HETEROCYCLIC CONSTITUENTS OF MEAT AROMA

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Heterocyclic compounds play an important role in roasted flavors and particularly in meat products. They result from non-enzymatic browning reactions between carbohydrates and aminoacids. Some have interesting organoleptic properties and very low thresholds. This review describes all volatile heterocyclic constituents identified in the flavor of meat and meat-related products.

Among about 3,000 known constituents of aroma,[1] *heterocyclic compounds deserve particular attention. They generally originate from odorless precursors of mostly high molecular weight, either enzymatically or - more frequently - by the action of heat. Accordingly, we come across these "breakdown" flavors in our daily food, consumed after cooking, baking or roasting. It is during this processing that heterocyclic compounds tend to be formed in large numbers* (Table I).

TABLE I. Distribution of heterocyclic volatiles in food flavors[2]

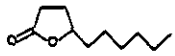
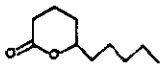
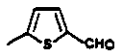
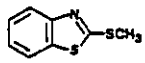
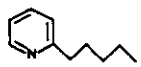
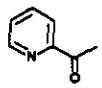
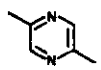
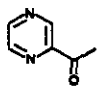
kinds of aroma	number of constituents identified		
	total	heterocycles	
roasted coffee	540	310 =	57%
roasted sesame seed	67	32	48%
roasted filberts	232	95	41%
processed meat	600	223	38%*
heated pork meat	281	96	34%
roasted peanuts	279	92	33%
cocoa	386	124	32%
tea	339	100	29%
potato chips	147	40	27%
peach	78	13**	17%
cooked chicken	183[3]	18	10%
pear	127	0	0
banana	226	0	0
cabbage	74	0	0

* this review

** essentially lactones

Owing to their characteristic odor, heterocycles contribute significantly to the flavor principle of processed foods. In fact, the potency of numerous heterocycles is such (Table 2) *that even in trace amounts their effect becomes fully apparent. Two recently published review articles discuss their relevance in the most important foodstuffs.*[4,5]

TABLE 2. Odor threshold data of meat aroma constituents (ppb in water)

	2-methylfuran (2)	3500 [6]
	2-[(methyldithio)methyl]furan (31)	0.04 [7]
	4-hydroxy-2,5-dimethyl-3(2H)-furanone (35) (FURANEOL®)	0.04 [8]
	maltol (36)	35000 [9]
	γ-*decalactone* (44)	88 [10]
	δ-decalactone (61)	160 [10]
	5-methyl-2-formylthiophene (84)	1 [11]
	2-acetylthiazole (143)	10 [11]
	2-acetyl-2-thiazoline (149)	1.3 [12]
	2-methylthiobenzothiazole (145)	5 [13]
	3,5-dimethyl-1,2,4-trithiolane (103)	10 [11]
	2-pentylpyridine (156)	0.6 [14]
	2-acetylpyridine (162)	19 [12]
	2,3-*dimethylpyrazine* (169)	400 [15]
	2,5-dimethylpyrazine (171)	1800 [16]
	2-acetylpyrazine (194)	62 [12]

At present, one of the most important problems in flavor chemistry is the investigation of meat aromas. Indeed, complete knowledge of their constituents would allow the creation of true-to-nature flavors and thus development of novel foodstuffs. These, in turn, are essential for an efficient control of undernourishment in general, and lack of proteins in particular, from which two billions of the world's population are at present suffering. There has been great progress, judging by the achievments of the past 10 years, but further efforts will be necessary in order to approach a solution to the problem. The aim of this report is not only to give a complete survey of the latest activities in meat-related heterocycles but to stimulate individual efforts in this particular field.

The exacting task of systematically investigating the substances responsible for the aroma of processed meat products (beef, pork, lamb and poultry for instance), could not be approached successfully before modern analytical procedures had reached a high level of sophistication. It is therefore no surprise that references on aroma constituents of products related to meat were practically non-existent before 1960. Several reviews sum up the extensive research in this field during the past 18 years.[17-23]

Meat aroma cannot be attributed to a single compound or a particular class of compounds. Indeed, the odor profile of a meat product is rather a sum of all the sensory effects produced by a large number of volatiles of different structures, present in a particular quantitative proportion. Past investigations, however, leave no doubt that heterocyclic compounds contribute significantly to the aroma impression of meat.

Of about 600 constituents known[24] *223 are heterocycles belonging to 26 dif-*

ferent basic skeletons (Fig. 1). *This paper reviews all the heterocycles discovered so far in meat-related flavors, classifying them by structural groups.*

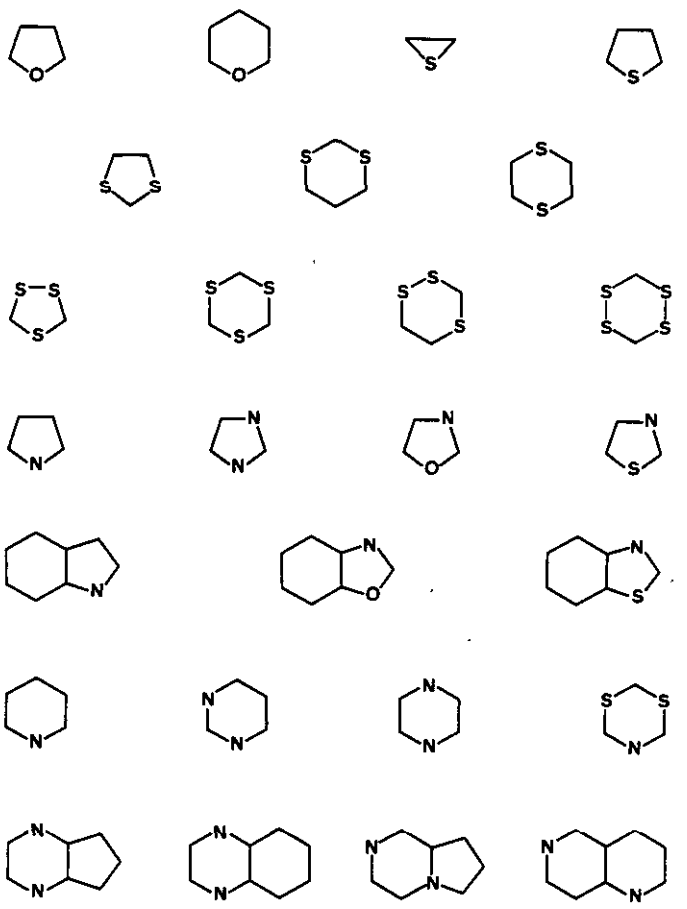


FIGURE 1. Basic skeletons of heterocyclic compounds found in meat flavors

Cyclic ethers are found in all food aromas which are produced in the course of a thermal process. Among these non-enzymatic "browning flavors"[25,26] the furanoid compounds occupy a privileged position, owing to their wide distribution and the diversity of their structures. They are usually formed by degradation of carbohydrates.[27,28] In coffee aroma alone 85 different furan derivatives have been found,[29,30] while the volatile part of bread containes 25[6] and caramel 37[31] representatives of this class.

Until 1967 furanoid compounds had not been reported to be present in the aroma of meat products.[32] Since then, 32 compounds of this class have been found in meat aroma (1 - 32) among which 18 compounds carry functional groups (15 - 32). Furan derivatives are found among the volatiles of boiled,[36] roasted[37] and canned beef[33] as well as in the aroma of cooked chicken.[21,32] The 23 furans from cooked port liver even amount to 29% of all its aroma constituents, next to the pyrazines (41%), they are the most frequently occurring class of compounds.[34]

As a rule, furan derivatives are considered to be important aroma constituents from a sensory point of view, and 60 of them have been admitted as food additives for human consumption in the USA as shown in the FEMA GRAS* list.[41] Furans that do not contain sulfur are mainly associated with a sweet, fruity, nutty and caramel-like odor impression,[4] none of them being meaty, so, although they are not considered to contribute significantly to the basic meaty aroma, they could contribute to the overall odor of broiled or roasted meat.[42] 2-Pentylfuran 7, presumably formed by autoxidation of 2(*E*),4(*E*)-decadienal,[32] is described as having a sweet and pungent odor.[33] In vegetable oil at concentrations up to 10 ppm it imparts a beany and grassy flavor impression.[17] The sensory value of furan deriva-

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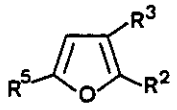
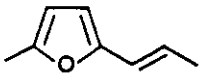
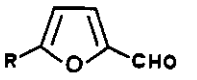
* FEMA = Flavoring Extract Manufacturers Association
GRAS = Generally Recognized as Safe



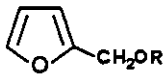
1 R^2,R^3,R^5 = H [33]
2 R^2 = CH_3; R^3,R^5 = H [32,33]
3 R^3 = CH_3; R^2,R^5 = H [33]
4 R^2 = C_2H_5; R^3,R^5 = H [32,34,35]
5 R^2 = C_3H_7; R^3,R^5 = H [32,33]
6 R^2 = C_4H_9; R^3,R^5 = H [32-34]
7 R^2 = C_5H_{11}; R^3,R^5 = H [32,36]
8 R^2 = C_6H_{13}; R^3,R^5 = H [32,37]
9 R^2 = C_7H_{15}; R^3,R^5 = H [32,37]
10 R^2 = C_8H_{17}; R^3,R^5 = H [37]
11 R^2,R^5 = CH_3; R^3 = H [33]
12 R^2=CH_3; R^5 = C_2H_5; R^3 = H [33]
13 R^2 or R^3 = C_6H_5; R^5 = H [34]



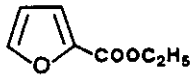
14 [33]



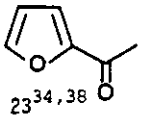
15 R = H [34]
16 R = CH_3 [34]



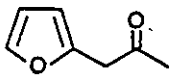
17 R = H [34]
18 R = COH [34]
19 R = $COCH_3$ [34]
20 R = COC_4H_9 [34]
21 R = COC_5H_{11} [34]



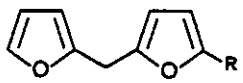
22 [34]



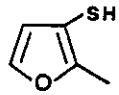
23 [34,38]



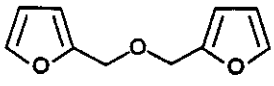
24 [34,39]



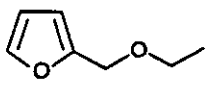
25 R = H [34]
26 R = CH_3 [34]



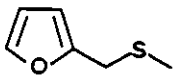
27 [40]



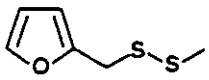
28 [34]



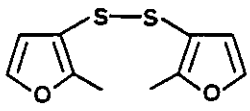
29 [34]



30 [34]



31 [34]



32 [40]

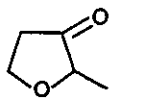
tives generally increases when further functional groups are introduced into the furan ring. The odor of 5-methyl-2-furaldehyde **16** is described as burnt, caramel-like and slightly meaty.[4] On the other hand, 1-(2-furyl)-propan-2-one **24** is said to have a rum-like smell. According to another source, the odor and taste of **24** is suggestive of radish.[43] The organoleptic properties of ethyl 2-furoate **22** are characterized as burnt, buttery and vanilla-like.[4] A certain importance is attributed to the two ketones **23** and **24** in the development of the complex sensation of the shallow-fried beef flavor.[39]

Sulfur-containing furanoids are formed through the thermal interaction of S-amino acids and carbohydrates. As a rule, in the pure state they possess a penetrating odor resembling burnt rubber which turns into a pleasant roasted note at high dilution. Furfuryl methyl disulfide **31**, for instance, identified in pressure-cooked pork liver[34] is the character impact compound of fresh white bread crust.[7]

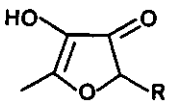
A wrong interpretation of spectral characteristics has led to the conclusion that "5-thiomethylfurfural" (the correct name should be 5-methylthiofurfural) was a constituent of boiled beef flavor.[36,44] This erroneous structural hypothesis was unfortunately considered as a certain identification in later articles.[45,46] A comparison with an authentic sample of 5-methylthiofurfural prepared in our laboratories[47] has definitly invalidated this hypothesis.

Furans do not solely contribute to the acceptance of an aroma but can also develop unpleasant sensory properties as soon as, due to external influences, they occur in a disproportionately high quantity compared with the remaining aroma constituents. During storage of canned beef, for instance, 2-ethylfuran **4** is relatively stable, whereas other flavor components are altered so that as a re-

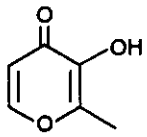
sult the undesirable odor qualities "acid, sour" and "whey butter-like" are strengthened.[35] 2-Pentylfuran 7 on the other hand is believed to be responsible for the characteristic off flavor of reverted soybean oil.[48]



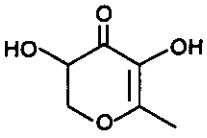
33 [34,44,49]



34 R = H [50]
35 R = CH_3 [50]



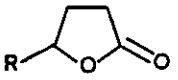
36 [47]



37 [51]

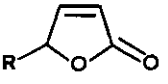
Compound 33 is the only tetrahydrofuran derivative which was found in meat products.[34,44] 2-Methyltetrahydrofuran-3-one 33 is widely distributed in roasted and manufactured products such as bread, coffee, peanuts, potato chips and rum. It has also been identified in tomatoes.[52] 4-Hydroxy-5-methyl-3(2H)-furanone 34 and its homolog 35 are important flavor constituents isolated from beef broth.[50] The sensory impression of 35 has been described as caramel-like,[53] burnt pineapple,[54] which turns into a strawberry-like note as dilution increases.[55] The odor of 34 is reminiscent of roasted chicory root[50] with an unmistakable undertone of maple sirup.[55] Compound 35, which was introduced on the market under the trade name FURANEOL®, was detected in the aromas of pineapple,[54] strawberry,[55] roasted almond,[56] sponge cake[57] and arctic bramble.[58] The pyrone derivative maltol 36, recently found in roasted beef flavor,[47] was already discovered in 1894 as one of the character impact compounds in malt.[58,59] Since then identified as an important flavor constituent in various thermally processed foodstuffs,[60] it serves as a standard of caramel odor. 2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one 37 has recently been detected in cooked meat.[51]

® = Registered trade mark of Firmenich SA.

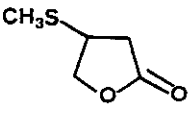


38 R = H [37]
39 R = CH_3 [36,37]
40 R = C_2H_5 [61,62]
41 R = C_3H_7 [37,61,63,64]
42 R = C_4H_9 [21,61,63,64]
43 R = C_5H_{11} [61,63]
44 R = C_6H_{13} [61,63,64,65]
45 R = C_7H_{15} [61,63]
46 R = C_8H_{17} [61,63,65]
47 R = C_9H_{19} [63]
48 R = $C_{10}H_{21}$ [63,64,65]
49 R = $C_{11}H_{23}$ [63]
50 R = $C_{12}H_{25}$ [63,65]

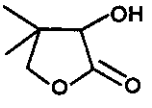
51 [66]



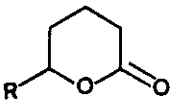
52 R = H [47]
53 R = C_2H_5 [47]



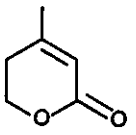
54 [24]



55 [24]



56 R = H [37]
57 R = CH_3 [63]
58 R = C_2H_5 [37]
59 R = C_3H_7 [37]
60 R = C_4H_9 [37,61]
61 R = C_5H_{11} [61,63,65,67]
62 R = C_6H_{13} [63]
63 R = C_7H_{15} [61,63,65,67]
64 R = C_8H_{17} [63]
65 R = C_9H_{19} [61,63,65,67]
66 R = $C_{10}H_{21}$ [63]
67 R = $C_{11}H_{23}$ [63,67]
68 R = $C_{13}H_{27}$ [65]

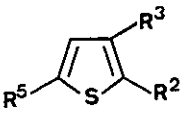


69 [24]

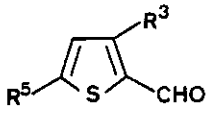
Lactones are known as being associated with meat aromas of all kinds. Among the γ-lactones are found all the normal members ranging from butyrolactone **38** to γ-hexadecalactone **50**. In the δ-series the complete range was observed even

up to δ-octadecalactone **56** - **68**.[61-63,65] Model experiments have shown that the lactones originate from the fat portions of the most varied sorts of meat. Either they occur preformed as 4- and 5-hydroxy fatty acids in their glycerides or they are formed by oxidative degradation from unsaturated long chain fatty acids.[61,65] Saturated fatty acids, aldehydes and alcohols can also serve as precursors.[68] The mechanism of the formation of lactones have been explained in a series of reviews.[69-71]

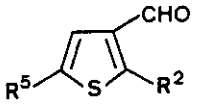
Saturated aliphatic lactones are widely distributed in aromas of foods of animal or vegetable origin.[72] Their characteristic and potent organoleptic properties, rather fruity and flowery, give rise to a certain freshness and in most cases an agreeable note. The odors of corresponding γ- and δ-lactones are essentially very similar and differ mostly in nuances only. Thus, the odor of γ-decalactone is characterized as "oily, peachy, nut-like", whereas δ-decalactone is described as "sweet, creamy and nut-like".[73] Among the unsaturated lactones only (Z)-6-dodecen-4-olide **51** has been reported to occur in lamb aroma from animals fed a lipid-protected dietary supplement, and is considered to be largely responsible for the sweet flavor note of that particular meat.[66] Recently, the two butenolides **52** and **53** as well as anhydromevalolactone **69** were isolated from roasted beef aroma.[24] β-Methylthio-γ-butyrolactone **54** found in the same type of flavor is presumed to be generated by the addition of methanethiol to 2-butenolide **52**. Lactone **54** is described as having a characteristic sulfur-like note of onions.[24] Pantolactone **55**, presumambly a degradation product of pantothenic acid and previously identified in Spanish sherry[74,75] is relatively abundant in the neutral fraction of beef aroma.[24]



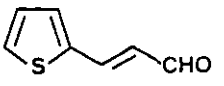
70 R^2,R^3,R^5 = H [33,76,77]
71 R^2 = CH_3; R^3,R^5 = H [33,34,76]
72 R^3 = CH_3; R^2,R^5 = H [33]
73 R^2 = C_2H_5; R^3,R^5 = H [76]
74 R^2 = n-C_4H_9; R^3,R^5 = H [76]
75 R^2 = t-C_4H_9; R^3,R^5 = H [78]
76 R^3 = t-C_4H_9; R^2,R^5 = H [78]
77 R^2 = C_5H_{11}; R^3,R^5 = H [33,76]
78 R^2 or R^3=C_8H_{17}; R^5 = H [76]
79 R^2 or R^3=$C_{14}H_{29}$; R^5 = H [76]
80 R^2 or R^3=CH_3; R^5 = H [33]
81 R^2,R^5= CH_3; R^3 = H [33]



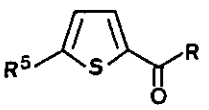
82 R^3,R^5 = H [34,36,44]
83 R^3 = CH_3; R^5 = H [34]
84 R^5 = CH_3; R^3 = H [34,76]



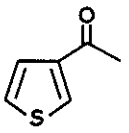
85 R^2,R^5 = H [34,76]
86 R^2,R^5 = CH_3 [34,76]



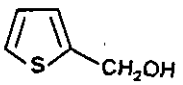
87 [34,76]



88 R = CH_3; R^5= H [34,76]
89 R,R^5 = CH_3 [34,76]
90 R = C_2H_5; R^5= H [76]
91 R = C_2H_5; R^5= CH_3 [76*]



92 [34,76]

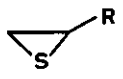


93 [76]

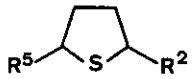
* *tentatively identified*

Although discovered as late as 1967 as aroma constituents in processed foodstuffs, the thiophenes already play a certain role as artificial flavoring agents.[79] During the last decade 24 individual components of this type (**70 - 93**) were detected in meat-related products alone. This class of compounds also occurs in black tea and coffee aroma, various onion products, and the aroma of various nut products.[5]

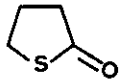
Although the thiophenes are considered to be odorants of unusually high potency, quantitative investigations have not yet been performed. However, it is significant that a usage level of 0.5 ppm is recommended for 5-methyl-2-thiophene-carboxaldehyde **84**, a compound having a cherry-like odor.[80] The odor of the 3-substituted aldehyde **83** is said to be reminiscent of saffron and that of the unsubstituted aldehyde **82** of benzaldehyde.[80] The odor of 2-acetylthiophene **88** in a syrup (1 g/100 l) has been described as onion-like, whereas in coffee it develops a malty, roasted note. In a syrup its homolog **90** is perceived as creamy and caramel-like.[80] The odor properties of alkyl-substituted thiophenes are normally described as being reminiscent of fried onions.[81]



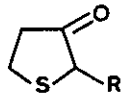
94 R = H [33]
95 R = CH_3 [33]



96 R^2 = CH_3; R^5 = H [78]
97 R^2,R^5 = CH_3 [78]



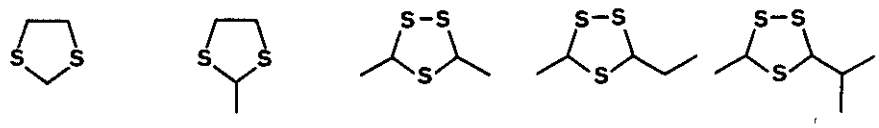
98 [47]



99 R = H [76]
100 R = CH_3 [76]

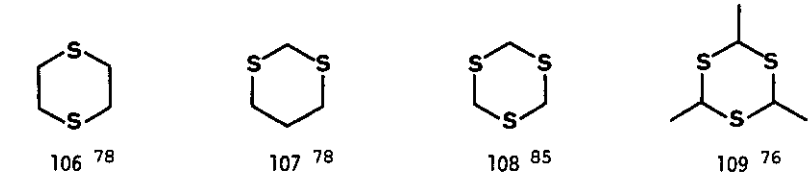
The cyclic sulfur compounds of non-aromatic nature **94** - **100** seem to be characteristic of some particular meat preparations. Thus, ethylene sulfide **94** and propylene sulfide **95** were found in canned beef,[33] the two tetrahydrothiophenes **96** and **97** in cooked meat[78] and the corresponding carbonyl derivatives **99** and **100** in pressure-cooked beef.[76] γ-Thiobutyrolactone **98** was detected in a commercial meat extract.[47] The lowest member (**94**) of the cyclic sulfur compounds is said to produce an odor impression of cooked cabbage.[33]

Among the five-membered cyclic poly-sulfur compounds, **101** - **103** were detected in boiled meat,[78,82] and 3-ethyl-5-methyl-1,2,4-trithiolane **104** and 3-isopropyl--5-methyl-1,2,4-trithiolane **105** occur in the aroma of beef extract,[24] all tri-

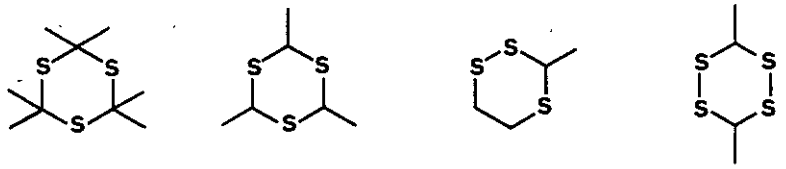


101 [78] 102 [78] 103 [82] 104 [24] 105 [24]

thiolane derivatives existing as diastereoisomers. When first discovered, 3,5-dimethyl-1,2,4-trithiolane **103** was described as having a characteristic odor of boiled beef[82] although this opinion was later questioned.[44] Trithiolane **103** is easily synthesized by reaction of acetaldehyde with sulfur and hydrogen sulfide in the presence of a primary amine.[83] This reaction is probably similar to that which takes place spontaneously in foodstuffs, since it was recently shown that the trithiolane derivative **103** results from the oxidation of bis-(1-mercaptoethyl)sulfide which is a key product formed in the reaction of acetaldehyde with hydrogen sulfide.[84]



106 [78] 107 [78] 108 [85] 109 [76]

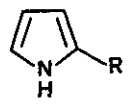


110 [76] 111 [14,76,86] 112 [24] 113 [87]

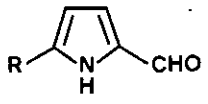
1,3-Dithiane **107** and 1,4-dithiane **106**[78] also occur in various sorts of beef aroma as do the two 1,3,5-trithianes **109** and **110**[76] and 3-methyl-1,2,4-trithiane **112**.[24] The qualitative contribution of **112** to meat flavor is said to be parti-

cularly remarkable, its effect being already noticeable at concentrations of the order of 0.05 to 0.5 ppm.[24]

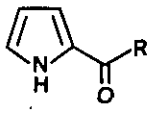
Trithioacetaldehyde **108**[85] is a constituent of chicken aroma, and 3,6-dimethyl-1,2,4,5-tetrathiacyclohexane **113** occurs in processed ham.[88] Thialdine **111**, which has a note typical of heated meat,[89] has so far been detected in beef aroma[76,86] and roasted lamb fat.[14]



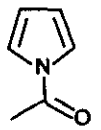
114 R = H [47]
115 R = CH_3 [47]



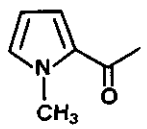
116 R = H [34]
117 R = CH_3 [34]



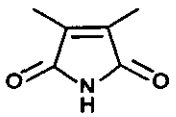
118 R = CH_3 [34,37]
119 R = C_2H_5 [34]



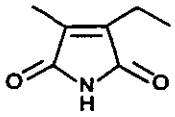
120 [34]



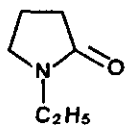
121 [39]



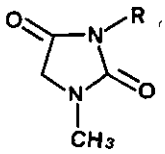
122 [24]



123 [24]



124 [38]



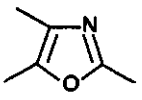
125 R = CH_3 [24]
126 R = C_2H_5 [24]

Among the "breakdown flavors" of various foodstuffs about 50 members of the pyrrole series have so far been detected. To a certain extent this class of substances also occurs in processed meat products. The lowest members **114** and **115** were found in a meat extract.[47] The carbonylated derivatives **116** - **120** were detected in cooked pork liver.[34] The aroma of cooked pork contains 1-ethyl-2-pyr-

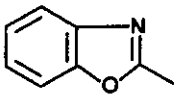
rolidone **124** as a typical constituent.[38] 2-Acetylpyrrole **118**,[37] together with the corresponding N-methyl derivative **121**,[39] was detected in beef products.

Ethyl-methylmaleinimide **123** detected for the first time in tobacco aroma [90] is, together with its lower homolog **122**, a constituent of meat aroma.[24]

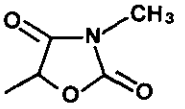
The two hydantoins **125** and **126** from roasted beef were previously unknown as flavoring agents.[24] Synthetic 1,3-dimethylhydantoin **125** is described as a compound having a peculiar acrid taste.[91]



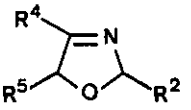
127 [92]



128 [5,47]



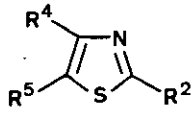
133 [24]



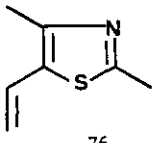
129 $R^2,R^4 = CH_3$; $R^5 = H$ [93]
130 $R^2,R^4,R^5 = CH_3$ [93,82,44]
131 $R^2,R^4 = CH_3$; $R^5 = C_2H_5$ [93]
132 $R^2,R^5 = CH_3$; $R^4 = C_2H_5$ [93]

Although since 1968 about 30 oxazole derivatives have been detected in aromas, 28 of which in coffee aroma alone,[29] meat aroma contains only 2,4,5-trimethyloxazole **127**[47] and 2-methylbenzoxazole **128**.[5] The flavor of **127** is close to that of boiled beef.[17] So far, oxazolines have been found to occur only in meat aroma. The four alkyl-substituted derivatives **129 - 132** seem to have a certain importance in the development of the flavor of cooked beef.[44,82,93] Reaction of acetaldehyde with acetoin in ammonia solution provides an easy synthesis of **130**.[94] This process can be considered as a model reaction in the roasting of meat since we have merely to substitute an amino acid for ammonia and assume a Strecker degradation as the central reaction.

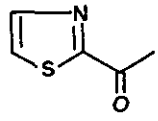
3,5-Dimethyl-1,3-oxazolidin-2,4-dione **133** was discovered for the first time in an aroma[24] when it was isolated from the volatiles of roasted beef.



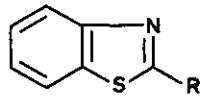
134 $R^2,R^4,R^5 = H$ [34,76]
135 $R^2 = CH_3$; $R^4,R^5 = H$ [76]
136 $R^4 = CH_3$; $R^2,R^5 = H$ [34,76]
137 $R^2,R^4 = CH_3$; $R^5 = H$ [76]
138 $R^2,R^4,R^5 = CH_3$ [14,76]
139 $R^2 = CH_3$; $R^4 = C_2H_5$; $R^5 = H$ [76]
140 $R^4 = CH_3$; $R^5 = C_2H_5$; $R^2 = H$ [76]
141 $R^2,R^4 = CH_3$; $R^5 = C_2H_5$ [14]



142 [76]



143 [34,76,95]



144 R = H [14,37]
145 R = SCH_3 [24]

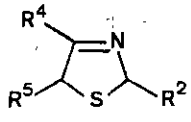
Today there is no longer any doubt about the importance of the thiazoles as constitutents of food aromas.[96,97] Thirteen representatives of this class have been included in the GRAS list of food additives.[97] The highest number of members of this class was found in the aromas of meat[76] and coffee.[98] Many of them are alkyl-thiazoles whose odor has generally been described as green, nutty and vegetable-like.[99] In meat products compounds **134 - 141** have been identified.

2,4-Dimethyl-5-vinylthiazole **142**, an important meat aroma constituent, has a strong, characteristic nut-like odor[100] and is used in flavor compositions[101] at a level of 0.1 - 0.5 ppm.[97] The 2-nor derivative of **142** has been recognized as character impact constituent of cocoa aroma.[100]

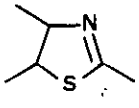
2-Acetylthiazole **143**, which was identified in pressure-cooked beef,[76] boiled potatoes,[102] cooked pork liver,[34] cooked asparagus,[103] dry red beans[104] and canned beef[95] as well as in the products of the model reaction between cy-

steine-cystine and ribose,[105] possesses a strong, characteristic nutty, cereal and popcorn flavor.[99]

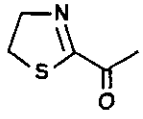
Benzothiazole **144** is abundant in aromas. Identified for the first time in a sterilized milk concentrate[106] in 1966, it was found in the following year in cocoa,[107] butter,[108] beer,[109] cranberries,[110] roast beef, roasted lamb fat[14,37] and Swiss cheese.[111] Subsequently, it was detected in more than a dozen other flavors. It is described as having a quinoline-like, rubbery odor.[97] 2-Methylthiobenzothiazole **145** has also been found recently in a meat flavor,[5] and imparts a relatively characteristic fatty and smoky odor to meat aroma.[24]



146 $R^2, R^4 = CH_3$; $R^5 = H$ [93]
147 $R^2, R^4, R^5 = CH_3$ [93]



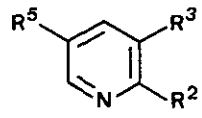
148 [14]



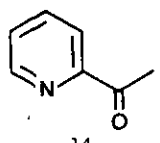
149 [76,112,113]

2,4-Dimethyl-3-thiazoline **146** together with the trimethyl derivative **147** identified in cooked beef,[93] was formed in a model reaction of glucose with hydrogen sulfide and ammonia.[114] Isolated from beef broth,[112,113] 2-acetyl-2-thiazoline **149** is described as having an intense odor of freshly baked bread crust, although it is not the character impact flavor component of this.[34] The sensory properties of 2,4,5-trimethyl-2-thiazoline **148** found in lamb fat flavor[14] have not yet been described.

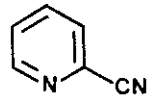
The importance of pyridine derivatives as aroma constituents has remained quite limited so far, although they are widely occurring in various "breakdown flavors" such as that of coffee[116] or barley.[117] Thirteen different substituted pyridines **150 - 162** were isolated from the basic fraction of the volatiles of



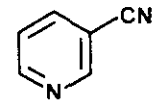
150 $R^2,R^3,R^5 = H$ [14]
151 $R^2 = CH_3$; $R^3,R^5 = H$ [14,38]
152 $R^3 = CH_3$; $R^2,R^5 = H$ [14]
153 $R^2 = C_2H_5$; $R^3,R^5 = H$ [14,115]
154 $R^3 = C_2H_5$; $R^2,R^5 = H$ [14]
155 $R^2 = C_4H_9$; $R^3,R^5 = H$ [14]
156 $R^2 = C_5H_{11}$; $R^3,R^5 = H$ [14,115]
157 $R^3 = C_5H_{11}$; $R^2,R^5 = H$ [14]
158 $R^2 = C_6H_{13}$; $R^3,R^5 = H$ [14]
159 $R^2 = CH_3$; $R^5 = C_2H_5$; $R^3 = H$ [14]
160 $R^2 = C_5H_{11}$; $R^5 = CH_3$; $R^3 = H$ [14]
161 $R^2 = C_5H_{11}$; $R^5 = C_2H_5$; $R^3 = H$ [14]



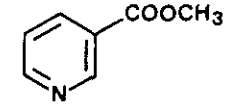
162 [14]



163 [47]



164 [47]

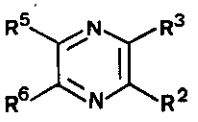


165 [47]

roasted lamb fat aroma,[14] among these 2-acetylpyridine **162** which has an odor of popcorn.[99] 2-Ethyl- and 2-pentylpyridine **153** and **156** had already been identified earlier in shallow-fried beef aroma.[115] The pentyl derivative **156** is said to possess a fatty or tallow-like odor and to have the extremely low threshold concentration of 0.6 ppb.[14] The formation of **156** was attributed to the thermal conversion of deca-2,4-dienal in the presence of ammonia or amines.[14] Strangely enough, it was possible to detect methyl nicotinate **165** besides nicotinonitrile **164** and pyridine-2-carbonitrile **163** in meat aroma.[47]

Pyrazines in foodstuffs seem to outshine all the preceding groups as to the structural variety and sensory importance. During the last 14 years more than a hundred papers have appeared on the identification of more than 50 different alkylpyrazines in about 30 natural or manufactured, cooked, roasted, or fermented products of vegetable or animal origin. Among the 43 pyrazines which have so far

been identified in cocoa there are no less than 27 alkylpyrazines of different degrees of substitution.[118] Some of them give an inimitable imprint to certain flavors. 3-Ethyl-2,5-dimethyl pyrazine **178**, for instance, is a contributor to the odoriferous principle of cocoa aroma.[107] It is also one of the most potent odorants derived from potato chips.[119] As a rule, alkylpyrazines produce roasted nut-like sensory impressions. It is curious to note that the chocolate-smelling alarm pheromone of an American species of *Odontomachus* (an ant species) mainly consists of alkylpyrazines.[120]



166 $R^2,R^3,R^5,R^6 = H$ [34,121]

167 $R^2 = CH_3$; $R^3,R^5,R^6 = H$ [34,121]

168 $R^2 = C_2H_5$; $R^3,R^5,R^6 = H$ [34,121]

169 $R^2,R^3 = CH_3$; $R^5,R^6 = H$ [34,121]

170 $R^2,R^5 = CH_3$; $R^3,R^6 = H$ [34,121]

171 $R^2,R^6 = CH_3$; $R^3,R^5 = H$ [34,121]

172 $R^2 = CH_3$; $R^3 = C_2H_5$; $R^5,R^6 = H$ [122]

173 $R^2 = CH_3$; $R^5 = C_2H_5$; $R^3,R^6 = H$ [34,121]

174 $R^2 = CH_3$; $R^6 = C_2H_5$; $R^3,R^5 = H$ [34, 121]

175 $R^2,R^5 = C_2H_5$; $R^3,R^6 = H$ [34]

176 $R^2,R^6 = C_2H_5$; $R^3,R^5 = H$ [121]

177 R^2,R^3, $R^5 = CH_3$; $R^6 = H$ [34,121]

178 $R^2,R^5 = CH_3$; $R^3 = C_2H_5$; $R^6 = H$ [34,121]

179 $R^2,R^3 = CH_3$; $R^5 = C_2H_5$; $R^6 = H$ [34,121]

180 $R^2,R^6 = CH_3$; $R^3 = C_2H_5$; $R^5 = H$ [34,121]

181 $R^2,R^3 = C_2H_5$; $R^5 = CH_3$; $R^6 = H$ [34,121]

182 $R^2 = CH_3$; $R^3,R^5 = C_2H_5$; $R^6 = H$ [34,121]

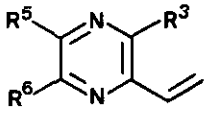
183 $R^2 = CH_3$; $R^3,R^6 = C_2H_5$; $R^5 = H$ [34,121]

184 $R^2,R^3,R^5 = C_2H_5$; $R^6 = H$ [34,121]

185 $R^2,R^6 = CH_3$; $R^3 = C_3H_7$; $R^5 = H$ [122]

186 $R^2,R^3,R^5,R^6 = CH_3$ [34,121]

187 $R^2;R^5,R^6 = CH_3$; $R^3 = C_2H_5$ [122]

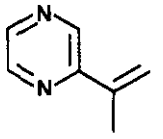


188 $R^3,R^5,R^6 = H$ [121]*

189 $R^3 = CH_3$; $R^5,R^6 = H$ [34]

190 $R^5 = CH_3$; $R^3,R^6 = H$ [34]

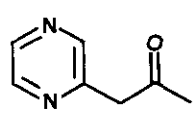
191 $R^6 = CH_3$; $R^3,R^5 = H$ [121]*



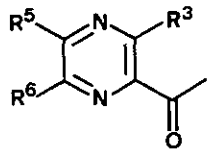
192 [121]*

* tentatively identified

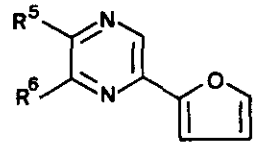
A particularly high number of alkylpyrazines is present in roasted meat aroma.[122] So far the 22 alkyl derivatives **166 - 187** and the 5 alkenyl derivatives **188 - 192** were identified.



193 [121]



194 $R^3,R^5,R^6 = H$ [34,121]
195 $R^5 = CH_3$; $R^3,R^6 = H$ [34,121]
196 $R^6 = CH_3$; $R^3,R^5 = H$ [34]
197 $R^3 = C_2H_5$; $R^5,R^6 = H$ [34]
198 $R^5 = C_2H_5$; $R^3,R^6 = H$ [34,121]
199 $R^6 = C_2H_5$; $R^3,R^5 = H$ [34]*



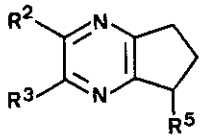
200 $R^5,R^6 = H$ [34]
201 R^5 or $R^6 = CH_3$ [34]

* tentatively identified

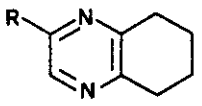
Among the pyrazines the acetyl derivatives **194 - 199** occupy a particular position as flavoring agents. They have a surprisingly intense and characteristic roasted note which is reminiscent of popcorn.[123] Acetylpyrazine **194** was identified for the first time in 1969 during an investigation on the components of sesame oil.[124] After having been tentatively identified in popcorn,[125] acetylpyrazine was isolated from roasted peanuts,[126] tobacco,[90] roasted filberts,[127] roasted sesame seed,[128] roasted coffee[29] and roasted almonds.[56] Six of these derivatives **194 - 199** are found in boiled beef[121] and pressur-cooked pork liver.[34]

1-(2-pyrazinyl)propan-2-one **193** was found in cooked beef[121] and among the products of a Maillard reaction.[129] When used in combination with thiazolidines and/or cyclohexenones, this pyrazine imparts a toasted and burnt note to foodstuffs.[130,131] Its utilization for modifying coffee flavor is patented.[131]

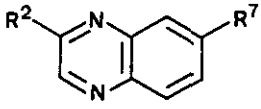
The first identification of 2-(2-furyl)pyrazine **200** was during the analysis of coffee flavor.[132] It seems to be the most widely distributed compound of this series having been found in cigarette smoke[133,134] and roasted foodstuffs such as filberts,[127] green tea,[135] almonds,[136] sesame seed,[128] cocoa[118] and together with its methyl derivative **201** also in pressure-cooked pork liver.[34]



202 $R^2,R^3,R^5 = H$ [34,121,137]
203 $R^2 = CH_3$; $R^3,R^5 = H$ [34,121,137]
204 $R^5 = CH_3$; $R^2,R^3 = H$ [34,121,137]
205 R^2(or R^3),$R^5 = CH_3$; R^3(or R^2) $= H$ [34, 121, 137]
206 $R^2,R^3 = CH_3$; $R^5 = H$ [137]
207 $R^2 = CH_3$; $R^3 = C_2H_5$; $R^5 = H$ [137]
208 $R^2,R^3,R^5 = CH_3$ [137]



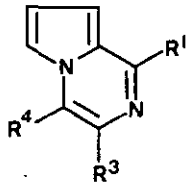
209 $R = H$ [34,121]
210 $R = CH_3$ [34,121]



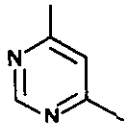
211 $R^2,R^7 = H$ [34]
212 $R^2 = CH_3$; $R^7 = H$ [34]
213 $R^7 = CH_3$; $R^2 = H$ [34]

Whenever bicyclic pyrazines are present in roasted food aromas, they represent typical notes of the organoleptic properties of grilled beef. The two basic components, cyclopentapyrazine **202** and 5,6,7,8-tetrahydroquinoxaline **209**, were first found in 1971 among the aroma substances of roasted peanuts. Then a series of their alkyl derivatives **203** - **208** and **210** were discovered in rapid succession in thermally processed foods such as green tea, cocoa, coffee and also roasted meat. The three quinoxalines **211** - **213** are found as flavor constituents in pork liver.[34]

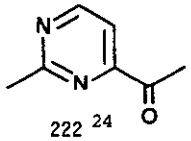
Among the model reaction products mentioned above[137] unsaturated bicyclic structures such as 5H-cyclopenta[*b*]pyrazines and 5-methyleno-6,7-dehydro-5H-cyclopenta[*b*]pyrazines have also been observed. Their synthesis[138] and their use as flavoring ingredients[139] have been described. Such products have roasted, grilled, burnt and animal notes interesting for the aromatization of meat and tobacco products.



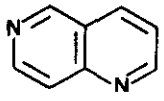
214 R^1,R^3,R^4 = H [140]
215 R^1 = CH_3; R^3,R^4 = H [140]
216 R^3 = CH_3; R^1,R^4 = H [140]
217 R^4 = CH_3; R^1,R^3 = H [140]
218 R^1,R^3 = CH_3; R^4 = H [140]
219 R^1,R^4 = CH_3; R^3 = H [140]
220 R^3,R^4 = CH_3; R^1 = H [140]



221 [24]



222 [24]



223 [24]

Recently,[140] a new bicyclic pyrazine skeleton was found in roasted meat flavor; seven alkylpyrrolo[1,2-a]pyrazines 214 - 220 were identified and the presence of higher homologs was suspected.

The three nitrogen derivatives 221 - 223 have been found for the first time in a flavor when identified in the volatiles of roasted beef.[24] Whereas 4,6-dimethylpyrimidine 221 has an odor similar to that of alkyl-substituted pyrazines, 4-acetyl-2-methylpyrimidine 222 has a very interesting grilled note and is

detectable at a level of 0.5 ppm. 1,6-Napthyridine **223** is also said to have a very characteristic odor and taste.

In spite of our thorough knowledge of the organoleptic properties of the 223 heterocycles discovered so far and of the about 370 non-heteroatomic meat-related constituents, the results are not sufficient for producing synthetically a true-to-nature meat aroma. In our laboratory 400 additional previously unknown constituents of roasted beef volatiles have been detected.[24] For the elucidation of their structures we often must reach the limits of the present analytical possibilities. The synthetically oriented chemist still has a vast field of activity before him to solve this difficult problem, where again, the heterocycles are of great relevance.

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