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Retention of aroma compounds in food matrices of similar rheological behaviour and different compositions

Anne-Marie Seuvre [a,b,*], Ellen Philippe [a], Sophie Rochard [c], Andrée Voilley [a]

[a] *ENSBANA, Laboratoire d'Ingénierie Moléculaire et Sensorielle des Aliments et des Produits de Santé, 1 Esplanade Erasme, F21000 Dijon, France*
[b] *IUT, Département Génie Biologique, Bd Dr. Petitjean, B.P. 17867, F21078 Dijon Cedex, France*
[c] *Degussa Flavour and Fruit Systems, Z.I. du Plan, B.P. 82067, F06131 Grasse Cedex, France*

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Abstract

Two matrices with a similar rheological behaviour but with a different composition have been developed: one containing carbohydrates (D-glucose, pectin and starch) and in the second one, called complex matrix, a lipid (triolein) was added. The release of six aroma compounds is quantified by using the measurements of partition coefficients at thermodynamic equilibrium. The role of lipid (triolein) on the retention of all the aroma compounds was pointed out. The effect of carbohydrates was more complex: in comparison with water, ethyl hexanoate and *trans*-2-hexenal were more retained whereas diacetyl, 2-pentanone and *cis*-3-hexenol were "repulsed" from the matrix. The kinetic study of the release from these matrices had shown a decrease of the initial rate of release by reference with water. From carbohydrates matrix, the decrease of the release for three compounds (ethyl acetate, ethyl hexanoate, 2-pentanone) seemed to arise from the variation of diffusion and/or retention by carbohydrates. For the three other aroma compounds (diacetyl, *cis*-3-hexenol and *trans*-2-hexenal) no variation of the initial rate was registered. The comparison of the release rates from carbohydrate and complex matrices indicated the role of lipids and the comparison of the release rates from water and complex matrix showed the combined effects of texture and lipids. The decrease of initial release rate was more important in presence of lipids than in presence of carbohydrates. The most important decrease was observed with the most hydrophobic compound.

Keywords: Retention; Release; Aroma compounds; Carbohydrate matrix; Lipid; Partition coefficient; Kinetic

1. Introduction

Foods are complex products containing volatile and non-volatile compounds with different structures. During the processes of fabrication the aroma compounds naturally present could be eliminated or modified, or new compounds could appear. To keep the natural note, aroma compounds may be introduced during or at the end of the fabrication process. The aroma of a food depends on the equilibrium between the different volatile compounds and their concentrations. The aroma also depends on the composition of the food matrix (Kinsella, 1989).

The chemical nature of the aroma compounds, the composition and the structure of the foods are the principal characteristics that influence the transfer of aroma compounds within the food and their release. Generally foods matrices are multiphasic, containing liquid (aqueous or lipidic), solid and vapour phases. The distribution of an aroma compound within a food depends on its affinity for these different phases and its ability to release in the vapour phase. The nature of the different non-volatile constituents such as proteins, lipids, carbohydrates, and salts have a great impact on the retention of the aroma compounds by the food matrices (Bakker,

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[*] Corresponding author. Tel.: +33 3 8039 6843; fax: +33 3 8039 6611. *E-mail address:* amseuvre@u-bourgogne.fr (A.-M. Seuvre).

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1995; de Roos, 1997; Fischer & Widder, 1997; Godshall, 1997; Guichard, 2002; Lubbers, Landy, & Voilley, 1998; van Ruth, King, & Giannouli, 2002).

Physicochemical interactions could take place between aroma compounds and food constituents. These interactions could modify the repartition of these aroma compounds inside the food. The retention and/or the release of the aroma compounds were influenced and thus their sensorial perception.

These last years, numerous low fat or sugar lightened foods have arisen and have required a new formulation. However, variation of the food composition leads to modifications of the structure and of physicochemical interactions established between volatile and non-volatile compounds.

Model food matrices have been prepared to understand these modifications. The aim was to separate the influence of the texture from that of the interactions. In this objective the two studied matrices had the same rheological behaviour but a different composition: one was called carbohydrate matrix containing principally carbohydrates and in the second one, named complex matrix, where lipids are added to carbohydrates.

2. Material and methods

2.1. Preparation of matrices

Mineral water in glass bottle (Volric, Danone, France) was used throughout the study.

2.1.1. Carbohydrate matrix

A mixture containing modified waxy corn starch (2.4%, w/w; National Starch & Chemical, Villefranche, France), pectin (LM, DE = 30.5: 0.4%, w/w, and HM, DE = 70.8: 0.9%, w/w, Degussa Texturant Systems, Baupte, France) and D-glucose (1.8%, w/w) was elaborated by Degussa Texturant Systems (Baupte, France). Citric acid (0.15%, w/w, Prolabo, Paris, France), trisodium citrate (0.05%, w/w, Prolabo, Paris, France) and tricalcium citrate (0.03%, w/w, Sigma–Aldrich Chemie GmbH, Steinheim, Germany) were dissolved in mineral water under constant agitation with a magnetic stirrer; then the mixture of carbohydrates was added. The matrix was heated and boiled for 5 min then cooled to a temperature of 35 °C. The rate of evaporation was controlled and a solution of potassium sorbate (0.05%, w/w, Degussa Texturant Systems, Baupte, France) in mineral water was used to adjust the concentrations. This matrix was developed to have the same rheological behaviour as stirred yoghurt.

2.1.2. Complex matrix

The complex matrix containing lipids and carbohydrates was prepared as for the carbohydrate matrix. The amount of water was replaced by a similar quantity of the 3.5% oil-in-water emulsion (described below). The carbohydrate concentration was the same as in the carbohydrate matrix (5.5%, w/w) and the lipid (triolein) concentration was 3.5%, w/w. The tricalcium citrate, which gives the carbohydrate matrix the desired behaviour, was not added to the complex matrix. The presence of triolein compensated for the rheological impact of this salt in the complex matrix.

Oil-in-emulsion was prepared in batches of 100 mL by homogenizing liquid triolein (3.5%, w/w) in water containing soybean lecithin (0.4%, w/w) as emulsifier (Emulpur N, Lucas Meyer GmbH, Hamburg, Germany) using an Ultra Turrax T25 homogenizer (Janke & Kunkel, IKA, Laborteknik, Staufen, Germany) at a rate of 24,000 rpm, for 20 min.

Triolein [1,2,3-Tris(*cis*-9-ostadecenoyl)glycerol; 65% purity] was purchased from Sigma–Aldrich Chemie (Steinheim, Germany) and purified by percolation through a column packed with magnesium silicate ($MgO:SiO_2 \approx 15:85$) of particle size 0.150–0.250 mm (60–10 mesh ASTM) (Floril, Merck, Darmstadt, Germany). The purified triolein was stored at 4 °C.

2.2. Characterization of the matrices

2.2.1. Emulsion characterization

To verify the stability of the emulsion viscosity and particle size distribution were determined.

Viscosity was measured using a rotational viscometer Rheomat 30 (Contraves, Zurich) equipped with MSO co-axial cylinders and a Rheoscan 20 programmer. The measurements were performed at 37.0 ± 0.5 °C.

Particle size distribution was determined at ambient temperature using a Malvern Mastersizer laser diffractometer (Hydro 2000 G, Malvern Instruments, Orsay, France), both before and after headspace measurements to verify the stability of the emulsion.

2.2.2. Carbohydrate and complex matrices characterization

Rheological behaviour was measured before and after headspace measurements using a dynamic stress rheometer (SR 5000, Rheometric Scientific Inc., Piscataway, USA) equipped with cone-and-plate geometry cone (acrylic, 40 mm diameter, nominal cone angle 0.04 rad., nominal gap 0.0508 mm) heated at 37 °C by a Peltier system. A humidity cover trap was used to avoid the evaporation of water during the measurements. A shear stress sweep ranging from 1 to 160 Pa was applied and the corresponding shear rate was measured. The flow curves giving shear stress σ (Pa) as a function of shear rate $\dot{\gamma}$ (s^{-1}) are characteristics of a shear-thinning behaviour. The power law equation $\sigma = K \cdot \dot{\gamma}^n$ allows the calculation of the consistency index K and the flow behaviour index n (Software RSI

Orchestrator, v 6.3.2., Rheometric Scientific, Copyright © 1997).

2.3. Flavour compounds

Six flavour compounds belonging to the strawberry flavour note (Zabetakis & Holden, 1997) or to cream note and with different physicochemical properties were chosen: two ethyl esters (C_4 and C_8), two ketones, an alcohol and an aldehyde. Degussa Flavours & Fruits Systems (Maxens, Grasse, France) supplied them. Their purities were higher than 98%. Their chemical formula, molecular weights, densities, boiling points and odour descriptors are presented in Table 1.

2.4. Determination of flavour compound characteristics

Physicochemical characteristics of flavour compounds were measured or estimated.

2.4.1. Hydrophobicity

The $\log P$ value describes the partitioning of an organic compound between *n*-octanol and water. The $\log P$ hydrophobicity constants were estimated using a group contribution method (Hansch & Leo, 1979). These values are the sum of the hydrophobic contributions of each functional group of the molecule.

2.4.2. Water solubility

The solubility limit was measured using the mutual solubility method (Subrahmanyam, Rari Prakash, & Gundu Rao, 1996). In sealed flasks, an excess of pure flavour compound was added to the water and allowed to equilibrate by gently stirring at 37.0 ± 0.5 °C. After 24 h, the mixture was centrifuged for 20 min at 4000 rpm. Each system was repeated in triplicate. Analysis of the aqueous phase was carried out using a gas chromatograph CP3800 series (Varian Analytical Instruments, Walnut Creek, USA) fitted with an FID. The chromatograph was equipped with an automatic CombiPal injection system and a 1.5-m stainless column (2.2 mm internal diameter) packed with Chromosorb W-AW 100–200 mesh with stationary phase of Carbowax 20M-10%. The operating conditions were as follows: nitrogen carrier flow rate 25 mL/min; hydrogen flow rate 33 mL/min; air flow rate 330 mL/min; injector temperature 190 °C; FID detector temperature 200 °C; isothermal oven temperature 90 or 100 °C according to flavour compound. The chromatograms were registered and the data treated using the Star Chromatography Workstation software (v5.31, Varian Associates Inc., Copyright © 1989–1998). The flavour compound concentrations in water ($\mathrm{g\,L^{-1}}$) were determined using a standard calibration curve.

2.4.3. Saturated vapour pressure

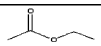
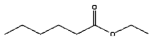
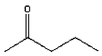
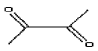
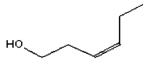
The saturated vapour pressure, P_i^S (Pa) represents the volatility of the pure compound at a given temperature. The saturated vapour pressure values were calculated using the software, MP.BPWIN (v1.27, SRC, Copyright ©, 1994–1997). Results were the mean values obtained by two methods using the boiling point: the Antoine method and the modified Grain method. This software gives accurate values for esters and ketones (Philippe, Seuvre, & Voilley, 2001).

2.5. Measurements of flavour partioning

2.5.1. Headspace analysis

Flasks (20 mL) and aromatized matrices were pre-equilibrated at 37 °C. The aromatized matrices (10 mL) were placed in the flasks closed with a cap fitted with a Teflon-coated seal. These were placed in an incubator at 37.0 ± 0.5 °C. Preliminary experiments of headspace analysis at different equilibrium times were used to ensure that the analysis for each sample was performed

Table 1
Flavour compounds and their molecular weights (M_w), densities (d), boiling points (bp), odour descriptors

	Chemical formula	Molecular formula	M_w ($\mathrm{g\,mol^{-1}}$)	Density (25 °C)	Bp (°C)	Odour descriptor[a]
Ethyl acetate (1)	$C_4H_8O_2$		88	0.91	75	Ethereal-fruity
Ethyl hexanoate (1)	$C_8H_{16}O_2$		144	0.89	168	Fruity, banana, pineapple
2-Pentanone (2) (pentan-2-one)	$C_5H_{10}O$		86	0.82	102	Wine, acetone-like
Diacetyl (2)	$C_4H_6O_2$		86	0.92	87	Butter, fat
cis-3-Hexenol (1) (hex-3-en-1-ol)	$C_6H_{12}O$		100	0.79	156	Grass, green
trans-2-Hexenal (1) (*trans*-hex-2-en-al)	$C_6H_{10}O$		98	0.78	43 at 1600 Pa	Green, leafy odour

(1) Strawberry flavour note.
(2) Cream flavour note.
[a] Furia and Bellanca (1975).

at equilibrium. A time of 48 h was sufficient to reach equilibrium for each matrix and flavour compound. To verify that no flavour compounds were formed during the incubation time, blank sample (non-aromatized) of carbohydrate and complex matrices were incubated and analysed. For each flask, 1 mL of the vapour phase above the matrix was removed from the headspace with a thermostated gas syringe and injected into an FID gas chromatograph CP3800 series using the same conditions of analysis as described previously. The same batch of matrices was used throughout an experiment. Each experiment was carried out at least three times using three different batches of matrix. The mass partition coefficient between gaseous phase and matrix was calculated $K_{\text{mass}} = C_g/C_m$, where C_g and C_m are, respectively, the flavour mass fractions (w/w) in the gas and in the matrix phase. The measurements were made at infinite dilution where the partition coefficients are not influenced by the flavour compound concentration (50 ppm, w/w).

2.6. Statistical analysis

The statistical analysis was carried out using the Statistical Analysis System software (Procedure GML, SAS Institute Inc., Cary, NC). A one-way analysis of variance followed by comparison of means by Student–Newman–Keuls test was applied to determine significant differences between the media headspace concentration. The significant level was $P < 0.05$ throughout the study.

3. Results and discussion

3.1. Characteristics of the matrices

The rheological behaviour target was that of a stirred yoghurt. These foods contain 3.5% fat (w/w) and in low fat yoghurt, fat is replaced with polysaccharides such as pectines to provide the same texture.

The carbohydrate and complex matrices were prepared in order to have two matrices with a similar rheological behaviour, close to that of stirred yoghurt, but with a different composition (with or without lipids). Physicochemical characteristics are given in Table 2. Both matrices presented a strong shear-thinning behaviour and similar consistency (K) and flow behaviour (n) indices. The apparent viscosities $\eta\ (\dot{\gamma} = 100\ \text{s}^{-1})$ at 37 °C were 0.17, 0.09 and 0.12 Pa s for the stirred yoghurt, the carbohydrate and the complex matrices, respectively, and the behaviour index n at 37 °C of yoghurt was 0.42.

3.2. Characteristics of the flavour compounds

The six flavour compounds differed in their physicochemical characteristics such as saturated vapour pressure, n-octanol–water partition coefficients ($\log P$), water solubility (Table 3).

3.2.1. Saturated vapour pressure

Whereas molar volume values were in the same order, saturated vapour pressure values (P_i^S) showed a large

Table 2
Physicochemical characteristics of carbohydrate and complex matrices

Matrix	Consistency index, K ($\dot{\gamma} = 1\ \text{s}^{-1}$) (Pa s^n; 37 °C)	Flow behaviour index, n (37 °C)	Dry matter[a] (%)	A_w (25 °C)	pH (25 °C)	Density[b] (g mL^{-1}) (25 °C)
Carbohydrate	0.81	0.59	5.3	0.990	3.53	1.204
Complex	0.87	0.51	8.9	0.976	3.50	1.039

[a] After 24 h in an oven at 102 °C.
[b] Measured by picnometry.

Table 3
Physicochemical characteristics of flavour compounds

	Molar volume[a] (cm^3 mol^{-1})	$\log P$[b] octanol/water (25 °C)	Saturated pressure vapour,[c] P_i^S (Pa; 37 °C)	Water solubility[d] (g L^{-1}; 37 °C)
Ethyl acetate	107	0.7	24,527	67.1
Ethyl hexanoate	196	2.8	500	0.5
2-Pentanone	121	0.8	9464	48.1
Diacetyl	101	−1.5	16,129	400.9
cis-3-Hexenol	129	1.3	317	14.7
trans-2-Hexenal	128	1.7	1866	16.5

[a, b] Estimated data.
[a] Reid et al. (1987).
[b] Hansch and Leo (1979).
[c] Estimated data, software MPBP.WIN, 1994–1997.
[d] Experimental data.

distribution. This value represents the ability of an aroma compound to pass from liquid to gaseous state. For compounds with similar molecular weight, the value of saturated vapour pressure could be different: ethyl acetate (M_w: 88 g mol^{-1}) and 2-pentanone (M_w: 86 g mol^{-1}) presented P_i^S values of 24,527 and 9464 Pa, respectively. Same kinds of observations were obtained by comparison of *cis*-3-hexenol (M_w: 100 g mol^{-1}) and *trans*-2-hexenal (M_w: 98 g mol^{-1}) with P_i^S values of 317 and 1866 Pa, respectively. The saturated vapour pressure did not depend on the molecular weight of a compound, but rather on the chemical functions (Philippe et al., 2001). Whereas P_i^S represents the volatility of a compound on the pure state, hydrophobicity and solubility in water indicate the partition of the compound in the aqueous and organic solvent phases.

3.2.2. Water solubility

The solubility influences the phenomenon of vapour–matrix and liquid–liquid partition. The most polar compound, diacetyl, is the most soluble compound in water. This diketone is able to establish interactions with water molecules such as H-bonding or van der Waals interactions. In the case of ethyl hexanoate, presenting the weakest value of water solubility, this kind of interactions will be difficult to establish, even in the presence of an ester function.

3.2.3. hydrophobicity

A positive log P value indicates the lipophilic character of the compound; only diacetyl presented a negative value, that showed its hydrophilic character. This compound presented the value of the highest water solubility.

3.3. Flavour partitioning at equilibrium

To study the interactions between aroma compounds and the matrices, Volvic mineral water was chosen as the reference system. A significant variation of the value of vapour–matrix partition coefficient indicates the presence of interactions between aroma compounds and non-volatile substances, characterized by a retention percentage R:

$$R = \frac{K_{\text{mass}}^{\text{water}} - K_{\text{mass}}^{\text{matrix}}}{K_{\text{mass}}^{\text{matrix}}} \times 100(\%),$$

where $K_{\text{mass}}^{\text{water}}$ are the vapour–water partition coefficients and $K_{\text{mass}}^{\text{matrix}}$ are the vapour–matrix partition coefficients.

A positive percentage value indicates an aroma compound retained by the matrix and a negative value a compound released by the matrix. The partition coefficients (K_{mass}) of flavour compounds between gaseous phase and matrices are presented in Fig. 1 as well as the retention percentages.

The aroma compounds did not present the same behaviour. Ethyl hexanoate was the least retained whereas *cis*-3-hexenol was the best retained compound. Ketones (2-pentanone and diacetyl) presented a comparable profile: a negative value of the retention percentage for the polysaccharidic matrix, indicating a flavour release, and positive value for the complex matrix, indicating that these flavour compounds are retained. The alcohol (*cis*-3-hexenol) showed a strong percentage of release (37%) from the carbohydrate matrix whereas no effect of the complex matrix was notable. Ethyl hexanoate (ester) and *trans*-2-hexenal (aldehyde) did not follow the profiles previously described: for both

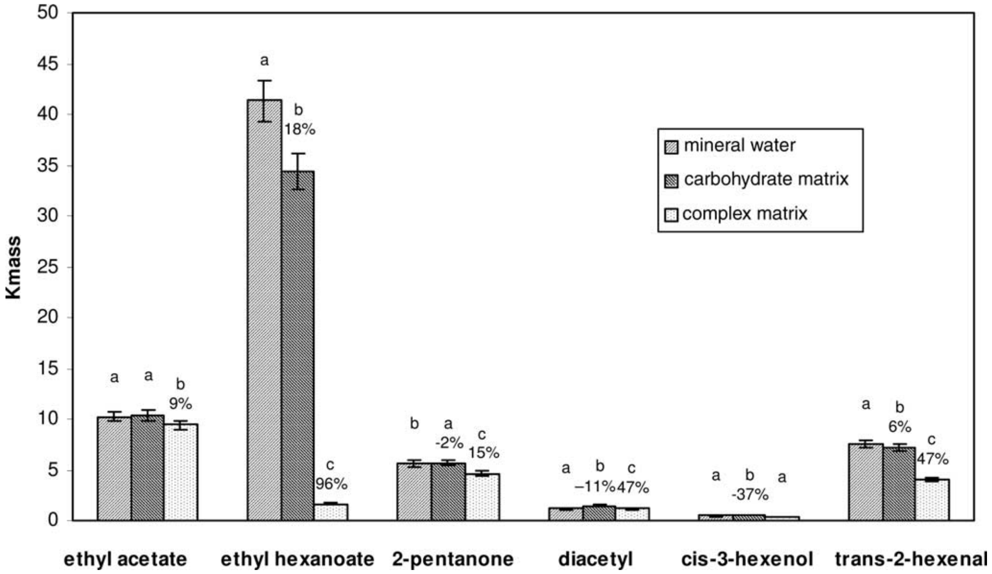


Fig. 1. Partition coefficient (K_{mass}) of flavour compounds between gaseous phase and matrices. a, b, c: Different letters mean that the results are significant at $P < 0.05$. %: A positive percentage value indicates a flavour compound retained by the matrix; a negative value indicates a flavour compound released by the matrix.

Table 4
Ratio of partition coefficients, K_{mass}, for flavour compounds in the different matrices at 37 °C, pH 7

K_{mass} matrix/K_{mass} matrix	Water/ Carbohydrate	Water/ Complex	Carbohydrate/ Complex
Ethyl acetate	NS	1.1	1.1
Ethyl hexanoate	1.2	25.1	20.5
2-Pentanone	0.9	1.2	1.2
Diacetyl	0.9[a]	1.1[a]	1.3[a]
cis-3-Hexenol	0.7[a]	NS[a]	1.3[a]
trans-2-Hexenal	1.1	1.9	1.8

NS: results are not significantly different at $P < 0.05$.

[a] For diacetyl and *cis*-2-hexenol the ratio was calculated from water at pH 3.52.

matrices (polysaccharidic and complex) the aroma compounds were retained but with a higher retention in complex matrix which contained lipids. These differences of behaviour could be explained by the differences of polarity and the chemical functions of the molecules. For ethyl acetate, only the effect of retention by the complex matrix was observed, arising from its affinity for lipids while for the other ester (ethyl hexanoate) both effects, carbohydrates and lipids, were observed.

In order to check on the influence of the composition of the matrices and that of the rheological behaviour on the release an/or the retention of aroma compounds, the two matrices have been developed having the same rheological behaviour. The effect of the different components could be pointed out by calculating the ratio between two partition coefficients (Table 4), in particular the effect of lipids and carbohydrates and their combination. The ratio between water K_{mass} and carbohydrate matrix K_{mass} shows the effect of carbohydrates; the ratio between water K_{mass} and complex matrix K_{mass} indicates both the carbohydrate and lipid effects; the ratio between carbohydrate matrix K_{mass} and complex matrix K_{mass} underlines the role of the lipids. When the ratio value is >1, a significant component effect on flavour retention is pointed out.

3.3.1. Carbohydrate effect

For all aroma compounds the ratio water K_{mass}/carbohydrate matrix K_{mass} presented a value near 1, but with opposite variation around this value. For ethyl hexanoate and *trans*-2-hexenal a higher retention is observed. The glucidic components of the matrix have a weak though significant effect. The retention of aroma compounds by polyosides is a phenomenon observed before (Godshall, 1997; Goubet, Le Quéré, & Voilley, 1998; Guichard, 2002). The decrease was attributed to the establishment of interactions (or possible complexation) between starch and aroma compounds (Escher, Nuessli, & Conde-Petit, 2000; Godet, Colonna, & Buleon, 1995; Rutschmann & Solms, 1990). Pectins also play a role on the retention with their thickening and gelling power (Guichard, Issanchou, Descourrieres, & Etiévant, 1991; Hansson, Andersson, & Leufvén, 2001).

The opposite release effect is observed for 2-pentanone, *cis*-3-hexenol and diacetyl. This phenomenon was observed in aqueous media containing small sugars, such as sucrose, with relatively polar aroma compounds (Le Thanh, Thibeaudeau, Thibaut, & Voilley, 1992; Nahon, Navarro y Koren, Roozen, & Posthymus, 1998; Perpète & Collin, 2000; Roberts, Elmore, Langley, & Bakker, 1996; Voilley, Simatos, & Loncin, 1977). This behaviour could arise from small sugars (D-glucose) contained in the carbohydrate matrix.

3.3.2. Lipids effect

The complex matrix contains triolein (3.5%, w/w) and soybean lecithin (0.4%, w/w) as emulsifier. All the ratios water K_{mass}/complex matrix K_{mass} and carbohydrate matrix K_{mass}/complex matrix K_{mass} were higher than 1 (except the ratio water K_{mass}/complex matrix K_{mass} where the values are not significantly different). The first ratio showed the effect of both carbohydrates and lipids and the second ratio the effect of lipids. Lipids (triolein and lecithin) were implicated in the retention: the ratios increased with the hydrophobicity, particularly with ethyl hexanoate; this effect of retention was observed before (de Roos, 1997; Piraprez, Hérent, & Collin, 1997). Triolein with its three fatty acid chains could establish interactions with hydrophobic compounds. Lecithin with its two fatty acid chains could also retain aroma compounds, but to a lesser degree.

3.4. Release kinetics of the aroma compounds

To study the release of the aroma compounds from the matrices, measurements have been realized on non-agitated matrices during time. Then the release is only the result of diffusion phenomenon through the matrices and of the transfer of the aroma compounds towards the vapour phase and of diffusion in the vapour phase.

The matrices are aromatized with 50 ppm (v/m) and 10 mL was immediately placed in sealed flasks. To study the influence of the nature of the aroma compound and the influence of the matrices on the kinetic of release, the K_{mass} kinetic curves were drawn (Fig. 2). On each curve a minimum of 14 experimental time values were realized. Only one measurement of the vapour phase was done on a same flask. Each point was done in triplicate. These measurements are realized in the three media (water, carbohydrate matrix and complex matrix). From water, the most hydrophobic ($\log P = 2.8$) aroma compound, ethyl hexanoate, presented the highest released quantity. Followed in the order of decreasing released quantity ethyl acetate ($\log P = 0.7$), *trans*-2-hexenal ($\log P = 1.7$) and 2-pentanone ($\log P = 0.8$). Diacetyl and *cis*-3-hexenol were the compounds the less released: diacetyl because of its log $P = -1.5$; *cis*-3-hexenol with a

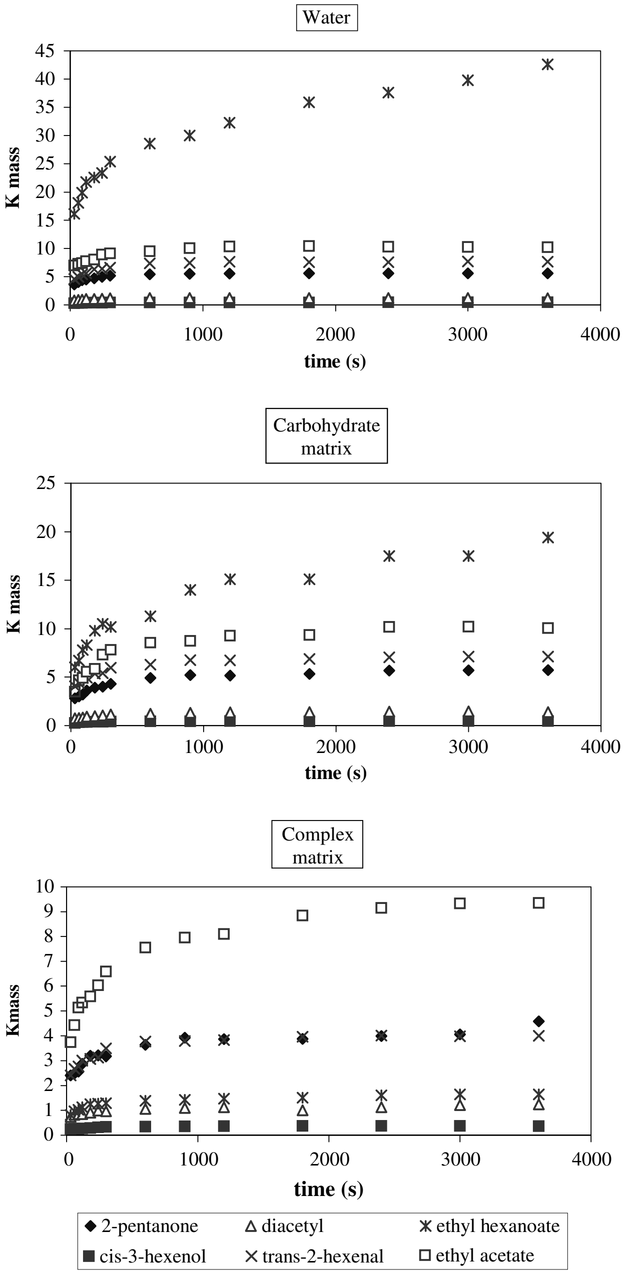


Fig. 2. Release of aroma compounds from water, carbohydrate matrix and complex matrix.

log $P = 1.3$ differed from the behaviour of *trans*-2-hexenal (log $P = 1.7$). The same order of quantities of released aroma compounds from the carbohydrate matrix was observed. The order of released quantities differed with the complex matrix where lipids intervened.

In Fig. 3 the release of the two esters from the three matrices was drawn. The behaviour of these two compounds belonging to the same chemical family differed strongly. For ethyl hexanoate, the effect of the carbohydrates was observed during the whole kinetic curve with a significant decrease of released aroma (2 times). For ethyl acetate, a smaller compound (Table 1), the effect of retention of the carbohydrate matrix is notable only in the first part of the curve. The carbohydrate matrix K_{mass} at equilibrium did not differ from that in water. For the two compounds the effect of the complex matrix (containing lipids) was significant but with a greater retention for ethyl hexanoate.

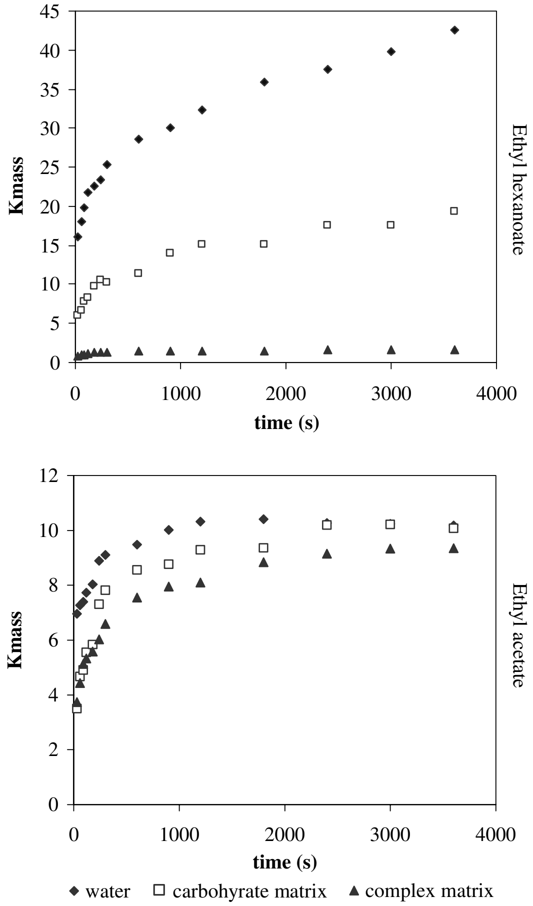


Fig. 3. Release of esters (ethyl acetate and ethyl hexanoate) from water, carbohydrate matrix and complex matrix.

The kinetic curves of release of two ketones from the three matrices were drawn in Fig. 4. In the case of 2-pentanone, the curves of release from water and from carbohydrate matrix could not be superposed: the release from water was more important in the first part of the curves until they intersected (at 35 min) before to reach their equilibrium where release from carbohydrate matrix was higher than that of water. This behaviour of repulsion was more marked in the case of diacetyl (a diketone) where the cross of the kinetic curves appeared in the first 5 min. The higher release from carbohydrate matrix compared to that from water could be explained by the repulsion effect of small saccharides which can compete with aroma in their interactions with water. The behaviour of these two ketones towards lipids also differed. The effect of retention of 2-pentanone by the

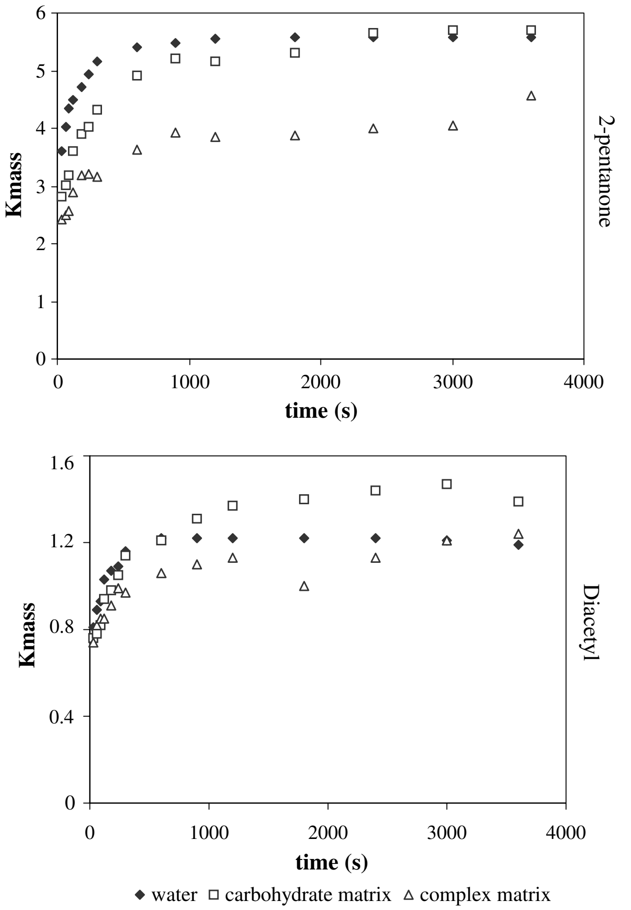


Fig. 4. Release of ketones (2-pentanone, diacetyl) from water, carbohydrate matrix and complex matrix.

complex matrix compared to the two other curves (in water and in carbohydrate matrix) was observed along the kinetic curves. The behaviour of diacetyl is more complex to explain. The release curves from water and from the complex matrix are nearer than that from carbohydrate matrix. Diacetyl has a great affinity for water (high water solubility: 400.9 g L^{-1}) and a weak log P (=−1.5). The effect of lipids on this compound was not strongly marked.

Fig. 5 presents the release of an aldehyde and an alcohol. For *trans*-2-hexenal, the effect of retention of carbohydrates was appreciable and that of lipids clearly observable with a decrease of 2 times of K_{mass} at equilibrium. In the case of alcohol, the effects of carbohydrates and lipids were opposite: carbohydrates increased the release and lipids retained the compounds compared to the behaviour in water.

To evaluate the influence of the nature of the aroma compounds on the release kinetic, the apparent initial rates (min^{-1}) were presented in Table 5. The apparent initial rate was calculated by the mean value of the K_{mass} in the matrices at time 0.5 min (Fig. 2). The value was the mean of a minimum of three measurements.

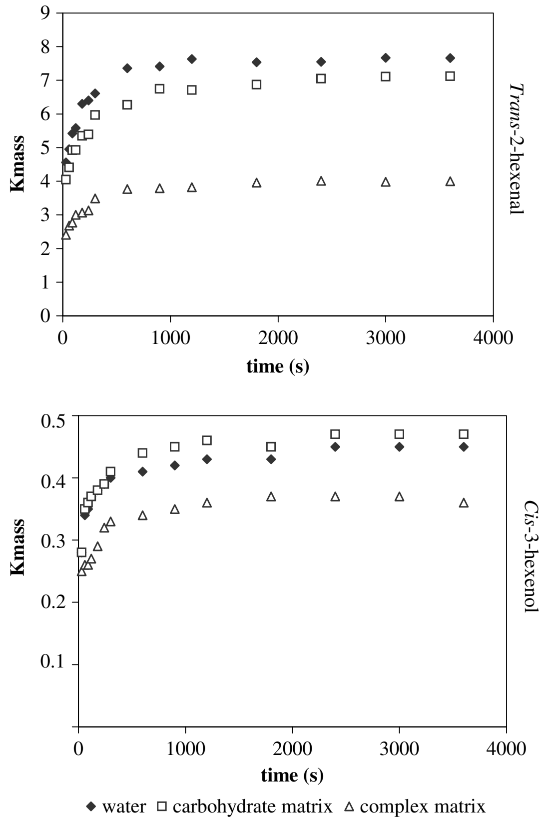


Fig. 5. Release of aldehyde (*trans*-2-hexenal) and alcohol (*cis*-3-hexenol) from water, carbohydrate matrix and complex matrix.

Table 5
Apparent initial rate (r_i^{app}) of release of the aroma compounds from the matrices (min^{-1})

r_i^{app}	Water	Carbohydrate matrix	Complex matrix
Ethyl acetate	13.9 ± 0.3 a	7.5 ± 0.3 b	7.0 ± 0.2 b
Ethyl hexanoate	32.2 ± 2.7 a	12.0 ± 0.2 b	1.62 ± 0.06 c
2-Pentanone	7.2 ± 0.3 a	5.6 ± 0.4 b	4.8 ± 0.1 c
Diacetyl	1.62 ± 0.04 a	1.52 ± 0.23 a	1.4 ± 0.4 a
cis-3-Hexenol	0.56 ± 0.05 a	0.56 ± 0.01 a	0.50 ± 0.02 b
trans-2-Hexenal	9.1 ± 0.4 a	8.1 ± 0.7 a	4.8 ± 0.9 b

The Student–Newman–Keuls statistical test was applied.
a, b, c: Different letters means that the results are significant at $P < 0.05$ for the considered aroma compound.

In water, *cis*-3-hexenol and diacetyl presented the slower release rates while ethyl hexanoate was the faster. The release rate followed the order: *cis*-3-hexenol< diacetyl $\ll$ 2-pentanone < *trans*-2-hexenal $\ll$ ethyl acetate $\ll$ ethyl hexanoate. The more hydrophilic compounds such as diacetyl or those that establish interactions with the water molecules (which due to be broken to permit the release in vapour phase) showed the lower release rate. For the hydrophobic compounds, such as ethyl hexanoate, the repulsion by the water molecules is immediate, that explains the high initial rate but the release is progressive and a long time is needed to reach equilibrium (Fig. 3, more than 1 h).

From the carbohydrate matrix, the release rates followed an order similar to that of water (except for ethyl acetate): *cis*-3-hexenol < diacetyl $\ll$ 2-pentanone < ethyl acetate < *trans*-2-hexenal $\ll$ ethyl hexanoate. By comparison with water the values had decreased and were statistically different for ethyl acetate, ethyl hexanoate and 2-pentanone. Rate release of ethyl hexanoate decreased more than 60%, ethyl acetate around 50% and 2-pentanone around 20%. Above a matrix, the first aroma compounds to be vapourized are those present at the interface matrix–vapour; when these compounds are in the vapour phase they are renewed at the interface and that is diffusion in the matrix which governs this renewal. These slower rates could be due to a decrease of diffusion of the aroma inside the carbohydrate matrix and to a retention effect.

From the complex matrix, the release rates did not follow the orders previously described. However, the lower rate remained for *cis*-3-hexenol. The order was as follows: *cis*-3-hexenol < diacetyl < ethyl hexanoate < *trans*-2-hexenal < 2-pentanone < ethyl acetate. Similar as in the carbohydrate matrix, diffusion partially participated to the decrease of the release rates. However, these two matrices were elaborated to have the same rheological behaviour. The observed differences could not been explained only by diffusion.

To observe the effect of the matrix on the release kinetic, the ratio of the apparent initial rates in two matrices were calculated (Table 6). A ratio upper 1 indicates an effect of the matrix on the decrease of the initial apparent rate. The ratios calculated with water cumulated the effect of diffusion and that of the affinity of the compound for the considered matrix. The different compounds presented a variety of behaviours.

The release rate of diacetyl did not seem to be affected by any matrix. The different ratios did not show a significant variation whatever the matrix, that indicated that the initial rate release was the same in the three matrices. Diacetyl was one of the studied compounds with the smaller molecular weight and the smaller molar volume. The diffusion of this compound through the meshes of the carbohydrate net was relatively easy. Then the affinity for the carbohydrate matrix did not differ from that of water. This compound presents a $\log P$ and a water solubility values which show its hydrophilic behaviour. This fact was supported by the ratios of the rates carbohydrate matrix/complex matrix and water/complex matrix, which would be modified if a lipid effect existed.

For ethyl acetate, the rate ratio water/carbohydrate matrix pointed out the influence of the carbohydrate; on the other hand, lipids did not seem to affect its initial behaviour since the rate ratio carbohydrate matrix/complex matrix showed no significant variation. The ratio water/complex ratio was explained by the effect of carbohydrates and certainly by the difference of diffusion in water compared to that in the matrix.

For 2-pentanone, the different ratios showed the effects of both carbohydrates and lipids; the initial rate ratio water/carbohydrate matrix was higher than 1 (1.3), and that of the ratio carbohydrate matrix/complex matrix varied in the same way (1.2); the ratio water/complex matrix showed the cumulate effects (1.5); however, the diffusion is also to take into account.

The behaviour of ethyl hexanoate was governed by same kind of considerations but in a larger extend: for this compound the release rate decreased 2.7 times in presence of carbohydrates; in presence of lipids, the rate decrease was more than 7 times and in the presence of both carbohydrates and lipids the rate decrease reached around 20 times. This behaviour is surprising because its affinity for lipids was known ($\log P = 2.8$), but that of carbohydrates was not well known; with these results the respective quantification of both influences was realized. However, the release of aroma compounds was not only governed by the interactions with the solutes but also by the diffusion in the matrices without forgetting the difference of diffusion in water compared to that in matrices.

For the two last studied compounds, *cis*-3-hexenol and *trans*-2-hexenal, the behaviours seemed to be comparable: no effect of carbohydrates and in presence of lipids a decrease of the release rates was induced with

Table 6
Ratio of apparent initial rates in different matrices

$r_i^{\mathrm{app}}/r_i^{\mathrm{app}}$	Water/Carbohydrate matrix	Carbohydrate matrix/Complex matrix	Water/Complex matrix
Ethyl acetate	1.9	NS	2.0
Ethyl hexanoate	2.7	7.4	19.9
2-Pentanone	1.3	1.2	1.5
Diacetyl[*]	NS	NS	NS
cis-3-Hexenol[*]	NS	1.1	1.1
trans-2-Hexenal	NS	1.7	1.9

The Student–Newman–Keuls statistical test was applied on a same matrix for all the compounds. NS: values are not significantly different at $P < 0.05$.

[*] Measurements were realized in water at pH 7.00. For the other compounds pH water was 3.52 as the pH of the carbohydrate and complex matrices.

a more marked effect of lipids in the case of *trans*-2-hexenal. The diffusion in water and in the two matrices seemed similar because no variation was noticed in the initial release rate from carbohydrate matrix and the two matrices have the same rheological behaviour.

4. Conclusion

The comparison of the release of aroma compounds with different physico-chemical characteristics from two matrices having the same rheological behaviour had shown the effect of carbohydrates and lipids separately and both combined by reference to water. The retention of aroma by the two matrices has been studied by thermodynamical and kinetic approaches. At equilibrium the comparison of the ratio between water K_{mass} and carbohydrates K_{mass} has shown the effect of carbohydrates: for ethyl hexanoate and *trans*-2-hexenal a higher retention is noticed; an opposite effect, a higher release, is observed for 2-pentanone, *cis*-3-hexenol and diacetyl and no variation is registered for ethyl acetate. The comparison of carbohydrates K_{mass} and complex K_{mass} pointed out the effect of lipids for all studied compounds. The kinetic study was conducted by comparison of the release kinetics in different matrices. The comparison of the release from water and from carbohydrate matrix pointed out that if a decrease of release existed, it arose from a variation of diffusion in the matrix (in relation to the difference of viscosity) and/or to the retention by carbohydrates. The comparison of the release kinetics from carbohydrate matrix and complex matrix pointed out only the retention by lipids because the two matrices had the same rheological behaviour. The comparison of release kinetics from water and complex matrix showed the variation of diffusion and the retention of lipids. The studied aroma compounds had their own behaviour towards these matrices. The initial release rate of diacetyl was not affected whatever the matrix. Ethyl acetate ethyl hexanoate and 2-pentanone showed a decrease of the release rate from carbohydrate matrix, however, the initial release rate of ethyl acetate was not affected by the presence of lipids, which showed that in a chemical family, aroma compounds could have a different behaviour. *cis*-3-Hexenol and *trans*-2-hexenal showed no difference of release rate from carbohydrate matrix compared to water, which indicated no retention effect of carbohydrate and diffusion similar to that observed in water. The rate decrease from complex matrix arose from the retention of lipids. To elaborate a new formulation of light foods, the variation of composition (considering a similar rheological behaviour) implicates a variation of the repartition of aroma compounds. The perceived aroma will depend on the presence of lipids (even in a weak quantity) and on the presence of carbohydrates with different possible roles: retention, release or no effect.

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