T, NITRITE AND THE FLAVOUR OF CURED COOKED HAM

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e lowering of fat contents in cooked cured ham produced by the meat industry sometimes results in "low fat, low flavour" foods. This y appear irrational as defatting is applied to external fat and not to intramuscular fat, the acknowledged flavour precursor. Experiments e carried out to detect possible implications of external fat in the development of the typical cured flavour of cooked ham.

ids were extracted from a "nitrite-fortified" cooked ham (1000 ppm instead of 120 ppm), produced at a pilot plant. Lipids extracted from ured pork leg, pure tripalmitin and triolein served as reference materials. They were treated with high concentration of nitrite (ratio 1/1). mparison of IR data obtained on animal fats gives evidence that intramuscular fat from cured samples contains nitro-derivatives and ch less oxidation products than uncured references. On the contrary, external fat appears neither oxidized nor nitrosated. Under the erimental conditions used, nitro-derivatives are formed when nitrite is reacted with triolein or extracted pork lipids but not with lmitin.

hough possible on a chemical basis, nitrite reaction with external fat was not traced in cured meat samples. This suggests that such a ction can only take place at a very limited extend. As a consequence, direct contribution through formation of high-impact flavour mpounds seems unlikely. Decrease in flavour intensity associated with external fat trimming off, must therefore result from an intricate eme involving external fat in different ways (barrier, solvent or precursor for active species) that have still to be sorted out.

TRODUCTION

wadays, the meat industry currently produces cooked cured ham with fat contents lower than 5%. Triggered in the eighties by the alleged sumer demand for foods low in calories, reduction of the fat contents is usually achieved by trimming off most of the external fat.

m the sensory point of view, low fat products sometimes deserve blame for lacking the typical cured flavour of ham. Considered in the ht of field observations, made by practitioners, suggesting that external fat plays an active role in the development of the characteristic vour of the finished product (GOUTEFONGEA and TOURAILLE), the claim of the learned consumers seems to make sense.

widely accepted that a number of sensorially active volatile compounds traced in food are end-products of the oxidative breakdown of aturated fatty acids. General schemes for flavour formation in cured meat products have been proposed. It is commonly assumed that the idative process implicating phospholipids of meat is severely impeded by nitrite, either through inhibition of the primary reaction ROSS and ZIEGLER, 1965; IGENE *et al.*, 1985) or through diversion of peroxides from the normal pathway (MOTTRAM, 1984). All posed routes share a common feature as they emphasize implicitly on intramuscular fat, especially phospholipids, that are not liable to be ected by trimming of the external fat.

ch a situation, in which experience of sensory experts opposes to modelized systems of the chemists, is certainly puzzling although not ceptional. Involved in an investigation on nitrite reaction with meat lipids, it appeared sensible to broaden the study beyond the scope of e sensitive intramuscular fat. Moreover, considering previous experiments that have evidenced a strong binding of some nitrogen-ntaining derivatives to fat in nitrite-treated adipose tissue (GOUTEFONGEA *et al.*, 1977) led us to carry out studies to the whole of pork .

ATERIALS and METHODS

Processed meat samples

ooked ham samples were produced at a pilot plant according to the customary practise with the sole exception that nitrite was added in an ght-fold excess (1000 ppm instead of 120 ppm). Adipose tissue was trimmed off. Lipids were subsequently extracted from meat and ipose tissue. The organic phase was washed with saline water (NaCl 0.71%) in order to remove residual nitrite and water-soluble purities and dried under nitrogen. The residue was dissolved in methylene chloride and stored deep-frozen until use.

Control samples

pids from uncured pork legs were extracted according to the procedure reported for cooked ham. Pure tripalmitin and triolein (Sigma, St. uis, Mo), were used as model fat samples.

*** Nitrosated model systems**

Pure lipid or uncured meat fat extracts (0.5 g) were suspended in 10 ml of 0.6 M acetic acid-sodium acetate buffer (pH = 5.6) and prote
sonicated with a 500W Sonic and Material Inc. pulse sonifier (20 kHz; titanium microtips; output 4; 40% duty cycle) for 15 minutes in
cold. Then, samples were transferred into nitrogen-flushed 50 ml conical flasks and the required amount of $NaNO_2$ (ratio ranging from 0.
to 0.62; w/w) added. Magnetically stirred reaction mixtures were incubated for 2 hours at 37°C. In the event of residual nitrogen oxid
samples were bubbled under nitrogen, extracted with methylene chloride and stored deep-frozen until use.

*** Experimental**

Nitrite-treated samples and their untreated counterparts were investigated by means of infra-red spectroscopy and gas-liqu
chromatography.

*** Infra-red spectroscopy.**

Spectra were recorded in a Fourier transform mode on a Nicolet DX-10 spectrometer. Measurements were carried out either on liquid fil
using sampling cells with **KBr** windows or on **KBr** pellets. The absorption band at 1712cm^{-1}, characteristic for the **C=O** bond of oleic ac
was taken as an internal standard and used for peak calibration.

*** Gas-liquid chromatography**

Methyl esters, prepared according to MORRISON and SMITH (1964) were chromatographed on a Delsi 700 gas chromatograph equipp
with a FID detector. The injector and detector temperatures were maintained at 250°C. Samples were analysed by using a 50m x 0.25m
bonded CP-Sil88 fused silica capillary column (Chrompack, Delft, Netherlands). Column temperature was 180°C and the inlet pressure
the hydrogen carrier gas was 0.6 bar. The output signal was integrated by means of a Delsi Enica 10 electronic integrator.

RESULTS and DISCUSSION

IR spectra of intramuscular lipids extracted from either cured or uncured meat were obtained. Some noticeable differences can be p
pointed when spectra are matched (Fig. 1). Cured samples do not display the strong wide band in the 3600-3100cm^{-1} region which is sho
by the uncured samples. The band can be attributed to a **-OH** bond. Other bands, indicating that intramuscular lipids of uncured me
contain much more oxygenated derivatives than cured samples, can be spotted in the 1250-1050cm^{-1} region. Intensity of these ban
generally increases during storage of uncured samples whilst cured samples are left unaffected. Hints can be found, in nitrite-treate
samples, of the formation of **N**-containing derivatives of fatty acids. Spectra of cured samples contain a weak absorption band at 1554cm
(interpreted as **C-NO2** groups) and a pair of coupled bands at 1646cm^{-1} and 1276cm^{-1} (interpreted as **C-ONO2** groups). Beside th
immediate inference that intramuscular fat is heavily implicated, these results are consistent with either schemes proposed previously t
account for cured flavour formation. Neither inhibition of oxidation nor formation of specific flavour compounds at the expense of oxidize
fatty acids can be ruled out in the light of the available data. Moreover, as mechanisms are not exclusive of each other, they may occu
jointly as a consequence of nitrite-fat reaction.

IR spectra obtained on external fat extracted from cured and uncured meat samples look very similar. They do not show any evidence fo
lipid oxidation nor reaction with nitrogen oxides. It can be concluded that under normal conditions used for cooked ham processing, external
fat is very stable. Whatever the scheme accepted to explain flavour formation in cooked cured meat product, external fat can hardly be
assigned as an effective flavour precursor. Removal of external fat may therefore be expected to have very little impact on the overall
flavour intensity. Observations based on sensory experience of consumers and professionals support the opposite conclusion, leading to thi
overlooked evidence that the sensorially active flavour can notably differ from what is expected on the basis of the flavour potential.

The question is raised to point out how external fat can contribute to the making of the characteristic flavour of cooked cured ham withou
involving lipid oxidation. Two proposals, implying the formation of character-impact components, can be made to try to answer the questio
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- First, external fat reaction with nitrite has occurred but instruments are not sensitive enough to detect the formed compounds.
- Second, external fat has not reacted and plays a role as a barrier protecting against volatilization of characteristic flavour compounds.

In the event of the first proposal is right, ability of external fat to react with nitrite has to be investigated. Assuming that nitrite reactivity
toward unsaturated fatty acids may be seriously lowered when involved in triglycerides, previous reports (ROSS *et al.*, 1987; DUMONT *et*
al., 1990) dealing with individual fatty acids were reexamined. IR spectrum obtained on triolein reacted with nitrite (molar ratio nitrite/oleic
acid; **R** = 1) is shown in Fig. 2, matched with the spectrum obtained on neat triolein. Evidence for the formation of **N**-containing derivatives
of fatty acids can be found in the presence of absorption bands at 1554cm^{-1} and 1369cm^{-1} (interpreted as **C-NO2** groups) and of coupled
bands at 1646cm^{-1} and 1276cm^{-1} (interpreted as **C-ONO2** groups).

Fig.1: I.R. Spectra of intramuscular lipids from ham.

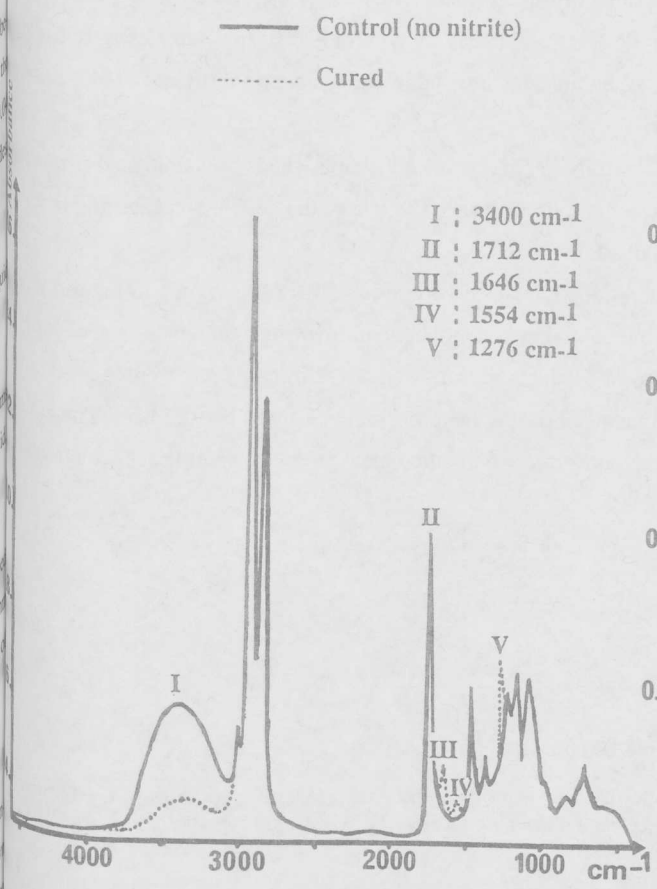


Fig.2: I.R. Spectra of Triolein.

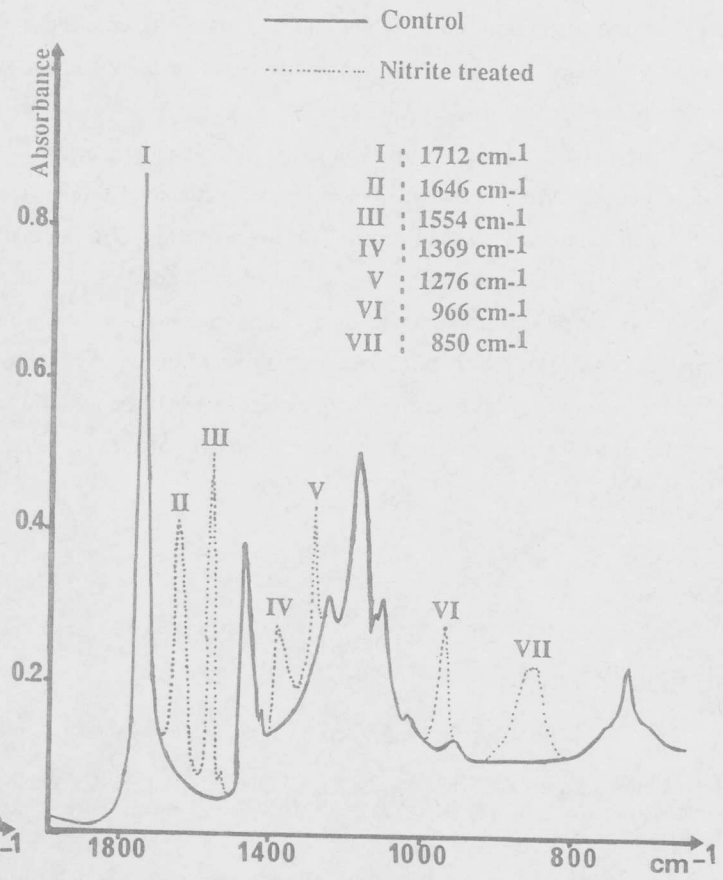


Fig.3: Isomerization of Δ9 double-bonds in triolein at different values of R= Nitrite/Oleic acid

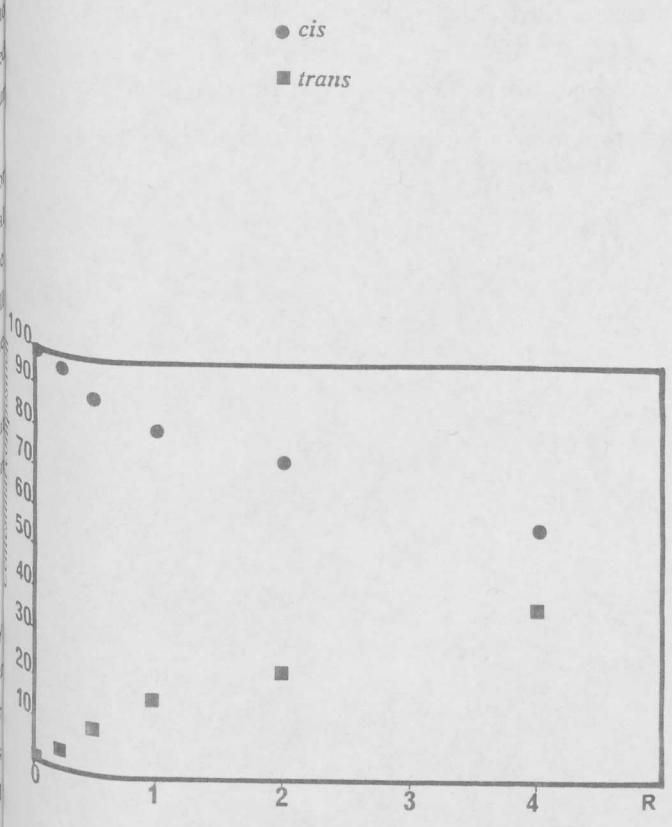
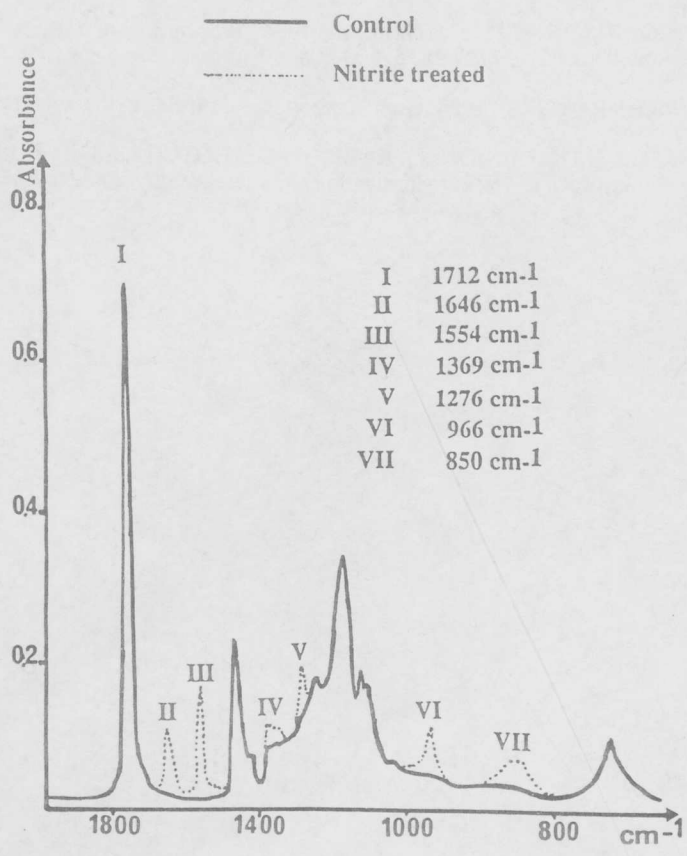


Fig.4: I.R. Spectra of extramuscular lipids extracted from ham, and thereafter nitrite treated.



Presence of an additional band at 966cm^{-1} indicates an appreciable extend of *cis-trans* isomerization of the double bond of oleic acid. the contrary, tripalmitin show no hint that reaction has taken place as IR spectra obtained on control and treated samples were identical can be concluded that, under the conditions used in the experiment, ester linkages are stable and reactions restricted to the unsatur moiety of the lipid molecule.

Fig. 3 shows that, as evidenced previously on individual fatty acids (DUMONT *et al.*, 1990) fairly high yields of elaidic acid (*trans* isom can be produced from oleic acid in model systems containing high concentrations of nitrite. The rate of the double bond shifting from the to the *trans* configuration can be modelized in the form $\mathbf{C = C_0 (1 - exp(-kR))}$.

IR spectrum obtained on external fat, extracted from pork leg and subsequently reacted with nitrite ($\mathbf{R = 1}$), is shown in Figure 4. It is very similar to the spectrum obtained on treated triolein. It can therefore be assumed that location rather than composition accounts for apparent absence of reactivity of external fat toward nitrite in cured meat products. Results suggest that, although possible on the basis chemical reactivity, nitrite reaction with external fat is certainly little involved during the processing of cured cooked ham. The actual of external fat (barrier, solvent or precursor for active species) in the flavour formation of cured meat products has still to be digged out.

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