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Formation of amylose complexes with C6-aroma compounds in starch dispersions and its impact on retention

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Abstract

Interactions between aroma compounds and starch matrices may increase the retention of aroma compounds. In particular, the linear amylose of starch, is able to form inclusion complexes with a wide variety of flavour compounds.

The retention of four C6 aroma compounds (hexanol, hexanal, *trans*-2-hexenal and 2-hexanone) in model starch dispersions was measured using the exponential dilution method. The complexing behaviour of these aroma compounds with amylose and two starch dispersions was studied by differential scanning calorimetry (DSC) and X-ray diffraction, to determine the relative importance of this factor.

The ability of hexanol and hexanal to induce a specific interaction with amylose is showed by both methods. This can explain their high retention in model starch dispersions. In contrast, the inability of 2-hexanone to interact with amylose explained its low level of retention.

Keywords: Starch; DSC; X-ray diffraction; Aroma compound; Exponential dilution

1. Introduction

Interactions between aroma compounds and other ingredients in the food matrix play an important role in the flavour perception of food products and consequently their acceptability to consumers (Druaux & Voilley, 1997). Not only starch is an important ingredient in all cereal products, but also, starch and starch derivatives are widely used as additives (thickener, stabiliser, texturing agent) or as flavour carriers. Thus, a fundamental understanding of aroma-starch interactions is useful to improve food flavouring and to develop new carriers for flavour encapsulation.

The interactions between starch and volatile molecules have been studied using a variety of techniques. Inclusion complexes of starch with different aroma compounds have been characterized by amperometric iodine titration (Nuessli, Conde-Petit, Trommsdorff, & Escher, 1995; Rutschmann & Solms, 1990a), X-ray diffraction, and differential scanning calorimetry (DSC) (Nuessli, Sigg, Conde-Petit, & Escher, 1997). Interaction parameters have generally been measured in starch solutions using the static headspace method (Jouquand, Ducruet, & Giampaoli, 2004; Le Thanh, Thibeaudeau, Thibaut, & Voilley, 1992) or binding profiles (Rutschmann, Heiniger, & Solms, 1989; Rutschmann & Solms, 1990b).

In recent studies, the ability of aroma compounds to form complexes with amylose, has been compared to their retention in starch-based matrices (Arvisenet, Le

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Bail, Voilley, & Cayot, 2002a). Complexing experiments were performed with amylose dispersions only. The aim of the present work was to study the influence of interactions between aroma compounds and amylose on aroma retention in model starch dispersions at a low concentration. The ability or inability of C6-aroma compounds to form complexes with amylose, related to their chemical function (hexanal; hexanol; *t*-2-hexenal; 2-hexanone) was demonstrated by DSC and X-ray diffraction. In parallel, the retention of these aroma compounds was measured by exponential dilution in starch dispersions at low concentration. Potato and corn starches were compared in order to determine the influence of internal lipids on aroma retention. The effects of amylose–aroma complexes on aroma retention in starch dispersions are discussed.

2. Materials and methods

2.1. Materials

Hexanol and 2-hexanone were obtained from Ega (France); *t*-2-hexenal and hexanal were obtained from Aldrich (St Quentin Fallavier, France). The physicochemical properties of the aroma compounds are shown in Table 1.

Potato amylose (type III) was obtained from Sigma (France), polymerization degree (DP) 841.

Potato and corn starches were kindly provided free of charge by Roquette Frères (Lestrem, France). The properties of these starches are shown in Table 2.

2.2. Preparation of model starch dispersions

Two model starch dispersions (potato or corn, 3% w/w) were prepared with distilled water (200 ml) in 250 ml Sovirel bottle. The mixture was stirred for 10 min and 25 ppm of aroma compounds were added to the bottle before being hermetically closed. The mixture was then heated for 45 min at 95 °C using a water bath, under magnetic stirring at 700 rpm. After cooling the mixture was stored at room temperature for 24 h before measurements were performed.

Table 2
Properties of starches

Starch	Water content (%)	Amylose (%)	Lipids (%)
Potato starch	12	28	0.65
Corn starch	16	25	0.09

2.3. Exponential dilution method

The activity coefficients of aroma compounds at infinite dilution were determined at 60 °C, using the exponential dilution method (Leroi, Masson, Renon, Fabries, & Sannier, 1977). The saturated vapour pressure at 60 °C was estimated by the Gomez–Thodos method (Espinoza-Diaz, Guetachew, Landy, Jose, & Voilley, 1999). The results are shown in Table 5.

Thirty milliliters of starch dispersion containing each aroma compound were introduced into a purge vessel (100 ml) maintained at 60 °C. Nitrogen was bubbled through the starch preparation at a constant flow rate (from 50 to 60 ml/min, depending on the aroma compound) and volatile compounds were released into the headspace (N_2 outlet). One milliliter of the vapour phase was manually injected at regular intervals, using a heated (120 °C) gas valve (Supelco). The gas chromatograph (Perichrom, France) was equipped with a flame ionization detector with a 15-m stainless steel column packed with Chromosorb® W-HP (80–100 mesh), coated with 10% Carbowax 20-M (Interchim, France). The chromatographic parameters were as follows: detector temperature: 250 °C; hydrogen flow-rate: 45 mL/min; air flow-rate: 450 mL/min; column temperature: 120 °C; nitrogen flow-rate: 18 mL/min. Chromatograms were recorded using the Winilab III software (Perichrom, France).

The intensity of the interactions was determined by the following equation (Landy, Druaux, & Voilley, 1995):

$$R = [1 - (\gamma^{\infty}_{\text{starch}}/\gamma^{\infty}_{\text{water}})] \times 100,$$

Table 1
Physicochemical properties of aroma compounds

Aroma compound	Purity (%)	Density	Molecular weight	Saturated vapor pressure at 25 °C (mm Hg)	Saturated vapor pressure at 60 °C (mm Hg)[c]	Solubility in water at 25 °C (g/L)	Log *P*
Hexanal	98	0.830	100	11.26[a]	58.52	4.8[b]	1.78[a]
2-Hexanone	98	0.812	100	11.6[a]	91.96	20[b]	1.38[a]
t-2-Hexenal	98	0.846	98	6.6[a]	29.64	5.3[a]	1.58[a]
Hexanol	99	0.814	102	0.928[a]	7.17	5.9[a]	2.03[a]

[a] Syracuse Research Corporation (2004).
[b] Chemexper Chemical Directory (2004).
[c] Estimated by the Gomez–Thodos method.

where γ^{∞}_{starch} is the activity coefficient of the aroma compound in starch dispersion; γ^{∞}_{water} is the activity coefficient of the aroma compounds in water.

2.4. X-ray diffraction analysis

In order to show the affinity of the four aroma studied with amylose, were prepared highly crystalline powders of amylose complexes with aroma (Le Bail, Rondeau, & Buléon, 2005).

2.4.1. "In vitro" complex preparation with amylose and aroma compounds

As hexanol, hexanal, *trans*-2-hexenal and 2-hexanone are slightly soluble in water, flavour compounds were added in excess to amylose solution for complexation experiments.

Before heating and mixing amylose and aroma, a nitrogen flow was first passed through the samples for 10 min to prevent their oxidation during heating.

Amylose was dispersed in pure water 1% (w/v) (200 mg/20 ml) at 160 °C for 45 min in a glass tube with a screw cap.

In 10 ml water, 1.68 g of aroma were preheated to 90 °C and added to amylose solution after its cooling at 80 °C. The final concentration was 6.25% (w/w) corresponding to molar ratio aroma/amylose: 11.14–11.45×10^3 (mol/mol). The mixture was then maintained at 90 °C for 10 min., cooled down to room temperature and stored for 48 h. The precipitate was then collected by centrifugation (625*g*) and the water content was adjusted at $a_w = 0.75$ over saturated NaCl solution. Wide-angle X-ray diffraction measurements were then performed.

2.4.2. Complexes in corn and potato starch dispersions

Complexes were also prepared using low concentration starch dispersions to highlight the influence of amylopectin. Two starches were studied, corn and potato, to show the competition between aroma and endogenous lipids of corn starch.

Starch and water were mixed for 10 min to give 3% (w/w) suspension and 7% of the aroma compound were added to the starch dispersion. The aroma concentration is shown in Table 3. A nitrogen flow was passed through the samples for about 10 min. Immediately thereafter, the vials were sealed and heated in an oil bath at 95 °C for 45 min under stirring.

The mixture was stored for 24 h. The gel obtained was removed and then conditioned by desorption of water by equilibration over saturated NaCl solution at a water activity $a_w = 0.75$ for 1 week. The film thus obtained was studied by X-ray diffraction.

2.5. X-ray diffraction measurements

X-ray diffraction data were collected using a diffractometer which operated in a transmission mode and powered by a XRG 3000 (Inel-France) generator running at 40 kV and 30 mA. A copper X-ray tube was used with a quartz monochromator, providing the Cu $K\alpha_1$ beam (0.15405 nm). One hundred milligram of samples, after equilibration time at $a_w = 0.75$, were sealed between two aluminum foils to prevent any significant change in the water content during the measurement. Diffraction intensities were recorded for a 2-h exposure period by a curve position sensitive detector (CPS 120 – Inel France). The resulting diffraction diagrams were normalised to the same total integrated area between 3° and 30° (2θ).

2.6. Differential scanning calorimetry measurements of aroma/potato starch complexes

DSC thermograms were recorded using an automated heat flux differential scanning calorimeter SETARAM DSC 121 (France). Stainless steel high pressure cells were used. The system was calibrated with indium and a pan containing 100 μL water was taken as reference.

Starch suspension at a concentration of 53 g dry starch/100 g dispersion were prepared at room temperature. The detection limits of the calorimeter to detect the formation of amylose–aroma complexes impose a high concentration of starch in the dispersion. Flavour substances were added to the starch dispersions at a concentration of 7% (w/w of dry starch). This concentration was chosen to favour a high amount of amylose/aroma complexes detected by DSC.

Samples and references were sealed in stainless steel high-pressure cells and two successive scans were run at 3 °C/min between 5 and 160 °C, separated by a cooling stage at about 10 °C/min.

Table 3
The different starch preparations with the corresponding aroma concentration and the method used

Method used	Exponential dilution	X-ray diffraction	DSC
% of dry starch (w/w)	3	3	53
Aroma concentration	2.5×10^{-3}% (w/w)	7% (w/w)	7% (w/w)
Temperature conditions	95 °C for 45 min	95 °C for 45 min	5–160 °C at 3 °C/min

3. Results and discussion

3.1. The following of potato starch/aroma complexes formation by DSC

Fig. 1 shows the melting thermograms obtained after heating potato starch dispersions in the presence of aroma compounds (hexanol, hexanal, 2-hexanone). The thermogram (Fig. 1(a)) corresponding to the reference (potato starch without aroma compound) was characteristic of the potato starch dispersion under low moisture conditions. It is well known that starch DSC curves usually contain multiple endotherms under low water content conditions (Colonna, Buléon, Mercier, & Lemaguer, 1982). In this case, two endotherms were observed at 63 and 71 °C (shoulder), corresponding to starch gelatinization.

Thermoanalysis is generally used to characterize amylose/lipid complex formation. Because the linear molecular structure of hexanal, hexanol, 2-hexanone and *t*-2-hexenal is comparable to that of short fatty acids, a similar behaviour could be expected with amylose. Nevertheless, as with Nuessli et al. (1997) not even one endothermic phase transition typical of amylose/lipid complexes could be detected for amylose/hexanol complexes (Fig. 1(c)). A broad endothermic phase transition with a maximum at 93 °C and an exothermic phase transition at around 100 °C occurred, followed by a second endotherm at 123 °C. This phenomenon could be explained by a superimposition of a broader endotherm and an exotherm corresponding to the crystallisation of amylose/hexanol complexes (Le Bail et al., 1999). The first part of the endotherm could correspond to the poorly crystalline complexes or to a decomplexing of amorphous complexes (Biliaderis, 1992). This phenomenon could have been superimposed on exothermic crystallization of new complexes into a more crystalline V_6 structure which could then melt at the higher temperature corresponding to the end of the endotherm. During the second run, a phase transition in the 110–125 °C range was detected; the melting of complexes was reversible when samples were heated to temperatures lower than 160 °C.

In contrast to hexanol (Fig. 1(c)), thermal analysis curves for hexanal complexes (Fig. 1(d)) only exhibited the gelatinization endotherm during the first run. On the other hand, an endotherm clearly appeared during the second heating at 107 °C. This second endotherm could be assigned to the presence of amylose/hexanal complexes and this result seems to prove that amylose/hexanal complexes are formed during the cooling phase. The different behaviours of hexanol and hexanal with amylose (at 53% dry starch) may indicate two mechanisms of complex formation.

Behaviour during the heating phase differed for 2-hexanone (Fig. 1(b)) and *t*-2-hexenal (thermogram not shown). No endotherm corresponded to the melting of amylose/aroma complexes and the thermal analysis curves were very similar to the reference (Fig. 1(a)).

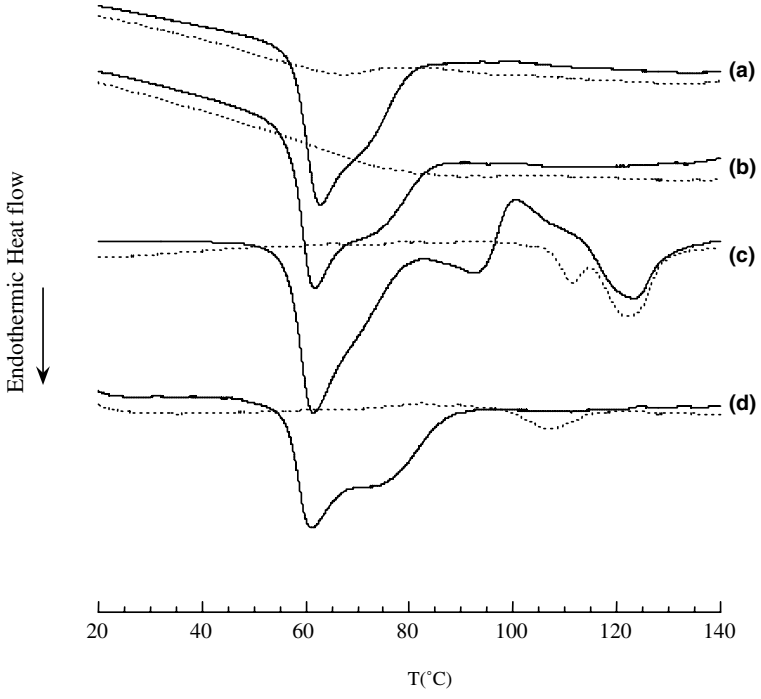

Fig. 1. DSC thermograms of potato starch at 47% of humidity without aroma compounds (a), with 2-hexanone (b), with hexanol (c) and with hexanal (d).

3.2. X-ray diffraction of amylose aroma complexes and starch dispersions aroma complexes

3.2.1. "In vitro" complexes

Amylose, the linear fraction of starch, forms crystalline complexes, known under the generic name of V amylose, with a variety of small ligands. In the literature, depending on the complexing molecule, different types of V amylose exist: iodine (Bluhm & Zugenmaier, 1981), dimethyl sulfoxide (Winter & Sarko, 1974), potassium hydroxide and potassium bromide (Senti & Winauer, 1952). The best-known and best described complex is V_h amylose, which is obtained with linear alcohols (Brisson, Chanzy, & Winter, 1991; Buléon, Duprat, Booy, & Chanzy, 1984; Le Bail, Bizot, Pontoire, & Buleon, 1995; Whittam et al., 1989) and monoacyl lipids (Godet, Tran, Delage, & Buleon, 1993; Godet, Bizot, & Buleon, 1995). It consists of a sixfold left-handed helix repeating at 0.80 nm, in which the complexing agent is included.

Three other crystalline types of complexes have also been highlighted with no linear alcohol. These complexes can initially be distinguished, using the constructive amylose helix. At present, two families are known (V_6 and V_8, where 6 and 8 represent the unit numbers of D-glycosyl per turn). For V_6 types, two trapping modes could be suggested: intra helices inclusion V_{6I} and intra–inter helices inclusion V_{6II}, V_{6III}, I, II and III represent varying volume between helices in the crystalline stacking. For V_{6I} (Brisson et al., 1991), the small molecules could be entrapped only into the cavity of the helix (Godet et al., 1995) and for V_{6II} and V_{6III}, the molecules could also be entrapped between helices.

Another possibility is a larger cavity with eight D-glucose residues per turn V_8, which allows the inclusion of bulky molecules (Winter, Chanzy, Putaux, & Helbert, 1998; Le Bail et al., 2005).

Characteristics X-ray diffraction patterns (V_{6I}, V_{6II}) are shown in Fig. 2 (Le Bail et al., 2005).

All X-ray results are summed up in Table 4. Fig. 3 shows the X-ray diffraction thermograms for the four "complexes" studied. The X-ray diagrams obtained with hexanol and hexanal are shown in Fig. 3(c) and (d). The reflections at (2Θ = 7.3; 9.3; 11.9; 13.3; 20.1; 21.2) were comparable to those obtained for amylose complexed with butanol (V_{6II} type, Fig. 2(c)) (Helbert & Chanzy, 1994).

An X-ray diffractograms (Fig. 3(b)) obtained with amylose precipitated with *t*-2-hexenal exhibited reflections characteristic of V_{6I} (V_h) type (Fig. 2(b)). During DSC experiments, amylose/*t*-2-hexenal complexes were not detected; it seems that these experimental conditions (low water content, presence of amylopectin, no stirring) did not favour complex formation with *t*-2-hexenal. Moreover, a time delay could be necessary

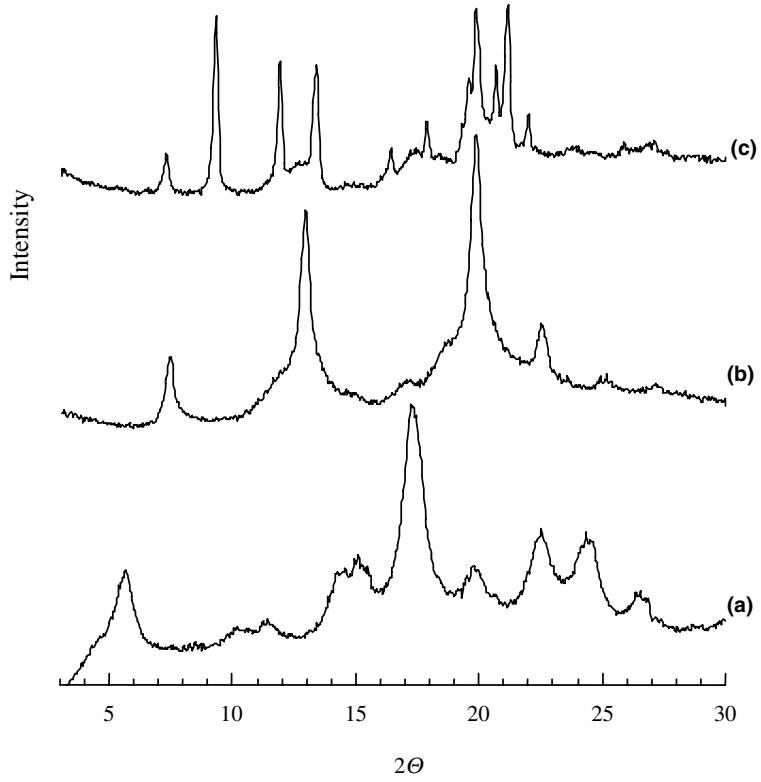

Fig. 2. Characteristics X-rays diffractograms of B-type structure (a), V_{6I} type structure (b) and V_{6II} type structure (c).

Table 4
X-ray crystalline types obtained for amylose, potato starch and corn starch dispersions with addition of 2-hexanone, *t*-2-hexenal, hexanol and hexanal

	Hexanal	2-Hexanone	*t*-2-Hexenal	Hexanol
Amylose dispersion	V_{6II} type	B type	V_{6I} type	V_{6II} type
Potato starch dispersion	V_{6II} type	B type	Amorphous V_{6I} type (traces)	V_{6II} type
Corn starch dispersion	V_{6II} type V_{6I} type	B type V_{6I} type (traces)	V_{6I} type	V_{6II} type V_{6I} type

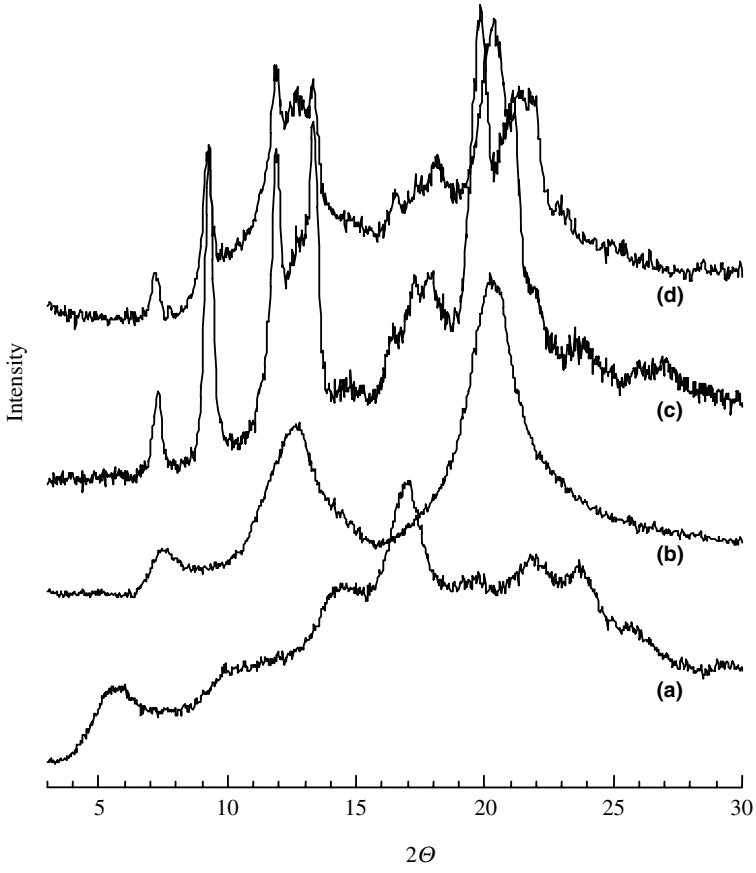

Fig. 3. X-rays diffractograms obtained for amylose dispersion crystallised with addition of 2-hexanone (a), *t*-2-hexenal (b), hexanol (c) and hexanal (d).

to favour the formation of amylose/*t*-2-hexenal complexes. Indeed, this time delay could be reached with X-ray diffraction experiments (48 h) and not with DSC experiments (60 min). Fig. 3(a) shows a wide-angle X-ray diffraction diagram for amylose/2-hexanone. The reflections obtained were characteristic of the B type (Fig. 2(a)), which show that amylose, in this case, had retrogradated, and indicated that 2-hexanone did not form complexes with amylose. This result was confirmed by the inability of 2-hexanone to form complexes with amylose during DSC experiments.

For these four compounds, the chemical function had an impact on the formation of the V type of amylose. It seems that the ketone function was able to prevent the formation of complexes with amylose.

3.2.2. Complexes in starch dispersions

In order to evaluate the influence of the amylopectin and endogenous lipids existing in corn starch, complexes were also prepared with low concentration starch dispersions. In potato starch dispersions, the X-ray diagram obtained without aroma compounds, and used as a reference, was characteristic of the B type. In the presence of 2-hexanone, the X-ray diffraction diagram showed a B-type, whereas hexanol and hexanal appear to be of the V_{6II} type (Fig. 4, Table 4).

The X-ray diagram of starch dispersion precipitated with *t*-2-hexenal displayed an amorphous spectrum with traces of V_{6I} type amylose (central diffusion $2\Theta = 20$). Thus the conditions for starch dispersion preparation seemed less favourable to forming complexes with amylose than the conditions used for "in vitro complexes".

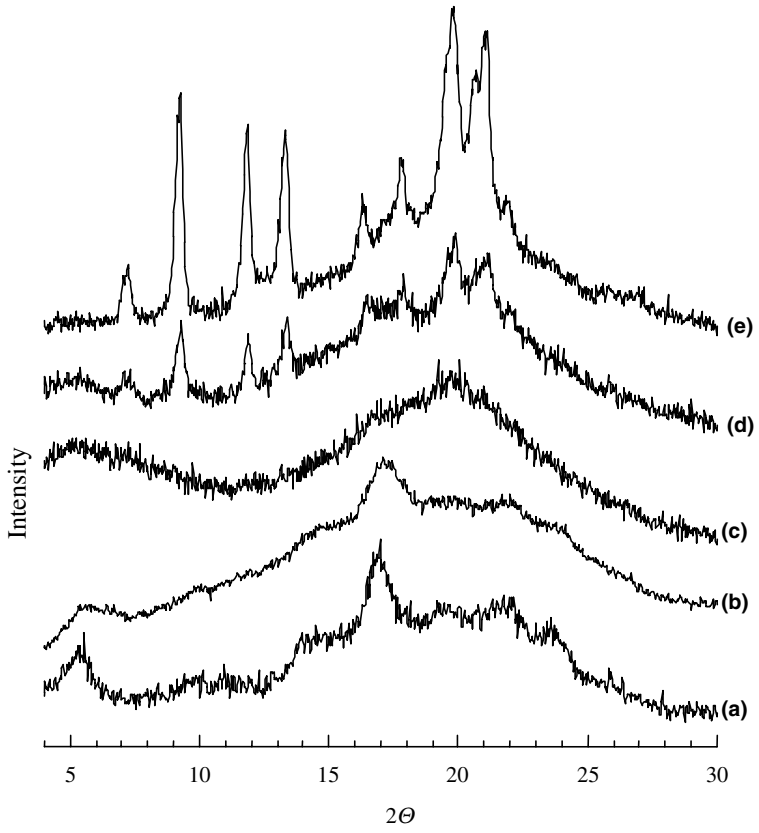

Fig. 4. X-ray diffractograms obtained for potato starch dispersion: without aroma (a), with 2-hexanone (b), *t*-2-hexenal (c), hexanol (d) and hexanal (e).

This result may involve a low affinity of *t*-2-hexenal for amylose.

Fig. 5 shows the X-ray diffraction diagrams of complexes obtained with corn starch dispersions. The X-ray diagram obtained without aroma compounds exhibited reflections characteristic of B and V_{6I} types (Fig. 5(a)). This result indicates that internal lipids in corn starch complexed some part of the amylose.

Hexanol and hexanal X-ray diffraction diagrams yielded a two phase structure: indeed, the two crystalline types V_{6I} and V_{6II} were simultaneously present and this result indicated that endogenous lipids, which are more available, took precedence over exogenous ligands, but without hindering the interactions with them.

The corn starch/hexanol complex, shows a strong crystallinity for the two crystalline types (V_{6I} and V_{6II}) present on the X-ray spectrum. The peaks are very thin and intense, in contrast to the corn starch/hexanal complexes.

This result could be explained by DSC experiments, where the amylose/hexanol complex had a crystallisation temperature close to that of the amylose/endogenous lipids of corn starch complexes. Thus, in corn starch dispersions, the formation of amylose/lipid complexes and amylose/hexanol complexes were in competition. As shown by DSC experiments, amylose/hexanal complexes crystallised during the cooling phase. Therefore, the amylose/lipid complexes formed first, hampering the formation of amylose/hexanal complexes.

When 2-hexanone was added to corn starch dispersions, the B-type of amylose was the principal form. This compound limited the formation of amylose/lipid complexes at this concentration. The 2-hexanone seems to favor the precipitation (retrogradation) of the amylose in the B-type to the detriment of the complexation of the endogenous lipids.

In the case of *t*-2-hexenal, the X-ray diagram exhibited reflections of a V_{6I} type. The presence of internal lipids seemed to favour complex formation with *t*-2-hexenal.

4. Retention of aroma compounds in low concentration starch dispersions

The activity coefficients of aroma compounds measured by the exponential dilution method, in water at 60 °C are shown in Table 5, these coefficients enabled the determination of aroma retention. The exponential dilution method was used to determine retention due to physicochemical interactions. Indeed, because this is a dynamic method in comparison with measurements

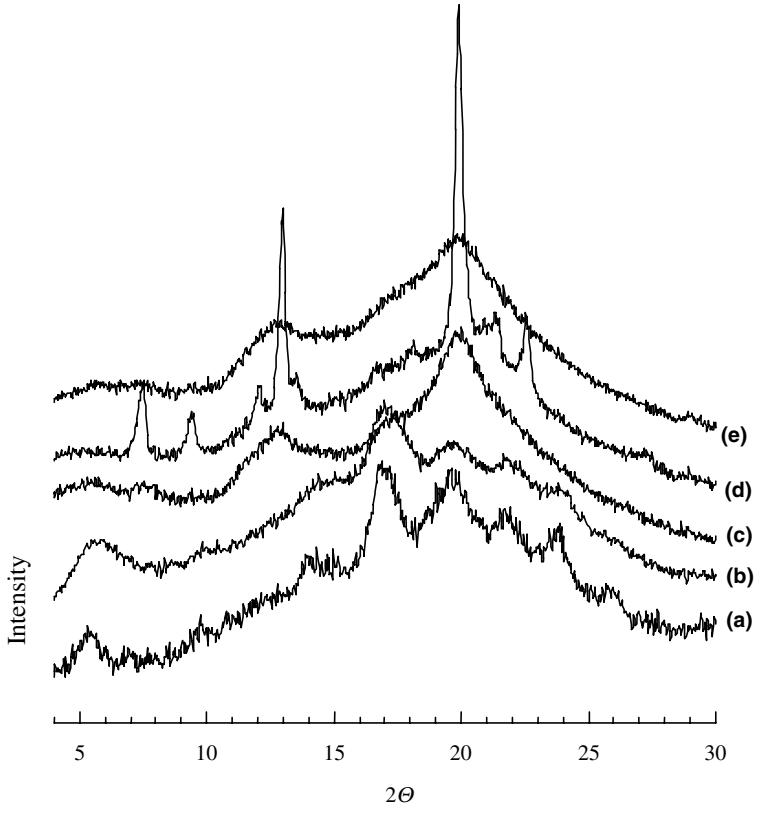

Fig. 5. X-ray diffractograms obtained for corn starch dispersion: without aroma (a), with 2-hexanone (b), *t*-2-hexenal (c), hexanol (d) and hexanal (e).

Table 5
Activity coefficients of aroma compounds in water, at 60 °C, measured by the exponential dilution method

Aroma compounds	Activity coefficients
2-Hexanone	345 ± 16
t-2-Hexenal	841 ± 28
Hexanal	1351 ± 64
Hexanol	1283 ± 63

made by static headspace, the kinetic effects which might have been involved in aroma retention were limited.

Fig. 6 shows the retention of aroma compounds by the two different starches. Retention appeared to be the same for each compound, whatever the type of starch. In the literature, starch type, and particularly the percentage of amylose (Arvisenet et al., 2002a), influences the retention of aroma compounds. Both starches used in our study contained the same percentage of amylose which could explain this result. However, aroma retention seemed to be slightly lower for corn starch dispersions, particularly with respect to hexanol. Competition between this compound and internal lipids

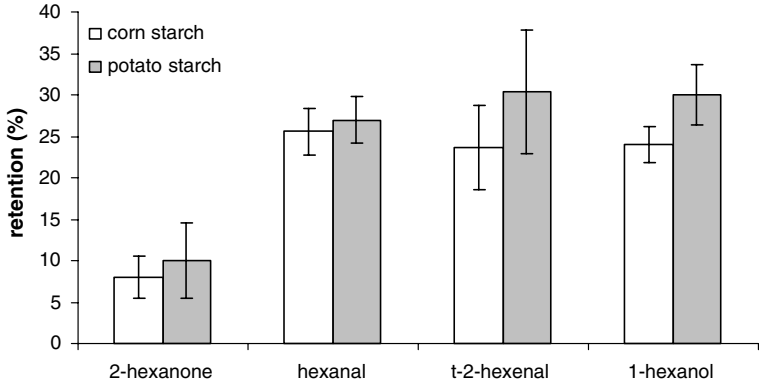

Fig. 6. Retention of aroma compounds in starch dispersions.

for amylose molecules may have occurred during the heating phase.

The retention of hexanal, *t*-2-hexenal and hexanol reached about 30%, while that of 2-hexanone was lower (about 10%). The better retention of hexanol, hexanal and *t*-2-hexenal may have been due to specific interactions with starch. In the case of hexanol and hexanal (which were able to form complexes with amylose in starch dispersions), their retention may have been due to such complexes. In contrast, the inability of 2-hexanone to form complexes with amylose could explain its low retention. The difference in hydrophobicity between hexanol, hexanal and *t*-2-hexenal did not seem to influence retention. In another system like maltodextrin solutions (10%, w/w) studied by Jouquand et al. (2004), retention mainly depended on the hydrophobicity of these compounds (hexanal > *t*-2-hexenal > 2-hexanone).

The case of *t*-2-hexenal is surprising, because this compound (which had a low affinity for amylose in crystallisation experiments) was retained to the same extent as hexanol and hexanal. This compound could interact with amylopectin through a mechanism other than complexing. Previous studies have demonstrated the importance of amylopectin to aroma retention (Arvisenet et al., 2002a; Arvisenet, Voilley, & Cayot, 2002b; Van Ruth & King, 2003). Moreover, Heinemann, Escher, and Conde-Petit (2003) showed by X-ray diffraction measurements that amylopectin could interact with δ-lactone by the formation of a V_{6I} helix.

5. Conclusion

The exponential dilution method used to limit the kinetic effects often involved in aroma retention demonstrated that hexanol, hexanal and *t*-2-hexenal were retained to a greater extent than 2-hexanone. Study of the physicochemical interactions between aroma compounds and starch at a molecular level (X-ray diffraction and DSC) provided a partial explanation of the results obtained using the dilution exponential method. Indeed, the ability of hexanol and hexanal to interact with amylose could explain their high retention. Interactions with amylopectin may participate in aroma retention in the case of *t*-2-hexenal.

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