

Influence of the nature and treatment of starch on aroma retention

A. Boutboul^{a,b}, P. Giampaoli^a, A. Feigenbaum^c, V. Ducruet^{b,*}

^aLaboratoire de Chimie des Substances Naturelles, ENSIA, 1 av. des Olympiades 91744 Massy cedex, France

^bSquAle, Laboratoire de Nutrition et Sécurité Alimentaire, INRA, 78352 Jouy-en-Josas cedex, France

^cUnité de Physicochimie et Biotechnologie des Polymères, INRA, Moulin de la Housse, 51687 Reims cedex, France

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Abstract

The retention of aroma compounds (*d*-limonene, ethyl hexanoate, octanal and 1-hexanol) on different starch matrices was measured using inverse gas chromatography. The starch materials were native, acetylated and pregelatinised corn starches, maltodextrin and extruded corn starches. The influence of the amylose content and of the physical characteristics of starch (specific area, particle shape and size) were studied. Whatever the type of starch, retention increased with the polarity of the flavour molecules in the sequence: *d*-limonene < ethyl hexanoate < octanal < 1-hexanol. Maltodextrin appeared to be the most efficient matrix for flavour retention, followed by pregelatinised starches, extruded high-amylose starch and finally granular starches (native and acetylated starches). Retention on native starches did not follow the amylose content, unlike that on extruded starches. Specific area was the main factor, which could explain the different behaviour of samples. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Starch and starch-based ingredients (modified starches, maltodextrins, β -cyclodextrins) are widely used in the food industry to retain and protect volatile compounds. They can act as carriers for aroma encapsulation, fat replacers and also emulsion stabilizers (Thomas & Atwell, 1999). Since new techniques and new carriers are needed in the field of flavour encapsulation, starch appears promising for its potential as a flavour adsorbent. Thus, many researchers have created new microporous starch materials with the aim of improving aroma retention (Glenn & Stern, 1999; Golovnya, Misharina & Terenina, 1998; Smelik, 1991). These starch materials may be used for specific applications such as the controlled release of flavour in a package headspace or the selective adsorption of impurities and bitter components (Zeller, Saleeb & Ludescher, 1999).

Interactions between aroma compounds and starch have mostly been measured in solutions using static headspace analysis (Le Thanh, Thibaudieu, Thibault & Voilley, 1992). Static headspace was also used to study the binding of volatiles on low water content starch materials such as native starch (Hau, Gray & Taylor, 1996), extruded starch

(Hau, Gray & Taylor, 1998) or microcellular foam starch (Buttery, Glenn & Stern, 1999), as well as the diffusion of flavour through encapsulation carriers such as maltodextrin (Whorton & Reneccius, 1995). In this work, inverse gas chromatography (IGC) was used to measure aroma–starch interactions. This efficient technique has made possible the characterisation of interactions between aroma compounds and polymers (Delarue & Giampaoli, 2000; Gavara, Catala & Hernandez-Munoz, 1997). Recently, the IGC technique has been improved by humidifying the carrier gas to reduce matrix dehydration (Aucejo, Pozo & Gavara, 1998; Boutboul, Giampaoli, Feigenbaum & Ducruet, 2000).

Interactions between aroma compounds and food involve three mechanisms: the partition of flavour molecules between different phases of the food product, the diffusion of flavour molecules through the food and matrix and the binding of flavour molecules to food components (Taylor, 1998). The binding of volatiles to starch has been classified into two types. On the one hand, starch has been shown to form inclusion complexes with different volatile molecules (Nuessli, Sigg & Conde-Petit, 1997; Rutschman & Solms, 1990). In these complexes, the flavour compound is entrapped in the amylose helix through hydrophobic bonding. On the other hand, polar interactions have been determined, which involve hydrogen bonds between the hydroxyl groups of starch and aroma compounds (Maier, 1972).

* Corresponding author. Tel.: +33-1-34-65-20-63; fax: +33-1-34-65-20-85.

E-mail address: vducruet@jouy.inra.fr (V. Ducruet).

The microstructure of the food matrix plays an important role in aroma retention (Druaux & Voilley, 1997; Goubet, Le Queré & Voilley, 1998). Many systematic studies have been carried out on aroma–carbohydrate interactions, but there have been few attempts to correlate aroma retention with the structural parameters of the polysaccharide matrix, such as glassy or rubbery state, crystalline regions (Whorton & Reneccius, 1995) or porosity (Buttery et al., 1999). In this investigation therefore, we first studied the physical characteristics of starch materials, such as particle size and shape, specific area, bulk density, physical state and water content. Secondly, the retention of aroma compounds on 10 starch matrices was measured using IGC and then correlated with structural parameters.

2. Materials and methods

2.1. Materials

2.1.1. Aroma compounds

d-Limonene was obtained from René Laurent (Le Cannet, France). Ethyl hexanoate, octanal and 1-hexanol were obtained from Sigma Aldrich Chimie (Saint-Quentin Fallavier, France). The purity of aroma compounds ranged from 98 to 99%.

2.1.2. Starch materials

The following starch materials were used: a standard corn starch with a 25% amylose content, a waxy corn starch (Waxilys® 200) with less than 1% amylose content, a high amylose corn starch (Eurylon® 7) with a 70–80% amylose content, a pregelatinised standard corn starch (Pregelflo® M), a pregelatinised waxy corn starch (Pregelflo® C), an acetylated standard corn starch (Cleargum® MG85) with a degree of substitution of 1.7–2.5%, and a maltodextrin (Glucidex® 12) with 11–14 dextrose equivalent. These seven starch materials were provided by Roquette Frères (Lestrem, France).

The three extruded starches were made from the three native starches: standard, waxy and high-amylase corn starch. Twenty-five kg of each native starch bearing the Roquette Frères label were supplied by Carrechim (Vincennes, France) and used for extrusion.

Each of the 10 samples was sieved prior to further evaluation by IGC.

2.2. Methods

2.2.1. Extrusion

The water contents of the three native starches used for extrusion (waxy, standard and high-amylase corn starch) were 14, 12 and 12%, respectively. Samples were processed by extrusion through a Clextral BC-45 co-rotating intermeshing twin-screw extruder. The feed rate of starch was 35, 25 and 25 kg h⁻¹, respectively. The respective rates of water injection were 0.12, 0.48 and 0.48 l h⁻¹. This

provided starches with a water content of 17, 16 and 16%, respectively, before extrusion. The temperature of the barrel was 160, 140 and 140°C, respectively. The temperature of the melt product in the die zone was 190, 185 and 195°C, due to the mechanical process. The screw–screw-rotating rate was 175 rpm. The final water content of extruded starch samples was 7.7%. The extruded material was formed into cylinders using a 4-mm circular die plate at the extruder exit. After cooling, the samples were packed into hermetic plastic bags and stored at 4°C. For each of the three experiments, 10-kg native starch was used and 1 kg extruded starch was taken from the middle fraction, so as to ensure stable extrusion parameters and thus stable products.

Each extruded starch (400 g) was roughly and rapidly crushed with a food crusher (Vitamix, Moulinex) by portions of 15 g. An IKA A10 grinder cooled by a circulating flow of water was then used to obtain a thinner powder. Finally, the extruded starch powder was sieved to obtain particle sizes between 40 and 63 µm.

2.2.2. Characterisation of starch materials

2.2.2.1. Scanning electronic microscopy. Each of the 10 starch samples (1% w/w) was suspended in 100% methanol and mixed for 2 h at room temperature. The suspension was then filtered with a Büchner filter and the starch was vacuum dried at room temperature for one night in a dessicator containing silica gel.

The dried starch samples were sprinkled onto double-sided adhesive tape attached to specimen tubs. They were then sputter-coated with gold, mounted and observed using a JEOL-JSM 5200 scanning electron microscope. The samples were examined at an accelerating voltage of 5 or 10 kV. Micrographs were taken at a magnification of 750.

2.2.2.2. Particle size. The starch samples were suspended in 95% ethanol and the size distribution of starch particles was measured at room temperature by light scattering, using a Mastersizer (Malvern Instrument, Orsay, France).

2.2.2.3. Specific area. The specific area of starch samples was determined by quantifying the amount of nitrogen adsorbed onto the surface of the solid (V) under different pressures, at the nitrogen boiling point, using the BET equation (Braunauer, Emmett & Teller, 1938). A minimum of five points (P/P_0 , V) were plotted, with relative pressures (P/P_0) ranging between 0.03 and 0.2. Prior to analysis, samples were purged for 48 h to reach a pressure lower than 20 µmHg. The surface of a nitrogen molecule was estimated at 16.2 Å².

2.2.2.4. Bulk density. The bulk density (ρ) of starch matrices in the IGC column was determined using Eq. (1):

$$\rho = m/(V - V_0) \quad (1)$$

where m is the mass of the stationary phase, V the volume of

the column, and V_0 the interstitial volume, calculated using:

$$V_0 = t_0 F \quad (2)$$

where t_0 is the retention time of a non-retained compound (methane) and F the carrier gas flow rate.

2.2.2.5. Complementary characterisations of extruded samples. The density of samples was measured by immersing the starch cylinders in a container of mustard seeds, using the protocol developed by Tharrault (1992). The volumetric expansion of extruded samples was calculated using the equations described by Launay (1994).

The physical state of extrudates was determined using dynamic mechanical and thermal analysis (DMTA). Extrudates were cut to obtain $(30 \times 10 \times 8) \text{ mm}^3$ parallelepiped. In order to prevent dehydration, the bars were lubricated with Teflon immediately prior to the analysis. The DMTA measurements were carried out with a Rheometric Scientific DMTA MK III analyser at 40°C . An oscillatory strain was applied to the sample at various frequencies ranging from 10^3 to $10^{-2} \text{ rad s}^{-1}$. The storage modulus (E'), loss modulus (E'') and viscoelastic ratio ($\tan \delta$) were measured as a function of the frequency.

2.2.3. Inverse gas chromatography

Glass columns ($11.5 \text{ cm} \times 4.5 \text{ mm i.d.}$) were deactivated with dimethyldichlorosilane (DMCS) before being packed with starch. Column packing was facilitated by combined application of an electric vibrator and a vacuum system. The mass of the stationary phase was 0.42 g for extruded high amylose corn starch, 0.74 g for maltodextrin and 1.15 ± 0.07 g for the other starch materials.

The starch column was placed in the oven of a Carlo Erba 6000 Vega II gas chromatograph and connected to the injector and detector with deactivated fused silica tubing (0.32 mm i.d.). The gas chromatograph, equipped with a flame ionisation detector (FID), was operated under isothermal conditions at a temperature of 40°C . The injector and detector temperatures were maintained at 250°C . The flow-rate of the carrier gas (nitrogen) was regulated at 20 ml min^{-1} . This flow rate provided a pressure of 1.3–2.2 bar at the head of the column, depending on the starch material (1.4 ± 0.1 bar for extruded starches and 2.05 ± 0.15 bar for the other starch materials). All experiments were performed under humid conditions, the carrier gas being bubbled in water, as described by Boutboul et al. (2000). Prior to the experiments, the starch column had been conditioned for 8 h with the carrier gas to reach a stable starch–water content at equilibrium, resulting in stable retention times.

Pure volatile compounds ($0.05 \mu\text{l}$) were injected in a splitless mode with a $0.5 \mu\text{l}$ Hamilton syringe (Supelco, Bellefonte, USA). Retention times were determined using Borwin 1.2 data acquisition software. Specific retention volumes V_g were calculated using Eq. (3), where t (min) was the retention time of the solute, t_0 (min) the retention

time of a non-retained compound (methane), F (ml min^{-1}) the carrier gas flow rate, m (g) the mass of the stationary phase and T (K) the temperature of the column. The James and Martin compressibility factor j was calculated using Eq. (4) where P_i and P_0 were the inlet and outlet pressures, respectively.

$$V_g = j \frac{(t - t_0)F}{m} \frac{273}{T} \quad (3)$$

$$j = \frac{3}{2} \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \quad (4)$$

All injections of aroma compounds were performed in triplicate. A variation of less than 10% variation was observed between the retention times for replicate injections. Column to column variations were lower than 10%.

2.2.4. Water content

The initial water content of the starch materials was determined by weighing the samples before and after heating for 1 h at 130°C .

The water content of starch materials in the column was measured after conditioning and verified after the IGC experiment by weighing the column.

All the water contents are reported on a wet weight basis.

3. Results and discussion

3.1. Characterisation of starch materials

3.1.1. Ultrastructure

Scanning electronic microscopy enabled observation of the ultrastructure of the starch materials, providing information on particle size, shape and particularly the integrity or loss of the initial granular structure of starch.

Fig. 1(a) shows native corn starch granules with round and polygonal shapes. The particles had a regular shape and size (5–15 μm diameter) and some of them formed aggregates.

Pregelatinised starches were produced from native starches by drum drying. This harsh physical treatment induced the loss of the granular integrity of starch and large fragments made from a dried and cut starch paste were observed by scanning electronic microscopy (Fig. 1(b) and (c)). The particles had heterogeneous shapes and sizes (5–50 μm long).

Maltodextrin was produced from native standard corn starch by partial enzymatic hydrolysis, purification and spray drying. This physical and enzymatic treatment also induced loss of the granular structure of starch. The scanning electron micrograph of maltodextrin (Fig. 1(d)) showed thin sheets of material.

The acetylation of starch is a mild chemical treatment, which did not affect the granular integrity of starch (Fig. 1(e)). Like native corn starch, particles had a regular shape and size (5–20 μm diameter).

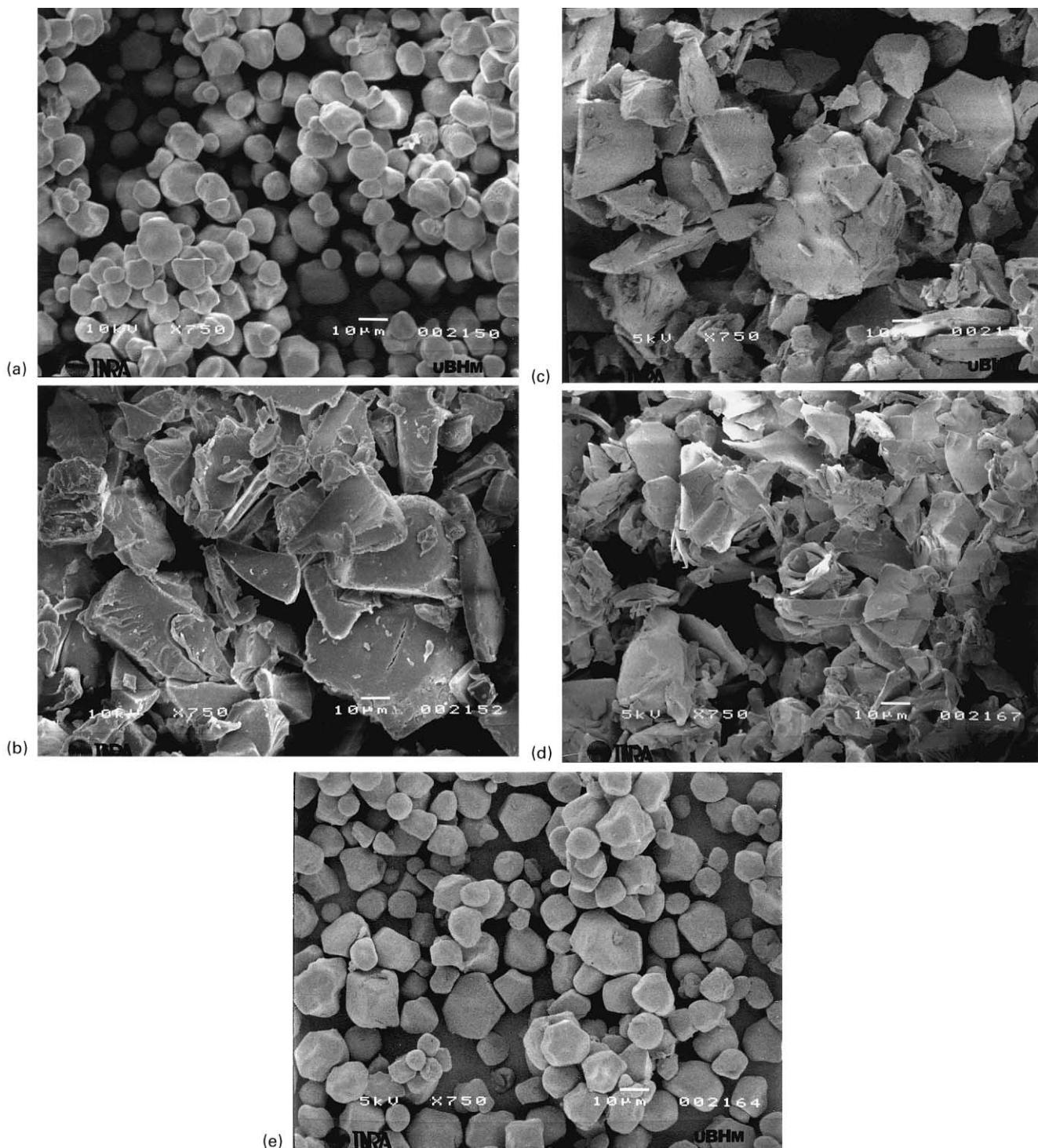


Fig. 1. Particles of corn starch materials: (a) native corn starch; (b) pregelatinised standard corn starch; (c) pregelatinised waxy corn starch; (d) maltodextrin; (e) acetylated corn starch.

During the extrusion-cooking of native starches, granules were gelatinised and molten (Fig. 2(a)–(c), ground starch extrudates). Particles from ground extrudates were very large ($>100 \mu\text{m}$ long) when compared with other starch materials and had quite a regular size and shape. Particles of high-amylose extrudates were thin chips (Fig. 2(a)) while

particles of standard and waxy extrudates were large blocks (Fig. 2(b) and (c)). Small fragments ($<10 \mu\text{m}$) could be distinguished between the blocks.

3.1.2. Particle size

Light scattering observation (Table 1) showed that the

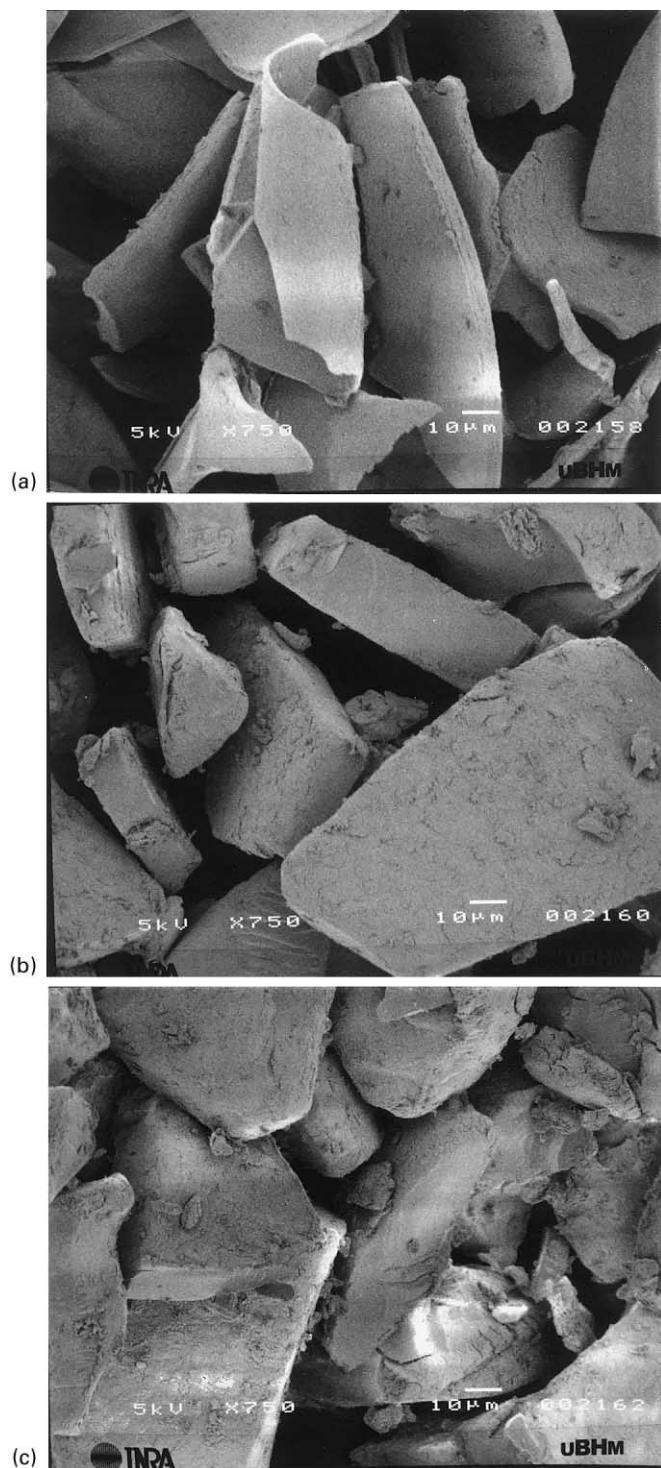


Fig. 2. Particles of ground extrudates: (a) extruded high-amylose corn starch; (b) extruded standard corn starch; (c) extruded waxy corn starch.

distributions of particle sizes of starch materials differed from the expected values (sieving 40–63 μm) and also from starch to starch. Sieving efficiency was affected by the aggregation of small particles and also by the irregular shape of particles. Some materials had spherical particles (granular starches), while others had rectangular or chip-shaped particles (extruded starches). Extruded corn starch

with a high amylose content had the thinnest but longest particles and so exhibited the largest particle size after sieving.

3.1.3. Specific area and bulk density

The mean specific area of granular starches (native and acetylated) was $0.44 \pm 0.07 \text{ m}^2 \text{ g}^{-1}$. These values are close to those determined by Karathanos and Saravacos (1993) for

Table 1

Physical characteristics of starch materials

		Particles size ^a (μm)	Specific area ± 0.03 ($\text{m}^2 \text{g}^{-1}$)	Bulk density (g cm^{-3})	Water content (%) Initial	Water content (%) IGC
Acetylated c.s. ^b		12–56	0.37	0.59	11.8	7.5
Native c.s.	Standard	10–46	0.40	0.65		
	Waxy	10–48	0.46	0.65	12.0 \pm 0.5	8 \pm 0.2
	High amylose	9–51	0.52	0.62		
Pregelatinised c.s.	Standard	11–69	0.51	0.62	7.5 \pm 0.1	7.1 \pm 0.1
	Waxy	10–64	0.54	0.66		
Maltodextrin		11–59	0.82	0.41	5	5
Extruded c.s.	Standard	26–108	0.30	0.62		
	Waxy	42–112	0.20	0.67	7.7 \pm 0.1	7.2 \pm 0.1
	High amylose	38–140	0.82	0.23		

^a For 80% of the particles.^b c.s. = corn starch.

waxy and high-amylose corn starch (0.39 and $0.49 \text{ m}^2 \text{ g}^{-1}$). With the exception of high-amylose corn starch, the specific area was reduced after extrusion-cooking, as previously described by Colonna and Buléon (1994). Maltodextrin and extruded high-amylose starch exhibited the highest specific areas ($0.82 \text{ m}^2 \text{ g}^{-1}$) and also the lowest bulk densities (0.41 and 0.23 g cm^{-3} versus $0.63 \pm 0.03 \text{ g cm}^{-3}$ for other starch materials). Specific area is dependent on the presence of fine pores and also on particle surface area, which increases as the density decreases (Karathanos & Saravacos, 1993), as we also observed. Furthermore, as shown by scanning electronic micrographs, particles of maltodextrin and extruded high-amylose starch both took the shape of thin chips, leading to a high specific area.

3.1.4. Physical state

The physical state of the matrix plays an important role in aroma retention (Whorton, 1995). It was therefore useful to know whether the starch materials were all in the same state.

The granular, pregelatinised sample and maltodextrin were in the glassy state under these conditions of low temperature (40°C) and low water content (5–8%) as widely described in the literature (Biliaderis, Page, Maurice & Juliano, 1986; Roos & Karel, 1991; Zelezna & Hoseney, 1987). We verified that the three extruded samples were in a glassy state under our conditions of humidity and temperature using DMTA.

3.1.5. Water content

Table 1 shows the water content of starch materials before and after IGC column conditioning. The different starch materials did not have the same initial water content (range: 5–12%). This water content depended on the nature and the treatment of starch. After IGC conditioning, the water content in each type of starch was different (5–8%) and was lower than or equal to its initial content. This result has already been reported in a previous paper (Boutboul et al., 2000) for Eurylon®7.

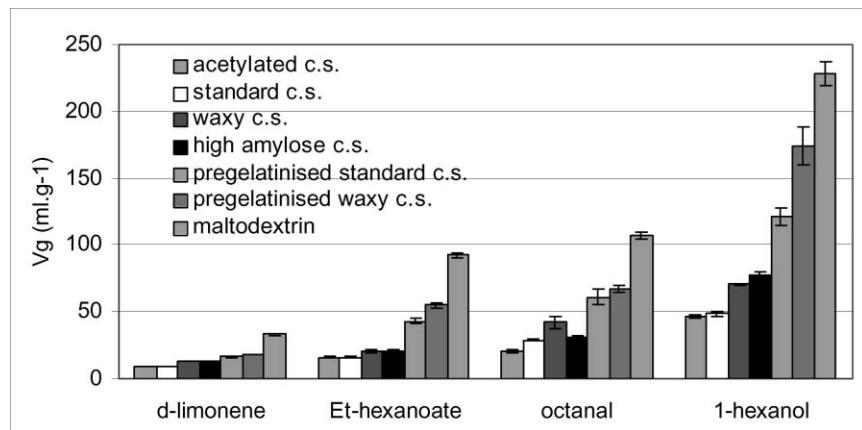


Fig. 3. Specific retention volume (V_g) of aroma compounds on different starch materials. c.s. = corn starch (humid conditions).

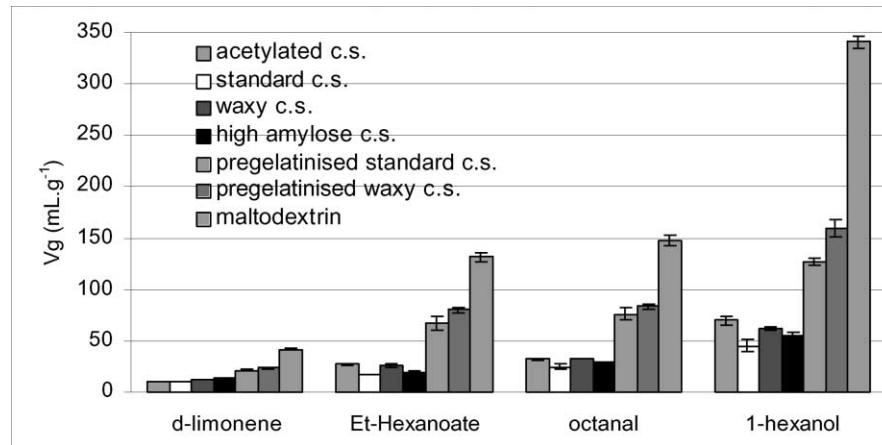


Fig. 4. Specific retention volume (V_g) of aroma compounds on different starch materials. c.s. = corn starch (dry conditions).

3.2. Aroma retention on native, acetylated, pregelatinised starches and maltodextrin

3.2.1. Influence of the nature and treatment of starch

The retention of aroma compounds was measured on different starch materials. The specific retention volumes (V_g) of four aroma compounds were plotted for the seven starchy materials (Fig. 3).

First, by whatever the type of starch employed, retention increased in the following sequence: *d*-limonene < ethyl hexanoate < octanal < 1-hexanol. Retention on starch increased according to the polarity of the flavour molecules, since starch is a polar stationary phase capable of forming hydrogen bonds with aroma compounds (Maier, 1972).

As for the behaviour of starch, three groups could be distinguished. The first group contained granular starches, including acetylated starch and the three native starches (standard, waxy and high-amylose corn starch); the second group contained pregelatinised starches (pregelatinised standard and waxy corn starch), and the third group, maltodextrin. Native starches displayed only minor differences and aroma retention did not follow the amylose content.

Aroma compounds were less well retained by granular starches. When focusing on a single aroma compound, such as ethyl hexanoate, a specific retention volume of about 20 ml g^{-1} on granular starches was determined. Starches, which have lost their granular structure, give rise to higher specific retention volumes for aroma compounds. This was the case with pregelatinised starches ($V_g \approx 50 \text{ ml g}^{-1}$ for ethyl hexanoate) and particularly with maltodextrin ($V_g \approx 90 \text{ ml g}^{-1}$).

Water content is one of the factors that can affect volatile retention. It was therefore important to know the exact water content of each starch sample in the column. The water content differed for each material (5–8%). In order to establish whether these differences in water content between the different samples would influence our results, we reproduced the same experiments under dry conditions (dry starches and dry nitrogen), where all the samples had the same water content ($\approx 0\%$).

When comparing the results obtained under humid conditions (Fig. 3) and under dry conditions (Fig. 4), we observed that the specific retention volume of aroma compounds on starch materials varied according to the water content.

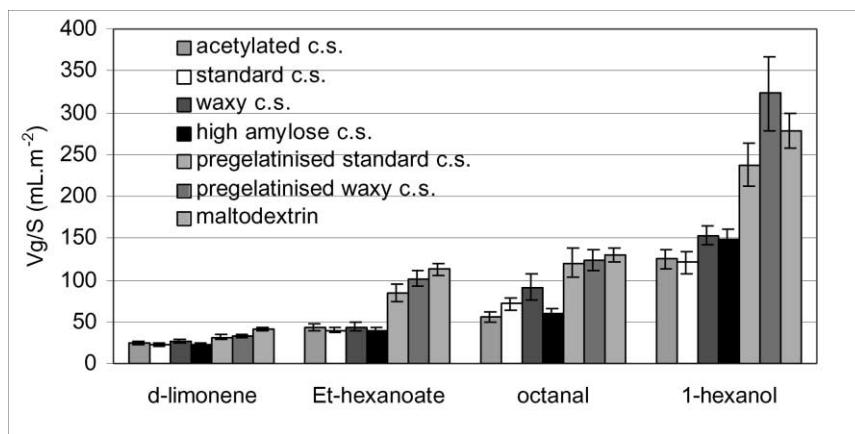


Fig. 5. Aroma retention on different starch materials corrected by the specific area of starch; ratio of the specific retention volume (V_g) to the specific area (S). c.s. = corn starch.

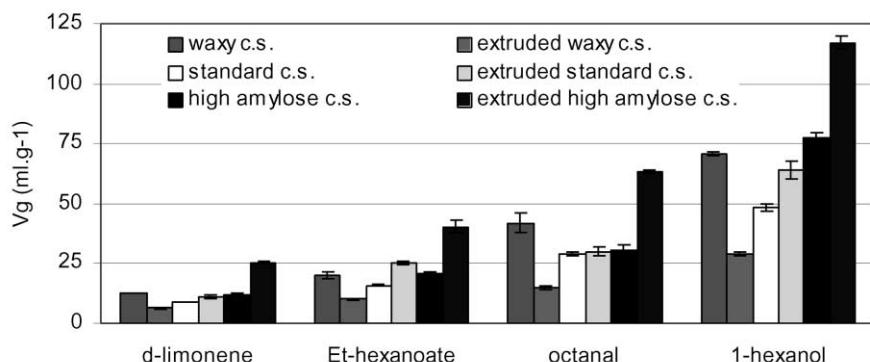


Fig. 6. Specific retention volume of aroma compounds on native and extruded starches. c.s. = corn starch.

However, starch matrices were classified on the basis of their ability to retain flavour. The same order was followed under dry and humid conditions and three groups could still be distinguished: native starches, pregelatinised starches and maltodextrin.

Under these experimental conditions (temperature, humidity), starch is in a glassy state and the low mobility of amylose molecules does not allow the formation of inclusion complexes with aroma. The aroma–starch interactions revealed by humidified IGC mainly resulted from an adsorption phenomenon involving hydrogen bonds. Furthermore, the partial diffusion of aroma compounds into the matrix, favoured by humid carrier gas, could be involved, as well as the partitioning of flavour between the gas phase and the water contained in starch.

3.2.2. Influence of the specific area of starch

In order to gain a clearer understanding of retention phenomena, the specific area of starch materials (Table 1) was correlated with aroma retention. Aroma retention increased with the specific area of starch, from acetylated starch to maltodextrin (Table 1 and Fig. 3). Hau et al. (1998) measured the influence of the surface area of wheat-extruded starch on diacetyl binding using static headspace analysis and observed a marked increase in binding capacity

when the surface area was increased by grinding the extruded sample.

Fig. 5 shows the ratio of the specific retention volume of aroma compounds to the specific area of starchy materials. V_g expresses the retention per gram of the stationary phase, V_g/S the retention per m^2 of stationary phase. A comparison of Figs. 3 and 5 shows that the differences between the starchy materials were attenuated, especially in the case of maltodextrin, which exhibited the highest specific area (Table 1). Two groups could then be distinguished: the group of granular starches (acetylated and native starches) and the group of non-granular starch materials (pregelatinised starches and maltodextrin). Thus, maltodextrin (Fig. 3) exhibited better retention than pregelatinised starches because of its higher specific area.

These results led us to conclude that the specific area of starch plays a major role in aroma retention. Starch is widely used as a flavour carrier and numerous studies have been carried out with the aim of improving the porosity and specific area of starch and hence the adsorption of aroma compounds (Zeller et al., 1999). Thus, microporous materials have been obtained by the gelatinisation of starch and drying with ethanol, producing specific areas of $50\text{ m}^2\text{ g}^{-1}$ (Glenn & Stern, 1999) and $100\text{ m}^2\text{ g}^{-1}$ (Smelik, 1991) and greatly improving aroma retention.

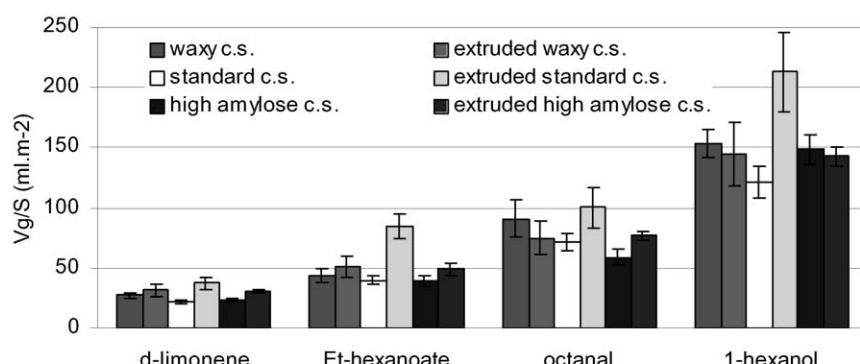


Fig. 7. Aroma retention on native and extruded starches corrected by the specific area of starch; ratio of the specific retention volume (V_g) to the specific area (S). c.s. = corn starch.

Table 2

Physical characteristics of extruded starches and 1-hexanol retention

Extruded corn starches	High amylose	Standard	Waxy
Extrudates density (g cm^{-3})	0.047	0.230	0.177
Volumetric expansion	9.54	1.95	2.47
Specific area ($\text{m}^2 \text{g}^{-1}$)	0.82	0.30	0.20
V_g of 1-hexanol (ml g^{-1})	120	65	30

However, specific area is not the only factor affecting retention. Other parameters may be involved, such as the accessibility of starch macromolecules to flavour compounds. In native starches, starch macromolecules (amylose and amylopectin) are associated in granular entities. When subjected to major treatment, starch granules are disrupted and the amylose and amylopectin chains become more available to aroma compounds. This may explain the higher retention of aroma compounds on non-granular starches than on granular starches.

3.3. Aroma retention on native and extruded starches

3.3.1. Influence of extrusion on aroma retention

The retention of aroma compounds on the three native starches was compared with retention on the three corresponding extruded starches (Fig. 6). For the four aroma compounds, an important decrease in the V_g was observed after extrusion for waxy corn starch ($70\text{--}30 \text{ ml g}^{-1}$ for 1-hexanol), no significant variation was seen with standard corn starch ($50\text{--}65 \text{ ml g}^{-1}$), and a marked increase was seen with high-amylose corn starch ($80\text{--}120 \text{ ml g}^{-1}$). If we focused on extruded starches, we observed that retention increased with the amylose content.

3.3.2. Influence of dimensional parameters and specific area

In order to gain a clearer understanding of retention phenomena, dimensional parameters and the specific area of extruded samples were measured (Table 2) and compared with aroma retention. The volumetric expansion of high-amylose starch melt was five and four times higher than those of standard and waxy starch melt. Chinnaswamy and Hanna (1988) had also observed an increase in volumetric expansion with the amylose content of starch using extrusion parameters close to ours (140°C and 15% water), but these results were closely dependent on the extrusion parameters (Launay, 1994). During the extrusion process, high-amylose samples were expanded more than waxy and standard samples, leading to a lower density. Consequently, the walls between air alveoli were thinner in high-amylose extrudates, leading to thinner fragments after grinding and thus a higher specific area ($0.82 \text{ m}^2 \text{ g}^{-1}$ to 0.30 and $0.20 \text{ m}^2 \text{ g}^{-1}$ for standard and waxy extruded starches). This phenomenon was confirmed by scanning electronic micrographs (Fig. 2(a)–(c)).

If the V_g was corrected by the specific area of the starch (Fig. 7), all starches (native and extruded) exhibited

Table 3

Ratio of the specific retention volume of 1-hexanol (V_g) on starch materials to that on standard corn starch ($V_{g,\text{standard}}$)

Starch material	$V_g/V_{g,\text{standard}}$
Extruded waxy c.s. ^a	0.60
Acetylated c.s.	0.96
Standard c.s.	1.00
Extruded standard c.s.	1.32
Waxy c.s.	1.46
High amylose c.s.	1.60
Extruded high amylose c.s.	2.42
Pregelatinised standard c.s.	2.50
Pregelatinised waxy c.s.	3.60
Maltodextrin	4.70

^a c.s. = corn starch.

approximately the same retention ($V_g/S = 135 \pm 15 \text{ ml m}^{-2}$ for 1-hexanol), except for extruded standard corn starch on which aroma compounds, and especially ethyl hexanoate and 1-hexanol, exhibited greater retention ($V_g = 215 \text{ ml m}^{-2}$ for 1-hexanol).

These results led us to conclude that specific area is the principal factor affecting aroma retention by extruded starches. The specific area of extruded starches is influenced by the macroscopic alveolar structure of extruded starches, which in turn is dependent upon extrusion parameters and the amylose content of native starches.

3.4. Comparison of the 10 starch materials in terms of their ability to retain aroma compounds

Because of substantial retention due to its alcohol functional group, 1-hexanol was chosen to compare starch materials. Starch materials were classified in increasing order (Table 3) in terms of their ability to retain this molecule, taking standard corn starch as reference material. The most efficient materials for flavour retention were firstly maltodextrin, secondly, pregelatinised waxy corn starch, and thirdly pregelatinised standard and extruded high-amylose corn starches.

4. Conclusion

IGC enabled the measurement of aroma retention on different starch materials. Aroma retention increased with the polarity of the flavour molecules and did not follow the amylose content for native starches. This led us to conclude that aroma–starch interactions mainly result from an adsorption phenomenon involving hydrogen bonds and not from inclusion complexes.

Aroma retention measured by IGC showed good correlations with the physical characteristics of starch materials and especially specific area. Aroma retention increased according to the specific area of starch.

Knowledge of the matrix structural factors influencing aroma retention could be of great interest for the food industry.

It would allow the selection of carriers, an improvement in specific carrier properties (specific area, porosity), and the optimisation of conditions for food processing in order to increase flavour retention.

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References

- Aucejo, S., Pozo, M. J., & Gavara, R. (1998). Effect of water presence on the sorption of organic compounds in ethylene–vinyl alcohol copolymers. *Journal of Applied Polymer Science*, 70, 711–716.
- Biliaderis, C. G., Page, C. M., Maurice, T. J., & Juliano, B. O. (1986). Thermal characterization of rice starches: a polymeric approach to phase transitions of granular starch. *Journal of Agricultural and Food Chemistry*, 34, 6–14.
- Boutboul, A., Giampaoli, P., Feigenbaum, A., & Ducruet, V. (2000). Use of inverse gas chromatography with humidity control of the carrier gas to characterize aroma–starch interactions. *Food Chemistry*, 71, 387–392.
- Bruauner, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60, 309–319.
- Buttery, R. G., Glenn, G. M., & Stern, D. J. (1999). Sorption of volatile flavor compounds by microcellular cereal starch. *Journal of Agricultural and Food Chemistry*, 47 (12), 5206–5208.
- Chinnaswamy, R., & Hanna, M. A. (1988). Relationship between amylose content and extrusion-expansion properties of corn starch. *Cereal Chemistry*, 65, 138–143.
- Colonna, P., & Buléon, A. (1994). Transformation structurale de l'amidon. In P. Colonna & G. Dellavalle, *La cuisson-extrusion* (pp. 18–43). Paris: Lavoisier Tec & Doc.
- Delarue, J., & Giampaoli, P. (2000). Study of interaction phenomena between aroma compounds and carbohydrate matrices by inverse gas chromatography. *Journal of Agricultural and Food Chemistry*, 48 (6), 2372–2375.
- Druaux, C., & Voilley, A. (1997). Effect of food composition and microstructure on volatile flavour release. *Trends in Food Science & Technology*, 8, 364–368.
- Gavara, R., Catala, R., & Hernandez-Munoz, P. (1997). Study of aroma scalping through thermosealable polymers used in food packaging by inverse gas chromatography. *Food Additives and Contaminants*, 14 (6 and 7), 609–616.
- Glenn, G. M. & Stern, D. J. (1999). Starch-based microcellular foams. US Patent Serial 5958589.
- Golovnya, R. V., Misharina, T. A., & Terenina, M. B. (1998). GC evaluation of flavour compound sorption from water solutions by corn starch cryotextures obtained by freezing. *Nahrung*, 42 (6), 380–384.
- Goubet, I., Le Queré, J. L., & Voilley, A. J. (1998). Retention of aroma compounds by carbohydrates: influence of their physicochemical characteristics and their physical state. A review. *Journal of Agricultural and Food Chemistry*, 46, 1981–1990.
- Hau, M. Y. M., Gray, D. A., & Taylor, A. J. (1996). Binding of volatiles to starch. In R. J. McGorin & J. V. Leland, *Flavor–food interactions ACS Symposium Series* 633 (pp. 107–117). Washington, DC: American Chemical Society.
- Hau, M. Y. M., Gray, D. A., & Taylor, A. J. (1998). Binding of volatiles to extruded starch at low water contents. *Flavour and Fragrance Journal*, 13, 77–84.
- Karathanos, V. T., & Saravacos, G. D. (1993). Porosity and pore size distribution of starch materials. *Journal of Food Engineering*, 18, 259–280.
- Launay, B. (1994). Expansion des matériaux amylacés en sortie de filière: caractérisation expérimentale et interprétation. In P. Colonna & G. Dellavalle, *La cuisson-extrusion* (pp. 166–199). Paris: Lavoisier Tec & Doc.
- Le Thanh, M., Thibeau-deau, P., Thibault, M. A., & Voilley, A. (1992). Interactions between volatile and non-volatile compounds in the presence of water. *Food Chemistry*, 43, 129–135.
- Maier, H. G. (1972). Bindung fluechtiger aromastoffe an lebensmittel. *Lebensmittel-Wissenschaft-und -Technologie*, 5, 1–6.
- Nuessli, J., Sigg, B., Conde-Petit, B., & Escher, F. (1997). Characterization of amylose-flavour complexes by DSC and X-ray diffraction. *Food Hydrocolloids*, 11, 27–34.
- Roos, Y., & Karel, M. (1991). Phase transitions of mixtures of amorphous polysaccharides and sugars. *Biotechnology Progress*, 7, 49–53.
- Rutschman, M. A., & Solms, J. (1990). Formation of inclusion complexes of starch with different organic compounds. V. Characterization of complexes with amperometric iodine titration, as compared with direct quantitative analysis. *Lebensmittel-Wissenschaft-und -Technologie*, 23, 88–93.
- Smelik, A. (1991). Modification of corn starch. Czechoslovak patent 272-971.
- Taylor, A. J. (1998). Physical chemistry of flavour. *International Journal of Food Science and Technology*, 33, 53–62.
- Tharrault, J.-T. (1992). Contribution à l'étude du comportement des farines de blé tendre en cuisson-extrusion bi-vis. Application à l'appréciation de leur valeur industrielle. Doctorat de l'Université de Paris 11, Paris 7, ENSIA, France.
- Thomas, D. J., & Atwell, W. A. (1999). *Starches*. Saint Paul, Minnesota: Eagan Press.
- Whorton, C. (1995). Factors influencing volatile release from encapsulation matrices. In S. J. Risch & G. A. Reineccius, *Encapsulation and controlled release of food ingredients* (pp. 134–142). Washington DC: American Chemical Society.
- Whorton, C., & Reineccius, G. A. (1995). Evaluation of the mechanisms associated with the release of encapsulated flavor materials from malto-dextrin matrices. In S. J. Risch & G. A. Reineccius, *Encapsulation and controlled release of food ingredients* (pp. 143–160). Washington DC: American Chemical Society.
- Zelevnak, K. J., & Hoseney, R. C. (1987). The glass transition in starch. *Cereal Chemistry*, 64 (2), 121–124.
- Zeller, B. L., Saleeb, F. Z., & Ludescher, R. D. (1999). Trends in development of porous carbohydrate food ingredients for use in flavor encapsulation. *Trends in Food Science & Technology*, 9, 389–394.