Flavor components of cured Pork products.

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61 volatile components were separated and caracterized from nitrite cured pork after heat treatment. Of these were 14 aldehydes, 6 ketones, 11 sulfur compounds and 5 furanes. 20 of these compounds have to our knowledge not previously been identified from pork products. The concentration of the characterized compounds were compared with their threshold concentrations of perception, and 10 sulfur compounds, 8 aldehydes, 2 ketones and 2 furans considered of importance as flavor compounds. The components were isolated from headspace above heated meat or by concentration of vacuumdestillates. The components were separated by gaschromatography, and characterized partly by refractiontime, partly by mass spectrometry. All the identified components were isolated from fresh as well as cured meat but in different concentrations.

With regard to sulfur compounds were the most volatile, like hydrogensulfide and methyl mercaptan, most aundant in vapors from fresh meat, while the less volatile disulfides were in higest concentrations in vapors from cured meat. Short chain carbonyls (C_2 - C_5) were in higest concentrations over cured meat and medium chain (above C_5) carbonyls over fresh meat.

Les components aromatiques des produits de porc salés.

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61 components inconstants de porc nitrit salé ont eté separés et caractérisés après traitment thermique. 14 de ces components étaient des aldehydes, 6 cetons, 11 composés sulfurés et 2 furans. A notre connaissance 20 de ces components ne sont pas avant identifiés de produits de porc. La concentration des produits caracterisés fût comparée à leur valeur de seuil d'odeur, et il faut soiligner que 10 composés sulfurés, 8 aldehydes, 2 cetons et 2 furons aient une grande importance pour l'impression aromatique. Les components sont isolés du volume d'air au-dessus du porc termique traité et à l'aide des déstillats de vacuum. Les produits sont separés par gazchromatographie et caracterisés par temps de réfraction et aussi par spectrometri en masse. Tous les components identifiés sont isolés tant de porc frais et de porc salé, mais en quantités differents.

Quant-aux composés sulfurés les plus inconstants, comme hydrogensulfid et methyl mercaptan étaients representés en la plus haute concentration dans des vapeurs de porc frais tandis que les moins inconstants disulfids en les trés haute concentration sur le porc salé. Les courte chaînes de carbonyles (C_2-C_5) etait representés en la plus haute concentration sur porc salé tandis que les plus longue chaînes (sur C_5) avaient la plus haute concentration sur porc frais.

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Aromakomponenten von gepökelt Schweineerzeugnisse.

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61 flüchtige Komponente waren entscheidet und charakterisiert im Nitrit gepökelt Schweinefleisch nach Wärmebehandlung. Aus diese waren 14 Aldehüde, 6 Ketonen, 2 Furane und 11 Schwefel verbindungen. 20 von diesser Komponenten sind, uns bekannt, nicht früher im Schweineerzeugnisse identifiziert worden. Die Konzentrationen der charakterizierte Komponente wurde mit ihren geruch grenzwert vergleicht. 10 Schwefelkomponenten, 8 Aldehüde, 2 Ketonen und 2 Furane schienen von bedeutung des Aromas zu werden. Die Komponenten waren Gaschromatografisch separiert und teils durch Refraktions Zeit, teils durch Massenspektrometrie karakterisiert. Alle die identificierte Komponente waren von sowohl frisch als gepökeltes Fleisch isoliert worden, aber in verschidene Koncentrationen.

Betreffend die Schwefel Komponenten, waren die meist flüchtige Komponenten (Hydrogen Sulfid und Methyl Merkaptan) anwesend in die högste Koncentrationen über das frische Fleisch. Die weniger flüchtige Disulfiden waren im högstem Koncentration über gepökeltes Fleisch. Die kurtz Kettige Karbonylen (C_2 - C_5) waren im högstem Koncentration über gepökeltes Fleisch gefunden, Karbonylen dagegen waren über C_5 im högstem Koncentration über frisches Fleisch gemessen.

Ароматные компоненты солённых продуктов свинины.

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6I летучий компонент разлагался от мяса свинины, посоленным нитритом, и после тепло-обработки характеризировался. Из них были I4 альдегидов, 6 кетонов, II серных соединений и 5 фуранов. На сколько нам известно 2о из этих веществ раньше не отождествились от продуктов мяса свинины. Концентрация характеризированных веществ сравнивали с пределной концентрацией запаха, и Iо серных соединений, 8 альдегидов, 2 кетона и 2 фурана считали большим значением аромата. Компоненты выделялись от объёма воздуха над тепло- обработанным мясом или концентрацией вакуум-дистиллятами. Компоненты разлагались газо-хроматографией и характеризировались частично временем рефракции, частично масс-спектрометрией. Все отождествленные компоненты были выделенные и от свежего мяса и от солённого мяса, но в различном количестве.

Насчёт серных соединений самые летучие, как сероводород и метиловый меркаптан, встречались в самой большой концентрации в паре свежего мяса. Мало-летучие дисульфиды встречались в самой большой концентрации в паре солённого мяса. Кратко-цепные карбонилы (c_2 - c_5)имели самую большую концентрацию над солённым мясом, а средне- цепные карбонилы (больше c_5) имели самую большую концентрацию над свежим мясом.

FLAVOR COMPONENTS OF CURED PORK PRODUCTS

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INTRODUCTION

In the present study the volatile compounds from heated pork were investigated.

The research was primarily centered I) on identifying the volatile compounds II) on determining their concentration in head space III) on finding which of the volatiles there can be of importance for the flavor impression IV) on finding the influence of nitrite on cured pork meat.

MATERIALS AND METHODS

All the meat came from the judging central for pork research in Ringsted. Only middles (loin and side) from pigs in the best category were used.

Preparation of the sample

The middles were divided transversively in 9 ribbons of same size. They were grouped in 3 portions of 3. The portions were cured in a brine with 2o % NaCl and different amounts of KNO_3 and $NaNO_2$: 1 % KNO_3 with o.1 % $NaNO_2$, 2/3 and 1/3 of that. The curing took place by $4^{o}C$ for 3 days. After this time the cured meat was stored by $3^{o}C$ for 18 days. Samples were taken out the 3rd, 16th and 21st day. The samples (1 kg) were cutted after the rind was removed. By Ultra x the fat % was measured and adjusted to 26 % with fat from the same sample.

Koncentration

A technique described by von Sydow et al. (197o) was used to concentrate the volatile compounds in the head space of the sample bottle: The head space was pressed through a U-shaped tube cooled with liquid nitrogen to $-196^{o}C$. This low temperature is resulting in the volatile compounds were held back. When the wanted amounts of head space (5oo ml) are led through the cold trap the tube is connected with the gaschromatograph and heated to $15o^{o}C$ in oil bath, hereby there will happen a momentanious injection of the compounds in the gaschromatograph.

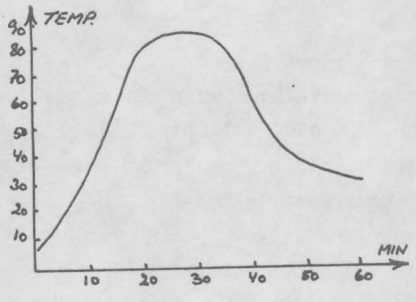

Fig. 1. The temperature in centre of sample during the heating and cooling period.

For massspectrometric identification a further concentration was necessary. Here two methods were used; vacuumdistillation of the most volatile compounds and steamdistillation of the less volatile compounds. To the vacuumdistillation 1.5 kg cutted meat was used mixed with 1.5 kg water. The distillation took place by 7 mm Hg and $2o^{o}C$ under constant stirring after initial degassing of the meat slurry at $0^{o}C$. The whole system was composed in glas-teflon (Sovirel). The distillation temperature was $0-2^{o}C$, and the volatile compounds were condensed in a cold trap by liquid nitrogen. Additional concentrations were made by redistillation of several concentrates.

To the steamdistillation there was also used 1.5 kg cutted meat mixed with 1.5 kg water. The sample was cooked in autoclave by 140°C in 30 min. The meat slurry was then steam-distilled until 200 ml was collected. This distillate was extracted three times with 200 ml distilled diethyl ether. The extract was dried over anhydrous sodium sulphate and concentrated to about 2 ml by careful distillation with reflux column.

Gas chromatography

The equipment consisted of a Perkin-Elmer Model 3920 with flame ionization detector (FID) and a Meloy flame photometric detector (FPD).

For analyzing the sulphuric compounds a glass colourn was used (3 m x 1/8" ID) packed with chromosorb 103 80/100 mesh. The temperature was programmed 40-190°C with a gradient of 4°C/min. after initial isothermal periods of 2 min. The carrier gas flow was 30 ml N_2/min.

When using the FID the samples were analyzed on open tubular glas column (20 m x 0.3 mm ID) of the WCOT type coated with Ucon 280 LB. The temperature was here programmed 20-190°C with a gradient of 2°C/min after initial isothermal periods of 4 min. The carrier gas flow was 2 ml N_2/min.

The calibrating of FDP with the different sulphuric compounds were made by taking 1-50 µl samples with a gas tight syringe from a gas volume (250 ml) containing a known amount of the concerned chemical compound. The absolute quantitative amount of the compound in every single gas chromatographical top was determined by reference compounds in approximately the same amount as in the samples. The hights of the tops were used as an expression of the samples amounts.

Mass spectrometry

The samples were analyzed in a combined gas chromatograph-mass spectrometer (Varian aerograph, Model 2700-Mat 311) with parallel detection in gas chromatograph and mass spectrometer. Glass columns were used (1/8" x 2 m) packed with chromosorb 103 80/100 mesh and chromosorb WAW-DMCS 80/100 mesh, coated with 8 % carbowax 1540. Mass spectra were recorded at 70 eV, and with 3 KV acceleration voltage. The temperature in the separator was 270°C and 230°C in the ion source.

RESULTS AND DISCUSSION

The identified volatile compounds in head space are specified in table 1.

methanol	ethanal	furan	methyl mercaptan
ethanol	propanal	2-methyl furan	hydrogen sulfide
1-butanol	n-butanal	2-acetyl furan	ethylene sulfide
1-hexanol	n-pentanal	2-pentyl furan	ethyl methyl sulfide
1-octanol	n-hexanal		thiophene
	n-heptanal	n-pentane	diethyl sulfide
	n-octanal	n-hexane	dimethyl disulfide
	n-nonanal	n-heptane	2-methyl disulfide
	n-decanal		2-methyl thiophene
	n-undecanal	benzene	ethyl methyl disulfide
	2-methyl propanal	toluene	diethyl disulfide
	3-methyl butanal	(o,m,p)-xylene	3,5-dimethyl-1,2,4-trithiolane
	benzaldehyde	ethyl benzene	
	furfural	trimethyl benzene	

Tabel 1: Compounds identified by gas chromatograph-mass spectrometer in head space

The retention times for the mass spectrometric identified compounds were examined on analytical pure compounds from Merck and Fluka.

The presence of NH_3 was shown by leading N_2 through meat slurry and from this through 2 N HCl. After evaporation, the whole residue showed positive Nessler reaktion.

Also volatile fatty acids were determined by steam distillation (Halvarson, 1972). 8 fatty acids were hereby identified: acetic acid, butyric acid, isobutyric acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid and decanoic acid.

Sensoric evaluation on some of the chromatographic eluates were made. It showed that not a single compound, but the simultaneous presence of several compounds give the specific flavor of the product.

Alle the identified components were isolated from fresh as well as cured meat but in different concentrations.

Some of the compounds determined during our investigations are not earlier found in pork meat, but, however, identified as compounds in pork liver (Mussinan and Walradt,1974), chicken meat (Wilson and Katz, 1972) and beef (Persson and von Sydow, 1973). In earlier investigations made by Kami (1969) and Swain (1972) some compounds, we could not find, are described. The difference are probably due to the different concentration methods. In addition to the identification of the volatile compounds there were made quantitative determinations. Concerning the sulfuric compounds (table 2.) the investigations showed methyl mercaptan and hydrogen sulfide,are present in fresh meat in the highest amount. The amount of the two compounds decrease with increasing quantity of nitrite and increasing curing period. Ethyl methyl sulfide and ethylene sulfide have nearly the same concentration in fresh and cured meat. The subsequent sulfuric compounds showed to be in highest amount in fully cured meat with high concentration of nitrite. The content is decreasing, when the curing period and/or the nitrite concentration are decreased.

compound	fresh meat	A_3*)	B_3	C_3	A_{I6}	B_{I6}	C_{I6}	A_{2I}	B_{2I}	C_{2I}	odor threshold ppb,v/v
methyl mercaptan	432	400	400	400	I30	I60	I73	I04	II0	I50	2.I
hydrogen sulfide	993	960	960	965	848	860	876	848	850	900	0.47
ethyl methyl sulfide	I6	I6	I6	I6	I6	I5	I6	I4	I4	I4	
ethylene sulfide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	4.0	4.0	5.0	
thiophene	I.2	I.3	I.3	I.3	I2	I2	I2	I2	I2	I2	
diethyl sulfide	I.4	I.6	I.4	I.4	II	I2	9.5	II	I0	II	
dimethyl disulfide	739	780	780	740	I949	I950	I747	20I6	2000	I962	7.6
2-methyl thiophene	2.3	2.5	2.3	2.3	9.2	9.2	9.2	9.2	9.5	9.I	
ethyl methyl disulfide	I.2	I.2	I.2	I.2	2.2	2.2	I.9	3.6	2.5	2.0	
diethyl disulfide	I.0	I.0	I.0	I.0	5.3	5.I	5.3	I3	II.5	5.8	
3,5-dimethyl-I,2,4-trithiolane	0.I	I.0	I.0	I.0	I.0	I.0	I.0	I.0	I.0	I.0	

Table 2: Sulfuric compounds and the absolute concentrations in head space. (ppb,v/v)
A: Addition of I% KNO_3 and I% $NaNO_3$
B: Addition of 0.66% KNO_3 and 0.66% $NaNO_3$
C: Addition of 0.33% KNO_3 and 0.33% $NaNO_3$
*) The number indicate the day from the beginning of the curing period.

When a metal column was used for gas chromatographical separation of the sulfuric compounds methyl mercaptan disappeared, while greater amounts of 3,5-dimethyl-I,2,4-trithiolane and 3,6-dimethyl-I,2,4,5-tetrathiolan were appearing. Both compounds are descreibed by Swain (I972) as flavour compounds in cured pork.The above mentioned results indicate the two com-

pounds, in any case partly, come from chemical reactions in the column. The fat content was in all the experiments held constant on 26%. Fat dissolves some sulfides and disulfides and are hereby lowering the vapor pressure. The amounts of aldehydes increase with increasing fat% because these chemical compounds among other things can be synthesised from fatty acids.By comparing the carbonyle content in fresh meat with cured meat, the tendency indicate, that short chain carbonyles until and including pentanal, were in highest concentrations over cured meat and medium chain carbonyles over fresh meat. This tendency was intensivated during the curing and was highest by full nitrite dose.These results are consistent with the theory about nitrites restrictive influence on the oxidation of fatty acids. Longer chained aldehydes and ketones come mainly from the degradation of fatty acids, while the short chaned carbonyles also come from degradation of proteins.

Fully satisfieng results about all the quantitative facts are not yet obtained.

Unsaturated carbonyles have not been detected.

Odor threshold data available in litterature have been compared with the actual concentrations of the volatiles in head space. By this comparing it is possible to predict something about the importance of the single compound to the flavour. Methyl mercaptan, hydrogen sulfide and dimethyl disulfide are present in amounts much higher than the odor thresholds, but all the other detected sulfuric compounds have probably also a consequence for the flavour. In the group of non-sulfuric compounds only few of the detected compounds seems to be of importance to the flavour, and it is aldehydes up to heptanal and the ketones 2,3-butandion and 2,3-pentandion.

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