Cheese Acids

Chemistry and application in flavor

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4-Methylnonanoic acid (FEMA# 3574, CAS# 45019-28-1) (**F-1**) occurs in heated lamb (mutton) and cheeses such as Pecorino Romano, and it has a fatty, meaty odor. Dating back to ancient Roman times, Pecorino Romano is one of the world's oldest recorded cheeses. *Pecorino* is an Italian word meaning from sheep's milk, and Romano indicates that this cheese is of Roman descent. The majority of Pecorino Romano is made in Lazio, Tuscany or Sardinia between November and June. These three regions have very similar pastures and breeds of sheep, ensuring consistent flavor and quality[b].

4-Methylnonanoic acid is one of the major contributors to the so-called "soo" odor of mutton, which is an unpleasant, fatty-goaty type note. It can be used in cooked lamb and mutton flavors for bakery and snack foods at 10 ppm, meat and dairy products at 5 ppm, and in soups and gravies at 2.5 ppm. Normal use levels in finished consumer product are up to 10 ppm[c].

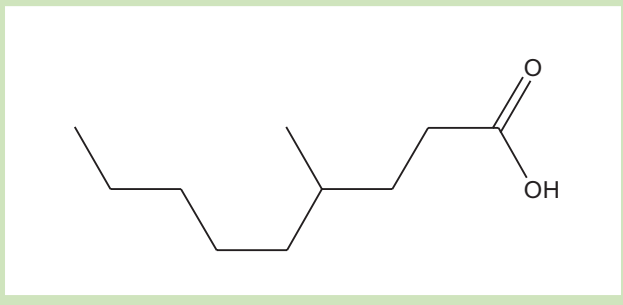
The formation of typical cheese flavors during natural ripening processes is not fully understood, but the majority of reactions last for an extended period of months and comprise oxidative, inter- and intramolecular, enzymatic or microbial reactions. Substrates are partially very reactive milk-based ingredients that are mainly transformed to volatile flavor-intensive compounds like esters, methyl-ketones, aldehydes, lactones, carboxylic acids and sulfur-containing products.

The effect of enzymes on flavor enhancement is also not fully understood, both in the intensity and in the characteristic odor notes. Aliphatic monoketones in flavors, their chemistry and application in flavor have been reviewed elsewhere.[1] This article is dedicated to the branched carboxylic acids in ewe's milk.

There are 30 different carboxylic acids identified in ewe's milk, of which the saturated branched acids are seen in **F-2**[d,e]. Additional three-branched acids with an incompletely defined substance occurring in ewe's milk are: methyldecanoic acid (CAS# 77017-96-0), methylheptanoic acid (CAS# 91433-72-6) and dimethyloctanoic acid (CAS# 82430-11-3).

(Continued on Page 35)

4-Methylnonanoic acid **F-1**



Physical Data for 4-Methylnonanoic acid[a]

Appearance: Colorless to pale yellow liquid

Molecular weight: 172.3

Molecular formula: $C_{10}H_{20}O_2$

Refractive index (n^{20}/D): 1.435–1.440

Specific gravity (D^{20}): 0.900–0.907

Boiling point: 292°C

Flash point: 116°C

[a] Data taken from Endeavour Specialty Chemicals Ltd. specifications.

[b] *www.igourmet.com/shoppe/prodview.aspx?prod=1962S* (Accessed Jan 5, 2012)

[c] Description from Treatt PLC.

[d] Information from VCF 00 Database Report, BACIS, The Netherlands; data by TNO, The Netherlands.

[e] Most information on organoleptic properties and uses (unless otherwise noted) are taken from FRM 2001 *Database of Flavour Raw Materials*, Boelens Aroma Chemicals Information Services, The Netherlands.

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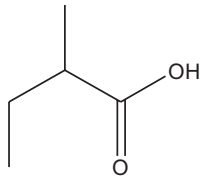
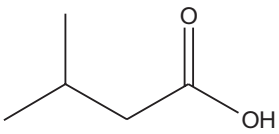
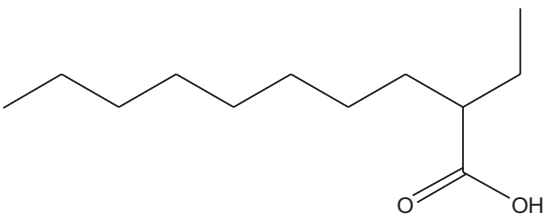
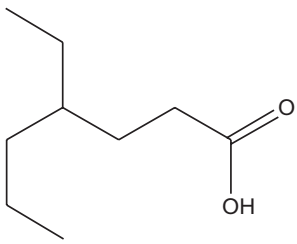
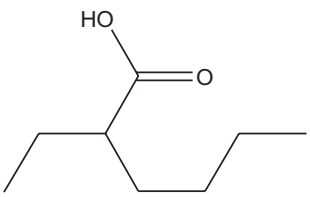
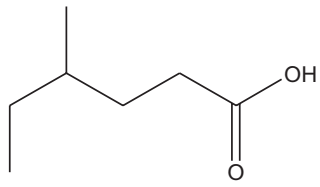
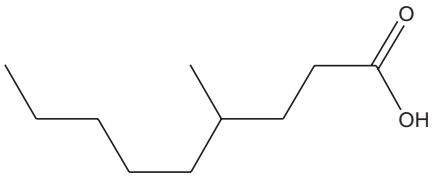
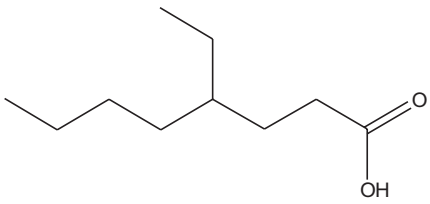
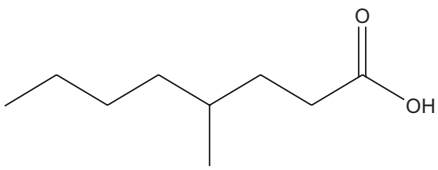
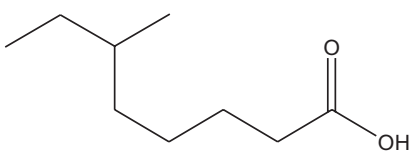
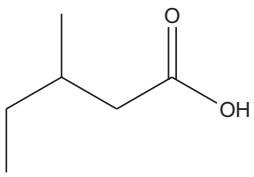
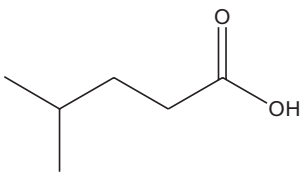
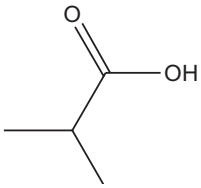
Structure/Name (FEMA# [if applicable], CAS#)	Occurrence	Organoleptic characteristics	Applications in flavors
 2-Methylbutanoic acid (FEMA# 2695, CAS# 116-53-0)	Widely found in nature—fruits, dairy, alcoholic and meat products	Fruity, sour, cheesy in dilution, acidic, sweaty, berrylike	Fruity, dairy flavorings; strawberry, cheese, raspberry and tropical nuances
 3-Methylbutanoic acid (FEMA# 3102, CAS# 503-74-2)	Butter, cheese	Acidic, cheeselike	Dairy flavorings
 2-Ethyldecanoic acid (CAS# 2874-76-2)		Soapy-waxy, slightly citrus, slightly woody[2]	
 4-Ethylheptanoic acid (CAS# 132735-95-6)		Hircine (goaty)[3]	
 2-Ethylhexanoic acid (CAS# 149-57-5)	Grape, papaya, raspberry, citrus, wine, beer, tea, mango, rice	Sour, caprylic	Fruity, citrus and alcoholic beverage flavorings

Carboxylic acids identified in ewe's milk

F-2 (cont.)

Structure/Name (FEMA# [if applicable], CAS#)	Occurrence	Organoleptic characteristics	Applications in flavors
 4-Methylhexanoic acid (CAS# 1561-11-1)	Cheese, lamb, mutton	Sourish, cheeselike connotation	Dairy, cheese and meat flavorings
 4-Methylnonanoic acid (FEMA# 3574, CAS# 45019-28-1)	Heated lamb (mutton)	Fatty, meaty	Meat (lamb) flavorings
 4-Ethyloctanoic acid (FEMA# 3800, CAS# 16493-80-4)	Cheese, mutton, lamb, costus root oil	Powerful animal character, goat-like; on extreme dilution (<0.1%) reminiscent of costus root	Dairy and cheese flavorings
 4-Methyloctanoic acid (FEMA# 3575, CAS# 54947-74-9)	Heated lamb (mutton)	Fatty, meaty, caprylic, waxy, creamy, lactonic with metallic nuances (at 20 ppm)	Dairy flavorings such as cheese, cream, butter and condensed milk
 6-Methyloctanoic acid (CAS# 504-99-4)	*Not applicable*		

Carboxylic acids identified in ewe's milk **F-2 (cont.)**

Structure/Name (FEMA# [if applicable], CAS#)	Occurrence	Organoleptic characteristics	Applications in flavors
 3-Methylpentanoic acid (FEMA# 3437, CAS# 105-43-1)	Apple, citrus oils, grape, etc.	Sour, cheeselike, fresh with fruity notes	Fresh top note for fruits, apple, strawberry and cheese flavorings
 4-Methylpentanoic acid (FEMA# 3463, CAS# 646-07-1)	Fruits, baked, dairy, roasted meat products	Pungent, cheeselike	Cheese flavorings
 2-Methylpropanoic acid (FEMA# 2222, CAS# 79-31-2)	Widely found in nature—fruits, cereals, alcoholic and meat products	Sour, caprylic, buttery, cheeselike, acidic, sour dairy, creamy, cultured dairy nuance (at 15 ppm)	Cheese, starter culture, caramel and butterscotch flavorings

(Continued from Page 30)

4-Methylnonanoic acid can be prepared by condensation of heptanal with pyrrolidine (FEMA# 3523, CAS# 25150-61-2) followed by addition of methyl acrylate (CAS# 96-33-3), hydrolysis and reduction (**F-3**).[4]

Due to the chiral center at position four, there are two enantiomers: (4S)-4-methyl-nonanoic acid (CAS# 128342-72-3), which has a more intensive odor than the (R)-enantiomer, reminiscent of mutton and goat. The (4R)-4-methylnonanoic acid (CAS# 124918-65-6) enantiomer has a weak, sweaty odor (**F-4**).[5]

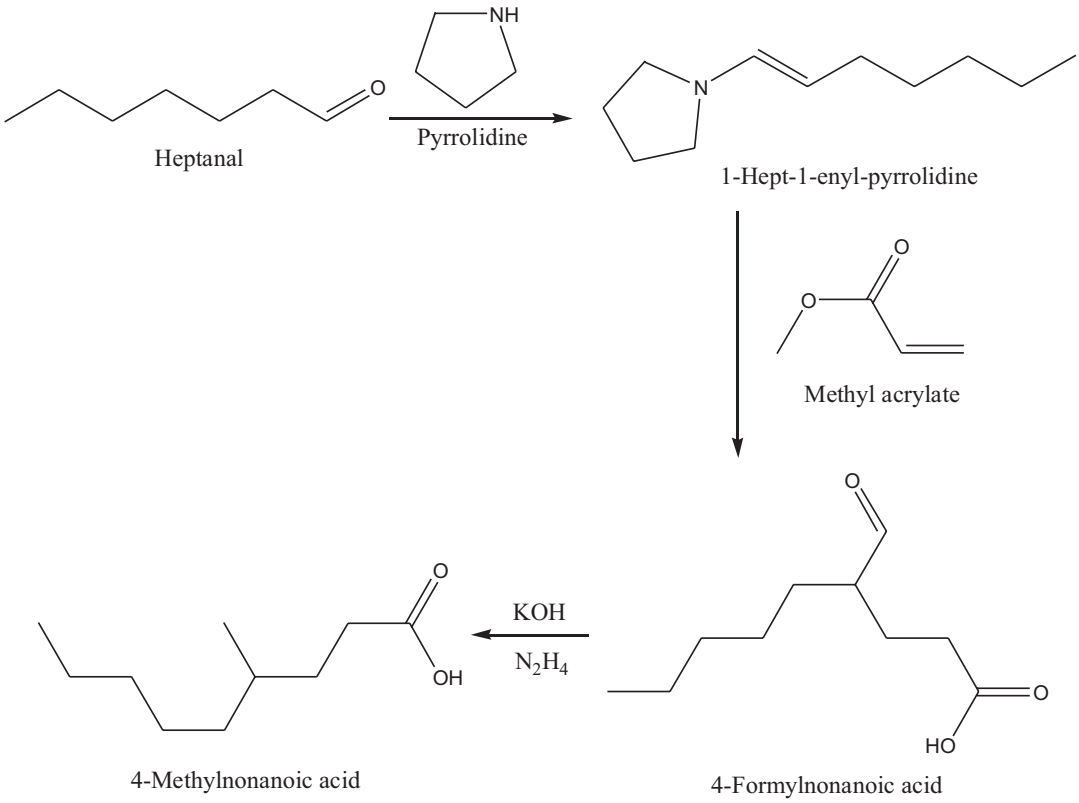
Cheese Flavors

Lipases derived from *mucor*-type molds play an important role in the manufacturing of cheese flavor concentrates (enzyme-modified cheese). Such natural flavor concentrates are used in dosages of 0.5–2.5% for cheese spreads, cheese pastry, cheese sauces and cheese-containing finished meals.[6] The use of enzyme-modified cheese flavors reduces the added amount of cheese by up to 90%, and therefore effects a significant price reduction in the end products. It is also possible to manufacture complex cheese flavors by fermentation of raw materials of cheese processing with defined microorganisms.

Roquefort and other blue cheese flavors fermented by the mold *Penicillium roqueforti* are currently in commercial production. This blue cheese mold is fermented in suspension in the submerged technique. Milk, whey or lipase-modified butterfat may serve as substrates. *Penicillium roquefortii* produces a protease and different lipases that also may be applied in isolated and purified form. The fermentation lasts several days and produces mainly methyl ketones and secondary alcohols with five to eleven carbon atoms. Important representatives are 2-hexanone (CAS# 591-78-6; fruity with a fungi undertone, somewhat meat- and butterlike), 2-heptanone (FEMA# 2544, CAS# 110-43-0; green fruity, spicy,

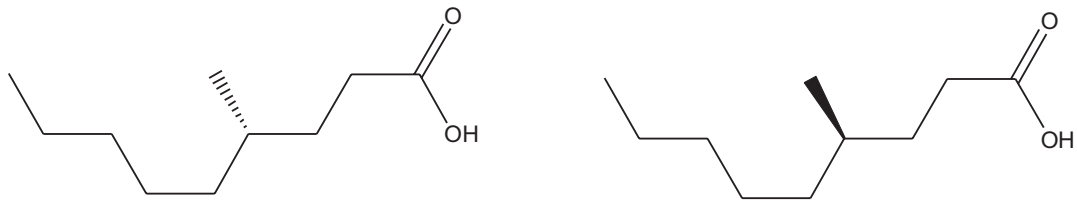
4-Methylnonanoic acid preparation by condensation of heptanal with pyrrolidine, followed by addition of methyl acrylate, hydrolysis and reduction

F-3



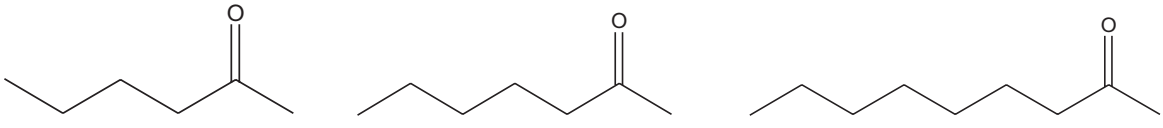
(4S)-4-Methylnonanoic acid and (4R)-4-methylnonanoic acid

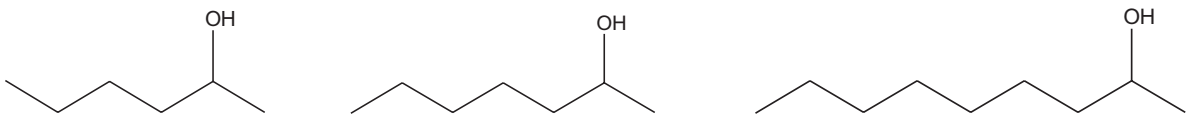
F-4



2-Hexanone, 2-heptanone and 2-nonanone

F-5





cinnamonlike, cheesy, coconut, waxy), 2-nonanone (FEMA# 2785, CAS# 821-55-6; green fruity, dairy, cheesy, buttery)(**F-5**), as well as the corresponding alcohols 2-hexanol (CAS# 626-93-7; mildly fermented, slightly fruity-fatty), 2-heptanol (FEMA# 3288, CAS# 543-49-7; mild, fresh, slightly oily, fatty) and 2-nonanol (FEMA# 3315, CAS# 628-99-9; waxy, soapy, musty with green fruity and dairy nuances)(**F-6**).

The isolation of the reaction mixture consisting mostly of volatile flavor substances is achieved after fermentation and heat activation of the mold-borne enzymes, e.g. by distillation and extraction. Gas chromatograms of the obtained flavor extracts compared with the flavor substances of naturally manufactured Roquefort cheese show a very good correlation in composition and concentration of the taste-delivering ingredients.[7] The blue mold flavor extracts are used mainly in the flavoring of cheese spreads or cheese-containing finished menus. Some other cheese flavors (provolone, Emmentaler and other miscellaneous cheesy flavor notes) can be obtained by fermentation of edible fats by means of microorganisms that are producing butter or propionic acid.

There is some experience concerning other milk and plant fats that may be fermented by microorganisms only on a laboratory scale. Examples are butter flavors' generation of diacetyl and acetoin by suitable bacteria cultures, which are derived from milk (*Streptococcus diacetylactis* and *Leuconostoc citrovorum*). Today, buttery flavors are especially important for dietetic foods, like fat-reduced butter, or for the fortification of plant fats, such as margarine.[8]

References

1. M Zviely, Aliphatic Monoketones, *Perfum Flavor*, 36(4), 46 (2011)
2. AM Pearson and TR Dutson (eds.), "Quality Attributes and Their Measurement in Meat, Poultry and Fish Products," *Advances in Meat Research* series, 9, Aspen Publishers, New York, 235 (1995)
3. TD Wyat, *Pheromones And Animal Behaviour: Communication By Smell And Taste*, Cambridge University Press, Cambridge, UK, 292 (2003)
4. W Jia, A Su, H Cao, and Z Wang, CN Pat 101786950 A 20100728, assigned to Faming Zhuanli Shenqing (2010)
5. V Karl, J Gutser, A Dietrich, B Maas and A Mosandl, Stereoisomeric flavour compounds LXVIII. 2-, 3-, and 4-alkyl branched acids, part 2: chirospecific analysis and sensory evaluation. *Chirality*, 6(5), 427–434 (1994)
6. GJ Moskowitz and SS Noelck, Enzyme Modified Cheese Technology. *J Dairy Sci*, 70, 1761–1769 (1987)
7. B Kunz, Trends in der Lebensmittelbiotechnologie. *Lebensmitteltechnologie*, P Czermak (ed.), GIT-Verlag, Darmstadt, Germany (1993)
8. H Ziegler (ed.), *Flavorings Production, Composition, Applications, Regulation*, Edit, H Ziegler, Wiley-VCH Verlag GmbH & Co. KGaA, Weinham, Germany (2007)

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