

## Tracer Aroma Compound Transfer from a Solid and Complex-Flavored Food Matrix Packed in Treated Papers or Plastic Packaging Film

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The objective of this work was to study the transfer of four aroma compounds (ethyl butyrate, ethyl hexanoate, *cis*-3-hexenol, and benzaldehyde) from a solid and complex-flavored food matrix (sponge cake) toward and through packaging films placed in indirect contact during storage in accelerated aging conditions (38 °C and 86% relative humidity gradient). The efficiency of treated papers relative to that of standard paper and plastic as barrier was tested. Before storage, aroma compound volatility in the sponge cake was measured, and similar values were found between aroma compounds, due to the fat content of the sponge cake. Whatever the aroma compound, permeability values during storage were similar for the same packaging film. The plastic film was the highest barrier, whereas calendering and coating treatments applied to treated papers decreased effectively their permeability. An opposite trend was observed for aroma compound sorption into packaging films during storage.

**KEYWORDS:** Aroma compound; sponge cake; packaging; partitioning; transfer; storage

### INTRODUCTION

One of the main roles of packaging is to protect foodstuffs against deterioration during storage. This function requires the control of small volatile molecules transfer, such as aroma compounds, gases, or water vapor. This control is generally obtained by selecting the best barrier packaging materials, that is, with the lowest solubility ( $S$ , kg m<sup>-3</sup> Pa<sup>-1</sup>) and permeability coefficients ( $P$ , kg m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup>). In spite of high barrier packaging development (multilayers, nanocomposites, SiO<sub>x</sub>-coated films), food products can still be submitted to deteriorations during shelf life due to mass transfers, and the choice of the most suited packaging for a given foodstuff is still difficult. Particularly, flavor transfer through packaging can lead to the modifications of foodstuff organoleptic quality and packaging material properties (1–3). Dury-Brun et al. (4) recently reviewed the factors affecting interactions (sorption, diffusion, permeation) between aroma and flexible packaging. Those factors are the nature and physicochemical properties of aroma compounds and packaging materials, as well as environmental conditions. Packaging materials are now better characterized for their flavor

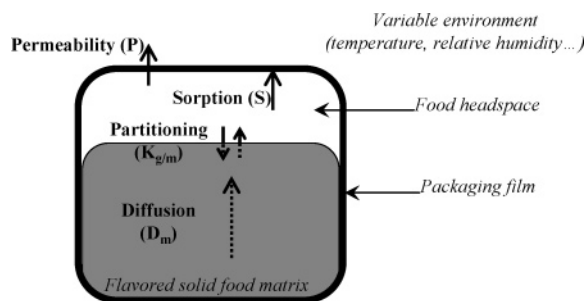
barrier property than in the past decades, and such characterization was generally established by use of pure aroma compounds more or less diluted in inert gases, in dynamic conditions, often far from storage reality and without the presence of the food matrix. Van Willige et al. (5, 6) showed the important role of the food matrix in their works about aroma compounds, milk ingredients, and plastic film interactions. To study the modifications of food flavor profile with packaging material transfer property, appropriate food model systems should be selected because most food products are complex. In most studies regarding aroma compound transfer through packaging materials, a few selected aroma compounds have been employed in more or less complex food model systems. Liquid models close to reality (fruit or vegetable juices, syrup, milk) or aqueous solutions containing some of the food ingredients (proteins, fats, carbohydrates) were mostly considered until now (1, 5–10). Fat seems to be the food component that affects flavor–packaging interactions in the higher extent, depending on fat composition and content, as well as simultaneous contact between fat, flavor, and packaging (5, 11). The effect of biopolymers such as proteins and carbohydrates on flavor–packaging interactions would be more linked to water available in the food model (6). Absorption of flavor molecules from a fatty aqueous model matrix into LLDPE was successfully modeled and then validated with whole milk by taking into

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**Figure 1.** Aroma compound physicochemical transfer from a flavored solid food matrix toward and through packaging placed in indirect contact.  $D_m$  is aroma compound diffusion through the food matrix,  $K_{g/m}$  is the gas (g) to matrix (m) partition coefficient,  $S$  and  $P$  are aroma compound sorption and permeability into and through packaging, respectively.

account flavor partitioning between the oily, aqueous, and polymer phases and hydrophobicity of flavor compounds (12). Predictive models for flavor absorption from foodstuffs to packaging films would require more knowledge about factors affecting flavor binding to food components and would have to take into account the nature of food and time of exposure. An orange juice model was particularly studied because aroma compound–packaging interactions were sensorially detected (7, 13). Such liquid models are generally easily made with good aroma compound solubilization and homogeneity of the obtained system. As the contact between such liquid food and packaging is direct, there is no partitioning step with headspace, and flavor interactions with packaging are enhanced and easily detected. On the contrary, aroma vapor transfer through packaging if released from a solid food matrix was little studied until now to the authors' knowledge. Flavor distribution in solid food matrices can be heterogeneous and difficult to optimize, particularly when thermal processing is involved in food production (14, 15). The retention of aroma compounds in solid food matrices placed in indirect contact with packaging films during their storage will be dependent not only on their stability in the food matrix (16, 17) but also on their transfers from the food to the packaging, which involve four steps (Figure 1): first, flavor transfer kinetic (diffusion) into the food; second, flavor partitioning (volatility) between the food and its headspace; third, flavor partitioning between the food headspace and the packaging (sorption); and fourth, flavor transfer kinetic through the packaging (permeation).

The objective of this work was to study the transfer of four aroma compounds (ethyl butyrate, ethyl hexanoate, *cis*-3-hexenol, and benzaldehyde) from a solid and complex-flavored food matrix (sponge cake) toward and through packaging films placed in indirect contact during storage in accelerated aging conditions (high temperature and relative humidity gradient). The efficiency of treated papers relative to that of standard paper and plastic as barrier packaging to prevent flavor loss from the sponge cake during storage was tested by determining aroma compound volatility from the sponge cake as well as their permeability and sorption through and into packaging films.

## MATERIALS AND METHODS

**Aroma Compounds and Solvents.** Flavoring of the sponge cake dough was carried out by using four aroma compounds (ethyl butyrate, ethyl hexanoate, *cis*-3-hexenol, and benzaldehyde) (Sigma-Aldrich, St Quentin Fallavier, France), purity  $\geq 98\%$ ; the sensory note and physicochemical properties (at 38 °C) are given in Table 1. Each aroma compound was added pure at 1000 mg/kg (w/w) in the dough before baking. The four aroma compounds were chosen from a previous work among the aroma compounds easily extracted by the solvent-assisted

flavor evaporation (SAFE) method and quantified by the standard addition method, after flavoring of the sponge cake with a mixture of 19 aroma compounds (18).

The four aroma compounds provide a range of values for solubility in water, hydrophobicity defined as the logarithm of the partition coefficient between octanol and water ( $\log P$ ), and pure compound saturated vapor pressure (Table 1).

Hexane with purity  $\geq 98.5\%$  (Merck) was used as extraction solvent. Hexadecane with purity  $\geq 98\%$  (Fluka) was used as internal standard.

Propylene glycol with 99.9% purity (Sigma-Aldrich Chemie GmbH) was used to dissolve aroma compounds.

**Sponge Cake.** The sponge cake dough was made of pasteurized liquid whole eggs [45 g/100 g, wet basis (wb), Agro-Doubs, Flagey, France] stored at  $-18$  °C, sucrose (25 g/100 g, wb, Béghin-Say), wheat flour (25 g/100 g, wb, Carrefour, Quetigny, France), palm oil (4 g/100 g, wb, Celys, Rezé, France), and sodium chloride (0.5 g/100 g, wb, Sigma-Aldrich, Seelze, Germany). Sodium azide (100 mg/kg, wb, VWR-Prolabo, Fontenay-sous-Bois, France) was added to prevent microbial spoilage.

After thawing of the whole eggs during 2 h at ambient conditions, sponge cake dough was prepared as stated by Pozo-Bayón et al. (18). Sodium azide was added at the same time as flour. Palm oil was melted at 50 °C in a water bath; then, after cooling at 40 °C, each pure aroma compound was added to the oil at a concentration corresponding to 1000 mg/kg of sponge cake dough. The whole was then immediately added to and mixed with the dough.

The dough was then baked at a fixed position in a revolving heat furnace (Rowenta TU284, Werke GmbH, Offenbach am Main, Germany) during 25 min at 170 °C. The cake was then allowed to cool at ambient conditions during 1 h and was then frozen at  $-18$  °C during 1 h to make easier the removal of the crust. Only the crumb was used in this study because baking of the sponge cake produces a superficial layer having a low moisture content compared to the crumb. Severe heating conditions in the surface dry layer cause Maillard browning reactions during baking, which produce different aroma compounds according to the combination of sugars and amino acids present in the food and temperature. The occurrence of those endogenous aroma compounds in the sponge cake was thus limited by using only the crumb.

**Packaging Films.** A heat-sealable coextruded biaxially oriented polypropylene film (BOPP) was provided by Mobil Plastics Europe and was used as a reference in this study.

Three different papers were used, two of them being treated papers (Table 2). Paper 1 is a simple sheet of cellulose. Paper 2 is a paper that has been impregnated (bulk treatment) with a hydrophobic substance (acrylic-based latex 1) on both sides and then supercalendered. Paper 3 is paper 2 that has been then coated (surface treatment) with the same weight of another hydrophobic substance (acrylic-based latex 2) on both sides, which provides a water vapor barrier and a dense surface to this paper (23).

Thickness ( $\mu\text{m}$ ), basis weight ( $\text{g m}^{-2}$ ), and density ratio (adimensional value) of the four films are given in Table 2. Thickness was measured at 25 °C and 50% relative humidity (RH) with a micrometer MI-20, with accuracy between 0.8 and 2.2  $\mu\text{m}$ . Mean basis weight was obtained by weighing 10 film samples of 10  $\text{cm}^2$  (after drying during 15 min at  $65 \pm 2$  °C for papers). Density ratio was calculated by dividing mean basis weight ( $\text{kg m}^{-2}$ ) by the product of mean thickness (m) and water density.

**Aroma Compound Volatility from the Sponge Cake before Storage.** The volatility of the four aroma compounds used to flavor the sponge cake was estimated from the gas to matrix mass partition coefficient ( $K_{\text{mass}}$ ) at concentration equilibrium, which was calculated by eq 1

$$K_{\text{mass}} = C_g/C_m \quad (1)$$

where  $C_g$  and  $C_m$  are the aroma compound mass fractions (w/w) in the gas and matrix phases, respectively.

To determine aroma compound partitioning between the headspace and the sponge cake, flavored sponge cake cylinders ( $8 \pm 1$  g but accurately weighed) were placed in glass cells ( $71 \pm 1$  mL but

**Table 1.** Aroma Compounds and Their Sensory Note as Well as Physicochemical Properties

aroma compound	sensory note <sup>a</sup>	BP <sup>b</sup> (°C)	density (kg m <sup>-3</sup> )	log P <sup>c</sup>	P <sub>v</sub> <sup>s</sup> (Pa) at 38 °C <sup>d</sup>	S <sub>water</sub> (g L <sup>-1</sup> ) at 38 °C <sup>e</sup>
cis-3-hexenol	green grass	156	848	1.61	317 <sup>ii</sup>	14.7 <sup>f</sup>
benzaldehyde	bitter almond	179	1045	1.64	274 <sup>g</sup>	6.9 <sup>g</sup> (at 25 °C)
ethyl butyrate	fruity, banana, pineapple	121	875	1.77	4506 <sup>hj</sup>	5.3 <sup>f</sup>
ethyl hexanoate	fruity, apple, banana	168	869	2.83	528 <sup>hj</sup>	0.5 <sup>f</sup>

<sup>a</sup> From ref 19. <sup>b</sup> Boiling point (19). <sup>c</sup> Estimated by ACD labs (Advanced Chemistry Development Software Solaris V4.67, 1994–2003 ACD). <sup>d</sup> Saturated vapor pressure at 38 °C. <sup>e</sup> Solubility (g L<sup>-1</sup>) in water at 38 °C. <sup>f</sup> From ref 20. <sup>g</sup> From ref 21. <sup>h</sup> From ref 22. <sup>i</sup> Estimated data (software MP. BPWIN, 1994–1997). <sup>j</sup> Estimated data from Antoine's equation.

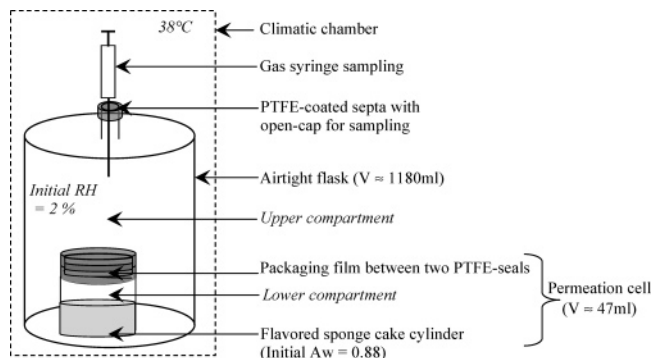
**Table 2.** Physical (Calendering) and Chemical (Impregnation or Coating) Treatments Applied to the Plastic Film and the Three Papers Used as Well as Their Mean Thickness, Mean Basis Weight, and Density Ratio (Adimensional)

packaging film	impregnation <sup>a</sup>	calendering <sup>a</sup>	coating <sup>a</sup>	thickness (μm)	basis weight (g m <sup>-2</sup> )	density ratio
BOPP	–	–	–	38.3 ± 0.8	36.3 ± 0.6	0.95
paper 1	–	–	–	77.3 ± 1.3	52.4 ± 0.2	0.68
paper 2	latex 1	++	–	30.5 ± 1.5	36.0 ± 0.2	1.18
paper 3	latex 1	++	latex 2	36.5 ± 1.0	41.7 ± 0.5	1.14

<sup>a</sup> –, no treatment; ++, supercalendering.

accurately measured), which were then closed with caps fitted with a PTFE-coated seal and stored at 38.0 ± 0.3 °C (WTB Binder GmbH climatic chamber, Tuttlingen, Germany). Three replicates were independently made. From preliminary experiments, it was checked that aroma compound concentration equilibrium between the sponge cake and its gas phase was obtained after 1 month of storage at 38.0 ± 0.3 °C. At equilibrium, 1 mL of the gas phase was sampled from the lateral entrance of the flask closed by a cap fitted with a PTFE-coated seal and the food matrix was then extracted by hexane. Hexane and an internal standard (hexadecane) were added to 0.2 g of sponge cake crumb, and the whole was stirred in ambient conditions during 14 h. The extract was then placed at –18 °C to freeze the fat, which could have been extracted by hexane. The extraction yield of the four aroma compounds by hexane was determined in preliminary studies by adding a known quantity (about 500 mg/kg) of each compound to nonflavored sponge cake samples (three replicates). The solvent extraction yield was 99 ± 3% for the four aroma compounds. Both the gas-phase sample and the extract were analyzed with a Shimadzu gas chromatograph (GC) 14B linked to a Shimadzu recorder–integrator. A split/splitless injector at 240 °C and a flame ionization detector (FID) at 250 °C were used. A stainless steel capillary column AquaWAX-DA (Alltech, 30 m × 0.32 mm × 0.25 μm) heated from 40 °C (3 min) to 240 °C (5 min) at a rate of 4 °C min<sup>-1</sup> was used. Helium was used as the carrier gas (linear velocity = 23 cm s<sup>-1</sup> at 40 °C), air and hydrogen flow rates were 350 and 48 mL min<sup>-1</sup>, respectively. Aroma compound concentrations in the gas phase and in the extract were determined using a standard calibration curve made in hexane.

The aroma compound partition coefficient between the sponge cake and its gas phase was compared to that obtained between a propylene glycol solution and its headspace because propylene glycol was the solvent of the 19 aroma compounds, among which were chosen the 4 compounds studied in this work (19). An aliquot of 20 ± 1 g (but accurately weighed) of an aqueous solution containing propylene glycol (5% w/w), 500 mg/kg ethyl butyrate, 300 mg/kg ethyl hexanoate, and 2500 mg/kg of both cis-3-hexenol and benzaldehyde was poured into 44 ± 1 mL (but accurately measured) glass flask (Supelco, Bellefonte, PA) equipped with a mininert valve (Supelco). The flask was then stored in a water bath at 38 ± 1 °C during 4 h to reach aroma compound concentration equilibrium between the solution and its headspace. Four replicates were independently made. At equilibrium, 1 mL of the gas phase was sampled by a gas syringe, as well as 1 μL of the liquid phase. Both were analyzed in a GC Chrompack CP 9000 linked to a Shimadzu recorder–integrator. A splitless injector at 190 °C and a FID at 200 °C were used. A polar packed column Carbowax 20M (80–100 mesh, 3 m length, 1/8 in. O.D.) heated from 80 °C (5 min) to 190 °C (10 min) at a rate of 7 °C min<sup>-1</sup> was used. Gas flow rates were 30 mL min<sup>-1</sup> for nitrogen (carrier gas), 25 mL min<sup>-1</sup> for hydrogen, and



**Figure 2.** Experimental system used to measure aroma compound permeability through packaging films if released from the flavored sponge cake placed in indirect contact at 38 °C and ΔRH = 86%.

240 mL min<sup>-1</sup> for air. Aroma compound concentrations in the gas and liquid phases were determined using a standard calibration curve made in hexane.

**Aroma Compound Transfer through Packaging in Indirect Contact with the Sponge Cake during Storage.** A static integral permeation method was chosen to measure aroma compound transfer through packaging because conditions are closer to those of a real packed foodstuff during storage than with dynamic permeation methods (24). The experimental system is shown in Figure 2. A cylinder of flavored sponge cake crumb (8 ± 1 g but accurately weighed, Ø 4.7 cm × h 3.8 cm) was fitted to the bottom of a glass-made permeation cell (47 ± 2 mL but accurately measured), leaving a headspace (lower compartment), the cell being then closed by a close-cap fitted with a PTFE-coated seal. The sample of packaging film, previously equilibrated at 90% RH in a desiccator over a BaCl<sub>2</sub> saturated solution, was placed between two PTFE seals (permeation area = 8.02 cm<sup>2</sup>) inside an open cap. The permeation cell containing the sponge cake sample and the open cap equipped with the film sample were then placed in a glove bag (Fisher Bioblock Scientific, Illirch, France) as well as a 1.1 L glass flask equipped with its lid and its rubber ring wrapped in PTFE. The glove bag was swept with dry nitrogen to decrease its RH until 2 ± 1% (hygrometer Dostmann electronic GmbH). The glove bag was then thermostealed (Multivac, Videmal, Blanot, France), the open cap containing the film sample was twisted on the permeation cell, and the whole system was placed in the 1.1 L flask, which was air tightly closed. This represented time zero of the experiment. The 1.1 L flask was then stored at 38.0 ± 0.3 °C in a climatic chamber (WTB Binder GmbH, Tuttlingen, Germany). Two milliliters of the gas phase (1133 ± 2 mL) was sampled with time (every 30 min for the most permeable packaging and every day for the least permeable) by means of an upper entrance

closed with an open cap equipped with a PTFE-coated seal. The sample was analyzed by GC according to the method described for determining the partition coefficient between the sponge cake and its headspace. Three replicates were made per film studied. From preliminary studies, it was checked that the whole sampling volume was negligible compared to the upper compartment volume and that sampling did not modify the aroma compound concentration in the upper compartment. The slope at initial time for the aroma compound permeation kinetic (represented by the cumulated mass in the upper compartment as a function of time) corresponded to transfer steady state and was determined by linear regression. From the slope, the aroma compound transmission rate (ACTR in  $\text{kg s}^{-1} \text{m}^{-2}$ ) across the film sample was determined by eq 2 and the aroma compound permeability (ACP in  $\text{kg m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ ) by eq 3

$$\text{ACTR} = \text{slope}/A \quad (2)$$

with the slope in  $\text{kg s}^{-1}$  and  $A$  the permeation area in  $\text{m}^2$

$$\text{ACP} = (\text{ACTR} \times e)/\Delta p \quad (3)$$

with  $e$  the thickness of the film sample (m) and  $\Delta p$  the aroma compound partial pressure gradient across the film sample (Pa). To determine  $\Delta p$ , it was checked that the aroma compound partial pressure in the upper compartment of the 1.1 L flask was initially negligible.  $\Delta p$  was then obtained from the aroma compound partial pressure in the food matrix headspace, which was constant during the time of the experiment. Indeed, it was checked that the food matrix acted as a reservoir for the aroma compound release by making mass balances of the four aroma compounds in the sponge cake before and after storage. The aroma compound partial pressure in the food matrix headspace was determined from its mass partition coefficient and by applying the perfect gas law.

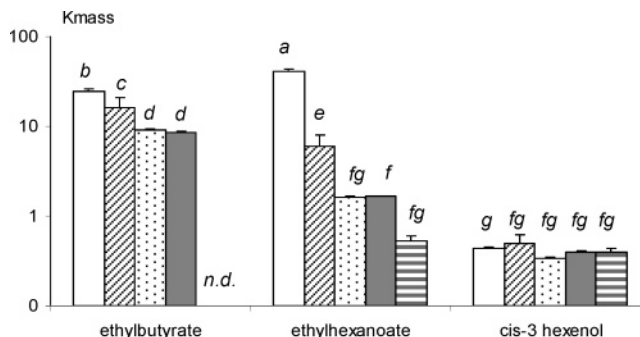
**Aroma Compound Sorption into Packaging in Indirect Contact with the Sponge Cake during Storage.** When aroma compound concentration equilibrium was reached by the integral permeation method, the packaging film permeation area was sampled and extracted by hexane in a closed flask, under magnetic stirring and at ambient conditions during 14 h. Chromatographic conditions were the same as those described for the aroma compound partitioning between the sponge cake and its headspace. The solvent extraction yield was  $99 \pm 3\%$  for all aroma compounds and packaging films. Sorption values ( $\text{kg}$  of aroma compound  $\text{m}^{-3}$  of packaging) were the mean of three replicates per packaging.

**Statistical Studies.** Differences among data means (aroma compound partition coefficients, permeability coefficients, sorption values, and concentrations in the sponge cake) were tested for statistical significance at the  $p < 0.05$  level using the ANOVA test, and the means were compared by using Fisher's LSD test of SAS software version 9.1 (Statistical Analysis System, SAS Institute Inc., Cary, NC).

## RESULTS AND DISCUSSION

**Aroma Compound Volatility from the Sponge Cake before Storage.** The rate and extent of flavor volatilization from a food matrix are mainly determined by the partition coefficient, which can be affected by the composition of the food and by resistance to mass transfer, the latter being affected by food structure (25). The mass partition coefficients ( $K_{\text{mass}}$ ) of ethyl hexanoate, *cis*-3-hexenol, and benzaldehyde between the sponge cake and the headspace were determined at 38 °C. The  $K_{\text{mass}}$  of ethyl hexanoate and *cis*-3-hexenol, presented in Figure 3, and the  $K_{\text{mass}}$  of benzaldehyde, the value of which was  $0.28 \pm 0.03$ , were not significantly different (at the  $p > 0.05$  level). As ethyl butyrate retention in the sponge cake was low ( $<5 \text{ mg/kg}$ ) and not repeatable, its  $K_{\text{mass}}$  could not be accurately determined.

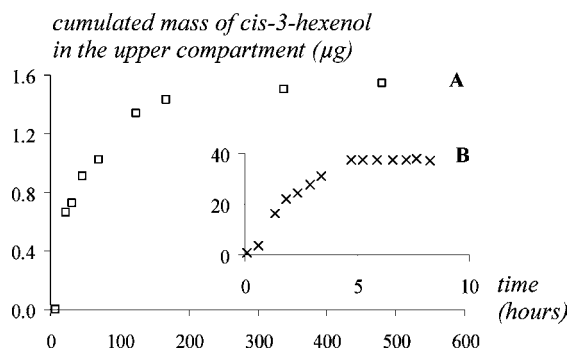
$K_{\text{mass}}$  values of ethyl hexanoate and *cis*-3-hexenol in the sponge cake were compared to their  $K_{\text{mass}}$  values from simpler and liquid model matrices such as water (20), a 5% (w/w) propylene glycol solution, and an emulsion of trioleine (3.5% w/w) in water with or without 5.5% carbohydrates (starch,



**Figure 3.** Ethyl butyrate, ethyl hexanoate and *cis*-3-hexenol mass partition coefficient for water (20) (first bar in each group), a propylene glycol aqueous solution (25) (second bar in each group), an emulsion of trioleine (25) (third bar in each group), an emulsion of trioleine with carbohydrates (25) (fourth bar in each group), and the sponge cake at 38 °C (fifth bar in second and third groups). The benzaldehyde mass partition coefficient was not represented, but its value was  $2.21 \pm 0.57$  for the propylene glycol solution and  $0.28 \pm 0.03$  for the sponge cake.  $K_{\text{mass}}$  is the mean of three replicates and is presented on a logarithmic scale. Bars with different letters (a–g) are significantly different at  $p \leq 0.05$ , and *n.d.* means not detected.

glucose, and pectins) (25) (Figure 3). Ethyl butyrate partitioning between those solutions and their headspace was considered for comparison. The  $K_{\text{mass}}$  for water was significantly higher than for the propylene glycol solution for these aroma compounds except for *cis*-3-hexenol, for which there was no significant difference between all liquid and solid model matrices. The  $K_{\text{mass}}$  values of ethyl butyrate and ethyl hexanoate in the emulsion of trioleine in water with or without carbohydrates were significantly lower than their  $K_{\text{mass}}$  values in water and in the propylene glycol solution. Ethyl hexanoate  $K_{\text{mass}}$  in the sponge cake was not significantly different from its  $K_{\text{mass}}$  in the emulsion of trioleine in water with or without carbohydrates. Benzaldehyde  $K_{\text{mass}}$  was significantly lower in the sponge cake ( $K_{\text{mass}} = 0.28 \pm 0.03$ ) than in the propylene glycol solution ( $K_{\text{mass}} = 2.21 \pm 0.57$ ).

According to De Roos and Graf (26), water, lipids, and ethanol have the strongest effect on the equilibrium headspace concentrations of flavor chemicals. Propylene glycol is likely to retain aroma compounds, therefore reducing their partition coefficient (27). With an aqueous solution containing 5% glycerol, another polyol, the volatility of methyl-3-butanol, methyl-3-propanol, ethyl hexanoate, and methyl-3-butyl acetate did not change compared to that of water (28). The retention of 2-methylbutanal and 3-methylbutanal decreased in solution if the ethanol content increased from 1 to 5%, and the effect was even significant for 0.5% ethanol content (29). The same trend was observed with esters such as ethyl hexanoate, isoamyl acetate, or ethyl acetate (30). The lower volatility of these compounds in polyethylene glycol 200, glycerol, or ethanol solutions than in water was linked to their higher solubility in these solutions than in water (31). This could indicate that the reduction of volatility of the four aroma compounds in the 5% propylene glycol solution would be due to their higher solubility in propylene glycol than in water and justified the use of this solvent to solubilize aroma compounds. Ethyl hexanoate and *cis*-3-hexenol  $K_{\text{mass}}$  values for the sponge cake were close to the  $K_{\text{mass}}$  values of those aroma compounds for an emulsion of trioleine (3.5% w/w) in water with or without 5.5% carbohydrates (25). This can be explained by the fat content of the sponge cake (9% w/w by taking into account fat from palm oil, eggs, and flour) (32; palm oil supplier, Celys, 2001). Indeed,



**Figure 4.** *cis*-3-Hexenol transfer kinetic through BOPP (A, □) and paper 2 (B, ×) at 38 °C and  $\Delta RH = 86\%$ .

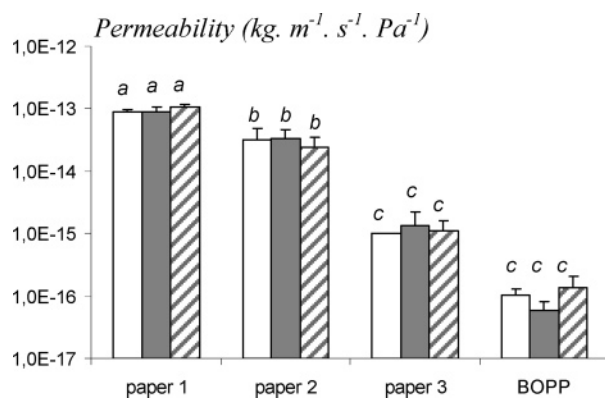
for most aroma compounds the effect of oil on their release is greater than that of other food components (33). The four aroma compounds were not retained in the baked sponge cake if palm oil was not present in the formula (18).

The maximum aroma compound concentration in the sponge cake headspace at the beginning of storage in an inert packaging film was thus estimated from  $K_{mass}$  to be  $265 \pm 35$  mg/kg (on a weight basis) for ethyl hexanoate,  $132 \pm 18$  mg/kg for *cis*-3-hexenol, and  $141 \pm 57$  mg/kg for benzaldehyde. These concentrations stand for aroma compound partial pressures of about some Pa in the sponge cake headspace. Although those aroma compound concentrations were higher than those used to flavor food matrices in reality, they were necessary to the study so that the flavored sponge cake should act as an infinite reservoir for aroma compound release and for detectable transfer through packaging films.

**Aroma Compound Transfer through Packaging Films in Indirect Contact with the Flavored Sponge Cake at 38 °C and 86% RH Gradient.** Aroma compound volatility was not influenced by the physicochemical properties of aroma compounds but was a function of the matrix composition, particularly fat presence. Knowing the initial composition of the headspace above the sponge cake, the efficiency of treated papers to that of standard paper and plastic as barrier packaging to prevent aroma compound losses from the flavored sponge cake during storage in accelerated aging conditions (38 °C and 86% RH gradient) was tested. Packaging barrier property was evaluated by determining aroma compound permeability and sorption with a permeation method integrating the flavored sponge cake placed in indirect contact.

**Aroma Compound Permeation.** The example of *cis*-3-hexenol transfer kinetic through paper 2 and BOPP is given in **Figure 4**. Transfer equilibrium was reached in less than 8 h for papers 1 and 2, in 4 days for paper 3, and in 10 days for BOPP. The aroma compound transfer through the different packaging films was thus fast at 38 °C and 86% RH gradient.

Ethyl hexanoate, *cis*-3-hexenol, and benzaldehyde permeability coefficients through the different packaging films at 38 °C and  $\Delta RH = 86\%$  are shown in **Figure 5** (ethyl butyrate transfer was not detectable). There was a clear effect of the type of packaging film on the permeability coefficients. The highest permeability values were found for paper 1 and were about  $1 \times 10^{-13}$  kg m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup>. They were in the same range of values as those found for a methylcellulose film at 25 °C and 0% RH for methylketones used at saturated vapor pressure (34), the difference of experimental conditions (aroma compound nature and concentration, packaging nature, temperature, and RH gradient) explaining this result. The permeability values were decreased by a factor of 3 between paper 1 and paper 2, due to the impregnation and calendering treatments applied to



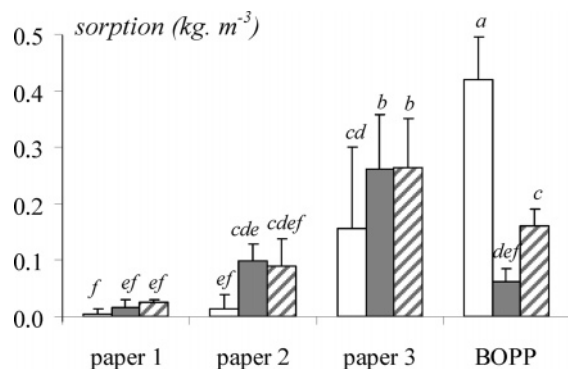
**Figure 5.** Ethyl hexanoate (white bars), *cis*-3-hexenol (gray bars), and benzaldehyde (hatched bars) permeability coefficients (kg m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup>) through the three papers and BOPP at 38 °C and  $\Delta RH = 86\%$ . Permeability coefficients are the mean of three replicates and are presented on a logarithmic scale. Bars with different letters (a–c) are significantly different at  $p \leq 0.05$ .

paper 2 (**Table 2**). The coating applied on the paper 2 surface to give paper 3 decreased by a factor 26 the aroma compound permeability. However, the permeability of paper 3, with the highest barrier to aroma compound transfer, was still 11 times higher than that of the plastic film. The improvement of small molecules barrier property of papers after their treatment was in accordance with the findings of Schuman et al. (35, 36) on the effect of precoating, calendering, and coating on water vapor and air permeability of papers. The BOPP aroma compound permeability was the lowest among the four packaging films with values close to those reported in the literature. BOPP permeability to *cis*-3-hexenol was  $0.07 \times 10^{-15}$  kg m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup> with *cis*-3-hexenol used at high diluted condition (<1 Pa) (37), which was close to our value ( $0.06 \times 10^{-15}$  kg m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup>).

There was no significant effect of aroma compound (ethyl hexanoate, *cis*-3-hexenol, and benzaldehyde) on the permeability values found for each packaging film. They were transferred at the same level for each packaging film. The fact that  $K_{mass}$  was on the same order between the three aroma compounds for the sponge cake (from 0.53 for ethyl hexanoate and 0.40 for *cis*-3-hexenol to 0.28 for benzaldehyde) could explain why their permeability values were close through each packaging film. Therefore, aroma compound physicochemical properties did not affect their permeability through packaging films in our conditions, probably due to the fat present in the sponge cake. It would be interesting to confirm the role of fat on aroma compound transfer from the food matrix toward and through packaging films by studying different fat contents of the sponge cake. The nature and treatments of packaging during their processing had a more important influence on aroma compound permeability than aroma compound physicochemical properties (**Table 2**).

The aroma compound transfer through the different packaging films was coupled to a water vapor transfer in the same direction due to the high RH gradient (2–88%), the initial water activity (GBX FA-st/1, Romans, France) of the sponge cake being  $0.88 \pm 0.01$ . In such conditions, the water vapor transfer could influence the aroma compound transfer through treated papers by plasticization of their cellulosic part (38).

**Aroma Compound Sorption.** To better understand packaging barrier property, sorption of ethyl hexanoate, *cis*-3-hexenol, and benzaldehyde in the different packaging films was determined at transfer equilibrium by solvent extraction. From results presented in **Figure 6**, the sorption values in the four packaging films were the opposite of their aroma compound permeability



**Figure 6.** Ethyl hexanoate (white bars), *cis*-3-hexenol (gray bars), and benzaldehyde (hatched bars) sorption ( $\text{kg m}^{-3}$ ) into the three papers and BOPP at transfer equilibrium at 38 °C and  $\Delta\text{RH} = 86\%$ . Sorption values are the mean of three replicates. Bars with different letters (a–f) are significantly different at  $p \leq 0.05$ .

order: the best aroma compound barriers (BOPP and paper 3) sorbed the highest quantity of aroma compounds. Very little sorption was detected in paper 1, and paper 2 presented an intermediate sorption behavior. Moreover, for each packaging film, some differences were found between the different aroma compound sorption values, whereas their permeability values were not significantly different (Figure 5).

The highest sorption value was found for ethyl hexanoate in BOPP. The hydrophobic nature of both ethyl hexanoate ( $\log P = 2.83$ ) and BOPP could explain that their mutual affinity was important. *cis*-3-Hexenol and benzaldehyde were sorbed to a lesser extent in BOPP, partly due to their lower hydrophobicity ( $\log P = 1.61$  and 1.64, respectively). On the contrary, those two aroma compounds were the most sorbed in papers 1 and 2, with the highest sorption found for paper 3. Although those papers were coated and/or impregnated by a hydrophobic latex-based substance (Table 2), the sorption was still higher for the most hydrophilic aroma compounds. Therefore, the different nature of aroma compounds can play a role in the preferential sorption. Latices are water-based systems that give films or coatings under a three-steps process: first, evaporation, particle concentration, and ordering; second, particle deformation; and third, polymer chain diffusion across particle boundaries (39). Latex coatings typically contain surfactants added to enhance the colloidal stability of the dispersion and to aid film formation (such as increase of the drying rate) (39, 40). When the latex coating dries, the surfactant could form a separate phase, which could interact with the sorbed water (41). As a high RH gradient was used in this study, such surfactant–water interactions could have occurred to a high extent and improved *cis*-3-hexenol and benzaldehyde affinity for papers 2 and 3. It would thus be of high interest to confirm this hypothesis by studying aroma compound permeability of films made solely from the acrylic latex-based substance, with high and low RH gradients.

Because opposite trends were obtained between permeability and sorption values for all packaging films, other phenomena seem to influence the permeability of aroma compounds through packaging films, particularly the diffusion step. It can be supposed that aroma compound diffusivity would be lower in BOPP because its structure is denser than in treated papers. Diffusivity of aroma compound through those packaging films will be studied in another work.

In future work, a sensitive olfactometry technique will be used to characterize aroma compound transfer through packaging films placed in indirect contact with a solid and complex

food matrix flavored with a more realistic aroma compound formulation (composition and concentration).

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