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Effects of Cyclodextrins on Deodoration of "Aging Odor"

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Abstract

Hexenal, octenal and nonenal are known causes of unpleasant body odor and are present at markedly increased levels in the middle-aged and elderly. The odor of such unsaturated aldehydes is therefore called "aging odor". The present study investigated the effects of cyclodextrins (CDs) on deodoration of crotonaldehyde, pentenal, hexenal, heptenal, octenal, nonenal, decenal, undecenal and dodecenal. α-, β- and γ-CD formed inclusion complexes with the majority of unsaturated aldehydes in aqueous solution. The γ-CD inclusion complex contained the highest amount of guest molecule. One molecule of γ-CD was estimated to include 1 molecule of short chain aldehyde and 2 molecules of long chain aldehyde. Deodorant testing was conducted by headspace gas analysis using sealed vials. All CDs decreased the concentrations of unsaturated aldehyde. With nonenal, the deodorant power of parent CDs was α-CD > β-CD > γ-CD, and that of chemically modified CD was Meβ-CD > HPβ-CD > G2β-CD > MCTβ-CD. CDs were demonstrated to reduce "aging odor". Meβ-CD was the most effective type of CD for the deodoration of "aging odor".

Abbreviations: CD, cyclodextrin; G2β-CD, 6-O-α-maltosyl-β-CD; Meβ-CD, methyl-β-CD; HPβ-CD, hydroxypropyl-β-CD; MCTβ-CD, monochlorotriazinyl-β-CD; pentenal, trans-2-pentenal; hexenal, trans-2-hexenal; heptenal, trans-2-heptenal; octenal, trans-2-octenal; nonenal, trans-2-nonenal; decenal, trans-2-decenal; undecenal, trans-2-undecenal; dodecenal, trans-2-dodecenal

Introduction

Hexenal, octenal and nonenal are formed through the oxidative degradation of unsaturated fatty acids in skin surface lipids. These unsaturated aldehydes, particularly nonenal, are known causes of an unpleasant greasy body odor and markedly increased levels have been demonstrated in the middle-aged and elderly [1]. The odor of such unsaturated aldehydes is therefore called "aging odor". The effectiveness of CDs in the deodoration of various compounds has been demonstrated by numerous researchers [2], however, very few studies have focused on the deodoration of aldehydes by CDs [3]. The aim of the present study was to select the most appropriate types of CD for forming inclusion complexes with and deodoration of 9 kinds of unsaturated aldehyde. Particular attention was paid to the deodoration of hexenal, octenal and nonenal.

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Materials and methods

Materials

Crotonaldehyde, pentenal, hexenal, heptenal, octenal, nonenal, decenal, undecenal and dodecenal were used as test odorants (Figure 1).

α-, β- and G2β-CD were products of Ensuiko Sugar Refining Co., LTD. G2β-CD contained 20% monomaltosyl-β-CD, 50% dimaltosyl-β-CD and 30% trimaltosy-β-CD. γ-CD, Meβ-CD, HPβ-CD and MCTβ-CD were produced by Wacker Chemie. Degrees of substitution of Meβ-CD, HPβ-CD and MCTβ-CD were 1.8, 0.9 and 0.4 on the glucose unit, respectively.

Inclusion complex formation

Five millimoles of unsaturated aldehyde was added to 10 ml of 100 mM α-CD, 10 ml of 100 mM α-CD, or 100 ml of 10 mM β-CD and mixed for 10 min at room temperature. Inclusion complexes precipitated during overnight incubation at room temperature. Precipitates were collected by centrifugation at 3000 rpm for 10 min at room temperature and freeze-dried. Powder was re-dissolved in water-diethyl ether with internal standard added. The diethyl ether phase was

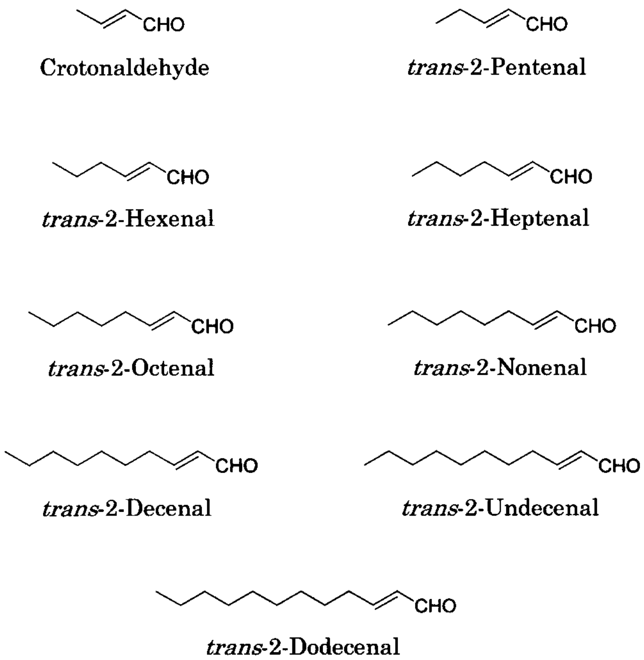

Figure 1. Chemical structure of unsaturated aldehydes.

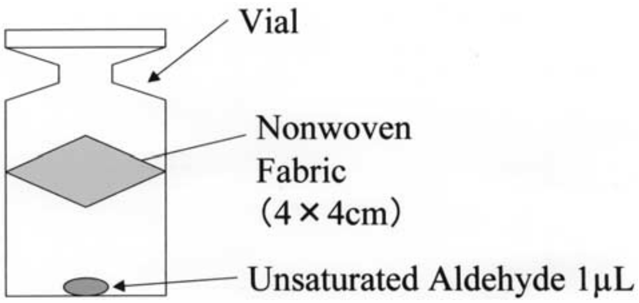

Figure 2. Illustration of headspace gas analysis.

analyzed by gas chromatography. Gas chromatography was run with a Shimadzu model GC-2010 equipped with an FID detector. Analysis was conducted in a TC-WAX fused silica capillary column (60 m × 0.25 mm I.D. GL Science Inc.) at 100 °C for crotonaldehyde, pentenal, hexenal and heptenal, at 130 °C for octenal and nonenal, at 170 °C for decenal, undecenal and dodecenal.

Deodorant test

One microliter of unsaturated aldehyde was placed in a vial (27 ml). A 4 × 4 cm square of nonwoven fabric was treated with 250 μl of 10 mM α-, β- or γ-CD, or 20% (w/v) G2β-CD, Meβ-CD, HPβ-CD or MCTβ-CD solution and carefully positioned in the vial, to avoid contact with the unsaturated aldehyde (Figure 2). The vial was sealed and left for 30 min at 40 °C. The headspace gas was then analyzed by gas chromatography. Gas chromatography was run with a Shimadzu model GC-14A. Other conditions were as mentioned above.

Table 1. Molar ratio of guest/CD in precipitate

	α-CD	β-CD	γ-CD
Crotonaldehyde	–*	–*	0.98
trans-2-pentenal	–*	–*	1.00
trans-2-hexenal	0.75	–*	1.04
trans-2-heptenal	0.51	0.82	1.18
trans-2-octenal	0.55	0.85	2.10
trans-2-nonenal	0.55	0.94	2.39
trans-2-decenal	0.48	0.62	1.56
trans-2-undecenal	0.40	0.39	1.18
trans-2-dodecenal	0.38	0.45	1.49

* No precipitation.

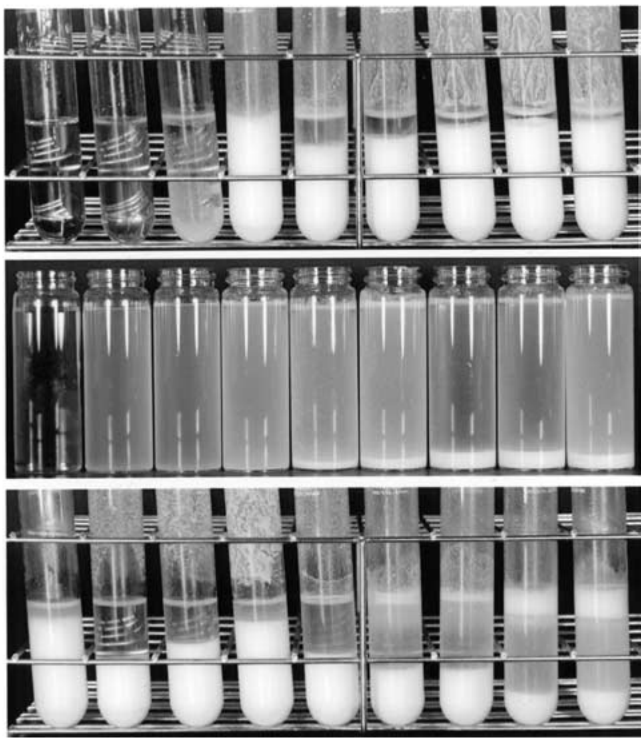

Figure 3. Photograph of inclusion complexes with unsaturated aldehydes. Upper, α-CD; middle, β-CD; lower, γ-CD. Aldehydes were left to right as follows; crotonaldehyde, trans-2-pentenal, trans-2-hexenal, trans-2-heptenal, trans-2-octenal, trans-2-nonenal, trans-2-decenal, trans-2-undecenal and trans-2-dodecenal.

Results and discussion

Inclusion complex formation

All combinations formed an inclusion complex precipitate with the exception of α-CD-crotonaldehyde, β-CD-pentenal, β-CD-crotonaldehyde and β-CD-pentenal (Table 1). The molar ratio of CD and unsaturated aldehyde was related to the alkyl chain length of the unsaturated aldehyde. The molar ratio of α-CD and heptenal – decenal was 2:1, and that of α-CD and undecenal – dodecenal was approximately 3:1. The molar ratio of β-CD and heptenal – nonenal was 1:1, and that of β-CD and decenal – dodecenal was about 2:1. The molar ratio of γ-CD and crotonaldehyde – heptenal was 1:1, while that of γ-CD and octenal – dodecenal was 1:2 – 2:2. γ-CD inclusion complex had highest amount of

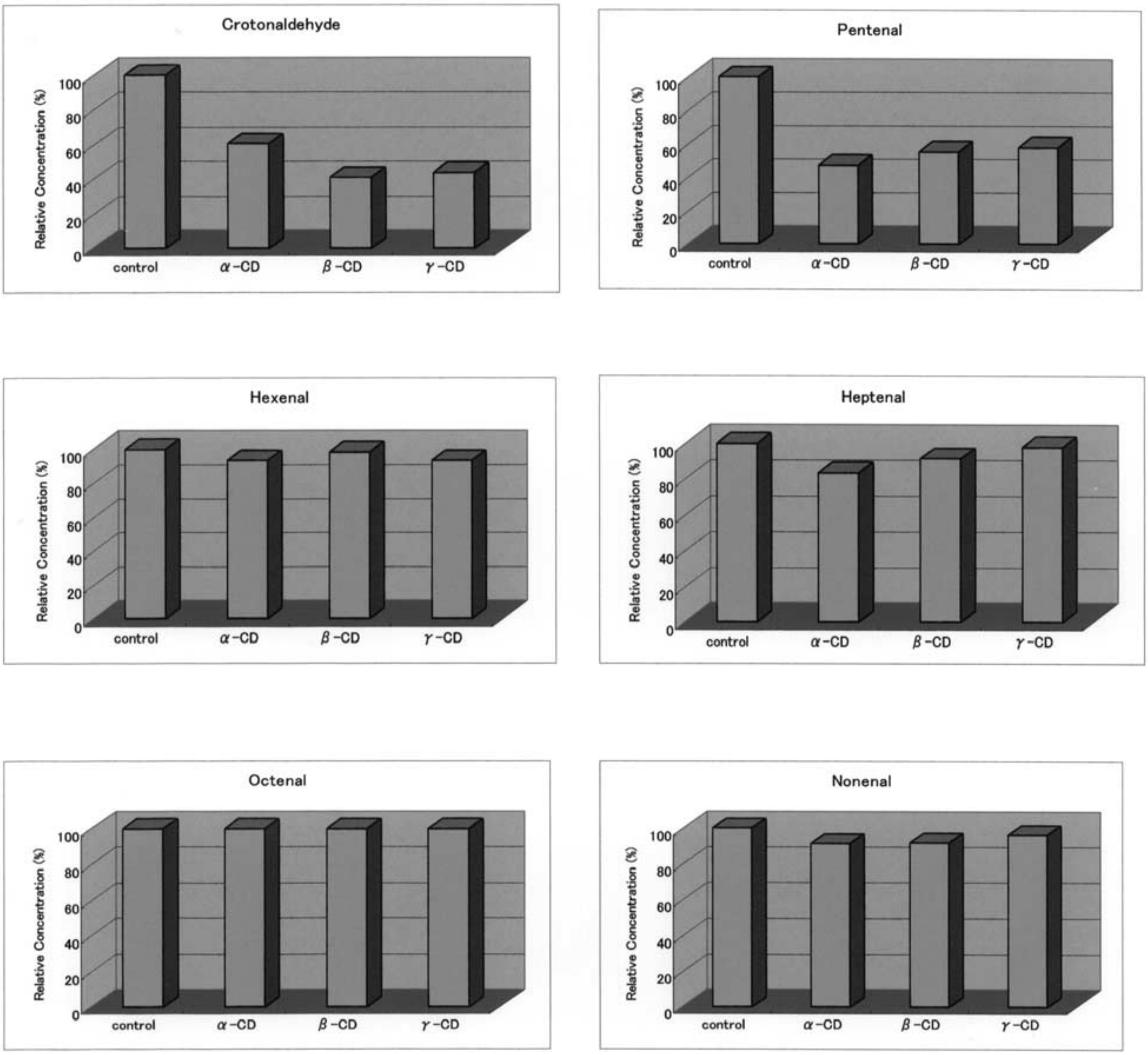

Figure 4. Relative concentration of unsaturated aldehydes in headspace gas with parent CD.

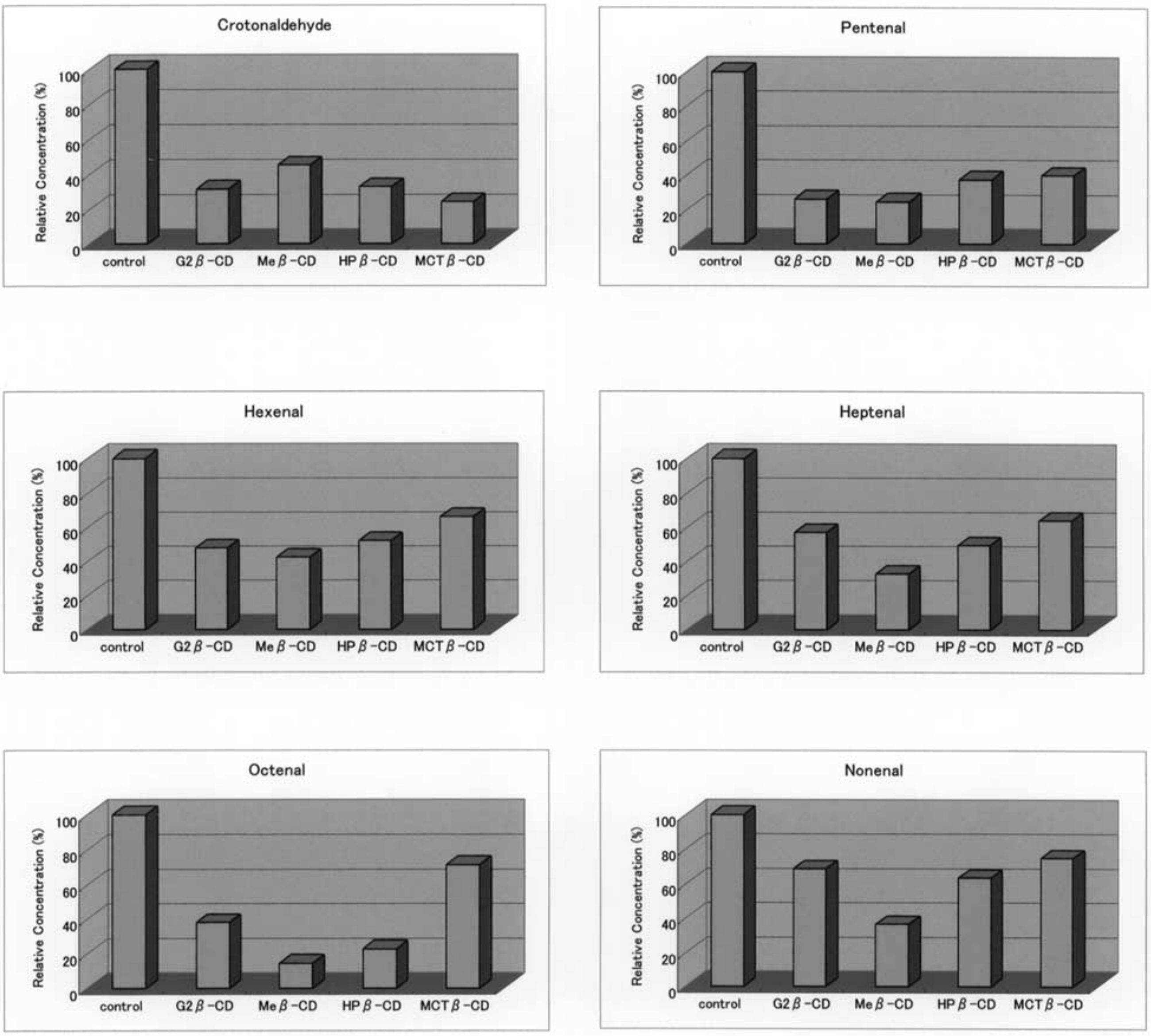

Figure 5. Relative concentration of unsaturated aldehydes in headspace gas with chemically modified CD.

guest molecule. One molecule of γ-CD was estimated to include 1 molecule of short chain aldehyde and 2 molecules of long chain aldehyde. Similar results were also obtained by Matsui et al. (4) and Mikuni et al. (5), who reported that γ-CD included 2 molecules of fatty acids.

Figure 3 shows a photograph of inclusion complex precipitates with unsaturated aldehydes. Both α- and β-CD formed increased amounts of precipitate with longer alkyl chain unsaturated aldehydes. γ-CD tended to form inclusion complexes with shorter alkyl chain unsaturated aldehydes.

Deodorant test

Figure 4 shows the relative concentration of unsaturated aldehydes in headspace gas with parent CDs. Concentrations of crotonaldehyde and pentenal were effectively reduced, whereas concentrations of other aldehydes were slightly reduced. α-CD was the most effective in reducing unsaturated aldehyde concentrations in headspace gas. In the inclusion complex formation tests, γ-CD encapsulated the largest amount of unsaturated aldehyde, probably due to the physical mixing of the two compounds.

Figure 5 shows relative concentration of unsaturated aldehydes in headspace gas with chemically modified β-CDs. All chemically modified β-CDs reduced the concentration of unsaturated aldehydes in the headspace gas. Meβ-CD was most effective with all aldehydes, with the exception of crotonaldehyde.

With specific regard to nonenal, the relative deodorant effectiveness of parent CDs was α-CD > β-CD > γ-CD, and that of chemically modified CDs was Meβ-CD > HPβ-CD > G2β-CD > MCTβ-CD.

α-, β- and γ-CD formed inclusion complexes with hexenal, octenal and nonenal. All CDs decreased the concentrations of unsaturated aldehyde in headspace gas, therefore reducing "aging odor". Meβ-CD was the most effective CD in the deodoration of "aging odor".

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