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EFFECT OF CYCLOMALTOHEPTAOSE ON AMYLOSE–LIPID COMPLEXES DURING WHEAT-STARCH PASTING*

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ABSTRACT

The V-type X-ray diffraction pattern associated with amylose–lipid complexes disappeared when an amylose–lysolecithin complex was heated in the presence of cyclomaltoheptaose. When cyclomaltoheptaose was added to wheat starch or an amylose–lysolecithin complex, the melting enthalpy of the amylose–lysolecithin complex was lessened. Turbidity measurements showed that cyclomaltoheptaose disrupted the amylose–lysolecithin complexes at temperatures above 65°. Using differential scanning calorimetry and turbidity measurements, a molar binding ratio for the cyclomaltoheptaose–lysolecithin complex of 3:1 was obtained. This complex appeared to dissociate over a temperature range of 33–37° in an excess of water.

INTRODUCTION

Although cereal starches contain only ~1% of lipid, this minor component greatly affects starch properties through formation of amylose–lipid complexes[1–3]. Addition of lipid lessens gelatinization and swelling, and prevents leaching of amylose from starch granules[4–6]. Conversely, it has been known that defatting increases swelling and solubility of the starch by disrupting amylose–lipid complexes[1,7]. Hizukuri and Takeda[8] also reported that addition of primary alcohols promotes gelatinization, presumably owing to the exchange of alcohols for lipids in the amylose–lipid complexes.

Cyclodextrins are known to form inclusion complexes with many lipids[9–12]. In previous work, it was found that cyclomaltoheptaose modifies the characteristics of wheat-flour dough[13], and exhibits a promotive effect on wheat-starch pasting: such starch characteristics as swelling power, solubility, amylose leaching, and viscosity were all increased in the presence of cyclomaltoheptaose[14]. The effects of cyclomaltoheptaose on wheat-starch pasting appear to be due to disruption of amylose–lipid complexes. The present work was undertaken to investigate the interaction of cyclomaltoheptaose with lysolecithin, a major component in wheat-

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starch lipid, and to measure the effect of cyclomaltoheptaose on the amylose–lysolecithin complex during wheat-starch pasting.

MATERIALS AND METHODS

Commercial wheat-starch (unmodified), cyclomaltoheptaose, 1-palmitoyl-L-α-lysophosphatidylcholine (synthetic), and potato amylose (type III) were obtained from Sigma Chemical Co., St. Louis, MO. The moisture content was calculated from the loss in weight after heating for 1 h at 130°. The moisture contents of cyclomaltoheptaose, wheat starch, defatted wheat-starch, and amylose were 11.6, 10.3, 13.0, and 13.7%, respectively. Defatted wheat-starch was prepared by extracting the wheat starch with water-saturated 1-butanol at 40°, as described previously[14].

Sample preparation

1. Amylose–lysolecithin complex. — The amylose solution was prepared by heating an amylose suspension in double-distilled water (10 mg/mL) for 30 min at 100° while stirring with a magnetic stirrer.

In preparing an amylose–lysolecithin complex (10:1 w/w), the lysolecithin solution (10 mg/mL) was added to the prepared amylose solution, and the mixture was heated for 1 h at 70° while stirring. Then, the mixture was kept for 1 h at room temperature and freeze-dried to afford the complex as a powder.

2. Cyclomaltoheptaose–lysolecithin mixture. — A cyclomaltoheptaose solution (15 mg/mL) and a lysolecithin solution (10 mg/mL) were mixed and then heated for 1 h at 70° while stirring. After this the mixture was kept for 1 h at room temperature and then freeze dried.

3. Amylose–lysolecithin–cyclomaltoheptaose mixture. — An amylose–lysolecithin–cyclomaltoheptaose mixture was prepared by adding a cyclomaltoheptaose solution (10 mg/mL) to the amylose–lysolecithin complex which had been heated for 1 h at 70° and kept for 1 h at room temperature. The amylose–lysolecithin–cyclomaltoheptaose mixture was heated for 1 h at 90° while stirring, kept for 1 h at room temperature, and freeze-dried.

X-Ray diffractometry. — Samples were hydrated overnight in a humidity chamber according to Zobel[15]. X-Ray diffraction patterns were recorded with a Philips model PW-1710, automated, X-ray powder diffractometer equipped with a curved graphite-crystal monochromator. Copper Kα radiation (1.54051 Å) was used with a time constant of 0.5 s, goniometer scan-speed of 0.10° 2θ/S (6.0° 2θ/min), and a chart speed of 10 mm/°2θ, voltage 40 kV, current 40 mA, over the angular range from 3 to 32° at room temperature.

Differential scanning calorimetry. — A Dupont model 990 thermal analyzer with a model 910 DSC cell base modified to give a maximum sensitivity of 5 $\mu cal.s^{-1}.in^{-1}$ was used. Temperature calibration and the calibration coefficient for the DSC cell were determined by using weighed samples of indium and sapphire

over a scanning range of 40–120°. A sample (1–2 mg, dry solids) was weighed into an aluminum hermetic pan, water (6–12 μL) was added by using a syringe, and then the pan was sealed. The moisture content in samples for DSC measurement was ~85%.

All samples were scanned at a heating rate of 10° min^{-1}, using instrument sensitivities of 0.02 and 0.05 $mcal.s^{-1}.in^{-1}$. After heating to 120°, cooling scans were carried out. The reference pan contained either water or sufficient sand to approximate the heat capacity of the sample. The cell was flushed with nitrogen at a rate of 45 $mL.min^{-1}$ for all experiments. The temperature was monitored throughout the scan using the second pen on the DSC recorder. The mV reading obtained was converted into °C by using thermocouple tables supplied with the instrument. To obtain peak areas, baselines were constructed as a single straight line from the beginning to the end of the peak, and the areas were determined by using a planimeter.

The binding ratio of the cyclomaltoheptaose–lysolecithin (palmitoyl) complex was studied by using various molecular ratios of cyclomaltoheptaose to lysolecithin. Cyclomaltoheptaose–lysolecithin complexes were prepared by freeze-drying the mixture of cyclomaltoheptaose and lysolecithin solutions. The enthalpies of melting of the complexes were measured and were then plotted as a function of the lyso-

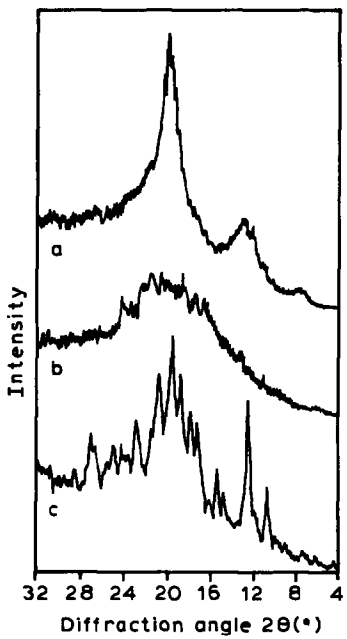


Fig. 1. X-Ray diffraction patterns of amylose–lysolecithin complex, powder mixture of amylose and lysolecithin, and amylose–lysolecithin–cyclomaltoheptaose mixture. [Key: a, amylose–lysolecithin complex (10:1 w/w); b, powder mixture of amylose and lysolecithin (10:1 w/w); and c, amylose–lysolecithin–cyclomaltoheptaose mixture (10:1:10 w/w) prepared with heating at 90°.]

lecithin:cyclomaltoheptaose ratio. Reproducibility of transition temperatures was generally ±0.5°, and that of ΔH, ±5%.

Turbidity measurements

1. Binding ratios and solubility of cyclomaltoheptaose–lysolecithin complex. — Samples were prepared by mixing a cyclomaltoheptaose solution (15 mg/mL) and a lysolecithin solution (10 mg/mL). The ratio of mixing was varied in order to obtain different ratios of cyclomaltoheptaose to lysolecithin. The total volume of each sample was made constant by adding water, the samples were vortexed for 1 min, and kept for 15 min, and the turbidity was measured at 520 nm by using a Zeiss spectrophotometer at room temperature.

Also, the turbidity of cyclomaltoheptaose–lysolecithin complex was measured as a function of temperature, using a Cary model 15 spectrophotometer. The temperature was increased from 20 to 85° and then decreased from 85 to 20°.

2. Effect of cyclomaltoheptaose on amylose–lysolecithin complex. — Amylose–lysolecithin complex (10:1 w/w; 5.5 mg) was suspended in 6 mL of water or cyclomaltoheptaose solution in a 10-mL screw-capped tube, and heated for 30 min at the desired temperature with frequent shaking. The turbidity was measured at 520 nm by using a Cary model 15 spectrophotometer at the heating temperature.

RESULTS AND DISCUSSION

X-Ray diffraction patterns. — Amylose–lysolecithin complex (10:1 w/w) showed the characteristic V_h (hydrated) type of pattern given in Fig. 1a. It had strong intensities at spacings of 6.92 and 4.48 Å. In contrast, the powder mixture of amylose and lysolecithin (10:1 w/w) showed a quite different pattern (see Fig. 1b). Thus, a physical mixture of solid amylose and solid lysolecithin was unable to form a complex. When amylose–lysolecithin complex was heated in water at 90° with cyclomaltoheptaose, the V-pattern was no longer apparent and the diffraction pattern was more complicated (see Fig. 1c). The lack of V-type diffraction spacings of the amylose–lysolecithin complex suggested that the cyclomaltoheptaose interfered with the formation of V-type crystals of the amylose–lysolecithin complex.

Differential scanning calorimetry (d.s.c.). — Cyclomaltoheptaose–lysolecithin complex showed an endothermic transition that started at 44.5°, peaked at 68°, and ended at 77°, with an enthalpy of 4.00 cal/g (see Table I and Fig. 2). This transition corresponded to the dissociation of the cyclomaltoheptaose–lysolecithin complex. On cooling after heating to 120°, there appeared an exothermic transition, which started at 57°, peaked at 53°, and ended at 41°, with an enthalpy of 2.68 cal/g. This transition indicated the association of cyclomaltoheptaose with lysolecithin.

From the characteristic saturation plateau for binding (see Fig. 3), the binding ratio for cyclomaltoheptaose–lysolecithin complex was found to be 3:1 (mol/mol). The binding ratio agreed with the finding that, on average, five CH_2 groups are coordinated to one cyclomaltoheptaose molecule during complex-formation[9].

Thermograms of the amylose–lysolecithin complex (10:1 w/w) had an endothermic transition that peaked at 103° and was spread over a temperature range of 88–112°, with an enthalpy of 4.91 cal/g (see Table I). On cooling after heating, there was an exothermic transition at 87°, which was spread over 93–77°, with an enthalpy of 4.39 cal/g. These transitions corresponded to melting and association of the complex, respectively. When cyclomaltoheptaose was added to the amylose–lysolecithin complex, and heated for 1 h at 90°, the resulting ternary system showed two endothermic transitions (see Fig. 4). The first transition, at 57.5°, and the second, at 98.5°, corresponded to melting of the cyclomaltoheptaose–lysolecithin complex and melting of the amylose–lysolecithin complex, respectively. These temperatures were slightly lower than those obtained from the respective binary system. Enthalpy values also were lowered in the ternary system, *i.e.*, the enthalpy for the melting of the amylose–lysolecithin complex was diminished to 1.74 cal/g of amylose (from 4.91 cal/g of amylose in the presence of cyclomaltoheptaose). Likewise, the enthalpy for the melting of the cyclomaltoheptaose–lysolecithin complex was lessened to 2.58 cal/g of cyclomaltoheptaose (from 4.00 cal/g of cyclomaltoheptaose in the presence of amylose).

Thermograms of wheat starch exhibited two endothermic transitions (see Fig. 5a). The gelatinization endotherm peaked at 64° and was spread over the range of

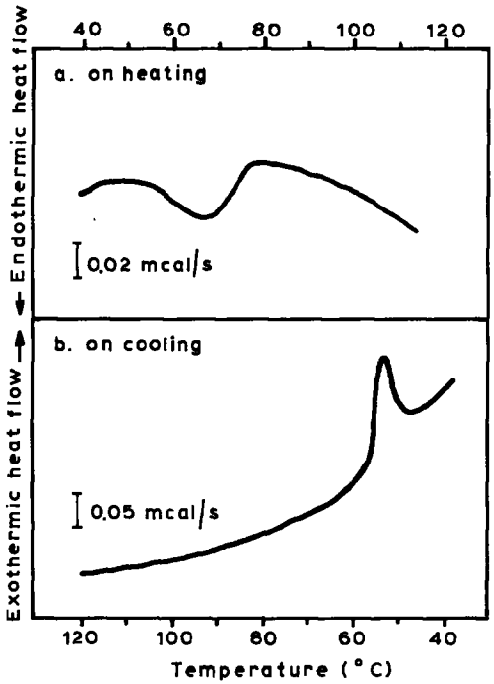


Fig. 2. Thermograms of cyclomaltoheptaose–lysolecithin complex obtained on heating and cooling. [Key: a, on heating, and b, on cooling, 0.95 mg of cyclomaltoheptaose–lysolecithin complex (10:1 w/w) + 6 μL of water.]

TABLE I

TRANSITION TEMPERATURES AND ENTHALPY VALUES[a] OF AMYLOSE–LYSOLECITHIN–CYCLOMALTOHEPTAOSE SYSTEM AND WHEAT-STARCH–LYSOLECITHIN–CYCLOMALTOHEPTAOSE SYSTEM

Sample	*Gelatinization*				*Melting of complex*			
	To	*Tp* (°C)	*Tc*	*ΔH* (cal/g)	*To*	*Tp* (°C)	*Tc*	*ΔH* (cal/g)
Cyclomaltoheptaose–lysolecithin (10:1 w/w)					44.5	68.0	77.0	4.00[b]
Amylose–lysolecithin (10:1 w/w)					88.0	103.0	112.0	4.91[c]
Amylose–lysolecithin–cyclomaltoheptaose (10:1:10 w/w)					37.0 81.5	57.5 98.5	71.0 107.5	2.58[b] 1.74[c]
Wheat-starch	54.5	64.0	75.5	2.34	85.0	95.5	101.5	0.44
Wheat-starch + cyclomaltoheptaose (1:1 w/w)	54.5	65.0	94.5	8.27				
Defatted wheat-starch	56.0	64.0	76.5	2.31				
Defatted wheat-starch + lysolecithin (10:1 w/w)	57.0	64.0	73.5	1.74	89.0	100.0	109.0	2.63
Defatted wheat-starch + lysolecithin + cyclomaltoheptaose (10:1:10 w/w)	56.0	66.0	80.5	3.18	90.0	100.0	108.5	0.85

[a]Mean values obtained from a minimum of duplicate determinations; reproductibility of transition temperatures was generally ±0.5°, and that of *ΔH* within ±5%. The moisture content in samples was ~85%; *ΔH* is expressed as calories per g of starch, except as otherwise noted; *To*, onset temperature; *Tp*, peak temperature; and *Tc* conclusion temperature. [b]As calories per g of cyclomaltoheptaose. [c]As calories per g of amylose.

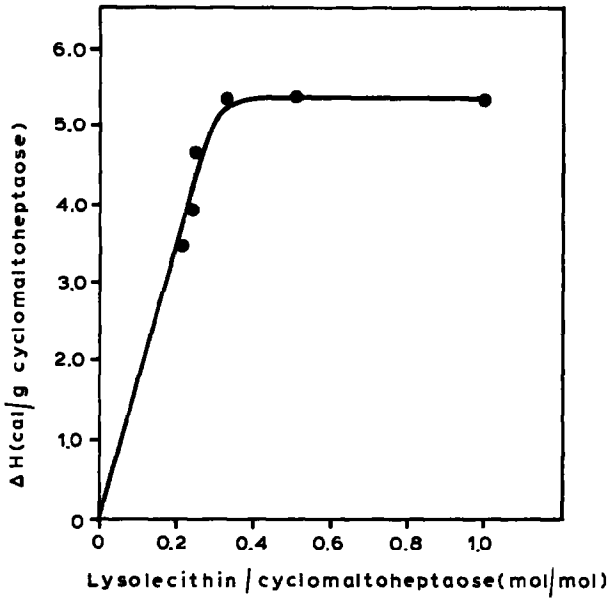


Fig. 3. Enthalpy of melting of cyclomaltoheptaose–lysolecithin complexes as a function of lysolecithin:cyclomaltoheptaose ratio.

54.5–75.5°, with an enthalpy of 2.34 cal/g of wheat starch (see Table I). This result was in good agreement with data reported by Kugimiya *et al.*[16] and Stevens and Elton[17]. The high-temperature endotherm, at 95.5°, with the range of 85–101.5°, had an enthalpy of 0.44 cal/g. This endotherm has been shown to be due to the melting of amylose–lipid complex in cereal starch[16,18,19].

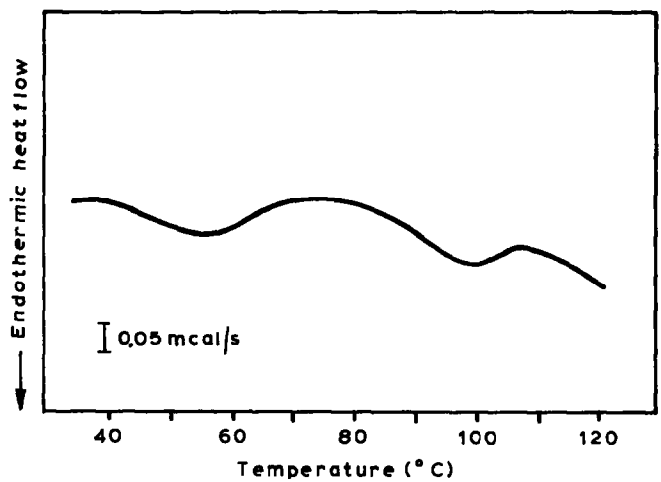


Fig. 4. Thermogram of amylose–lysolecithin–cyclomaltoheptaose mixture. [2.00 mg of amylose–lysolecithin–cyclomaltoheptaose mixture (10:1:10 w/w) prepared with heating at 90° + 12 μL of water.]

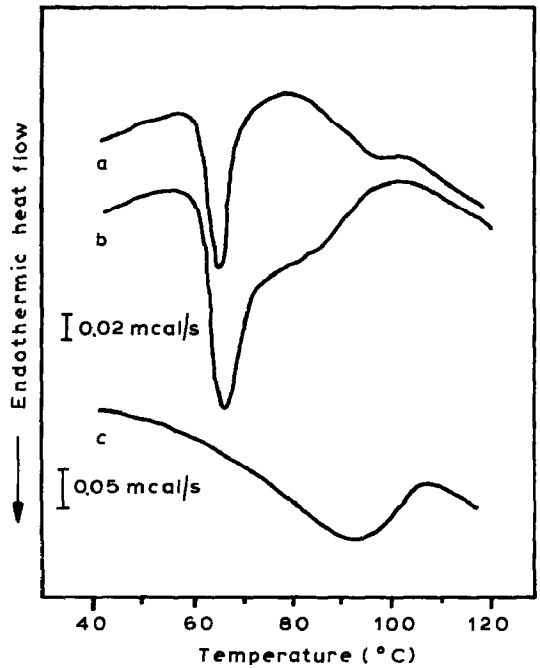


Fig. 5. Thermograms of wheat starch in the presence of cyclomaltoheptaose. [Key: a, 1.00 mg of wheat starch + 6 μL of water; b, 0.99 mg of wheat starch + 1.02 mg of cyclomaltoheptaose + 12 μL of water; c, 1.84 mg of cyclomaltoheptaose + 12 μL of water.]

Addition of cyclomaltoheptaose to wheat starch resulted in a larger endotherm at 65°, compared to the gelatinization endotherm of wheat starch only (see Fig. 5b). The endothermic transition for melting of the amylose–lipid complex disappeared. Based on the disappearance of the endothermic transition for the melting of the amylose–lipid complex, it was concluded that the presence of cyclomaltoheptaose interfered with the formation of amylose–lipid complex or promoted disruption of the amylose–lipid complex. This effect is similar to that of defatting of starch, as it has been reported that defatting eliminated or lowered the endothermic transition near 100° for melting of amylose–lipid complexes in cereal starches[16,18–20].

In defatted wheat-starch, there was an endothermic transition at 64°, but no endothermic transition for melting of amylose–lipid complex was observed, despite the fact that the defatted wheat starch contained 0.4% of lipid (see Fig. 6a).

With the addition of lysolecithin to the defatted wheat-starch, there appeared a pronounced endothermic transition for the melting of amylose–lysolecithin complex at 100° (see Fig. 6b). This temperature was slightly higher than that for the amylose–lipid complex in native wheat-starch.

When cyclomaltoheptaose and lysolecithin were added together to the defatted wheat starch, there was an increase in gelatinization enthalpy and a

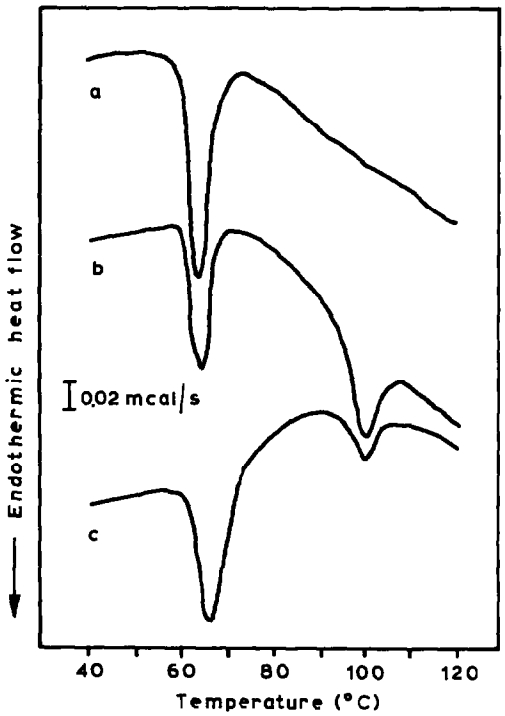


Fig. 6. Thermograms of defatted wheat-starch in the presence of lysolecithin, or cyclomaltoheptaose, or both. [Key: a, 0.96 mg of defatted wheat-starch + 6 μL of water; b, 1.02 mg of defatted wheat-starch + 0.10 mg of lysolecithin + 6 μL of water; and c, 0.93 mg of defatted wheat-starch + 0.11 mg of lysolecithin + 0.92 mg of cyclomaltoheptaose + 12 μL of water.]

diminution in enthalpy of the amylose–lysolecithin complex, compared to the defatted wheat-starch–lysolecithin system (see Fig. 6c and Table I). The lowering in the enthalpy of melting of the amylose–lysolecithin complex in the presence of cyclomaltoheptaose indicated that cyclomaltoheptaose interfered with the formation of amylose–lysolecithin complex in wheat starch.

Turbidity measurements. — Turbidity measurements have been used to confirm the existence of a complex of lipid with cyclomaltodextrins[21,22]. A cyclomaltoheptaose solution having a concentration of 1.00%, and a lysolecithin solution with a concentration of 0.03–0.30%, were used in this study. Both solutions showed 100% transmittance at room temperature (20°). Hence, the appearance of turbidity caused by crystal formation was considered to be evidence for an inclusion complex[21–23].

Fig. 7 shows the turbidity curves of solution mixtures of cyclomaltoheptaose and lysolecithin, measured at 20°. Maximum turbidities were obtained at a ratio of ~3:20 (w/w) for lysolecithin:cyclomaltoheptaose. This ratio corresponds to a molecular ratio of ~1:3, which is consistent with the result obtained by d.s.c. (see Fig. 3).

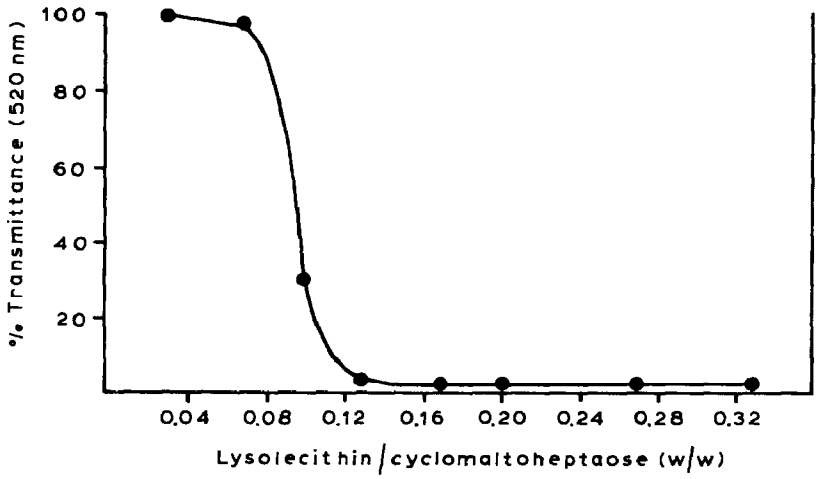


Fig. 7. Turbidity of solution mixture of cyclomaltoheptaose and lysolecithin as a function of lysolecithin cyclomaltoheptaose ratio (at 20°). [Concentration of sample mixture: cyclomaltoheptaose, 1.0%; lysolecithin, 0.03–0.3%.]

Fig. 8 shows the turbidity curve of the cyclomaltoheptaose–lysolecithin complex (10:2 w/w) as a function of temperature. As the temperature of solution of the cyclomaltoheptaose–lysolecithin mixture was increased from 20°, the solution was still turbid until the temperature reached 33°. Above 33°, however, turbidity started decreasing, and the solution was clear above 37°.

As the temperature of the solution was decreased from 85°, the solution was

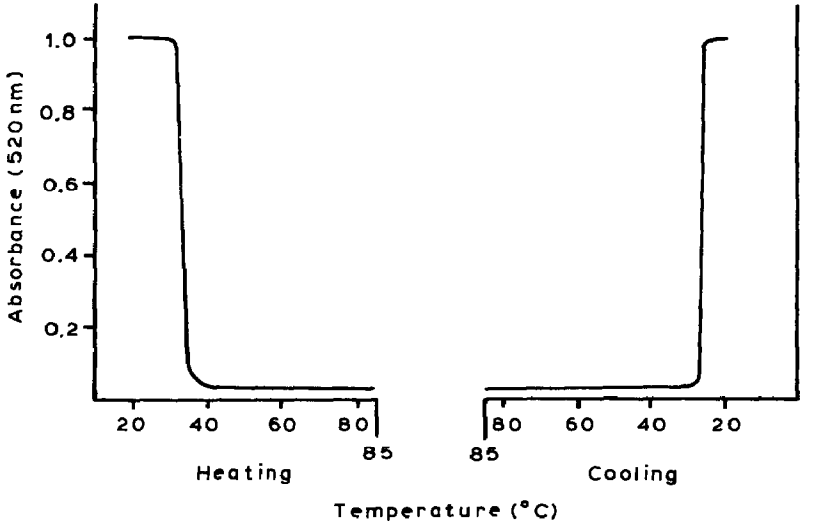


Fig. 8. Turbidity of cyclomaltoheptaose–lysolecithin complex as a function of temperature. [Cyclomaltoheptaose:lysolecithin = 10:2 (w/w); concentration of sample, 9.6 mg/mL.]

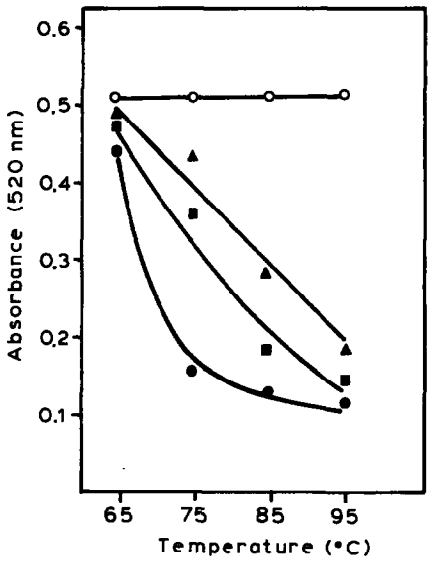
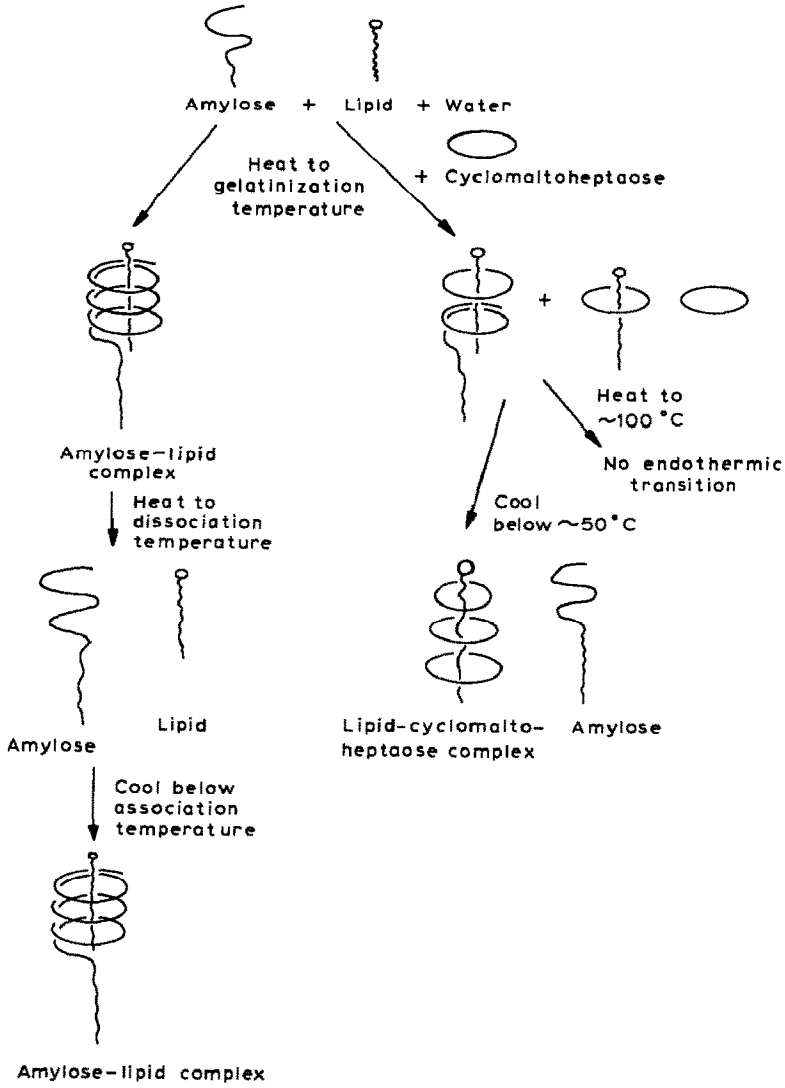


Fig. 9. Effect of cyclomaltoheptaose on the turbidity of amylose–lysolecithin complexes at various temperatures (measured at the heated temperatures). [Amylose:lysolecithin = 10:1 (w/w); concentration of amylose–lysolecithin complex: 0.9 mg/mL. Key: ○, 0% cyclomaltoheptaose; ▲, 0.5% cyclomaltoheptaose; ■, 1.0% cyclomaltoheptaose; and ●, 1.5% cyclomaltoheptaose.]

still clear down to 27°, and then, below 27°, the turbidity started increasing; maximum turbidity was obtained at 26°. Considering the fact that there was no crystal formation for either 0.8% cyclomaltoheptaose (alone) or 0.16% lysolecithin (alone) down to 20°, the appearance of turbidity implied formation of a complex of cyclomaltoheptaose with lysolecithin.

Without cyclomaltoheptaose, a solution of amylose–lysolecithin complex that had been heated for 30 min at 95° was still turbid. This indicated that the amylose–lysolecithin complex could not be dissociated at 95° (see Fig. 9). This was also observed by d.s.c. (see Table I). However, the solution became clear when heated in the presence of cyclomaltoheptaose. The decrease in turbidity was promoted by increased heating temperature and increased concentration of cyclomaltoheptaose. At 1.5% of cyclomaltoheptaose and 75°, the turbidity decreased by ~70% from that of the amylose–lysolecithin solution. Accordingly, this result suggested that dissociation of amylose–lysolecithin complex could occur in the presence of cyclomaltoheptaose before its melting temperature (near 100°) is reached. The degree of dissociation depended on the heating temperature and the concentration of cyclomaltoheptaose. All the amylose–lysolecithin complex seemed to be dissociated at 1.5% of cyclomaltoheptaose and 95°, judging from the turbidity of the amylose solution itself (A = 0.115).



Scheme 1. Representation of amylose–lipid interaction in the absence and presence of cyclomaltoheptaose.

GENERAL DISCUSSION

Scheme 1 is a representation of what may be occurring when amylose and lipid in wheat starch undergo heating in the absence and the presence of cyclomaltoheptaose. In the absence of cyclomaltoheptaose, formation of the amylose–lipid complex occurs above the gelatinization temperature and dissociation does not take place until the melting temperature of the complex is attained. Cyclomaltoheptaose interferes with amylose–lipid complexes, thus lowering the proportion of these complexes in the system.

As the temperature of a starch paste is increased above the gelatinization temperature, lipid entrapped among starch molecules becomes mobile[1]. Amylose interacted with lipid to form an amylose–lipid complex after gelatinization, as suggested by Kugimiya *et al.*[16] and Kugimiya and Donovan[20]. From the d.s.c. experiments it thus appeared that the presence of cyclomaltoheptaose interfered with the formation of amylose–lipid complexes. As the temperature of the starch paste is increased up to 95°, amylose–lipid complexes, which are naturally present, or formed above the gelatinization temperature, or both, cannot be dissociated until the melting temperature of the complex is reached. In the presence of cyclomaltoheptaose, however, amylose–lipid complexes either were prevented from forming or were dissociated at temperatures lower than their melting temperaures.

As the starch paste cools to room temperature (20°), amylose molecules reassociate with lipid[1]. Turbidity measurements, X-ray diffraction patterns, and d.s.c. experiments suggested that cyclomaltoheptaose interferes with the association of amylose and lipid during cooling. As a result, freed amylose could be leached from starch granules, resulting in increased solubility and swelling power.

The interfering effect of cyclomaltoheptaose on complex-formation between amylose and lipid could be explained by the fact that cyclomaltoheptaose can form inclusion complexes with lipids[9–12,24]. The results of d.s.c. and turbidity experiments indicated that, above the starch-gelatinization temperature, cyclomaltoheptaose–lysolecithin complexes are dissociated. Nevertheless, cyclomaltoheptaose seemed to interfere with amylose–lipid complexes during pasting. It is possible that affinity of cyclomaltoheptaose for lipid at a value less than the 3:1 ratio observed for the cyclomaltoheptaose–lysolecithin in melting transition prevents the association of amylose and lipid. Furthermore, it is also possible that cyclomaltoheptaose interferes with association amongst amylose–lipid complexes, resulting in prevention of precipitation. In this study, it was not possible, however, to differentiate between these possibilities. Because cyclomaltoheptaose possesses a hydrophobic character[25,26], it is possible that cyclomaltoheptaose could disrupt the hydrophobic association between amylose and lipid, as is the case for 1-butanol[8]. Gerlsma[27] suggested that non-clustered water molecules adjacent to the nonpolar solute molecules disrupt hydrogen bonds. Therefore, in a similar way, cyclomaltoheptaose could disrupt intra- and intermolecular hydrogen bonds within starch molecules. This could facilitate water hydration of starch and enhance the swelling and solubilization of the starch granules.

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