

Sulfur compounds in dairy products: lipophilicity and retention by lipids or fat-mimics

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INTRODUCTION

In food flavor acceptability, essential are not only the nature and the concentration of the aroma compounds but also their interactions with non-volatile macromolecules such as sugars, proteins, and lipids. Of all food ingredients, lipids probably have the strongest organoleptic impact as demonstrated in many model systems. Recently, we have studied the interactions between lipids and several aroma compounds (aldehydes, methylketones, esters, and dimethyldisulfide) in a real food system composed of fresh cheese, triolein, and water (Piraprez et al., 1998a). The concentration of "free" ligands was measured with a dynamic headspace-gas chromatographic system. From our results, we conclude that retention of all flavouring molecules increases with the amount of triolein. This phenomenon is highly influenced, however, by the structure of the aroma compound, as demonstrated by RP-HPLC lipophilicity determinations. Within the same chemical family there exists a linear relationship between the lipophilicity index k_w and retention.

In the present work, flavour retention was investigated in a large series of sulfur compounds including thioesters (S-methylthioacetate, S-ethylthioacetate, S-ethylthiopropionate, S-methylthiobutanoate, and S-butylthioacetate), sulfides (ethyl sulfide and isopropyl sulfide) and, disulfides (dimethyldisulfide and diethyldisulfide) which are organoleptic compounds in many cheeses (Dumont et al., 1976, Cuer et al., 1979). First, we have studied the influence on aroma retention of increasing amount of fat in the fresh cheese sample. Secondly, the impact of the use of polysaccharide as fat-mimic has also been considered. Two kinds of polymers have been studied: inulin and starch from various origins. In order to quantify the aroma retention we've had recourse to an hyphenated dynamic headspace injector-gas chromatographic system (Purge and Trap injector).

RESULTS AND DISCUSSION

Study of the influence of the lipidic content on aroma retention. Experiments were conducted in a real food matrix composed of fresh cheese, triolein and water. Triolein has been chosen as the lipidic model. Blends of fresh cheese, triolein and ultrapure water have been prepared with increasing amounts of lipids and a parallel decrease of water. For each triolein content, volatile compounds have been added with increasing concentrations just before the dynamic headspace analysis.

The linear relationship between chromatographic areas and aroma concentrations have been drawn for each flavouring substance and each triolein ratio. The inverse of the relative retention was calculated by dividing the slope of the sample containing triolein by the slope obtained for the sample without triolein (Piraprez et al., 1998a).

Results obtained for thioesters, sulfides and disulfides confirm those previously obtained for other aroma families: retention is higher in high lipidic media, especially when high lipophilic compounds are considered (Figure 1). For thioesters, the following equation can be used: retention (10 %) = 0.06 k_w ($r^2 = 0.909$).

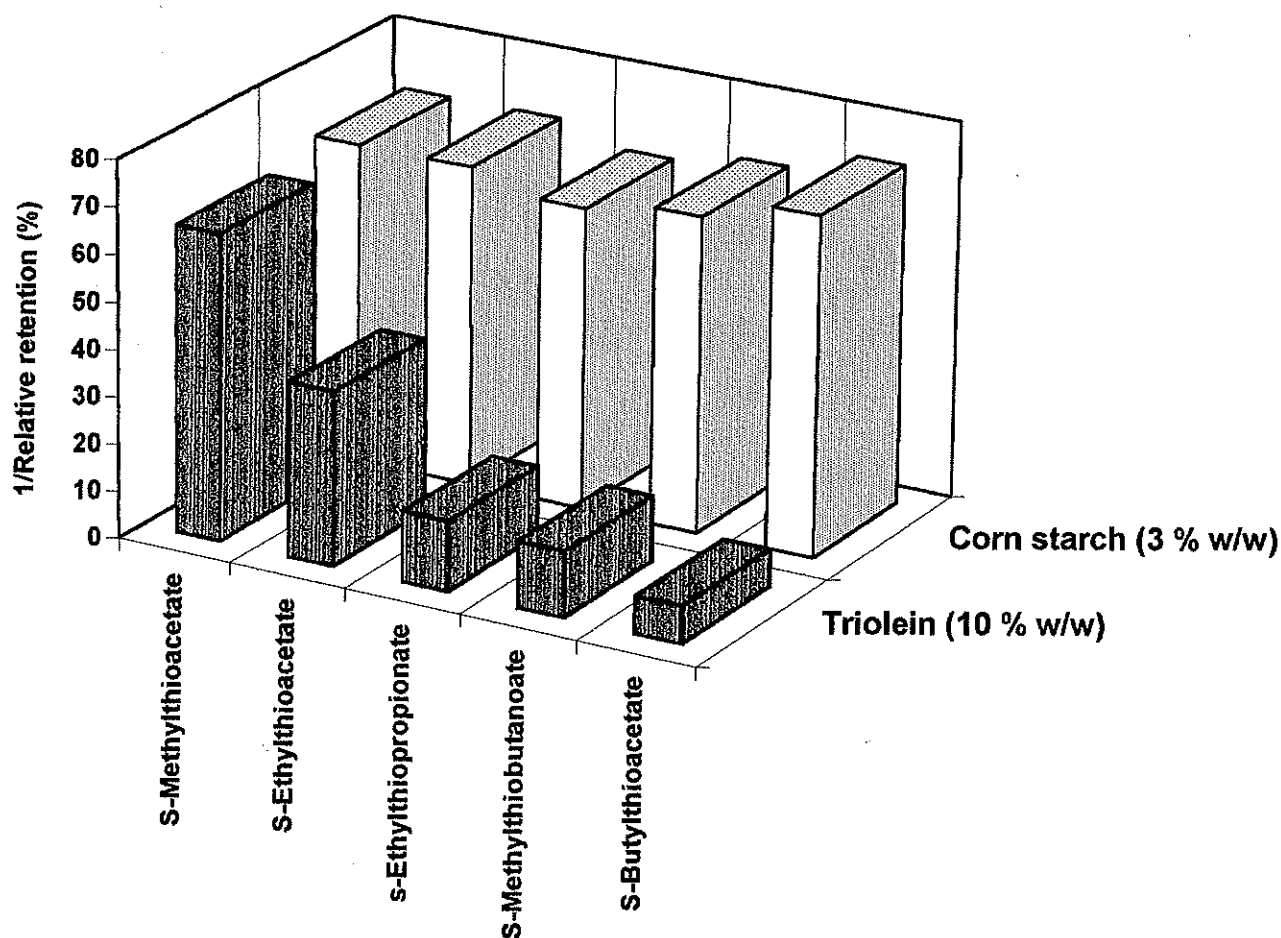


Figure 1. The inverse of the relative retention of thioesters added in fresh cheese samples containing 3 % w/w of corn starch or 10 % w/w of triolein.

Study of the influence of the use of a fat-mimic on aroma retention. In order to produce diet product with acceptable organoleptic properties, the influence of fat-mimic has been investigated by using the same methodology. Two polysaccharides already used in dairy industries have been chosen for those experiments: inulin and starch.

Impact of inulin on aroma retention. Inulin is a fructan polysaccharide where the fructose moieties are linearly linked by β -D-(2 \rightarrow 1) bonds with a few number of branched β -D-(2 \rightarrow 6) fructose units and one terminal glucose unit (GF_n). The degree of polymerisation is dependent on the plant source and varies from 2 to 70 units for inulin issued from chicory roots. Long Chain (LC) type inulin, free of oligosaccharides has been selected. Due to interactions with water molecules, the viscosity of the samples gradually increase with the inulin content. The creamy and fat-like texture of those systems lead to use inulin as a fat-mimic in dairy products.

Samples with increasing concentrations of inulin have been analysed (Piraprez et al., 1998b). As depicted for S-butylthioacetate (Figure 2), increase in the inulin content

influences very poorly the behaviour of the thioester within the fresh cheese matrix, in spite of the increasing viscosity. Even at 10 % inulin, no significant decrease in the slope of the calibration curve is observed. The same results have been obtained for the other thioesters, sulfides and disulfides. Reformulation of diet product containing inulin will have to take into account such differences.

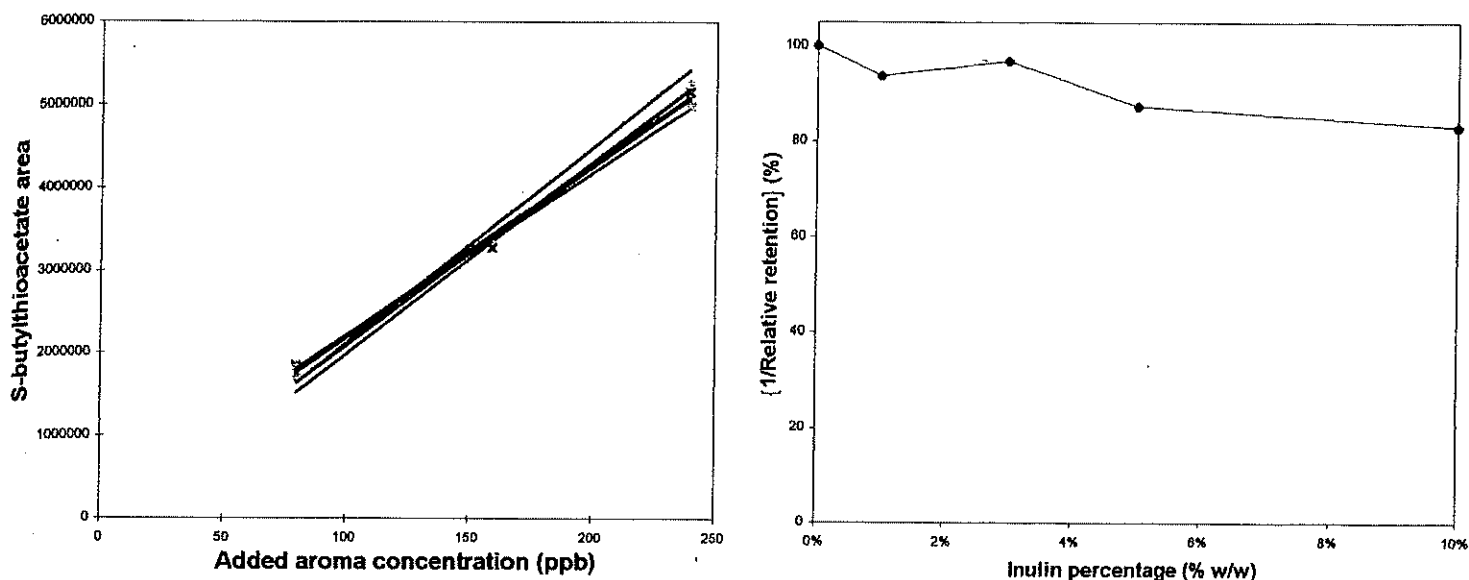


Figure 2. (a) Linear relationships between chromatographic areas and S-butylthioacetate concentrations at different percentages of inulin. (b) Relationship between the inverse of the relative retention (%) and the percentage of inulin (%).

The influence of the presence of both inulin and triolein within the sample has also been tested. For this experiment, samples containing fresh cheese (20 % w/w), inulin (10 % w/w), triolein (10 % w/w) and water (60 % w/w) have been prepared. In all cases, the aroma retention revealed to be identical compared to inulin-free samples with the same triolein ratio.

Impact of starch on aroma retention. Three kinds of starch from different plants which differed in amylose content and the molecular weight of the amylose (Table 1) have been tested. Modified starch widely used in dairy industries could not be analysed because of the foaming properties of the solution.

Table 1. Characteristics of the starch analysed.

Plant source	% amylose	M.W. _{amylose} (g/mol)
Potato starch	25	300 000
Corn starch	25	20 000
Waxy corn starch	1	/

Several authors have shown that amylose is able to form inclusion complexes with aroma compounds (Rutschmann et al., 1989; Nuessli et al., 1996). Nevertheless, all those experiments were realised in model systems. Are those results also valid in a more complex matrix such as fresh cheese?

Blends of fresh cheese (20 % w/w), starch (3 % w/w) and water (77 % w/w) were therefore prepared. The starch powder was mixed to water with an Ultra-Turrax (Janke & Kunkel GmbH, Ika-labortechnik, Ultra-Turrax T25; 24 000 rpm) for 2 min at 4 °C. Thereafter, the suspension was heated at 1 bar overpressure (121 °C) for 30 min (Nuessli et al., 1996). After the heat treatment, fresh cheese was added to the starch solution and mixed with the Ultra-Turrax (24 000 rpm) for 2 min. The blend was then stored at 4 °C until used in the headspace experiments. Ten minutes before the dynamic headspace analysis, the aroma compounds were added in the sample.

Results obtained for S-butylthioacetate are summarized in figure 3. In all cases, the retention by starch is far lower than the one measured in triolein media. However, significant differences can be detected between our three types of starch. Retention of aroma compounds by corn starch is greater than the one measured for potato or waxy corn starch. The latter, containing only one percent of amylose logically behaves like inulin. For amylose-rich systems, the weight of the linear α -D-(1 \rightarrow 4) glucopyranoside seems to be determinant for flavour retention intensity, the lower the molecular weight, the higher the retention. Furthermore, the interactions of aroma with polysaccharides highly depends on temperature. Even for corn starch, retention is no more observed at 60 °C.

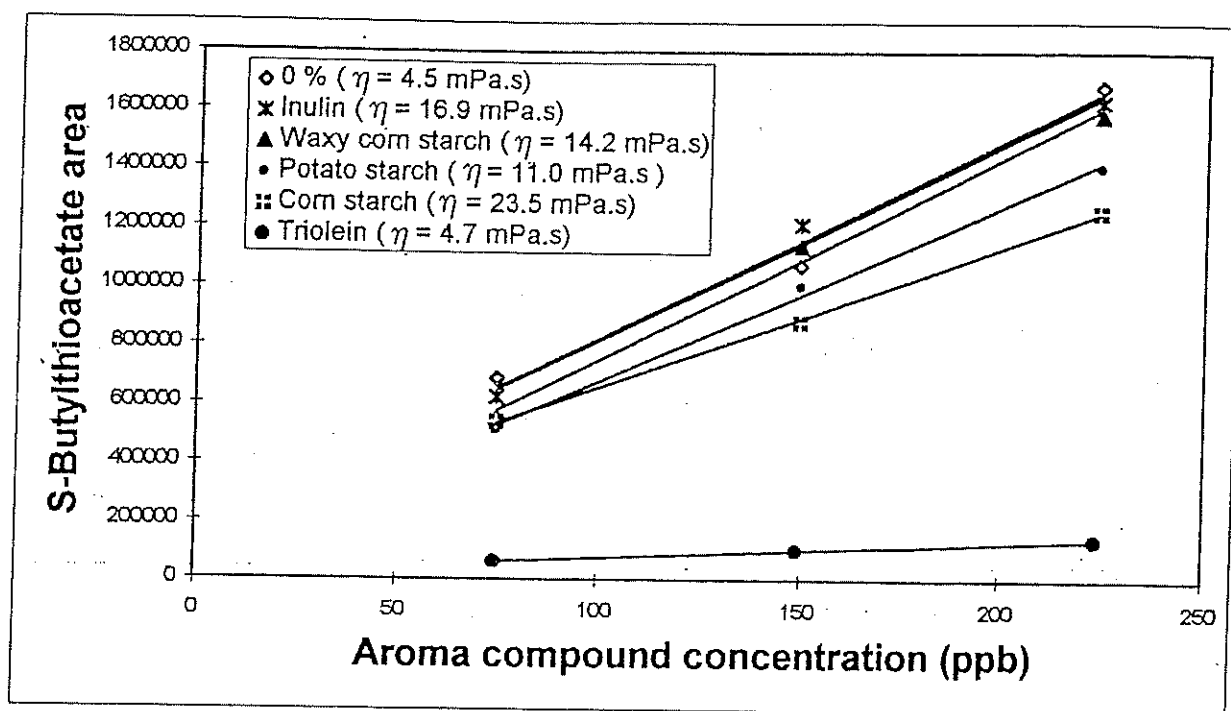


Figure 3. Linear relationships between chromatographic areas and S-butylthioacetate concentrations within the fresh cheese sample; η : dynamic viscosity of the sample (mPa.s).

The same trends has been obtained for all the other sulfur compounds studied. As shown in Figure 1, where the flavouring compounds have been classified by increasing lipophilicity, reformulation will be vital, mainly for high lipophilic molecules.

CONCLUSION

As previously obtained for other aroma families (methylketones, aldehydes and esters), retention of flavouring compounds by triolein increases with the lipophilicity of the aroma compounds (Piraprez et al., 1998a). Within the same chemical family there exists a linear relationship between the lipophilicity index k_w and retention. Therefore, it's possible to predict the retention of a flavouring substance in a lipidic food matrix knowing its lipophilicity. Opposite to this phenomenon, it's very difficult to predict the intensity of the retention of flavour compounds in a polysaccharidic media. Inulin and waxy corn starch don't interact with the sulfur compounds while corn starch retained them probably through inclusion complexes within amylose. Potato starch containing amylose with a higher molecular weight than corn starch interacts to a lesser extent than corn starch. According to these results, smaller amounts of flavouring compounds should be present in the diet product containing polysaccharide to induce similar perception. However, reformulation of the dairy product will have also to take into account probable deviations in time-intensity profiles.

LITERATURE CITED

Cuer, A.; Dauphin, G.; Kergomard, A.; Roger, S.; Dumont, J-P.; Adda, J. Flavour properties of some sulphur compounds isolated from cheeses. *Lebensm. Wiss. Technol.* **1979**, *12*, 258-261.

Dumont, J-P.; Degas, C.; Adda, J. L'arôme du Pont l'Evêque. Mise en évidence de constituants volatils quantitativement mineurs. *Le Lait* **1976**, 553-554, 177-780.

Nuessli, J.; Conde-Petit, B.; Trommsdorff, U.R.; Escher, F. Influence of starch flavour interactions on rheological properties of low concentration starch systems. *Carbohydr. Polym.* **1996**, *28*, 167-170.

Piraprez, G.; Herent, M-F.; Collin, S. Flavour retention by lipids measured in a fresh cheese matrix. *Food Chemistry*, **1998a**, *61* (1/2), 119-125.

Piraprez, G.; Gijs, L.; Spinnler, H. E.; Collin, S. Sulfur compounds in dairy products: flavor properties, lipophilicity and retention by lipids or fat-mimics. Submitted, **1998b**.

Rutschmann, M. A.; Heiniger, J.; Pliska, V., Solms, J. Formation of inclusion complexes of starch with different organic compounds. I. Method of evaluation of binding profiles with menthone as an example. *Lebensm. Wiss. Technol.*, **1989**, *22*, 240-244.