Aroma-active secondary oxidation products of butter

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Abstract

Butter contains vitamins, minerals and unsaturated lipids, such as polyunsaturated fatty acids (PUFA) and conjugated linoleic acids (CLAs). However the oxidative stability and consequently the shelf-life of milk products are inversely correlated with their PUFA and CLA content.

The objective of this study is the evaluation of the oxidative stability and sensory quality of PUFA/CLA-enriched butter versus conventional butter, with both types of butter being produced at ALP. For this purpose, new chemical and sensory-based methods will be developed, as well holistic complementary methods.

This paper focuses on a preliminary study achieved using conventional butter, subjected to a long storage and to oxygen and light exposure, to develop a gas chromatography olfactometry (GC-O) method able to detect the aroma-active compounds originated from oxidation. This will be one of the methods used for the evaluation of the oxidative stability of PUFA/CLA-enriched butter.

Introduction

In the frame of the EU Research Project "QualityLowInputFood" (QLIF), Work Package 5.3, ALP addresses the topic of processing strategies and examines the potential effects of processing on nutritionally high-value milk components, such as PUFA and CLA. They are desirable constituents of milk products for their beneficial effects on human health (Whingham et al., 2000). PUFA and CLA are naturally present in milk from ruminants but their content can be further increased to obtain dairy products with a higher nutritional value. PUFA/CLA enriched butter was produced at the ALP pilot plant, supplementing the diet of cows with sunflower seeds, rich in unsaturated fatty acids (Collomb et al., 2004). Conventional butter (not enriched in PUFA/CLA) was also produced and compared to the PUFA/CLA-enriched butter. These suitable components in milk fat may, however, cause faster oxidation and thus shorter shelf-life of butter. For this reason, the oxidative stability and the sensory quality of PUFA/CLA enriched butter are investigated and new chemical and sensory-based methods are developed at ALP. In addition, holistic methods are developed by a research group at the University of Kassel, partner of ALP. The present part of the project focuses on the development of an instrumental combined to a sensory method, gas chromatography olfactometry (GC-O), able to compare the aroma profiles of the PUFA/CLA-enriched butter to the conventional butter. In this first study a GC-O method was developed using conventional butter samples, subjected to a long storage

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or to oxygen and light exposure, to test the sensitivity of this method to the aroma compounds originate from oxidation. The GC-O method was able to characterise the aroma profile of the oxidised kinds of butter and to detect the odour-active compounds formed from lipid oxidation. This method will be applied to monitor the oxidation of PUFA/CLA-enriched butter during storage and to define the shelf-life of this product.

Materials and methods

Conventional sweet cream butter was produced in March 2006 at the ALP pilot plant. This butter was then analysed fresh, after storage of 1, 8, 20 and 35 days at 6°C and after induced oxidation by oxygen and light. Oxidised butter samples were obtained by exposure of fresh butter to a continuous flow of oxygen for 1, 3 and 12 hours and to fluorescence light (Philips TL40W/33RS) with an intensity of 2000 lx. The room temperature was in both cases 6°C. The aroma compounds were extracted by solid phase microextraction (SPME). After extraction, the fiber was desorbed in the injection-port of a gas chromatograph which was equipped with a mass selective detector, a flame ionisation detector and a sniffing port for the olfactometric analysis. The GC-O analysis was carried out by three trained panellists.

Results

A total of 19 odour-active compounds were detected in the headspace of the fresh butter by GC-O. The odour-active compounds of this butter were diacetyl, giving a buttery and creamy odour, 2-methylbutanal, with milk and chocolate notes, 2-methyl-3-furanthiol, with meaty odour and 2-nonanone, characterised by a hot milk odour. The aroma profile of the butter changed during storage, showing after 35 days, fatty, oily, fried and rancid notes, mainly due to lipid oxidation. Acetic and hexanoic acid as well as hexanal and (*E,E*)-2,4-decadienal are mainly responsible for the odour impression of long term stored butter. Table 1 compares the odour-active compounds found in the fresh butter with those of butter stored for 35 days. Butter samples subjected to oxygen and light exposure developed quickly off-flavours. The GC-O analysis showed that the butter exposed to oxygen for 12 h developed a fatty odour, probably due to (*E*)-2-hexenal and decanal, as well a sweaty odour, originated from pentanoic acid. Intense green, metallic and rancid notes characterised the butter exposed to the light. In the samples exposed for 12 hours aldehydes and ketones, such as pentanal, hexanal, (*Z*)-3-hexenal and 3-pentanone, 3- and 2-hexanone, play an important role, conferring chemical, green and metallic odours. A potato-like odour was detected only in the light-exposed samples, due to the methional. Table 2 summarises the GC-O results found for the butter samples exposed to oxygen and light.

Discussion

Many studies are already accomplished on butter aroma, but only few have used GC-O to evaluate the oxidative stability of butter. Butter samples showed a change in flavour during 35 days of storage, mainly due to off-flavours developing from lipid oxidation. Hexane and hexanal that increase during storage may considered as markers of oxidative processes. Hexanal, originating from autoxidation of linoleic acid, often predominates in the volatile fraction of oxidised foods (Belitz et al 2004) and was already chosen as an indicator of lipid oxidation in butter during storage (Christensen and Holmer 1996). (*E,E*)-2,4-Decadienal, responsible for fried-oily odour in butter stored for 35 days, was also found as off-flavour in butter oil stored 42 days at room

temperature (Widder et al. 1991). After 35 days of storage, butter showed a more intense mushroom notes, due to an increasing of 1-octen-3-one, developed from linoleic acid (Ullrich and Grosch 1987); these findings are in agreement with other authors (Widder 1994, Widder et al. 1991, Badings 1970). Butter samples were sensitive to oxygen and particularly to light that induced green, fatty and metallic notes. Pentanoic acid and decanal were only found in samples exposed to oxygen. Methional, with a boiled potato-like odour, was only detected in samples exposed to fluorescence light. This compound from the photodecomposition of methionine, is mainly responsible for the light-activated flavour in dairy products (Bosset et al. 1993, Azzara and Campbell 1992).

Conclusions

This preliminary study demonstrated that GC-O analysis is able to characterise the aroma and detect the odour differences in fresh butter, stored butter and butter exposed to oxygen and light. This GC-O analysis will be used to study the odour-active compounds originating from oxidative processes in the PUFA/CLA-enriched butter and conventional butter. These results will be compared to those obtained with chemical, sensory and holistic methods and the shelf-life of the two types of butter will be evaluated.

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Disclaimer

References

Azzara C.D. and Campbell L.B. (1992): Off-flavour of dairy products. In Charalambous G. (ed.): Off-Flavors in Foods and Beverages. Elsevier Science Publishers B V, Amsterdam, p 329-374.

Badings H.T. (1970): Cold-storage defects in butter and their relation to the autoxidation of unsaturated fatty acids. Neth. Milk Dairy J. 24:147-245.

Belitz H-D., Grosch W., Schieberle P. (2004): Food Chemistry. Springer, Berlin, p 201.

Bosset J.O., Gallmann P.U., Sieber R. (1993a): Influence de la translucidité de l'emballage sur la conservation du lait et des produits laitiers – un article de revue. Lait 73:3-49.

Collomb M., Sieber R, Bütikofer U. (2004): Lipids 4:355-364.

Christensen T.C. and Holmer G. (1996): GC/MS analysis of volatile aroma components in butter during storage in different catering packaging. Milchwissenschaft 51:134-139.

Ullrich F. and Grosch W. (1987): Identification of the most intense volatile flavour compounds formed during autoxidation of linoleic acid. Z. Lebensm. Unters. Forsch. 184:277-282

Whingham L.D., Cook M.E., Atkinson R.L. (2000): Conjugated Linoleic Acid: Implications for Human Health. Pharmacol. Res. 42:503-510.

Widder S., Sen A., Grosch W. (1991): Changes in the flavour of butter oil during storage. Z. Lebensm. Unters. Forsch. 193:32-35.

Widder S. (1994): Oxidativer Verderb von Butterschmalz-Einfluss von Antioxidantien. Ph.D. Thesis, Technical University of Munich, Germany.

Tab 1: Selected odour-active compounds detected in fresh butter and in 35 days stored butter

RI	Odour descriptor	Fresh	35 days	Compounds
581	butter, cream	x	x	2,3 Butandione (Diacetyl)
645	milk, chocolate	x		2-Methylbutanal
708	acetic, vinegar		x	Acetic acid
800	green		x	Hexanal
867	meat, broth	x		2-Methyl-3-furanthiol
902	soapy	x	x	Heptanal
980	mushroom	x	x	1-Octen-3-one
997	cheese, rancid		x	Hexanoic acid
1091	hot milk	x		2-Nonanone
1163	green	x	x	(*E*)-2-Nonenal
1170	hay	x	x	(*Z*)-2-Nonenal
1293	fried oil		x	(*E,E*)-2,4-Decadienal

RI= linear retention index determined on a HP-5MS capillary column

Tab 2: Selected odour-active compounds detected in butter exposed to oxygen and to fluorescence light for 12 h

RI*	Odour descriptor	O_2	Light	Compounds
581	butter, cream	x	x	2,3 Butandione (Diacetyl)
650	chemical		x	3-Pentanone
715	green		x	Pentanal
775	green, metallic		x	3-Hexanone
791	green		x	2-Hexanone
800	green, fresh		x	(*Z*)-3-Hexenal
800	green, metallic	x	x	Hexanal
820	boiled potato		x	Methional
841	grass, fatty	x	x	(*E*)-2-Hexenal
852	green		x	(*E*)-2-Hexenol
857	flower, green	x	x	(*Z*)-3-Hexenol
902	soapy, fatty	x	x	Heptanal
915	sweaty	x		Pentanoic acid
980	mushroom	x	x	1-Octen-3-one
1090	mushroom	x	x	3,5-Octadien-2-one^T
1181	green, metallic	x	x	(E)-4,5-Epoxy-(E)-2-octenal^T
1211	fatty	x		Decanal

RI= linear retention index determined on a HP-5MS capillary column

T= tentatively identified, based on comparison of the mass spectra with the ones of a mass spectra library.