

Retention of Aroma Compounds by Carbohydrates: Influence of Their Physicochemical Characteristics and of Their Physical State. A Review

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Many aroma compounds, used to flavor food products, are used in a solid state, after encapsulation. Carbohydrates are the most common matrices used to entrap these volatiles. It has been observed that depending on the aroma compound and the carrier, efficiency can vary. This article reviews the influence of physicochemical properties of both the volatiles and the carriers on retention. The latter depends on the functional groups of the aroma compound. Moreover, it increases with molecular weight and decreases with the polarity and relative volatility of the aroma compound. This behavior can be explained by the effect of these properties on the diffusion of the aroma compound through the matrix and on the ability of the volatile to form small drops. The physicochemical properties of the carrier are important too. Retention of the aroma compound increases with the molecular weight of the carrier until an optimum is reached and then decreases for very high polymerization degrees. Viscosity, solubility, and film forming properties improve the retention ability. The effect of these parameters is discussed according to their effect on the diffusion of the volatiles. The state of the carrier has to be taken into account too. The amorphous state provides the highest retention, collapse results in losses of aroma, and crystallization leads to the greatest losses of flavors.

Keywords: *Aroma compound; β -cyclodextrin; maltodextrin; retention*

1. INTRODUCTION

Sensory attributes are critical for the acceptance of food by consumers. Among them, aroma is of capital importance and may determine whether a product will be preferred to another. Consequently, aroma compounds are often added to improve sensory qualities or to hide off-flavors.

Many of these volatile compounds are encapsulated in solid carriers to increase their protection, control their release, reduce evaporation, and promote easier handling (Balassa and Fanger, 1971; Dziezak, 1988; Versic, 1988; Shahidi and Han, 1993; Reineccius, 1995; Risch, 1995b; Eckert, 1995). The encapsulation matrix can be selected from a wide variety of polymers, depending on the core material and desired characteristics of the microcapsule. Nevertheless, the ability of carbohydrates to retain volatiles during drying processes make them the most commonly used as coating materials (Shahidi and Han, 1993; King, 1995).

Several processes have been developed to encapsulate flavors (Balassa and Fanger, 1971; Chandrasekaran and King, 1971; Dziezak, 1988; Jackson and Lee, 1991; King, 1995; Dezarn, 1995; Risch, 1995a; Bhandari and D'Arcy,

1996). The two major processes are spray-drying and extrusion, the main carriers being maltodextrins, arabic gum, and modified starches (Young, 1986; Dziezak, 1988; Jackson and Lee, 1991; Eckert, 1995). Since the use of β -cyclodextrins has been approved in Japan, France, Holland, Spain, and Hungary and is under FDA consideration in the United States (Szejtli, 1997; Anantha and Milford, 1997), inclusion complexing can be used too (Qi and Hedges, 1995; Hedges et al., 1995). Another technique less used is freeze-drying. They all lead to a dry flavored carbohydrate matrix.

To control sensory qualities of foodstuff, it also appears necessary to understand the mechanisms involved in the retention and release of volatiles by carbohydrates. This would allow us to understand why some aroma compounds are better retained than others, leading to unbalanced flavor, and why some carriers are more efficient than others.

Numerous studies (Qi and Hedges, 1995; Hedges et al., 1995; Thijssen, 1965; Flink and Karel, 1970a; King and Massaldi, 1974; Rosenberg et al., 1990; Voilley and Loncin, 1978; Voilley and Simatos, 1980) have been done in order to explain how volatiles are retained. It has been recognized that operating conditions and the nature of both the flavorant and the carrier are determinant factors.

Operating conditions have been extensively studied, and their effect is now better understood.

When spray-drying is considered, the solid content of the dryer (Menting and Hoogstad, 1967; Reineccius and Coulter, 1969; Blakebrough and Morgan, 1973; Tsujim-

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oto et al., 1984; Reineccius, 1988), processing temperatures (Rulken and Thijssen, 1972; Thijssen, 1972; Tsujimoto et al., 1984; Anker and Reineccius, 1988; Rosenberg et al., 1990), and the particle size (Brooks, 1965; Rulken and Thijssen, 1972) have been shown to modify retention. When freeze-drying is considered, freezing and drying rates, sample composition and dimensions, the frozen core temperature, and the rate of heat input can influence retention (Flink, 1975; Kerkhof and Thijssen, 1975; Gero and Smyrl, 1982; Gerschenson et al., 1979; King and Massaldi, 1974; Etzel and King, 1980; Chen et al., 1993).

But whatever the process considered, it has also been shown that the nature of the aroma compound and of the carrier are determinant (Voilley and Simatos, 1980; Rosenberg et al., 1990). Interactions between volatile compounds and starch (Rutschmann et al., 1989; Rutschmann and Solms, 1990a–g; Solms and Guggenbuehl, 1990; Friedman, 1995; Nuessli et al., 1995) or cyclodextrins (Szejtli, 1984; Szejtli, 1985; Reineccius and Risch, 1986; Shieh and Hedges, 1996; Hedges et al., 1995; Nah et al., 1996; Kano, 1993) have received much more attention than interactions between flavors and maltodextrins or corn syrup solids. Consequently much more is known on the binding of flavors by starch than by other carbohydrates (Godshall, 1997). The nature of interactions between volatiles and cyclodextrins still needs explanation, and little is known about the way in which maltodextrins and corn syrup solids interact with ligands (Wulff and Kubik, 1992; Matheis, 1993; Furuta et al., 1994; Wender et al., 1994).

Since the effect of processing conditions have been extensively studied and since interactions between starch and volatiles have already been reviewed (Godshall and Solms, 1992), this paper will focus on the retention of volatile compounds by carbohydrates, starch excepted.

The influence of the physicochemical characteristics of the aroma compound will be exposed in the first part of this review, and the influence of the nature and physical state of the carrier on retention will be examined in the second part of this paper.

2. INFLUENCE OF THE PHYSICOCHEMICAL CHARACTERISTICS OF THE AROMA COMPOUND ON RETENTION

When the same carbohydrate is used as carrier, it has been observed that the retention rate varies according to the aroma compound encapsulated. This can lead to an unbalanced aroma (Reineccius and Risch, 1986; Dornier et al., 1990). Several physicochemical characteristics of the volatile compound could partly explain these differences. The effects of the main factors, molecular weight, the presence of different chemical groups, polarity, and the relative volatility of aroma compounds, will be successively discussed.

2.1. Molecular Weight and Steric Hindrance. *Molecular Weight (MW) of the Aroma Compound Influences Retention.* The higher the molecular weight, the lower the losses.

This behavior has been observed for esters spray-dried with gum arabic (Rosenberg et al., 1990). Several solid contents and concentrations of ester were tested and ethyl hexanoate (MW = 144) was always better retained than ethyl butyrate (MW = 116). Furthermore, when stored at different relative humidities (between 11 and

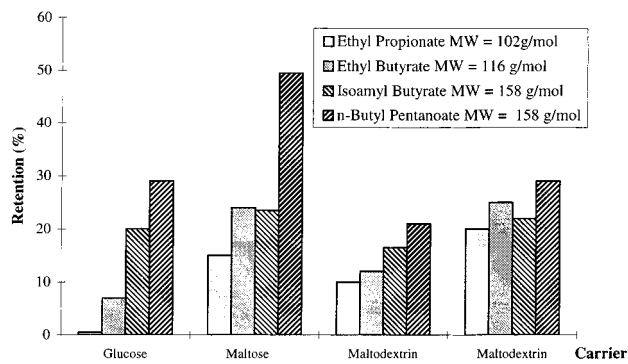


Figure 1. Influence of the molecular weights of aroma compounds on their retention.

97%), ethyl hexanoate was always more efficiently entrapped than ethyl butyrate.

The same trend has been noticed for a mixture of 16 aroma compounds encapsulated on glucose, maltose, or corn syrup solids of 28.5 and 41.4 dextrose equivalent (DE, reducing power expressed as grams of glucose per 100 g of dry matter) (Voilley, 1995) (Figure 1). The retention rate of isoamyl butyrate (MW = 158) or *n*-butyl-pentanoate (MW = 158) was higher than that of ethyl butyrate (MW = 116) or ethyl propionate (MW = 102) on all carriers, except on maltose and DE 28.5 corn syrup solid. On maltose, 24% of ethyl butyrate remained encapsulated against 23.5% for isoamyl butyrate. DE 28.5 corn syrup solid retained slightly more ethyl butyrate (25% of the initial amount added) than isoamyl butyrate (22%). Whatever the carrier, the amount of ethyl butyrate (MW = 116) encapsulated was greater than that of ethyl propionate (MW = 102). Except for the two cases mentioned above, retention increased with the molecular weight of the aroma compound in the following order: ethyl propionate (MW = 102) < ethyl butyrate (MW = 116) < *n*-butyl pentanoate, isoamyl butyrate (MW = 158).

These results could be explained by the greater ability of low molecular weight compounds to diffuse through the matrix during drying. Indeed, since the molecule is not linear, molecular weight and molecular size are linked and this latter is the primarily factor determining diffusion. When the molecular weight of the volatile increases, its molecular size increases and its diffusion rate also slows. As a consequence the aroma compound does not reach the matrix surface as readily. Retention of high molecular weight flavorants is also favored (Reineccius, 1988).

When β -cyclodextrins are chosen as the carrier, steric hindrance of the aroma compound determines whether the host can be included in the cavity. Indeed, β -cyclodextrins are made of seven D-glucose units forming a 7 Å diameter cavity (Szejtli, 1988; Shieh and Hedges, 1996). An internal volume of 262 Å³ has been calculated for β -cyclodextrins (Szejtli, 1988). These molecules seem to be flexible to some extent (Dodziuk and Nowinski, 1994). Nevertheless, too-bulky hosts cannot be completely accommodated inside (Szejtli, 1997). To the contrary, it has been reported that too-small hosts are badly retained (Reineccius and Risch, 1986). Complexation constants of several alcohols with β -cyclodextrins have been shown to increase as follows: methanol < ethanol < 2-propanol < 1-butanol (Nah et al., 1996). The higher the molecular weight, the stronger the binding of the host to the cyclodextrin. Similar results have

been observed for a set of alicyclic carboxyl acids (Eftink et al., 1989) or ketones (Tee et al., 1996). The low stability of complexes with small compounds could be explained by the fact that they do not provide sufficient contact with the wall of the cavity and the strength of the binding is also lowered (Eftink et al., 1989).

Many authors (Matsui and Mochida, 1979; Cromwell et al., 1985; Eftink et al., 1989; Tee et al., 1996) have also studied complexation of organic compounds with β -cyclodextrins in aqueous solution and deduced that steric hindrance of the guest was an important parameter in the association constant.

Less research has been done on the stability of dried complexes, but it has been put into evidence too that this one can be related to steric hindrance of the guest (Sanemasa et al., 1994). In a recent survey, 22 different organic compounds were complexed by β -cyclodextrins and the stability of these complexes was studied during a 2 weeks drying period (Sanemasa et al., 1994). It was observed that the stability was related to the volume of the guest. Provided it can be included in the cavity, the bulkier the guest is, the more stable the complex is.

Moreover, the shape of the guest molecule seems to be more important than molecular weight for complexation (Inoue et al., 1993; Hedges et al., 1995). It has been shown that, for substituted naphthalenes, the position of the substituent was determinant for the stability of the complex (Inoue et al., 1993). This can be explained by the fact that the shape of the guest determines the importance of the contact area with the cyclodextrin cavity. It also influences the strength of the binding to the host.

Moreover, the amount and nature and also the strength of these interactions will be determined, to some extent, by the nature and amount of functional groups of the volatile guest.

2.2. Chemical Groups. Comparison of the retention of several classes of aroma compounds, published by different authors (Rosenberg et al., 1990; Le Thanh, 1992; Voilley, 1995; Fleuriot, 1991), led us to notice some trends concerning the relationship between chemical groups and retention rate. We will also review the observations made on several alcohols, ketones, esters, aldehydes, and acids entrapped by polysaccharides.

Among the chemical functions reviewed, alcohols are usually the best retained compounds by carbohydrates. Propanol and 1-hexanol have been shown to be better sorbed on maltodextrins or β -cyclodextrins than diacetyl (a diketone) and ethyl acetate (an ester) (Le Thanh, 1992). A mixture containing these aroma compounds was sorbed on β -cyclodextrins or on DE 20, DE 31, or DE 61.5 maltodextrins. It was observed that 2-propanol and 1-hexanol represented respectively 12 and 9% of the total of the volatiles sorbed, whereas diacetyl and ethyl acetate represented respectively 7 and 5% of the total amount of volatiles (Le Thanh, 1992). When these amounts are expressed on a molar basis, the same order is kept: 2-propanol > 1-hexanol > diacetyl > ethyl acetate with respective molar fractions of 17, 7.5, 6.9, and 4.8%.

In another study, benzylic alcohol has been shown to be the most retained volatile during the freeze-drying of glucose, maltose, or DE 28.5 and DE 41.4 corn syrup solids flavored with a mixture of 16 compounds (Voilley, 1995). The retention rate of benzylic alcohol varied between 45 and 83%, depending on the carrier considered, but was always higher than those of the four esters

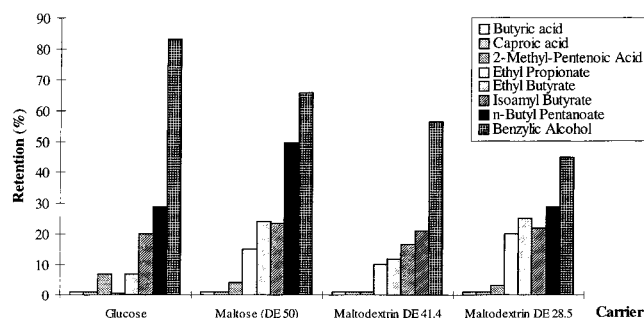


Figure 2. Influence of the chemical functions of volatiles on their retention.

(ethyl propionate, ethyl butyrate, isoamyl butyrate, and *n*-butyl pentanoate), which varied between 0.5 and 49.5%, or those of the three acids (butyric, caproic, and lactic acids), which were lower than 7% (Figure 2).

The same trend, a higher retention of alcohols than other compounds, has also been observed when encapsulating a mixture of 10 volatiles in β -cyclodextrins. Linalool was the most retained compound among the mixture including five esters, two aldehydes, γ -decalactone, and butyric acid (Fleuriot, 1991). Its retention rate, expressed as the amount of encapsulated compound on the added amount, was equal to 44%, whereas those of the other compounds were lower than 33%. A decreasing retention rate in the order alcohol (eugenol) > aldehyde (cinnamaldehyde) > ketone (3-octanone) > acid (nonanoic acid) has been reported too, in starch extrudates flavored using β -cyclodextrins-complexed aroma (Anantha and Milford, 1997).

But there are some exceptions to this trend. Indeed only 21% of octenol and 33% of octanol added were entrapped in DE 36.5 maltodextrins, whereas 41% of octanal remained in the dried matrix (Bangs and Reineccius, 1981). In this case, the aldehyde losses were also smaller than those of the alcohols.

When ketones are studied, they seem to be less retained than alcohols, similarly to esters and more efficiently than acids.

Flink and Karel (1970b) have put into evidence that retention of methanol, ethanol, *n*-propanol, 2-propanol, *n*-butanol or *tert*-butyl alcohol was greater than that of acetone on freeze-dried glucose, saccharose, lactose or dextran.

In another study it has been shown that more octanol (81%) and octenol (61%) than octanone (46%) were encapsulated in freeze-dried DE 10 maltodextrins (Bangs and Reineccius, 1981). Here again, the ketone was less retained than alcohols.

These results are in agreement with those obtained by Maier (1972). He observed that sorption of ketones by various food components, including carbohydrates, was lower than those of alcohols of comparable chain length.

But the opposite has been observed, when retentions of diacetyl (a diketone), 2-propanol, and hexanol were compared on glucose or maltodextrins (Le Thanh, 1992). Indeed, 15% (22% on a molar basis) of the sorbed volatiles was represented by acetone, whereas the proportion of 2-propanol and 1-hexanol only reached 12 and 9% (17 and 7.5% on a molar basis), respectively.

When the retentions of ketones and esters are compared, it has been observed that there were few differences between diacetyl and ethyl acetate retention rates

(7% against 5%) when they were sorbed on maltodextrins (Le Thanh, 1992).

In a decreasing retention rate order, esters seem to be the third class of compounds, although differences with ketones seem to be weak. In a comparison of different types of carriers, they seem to be better retained than acids.

Methyl propionate, methyl butyrate, isoamyl butyrate, and *n*-butyl pentanoate have also been shown to be more efficiently retained than butyric, caproic, or 2-methyl-2-pentenoic acids in glucose, maltose, or DE 41.4 and 28.5 corn syrup solids (Voilley, 1995). Indeed 10–49.5% of these different esters were entrapped, whereas, whatever the carrier, less than 7% of the acids were recovered in the dry matrix. The only exception was retention of 2-methyl-2-pentenoic acid on glucose, which reached 7% and was greater than those of ethyl propionate which equaled 0.5% on the same carrier (Voilley, 1995).

Methyl hexanoate, methyl cinnamate, ethyl hexanoate, and hexyl acetate have been shown to be better retained than aldehydes and γ -decalactone by β -cyclodextrins when a mixture of these compounds has been encapsulated (Fleuriot, 1991). The respective retention rates of these compounds were 21, 33, 32, and 27% for the esters, 1 and 6% for the aldehydes, and 15% for the lactone.

But there are exceptions to the trend usually observed. Ethyl acetate was less sorbed on maltodextrins than benzaldehyde, 2-propanol, 1-hexanol, or diacetyl. They represented respectively 5% of the volatiles sorbed against 52, 12, 9, and 7% (Le Thanh, 1992).

When attention is focused on aldehydes, there are great differences depending on the compound considered. Benzaldehyde has been shown to be three to four times better sorbed on maltodextrins than acetone, 2-propanol, 1-hexanol, diacetyl, or ethyl acetate. They represented respectively 52, 15, 12, 9, 7, and 5% of the total amount of volatiles sorbed (42, 22, 17, 7.5, 6.9, and 4.8% on a molar basis) (Le Thanh, 1992).

But, conversely, a lower retention of aldehydes compared to other chemical classes of compounds has been reported, as can be seen on the two following examples. Less *trans*-2-hexenal than alcohols or esters was entrapped in freeze-dried maltodextrins (Voilley, 1995). Hexanal and *trans*-2-hexenal were less retained (1 and 6% of retention) than alcohols, esters, and γ -decalactone (more than 15% of retention) when these compounds were encapsulated in β -cyclodextrins (Fleuriot, 1991).

No clear trend has been found for retention of this class of compound. In the studies reviewed, several parameters varied at the same time as chemical function and did not allow us to clearly define the effect of the presence of the aldehyde function.

A clearer picture can be described for acids. Those reviewed were poorly retained whatever the carrier. The retention rates of butyric acid, caproic acid, and 2-methylpentenoic acid were lower than 7% on freeze-dried glucose, maltose, or DE 28.5 and DE 41.4 corn syrup solids (Voilley, 1995).

From the reviewed studies, it also seems that the retention decreases according to the functional groups of the aroma compound, in the following order: alcohols > ketones = esters > acids. But the exceptions to the general trend clearly indicate that taking into account the chemical functions of the aroma compound is not sufficient. Moreover an aroma compound can hold

several different chemical functions, and therefore a more global descriptor must be used. Polarity could fill this requirement as it reflects the presence of different chemical groups on the aroma molecule.

2.3. Polarity. The retention of volatiles depends on their polarity: the more polar being the less retained (Rosenberg et al., 1990; Voilley, 1995).

Under the same conditions, the amount of ethyl hexanoate entrapped by spray-dried gum arabic was greater than those of ethyl butyrate. Moreover, this trend was observed for several relative humidities (Rosenberg et al., 1990).

Similarly, retention of *n*-butyl pentanoate was higher than that of ethyl butyrate, which was higher than that of ethyl propionate on freeze-dried glucose, maltose, or DE 28.5 and DE 41.4 corn syrup solids (Voilley, 1995).

These results could be explained by the greater solubility of polar compounds in water. As a consequence they would be able to diffuse more easily through the matrix during drying compared to apolar compounds. Indeed, retention of aroma compounds during dehydration can partly be explained by a diffusion mechanism (Thijssen, 1965). Aroma compounds and water are lost by diffusion through the matrix, but when the water content is lowered, the diffusion coefficients of volatile compounds decreases much more sharply than those of water. The water concentration gradient builds up during the dehydration process until a dry crust is formed at the surface of the matrix. This acts as a semipermeable membrane, preventing volatiles losses. The polar volatiles are more soluble in water and can also diffuse more easily through the matrix, which can explain their lower retention (Rosenberg et al., 1990).

Additionally, another phenomenon can be involved in volatiles losses. Above solubility limits, aroma compounds can associate to form small drops in the matrix and these volatiles could then be lost by stripping (Rosenberg et al., 1990). When spray-drying is considered, this latter phenomenon is enhanced by internal mixing that may bring the volatile to the surface of the capsule. It is also thought that, for rather polar compounds, such as ethyl propionate and ethyl butyrate, retention could be due to the combination of two mechanisms: molecular diffusivity of the water-soluble fraction and droplet stripping (Rosenberg et al., 1990).

When β -cyclodextrins are considered as carriers, the polarity of the aroma compound has to be taken into account for the complex stability. Molecules of β -cyclodextrins are made of seven α -1 \rightarrow 4 linked D-glucose units. They are torus shaped, and their internal cavity is walled by glycosidic oxygen atoms and hydrogen atoms. These bring a hydrophobic character to the cavity (Lichtenthaler and Immel, 1996a) which allows apolar organic molecules or part of molecules to be included inside (Szejtli, 1985; Hedges et al., 1995; Shieh and Hedges, 1996). The strength of the complex depends on the polarity of the guest molecule (Ito et al., 1988). It has been reported that the general requirement for complexation is a hydrophobic, nonpolar group attached to a more polar moiety (Ring and Whittam, 1991). Moreover, binding becomes stronger as the contact of hydrophobic groups with the cavity increases (Cromwell et al., 1985; Eftink et al., 1989; Hedges et al., 1995).

From the above data it appears that the chemical groups and also polarity of the aroma compound are

Table 1. Effect of Aroma Compound Characteristics on Retention by Carbohydrates

increase of retention with	decrease of retention with
molecular weight	polarity
functional groups: acids < aldehydes < esters ≤ ketones ≤ alcohols	relative volatility

important for diffusion of the volatile and stability of the complexes and consequently for retention. It has been seen in the previous paragraphs that molecular weight plays a role too. These characteristics influence the volatility of the compound. The link between volatility and retention has also been studied.

2.4. Relative Volatility. Volatility reflects the ability of a compound to reach the gaseous phase. It can be evaluated by measuring the vapor pressure of the pure compound.

Flink and Karel (1970b) have noticed that when sugars were used as carriers, the vapor pressure was not the decisive factor determining the level of retention; when dextran is the carrier, no direct correlation with volatility can be found.

Relative volatility characterizes the capacity of a compound to reach the gaseous phase when this compound is introduced in solution or in a mixture. It can be estimated thanks to the vapor pressure of the compound above the solution or mixture studied. It takes into account both the molecular weight and the polarity but also the interactions with the carrier.

Bangs and Reineccius (1981) have shown that retention of octanol, octenol, octanone, and octanal were related to their relative volatility when they were mixed with maltodextrins and spray-dried. Retention of these four different aroma compounds was reported against their relative volatility in the mixture before drying. It was observed that the higher the relative volatility is, the lower the retention. Similar results have been found by Saravacos and Moyer (1968). They concluded that, during freeze-drying and vacuum-drying, the retention of volatiles depends on the relative volatility of the selected compounds, those having a high relative volatility being the less retained.

From the previous results it can be seen that retention of volatiles depends on their steric hindrance, their polarity, and their relative volatility. These different parameters act on the capacity of the volatile to diffuse through the matrix and on its ability to form small pools. Their effects on retention are summarized in Table 1. They also partly determine the type and amount of interactions with the carrier.

3. INFLUENCE OF NATURE AND OF PHYSICAL STATES OF THE CARRIER ON RETENTION

When a single aroma compound is considered, it has been observed that retention varies according to the nature and physical state of the carrier.

Among carbohydrates used for encapsulation, maltodextrins, corn syrup solids, arabic gum, and modified starches are the most common but β -cyclodextrins and sucrose are used too (Shahidi, 1993; Kubik and Wulff, 1993). Their physicochemical characteristics and physical state can influence the diffusion of volatiles through the matrix. We will review successively the different characteristics that can affect retention: molecular weight, conformation, chemical functions, and the physical state of the carrier.

3.1. Molecular Weight. The molecular weight of the carrier influences the rate of retention. When

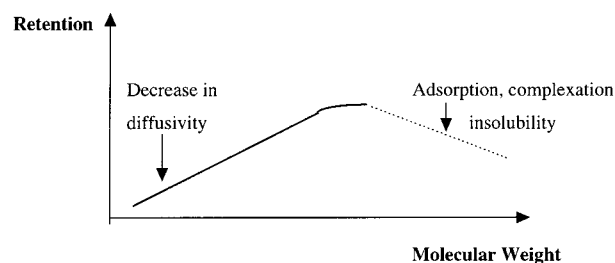


Figure 3. Influence of the molecular weight of the carrier on the retention of volatiles.

maltodextrins are considered, the lower the dextrose equivalent and also the higher the average molecular weight are, the more volatiles are entrapped.

Bangs and Reineccius (1981) have shown that the retention of a mixture of 12 aroma compounds depends on the DE of the maltodextrins and decreases as follows: DE 10 > DE 15 > DE 20 > DE 25 > DE 36.5. The only exception to this trend was found for DE 5 maltodextrins which retained slightly less aroma compounds than DE 10 maltodextrins, but this difference was not significant at the 5% level. Other studies have reported an increase in aroma entrapment when the average molecular weight of the carrier increase (Voilley and Simatos, 1980; Reineccius and Coulter, 1969; Voilley, 1986).

The greater retention observed with high a molecular weight carrier could be explained by a reduction of diffusivity of the solute during drying (Voilley, 1975) and an increase in the rate of formation of a dry crust at the surface of the carrier (Bangs and Reineccius, 1990).

Nevertheless, it has been noticed that for very high degrees of polymerization retention rates decrease with the molecular weight of the carrier (Voilley, 1975). When sugars (glucose, saccharose, and fructose) were used as carriers, more acetone was retained when molecular weight of the carrier increases. Conversely, when dextrans were used as carriers, less volatiles were entrapped when the molecular weight increased (Voilley, 1975). The same evolution has been shown for retention of a set of alcohols on sugars or dextran (Flink and Karel, 1970b). The variation of retention according to molecular weight could also be represented by Figure 3.

The increase in retention can be attributed to the reduction of diffusivity of the volatile in the matrix, whereas, for the highest degrees of polymerization, other phenomena such as interactions, insolubilizations, or inclusions are to be taken into account and could explain inversion of the initial trend (Voilley et al., 1977).

3.2. Conformation. Conformation of the carrier can greatly influence the retention of volatiles. This can be observed in comparing the retention ability of maltodextrins and β -cyclodextrins.

These two polymers are made of D-glucose units bound by α -1 \rightarrow 4 linkages. They differ in that β -cyclodextrins are constrained cyclic polysaccharides of seven glucose units (Saenger, 1988), whereas dextrans are mixtures of linear polymers of different chain lengths with considerable conformational mobility in solution (Szejtli, 1984; Kenyon and Anderson, 1988; Neszmélyi and Hollo, 1987, 1989, 1990; Pérez, 1993; Kenyon, 1995; Hedges et al., 1995; Shieh and Hedges, 1996). The similarity between these two carriers suggests that at least part of the mechanisms of interaction between host and guest may be common (Ring and Whittam, 1991). Hydrophobic and van der Waals interactions could be involved in the retention of volatiles by both maltodex-

trins and β -cyclodextrins (Matsui and Mochida, 1979; Solms and Guggenbuehl, 1990; Ivanov and Jaime, 1996; Kano et al., 1992; Kano, 1993; Langourieux and Crouzet, 1994; Lichtenthaler and Immel, 1995, 1996a,b). Other binding forces such as hydrogen bonds (Saenger and Steiner, 1993; Steiner et al., 1992), electrostatic ones, changes in the conformational energy, or the return of high-energy water to the bulk phase could be involved in the differences observed in the capacity of the retention of these carriers (Tabushi et al., 1978; Kano, 1993). The amount and nature of these interactions also depend on the amount and nature of chemical groups held by the carrier.

3.3. Chemical Groups. Properties of the carrier will depend on its chemical composition. The nature of the carrier can influence retention in that it will determine the viscosity for a given solid level (Reineccius, 1988). If the viscosity is low, internal mixing in the matrix can occur during drying and delays formation of the semipermeable surface. This delay permits greater aroma losses. Therefore, at the same infeed solids content, one would expect greater aroma retention for a high viscosity infeed material (Reineccius, 1988).

Moreover, the nature of the carrier will determine its emulsification and film forming properties and also its ability to entrap volatiles (Bangs and Reineccius, 1990; Sheu and Rosenberg, 1995). Gum arabic, which has higher emulsification properties than maltodextrins, has been shown to be more efficient in the retention of volatiles (Thevenet, 1988, 1995; Reineccius, 1991). When a mixture of ethyl propionate, ethyl butyrate, orange oil, cinnamic aldehyde, and benzaldehyde was encapsulated in a blend of gum arabic and maltodextrins, it was observed that the general trend was an increase in retention when the gum arabic fraction increased (Reineccius, 1991). Rosenberg explained the superior retention properties of gum arabic versus maltodextrins by its emulsification properties and its tendency to form films at the interfaces between the emulsion phases (Rosenberg et al., 1990).

Moreover, when a chemical class of carrier is considered, the amounts of chemical functions of the carrier have to be taken into account too. It has been shown that aroma retention in strawberry jam depends on the degree of esterification of the pectin added. A decrease in the degree of esterification led to an increase in the retention of methyl and ethyl butanoate, nonanal, and hexanoic acid (Guichard, 1996).

Similar results have been observed when pectins of different degrees of methylation were flavored with ethyl acetate, ethyl butyrate, methyl anthranilate, or acetic acid and freeze-dried (Saravacos and Moyer, 1968). It was noticed that low methylated pectins, which are more acidic than pure pectin, retain less aroma compounds.

3.4. Influence of the Physical State of the Carrier. Retention of aroma compounds depends not only on the nature of the aroma and the carrier but also on the physical state of the latter.

3.4.1. Amorphous State. Carbohydrate matrices can be either in an amorphous or crystalline state, which respective capacity of retention will be reviewed now. When the matrix has been rapidly dehydrated and a low water activity has been reached, as for example after spray-drying or freeze-drying, it is believed that carriers are in the glassy state (Roes and Karel, 1991a-c; Whorton and Reineccius, 1995). This is characterized

by a very low mobility of the carrier molecules. Due to this low mobility, release of the encapsulated materials is primarily via Fickian diffusion through the pores in the matrix. The amount of volatile released will also depend on the composition of the matrix, pore size, particle size, and the thickness and area of wall around the entrapped volatiles. As a consequence, while the matrix is in the glassy state, release or retention of volatiles depends more upon the rate at which aroma can migrate to the surface than upon the relative volatility of the aroma (Whorton, 1995).

When the plasticizer content, for example water content, increases, a transition occurs from the solid glassy to a liquid-like rubbery state. The hydrogen bonds which are responsible for the main structural forces in dried amorphous products are weakened. Molecular mobility and diffusion increase (Voilley, 1986; Whorton, 1995). Depending on the water uptake, some swelling and bridging of the particles or a dissolution of the wall polymer can occur (Rosenberg et al., 1990; Cooke, 1991). These morphological changes have been confirmed by scanning electron microscopy on spray-dried flavored gum arabic (Rosenberg et al., 1985, 1990; Whorton, 1995). The larger volatile losses are observed for this state of the carrier compared to glassy or collapsed ones. These variations in aroma retention could be explained by the destruction of microregions immobilizing the volatiles and by development of the diffusion of aroma (Flink and Karel, 1970b, 1972; Chirife and Karel, 1974; Rifai and Voilley, 1991).

With increasing water content, collapse may occur when plasticization of the carrier decreases the viscosity to the extent that the polymer matrix is unable to support itself against gravity. A strong dependence of the rate of collapse on temperature has been shown (Levi and Karel, 1995). It has been put into evidence that this rate can be predicted using the Williams-Landel-Ferry (WLF) equation (Levi, 1995).

When it happens, porosity is lost, reducing diffusion through the matrix. In some cases, collapse can result in reencapsulation of the aroma compound (Labrousse et al., 1992; Whorton and Reineccius, 1995). In this state, the release level resembles again Fickian diffusion.

3.4.2. Crystalline State. As seen above, collapse occurs when the water content increases, but, depending on the carrier used, crystallization may follow.

It has been shown that the transition from the glassy state to the crystallized one results in a loss of volatiles (Rifai and Voilley, 1991; Labrousse et al., 1992).

For instance, it has been observed that methyl linoleate oil encapsulated in model food powder was completely released upon crystallization of sugars (Labrousse et al., 1992). Similar observations have been done by Flink and Karel (1972), To and Flink (1978), and Shimada et al. (1991).

Crystallization requires the holding temperature to be above the glass transition temperature of the carrier considered. The time for occurrence depends on the difference between the holding temperature, T , and the glass transition temperature, T_g : $(T - T_g)$ (Levine and Slade, 1989; Levi and Karel, 1995; Senoussi et al., 1995). It occurs when viscosity is low and polymers have sufficient mobility to associate and form crystalline junctions. The rate can be predicted by the Williams-Landel-Ferry equation. Crystallization leads to a cross-linking effect, which results in the reduction of the

Table 2. Effect of Physicochemical Characteristics of the Carrier on the Retention of Aroma Compounds

increase of retention with	decrease of retention with
molecular weight for low molecular weights such as sugars and starch hydrolysates	molecular weight for high molecular weights such as starch and dextrans
viscosity	physical state:
emulsifying properties	amorphous > crystalline
film forming properties	

area between polymer chains. Volatiles are also forced from the crystallized matrix to the surface, and the retention of the aroma compound decreases (Labrousse et al., 1992; Levi, 1995).

From the above data it can also be seen that the amorphous state is the most efficient for retention of volatiles, the collapsed state leads to a loss in flavors, and crystallization results in the largest release of the encapsulated compounds.

The effects of carrier physicochemical characteristics on the retention of volatiles are summarized in Table 2.

4. CONCLUSION

Retention of aroma compounds is a complex phenomenon in which several factors take part. Operating conditions have been shown to play a role and have been extensively studied. But independently of the process chosen, retention varies with the nature of the aroma and of the carrier and with the state of this latter.

When the volatile is considered, chemical function and also polarity, steric hindrance, and relative volatility have been shown to be important. But the trends observed in comparing the retention of various compounds put into evidence that this topic still needs explanation.

When the carrier is considered, it has been shown that retention was influenced by its chemical functions, its molecular weight, and the state of the carrier.

The variation of the retention observed according to the kind of volatile and carrier used could be due to changes both in the nature and number of interactions between the carrier and the volatiles. Some polysaccharides such as starch or β -cyclodextrins have been largely studied. As a consequence, the mechanisms involved in complexation by these carriers is better understood but little is known of the nature of interactions between volatiles and maltodextrins or corn syrup solids, carriers widely used however. More information on the nature and amount of interactions occurring between such carriers and volatiles could also bring us some clues on the explanation of differences of efficiency among carriers.

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Received for review August 18, 1997. Revised manuscript received January 12, 1998. Accepted February 19, 1998.

JF970709Y