Evidence of Starch Inclusion Complexation with Lactones

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Starch, in particular the linear amylose, is able to form inclusion complexes with a wide spectrum of ligand molecules, among them flavor compounds. The complexing ability of a homologous series of γ- and δ-lactones with potato starch was followed by amperometric iodine titration, differential scanning calorimetry, and wide-angle X-ray diffraction measurements. Lactones with a linear chain of a size $\geq C_5$ form inclusion complexes with starch, whereas lactones with a short linear chain, such as γ-heptalactone, show poor complexing ability. The thermal stability of starch−lactone complexes increases with increasing chain length of the lactone. In general, lactones induce the formation of V_h helices. Only δ-decalactone complexes with starch were not definitely identified as V_h amylose helices. Complexation of starch dispersions with lactones induce turbidity and gelation or phase separation, both phenomena being the result of microphase separation.

Keywords: *Starch; amylose; lactone; inclusion complex*

INTRODUCTION

Amylose is able to form inclusion complexes with a wide spectrum of ligand molecules, for instance with flavor compounds (*1*−*8*). The addition of complexing ligands induces the formation of V-type amylose helices. Earlier investigations suggested the existence of amylose helices with 6, 7, or 8 glycosyl residues per helical turn (*9*−*11*), whereas more recent studies question the existence of helices with 7 glycosyl residues per helical turn (*12*). Linear ligands are thought to be located in the hydrophobic cavity of the amylose helix. In contrast, bulky ligands such as *n*-butanol and *n*-pentanol may be located between the amylose helices (*13*). Different methods are described in the literature for detecting amylose inclusion complexation. The most frequently applied methods are X-ray diffraction (*14*), NMR (*15*, *16*), CD (*17*), iodometric titration (*18*), and differential scanning calorimetry (DSC, *19*). Furthermore, the binding capacity of starch and the dissociation constants have been established for several ligands based on analytical determination on the bound ligands (*20*).

Lactones are important flavor compounds and their molecular structure suggests that complexation with amylose is possible. Recently, Guzmann (*16*) concluded that δ-decalactone forms inclusion complexes with amylose as detected by CD- and ^{1}H-NMR spectroscopies. Figure 1 shows the molecular structures of γ- and δ-decalactone. Lactones are cyclic esters with five- or six-membered rings and a linear chain. The size of the linear chain increases with increasing molecular weight of the lactone which, in turn, determines the water solubility and the flavor properties as presented in Table 1 (*21*, *22*). As natural flavors, these compounds occur in fruits such as apricot, peach, and coconut and in butter.

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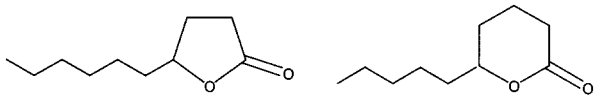

Figure 1. Molecular structure of γ-decalactone (left) and δ-decalactone (right).

The aim of the present study was to investigate the complexing ability of a homologous series of γ- and δ-lactones with starch. A low-concentration potato-starch dispersion was selected as the food model system. The interaction between starch and lactones was followed by amperometric iodine titration, DSC, and wide-angle X-ray diffraction measurements.

EXPERIMENTAL PROCEDURES

Materials. Native potato starch was obtained from Blattmann and Co., Wädenswil, Switzerland. γ-Heptalactone, γ-nonalactone, γ-decalactone, γ-dodecalactone, δ-decalactone, and δ-dodecalactone were supplied by Fluka, Buchs, Switzerland.

Sample Preparation. Starch dispersions at a concentration of 2 g dry starch/100 g dispersion were prepared by heating native potato-starch suspensions in cans in a retort at 1 bar overpressure (121 °C) for 30 min. Thereafter, the starch dispersions were cooled to room temperature. The flavor substances were added to the starch dispersions at concentrations ranging from 0 to 1000 mmol/mol glucose. The flavor substances were weighed into glass jars with a total volume of 60 or 100 mL, and 50 g of starch dispersion at room temperature was added. The jars were closed with caps and the mixture was shaken for 20 s ± 10 s. The jars were kept at 25 °C ± 2 °C for 24 h. For DSC and X-ray measurements the samples were frozen in the jars in a freezer at −25 °C and subsequently freeze-dried (Sécfroid, Lausanne, Switzerland).

Iodine Binding Capacity (IBC). The iodine binding capacity was determined by amperometric titration using a Polarizer E585, Potentiograph E567, and Dosimat 655 from Methrom (Herisau, Switzerland). The voltage of polarization was set to 140 mV and the attenuation of the polarizer was set to 5 mA. A 30-g sample containing 100 mg of starch (S_{tot}), 1 mL of 1 mol/L HCl, and deionized water was titrated with

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Table 1. Physicochemical and Sensory Properties of Lactones (*22*)

lactone	empirical formula	molecular weight (g/mol)	water solubility	flavor properties
γ-heptalactone	$C_7H_{12}O_2$	128	almost insoluble	sweet, nut-like, caramel
γ-nonalactone	$C_9H_{16}O_2$	156	insoluble	strong, coconut
γ-decalactone	$C_{10}H_{18}O_2$	170	slightly soluble	fruity, peach-like
γ-dodecalactone	$C_{12}H_{22}O_2$	198	insoluble	fatty, peachy
δ-decalactone	$C_{10}H_{18}O_2$	170	almost soluble	oily, peachy
δ-dodecalactone	$C_{12}H_{22}O_2$	198	insoluble	fresh fruity, oily

0.005 mol/L iodine solution (Titrisol, Merck) at a titration rate of 1 mL/min. The dispersion was constantly stirred during titration. The amount of bound iodine (I_b) was evaluated graphically as described by Hollo and Szejtli (*23*) and the IBC was calculated as

$$IBC = \frac{I_b}{S_{tot}} \times 100 \text{ [mg iodine/100 mg dry starch]} \quad (1)$$

Differential Scanning Calorimetry. The freeze-dried samples were rehydrated to 30 g dry matter/100 g. Samples of 30−40 mg were weighed into pressure pans (Perkin-Elmer, Norwalk, CT). The measurements were carried out on the 2910 DSC (TA Instruments, Felton, CA) that had been calibrated with indium and an empty pan as reference. The samples were heated at a rate of 10 °C/min from 4 to 160 °C with a nitrogen flush (40 cm^3/min). After cooling the sample to 4 °C with an average cooling rate of ∼20 °C/min, a second run was performed. Phase-transition characteristics were evaluated using the TA Instruments software program. The enthalpies are given in J/g dry starch sample.

Wide-Angle X-ray Diffraction Measurements. The moisture content of the freeze-dried samples was adjusted to 10−15 g/100 g moist sample by keeping the freeze-dried powder over water for 90 min in a closed vessel. Therefore, the samples were compressed into tablets of about 1-mm thickness and a diameter of 13 mm. The tablets were fixed on a sample holder. The measurements were carried out in the transmission mode on a powder diffractometer (Siemens Kristalloflex D500, Karlsruhe, Germany) using CuKα radiation (1.54 Å) with 35 mA and 40 kV. A divergence slit of 2 mm and a receiving slit of 1 degree were chosen. The relative intensity was recorded in a scattering angle range (2θ) of 4 to 30 degrees with a scintillation counter at a scanning speed of 0.02 degrees/min.

RESULTS AND DISCUSSION

Potato starch was selected because it is free of internal lipids and the occurrence of retrogradation is retarded at low concentrations. The potato-starch dispersion at a concentration of 2 g/100 g dispersion was considered as a model of aqueous food systems where starch is used as thickener, such as sauces, custards, and fillings. The potato-starch dispersions were prepared by a thermal treatment which promoted the solubilization of starch without complete disintegration of the granular structure (*24*).

Assessment of Starch Inclusion Complexation in Aqueous Systems. The complexation behavior of lactones in aqueous systems was followed by amperometric iodine titration, which has been described as a sensitive method for following starch complexation (*2*, *5*, *18*, *25*, *26*). The influences of the different γ- and δ-lactones on the IBC of potato starch dispersions are shown in Figures 2 and 3, respectively. Starch dispersions complexed with γ-nonalactone, γ-dodecalactone, δ-decalactone, and δ-dodecalactone showed bulk-phase separation at certain concentrations. Such dispersions were mixed before determining the IBC.

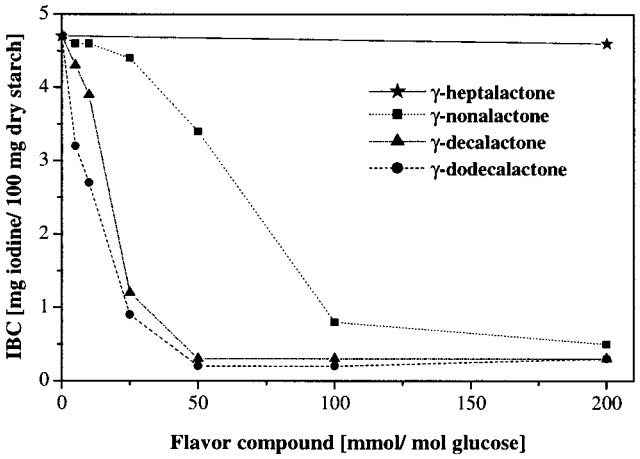

Figure 2. Influence of γ-lactone concentration on the IBC of potato-starch dispersions at 2 g dry starch/100 g dispersion.

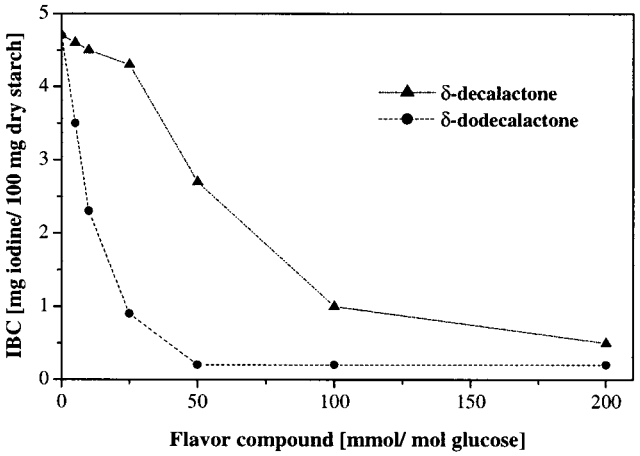

Figure 3. Influence of δ-lactone concentration on the IBC of potato-starch dispersions at 2 g dry starch/100 g dispersion.

The IBC of potato starch dispersion at a concentration of 2 g/100 g without lactone addition was 4.7 ± 0.1 mg iodine/100 mg dry starch which corresponds to an amylose content of 24 g/100 g dry starch, if an IBC of 19.5 g iodine/100 mg dry starch is assumed for pure amylose. The IBC of all starch dispersions decreased with increasing flavor concentration, except in the case of γ-heptalactone. The latter lactone did not significantly reduce the IBC of potato starch dispersion at a concentration of 200 mmol/mol glucose. At a concentration of 1000 mmol γ-heptalactone/mol glucose the IBC value decreased to 4.2 mg iodine/100 mg dry starch (data not shown). In contrast, γ-nonalactone at a concentration of around 200 mmol/mol glucose reduced the IBC to 0.5 mg iodine/100 mg dry starch. Even lower concentrations of γ-decalactone and γ-dodecalactone, that is, around 50 mmol/mol glucose, were necessary to reduce the IBC to 0.3 mg iodine/100 mg dry starch. δ-Decalactone and δ-dodecalactone also reduced the IBC of potato starch

showing a behavior similar to that of γ-nonalactone and γ-dodecalactone, respectively.

The decrease of the IBC of potato starch dispersions in the presence of lactones indicates the formation of amylose−lactone inclusion complexes. On the basis of the results of amperometric iodine titration γ-heptalactone does not seem to form inclusion complexes, whereas all other investigated lactones are able to form inclusion complexes. In the case of γ-heptalactone it cannot be excluded that inclusion complexes with very low stability, that is, with high dissociation constants, are formed. It is conceivable that ligands with low binding stability are displaced by iodine. To some extent iodine can also bind to amylose that is saturated with a ligand by entering the helix perpendicularly to the axial plane (*27*).

It has been shown that the binding capacity and the binding stability of amylose−ligand complexes depends on the length of the included hydrocarbon chain as shown with a homologous series of *n*-aliphatic alcohols (*2*). This also applies to starch−lactone complexes because shorter carbon chains required higher ligand concentration for saturation of amylose as detected by iodine titration. For instance, a higher δ-decalactone concentration was necessary for saturation of the amylose fraction compared to γ-decalactone, the latter possessing a longer carbon chain. On the other hand, lactones with the same carbon chain lengths, such as γ-nonalactone and δ-decalactone, present similar complexation behaviors as detected by iodine titration.

Amperometric iodine titration of starch/lactone systems allows following of the complexation process and gives quantitative information on the extent of amylose complexation. Rutschmann and Solms (*5*) found a close correlation between the IBC of starch/monostearate systems and the amount of "bound" monostearate as determined by chemical analysis. They concluded that for linear ligands iodometric methods can successfully be applied for quantitative investigation of starch complexation. However, the exact amounts of ligand molecules included in the helical segments of amylose cannot be evaluated directly from the results of iodine titration.

Thermal Behavior of Starch/Lactone Systems. For the DSC measurements, the lactones were added to starch at excess concentrations so that saturation of the amylose fraction was possible. In the case of γ-heptalactone, where no complexation was detected with iodine titration, a rather high lactone concentration of 1000 mmol/mol glucose was selected. The samples were freeze-dried and rehydrated to a moisture level of 70 g/100 g wb which resulted in transitions above the resolution level of the instrument without promoting secondary recrystallization processes during the measurement (*28*). DSC thermograms of dispersions complexed with γ- and δ-lactones are shown in Figure 4. Freeze-dried and rehydrated potato starch dispersion without the addition of lactone served as a reference and its thermogram is also presented in Figure 4. Approximate values for melting temperatures and enthalpies are summarized in Table 2. The reproducibility of the maximum melting temperature was better than that of the corresponding melting enthalpy, the variation coefficent assuming values of 0−8% and 0−35%, respectively.

The DSC thermogram of a freeze-dried and rehydrated potato-starch dispersion without addition (reference) presented no phase-transition, indicating that no retrogradation occurred and no complexes were present. γ-Heptalactone, γ-decalactone, and δ-dodecalactone showed two endothermic phase-transitions in the first run. The peak temperatures were between 89 and 117 °C and involved enthalpies were between 0.04 and 0.28 J/g dry substance. The transitions were broad, covering a range of 20 to 50 °C. In all cases, only one peak was observed in the second run. Similar results were obtained for γ-dodecalactone which presented two endothermic transitions in the first run that appeared at 72 and 105 °C, but three endothermic transitions in the second run at 71, 100, and 117 °C. γ-Nonalactone and δ-decalactone showed endothermic transitions at 91 and 112 °C with enthalpies of 0.32 and 0.77 J/g dry substance, respectively. The described thermal events were also observed in the second heating run.

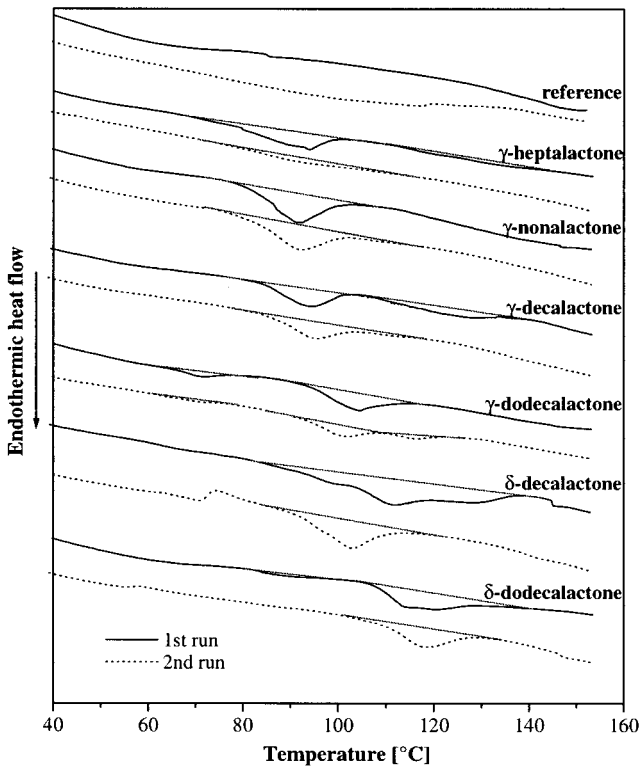

Figure 4. DSC thermograms of freeze-dried and rehydrated potato-starch dispersions without the addition of a ligand (reference), and with γ-hepta-, γ-nona-, γ-deca-, γ-dodeca, δ-deca-, and δ-dodecalactone.

On the basis of the temperatures and enthalpies of the endothermic phase-transitions, and the fact that the transitions are reversible, it is concluded that the thermal events reflect the dissociation of amylose−lactone complexes. It can be excluded that the transitions are originated by retrograded starch because the reference presented no peaks. Furthermore, melting of excess lactones is not thought to contribute to the observed thermal event as pure lactones present no phase-transitions between 20 and 100 °C. DSC measurements of starch with a homologous series of γ-lactones suggest that increased chain length of the ligand results in increased thermal stability. This was also observed with amylose−fatty acid complexes (*29*). In the case of γ-heptalactone the DSC measurements suggest complexation with starch, although the results of iodometric titration failed to indicate complexation. Nüssli (*7*) found similar results for starch/hexanal systems,

Table 2. Thermoanalytical Behavior of Freeze-Dried and Rehydrated Potato-Starch Dispersions with Addition of Lactones (average of 2 to 3 replicates)

lactone	concentration (mmol/mol gl)	run	endothermic phase transition temperatures [°C]			enthalpy (J/g db)	
γ-hepta-	1000	1	90	117[a]		0.19	0.19
		2	92			0.10	
γ-nona-	200	1	91			0.32	
		2	91			0.25	
γ-deca-	50	1	95	127[a]		0.23	0.11
		2	96			0.22	
γ-dodeca-	100	1	72 105		0.05	0.25	
		2	71 100	117	0.02	0.08	0.03
δ-deca-	200	1	112			0.77	
		2	104			0.39	
δ-dodeca-	100	1	89 115		0.04	0.28	
		2	117			0.29	

[a] Not always detectable.

that is no evidence of complex formation by iodometric titration, but a small endothermic phase-transition at 76 °C.

Most starch/lactone systems yield one broad endothermic transition or several phase transitions. Most likely the multiple melting transitions reflect the heterogeneity of the supramolecular starch structure. Thus, the investigated starch systems have to be considered as metastable systems which are inclined to reorganization during sample preparation and upon heating in DSC. Other authors also found bimodal-melting endotherms for amylose−lipid complexes resulting from amorphous and crystalline fractions of complexes (*30*, *31*).

No correlation was found between the chain length of the lactones and the melting enthalpy of starch/lactone systems. The melting enthalpies of starch−lactone complexes were rather low compared to those of other starch−flavor complexes (*6*). In the second heating run even lower melting enthalpies of starch complexes were found. It is conceivable that the volatility of lactones contributed to an increase of lactone concentration in the headspace of the DSC pan thereby reducing their availability for complexation. It should be noted that the melting enthalpy of inclusion complexes depends on the extent of complexation, that is, on the amount of ligand, but also on the crystalline organization of the complexes.

Crystalline Structure of Dry Starch/Lactone Systems. The crystalline structure of starch−lactone complexes was characterized by X-ray diffraction. For this purpose, the starch systems were freeze-dried. The moisture content of the freeze-dried samples was adjusted to between 10 and 15 g/100 g. Freeze-dried potato-starch dispersion without the addition of lactones served as reference. The diffraction diagrams of the reference and of the starch/lactone systems are presented in Figure 5.

The X-ray diffraction diagram of freeze-dried potato-starch dispersions without addition of lactones (reference) can be described as an amorphous halo. This indicates that no retrogradation of starch occurred during sample preparation. Therefore, the diffraction diagrams of samples with flavors were corrected by subtracting the amorphous halo of a reference potato-starch dispersion.

The X-ray diffraction diagram of potato starch in the presence of γ-heptalactone showed a small broad reflection at 20 degrees which suggests that the ligand is not able to form stable complexes. All other investigated γ-lactones resulted in X-ray diffraction diagrams with

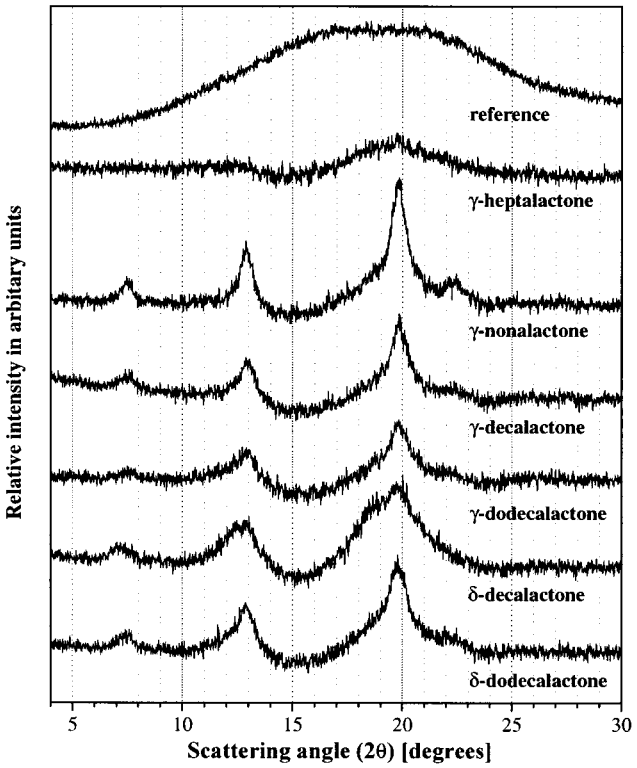

Figure 5. X-ray diffraction diagrams of freeze-dried potato-starch dispersions without the addition of a ligand (reference), and with γ-hepta-, γ-nona-, γ-deca-, γ-dodeca, δ-deca-, and δ-dodecalactone.

reflections at 7.5, 13.0, and 20.0 degrees. The scattering angles agree well with those described for the V_h amylose with reflections at 7.5, 13.0, and 20.0 degrees (*9*). It is concluded that γ-nonalactone, γ-decalactone, and γ-dodecalactone induce V_h type amylose helices which are characterized by single helices with 6 D-glycosyl residues per turn. In the case of γ-heptalactone very limited complexation may have occurred, the extent of complexation being below the resolution level of X-ray diffraction.

Addition of δ-dodecalactone to potato starch resulted in a system with reflections at 7.5, 13.0, and 20.0 degrees. Again, this indicates the formation of V_h type amylose helices. In contrast, potato starch with addition of δ-decalactone showed a small reflection at 7.0 and broad reflections from 12.0 to 13.0 and from 18.0 to 20.0 degrees. The described X-ray pattern may be interpreted as a V_h or another type of V amylose helix. The latter may be an intermediate helix as found by Buléon et al.

(*12*) for amylose−2-propanol complexes. The complexation of amylose with 2-propanol may yield a $V_{2\text{-propanol}}$ type X-ray pattern which converts readily into the well-known V_h amylose. On the basis of this fact, Buléon et al. (*12*) came to the conclusion that the amylose helix with 7 glycosyl residues per turn as described by Yamashita and Hirai (*10*) consists, in fact, of 6 glycosyl residues per turn. Other bulky flavor molecules such as geraniol were also found to form single helices of the $V_{2\text{-propanol}}$ type (*7*). In connection with starch−lactone complexes it is remarkable that only δ-decalactone presented a slightly different X-ray diffraction pattern. This is possibly linked to the interaction of the ligand with water as δ-decalactone is the only investigated lactone which is water soluble.

Structure−Property Relationships of Starch−Lactone Complexes. The characterization of starch/lactone systems by iodometric titration, DSC, and X-ray diffraction indicates that lactones with a linear chain of a size ≥ C_5 are able to form inclusion complexes with starch. Complexes are primarily formed with the linear starch fraction amylose, but a limited complexation with the side chains of amylopectin cannot be ruled out. The complexing ability of lactones has been confirmed with three different methods. Amperometric iodine titration has the advantage that it allows quantification of the extent of starch complexation in aqueous systems and does not require drying of the sample. DSC and X-ray diffraction are also suitable methods for assessing the complexing ability of a ligand. Both methods require freeze-drying of the sample with the risk of artifacts. Furthermore, quantitative analysis of starch complexes is difficult. Nevertheless, DSC and X-ray diffraction are widely applied methods for assessing starch complexation.

γ-Heptalactone is a borderline case regarding the complexation ability. The DSC results suggest that γ-heptalactone induces the helication of amylose. However, the stability of the starch−lactone complex is low because the ligand might be readily excluded from the helical cavity by a better complexing agent such as iodine. A similar situation is found with hexanal, with the difference that hexanal is able to induce the crystalline V_h amylose structure (*7*), whereas this is not the case for γ-heptalactone. Thus, DSC is more sensitive than amperometric iodine titration for the assessment of starch inclusion complexation. When comparing DSC and X-ray diffraction it is important to note that the two methods assess different structural levels. The enthalpy change of starch systems reflects the loss of order at the helical level rather than the disorganization of crystals, whereas X-ray diffraction gives information on the crystalline structure. This applies to retrograded amylopectin with a double helical structure (*32*) and also to amylose inclusion complexes as shown by Biliaderis and Galloway (*31*). The latter authors proved that amylose−monoglyceride complexes may exist in an amorphous form which yields an amorphous halo with X-ray diffraction, but present an endothermic melting transition around 90 °C as detected by DSC.

The investigated starch−lactone complexes are similar in terms of X-ray diffraction pattern, but large differences were found regarding thermostability, melting range, and melting enthalpy. The comparison of DSC curves of γ-nonalactone and δ-decalactone complexes, which show different thermal behavior despite identical chain length, suggests that not only the length of the linear chain, but also the ring structure, of lactones has an influence on the thermostability of the complexes. Furthermore, the solubility of the ligand may determine the properties of starch complexes. For instance, δ-decalactone, a ligand with good solubility in water, forms complexes with rather high enthalpy change upon melting and an X-ray pattern which is slightly different from all other investigated lactone complexes.

By analogy with complexing fatty acids it may be assumed that the linear carbon chain of lactone molecules is included in the amylose helix (*14*), whereas the pyranose or furanose ring is positioned outside. However, the fact that γ-nonalactone, with a rather short linear chain consisting of five carbon atoms, forms stable complexes speaks against this assumption. For instance, an investigation with a homologous series of aldehydes showed that hexanal does not form stable complexes, whereas octanal and decanal give stable complexes (*7*). Therefore, it is possible that the whole lactone molecule is positioned inside the amylose helix. Guzmann (*16*) even suggested that two antiparallel-oriented molecules of δ-decalactone are accommodated in the amylose helix.

It should be added that the complexation of starch with lactones also influences the macroscopic properties of the aqueous dispersions. Visual inspection of the systems revealed that the addition of lactones induced turbidity of the starch dispersions. Lactones promoted the formation of precipitate or a soft gel. Gelation of the starch dispersion was found with γ-decalactone, γ-dodecalactone, and δ-dodecalactone. The colloidal properties of aqueous starch systems are determined by polymer−solvent interactions (*33*). Water is a rather poor solvent for starch, in particular for amylose. The tendency of amylose to minimize the interaction with water is the driving force for the creation of supramolecular structures, which in turn determines the macroscopic properties. The formation of inclusion complexes with amylose further reduces the solubility of amylose in water because helical polymers possess little configurational entropy. The result of unfavorable interactions between amylose complexes and water is phase separation into polymer-rich and polymer-poor domains. Microphase separation is manifested by the appearance of turbidity. Upon further demixing, bulk-phase separation may occur as observed in potato starch dispersions in the presence of lactones with short linear chains. Other ligands such as geraniol and carvone also promote bulk-phase separation of starch, that is, the formation of a precipitate (*7*). The gelation of starch, which may be induced by lactones with linear chains ≥ C_5 is most probably also the result of microphase separation. The complexation-induced gelation of starch has been found with emulsifiers (*26*) and with flavor substances such as decanal and fenchone (*7*). Similarly to the latter systems, gelled starch−lactone dispersions can be described as three-dimensional networks of amylose aggregates.

Finally, it should be added that the described starch/lactone systems are far from being in an equilibrium state after an aging period of 24 h as manifested by the colloidal behavior. From a thermodynamic point of view, the structural changes upon aging of starch/lactone systems reflect the passage to a state of lower free energy. Besides the experimental time scale, the temperature is decisive for the rate of complex formation

which, in turn, has an influence on the supramolecular structures of starch.

CONCLUSIONS

γ- and δ-Lactones are able to form inclusion complexes with starch, in particular with amylose. The extent of starch complexation, as well as the thermal behavior and the structural properties of the complexes, are determined by the physicochemical properties of lactones, that is, their molecular weight, length of the linear chain, solubility, etc. On the other hand, the experimental results show that an unambiguous assessment of the complexing ability of a ligand and a comprehensive description of the structural organization of starch inclusion complexes requires the combination of different methods. In the present investigation the combination of amperometric iodine titration, DSC, and wide-angle X-ray diffraction proved to be successful for the evaluation of the complexing ability of lactones. However, several aspects of starch complexation are still not clear, such as the exact arrangement of lactones in the amylose helix. Furthermore, the relationship between the molecular structure of starch inclusion complexes and the colloidal behavior of aqueous starch dispersions at the macroscopic level requires further research. A detailed investigation of starch inclusion complexes is justified by the significance of starch−flavor interactions in foods. For instance, the question of how starch affects flavor retention and release in low-fat food products has become increasingly important (*34*).

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