Effect of Cooking and Drying on Carbonyls of Oil Sardine

K.AMMU and K.DEVADASAN
Central Institute of Fisheries Technology, Cochin - 682 029

Changes in the total as well as major individual carbonyls of oil sardine during steam cooking, oven drying, sun drying and freeze drying are presented. Carbonyls extracted with hexane were converted to their 2:4 dinitro phenyl hydrazone (DNPH) derivatives and were separated into major classes by column chromatrography on celite/ magnesia. Individual carbonyls were then identified by capillary gas chromatography of the DNPH derivatives. Dehydration and heating increase the carbonyl production from highly unsaturated fish lipids. The carbonyls produced react with other muscle constituents leading to complex changes. The influence of the mode of dehydration on these different aspects and their net effect on flavour are discussed.

Heat treated and dehydrated fat samples undergo easy oxidation leading to production of carbonyls. In the case of the highly unsaturated fish oils, such changes can be pronounced with noticeable changes in the flavour. Since many of the fish processing operations involve cooking, changes in the carbonyl profile of the fish during cooking is very important. Fat in dehydrated samples is easily oxidised resulting in rancid flavour. The influence of the method of dehydration on the extent of carbonyl production is one of the aspects that has not been studied in detail. Production of carbonyls and their subsequent reaction with other muscle constituents play a vital role in determining the final flavour of the product. This paper reports the results of a study on the effect of cooking as well as different dehydration methods on the carbonyl content in oil sardine muscle.

Materials and Methods

Fresh oil sardines *(Sardinella longiceps)* were procured from local fish landing centres. Carbonyls were extracted from a portion of the fish immediately. Another portion of fish was cooked in steam at 1.1 kg/cm² pressure for 10 min. Meat from another portion was minced well in a laboratory model meat mincer. The minced meat was divided into three portions. One portion was dried in sun to a moisture level of 3.4%. The second portion was dried in air oven at 80–85°C till the moisture content came down to 4%. The third portion was frozen and freeze dried in a Toshniwal model lyophiliser to a moisture content of 2%.

10 g of cooked muscle was minced well with enough anhydrous sodium sulphate in a mortar and extracted repeatedly with carbonyl free hexane to yield total carbonyls. In the case of dried samples powdered dried muscle was directly extracted with carbonyl free hexane. Conversion of the extracted carbonyls to the dinitrohenyl hydrazone (DNPH) derivatives, separation of the total carbonyls into major classes by column chromatography on celite 545/magnesia and identification of individual carbonyls by capillary gas chromatography were done by the methods reported earlier (Ammu *et al.*, 1986).

Results and Discussion

Table 1 presents the changes in total extractable carbonyls and in major groups like saturated monocarbonyls, 2-enals, dicarbonyls etc.and the fraction having absorption maximum at 380–385 nm (presumably unsaturated ketones and 2:6 dienals) in the muscle of oil sardine during cooking, after drying in sun, in an air oven at 80–85°C and in a freeze drier.

Monocarbonyls are known to have greater influence on flavour. In fresh fish, 58% of the total carbonyls were saturated mono-

carbonyls the rest being dicarbonyls. 2-enals, unsaturated ketones, 2:4 dienals, 2:6 dienals etc. were not detected.

Steam cooking is found to increase the extractable carbonyl content by 53.6%. 61% of the total extractable carbonyls of cooked muscle was saturated monocarbonyls, whereas 34% was dicarbonyls. About 5% of the total carbonyls were 2-enals (Table 1). Dicarbonyl fraction registered a 27% increase during cooking whereas saturated monocarbonyls increased by almost 62% from the original value. Heating in presence of air is known to increase the carbonyl content in the case of beef and pork fat (Hornstein & Crowe, 1960). However, the notable feature during cooking of fish muscle is the formation of 2-enals. It seems reasonable to conclude that 2 enals, even in minor quantities, may be contributing significantly to the overall characteristic cooked flavour. Hrdlicka & Pokorny (1962) observed that oxidation of oleic, linoleic and erucic acids at 180°C resulted in the production of n-alkanals and alk-2-enals. Oil sardine lipids, though not rich in linoleic and erucic acids are rich in oleic acid. 2-enals may be produced from oleic acid which accounts for 10–15% of the muscle lipid fatty acids of oil sardines (Gopakumar & Nair, 1966; Viswanathan Nair *et al.*, 1979). But Hrdlicka & Pokorny (1963) reported that oxidation of several natural fats at 180°C showed a different trend. Saturated compounds (with ketones predominating) and a number of dienals were produced from highly unsaturated fats. In the present study the highly unsaturated sardine lipids were heated in steam under pressure which again may be changing the picture.

The three methods of drying tried, gave different results with regard to the carbonyl content of the products (Table 1). The sample dried at 85°C in air oven showed an increase of 89% in the total carbonyls. 40% of the total carbonyls of this sample was saturated monocarbonyls and 40% dicarbonyls, the balance being the fraction with absorption maximum at 380–385 nm. Sun dried samples recorded 344% increase in total carbonyls. This sample showed the presence of saturated monocarbonyls (25%), 2 enals (9%), 2:6 dienals and unsaturated ketones (44%) and dicarbonyls (22%). Total carbonyls in freeze dried samples showed an increase of 558%. 67.5% of these were saturated monocarbonyls and 22% 2 enals. 10.5% of the total carbonyls in freeze dried samples were accounted by idicarbonyls (Table 1).

Drying invariably results in browning, its extent varying with the conditions of drying. The products of browning reactions can interfere with the absorbance when the DNPH deivatives of carbonyls from these samples are estimated spectrophotometrically. Moreover, the E values taken for calculation of total carbonyls (E = 22,500) also may not be the appropriate value in the case of

Table 1. *Changes in the total and major classes of carbonyls in oil sardine during cooking and drying (values in μ moles/100 g muscle)*

Samples	Total carbonyls	Saturated aldehydes and ketones	2 enals	Compounds with absorption maximum at 380–385 nm	Dicarbonyls (by difference)
Fresh	36.0	21.0	—	—	15.0
Cooked	55.3	34.0	2.6	—	18.7
Oven dried	68.0	27.8	—	13.5	26.7
Sun dried	160.0	40.0	15.0	70.0	35.0
Freeze dried	237.0	160.0	52.0	—	25.0

Note: 1. Calculated from standard E values at appropriate wave lengths. For the fraction at absorption maximum at 380–385 nm E value is taken as 22,500
2. All values expressed on wet weight basis

carbonyls from dried samples due to the interference from the browning compounds extracted by hexane along with the carbonyls.

Browning reactions occurring during drying can cause other problems also. These involve reactions of carbonyls with other muscle constituents like sugars, amines etc. thereby reducing the net available carbonyls. In oven dried samples, browning is maximum and available carbonyls was minimum. Freeze drying resulted in minimum browning and this gave the highest values for total extractable carbonyls. The absence of the 2-enals fraction in the oven dried samples also support the fact that browning reactions and interactions among the flavour compounds occur when fish muscle is heated in the presence of oxygen. Burton *et al.* (1963) examined the browning potentialities of a wide range of carbonyl compounds and obtained most rapid browning with alk-2-enals. These reactions may be relatively less during sun drying compared to oven drying which explain the higher amounts of extractable carbonyls in sun dried samples.

Freeze drying, on account of the low temperature and vacuum, normally can not be expected to favour production of carbonyls. However freeze dried sample becomes a porous mass which on subsequent exposure to air easily gets oxidised leading to the production of significant amounts of carbonyls. But unlike in sun drying and oven drying these carbonyls do not become unavailable as reaction with other muscle constituents will be very slow or nil in this case. The net available carbonyl content is thus maximum in freeze dried samples. The milder conditions of oxidation of the lipids of the porous freeze dried fish muscle probably do not result in fatty acid chain breakage and production of lower carbonyls. On the other hand, higher carbonyls are the probable end products. But in this study, many of the probable higher carbonyls were not identified due to lack of authentic reference standards. This probably explains, the small increase in the identified individual carbonyls in the freeze dried sample (Table 2) in spite of the substantial increase in total bcaronyls.

Table 2. *Changes in the content of major individual carbonyls during cooking and drying of oi sardine (% increase or decrease from the values for fresh fish)*

Carbonyl compound	Cooked	Oven dried	Sun dried	Freeze dried
Formaldehyde	+ 345.0	+ 173.0	+ 219.0	+ 158.0
Acetaldehyde	+ 70.0	+ 612.0	+1056.0	— 100.0
Propionaldehyde	+ 375.0	+ 520.0	+1794.0	+ 133.0
Isobutyraldehyde	+ 603.0	— 100.0	— 100.0	+ 655.0
Butyraldehyde	+ 141.0	+ 71.4	+ 12.0	+ 56.0
Isovaleraldehyde	+ 230.0	+ 499.0	+ 977.0	— 95.0
Valeraldehyde	+ 708.0	+1136.0	+2647.0	+ 124.0
Hexaldehyde	—	—	—	+ 37.0
Heptaldehyde	—	—	—	+ 21.0
Octaldehyde	+1104.0	—	+2140.0	—
Pelargonaldehyde	— 100.0	+1481.0	+2303.0	+ 51.0
Acetone	— 100.0	— 100.0	— 100.0	+ 120.0
Methyl ethyl ketone	+ 66.2	+ 3.1	+ 105.0	— 100.0
2 pentanone	— 100.0	+ 183.0	+ 100.0	+ 76.0
3 heptanone	+ 777.0	+1068.0	+ 436.0	— 100.0
4 heptanone	—	+3170.0	—	—
2 heptanone	+ 972.0	+1171.0	+ 599.0	+ 121.0
Octanone	— 100.0	— 100.0	+ 548.0	— 60.4
Heptyl methyl ketone	— 100.0	— 100.0	— 100.0	— 100.0

All values calculated on wet weight basis
+ = % increase; — = % decrease

All the three methods of drying, in general, lead to an increase in saturated aldehydes. In the case of oven dried and sun dried samples, 2-heptanone and 3-heptanone showed significant increase. Oven dried samples showed a remarkable increase in 4-heptanone also. As these were not present in freeze dried samples their role can be inferred to be in imparting the baked flavour of oven and sun dried fish. Increase in the aldehydes especially propionaldehyde, valeraldehyde and pelargonaldehyde, was remarkable in oven dried and sun dried samples. Freeze drying on the other hand, resulted in marginal increase of these compounds, probably due to reasons already explained above. But freeze drying was found to result in the production of hexaldehyde, heptaldehyde etc. which might have undergone further degradation or reaction during the other drying methods (Table 2).

Sun drying and freeze drying were found to produce 2-enals also. Crotonaldehyde and 2-pentenal were identified in sun dried samples. Sun dried and freeze dried samples showed the presence of a compound which can be 3–hexenal. But this needs further confirmation. Josephson *et al.* (1984) postulated that 3-hexenal can be formed in fish from eicosapentaenoic acid. Freeze dried samples had in addition to these, 2–hexenal and 2–heptenal.

Dienals and unsaturated ketones (380–385 nm) were seen only in sun dried and oven dried samples. Sardine lipids with its high content of $C_{20:5}$ and $C_{22:6}$ acids could be expected to have more dienals. But this was not found to be the case. In the case of oil sardine which exhibits remarkable seasonal changes in the nature and content of muscle lipids, season of catch is also a fact causing variations in the carbonyl profile (Viswanathan Nair, 1981).

The authors are thankful to Shri M. R. Nair, Director, Central Institute of Fisheries Technology for his encouragement and permission to publish this paper. Thanks are due to the Dairy Research Laboratory of the CSIRO, Australia for providing the DNPH derivatives of several carbonyls for use as reference standards.

References

Ammu, K., Viswanathan Nair, P. G. & Devadasan, K. (1986) *Fish. Technol.* 23, 134

Burton, H. S., McWeeny, B. J. & Biltcliffe, D. O. (1963) *J. Sci. Fd Agric.* 14, 911

Gopakumar, K. & Nair, M. R. (1966) *Fish. Technol.* 3, 21

Hornstein, I. and Crowe, P. F. (1960) *J. Agric. Fd Chem.* 8, 494

Hrdlicka, J. & Pokorny, J. (1962) *Potravinarska Technologie.* 6, 161

Hrdlicka, J. & Pokorny, J. (1963) *Potravinarska Technologie.* 7, 113

Josephson, D. S., Lindsay, H. C. & Stuiber, D. A. (1984) *J. Agric. Fd Chem.* 32, 1350

Viswanathan Nair, P. G., Antony, P. D. & Gopakumar, K. (1979) *J. Fd Sci. & Technol.* 16, 151

Viswanathan Nair, P. G. (1981) *Studies on the Lipid Composition of Marine, Freshwater and Shell Fishes.* Ph. D. Thesis, University of Kerala