

Aroma-active compounds of butter: a review

Silvia Mallia · Felix Escher · Hedwig Schlichtherle-Cerny

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Abstract This review article shows that more than 230 volatile compounds have been identified in butter, however, only a small number of them can be considered as key odorants of butter aroma. Gas chromatography olfactometry was used to determine the character impact odorants of different kinds of butter. Sweet cream butter is characterised by lactones with fruity and creamy notes and by sulphur compounds, having corn-like and garlic odours. The key odour compounds of sour cream butter are diacetyl (buttery-like), butanoic acid (cheesy) and δ -decalactone (peach), mainly due to lactic acid bacteria fermentation. The aroma of butter oil is characterised by aldehydes, such as (*E*)- and (*Z*)-2-nonenal and (*E,E*)-2,4-decadienal, conferring green and oily notes. Olfactometric studies of heated butter showed the formation of new aroma compounds during heating, such as 3-methylbutanoic acid (cheesy), methional (potato-like) and 2,5-dimethyl-4-hydroxy-3-(2*H*)-furanone (caramel-like). High temperature treatment of butter can also induce off-flavour development. Off-odours in

butter originate from autooxidative and as well as from lipolytic reactions, microbial contamination and animal feeding.

Keywords Butter · Aroma · GC-O · Gas chromatography · Olfactometry · Off-flavour

Abbreviations

AEDA	Aroma extract dilution analysis
BO	Butter oil
CharmAnalysis TM	Combined hedonic aroma response measurement
DMS	Dimethyl sulphide
DMTS	Dimethyl trisulphide
FD	Dilution factor
FID	Flame ionisation detector
GC × GC	Two dimensional gas chromatography
GC-MS	Gas chromatography mass spectrometry
GC-O	Gas chromatography olfactometry
OAV	Odour activity value
SIDA	Stable isotope dilution assay
SNIF	Surface nasal impact frequency
SoCB	Sour cream butter
SPME	Solid phase microextraction
SwCB	Sweet cream butter
TOF-MS	Time-of-flight mass spectrometry

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S. Mallia · H. Schlichtherle-Cerny (✉)
Agroscope Liebefeld-Posieux Research Station ALP,
Schwarzenburgstrasse 161, 3003 Berne, Switzerland
e-mail: hedwig.schlichtherle-cerny@alp.admin.ch

F. Escher
Institute of Food Science and Nutrition, Food Technology
and Sensory Science, ETH Zurich, 8092 Zurich, Switzerland

Introduction

Butter is a traditional food, which is widely consumed all over the world, directly or as an ingredient in

processed foods such as pastries and convenience dishes. Its nutritional value, due to a high content of fats, vitamins and minerals, and its unique and pleasant flavour make butter particularly appreciated by the consumers.

The nature of this flavour has since long intrigued chemists and flavourists who studied the aroma compounds of butter extensively and tried to reproduce an “artificial” butter aroma [1–4]. Various review articles of butter aroma are also available [5–9].

Different methods have been used for the isolation of the volatile compounds of butter, mainly consisting in steam distillation and high-vacuum distillation techniques [2, 10] and static and dynamic headspace methods, such as solid phase microextraction (SPME) [11, 12], static headspace analysis [13, 14], simultaneous purging-solvent extraction [15, 16] and using a purge and trap system [12]. Gas chromatography coupled to mass spectrometry (GC-MS) is the separation technique usually applied for the identification and quantification of volatile compounds in butter and generally in foods [10, 11, 17, 18].

The aroma composition of butter depends on animal feeding [5, 19], season of production [11, 20], manufacturing process [21] and storage conditions [22–24]. Depending on the manufacturing process, three main types of butter exist, each having a specific flavour: sour cream butter, obtained from cream inoculated with starter cultures; sweet cream butter, derived from unfermented cream; acidified cream butter, produced with sweet cream, that is acidulated in a subsequent step with lactic acid and a flavour concentrate.

Removing the aqueous phase from butter by decantation or evaporation yields butter oil, an important product. The aroma of butter oil was also widely studied over the years [10, 22, 23]. In an early study on the volatile composition of sweet cream butter, Siek and Lindsay [25] identified over 100 compounds in the steam distillates from butter-fat, including alkanals, alkanones, alcohols, esters, hydrocarbons and aromatic compounds. Stark and co-workers [4, 26–28] did several studies on a top quality Australian butter oil, obtained from sweet cream. They identified alkanones, alkanolic acids, δ -lactones, phenolic compounds, dimethyl sulfone, indole and 3-methylindole (skatole) and used flavour threshold studies to detect which compounds contribute to the aroma of butter oil. Their conclusion was that decanoic acid, lauric acid, δ -octalactone, δ -decalactone, indole, and skatole are important volatile compounds for the butter oil aroma, whereas the phenolic compounds are of only borderline significance.

The flavour of sour cream butter is composed of aroma compounds, which also occur in sweet cream butter and additionally those from starter cultures [8]. The reproduction of the flavour of sour cream butter was attempted by Lindsay and co-workers [29] and later by Badings [30], who found 2,3-butanedione (diacetyl), acetic acid and lactic acid as the most important aroma compounds, stemming from the metabolism of the lactic acid bacteria. δ -Dodecalactone, δ -decalactone, γ -decalactone, hydrogen sulphide and dimethyl sulphide, derived from sweet cream butter, also contribute to the flavour of the cultured butter [30]. Another study on sour cream butter aroma [31] confirmed the identification of lactones as the main volatile components of this butter type. In addition 2-methylketones and alcohols were found as important contributors. Additionally Shooter and co-workers [11] accomplished a selective study on volatile sulphur compounds in butter, showing an increase of methanethiol and dimethyldisulfide concentration in spring butter, due to the pasture composition, and a significant decrease of these compounds during storage.

An extensive study to identify the aroma compounds present in the water fraction of butter [16] found 23 compounds, such as 1-methoxy-2-propanol, 3-hydroxy-2-butanone, 1-ethoxy-2-propanol, 2,3-butanediol, butanoic acid and benzoic acid. It was observed that the heat treatment of butter at 170 °C for 5 min induces rapid formation of 2,5-dimethyl-4-hydroxy-3-(2H)-furanone and 3-hydroxy-2-methyl-pyran-4-one (maltol). The same research group recently improved the identification of flavour compounds in butter [32], using two-dimensional gas chromatography (GC \times GC) coupled to flame ionisation (FID) and time-of-flight mass spectrometric (TOF-MS) detection. This led to the detection of aldehydes, 2-enals, ketones, alcohols, fatty acids and lactones, which were not identified in the first study. Furan derivatives and heterocyclic compounds such as pyrroles and pyridines were exclusively found in the heat-treated samples.

The effect of storage on the volatile fraction of butter was evaluated by Christensen and Holmer [24] and by Povolo and Contarini [12]. The first authors studied the oxidative rancidity in butter during 14 weeks and chose hexanal as an indicator for lipid oxidation. Povolo and Contarini, using a purge and trap technique as well as SPME, identified 48 aroma compounds in butter, belonging to the chemical classes of ketones, aldehydes, alcohols, esters, acids, sulphur compounds, hydrocarbons and terpenes.

More than 230 volatiles have been identified as natural constituents of butter [33], but only a small

number of those is recognised as key odorants of butter flavour [34]. The study of the odour-active compounds, which actually contribute to the aroma of a specific food, is possible using instrumental methods in combination with sensory techniques. The application of gas chromatography-olfactometry (GC-O), using the human nose as a detector, provides both odour descriptors and odour activity measurement.

The human nose can be more sensitive than an instrumental detector, having in fact a detection limit down to 10^{-19} moles for certain odorants [35]. During olfactometric analysis, a trained panelist describes the odour quality and indicates the duration of the odour perception [36, 37].

Several GC-O methods are available to estimate the importance of a particular aroma compound in food: aroma extract dilution analysis (AEDA) [38], based on serial dilutions until an odour is no longer perceivable; CharmAnalysisTM (combined hedonic aroma response measurement) [39], also based on serial dilutions of the aroma extract; Osme (from the Greek word meaning odour) [40, 41], consisting of the analysis of a single concentration of the extract, to establish quality, duration and odour intensity; surface nasal impact frequency (SNIF) [42], based on the detection of odour frequencies by a panel of trained sniffers. Although olfactometric analysis may be dependent on subjective factors related to the psychophysical conditions of the panelist, it can result in reproducible measurements, if the panelists are trained with reference chemicals and agreed on the odour attributes.

The aim of this work is to review the character impact odour compounds of sweet cream butter, sour cream butter and butter oil, identified by GC-O analysis. Potent odorants generated during heating of butter will also be discussed. The last part is dedicated to the off-flavour formation in butter, which may be related to lipid oxidation, lipolysis and microbial growth, occurring during butter manufacturing, packaging and storage.

Odour-active compounds in butter

The character impact odour compounds of butter primarily originate from the cream used to make it. Up to now, however, only few publications exist on the aroma of cream. Haverkamp and co-workers [43] found (Z)-4-heptenal to be important for the cream flavour. Pionnier and Hugelshofer [44] analysed cream from different processes (pasteurisation, sterilisation, UHT) and having different fat levels by GC-O. They identified 35 key odorants, such as diacetyl (buttery),

2-pentanone (caramel-like, cream-like), 2-heptanone (dairy-like), 3-hydroxy-2-butanone (buttery), dimethyl trisulfide (cabbage-like), 2-nonanone (hot milk-like), acetic acid (acidic), furfural (caramel-like), butanoic acid (cheese-like). The aroma of cream is mainly due to the contribution from the aqueous phase of milk and from the fat globule membrane [8], while butter aroma is primarily derived from the volatile compounds present in the fat fraction.

Sweet cream butter

The key aroma compounds of sweet cream butter (SwCB) were studied by AEDA by Budin and co-workers [45] and by Peterson and Reineccius [13]. In the first study, lactones, ketones and aldehydes were found to have high aroma dilution factors: δ -decalactone (512), δ -dodecalactone (256), (Z)-6-dodecen- γ -lactone (128), 1-hexen-3-one (256), 1-octen-3-one (128), (E)-2-nonenal (64), (E,E)-2,4-decadienal (64), *trans*-4,5-epoxy-(E)-2-decenal (64) and (Z)-2-nonenal (32). Interestingly skatole was also found as key odorant of SwCB, showing an aroma dilution factor of 128.

Peterson and Reineccius identified by headspace analysis δ -decalactone, 1-hexen-3-one, 1-octen-3-one, (E)- and (Z)-2-nonenal and skatole as potent odorants of SwCB, which is in agreement with the study of Budin and co-workers. Additional aroma compounds were hydrogen sulphide, acetaldehyde, dimethyl sulphide, diacetyl, hexanal, 2-methylbutanal, 3-methylbutanal, butanoic acid, dimethyl trisulphide, hexanoic acid, δ -hexalactone, nonanal, δ -octalactone and γ -dodecalactone. Quantification of key odorants was performed by purge and trap-GC-MS using standard addition. The identified volatile compounds were added, according to their concentrations, to a model system to reconstitute the aroma of SwCB. Nineteen panellists rated the similarity of the aroma of the butter model versus the fresh butter obtained directly from the manufacturing plant, which was used as reference. The sensory analysis indicated that the butter model was significantly different from the reference, but it was ranked the same in similarity as an unsalted commercial butter. According to Peterson and Reineccius [13], SwCB was characterised by δ -octalactone, δ -hexalactone and γ -dodecalactone. In particular, δ -hexalactone and γ -dodecalactone had creamy and peach-like odours, respectively, but were identified in SwCB only by Peterson and Reineccius. The authors found, additionally, dimethyl sulphide (DMS) and dimethyl trisulphide (DMTS) as key odorants, which have already been detected by GC-O in milk and treated milks [46, 47], however not in butter. Day and

co-workers [20] identified DMS in butter already earlier and considered it a desirable component that smoothes the strong flavour of diacetyl.

In a study carried out by Schieberle and co-workers [48], the overall odour impression of SwCB was evaluated by a trained sensory panel and compared with the odorants of different types of sour cream butter (SoCB). The results showed that the diacetyl concentration is lower without a fermentation process as in SwCB, resulting in an overall mild and sweet odour impression. Odour activity values (concentrations of the odorants divided by their odour thresholds) were calculated: diacetyl (<2), δ -decalactone (32), butanoic acid (19), (Z)-6-dodecen- γ -lactone (<1), hexanoic acid (<1). Table 1 summarises the concentrations, odour thresholds and odour activity values of odour-active compounds found in SwCB by the different authors.

Sour cream butter

Schieberle and co-workers [48] studied different kinds of butter: sour cream butter (SoCB), Irish SoCB, German farm SoCB and cultured butter and compared them with SwCB.

An AEDA of Irish SoCB, showing the most intense odour during a preliminary sensory analysis, revealed 18 odour-active compounds: diacetyl, 1-penten-3-one, hexanal, 1-octen-3-one, (Z,Z)-3,6-nonadienal, (E)- and (Z)-2-nonenal, (E,E)-2,4-nonadienal, (E,E)-2,4-decadienal, γ -octalactone, *trans*-4,5-epoxy-(E)-2-decenal, skatole, δ -decalactone, (Z)-6-dodecen- γ -lactone, acetic acid, butanoic acid, hexanoic acid and an unknown compound with fatty-nutty odour. δ -Decalactone, (Z)-6-dodecen- γ -lactone and diacetyl, which had the highest dilution factors (FD) of 4096, 512 and 256, respectively, were quantified by stable isotope dilution assay (SIDA). Butanoic as well as hexanoic acid, which were major compounds in the acidic fraction of the volatiles, were quantified using unlabeled standards. Table 1 lists the most important odour-active compounds of SoCB. Sunflower oil was spiked with diacetyl, δ -decalactone and butanoic acid at the same concentrations occurring in cultured butter that was chosen as standard for the most typical butter odour. The results indicated that the sunflower oil containing the three odorants exhibited an aroma note, which in quality and intensity was very similar to the odour of the cultured butter.

The higher amounts of diacetyl, δ -decalactone (Z)-6-dodecen- γ -lactone, butanoic and hexanoic acids in SoCB, might result from the lactic acid bacteria, which are added to the cream during production.

Volatile compounds of traditional SoCB, such as Ghee [49] and in particular of Smen, a fermented

butter produced in Morocco and in other Arab countries, were studied by GC-O [50]. The results of an AEDA indicates butanoic and hexanoic acid as potent odorants. The primary mechanism of aroma development in this product is lipolysis.

Butter oil

Widder and co-workers [22, 23] investigated the key odorants of butter oil (BO), using vacuum distillation for the isolation and GC-MS combined with olfactometry for the identification of the volatile compounds. Sixteen potent odorants were identified by AEDA: diacetyl, acetic and butyric acid, 1-hexen-3-one, (Z)-3-hexenal, 1-octen-3-one, (Z)-1,5-octadien-3-one, guaiacol, (Z)- and (E)-2-nonenal, (E,E)-2,4-decadienal, skatole, 4-hydroxy-3-methoxybenzaldehyde (vanillin), (Z)-6-dodecen- γ -lactone, δ -octalactone and δ -decalactone. Vanillin has been reported by the authors for the first time in BO. The most important aroma compounds with the highest FD factors were 1-octen-3-one (FD = 128), (Z)-3-hexenal (64), (Z)-2-nonenal (64), (E)-2-nonenal (32) and (E,E)-2,4-decadienal (32) [22].

In the same study, the odour-active compounds of fresh BO were compared with those in BO after 42 days storage at room temperature. The FD factors of the carbonyl compounds formed by lipid peroxidation increased. This topic will be discussed later concerning oxidative off-flavours formed during storage.

Table 1 summarises the major odour-active compounds found in BO, SwCB and SoCB and describes their odour quality. Concentrations, nasal and retronasal odour thresholds in oil and OAVs of the odour compounds are listed, when available. The odour threshold data vary from author to author [23, 33, 48, 51–59], especially for (E) and (Z)-2-nonenal, 2-methylbutanal, hexanal and nonanal. The retronasal odour threshold of (E)-2-nonenal, for example, varies from 0.066 [57] to 66 mg/kg oil [23]. The chemical structures of selected odour-active compounds of butter and BO are represented in Fig. 1.

Odour-active compounds in heated butter

Butter generates potent odorants during heating [60]. Although the volatile composition of heated butter is well known and more than 170 compounds have been identified [33]; only few studies have identified and quantified the odour-active compounds responsible for its aroma. Budin and co-workers [45] studied odorants in heated SwCB using AEDA. The volatile fraction of butter, heated to 105–110 °C for 15 min, was isolated

Table 1 Odour-active compounds in sweet cream butter (SwCB), sour cream butter (SoCB) and butter oil (BO) as determined by gas chromatography-olfactometry

No ^a	Compound	Odour quality	Concentration (µg/kg butter)			Odour threshold (mg/kg oil) ^b		OAV ^c
			SwCB ^d	SoCB ^e	BO ^{f,g}	nasal	retronasal	
	Acids							
1	Butanoic acid	Buttery, sweaty, cheesy, rancid	192	4480	nq	0.135 ^e		19 ^q ; 33 ^e
	Hexanoic acid	Pungent, musty, cheesy, acrid	732	1840	nq	5.4 ^e		<1 ^e , ^q
	Aldehydes							
2	2-Methylbutanal	Chocolate, fruity	4.9	–	–	0.0022 ^h ; 0.140 ⁱ	0.0082 ^h ; 0.023 ^{i,j}	
	3-Methylbutanal	Chocolate	11.9	–	–	0.0054 ^k ; 0.013 ⁱ	0.0108 ^k	
3	Hexanal	Green, fatty	29	nq	nq	0.120 ⁱ ; 0.300 ^l	0.073 ^m ; 0.190 ⁿ	
4	Nonanal	Waxy, fatty, floral	43	–	–	1 ^l ; 13.5 ^o	0.26 ^o	
5	(<i>E</i>)-2-Nonenal	Green, fatty, tallowy	10	nq	6.75	0.9 ^l	0.066 ^m ; 66 ^f ; 45 ^f (BO)	<1 ^f
	(<i>Z</i>)-2-Nonenal	Green, fatty	nq	nq	0.2	0.0045 ^l	0.0006 ^m ; 0.6 ^l ; 3 ^f (BO)	<1 ^f
	(<i>Z</i>)-4-Heptenal	Green, fatty, cream, biscuit-like	nq	nq	0.3	0.002 ^o	0.001 ^o ; 0.75 ^l ; 3.5 ^f (BO)	<1 ^f
	Ketones							
6	2,3-Butanedione	Buttery	6.6	620	nq	0.0045 ^e ; 0.010 ^k	0.01 ^k ; 0.055 ⁿ	2 ^q ; 138 ^e
	1-Hexen-3-one	Vegetable-like, metallic	0.004	–	nq			
7	1-Octen-3-one	Mushroom-like	0.58	nq	1.1	0.010 ^l	0.3 ^l ; 3 ^f (BO)	<1 ^f
	Lactones							
	δ-Hexalactone	Creamy, chocolate, sweet aromatic	47.9	–	–			
	δ-Octalactone	Coconut-like, peach	72.8	–	nq			
8	δ-Decalactone	Coconut-like, peach	1193	5000	nq	0.4 ^k ; 0.12 ^e	1.4 ⁿ ; 1.6 ^k	32 ^q ; 42 ^e
9	γ-Dodecalactone	Peach	441	–	–			
	(<i>Z</i>)-6-Dodeceno-γ-lactone	Peach	–	260	nq	0.25 ^e		<1 ^q ; 1 ^e
	Sulphur containing compounds							
10	Dimethyl sulphide	Corn-like, fresh pumpkin	20	–	–	0.0012 ^p	0.0023 ^p	
11	Dimethyl trisulphide	Garlic, sulphury	17.4	–	–	0.0025 ^p	0.0042 ^p	
	Nitrogen containing compound							
12	3-Methyl-1H-indole (Skatole)	Mothball, fecal	12.6	nq	nq	0.0156 ^k	0.05 ^k	

nq compound detected but not quantified

^a Numbers refer to Fig. 1

^b Thresholds in vegetable oil, except for BO odour threshold determined in butter oil

^c Odour activity value (ratio of concentration to odour threshold) for SoCB and BO

^d Literature data (concentration determined by standard addition method) according to [13]

^e Literature data refer to Irish sour cream butter (concentration determined by SIDA), according to [48]

^f Literature data refer to fresh butter oil (concentration determined by SIDA) according to [23]

^g Literature data according to [22]

^h Odour threshold according to [59]

ⁱ Odour threshold according to [56]

^j Odour threshold according to [58]

^k Odour threshold according to [53]

^l Odour threshold according to [51, 52]

^m Odour threshold according to [57]

ⁿ Odour threshold according to [33]

^o Odour threshold according to [55]

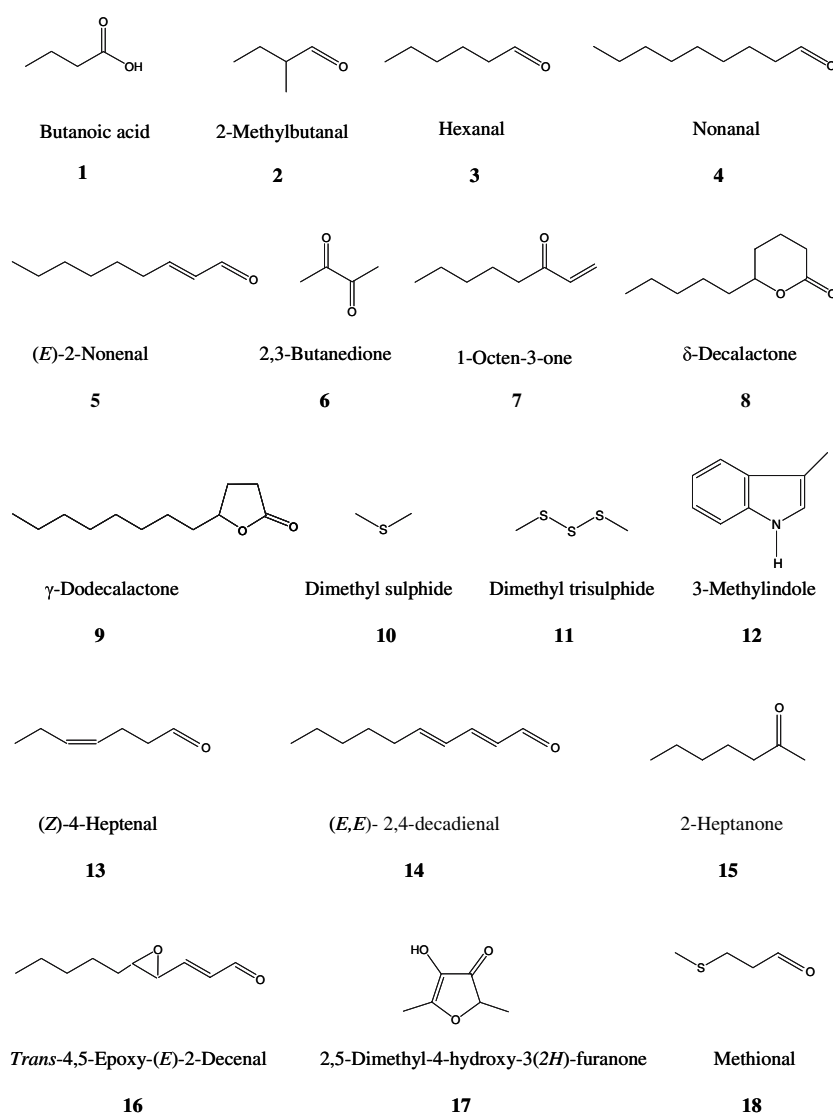
^p Odour threshold according to [54]

^q Literature data refer to sweet cream butter according to [48]

by high vacuum distillation. The odorants with the highest aroma dilution factors were 1-hexen-3-one, 1-octen-3-one, (*E*)-2-nonenal, (*Z*)-2-nonenal, (*E,E*)-2,4-

decadienal, *trans*-4,5-epoxy-(*E*)-2-decenal, 2,5-dimethyl-4-hydroxy-3-(2*H*)-furanone, methional, δ-octalactone, δ-decalactone, δ-dodecalactone and skatole.

Fig. 1 Chemical structures of potent odour-active compounds of butter



The quantification of ten odour-active compounds was performed by SIDA and the OAVs were also calculated. The data are shown in Table 2. The key aroma compounds of heated butter were compared with those of fresh butter: δ -decalactone, skatole, 1-octen-3-one, (E)- and (Z)-2-nonenal, (E,E)-2,4-decadienal and *trans*-4,5-epoxy-(E)-2-decenal had higher aroma dilution values in heated butter.

Schieberle and co-workers [48] determined the sensory threshold of δ -decalactone as 120 $\mu\text{g/kg}$ sunflower oil. It is present in heated butter approximately 50 times above its threshold, which suggests that it is the most important odorant in heated butter [45]. Due to their OAVs, 1-octen-3-one, methional, 2,5-dimethyl-4-hydroxy-3-(2*H*)-furanone and *trans*-4,5-epoxy-(E)-2-decenal were found to contribute to heated butter aroma. These results are in general qualitative agreement with those from Dickerson [61], who found 1-hexen-3-

one, 1-octen-3-one, methional, δ -octalactone, δ -decalactone, 2,5-dimethyl-4-hydroxy-3-(2*H*)-furanone, butanoic acid and skatole important for the aroma of heated butter. The quantitative results of Budin [45], obtained by isotope quantitation, are different from those of Dickerson [61], who found higher concentrations for 1-hexen-3-one, 2,5-dimethyl-4-hydroxy-3-(2*H*)-furanone and δ -octalactone using a sensory panel. Peterson and Reineccius [14] studied the key aroma compounds of heated butter, using static headspace analysis, and confirmed methional, (E)-2-nonenal, 1-hexen-3-one, 1-octen-3-one, δ -octalactone, δ -decalactone, 2,5-dimethyl-4-hydroxy-3-(2*H*)-furanone and skatole as potent odorants. In addition, they found hydrogen sulphide, methanethiol, acetaldehyde, diacetyl, 2-heptanone, dimethyl trisulphide, nonanal, butanoic acid, 3-methylbutanoic acid, δ -hexalactone and hexanoic acid. According to these authors,

Table 2 Odour-active compounds in heated cream sweet butter as determined by gas chromatography-olfactometry

No ^a	Compound	Odour quality	Concentration (µg/kg heated butter)
1	Acids		
	Butanoic acid	Buttery, sweaty, cheesy, rancid	353 ^b
	3-Methylbutanoic acid	Cheesy	39 ^b
	Hexanoic acid	Pungent, musty, cheesy, acrid	1137 ^b
4	Aldehydes		
	Nonanal	Waxy, fatty, floral	83 ^b
	Methional	Cooked potato	0.95 ^b , 2.8 ^c
5	(<i>E</i>)-2-Nonenal	Green, fatty, tallowy	43 ^b
14	(<i>E,E</i>)-2,4-Decadienal	Fatty	13 ^c
16	<i>trans</i> -4,5-Epoxy-(<i>E</i>)-2-decenal	Metallic	2.7 ^c
6	Ketones		
	2,3-Butanedione	Buttery	3.8 ^b
	2-Heptanone	Blue cheese	1294 ^b
15	1-Hexen-3-one	Vegetable-like	0.69 ^c
7	1-Octen-3-one	Mushroom-like	6 ^b , 98.7 ^c
8	Lactones		
	δ-Hexalactone	Creamy, chocolate, sweet aromatic	218 ^b
	δ-Octalactone	Coconut-like, peach	258 ^b , 578 ^c
	δ-Decalactone	Coconut-like, peach	2633 ^b , 5730 ^c
17	Miscellaneous compounds		
	2,5-Dimethyl-4-hydroxy-3-[2 <i>H</i>]-furanone	Sweet, caramel-like	233 ^b , 58.7 ^c
12	3-Methyl-1 <i>H</i> -indole (Skatole)	Mothball, fecal	24 ^b , 5 ^c

^a Numbers refer to Fig. 1^b Concentration determined by the standard addition method [14]^c Concentration determined by SIDA [45]

3-methylbutanoic acid (cheese-like odour), methional (potato-like), 2,5-dimethyl-4-hydroxy-3-(2*H*)-furanone (caramel-like) and 2-heptanone (blue-cheese) characterise the odour of heated butter. These compounds were not detected in fresh SwCB. On the other hand, odorants such as 2- and 3-methylbutanal, hexanal, γ -dodecalactone and DMS, found in the fresh SwCB, were not detected in heated butter. Ketones and especially lactones, which are present in fresh butter at subthreshold levels [62], show higher concentrations in heated butter and are hypothesised as being part of the pleasant flavour that is associated with many baked products containing butter. The aroma of heated butter as an ingredient in puff pastries was studied by Gas-senmeier and Schieberle [63] using AEDA. They reported δ -decalactone, (*E*)-2-nonenal, 4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone, butanoic acid, 3- and 2-methylbutanoic acid as the most potent odorants. The key odours of heated butter and their concentration, found in the different studies, are summarised in Table 2.

Butter off-flavours

The desirable and unique aroma of butter depends on a delicate balance of the concentrations of compounds

having a low odour threshold [4, 34]. Interactions between volatile and non-volatile compounds and the food matrix are also important. Any distortion of this balance by addition or deletion of aroma components can result in an off-flavour [4]. The development of off-flavours can go in parallel with loss of the nutritional quality (loss of vitamins, oxidation of unsaturated lipids) and sensory characteristics of butter and can lead consequently to significant economic losses [19].

Therefore, the identification and the origin of off-flavours in butter and butter oil have been the subject of several investigations [23, 64, 65] and reviews [19, 66–68]. Off-flavours in butter may have different origin and be related to lipid oxidation, lipolysis and microbial growth, occurring during butter manufacturing, packaging and storage. Transmitted off-flavours, caused by the transfer of substances from feed and environment into the butter, will also be discussed.

Oxygen induced off-flavours

Oxidised off-flavours in butter and dairy products have been described as cardboard-like, metallic, oily, fishy, painty and tallowy [69, 70]. These off-flavours originate from compounds produced during autoxidation of milk fat.

Autoxidation involves the conversion of unsaturated fatty acids, in the presence of oxygen, to hydroperoxides, which decompose into various flavourful compounds [67]. The autoxidation rate in butter depends on the fatty acid composition (e.g. linoleic acid oxidises ten times faster than oleic acid), presence of antioxidants (α -tocopherol, ascorbic acid and carotenoids) and pro-oxidants (peroxides and heavy metals). Pro-oxidants, like iron and copper ions, can be naturally present in butter or originate from the metal equipments used during butter manufacturing. The oxidation rate is also due to external factors, such as oxygen pressure, temperature, light exposure and moisture. The phospholipids that form the fat globule membranes, containing unsaturated fatty acids, are highly susceptible to oxidation. They may come into contact with prooxidants such as copper, especially present in the serum phase, because of their position at the fat/water interface [64, 71]. In the first phase of the autoxidation, molecular oxygen reacts with unsaturated fatty acids to produce hydroperoxides (primary oxidation products) and free radicals, both of which are very reactive. The primary products of autoxidation are odourless, e.g. linoleic acid hydroperoxides [72]. The reactive products of the initiation phase react with additional lipid molecules to form other reactive chemical compounds. The termination phase of the autoxidation leads to the formation of relatively stable compounds such as hydrocarbons, aldehydes and ketones. These compounds are secondary oxidation products and some of them are characterised by an intense odour, which can cause off-flavour at higher concentrations.

Different studies were accomplished about oxidised off-flavours formed in butter during prolonged storage. Badings studied the auto-catalytic oxidation of unsaturated fatty acids that causes flavour defects in butter during cold storage [64,71]. In these studies, van der Waarden [73] is referenced to be the first to present conclusive evidence that cold-storage defects in butter are caused by oxidative degradation of lipid components. Butter samples with “trainy” off-flavour were analysed by Badings who correlated odour thresholds and quantitative data of the potent odorants to explain their contribution to the butter off-flavour. Among the odour compounds present in trainy butter, at concentrations higher than their flavour threshold, there were: hexanal (green), heptanal (oily, putty), (*E*)-2-nonenal (tallowy, cucumbers), (*E,E*)-2,4-heptadienal (metallic, fried), (*Z*)-4-heptenal (creamy, putty), (*E,Z*)-2,4-decadienal (fried), (*E,Z*)-2,6-nonadienal (fresh cucumbers), 1-octen-3-ol (metallic) and 1-octen-3-one (mushroom). Badings explained that the precursors of

these compounds are arachidonic, linoleic and especially linolenic acid, which contribute most to the “trainy” flavour of cold-stored butter.

Hexanal, originating from autoxidation of linoleic acid often predominates in the volatile fraction of oxidised foods [72] and was chosen as an indicator of lipid oxidation in butter during storage [24]. (*E*)-2-Nonenal and 1-octen-3-one easily form by oxidation of linoleic acid [64]. The metallic off-flavour in butter can be explained by 1-octen-3-one and 1,5 (*Z*)-octadien-3-one [65, 74].

Widder [23] studied the off-flavour compound formation in BO by AEDA. This principle proved useful when comparing samples affected by off-notes and samples without odour defects [75]. The odour profiles of different samples, stored at 35 °C for 0, 42, 90 and 120 days, respectively, were compared. The results were consistent with the findings of Badings [64]. The dilution factors of (*E*)-2-nonenal, (*Z*)-2-nonenal, (*Z*)-4-heptenal and 1-octen-3-one increased proportionally with the storage period. The amounts of these compounds increased also in the presence of copper ions acting as pro-oxidants. They decreased when antioxidants, such as α - and γ -tocopherol, BHA and BHT were present.

Another AEDA study [22] showed that nine odour-active carbonyl compounds were responsible for off-flavours in BO, stored for 42 days at room temperature. Hexanal, (*Z*)-3-hexenal, 1-octen-3-one, (*Z*)-1,5-octadien-3-one, nonanal, (*Z*)- and (*E*)-2-nonenal, (*E,E*)-2,4-nonadienal, (*E,E*)-2,4-decadienal and in particular, 1-octen-3-one (FD = 1024), (*E*)-2-nonenal (256) and (*Z*)-1,5-octadiene-3-one (256) showed the highest FD factors.

Ullrich and Grosch [76] demonstrated that (*Z*)-1,5-octadiene-3-one originates from linolenic acid. Widder and Grosch [77] proved the formation of (*Z*)- and (*E*)-2-nonenal from autoxidised (*Z*)-9-hexadecenoic acid (palmitoleic acid). Their sensory study of BO led to the conclusion that a mixture of (*Z*)- and (*E*)-2-nonenal was responsible for the cardboard off-flavour [78]. The off-note was observed when the OAVs surpassed a value of 0.5 for each of the two nonenals. Further studies with and without antioxidants proved the two nonenals as suitable indicators for the cardboard-like off-flavour of BO.

Light-induced off-flavours

Off-flavour in butter and dairy products exposed to light can be generated by protein degradation, which causes burnt, cabbage and mushroom-like odours and by photo-induced lipid oxidation, yielding cardboard,

metallic, tallowy and oily off-notes [19]. Photo-oxidation takes place when photo-sensitisers such as riboflavin are activated in foods and react with a substrate like an amino acid or lipid, generating substrate radicals in the so-called photo-oxidation type I reaction. The sensitiser can also activate oxygen to its singlet state, which then starts a photo-oxidation type II chain reaction [72].

Methional, from photodecomposition of methionine, is mainly responsible, together with mercaptanes, for the light-activated flavour in dairy products [19, 79].

Grosch and co-workers [67] studied BO exposed to fluorescent light for 48 h, using AEDA. Under these conditions, BO developed green, strawy and fatty off-notes, which were mainly due to the formation of 3-methylnonane-2,4-dione derived from furan fatty acids, 4,5-epoxy-(*E*)-2-decenal and high concentrations of (*E*)-2-nonenal and (*E,E*)-2,4-decadienal. It is evident that the packaging of butter has a fundamental role in the protection against light and oxygen.

Heating-induced off-flavours

Heating-induced off-flavours have been described in dairy products [80] as cooked, burnt, sulphurous and caramelised. These off-flavours can be formed during pasteurisation at temperatures above 76.7 °C [81] or during high temperature treatment leading to a Maillard reaction.

Ellis and Wong [82] demonstrated that higher levels of lactones in BO are due to increased temperatures at prolonged heating times. Certain lactones can cause an undesirable coconut-like off-flavour [83]. Lee and co-workers [15] accomplished a study on SwCB, heated at 100, 150 and 200 °C for 5 h. The highest temperature determined an increase in the number of volatile compounds in butter. In particular aldehydes and ketones increased significantly at 200 °C, suggesting that lipid degradation was the major reaction occurring in butter during heating. Heterocyclic compounds including thiazoles, pyrroles and pyridines, were found in butter heated above 150 °C. These volatiles contribute significantly to the heated butter flavour because of their low odour thresholds [84]. However, the long heating period of 5 h used in this study does not compare to usual household or manufacturing processes. Gassenmeier and Schieberle [63] found 4,5-epoxy-(*E*)-2-decenal, having metallic odour, and (*E,Z*)-2,4-decadienal, which is fat and green smelling, as most important odorants in puff-pastries prepared with butter, baked for 12 min at 180 °C. They suggested that both aldehydes arise from peroxidation of linoleic acid during heating. The same authors reported

4,5-epoxy-(*E*)-2-decenal to be formed from 13-hydroxy-9,11-octadecadienoic acid and 9-hydroperoxy-10,12-octadecanoic acid, which are precursors isolated from thermally treated fat, such as baking shortening [85].

Lipolysis-induced off-flavours

Lipolysed off-flavours, often described as goaty or soapy, are caused by lipoprotein lipases, enzymes naturally present in the skim part of milk. The lipases are normally occluded by protein, e.g. casein micelles, preventing direct contact with the fat globules. When the double layer membrane protecting the fat globule is disrupted, by agitation or churning, lipolysis can take place causing rancid odour notes. These off-flavours are mainly due to the increase in free fatty acids [86, 87].

Schieberle and co-workers [48] analysed a sour cream butter manufactured traditionally in a farm by AEDA. The sample showed a rancid and sweaty odour, which was due to high concentrations of butanoic and hexanoic acids formed by lipolysis. The presence of lipases in butter can also be caused by external microbial contamination.

Apart from the development of off-flavour compounds, lipolysis can also reduce the churning efficiency of cream [88]. A pasteurisation process of at least 76.7 °C for 16 s is in general sufficient to prevent the lipolysis-induced off-flavour [89].

Microbial off-flavours

Microbial off-flavours in butter are the results of metabolites produced by microorganisms in the raw milk, prior to pasteurisation, or due to successive contaminations, occurring during manufacturing and storage.

Musty off-flavour in cream or butter is often due to 2-methoxy-3-alkylpyrazine produced by *Pseudomonas taetroleus*, which is a psychrotrophic strain [90]. Malty off-flavour is occasionally found in butter caused by the production of 3-methylbutanal and 2-methylbutanal by *Streptococcus lactis* var. *maltigenes* [91]. The presence of yeasty off-flavour in butter is the evidence that inferior microbiological quality cream was used [19].

The pasteurisation destroys bacteria responsible for microbial off-flavour; nevertheless heat-resistant bacteria lipases may remain active producing off-flavours [19]. In butter, the microbiological development is generally limited, due to the presence of a strongly dispersed water phase [92] and low storage temperature. The microbial-related off-flavours can be prevented by the use of good-quality sweet cream with proper sanitation during storage and processing [19].

Taint off-flavours

These off-flavours can be carried over into the butter from the environment, via the milk [93] or directly by external flavour absorption [19].

Off-flavours in dairy products originating from animal feeding can cause serious aroma defects. Among the feeds that are known to transfer off-flavours to milk products are fermented silage, musty hay or silage [94] and alfalfa. They contain (*E*)-2-hexenal, (*E*)-3-hexenals and (*E*)-3-hexenols [95], which impart a green flavour to dairy products.

Butter tainted by the cruciferous weed *Coronopus didymus* L. in feedstock is reported to contain sulphur compounds, such as benzylmethyl sulphide, benzyl sulphide, benzyl isothiocyanate, benzyl cyanide, indole and skatole. In particular, benzylmethyl sulphide and benzyl sulphide were considered the principal contributors to the weed off-flavour [5].

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