4:9 Volatile compounds arising from the reaction of sodium nitrite with pork during curing.

D.S. MOTTRAM
ARC Meat Research Institute, Langford, Bristol, U.K.

Introduction

Sodium nitrite is an essential additive in the manufacture of cured meats. Although it is only present at a level of 50-150 mg/kg in the cured product it is responsible for the characteristic pink colour of cured meats; it provides microbiological stability; and it imparts a characteristic flavour to the meat over and above any flavour which may be imparted by smoking. In a number of reports comparing the sensory properties of cured meats prepared with and without sodium nitrite clear differences between the products have been found (1,2). A sensory study of the effect of the concentration of sodium nitrite in bacon upon the flavour (3) showed an increase in bacon flavour with increasing nitrite concentration.

There have been very few reports on the chemical nature of flavour volatiles released from cured meats and none adequately explain the observed sensory differences between products prepared with and without sodium nitrite. It has been reported that cured pork contained lower amounts of aliphatic aldehydes than the uncured meat (4), and differences in amounts of thiols in cured and uncured pork have also been found (5). Recently, Ho et al. (6) found 135 substances in the volatiles of fried bacon, although cured flavour was not attributed to any individual compound. Although quantitative differences in aldehydes and thiols may play some part in the aroma differences between cured and uncured meat, the nitrite ion is a reactive species and could be expected to react with other flavour precursors to give hitherto un-identified compounds which may contribute to cured flavour.

Recent work at this laboratory has shown the presence of certain organic nitrates and nitriles in the volatiles of bacon (7,8). This paper reports the presence of nitriles and nitrates in various cured pork products containing a range of sodium nitrite concentrations, and gives evidence for possible mechanisms involved in their formation.

Materials and Methods

Bacon was prepared by a slice cure method (7) in which slices of pork loin were suspended in a brine containing NaCl and $NaNO_2$. Two levels of $NaNO_2$ were used which gave products containing residual $NaNO_2$ levels of 220 and 1060 mg/kg. A nitrite-free salt pork was also prepared and slices of uncured pork were taken. Minced lean samples (250g) from each treatment were boiled for 3h in a Likens-Nickerson continuous steam distillation - solvent extraction apparatus using purified diethyl ether as the solvent (9). Samples were also fried for 10 min in a pan at 170°C before the volatiles were extracted in a similar way.

Comminuted cured pork products containing 2% NaCl and either 200 or 1000 mg/kg $NaNO_2$ were also prepared in 100g batches by mixing minced lean pork (60g) with an aqueous solution (30g) containing NaCl and $NaNO_2$. After storing for 3 days at +5°C the products were boiled and the volatiles extracted as described above.

Volatiles from the reaction of pork lipid with aqueous $NaNO_2$ were also analysed. Rendered pork fat (50g) was boiled for 3h with an aqueous citrate buffer (500 ml) at pH 5.0 containing $NaNO_2$ (3.45g) in the Likens-Nickerson apparatus with purified diethyl ether as the extracting solvent.

The volatile extracts from all the samples were concentrated to 250 µl and analysed by gas chromatography - mass spectrometry (g.c.-m.s.) on a Finnigan 4000 instrument using a 50m x 0.32 mm i.d. silica column coated with CP Wax 57CB (Chrompak Ltd.).

Results and Discussion

The range of volatile compounds expected from cooked meat (i.e. aldehydes, alcohols, ketones, furans, pyrazines, etc.) were found in all samples. In addition a number of novel N-containing compounds were obtained from the cured meat volatiles which were absent from the uncured pork and the pork cured without nitrite. These comprised alkanenitriles, benzonitrile, phenylacetonitrile and alkyl nitrates (Table 1).

TABLE 1

Concentrations (ppm in meat) of nitriles and nitrates in volatile extracts of cured pork.

	Bacon: slice-cured				Comminuted meat	
	Boiled		Fried		Boiled	
Sodium nitrite	220[a]	1060[a]	220[a]	1060[a]	200[b]	1000[b]
Hexanenitrile	-	30	25	120	-	7
Heptanenitrile	3	80	10	720	-	2
Octanenitrile	3	9	tr	70	-	3
Nonanenitrile	3	10	1	45	-	tr
Decanenitrile	-	2	-	3	-	-
Undecanenitrile	-	8	-	6	-	-
Dodecanenitrile	tr	20	-	20	-	3
Tridecanenitrile	1	65	-	110	-	15
Tetradecanenitrile	-	80	8	70	55	100
Pentadecanenitrile	30	510	15	520	-	5
Hexadecanenitrile	90	45	-	30	-	-
Heptadecanenitrile	-	70	-	40	-	10
Benzonitrile	2	20	1	15	1	1
Phenylacetonitrile	tr	2	tr	3	tr	
Pentyl nitrate	2	2	15	5	-	-
Hexyl nitrate	7	5	4	6	-	-
Heptyl nitrate	-	-	30	15	-	2
Octyl nitrate	20	20	30	15	1	

a residual $NaNO_2$ analysed 3 days after curing
b amount added to pork
tr trace (< 1 ppm)
- not found (detection limit approximately 0.1 ppm)

In order to determine if the formation of these compounds was affected by nitrite concentration, meat products were prepared with higher residual nitrite levels than those normally permitted in cured meats. These high nitrite samples contained twelve alkanenitriles, several of which were absent from samples containing lower nitrite concentrations, and the levels of both alkane and aryl nitriles were considerably greater in the samples containing high amounts of nitrite. However, the alkyl nitrates were not significantly influenced by the nitrite concentration. Frying resulted in the highest levels of nitriles whilst the comminuted cured meats, which contained less fat than the slice-cured bacon, contained the lowest levels.

The aroma properties of these nitrogen compounds suggest that they are not responsible themselves for cured flavour. The aliphatic nitrates and nitriles appear to have relatively high odour thresholds (> 1 part in 10^6 parts water) and odours similar to aliphatic alcohols and aldehydes respectively. Although benzonitrile and phenylacetonitrile appear to have lower odour thresholds, their aromas are very similar to benzaldehyde which is found in relatively large amounts in the volatiles of all cooked meats. However, the reactions by which the compounds are derived may have great importance in the formation of other as yet unidentified compounds contributing to cured flavour.

The most likely origin of these nitrogen-compounds is from the reaction of $NaNO_2$ with lipids. When comminuted cured pork was prepared with 15N labelled sodium nitrite the volatiles from the boiled meat contained nitriles and nitrates with mass spectra showing molecular ions and nitrogen-containing fragments with m/z one mass unit higher than the spectra of compounds obtained from the normal nitrite cures. This confirmed $NaNO_2$ as the source of the nitrogen rather than from nitrogenous components of meat.

When rendered pork fat was boiled with an aqueous solution of $NaNO_2$ buffered at pH 5.0, benzonitrile and aliphatic nitrates and nitriles were found (Table 2).

TABLE 2

Nitrogen compounds obtained from the reaction of rendered pork fat with nitrous acid at pH 5.0

Pentanenitrile	Benzonitrile
Hexanenitrile	
Heptanenitrile	Pentyl nitrate
Octanenitrile	Hexyl nitrate
Nonanenitrile	Heptyl nitrate
Decanenitrile	Octyl nitrate
Undecanenitrile	
Dodecanenitrile	
Tridecanenitrile	
Pentadecanenitrile	
Heptadecanenitrile	

The alkyl nitrates probably result from the reaction of nitrous acid, or free radical species derived from nitrite, with the free radical intermediates obtained in the thermal oxidation of unsaturated fatty acids, e.g.:

$$R\text{-}CH_2\text{-}CH{=}CH\text{-} + O_2 \longrightarrow R\text{-}CH(OOH)\text{-}CH{=}CH\text{-}$$

$$R\text{-}CH(OOH)\text{-}CH{=}CH\text{-} \longrightarrow R\text{-}CH{\bullet}$$

$$R\text{-}CH{\bullet} + O_2 + RH \longrightarrow R\text{-}CH\text{-}OOH + R{\bullet}$$

$$R\text{-}CH\text{-}OOH \longrightarrow R\text{-}CH\text{-}O{\bullet}$$

$$R\text{-}CH\text{-}O{\bullet} + NO_2 \longrightarrow R\text{-}CH\text{-}ONO_2$$

A mechanism for the formation of nitriles involving nitrite and lipids is not so obvious. However, a possible route involves the C-nitrosation of a methylene group in the aliphatic chain of a fatty acid, which is activated by an adjacent carbonyl, carboxyl or similar group. Thermal degradation of the resulting oxime could give the CN group.

$$R\text{-}CH_2\text{-}CO\text{-} \xrightarrow{\text{nitrosation}} R\text{-}\underset{\underset{NO}{|}}{CH}\text{-}CO\text{-} \rightleftharpoons R\text{-}\underset{\underset{NOH}{||}}{C}\text{-}CO$$

$$R\text{-}\underset{\underset{NOH}{||}}{C}\text{-}CO\text{-} \xrightarrow{\text{heat}} R\text{-}C{\equiv}N$$

Although these nitriles and nitrates may not themselves be responsible for cured meat flavour, their presence in the volatiles of cured pork demonstrates novel reactions which may give rise to other compounds associated with the flavour of cooked cured meat.

References

1 D.B. MacDougall, D.S. Mottram and D.N. Rhodes, Contribution of nitrite and nitrate to the colour and flavour of cured meats. J. Sci. Food Agric., 26 (1975) 1743-1754.

2 J.I. Gray, B. MacDonald, A.M. Pearson and I.D. Morton, Role of nitrite in cured meat flavour: a review. J. Food Prot. 44 (1981) 302-312.

3 F.H. Heidemann and J. Wisemer-Pedersen, A study of some relations between organoleptic and chemical-physical data. Proc. 23rd European Meeting Meat Res. Workers, Moscow, 1977, pp.F1:7-F1:11.

6 C.-T. Ho, K.N. Lee and Q.Z. Jin, Isolation and identification of volatile flavour compounds in fried bacon. J. Agric. Food Chem., 31 (1983) 336-342.

7 D.S. Mottram, S.E. Croft and R.L.S. Patterson, Volatile components of cured and uncured pork: the role of nitrite and the formation of nitrogen compounds. J. Sci. Food Agric. 35 (1984) 233-239.

8 D.S. Mottram, Organic nitrates and nitriles in the volatiles of cooked cured pork. J. Agric. Food Chem. 32 (1984) 343-345.

9 D.S. Mottram and D.J. Puckey, Artefact formation during the extraction of bacon volatiles in a Likens-Nickerson apparatus. Chem. Ind. (London), 1978 385-386.