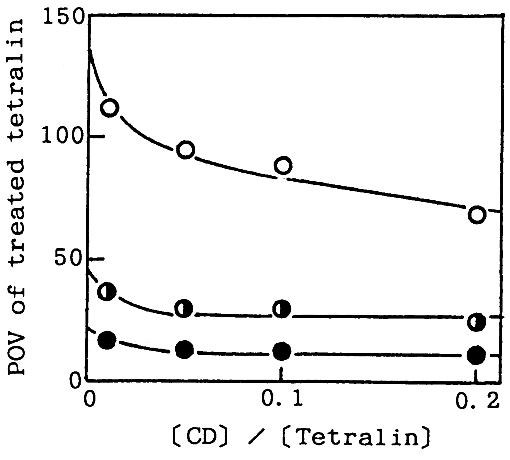

Fig. 4. Selective inclusion of tetralin hydroperoxide by γ-CD.

From Fig. 2, a decrease in the POV of the tetralin after treatment with α-CD was not clearly seen. Whereas, from Figs. 3 and 4, the POV of the tetralin treated with β- or γ-CD had apparently decreased. The most remarkable effect was seen in the case of β-CD. From these facts, it is suggested that β- and γ-CD form inclusion complexes with tetralin hydroperoxide with high selectivity.

Figure 5 shows the TLC analyses of refined tetralin (POV=2.8), autoxidized tetralin (POV=135.4), and the tetralin treated with β-CD (POV=50.4). (TLC plates: Kieselgel 60 F_{254} Merck; eluent: $CHCl_3$)

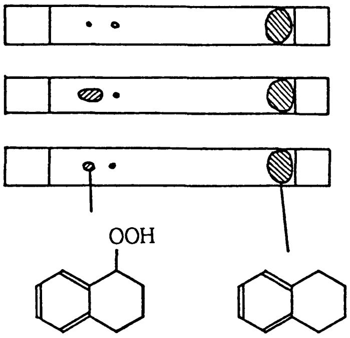

Fig. 5. TLC analyses of tetralin treated with CD.

As seen in Fig. 5, the amount of component (Rf=0.16) was decreased by selective inclusion of β-CD. Chromatographically isolated product of Rf=0.16 was determined to be tetralin monohydroperoxide.[9]

It was also found that CD can form an inclusion complex with tetralin. The inclusion complex was prepared by adding 13.2 mg (1.0×10^{-4} mol) of tetralin to 1.0×10^{-1} mol·dm^{-3} α-CD aqueous solution (1 cm^3) or 1.0×10^{-2} mol·dm^{-3} β- or γ-CD aqueous solution (10 cm^3) with stirring at 25 ℃. After stirring for 1 h, the white precipitates were filtered and washed with 10 mL of water and 10 mL of $CHCl_3$ to give the inclusion complex of tetralin and CD. The molecular structure and molar ratio of CD to tetralin were determined by ^{1}H NMR spectroscopy.[10] Table 1 shows the yields and molar ratio of the adduct. β- and γ-CD formed inclusion complexes with tetralin having a molar ratio of approximately 1:1. On the other hand, two and a half α-CD molecules were needed to form an inclusion complex with one tetralin molecule, but the yield was lower than those of β- and γ-CD.

Table 1. Inclusion complexes of CD with tetralin

Host	Yield / %	Molar ratio [CD] : [Tetralin]
α-CD	12.7	2.5 : 1
β-CD	48.8	1.1 : 1
γ-CD	31.1	0.9 : 1

It was found that CD formed inclusion complexes with both tetralin and tetralin monohydroperoxide, but β- and γ-CD formed complexes with tetralin monohydroperoxide more selectively than only tetralin. It seems that this recognizing ability of CD to the tetralin monohydroperoxide was ascribed to the high stability of the inclusion complexes of CD with tetralin monohydroperoxide due to their hydrogen bonding between host and guest molecules.

This recognizing ability of CD may be applied to the refining of oils or petroleum products with saving energy. Furthermore, CD is expected to be applied to the model of an enzyme which decomposes hydroperoxides such as glutathione peroxidase.

References

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8) Peroxide value (mequiv./kg), "Standard Methods for Analysis of Oils, Fats, and Derivatives," 2.4.28.1-81, Jpn. Oil Chem. Soc., (1981).
9) Found: C, 73.21; H, 7.38%. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37%. IR (Capi.), 3440 cm^{-1} (O-O-H), 2935, 2870 cm^{-1} (CH_2), 1490, 1590 cm^{-1} (arom.). ^1H NMR, 1.4-2.9 (6H, CH_2), 5.0 (1H, CH), 6.9-7.6 (4H, arom.), 8.2 (1H, O-O-H). ^{13}C NMR, 18.4, 26.7, 29.3 (CH_2), 81.0 (CH), 125.9, 128.4, 129.1, 130.7, 132.8, 139.0 (arom.)
10) The molar ratio of CD to tetralin was determined by ^1H NMR. For example, spectral data of the inclusion complex of α-CD with tetralin is as follows. α-CD: 3.1-4.0 (C2$\underline{H}$, C3$\underline{H}$, C4$\underline{H}$, C5$\underline{H}$, C6$\underline{H_2}$), 4.5 (O6$\underline{H}$), 4.7 (C1$\underline{H}$), 5.4, 5.6 (O2$\underline{H}$, O3$\underline{H}$). Tetralin: 1.7 (CH_2-C$\underline{H_2}$-C$\underline{H_2}$-CH_2), 2.7 (Ar-C$\underline{H_2}$-CH_2), 7.1 (arom.)

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