Lipid changes during the canning of mackerel

LIPID CHANGES DURING THE CANNING OF MACKEREL

by

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A Master's Thesis

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DEDICATION

To Mary for support and understanding.

ABSTRACT

Mackerel, Scomber scombrus, were filleted and fillets from one side of each fish were stored at -25°C. Fillets from the other side were immersed in saturated brine for 10 minutes and canned either in simulated tomato sauce (pH 4.7) or 2% brine.

Effects of the brining, heat processing and storage were studied. Iodine, Peroxide, Acid and Saponification Values in both canned and uncanned fillets were determined. The fatty acid profile was also determined for some of the samples. The analyses were carried out both on fillets with and without skin.

The analyses have shown slight changes between the canned and uncanned fillets. The brining process increases the Peroxide Values with an average of 28%, whereas the heat processing decreases the Peroxide Values by an average of 38%. No major changes were observed in the fatty acid composition, except for thymnodonic acid (20:5) which decreased about 4% due to heat processing.

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1. INTRODUCTION

The world catch of Scomber species in 1979 was 762 thousand tonnes of Atlantic mackerel, Scomber scombrus, and 2,571 thousand tonnes of the closely related Pacific mackerel, Scomber japonicus (FAO, 1980). The combined total of these species, 3,333 thousand tonnes represents about 5% of the total world fish catch. S. japonicus ranked 4th among the species of fish caught in 1979 and S. scombrus ranked 12th (Anon., 1981). About 30% of this catch is canned for human consumption (FAO, 1981). Mackerel is usually canned as steaks or in fillets in either brine, oil or tomato sauce (Tanikawa, 1971; Keay, 1979).

Mackerel has a high lipid content ranging from 1.0 to 23.5% (Murray and Burt, 1969) and 25.8% of the fatty acids in the lipids are polyunsaturated (Ackman, 1980). Polyunsaturated fatty acids are very susceptible to autoxidation resulting in the development of undesirable flavours and among the factors influencing the rate and course of autoxidation are exposure to air, high salt concentrations and high temperature (Mabrouk and Dugan, 1960; Lea, 1962a; Ahn et al., 1978).

Kinsella et al. (1975) pointed out that during the compilation of nutrient tables on fish and fish products, there is a need for data describing changes in fatty acids with processing (including canning), since lipids in fish vary widely as a function of species, season, etc. O'connor (1977) also suggested that more work should be carried out on nutritional and quality problems associated with thermal processing of foods including fish. Hansen (1977) emphasized that a study of the stability of nutrients during processing and storage is required. However little work has been reported following up these suggestions (Andrade and Lima, 1980). Among the few studies reported on changes in the lipids of flesh

foods during canning is that of Korzenoiowski (1971), who found decomposition of 40% of the phospholipids, an increase of 15% in the fatty acid content and significant changes in the triglycerides and cholesterol during the heat processing of canned pork and beef. Although Roubal (1963) observed no marked degradation of the polyunsaturated fatty acids during the canning of 4 species of tuna, Andrade and Lima (1980) reported decreases in myristic, pentadecanoic, palmitoleic, heptadecanoic acids and increases in palmitic, oleic and linoleic acids, during the canning of mandi (Pimelodus clarias), a Brazilian freshwater fish, in oil and tomato sauce packs.

The work described in this report was carried out in order to find out if significant changes in the lipids of mackerel (S. scombrus) occur in canning, both during pre-process brining operations and during the sterilisation process.

2. LITERATURE SURVEY

2.1 Lipids

Lipids are one of the three major classes of food components the others being carbohydrates and proteins. They have been known since ancient times and found utility because of their unique physical properties (Weiss, 1970). Lipids are found as depot fats in the adipose tissue of animals, in the oil glands of various plants and as dispersed fats. Initially a fat was defined as the oleaginous material which was solid at room temperature, while the liquid form was called an oil. Later lipids were defined as a heterogenous group of naturally occurring substances which are soluble in organic solvents such as ether, petroleum ether or chloroform (Aurand and Woods, 1973). However for practical purposes the lipids are normally grouped into the lipid classes, that is, triglycerides, phospholipids, free fatty acids and unsaponifiable matter.

2.1.1 Lipid classes

2.1.1.1 Triglycerides

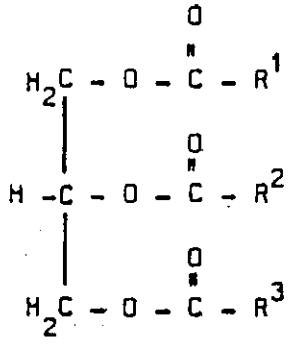
Triglycerides constitute the major lipid fraction of most animals, including fish, and most higher plants. For example about 90% of the total lipid in mackerel flesh is triglyceride (Hardy and Keay, 1972). Triglycerides are mainly found as depot fats in fish and represent only 0.1 to 0.2 % levels as cellular lipids (Ackman, 1974).

The triglyceride general structure is shown in Fig. 1, where the fatty acids esterified to the glycerol, R^1COOH, R^2COOH and R^3COOH, have saturated and unsaturated unbranched chains C_4 to C_{24}. Fatty acids are named according to the IUPAC rules for the nomeclature of Organic Chemistry (IUPAC, 1965). However Guarnieri and Johnson (1970) have adopted for convenience and brevity a short-hand designation of unsaturated fatty acids, in which the chain length is given, followed by a colon, and the number of double bonds in the molecule. The number following the letter ω (omega) or Δ (delta) indicates the number of carbon atoms between the terminal double bond and the methyl group or carboxyl group respectively. If more than one double bond is present in the molecule, a divinyl methane rhythm $\left[CH-CH_2-CH\right]$ is normally maintained in natural fatty acids.

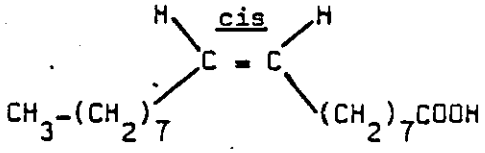
The saturated fatty acids esterified in natural triglycerides conform to the general formula $C_n H_{2n+1} COOH$, where "n" is an integer, as shown in Table 1. The most common saturated fatty acids found in animal and fish oils are palmitic (16:0) acid, stearic (18:0) acid and in lesser amounts myristic (14:0) acid (Tsuchiya, 1961). Saturated fatty acids of less than 16-carbon chain length are found in plant and milk fats (Weiss, 1970). Fish oils contain approximately 15 to 40% (of the weight of total fatty acids) of saturated fatty acids (Tsuchiya, 1961).

The unsaturated fatty acids esterified in natural triglycerides show two types of isomerism, geometric (cis, trans) and positional (difference in position of the double bond). Oleic acid and elaidic acid (see Fig. 1) are examples of naturally occurring geometric isomers. Most naturally occurring unsaturated fatty acids exist with cis double bonds, however trans double bonds are predominant in ruminant milk fats and in catalytically hydrogenated fats

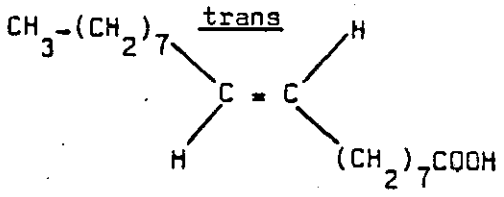
Figure 1 The general structure of triglyceride and an example of fatty acid geometric isomerism



triglyceride general structure



oleic acid (mp 14°C)



elaidic acid (mp 44°C)

Table 1 Some naturally occurring fatty acids

Systematic name	Common name	Formula	Short hand designation	
		Saturated fatty acids		
n-Butanoic	Butyric	$CH_3.(CH_2)_2.COOH$	4:0	
n-Dodecanoic	Lauric	$CH_3.(CH_2)_{10}.COOH$	12:0	
n-Tetradecanoic	Myristic	$CH_3.(CH_2)_{12}.COOH$	14:0	
n-Hexadecanoic	Palmitic	$CH_3.(CH_2)_{14}.COOH$	16:0	
n-Octadecanoic	Stearic	$CH_3.(CH_2)_{16}.COOH$	18:0	
		Unsaturated fatty acids	ω system	Δ system
Hexadec-9-enoic	Palmitoleic	$CH_3.(CH_2)_5.CH{=}CH.(CH_2)_7.COOH$	16:1ω7	16:1 Δ9
Octadec-9-enoic	Oleic	$CH_3.(CH_2)_7.CH{=}CH.(CH_2)_7.COOH$	18:1ω9	18:1 Δ9
Octadec-11-enoic	Vaccenic	$CH_3.(CH_2)_5.CH{=}CH.(CH_2)_9.COOH$	18:1ω7	18:1 Δ11
Octadeca-9:12-dienoic	Linoleic	$CH_3.(CH_2)_4.(CH{:}CH.CH_2)_2.(CH_2)_6.COOH$	18:2ω6	18:2 Δ9
Octadeca-9:12:15-trienoic	Linolenic	$CH_3.CH_2.(CH{:}CH.CH_2)_3.(CH_2)_6.COOH$	18:3ω3	18:3 Δ9
Eicosa-5:8:11:14 tetraenoic	Arachidonic	$CH_3.(CH_2)_4.(CH{:}CH.CH_2)_4.(CH_2)_2.COOH$	20:4ω6	20:4 Δ5
Eicosa-5:8:11:14:17 pentaenoic	Thymnodonic	$CH_3.CH_2.(CH{:}CH.CH_2)_5.(CH_2)_2.COOH$	20:5ω3	20:5 Δ5
Docosa-11-enoic		$CH_3.(CH_2)_9.CH{=}CH.(CH_2)_9.COOH$	22:1ω11	22:1 Δ11
Docosa-4:7:10:13:16:19-hexaenoic		$CH_3.CH_2.(CH{:}CH.CH_2)_6.CH_2.COOH$	22:6ω3	22:6 Δ4

(De Man, 1976). Positional isomerism occurs in many naturally occurring unsaturated fatty acids, for example 18:1ω7 is found to occur in fish oils in addition to 18:1ω9 (Ackman, 1974). Fatty acids with non-conjugated double bonds can rearrange to give conjugated double bonds on heating at high temperature, heating with alkali and also during autoxidation. The most common unsaturated fatty acids found in animal and fish triglycerides are oleic (18:1ω9) acid, palmitoleic (16:1ω7) acid, thymnodonic (20:5ω3) acid, docosaenoic (22:1ω11) acid, docosapentaenoic (22:5ω3) acid and docosahexaenoic (22:6ω3) acid (Ackman, 1980).

The distribution of fatty acids in the triglyceride molecule seems to be governed by chain length and unsaturation. In fish lipid triglycerides there are usually polyunsaturated fatty acids, such as 20:5ω3 or 22:6ω3, in the 2 position, a saturated or monounsaturated fatty acid in the 1 position, and often a monounsaturated fatty acid in the 3 position (Malins and Wekell, 1970), whereas in vegetable oils the saturated fatty acids have a tendency to occupy the 1 and 3 positions (De Man, 1976).

2.1.1.2 Phospholipids

All natural fats and oils contain some phospholipid. The lowest amounts are present in lard and beef tallow. In some crude vegetable oils, such as cottonseed, corn and soybean oils, phospholipids may be present at levels of 2 to 3% (De Man, 1976). Fish, crustacea and molluscs have approximately 0.7% total phospholipids in their muscle (Ackman, 1974). The phospholipids occur as basic

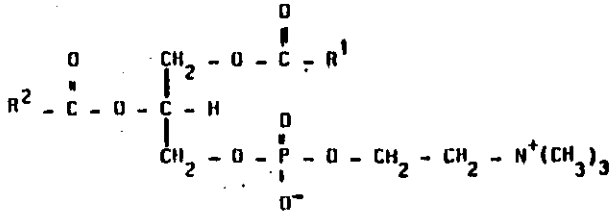
units in cellular structure and their fatty acids are generally more unsaturated than those of the triglycerides (Stansby, 1973), for example 60% of the fatty acids in the phospholipids of Atlantic menhaden (Brevoortia tyrannis) are unsaturated compared to 55% in triglycerides (Ackman et al., 1976).

The phospholipids include the phosphoglycerides (lecithin, cephalin and plasmalogens), the sphingolipids (sphingomyelins), and the phosphoinositides (Aurand and Woods, 1973).

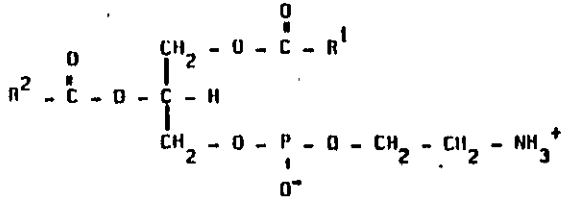
Lecithins are glycerol esters of two fatty acids and phosphoric acid combined with choline (see Fig. 2). Lecithins occur in nerve tissue, egg yolk, soybeans, liver and many crude vegetable oils. Their function in tissues is reported as keeping nonpolar molecules, such as sterols, in emulsified state (Aurand and Woods, 1973). Cephalin (see Fig. 2) is similar in structure to lecithin but with ethanolamine replacing choline. Cephalins are known to contain more unsaturated fatty acids than lecithins (Lea, 1962a). Phosphatidyl serine is also classified as a cephalin, since on decarboxylation it can form phosphatidyl ethanolamine (Weiss, 1970). The plasmalogens are substances present in the membranes of muscle tissue, brain and heart. They differ from lecithins and cephalins in that the fatty acid in the α-position is replaced by an α, β-unsaturated ether (see Fig. 2). The sphingolipids contain sphingosine (a long-chain unsaturated amino alcohol) in contrast to the other phosphatides which have glycerol as part of their structure (Aurand and Woods, 1973). Sphingomyelin is the most common sphingolipid (see Fig. 2).

The inositol (phosphoinositides) phosphatides are compounds which contain the cyclic hexahydroxy alcohol inositol, attached to the phosphate.

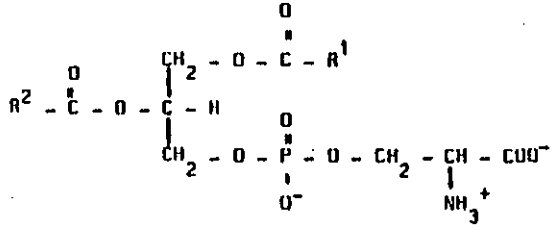
Figure 2 Structures of some phospholipids



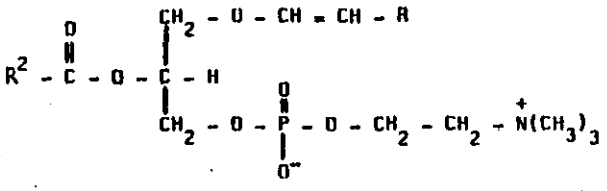
L - α-lecithin



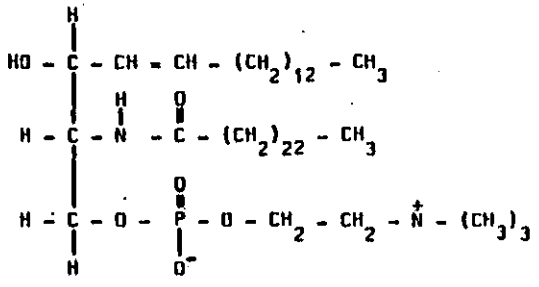
L-α-cephalin



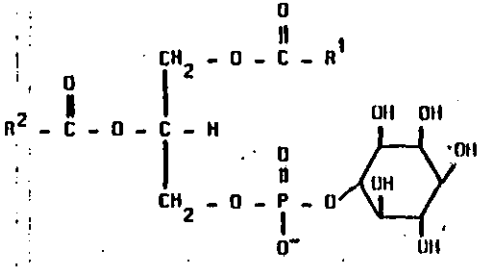
L-α-phosphatidyl serine



a plasmalogen



sphingomyelin



phosphatidyl inositol

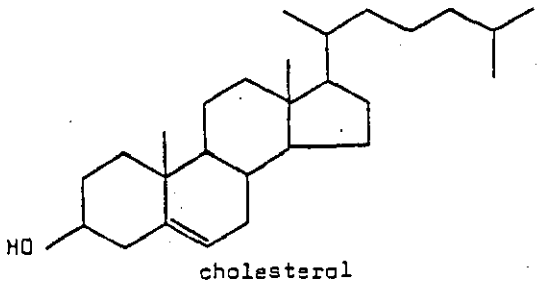
2.1.1.3 Free fatty acids

Free fatty acids occur in fresh animal lipids in minor quantities (Tsuchiya, 1961), for example in fresh rockfish muscle free fatty acids occur at levels of 0.04 to 0.07g/100g tissue (Wood et al., 1969). Storage, heat treatment and other types of processing can lead to an increase in the amount of free fatty acids. For instance, free fatty acids in minced cod fillets can increase from 4 to 40% during 20 days of storage at $-7^{o}C$ (Matthews et al., 1980).

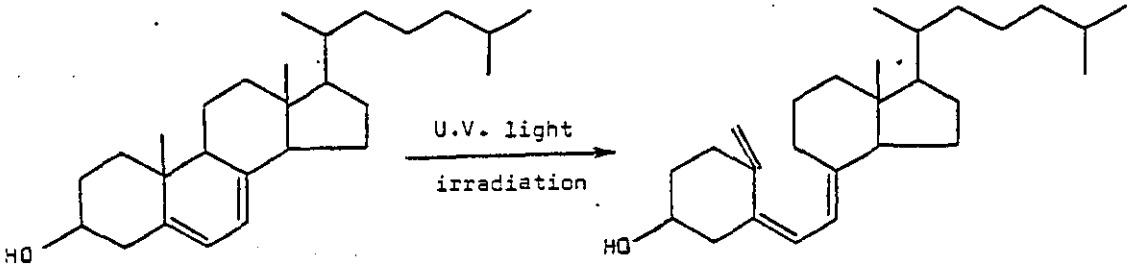
2.1.1.4 Unsaponifiable matter

The unsaponifiable matter of lipids consists of many different groups of compounds including the sterols, hydrocarbons and waxes. The sterols constitute the major group of compounds in the unsaponifiable matter of fats and oil (Meyer, 1960), representing about 64% of the unsaponifiable matter for corn oil (De Man, 1976), about 93 to 96 for fish lipids and 25 to 99% for shellfish lipids (Ackman, 1974). Cholesterol is the most common sterol in animal fats, and it has been associated with diseases of the heart and arteries (Jones, 1974). Cholesterol (see Fig. 3) is utilized in the biosynthesis of the adrenocortical hormones which are important in the development of secondary male and female sex characteristics (Aurand and Woods, 1973). Plant fats and oils contain phytosterols such as β-sitosterol, campesterol and stigmasterol. Although fish sterols are considered

Figure 3 Structures of some sterols and hydrocarbons

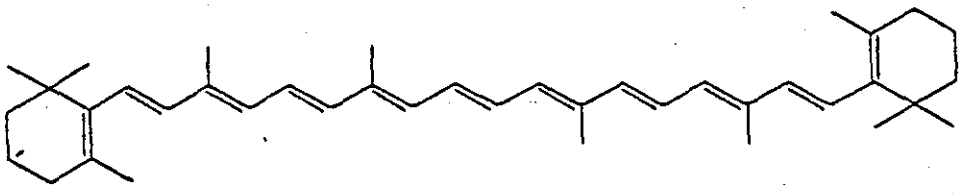


cholesterol

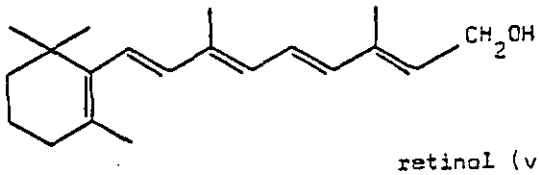


7-dehydrocholesterol

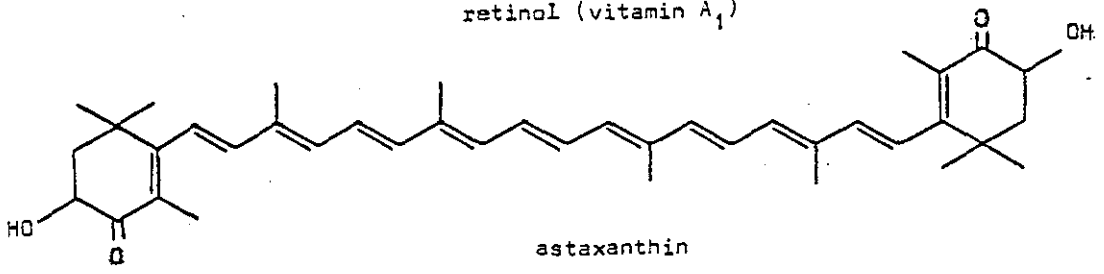
cholecalciferol (vitamin D_3)



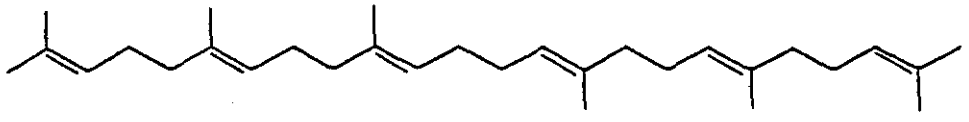
β -carotene



retinol (vitamin A_1)



astaxanthin



squalene

to be mainly cholesterol and derivatives, shellfish contain a number of phytosterols derived from their basic diet of unicellular plants (algae) (Kovacs et al., 1978).

Pearson (1978) reported that the cholesterol content of salt water fish is within the range of 26 to 68 mg/100g of flesh; prawns, 158 mg/100g and molluscs 57 to 77 mg/100g. Vitamin D_3, derived from 7-dehydrocholesterol is present in fatty fish muscle at levels of 300 to 1700 IU/100g and 4700 IU/100g in eel (Ikeda, 1980).

The hydrocarbon fraction includes coloured materials. The carotenes are present in several fats of vegetable origin and the cow concentrates it from the grass it eats in the milk fat (Weiss, 1970). Natural carotene is a mixture of three isomers alpha, beta and gamma. The natural mixture usually contains 85% β, 15% α and trace of γ-carotene. β-Carotene (see Fig. 3) can be metabolized to give two molecules of vitamin A_1. Vitamin A_1 also occurs naturally in several edible lipids including fish lipids. Carotenoids in fish include astaxanthin which contributes to the distinctive colour of salmonid flesh and crustacea (Katayama et al., 1972). Another component of the hydrocarbon fraction is squalene. Squalene occurs in fish liver and olive oil and has been found at levels of 3 to 45% in the liver oil of the basking shark, Cetorhinus maximus (Tsuchiya, 1961).

Waxes are esters of long-chain monohydroxy alcohols and fatty acids (Aurand and Woods, 1973). Natural waxes also contain paraffins, hydroxylated and unsaturated fatty acids, secondary alcohols and ketones. Waxes are widely distributed in nature

but they never occur abundantly. Fruit waxes often contain cyclic compounds of triterpenoid types, such as ursolic acid, which coats the surface of apples, grapes, etc. In animals waxes cover the surface of hair, wool and feathers. Some fish have wax esters as part of their body lipids, for example, in barracudina, Paralepsis rissoi kroveri, 85% of the total lipid is present as wax esters (Ackman et al., 1972).

2.1.2 Deterioration of lipids

Deterioration of lipids in foodstuffs occurs either by direct chemical reaction or through the intermediate agency of enzymes present in the raw tissues or produced by the activity of micro-organisms (Lea, 1962b). When it occurs through the autoxidation of unsaturated fatty acid glycerides in atmospheric oxygen, it is called lipid oxidation and off-flavours are referred to as oxidative rancidity. This is discussed in more detail below. When it occurs through the hydrolysis of the ester linkage enzymically or chemically it is called lipolysis and off-flavours, due to short chain fatty acids, are referred to as hydrolytic rancidity (Aurand and Woods, 1973). This is discussed in more detail below. In addition, at temperatures higher than 200^{o}C thermal polymerization, in the absence of air, and thermal oxidation, in the presence of air, may also take place (Perkins, 1960).

2.1.2.1 Lipid oxidation

Lipid oxidation is the most important type of deterioration of lipids in foods. The unsaturated bonds present in lipids are subject to oxidation as a result of their contact with even traces of oxygen (De Man, 1976). Oxidative deterioration of lipids results in the partial loss of vitamins, such as A, D, E, K and essential fatty acids and the development of pungent and offensive off-flavours (Aurand and Woods, 1973).

The general mechanism of lipid oxidation is well-established as a free radical chain reaction (Bateman, 1954; Swern, 1960; Labuza, 1971; Hardy, 1980). Three stages are involved: initiation, propagation and termination as shown in Fig. 4.

Initiation: In this stage hydrogen is abstracted from the methylenic carbon atom adjacent to a double bond in the unsaturated fatty acid chain (MH), yielding a free radical ($M^{\bullet}$). In the case of polyunsaturated lipid chains this can normally be stabilised by resonance (Labuza, 1971) (see Fig. 5 for resonance stabilisation of a free radical from a 1-cis,4-cis-diene system). The mechanism of this initiation step is not well established (Hardy, 1980) and heavy metal catalysis and bi- and termolecular reactions between substrate and oxygen (Ingold, 1961) have all been proposed.

Propagation: Once a free radical is formed, it can combine with oxygen to form a peroxy free radical, which in turn can abstract hydrogen from another unsaturated fatty acid chain (MH) to yield a hydroperoxide (M-O-O-H) and a new free radical ($M^{\bullet}$) initiating another reaction (see Fig. 4). The hydroperoxides produced in largest amounts from polyunsaturated fatty acid chains

Figure 4 General mechanism for the autoxidation of an unsaturated fatty acid chain (MH)

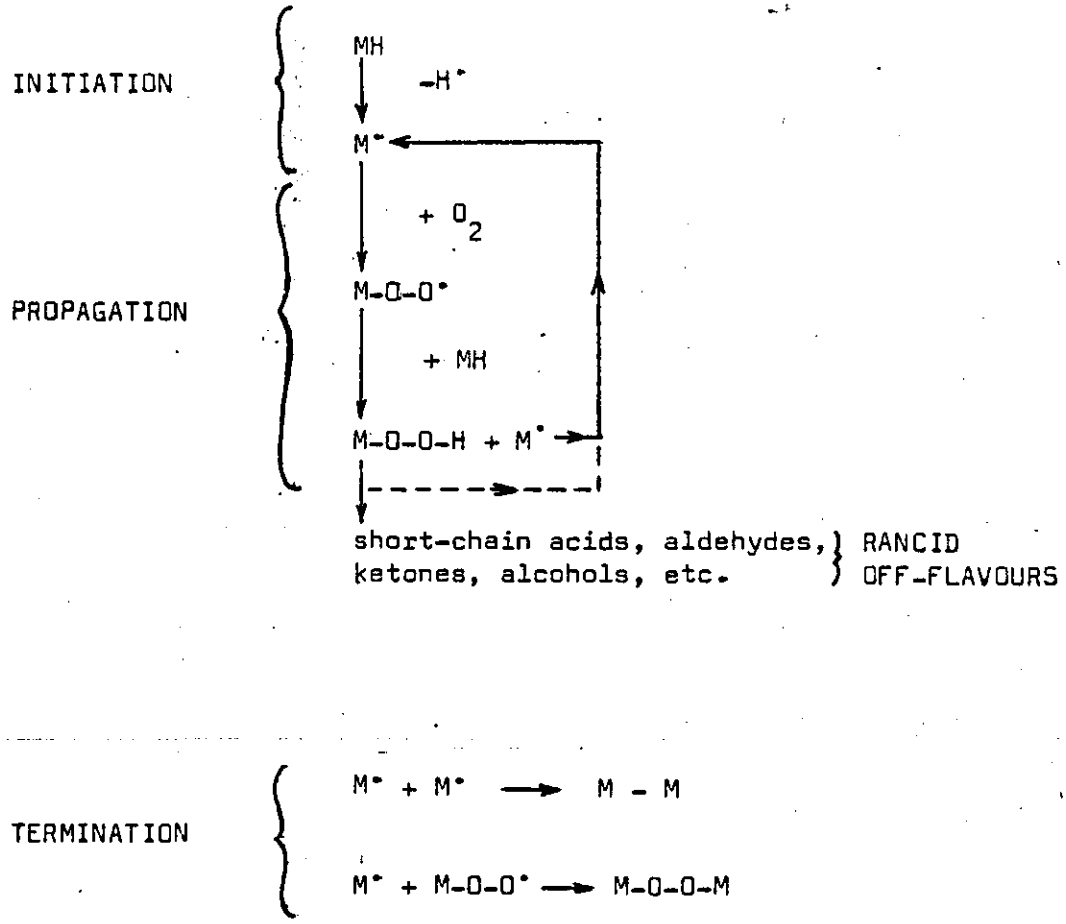
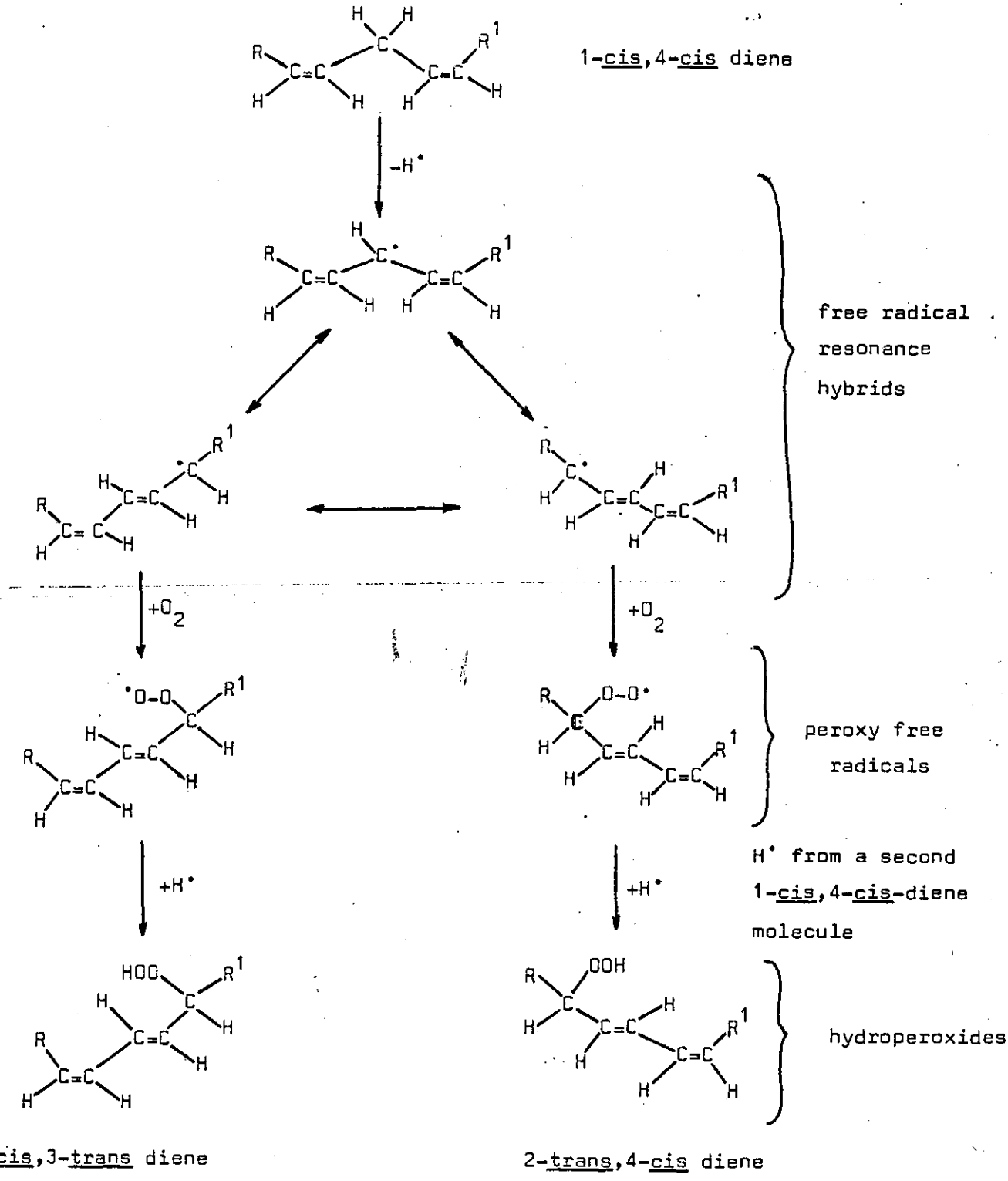


Figure 5 Mechanism for the autoxidation of a 1-cis, 4-cis-diene system e.g. a linoleate



are those in which double bond migration has occurred, for example, a 1-cis,4-cis-diene system rearranges to give 1-cis,3-trans or 2-trans,4-cis-diene hydroperoxides as shown in Fig. 5. The hydroperoxides produced are very unstable and decompose to form short chain acids, aldehydes, alcohols and ketones. These secondary oxidation products are responsible for the rancid off-flavours (Labuza, 1971). Hydroperoxide decomposition products include free radicals which can catalyse the autoxidation of further fatty acid chains.

Termination: The reaction can be terminated if the free radicals react with other free radicals to yield non propagating products; two examples of such reactions are shown in Fig. 4. The termination mechanism is important not only in controlling the rate, but also in deciding the nature of the primary products. A fast termination reaction will tend to reduce the amounts of hydroperoxide formed with a relative increase in other products such as peroxides, alcohols and ketones, whereas in slow termination reactions, hydroperoxides will predominate (Hardy, 1980).

The factors affecting the rate of lipid oxidation have been reviewed by a number of workers (Schultz et al., 1962; Labuza, 1971; Hardy, 1980), and include the following: composition of the lipid, availability of oxygen, temperature, moisture, radiation, pro-oxidants and antioxidants.

Composition of the lipid: The rate of lipid oxidation is not directly related to the total number of double bonds present in a fixed weight of the lipid (as measured by the Iodine Value) since it also depends on the distribution of double bonds between molecules (Aurand and Woods, 1973), for example, a linolenate

derivative (with 3 double bonds per chain) reacts about 25 times as fast as an oleate derivative (with 1 double bond per chain) (Meyer, 1960). The distribution of fatty acids in natural triglycerides also affects the rate of oxidation. In fish oils, unsaturated fatty acids in the 2 position of the glyceride molecule oxidize less rapidly than those in the 1 or 3 position (Hardy, 1980).

Availability of oxygen: Oxygen is necessary for autoxidation of lipids, thus its removal from a fat or food will prevent autoxidation. It has been reported that at low oxygen pressures, the rate of oxidation is approximately proportional to the pressure (Labuza, 1971). Thus exposure of lipid surfaces such as fillets, minces and gutted fish to oxygen will increase the rate of oxidation whereas lipids within the tissues will oxidize at a slower rate (Bligh and Regier, 1976). Oxygen-impermeable packaging can be used to retard lipid oxidation or packaging with an inert gas such as nitrogen.

Temperature: The effect of increasing temperature on the rate of autoxidation is slightly greater than for most chemical reactions, because it accelerates both the chain propagation and hydroperoxide decomposition reactions (Aurand and Woods, 1973). With subzero temperatures, for every 10°C reduction the oxidation rate falls by a factor of 2 or 3 (Hardy, 1980). Frozen fatty fish such as herring or mackerel can be stored up to 6 months at -30°C before rancid off-flavours become obtrusive (Hardy and Smith, 1976), compared with only a week or two at 0°C or above.

Moisture: Dehydration of foods, thus reducing the water activity to low values, is an effective method of preventing microbiological spoilage. However drying foods to very low water

activities renders them very susceptible to lipid oxidation. Increasing or lowering the water activity from about 0.3 (see Fig. 6) accelerates the rate of lipid oxidation. This has been explained by Labuza (1971) in terms of the ability of water to act as a solvent, to mobilize reactants and to interact either chemically or by hydrogen bonding with the reactants or other species.

Radiation: All forms of light and ionizing radiation are powerful accelerators of lipid oxidation. Ultraviolet and short wave visible light probably function mainly by photolysis of peroxides to chain-starting free radicals. Baldrati et al. (1978) reported an increase in lipid oxidation in irradiated chill stored fish, presumably due to the destruction of microbial oxygen users and introduction of free radical forming precursors.

Pro-oxidants: Transition metals which possess two or more valence states with suitable oxidation potentials both decrease the induction period and increase the rate of lipid oxidation. These metals include copper, iron, cobalt, manganese, nickel, etc. (Ke and Ackman, 1976). For example Castell and Spears (1968) found that copper, iron and vanadium were the most active catalysts in the development of rancidity in blended fish muscle. Haemo-proteins react with hydroperoxides to produce radicals and initiate autoxidation (Waters, 1971), thus haemoglobin acts as pro-oxidant in a wide range of food systems. In deboned poultry as well as deboned fish flesh haemoproteins can increase oxidative changes (Lee et al., 1975; Lee and Toledo, 1977).

Common salt (sodium chloride) shows an important accelerating effect on lipid oxidation in some food systems, apparently because of an activating influence on pro-oxidants already present although its effect may also relate to the water activity of the foodstuff (Mabrouk and Dugan, 1960).

Figure 6 Stability of foods as a function of water activity (Labuza, 1971).

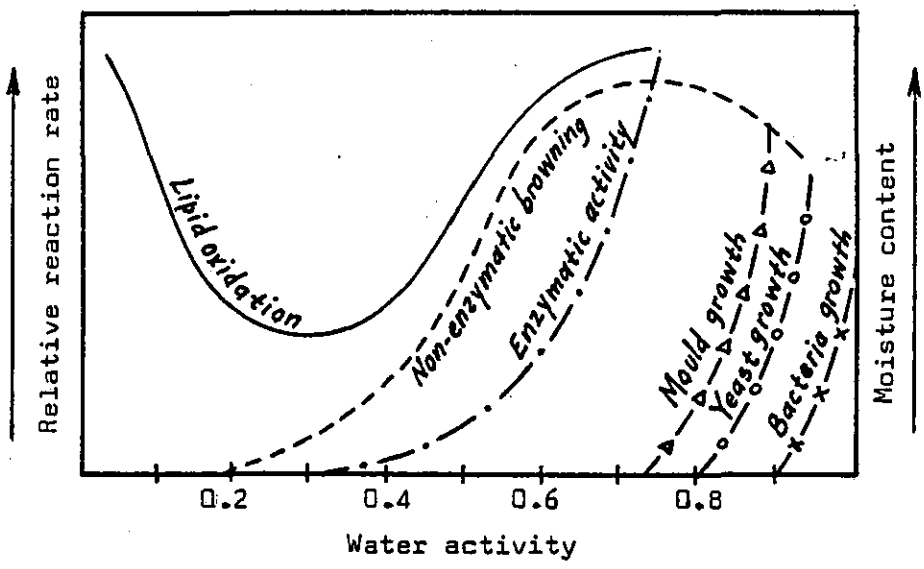
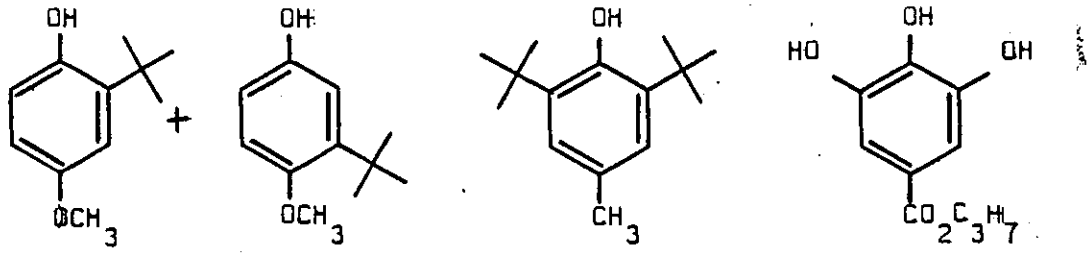
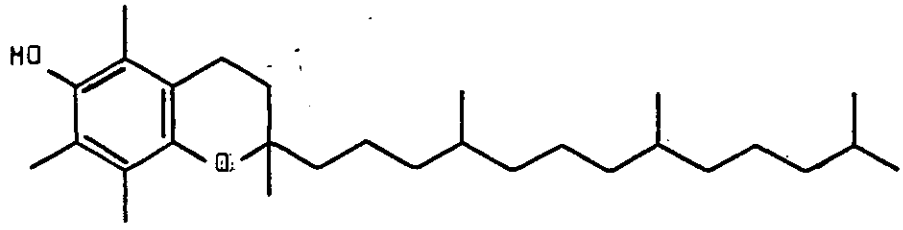


Figure 7 Phenolic antioxidants



BHA BHT PG



α -tocopherol

Enzymes, such as lipoxygenases and peroxidases, which are found widely in higher plants, can also catalyse lipid oxidation.

Antioxidants: Lipid oxidation in foods can be retarded by chemical compounds known as antioxidants. The chemical antioxidants act as: a) free radical terminators, for example, synthetic compounds such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and naturally occurring compounds such as α-tocopherol (see Fig. 7); or b) chelaters of metal ion catalysts, for example, ethylenediaminetetra acetic acid (EDTA), citric acid and various forms of ascorbic acid (Labuza, 1971). Ascorbic acid is also thought to act as an oxygen scavenger (Schuler, 1980). The free radical terminators are in general hindered phenolic compounds that form stable free radical intermediates on donation of hydrogen radicals to autoxidation free radical intermediates (Sherwin, 1978). These stable free radical intermediates are not able to initiate further autoxidation of fatty acid chains, but react with other free radicals in termination steps. The number of synthetic antioxidants permitted in foods is limited (De Man, 1976) and the concentrations strictly regulated because of toxicity problems (Sherwin, 1978). Naturally occurring lipids contain about 1 to 100 mg/100g of tocopherols (vitamin E). Animal lipids contain only α-tocopherol whereas vegetable lipids contain a mixture of α, β, γ and δ-tocopherols (Paul and Southgate, 1978).

In fish products, a wide range of compounds have been used as antioxidants such as ascorbic acid, sodium erythrobate, riboflavin derivatives, citric acid, glutamates and a whole variety of phenolic substances (Hardy, 1980 and references therein). Ethoxyquin

is commonly used to retard lipid oxidation in fish meal (Windsor and Barlow, 1981).

2.1.2.2 Lipolysis

Lipolysis can occur non-enzymically, particularly under processing conditions which involve high temperatures or extreme pH values, or enzymically. Lipolytic enzymes, lipases and phospholipases, in a stepwise process, produce free fatty acids, from triglycerides and phospholipids respectively. There are several different types of lipases and phospholipases that differ in their modes of action (Richardson, 1976).

Although free fatty acids produce undesirable off-flavours particularly in dairy products, where short-chain fatty acids are produced (Hampson and Hudson, 1961), no correlation has been established between the production of free fatty acids and the development of off-flavours in stored frozen fish and fishery products (Hardy, 1980) in which the free fatty acids are C_{14} and above.

2.1.3 Lipids in fish

2.1.3.1 General composition of fish

The chemical composition of fish flesh is very similar to that of the flesh of land animals. The principal constituents are: water 66 to 84%; protein 15 to 24% and lipids, 0.5 to 25%

(Jacquot, 1961; Stansby, 1973). The minor constituents include carbohydrate, which in white fish flesh is usually less than 1%, but in the dark muscle of some fatty species it may reach 2%. Minerals, accounted for by ash, rarely exceed 2%. Fish also contain water-soluble and fat-soluble vitamins. The water-soluble vitamins, other than vitamin C, are found in nutritionally significant amounts in fish and are generally evenly distributed within the fish (Murray and Burt, 1969). Of the fat-soluble vitamins, A and D are the most important in fish since they exist in relatively high quantities compared with other foodstuffs particularly in the liver and the gut.

2.1.3.2 Variability in total lipid content

The lipid content of fish varies in amount more than any other major chemical component. It may range from a minimum of 0.5 to a maximum of 25% (Stansby, 1973). The lipid content varies from species to species and even within the same species from one individual to another. The factors affecting this variation are numerous being either of intrinsic nature bearing upon genetics, morphology and physiology; or environmental, relating to the living conditions, particularly the feeding of the fish (Stansby and Olcott, 1963; Ackman, 1980).

Jacquot (1961) suggested classifying species of fish according to their lipid content into 3 categories: fatty fish with an average lipid content of 10%, semi-fatty fish with 2.5% and lean with 0.5%. Jacquot warned however not to draw too strict lines between these categories because of the range within species and

individual variations. Lean fish which have very low lipid content in the flesh have considerable lipid stored in their livers, for example cod and haddock have livers which sometimes represent 10% of the total weight of the fish and contain 50 to 80% lipid (Stansby, 1973).

The seasonal variation of the lipid content of the fish is mainly due to the stage of sexual development and feeding conditions. For example, during the spawning period fish cease feeding and the lipid content falls. Atlantic sardine contains 2% of lipids in the spring before spawning and 8.6% in the fall (Jacquot, 1961); Atlantic mackerel, Scomber scombrus, contains 6.3% of lipid in the summer at spawning time and 23.4% in the winter (Hardy and Keay, 1972).

The lipid content of the flesh (skinless, boneless fillets) varies from one part to another. There is a tendency for segments near to the head of a fish to have a higher lipid content than those near the tail, for example pink salmon (Oncorhynchus gorbuscha) has nearly twice as much lipid in a slice near the head as in a slice near the tail (Stansby, 1962). The dark flesh which occurs usually in small areas, such as beneath the skin and the lateral line has usually higher lipid content than the white flesh (Love, 1970). The belly flap also has a high concentration of lipids, perhaps because it cannot take an active part in swimming so makes a convenient lipid storehouse (Karrick and Thurston, 1964). For example, in halibut, Hippoglossus hippoglossus, the lipid content in the belly flap is about 4.8% whereas in the muscle it ranges from 1.3 to 1.2% (Mannan et al., 1961), and in mackerel, Scomber scombrus, the belly flap contains 29% lipid

against 18% in the dark muscle and 7.6% in light muscle (Ackman and Eaton, 1971). No consistent difference has ever been found in lipid or other constituents between the left and right fillets of the same fish (Love, 1970).

2.1.3.3 Lipid classes and fatty acids

The lipids in fish exist as depot and non-depot lipids. The former, mainly triglycerides, are regarded as energy reserves which the fish can use when food is unavailable (Lovern, 1962). The non-depot lipids are the phospholipids and sterols which occur as basic units in cellular structure (Stansby, 1973). Most fish species have about 0.7% phospholipids and in some, such as cod, it forms nearly all the lipid content in the flesh (Ackman, 1974).

Fish lipids present a source of different kinds of fatty acids to those supplied by plant and other animal sources. Whereas vegetable oil fatty acids contain mainly one or two double bonds, with small amounts of three and four double bonds, those from fish lipids contain a substantial percentage with five and six double bonds (Cruger, 1967). The fatty acids found in fish lipids have been discussed above (see section 2.1.1) and will be discussed in more detail for mackerel below.

2.1.3.4 Importance of fish lipids in nutrition

Fish has been reported to be effective in reducing serum

cholesterol levels (Peifer, 1967), as shown in Table 3. It is apparent that for each species, man, rat, chicken and mouse, fish oils lowered serum cholesterols to a greater extent than did corn oil or linoleate. The extent of lowering of serum cholesterol level was about twice as great for the fish oil as for the corn oil or lineoleate for man and for the rat, and range up to 12 times as great in the chicken. Jones (1974) indicated that ingestion of polyunsaturated lipids not only decreases the serum cholesterol level but also other factors which induce atherosclerosis are brought to a lower level. Von Lossonszy et al., (1978) reported that monks and nuns who ate 200 g of mackerel (contributing 54 g lipid) per day for three weeks, lowered their serum cholesterol significantly compared to a similar period when cheese was the dietary supplement. The average difference was 16 mg/100 cm^3, that is about an 8% fall. The penta-, or hexaene fatty acids present in fish lipids are more effective as cholesterol depressants than dienes which are the main polyunsaturated fatty acids of vegetable oils (Stansby, 1973).

The essential fatty acids which are known to support growth and cure dermal symptoms, linoleic (18:2ω6) acid, and arachidonic (20:4ω6) acid, are present in fish. Linoleic (18:2ω6) acid itself amounts to about 2% of the total fatty acids while arachidonic (20:4ω6) acid, which is absent from most vegetable oils, amounts to about 1% (Ackman, 1974).

Docosahexaenoic (22:6ω3) acid is present in fish lipids at levels up to 10% in the triglyceride fraction and 40% in the phospholipid fraction (Ackman, 1980). Although it has not been shown to have special nutritional significance (Stansby, 1973),

Table 3 Comparative effects of fish oil with corn oil or linoleate on serum cholesterol depression in man and animals (Peifer, 1967)

Species	Reference	Test lipid	Proportion of test lipid to total dietary lipid %	Test period weeks	Lowering of serum cholesterol %
Man	Ahrens et al., 1959	corn oil	100.0	6	-29
		menhaden oil	100.0	8	-57
Rat	Peifer et al., 1960	linoleate	33.3	4	-31
		menhaden oil	33.3	4	-51
		tuna oil	33.3	4	-59
Chicken	Kahn et al., 1963	corn oil	50.0	1	-5
		cod liver oil	50.0	1	-63
Mouse	Howe and Bosshardt, 1962	linoleate	100.0	1.7	-4
		corn oil	100.0	1.7	-4
		cod liver oil	100.0	1.7	-26

it is a very important fatty acid in the brain and nervous system lipids (Ackman, 1980). Another polyunsaturated fatty acid present in fish is eicosapentanoic (20:5ω3) acid which has been indicated as a protective against thrombosis (Dyerberg et al., 1978), but this fatty acid can be synthesized from docosahexaenoic acid or linolenic (18:3ω3) acid.

2.1.3.5 Lipid changes during processing and storage

In this section the work reported on lipid changes during storage and processing of fish is reviewed, with particular emphasis on frozen storage and on thermal processing, since most studies have concerned these two aspects.

During the storage of frozen fish, the major change in lipids is that of lipolysis which occurs mainly in the phospholipid fraction (Lovern and Olley, 1962). Oxidation is extremely slow, however it can reduce the acceptability of both fatty and lean fish, for example, in cod flesh the production of hep-cis-4-enal during cold storage makes the fish less acceptable (Hardy et al., 1980 and references therein). Mathews et al. (1980) reported values of about 40% for free fatty acid in the lipid of cod mince (which is mainly phospholipid) stored at $-7^{o}C$ for 10 days.

Frozen Indian mackerel, Rastrelliger kanagurta, stored at $-18^{o}C$ for about 150 days showed a decrease in the phospholipid concentration, the hydrolysis rate being at a maximum early in the storage period (up to 60 days) and decreasing later. Changes in free fatty acid concentrations were inversely proportional to those in phospholipid concentrations. The concentration of

phosphatidyl serine remained approximately constant throughout storage. Iodine Values decreased from 170 to 130 during the storage period. Changes in lipid fractions other than phospholipids and free fatty acids were small (Viswanathan Nair et al., 1976). Analyses carried out during the storage of frozen chub mackerel (Scomber japonicus) fillets for 75 days at -15°C treated with sodium chloride and with ascorbic acid showed higher Peroxide Values and Acid Values for the sample with sodium chloride and lower values for samples treated with ascorbic acid in comparison with controls. Palmitic, stearic and oleic acids decreased during storage for both treated and control samples (Ahn et al., 1978).

Repeated cooking and processing in a super-light frequency electric cabinet did not produce any major changes in the composition of phospholipids of carp (shiner) and pike muscle, although slightly reduced amounts of phosphatidyl chlorine and phosphatidyl ethanolamine were reported (Bastavizi and Smirnova, 1972). Quaglia et al. (1974) found a decrease in unsaturated fatty acids and increase in the saturated on roasting at 220°C to 240°C for 40 minutes, frozen fish (dentex), whereas boiling at 100°C for 35 minutes, gave opposite results. They assumed that the roasting treatment involved mostly oxidative processes while lipolysis and polymerisation prevail in the boiling treatment. Thermal processing at 121°C for 10 minutes in an autoclave alone and in combination with frozen storage of blue crab (Callinectes sapidus) meat, resulted in only slight changes in the lipid fractions and losses of polyunsaturated fatty acids were insignificant (Giddings and Hill, 1975). Strokova and Smirnova (1976) reported that frozen

fish (Seriolla maculata, Seriolla tinro and Epighonus atherinoides) kept at -18°C for 2, 4 and 6 months, processed by boiling or high frequency waves (no times or temperatures are indicated) showed progressive hydrolytic breakdown of triglycerides with time lapse; while phospholipids and glycolipids were reduced by oxidation. Minced carp tissue cooked by baking at 190°C for 14 minutes and deep fat frying at 190°C for 4 minutes and then stored at -18°C for periods up to 8 weeks showed decreased phospholipid levels, whereas the free fatty acids increased (Mai and Kinsella, 1979). Little lipid change during the cooking by baking at 190°C for 14 minutes, pan frying at 163°C for 8 minutes and deep frying at 190°C for 4 minutes of breaded and non-breaded trout (Salvelinus namacush), white sucker (Catastomus commersonni) and bluegill Lepomis macrochirus) fillets was reported by Mai et al. (1978), however the cholesterol content decreased following cooking by the three methods.

When fish are processed by hot smoking the smoke does not appear to affect the rate of oxidation. Comparison of the oxygen uptake of hot smoked dried West African herring (Sardinella aurita) under different time-temperature conditions indicated that the final moisture content is the predominant factor affecting rate of oxidation and not the smoking as was initially thought (Woolfe, 1975). The composition of lipid classes and the fatty acid profile of the total lipids in fresh and smoked esturion (Ascipencer sturio), herring (Clupea harengus), shark (Squalus acanthias), eel (Anguilla anguilla) and cod (Gadus morhua) were similar. However the lipids of fresh fish appeared to contain more eicosapentaenoic (20:5) and docosahexaenoic (22:6) acids than those of smoked fish (Meizes and Reichwald, 1973).

There is very little information available on the effect of the canning process on fish lipids. Roubal (1963) observed no marked degradation of the polyunsaturated fatty acids during the canning of 4 species of tuna, albacore tuna (Thunnus germo), blue fin tuna (Thunnus thynnus), and skipjack tuna (Katsuwonus pelamis). However, the total lipids, free fatty acids and cholesterol levels tended to be lower in mandi (Pimelodus clarias) canned in oil than in the fresh fish (Andrade and Lima, 1980). Canning was reported to cause a decrease in myristic, myristoleic, pentadecanoic, palmitoleic, heptadecanoic and heptadecenoic acids and increase in palmitic, oleic and linoleic acids. In mandi canned in tomato sauce and smoked mandi fillets canned in oil, the total lipids and cholesterol decreased on storage and changes were also reported in the component fatty acids. These authors noted that "The changes observed during processing and storage cannot be explained at present."

To summarise the lipid changes that occur during storage and thermal processing, the following points can be stated: During frozen storage rapid lipolysis of phospholipids occurs and slow lipid oxidation. The lipid oxidation leads to off-flavours after extended storage for both fatty and lean fish. During thermal processing including canning, no clear picture emerges for lipid changes and many results cannot be readily explained and in some cases are contradictory.

2.2 Mackerel

The name mackerel is used in the United Kingdom for the species Scomber scombrus, but the name can also be used for any species of Scomber offered for retail sale (Keay, 1979). S. scombrus is called Atlantic mackerel to distinguish it from Scomber japonicus which is called chub, Spanish or Pacific mackerel.

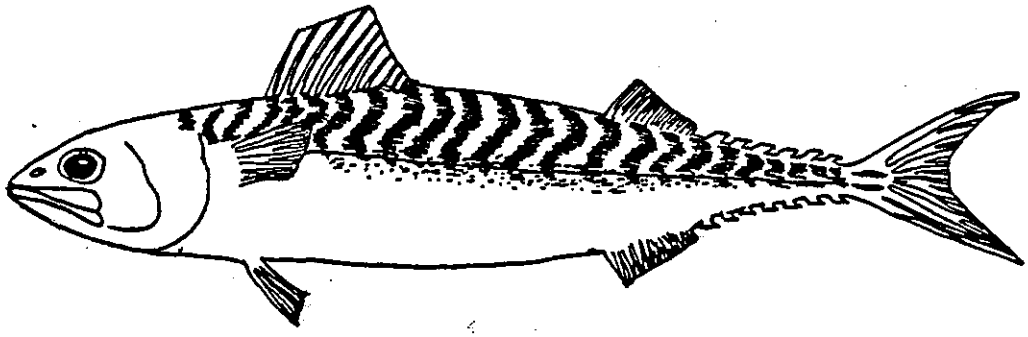
The distinguishing features between S. scombrus and S. japonicus are that in the former, the number of spines in the first dorsal fin is 11 to 13 and in the latter 9 to 10. There is a swimbladder in the S. japonicus but not in the S. scombrus. The dorsal fins are widely separated in the S. scombrus and its back has a dark S-shaped line (see Fig. 8) whereas the S. japonicus has faint wavy lines and numerous dusky rounded spots in the sides and belly (Wheeler, 1978).

Other species of Scomber and species of Rastrelliger, Scomberomorus and Auxis are also described as mackerel in many parts of the world (FAO, 1980; Keay, 1979) although the total catch of these fish are well below those of S. scombrus and S. japonicus (see section 2.2.2).

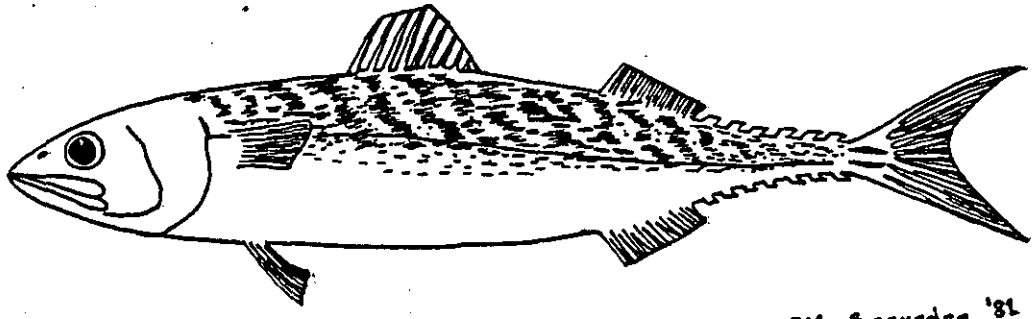
2.2.1 Characteristics of the Atlantic mackerel

The Atlantic mackerel, S. scombrus, has a relatively slender body but rounded in cross section. It has two dorsal fins, the one nearest head with 11 to 13 spines and one nearest the tail with 11 to 13 rays (Lythgoe, 1971). A series of 5 to 6 small finlets lie between the second dorsal and anal fins to reduce

Figure 8 Atlantic and Pacific mackerel



Atlantic mackerel (Scomber scombrus)



Pacific mackerel (Scomber japonicus) F.M. Saavedra '81

turbulence about the propulsive tail (Miller, 1980). The tail fin has 2 small keels at the bases of the fin but none on the side of the tail (Wheeler, 1978).

The Atlantic mackerel has a brilliant blue-green colouration on the back with 23 to 33 zebra-like stripes (Keay, 1979), which are sometimes broken into spots as shown in Fig. 8. The lower sides and belly are white with pinkish and gold reflections (Lythgoe, 1971; Wheeler, 1978).

In their first year mackerel may reach a length of 15 cm, and at 3 years old when they are sexually mature, about 30 cm (Christensen, 1978). The average length of mature mackerel is 40 cm and average weight 680 g, although they can reach 66 cm and weigh 3300 g (Wheeler, 1978).

Atlantic mackerel are found in shoals in the temperate Atlantic and Mediterranean waters from Morocco to Norway and from the Azores to the Black Sea (Hureau and Monod, 1973; Burton, 1975); as well as off the coast of Canada and U.S.A., from Triangle Harbour Labrador to Cape Hatteras, North Carolina (Scott, 1966). Mackerel are alternatively epipelagic and meso-demersal in depths up to 200 m-250 m (Hureau and Monod, 1973). They are highly migratory, making inshore and offshore migrations (Wheeler, 1978). In the late spring, through summer and early autumn large shoals occur close inshore to spawn and feed (Keay, 1979). In winter they move into deeper water offshore at the edge of the continental slope where they keep close to the bottom (Lythgoe, 1971), they do not feed during this time but they are not totally inactive either, they rise and disperse during darkness (Keay, 1979). Their food varies; they take planktonic crustaceans, fish eggs and larvae

(Miller, 1980). They also feed on smaller fishes such as sprats.

Mackerel spawn in summer, the spawning season covering most months from May to August (Wheeler, 1978). The older larger fish start spawning first. The average sized female (30 cm) produces up to 500,000 eggs (Scott, 1966). The size of the eggs varies from 1.0 to 1.2 mm and each has a single small oil drop, which helps it to float in the upper water layers until it hatches usually in two days (Jenkins, 1958). It is thought that some mackerel may live for 20 years (Lythgoe, 1971).

2.2.2 Mackerel fisheries

The Atlantic mackerel can be caught throughout the year. In the United Kingdom the fishing season is from February to October and in winter in the South West from October to March (Keay, 1979). The fishing methods vary. Drift-net fishing has declined since the second world war and has been replaced by "feathering" (Bolster, 1974). This handline fishing consists of a set of up to 24 hooks attached to a nylon line, about 30 cm apart. The hooks are dressed with hackle feathers from the necks of domestic poultry which have been dyed with bright colours. When fishing, the lines are moved up and down in the water. Purse seining is the most important method of capturing mackerel in quantity off the west of Scotland in late summer, midwater and bottom trawling remains the most important method of capture in the Cornish fishing area (Keay, 1979).

Landings and value of mackerel in the United Kingdom are shown in the Table 4 during the years 1970 to 1979. In that period the catch increased over 60 times mainly as a result of

Table 4 United Kingdom mackerel landings 1970-1979 (Keay, 1979; FAO, 1980)

Year	British vessels				Foreign vessels	UK Total	
	England and Wales 000t[1]	Scotland 000t	N.Ireland 000t	Total 000t	000t	000t	£'000[2]
1970	3.4	1.0	0.2	4.6	0.7	5.4	259
1971	4.8	1.4	0.3	6.5	0.8	7.3	357
1972	6.9	1.8	0.1	8.8	1.7	10.5	457
1973	13.1	8.2	0.1	21.4	1.7	23.1	1160
1974	21.2	8.8	0.1	30.1	1.0	31.1	1486
1975	31.6	16.7	0.1	48.4	0.3	48.7	2309
1976	57.4	29.6	0.1	87.1	0.2	87.3	5264
1977	132.4	54.2	0.1	186.7	0.2	186.9	14673
1978	213.5	107.4		320.9			
1979	245.0	108.4		353.4			

(1) thousand tonnes

(2) thousand pounds

the declining stocks of other common food fish species such as herring. Table 5 gives the total world catches of Atlantic mackerel and other mackerel species. It can be seen that the UK catch of Atlantic mackerel in 1979 (353,400 tonnes) represented about 45% of the total world catch. Other countries with large catches of Atlantic mackerel in 1979 were Norway (125,800 tonnes), Netherlands (63,400 tonnes), France (39,200 tonnes) and Faroe Islands (38,525 tonnes). As can be seen from Table 5, over 3 times as much of the closely related chub mackerel was caught as Atlantic mackerel. Japan accounted over 60% of the chub mackerel catch (1,591,700 tonnes), followed by the USSR (287,400 tonnes) and China (250,000 tonnes). Rastrelliger spp. and other mackerel-like fishes represent only about 10% of the total mackerel catch.

2.2.3 Lipid content of mackerel

The mackerel is a fatty fish with proximate composition of the flesh reported as water: 60-74%, lipid: 1.0-23.5% and protein 16-20% (Murray and Burt, 1969). The sum of lipid and water remain fairly constant with not more than ± 1.8% variation (Ueda, 1976). The lipid content varies with season (Stansby, 1973). Hardy and Keay (1972) reported 23.4% lipid content in December and 6.3% in June for Cornish mackerel (S. scombrus) and an inverse linear relationship was observed between lipid and water content as shown in Figure 9. The lower lipid content values occurred prior to

Table 5 Catches of mackerel species in metric tonnes (FAO, 1980)

Species	1976	1977	1978	1979
Atlantic mackerel (*Scomber scombrus*)	1,077,299	687,711	712,427	761,735[F]
Chub mackerel (*Scomber japonicus*)	1,699,317	2,304,454	2,851,783	2,571,075[F]
Short mackerel (*Rastrelliger brachysoma*)	31,314	21,937	25,183	17,914
Indian Mackerel (*Rastrelliger kanagurta*)	111,356	147,821	185,488	164,510[F]
Indian mackerel (*Rastrelliger* spp.)	149,377	152,239	177,561[F]	177,347[F]
Other Mackerel-like fish (*Scombroidei*)	15,900[F]	20,619[F]	27,547[F]	23,325[F]
Total	3,084,563	3,334,781	3,979,989	3,715,906

F = FAO estimates.

Figure 9 Seasonal variation in composition of Cornish mackerel (Keay, 1979)

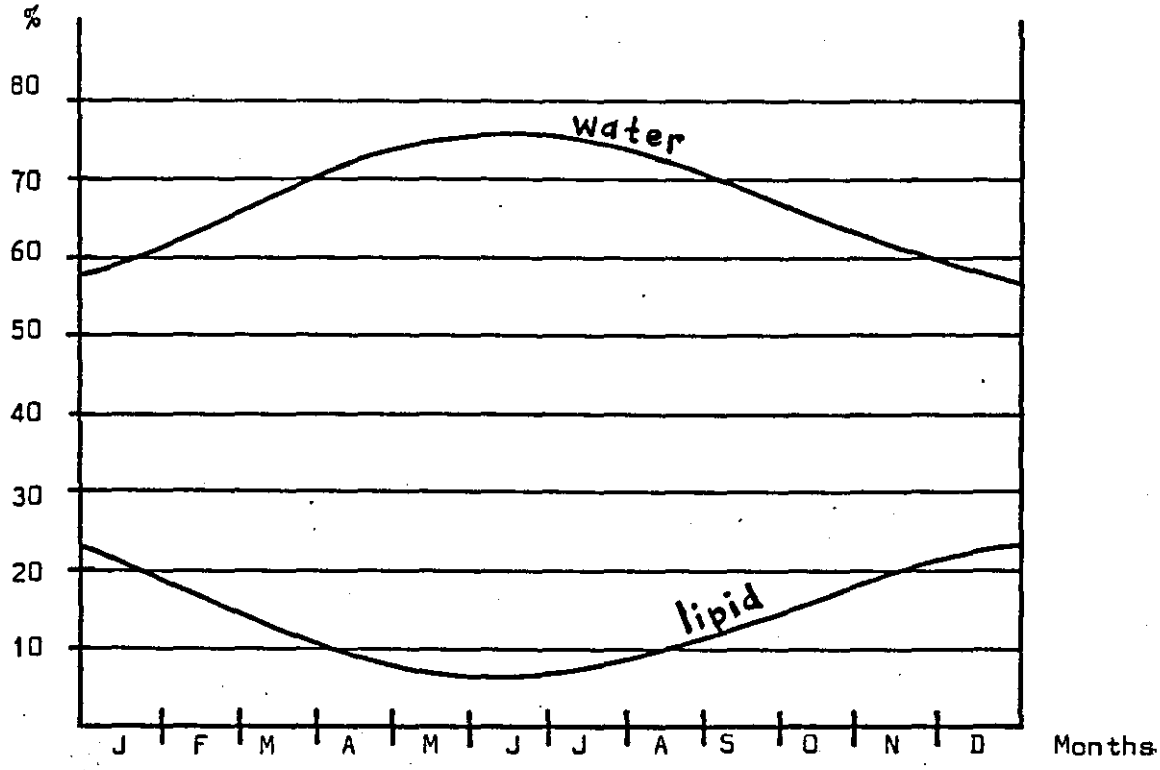
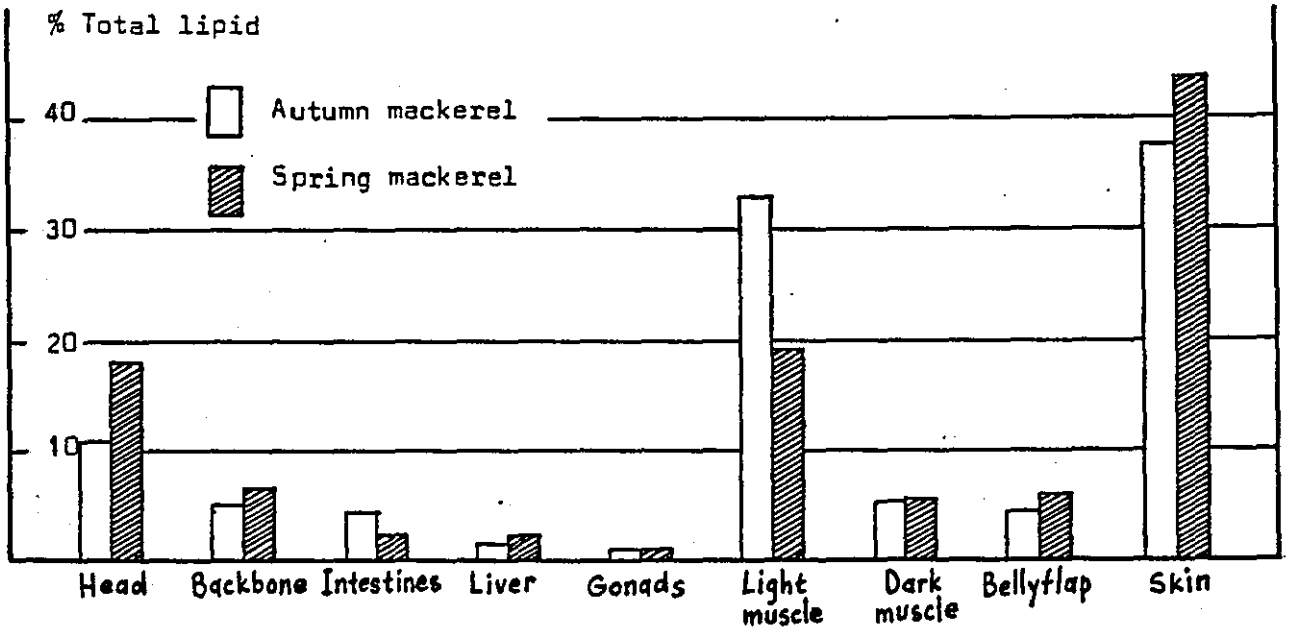


Figure 10 Distribution of total lipid in various body parts and organs of mackerel, S. scombrus (Ackman, 1980)



and during the spawning which takes place mainly from March to July. The higher values are related to the nutritional status of the mackerel. During the Autumn, mackerel feed heavily thus the lipid content is usually higher than in spring (Ackman and Eaton, 1971).

The distribution of lipid in the body of mackerel (S. scombrus) is very uneven as shown in Fig. 10 it is notable that the skin can total 40% of the lipid in the whole fish and can be up to 50% lipid (Ackman, 1980).

Variation in lipid content with size has also been reported for mackerel. For a batch of mackerel, caught in October in larger fish (>34 cm) the liver and muscle had a higher lipid content, average values for liver being 18.2% and for muscle 15.5% than smaller fish (<34 cm), average values for liver being 14.2% and for muscle 6.9% (Maslennikova, 1976). Maslennikova (1974) reported that lipid content increase with maturity and that female fish have a higher fat content than male fish, the difference being greatest in gonad tissue. However Hardy and Keay (1972) found higher values of lipid in male mackerel than female, 24.1% vs. 21.6% in December and 9.1% vs. 3.9% in June respectively. The lipid content in the gonad in male fish was higher than female in December but lower in June (4.3% vs. 2.1% and 2.1% vs. 4.8% respectively).

The composition of the lipid in mackerel also varies with season and type of muscle as shown in Table 6. The dark muscle was reported by Ackman and Eaton (1971) to contain 1.6% polar lipids (phospholipids) and the light muscle 0.5%. Similar percentage contents of phospholipids have been found in comparable muscles in other species, including lean fish such as cod (Ackman,

Table 6 Differences in lipid composition between light and dark muscle and with season, in some mackerel species

Species	S. scombrus[1]		S. scombrus[2]		S.scombrus[3]	S.japonicus[4]	
Sample	Dec.	June	Light m.	Dark m.	Dorsal m.	Aug.	Jan.
Total lipid (g/100g sample)	24.1	9.1	10.2	14.4	2.1	10.8	15.5
Polar lipid (g/100g sample)	0.84	0.88	0.5	1.6	0.85	1.1	0.99
Neutral lipid (g/100g sample)	22.2	7.9	9.1	10.7	1.23	9.4	14.4
% triglyceride in NL	97	91	90	74	-	-	-
% sterol in NL	3	4	-	-	-	-	-

(1) Hardy and Keay (1972)

(2) Ackman and Eaton (1971)

(3) Viviani et al. (1967)

(4) Ueda (1976)

1974). The phospholipid does not show the wide seasonal variation of the neutral lipid which is nearly all triglyceride.

The fatty acid composition of the lipids of mackerel (S. scombrus) from different tissues and types of lipids have been reported (Ackman and Eaton, 1971; Hardy and Keay, 1972; Viviani et al., 1968) and are summarized in Table 7. Palmitic acid (16:0) is the principal saturated fatty acid followed by myristic acid (14:0) and stearic acid (18.0) which is typical of marine fish fatty acids (Ackman, 1980). The main monoethylenic fatty acid is oleic acid (18:1). The essential fatty acids, linoleic acid (18:2ω6), and arachidonic acid (20:4ω6) are present in minor proportions (about 2% and 0.5 to 1% of the total respectively). The polyunsaturated fatty acids, 20:5ω3, 22:5ω3 and 22:6ω3, which are typical of marine organisms are present at about 20% in the triglycerides and 40% in the phospholipids.

2.3 Fish canning

2.3.1 General aspects

Canning may be defined as the packing of foods in hermetically sealed containers and obtaining "commercial sterility" (Hersom and Hulland, 1980). Commercial sterility, in turn, is defined as that degree of sterility necessary to destroy the most harmful types of bacteria (pathogens) and those that might cause spoilage of the canned food. Micro-organisms, whether in spore or vegetative form, can be inactivated at a logarithmic rate by heat once a

Table 7 Comparison among weight percent composition of major fatty acids from different tissues of mackerel (S. scombrus)

Fatty acid	14:0	16:0	18:0	16:1	18:1	20:1	22:1	18:2ω6	18:3ω3	18:4ω3	20:4ω6	20:5ω3	22:5ω3	22:6ω3
% lipid, season, tissue & lipid type	Principal Neutral Lipid Acids													
14.4% Fall, dark meat, triglyceride[1]	4.2	16.9	3.0	5.1	16.4	7.9	12.5	1.6	1.4	2.4	0.4	6.6	1.5	11.1
10.2% Fall, light meat, triglyceride[1]	5.0	15.1	3.9	5.5	23.9	5.9	5.6	1.4	1.3	2.1	0.4	7.6	1.4	13.4
8.7% Spring, dark meat, total lipid[1]	5.7	16.3	3.2	5.9	15.3	8.4	13.0	1.5	0.6	1.3	0.6	7.1	1.3	11.4
2.2% Spring, light meat, total lipid[1]	4.9	16.0	3.5	5.4	13.4	9.1	12.2	1.8	0.9	1.7	0.6	7.6	1.6	14.1
21.6% Fall, body flesh, triglyceride[2]	4.6	16.3	3.7	5.1	24.9	6.3	8.3	2.1		2.9	-	8.3	-	10.9
3.9% Spring, body flesh, triglyceride[2]	5.5	20.1	4.0	6.0	26.0	6.4	8.7	2.2		2.2	-	6.2	-	5.6
7.3% Fall, triglyceride[3]	4.2	11.5	6.1	8.9	24.3	4.2	3.2	1.7	-	1.4	0.7	7.4	1.2	18.2
1.2% Spring, triglyceride[3]	7.1	25.7	6.7	6.4	18.0	3.5	5.7	0.9	-	trace	trace	7.8	0.3	12.4
	Principal Polar Lipid Acids													
1.6% Fall, dark meat, polar lipid[1]	0.9	14.6	13.1	1.4	14.4	3.4	1.5	3.0	1.2	0.3	1.0	7.2	1.7	29.5
0.5% Fall, light meat, polar lipid[1]	0.5	20.4	7.4	1.8	9.2	1.6	1.0	1.6	0.5	0.2	1.7	10.7	1.6	36.3
1.0% Fall, body flesh, phospholipid[2]	1.9	20.6	6.4	1.8	11.1	1.5	0.8	1.1		0.2	-	12.3	-	34.2
0.8% Spring, body flesh, phospholipid[2]	0.4	18.8	7.3	1.7	9.7	1.1	1.0	1.6		0.3	-	12.5	-	39.8
Fall, body flesh, phospholipid[3]	0.9	12.8	14.4	3.0	14.2	1.1	3.2	1.5	-	0.4	0.6	7.0	1.4	30.7
Spring, body flesh, phospholipid[3]	1.1	24.2	12.4	2.4	12.7	0.7	3.4	1.2	-	trace	trace	7.0	1.1	25.5

(1) Ackman & Eaton, 1971

(2) Hardy and Keay, 1972

(3) Viviani et al., 1968

predetermined minimum temperature is reached. As the temperature increases, the time required for microbiological destruction decreases. However in practice over-processed food will be nutritionally and organoleptically inferior (Brennan et al., 1979), thus parameters of suitable thermal processes must be estimated on the basis of assumptions regarding the heat resistance of the spoilage micro-organisms and a knowledge of the temperature history of the food during processing. The parameter most commonly used is the Fo value (see Brennan et al. (1979), for definition and discussion of Fo values).

Low acid foods, pH greater than 4.5, such as fish will support the growth of pathogenic heat resistant spore formers like Clostridium botulinum, which is capable of producing a highly lethal toxin. These foods must therefore be processed to reduce to virtual insignificance the chance of such spores surviving the process. This is attained if the coldest point in the can receives a minimum process of 10 minutes at 121°C (Stumbo, 1973). Such a process will also kill all other micro-organisms capable of producing canned food spoilage under normal conditions of canned food handling and storage (Lopez, 1969).

Canned fish production has increased about five fold since 1938 (Bligh, 1980) and utilizes about 14% of the total fish catch which is about 20% of fish for human consumption (see Table 8).

Many of the problems in fish canning can be related to the quality of the raw material. Physical damage, autolysis, belly-burst, discolouration, off-odours and contamination can all ruin the raw material for canning (Connell, 1980). Processing conditions must be rigidly controlled for each individual species and product to ensure product uniformity and quality (Burgess et al., 1965). In some fatty pelagic species the lipid content often determines the quality of the end product, for example the lipid

Table 8 Disposition of world fish catch 1975-1979 (FAO, 1981)

Disposition[1]	1975		1976		1977		1978		1979	
	Weight	%	Weight	%	Weight	%	Weight	%	Weight	%
Total world catch	66.5	100	69.9	100	69.2	100	70.5	100	71.3	100
For human consumption	46.0	69.2	47.9	68.6	49.3	71.3	49.3	70.0	49.5	69.5
Marketing fresh	13.8	20.8	14.2	20.3	15.5	22.4	15.0	21.1	14.6	20.4
Freezing	13.3	20.0	14.6	21.0	14.6	21.0	15.0	21.2	15.1	21.2
Curing	9.6	14.5	9.7	13.9	9.8	14.2	9.8	13.9	9.9	13.9
Canning	9.2	13.9	9.4	13.4	9.5	13.7	9.7	13.8	10.0	14.0
For other purposes	20.5	30.8	22.0	31.4	20.0	28.7	21.2	30.0	21.8	30.5
Reduction	19.5	29.3	21.0	30.0	19.0	27.3	20.2	28.6	20.8	29.1
Miscellaneous purposes	1.0	1.5	1.0	1.4	1.0	1.4	1.0	1.4	1.0	1.4

(1) Weights are given in million metric tonnes.

content of sardines should lie between 7 to 15% for a good quality product (Connell, 1980).

2.3.2 Mackerel canning

Canned mackerel in the years 1977 to 1979 formed about 10% of the total production of canned fish (see Table 9) as notified to the FAO (FAO, 1981). The figures do not include the USSR, which produces over one million metric tonnes per year of canned fish, and some other countries which produce relative small amounts. In addition, the miscellaneous canned fish probably includes considerable amounts of canned mackerel. However it is clear that canned mackerel is one of the most important types of canned fish.

Table 10 gives figures for the production of canned mackerel by countries in metric tonnes in 1977 to 1979, again excluding the USSR and some other countries (FAO, 1981). The total production of Atlantic mackerel notified to FAO was over 20,000 tonnes, with the main producing country being Denmark. The total production of the closely related Pacific mackerel was over 200,000 tonnes, with the main producing country being Japan. It should be noted that the Pacific mackerel is far more widely distributed than the Atlantic mackerel (Wheeler, 1978). The actual world total for canned Atlantic and Pacific mackerel would be far higher if "canned mackerel (not identified)", "miscellaneous canned fish" and the USSR production could be taken into account.

Table 9 World production of canned fish (limited data excluding USSR and some other countries) (FAO, 1981)

Groups(1)	1977		1978		1979	
	Weight	%	Weight	%	Weight	%
Salmon, trout, smelt, etc.	109.918	4.0	100,720	3.4	93,000	3.1
Herring, sardine, anchovy, etc.	504,547	18.5	512,829	17.5	549,898	18.3
Tuna, bonito, billfish, etc.	528,997	19.4	611,654	20.8	585,646	19.4
Mackerel	288,124	10.5	307,989	10.5	290,569	9.6
Miscellaneous canned fish	1,300,288	52.4	1,397,736	47.8	1,491,319	49.6
Grand Total	2,731,874	100.0	2,930,928	100.0	3,010,432	100.0

(1) Weights are given in metric tonnes.

Table 10 Production of canned mackerel by countries in metric tonnes 1977-1979 (limited data excluding USSR and some other countries) (FAO, 1981)

	Country	1977	1978	1979
Pacific mackerel (Scomber japonicus)	Argentina	400	400	400
	Brazil	1,976	1,154	1,154
	Japan	211,000	222,100	203,800
	Morocco	4,644	5,654	3,961
	Peru	4,800	8,700	11,600
	S. Africa	1,800	2	248
	Total	224,620	238,010	221,163
Atlantic mackerel (Scomber scombrus)	Belgium	200	30	40
	Canada	1,745	692	900
	Denmark	12,200	14,200	14,200
	Netherlands	4,00	3,300	3,400
	Norway	2,400	2,200	2,200
	Sweden	237	249	245
	Total	20,782	20,671	20,989
Mackerel (Not identified)	France	28,400	30,400	32,100
	Korea Rep.	3,262	5,300	3,200
	Portugal	5,197	4,235	4,160
	Spain	5,863	8,931	8,931
	S. Africa	-	437	26
	Total	42,722	49,303	48,417
Grand Total		288,124	307,989	290,569

The canning of mackerel presents a number of technical problems, especially the large variation of lipid content, the high enzyme activity and often the large size of the catch (Seno, 1974). Mackerel containing about 10% of lipid will develop off-flavour after 1 to 2 days at 10°C (Keay, 1979). Mackerel for canning should not be kept in ice for more than 4 to 5 days (McLay, 1970; Balachandran and Nair, 1977). Seno (1974) recommended the following limits for mackerel as raw material for canning: 6 to 10 hours at 20°C, 48 hours at 0°C, 2 months at -18 to -20°C and 3 months at -30°C. Mackerel may be canned as steaks or as fillets in a variety of sauces. Tanikawa (1971) reported 6 types of canned mackerel produced commercially in Japan, and those prepared in oil and in tomato sauce are exported. McLay (1970) indicated that mackerel in tomato sauce, in oil, in natural style (juices) and smoked mackerel in oil are acceptable to British tastes. Mackerel in brine, in tomato sauce and in oil are the most common preparations (Da Costa, 1974).

Canning of mackerel involves the following operations:

pre-treatment, brining, filling and seaming, and processing.

Pre-treatment: The mackerel, either fresh, stored in ice, or thawed, are dressed by splitting longitudinally along the ventral side, removing the head and viscera, followed by washing the belly cavity. The black skin is removed from the belly wall, and traces of blood along the backbone are brushed away, and the carcase allowed to drain (Tanikawa, 1971). The drained fish are then cut into steaks of length to suit the pack; for example, 6 to 7 cm long are suitable for a 200g cylindrical can (Keay, 1979), or they can be filleted.

Brining: The cut pieces of fish or fillets are soaked in brine in order to extract the blood (Tanikawa, 1971), which also brightens the appearance of the fillets (Burgess et al., 1965) and reduces the breakdown of collagen in the tissue. The brining process is inversely related to the firmness of the canned fish (Perovic, 1977). There is no standard treatment and slight differences occur according to the size and condition of the fish (Van den Broek, 1965). Tanikawa (1971) recommended soaking the steaks for 20 to 30 minutes in 3% brine and then for 10 minutes in 10 to 16% brine. For mackerel fillets soaking in saturated brine for 6 and 10 minutes has been suggested (Keay, 1979). The temperature of the brine is recommended to be lower than 10°C (Seno, 1974). The brining also avoids the formation of "curd" in the canned product. Such "curd" is the coagulation of soluble proteins in the mackerel tissue which if not removed will give turbidity to the liquid medium (brine or oil) in the can, hence affecting the quality of the product.

Filling and Seaming: After brining, the steaks or fillets are rinsed with fresh water, drained for 10 to 30 minutes and packed tightly in the container. The weight is controlled according to the size of the container and an excess of 2 to 5g added to allow for shrinkage (Seno, 1974). Exhausting is carried out with steam for 10 minutes, in order to eliminate some water from the tissues, which gives better texture and presentation to the product (Stansby, 1963); the water which comes from the tissues is then poured off. However in some cases this practice is avoided when mackerel is canned in brine or natural juices (Van den Broek, 1965). Brine, tomato sauce or oil is then added and the cans are vacuum

seamed and retorted as soon as possible. Tanikawa et al. (1952) found that the maximum holding time of packed mackerel is 40 minutes. If this time is prolonged, bacterial decomposition may occur before the processing.

Processing: The heat processing given is according to the size of the cans as indicated in Tables 11 and 12. All cans used in mackerel products are lacquered inside in order to prevent contamination of the flesh from the metal of the can. After processing and cooling the cans are wiped or dried in hot air, labelled and packed in boxes ready for distribution.

Table 11 Heat processing for canned mackerel in brine

Can size	pH	Initial temp.(°C)	Processing temp.(°C)	Pressure (lb/in^2)	Processing time (min)	Come up time (min)	
1P long	6.0	13.0-15.0	112.6-115.8	8.0-10.5	110	5-20	(1)
½P long	5.7-6.5	10.0-90.0	114.0-115.8	9.0-10.5	80-90	5-25	
1P flat	5.7-6.5	13.0-75.0	115.2-115.8	10.0-10.5	100-120	13-25	
½P flat	5.7-6.5	20.0	114.0-115.8	9.0-10.5	90-100	10-30	
Flat 1			115.2-115.8	10.0-10.5	100-120		(2)
Flat 2			114.9-115.8	10.5	90-100		
200g cylindrical			115		90		(3)
200g oval			115		60		
225g cylindrical			115		90		(4)

Table 12 Heat processing for canned mackerel in tomato sauce

Can size	pH	Initial temp.(°C)	Processing temp.(°C)	Pressure (lb/in^2)	Processing time (min)	Come up time (min)	
⅓P long	4.2-5.8	50.0-80.0	111.3-115.8	7.0-10.5	70-90	12-30	(1)
115g club			115		70		(4)

(1) Seno, 1974
(2) Keay, 1979
(3) Tanikawa, 1971
(4) McLay, 1970

2.4 Aims of the present work

This work aims at:

1) Assessing changes in mackerel lipids caused by the brining operation and further refrigerated, and frozen storage.

2) Determining the effect of heat processing on the mackerel lipids.

3) Assessing the effect of storage after canning on the mackerel lipids.

3. EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Fish

The mackerel, Scomber scombrus, were caught off the Cornish coast by the line and feather lure technique. They were unloaded and iced in Falmouth and transported in a refrigerated lorry to Grimsby Docks and then to the food laboratory of Grimsby College of Technology, where they were organoleptically assessed, sorted, re-iced and stored in a refrigerator at $4^{o}C$ for 12 hours before processing.

3.1.2 Other materials

a) Food grade salt manufactured by British Salt Ltd., Middlewich, United Kingdom was used in the preparation of brine solutions.

b) The cans used were U8 open top processed food cans, size 300 x 207 produced by Metal Box Ltd.

c) Low density polyethylene, 35.5 gm^{-2} was used to prepare plastic pouches.

3.1.3 Equipment

The following pieces of equipment were used in the experiments:

a) A MB-1A vacuum closing machine made by Metal Box Ltd., was used to seam the cans.

b) A vertical stationary retort, made by Leeds and Bradford Boiler Co., was used in the sterilization in conjunction with an Ellab A/S Elektrolaboratoriet recorder type Z9CT-F for the Fo value evaluation.

c) The mackerel fillets were frozen in a blast freezer made by Woods Ltd., Leeds.

d) An EIL pH meter model 38B was used in the preparation of the simulated tomato sauce.

e) A portable hand sealer made by N.V. Machinef Abriek, Warmer Holland was used in the sealing of plastic pouches.

f) In the total lipid extraction an Ultra-turrax type homogeniser TP-18/10 made by Junkie and Kunkel, Germany, an MSE super-minor centrifuge, a Quickfit rotary film evaporator and an Edwards single stage speedivac high vacuum pump were used.

g) A Perkin Elmer F11 gas chromatograph was used in the fatty acid profiling.

h) A Unicam ultraviolet spectrophotometer model SP800A was used in the conjugable oxidation products (COP value) determination.

3.2 Methods

3.2.1 Biometric determinations on the fish

The length of the mackerel was measured as the distance between the anterior tip of the head and a line drawn between

the posterior tips of the caudal fins as shown in Fig. 11. The whole fish (total weight) and the fish without viscera and gills (eviscerated weight) were weighed to the nearest 0.1g. The sex of the fish was determined by visual examination of the gonads.

3.2.2 Can filling solutions

The simulated tomato sauce was a buffer solution of pH 4.7 prepared according to Vogel (1961), combining a 0.01M acetic acid with a 0.01M sodium acetate solution in a proportion 1:1. A 2% brine solution was prepared by dissolving 20.25g of food grade salt in a litre of distilled water (Hodman and Weast, 1961).

3.2.3 Production of canned mackerel

Each mackerel in a batch was measured, weighed and filleted. The belly flaps were removed and the fillets were trimmed (see Fig. 12) in order to achieve the same weights within each batch. One fillet from each fish was packed in a plastic pouch, sealed and frozen at -35°C in a blast freezer for 4 to 5 hours and then stored in a low temperature cabinet at -25°C. The fillets treated in this way are referred to as "raw" in the results tables. The other fillet from each of the fish was soaked in a saturated brine solution at 12 to 14°C for 10 minutes, then it was rinsed with fresh water and drained for 30 minutes at room temperature

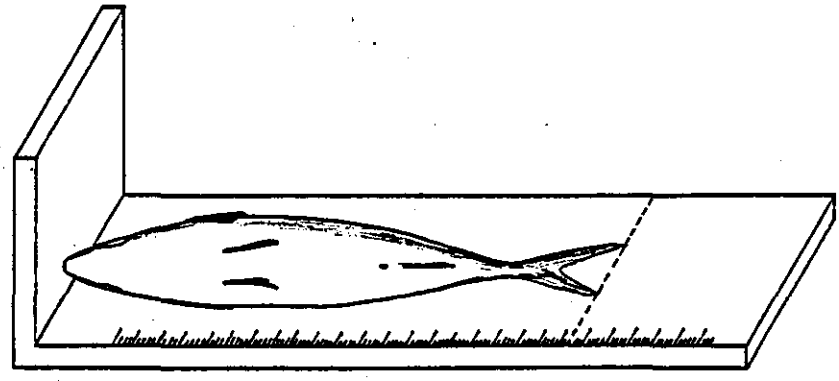


Figure 11 Mackerel length measurement

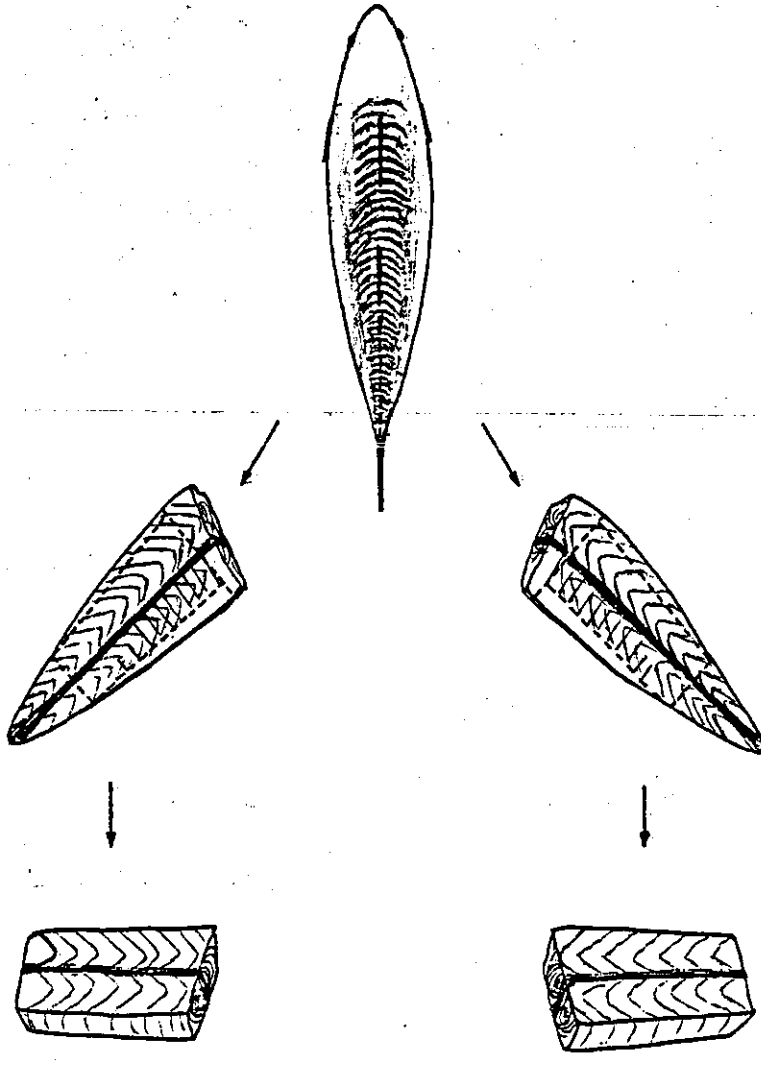


Figure 12 Filleting and trimming mackerel

(about 20°C). The fillets treated in this way are referred to as "brined" in the results tables.

The "brined" fillets were placed in U8 cans, filled with either 2% brine solution or simulated tomato sauce (pH 4.7) to give 210g specified net weight (Metal Box, 1978), and immediately vacuum seamed. The sterilization was at 115°C for about 85 to 95 minutes and to a Fo value of 14 ± 0.6. After cooling with cold water, the cans were wiped, dried and stored at room temperature.

3.2.4 Preparation of samples for analysis

The frozen fillets ("raw" as well as "brined") were thawed at room temperature, minced using a surgical scalpel and thoroughly mixed.

The canned samples were weighed, drained for 30 minutes and the fillets were then mashed.

3.2.5 Moisture determination

The moisture was determined by method 2.2A (determination of moisture by drying in an open dish) described by Pearson (1973).

3.2.6 Total lipids determination

Total lipids was determined by a modified Bligh and Dyer method. Approximately 25g of minced fish flesh was accurately weighed into a 250 cm^3 homogenising flask. The flask was placed in an insulated container and surrounded with crushed ice. 25 cm^3 of distilled water, 50 cm^3 chloroform, 100 cm^3 of methanol, 0.5g of antioxidant (butylated hydroxy toluene) were added and the mixture was homogenised for 2 minutes. A further 50 cm^3 of chloroform was added and the mixture homogenised for 30 seconds. Finally 50 cm^3 of water was added and the mixture homogenised for a further 30 seconds. The homogenate was poured into glass centrifuge flasks, centrifuged for 20 minutes at 3000 rpm. and the top layer (water-methanol) was removed by suction. The bottom (chloroform) layer was transferred to a burette, an exact volume was run off into a tared 250 cm^3 round-bottom flask and the solvent evaporated using a rotary film evaporator. The residue was dried to constant weight using a high vacuum pump. The total lipid was calculated from the formula.

$$\text{Total lipid (\%)} = \frac{C \times A \times 100}{B \times W}$$

Where: A = Total volume of chloroform added in cm^3

B = Volume of chloroform evaporated layer in cm^3

C = Weight of residue in g

W = Weight of sample in g

The determinations were carried out in duplicate.

The lipid obtained was stored at -25°C until required for further analysis.

3.2.7 Iodine Value

The iodine value was determined by the method 4.2 described by Pearson (1973). Approximately 0.1g of lipid was accurately weighed into a 250 cm^3 ground glass stoppered conical flask, 15 cm^3 chloroform was added and the flask was shaken until the lipid dissolved. 25 cm^3 of Wijs solution was added, the flask stoppered, swirled and placed in a darkened location for 30 minutes. Then 10 cm^3 of 10% potassium iodide solution and 50 cm^3 of distilled water were added, and the solution titrated with 0.1N sodium thiosulphate until a very pale yellow colour was observed. One to two cm^3 of 1 % starch solution as indicator was added and titration continued until the blue colour disappeared. The iodine determination was carried out in duplicate and also a blank for each separate sample was determined.

The iodine value was calculated from the formula:

$$\text{Iodine Value} = \frac{1.269\ (B-S)}{W}$$

Where: B = Titration of blank in cm^3
S = Titration of sample in cm^3
W = Weight of lipid in g.

3.2.8 Peroxide Value

The peroxide value was determined by Lea's rapid method (Pearson, 1973). Approximately 1.0g of lipid was accurately

weighed into a clean dry boiling tube, about 1.0g of (powdered) potassium iodide and 20 cm^3 of the solvent mixture, glacial acetic acid:chloroform (2:1 v/v) were added. The tube was placed in a boiling water bath for 1 minute, afterwards the contents were poured into a flask containing 20 cm^3 of 5% potassium iodide solution. The tube was rinsed twice with 25 cm^3 of water and the rinsings transferred to the flask containing the potassium iodide. The contents of the flask were titrated with 0.002N sodium thiosulphate using 1 % starch solution as indicator and carrying out a blank at the same time.

The peroxide value was calculated from the formula:

$$\text{Peroxide Value (meq/kg of lipid)} = \frac{2\,(S-B)}{W}$$

Where: B = Titration of blank in cm^3
S = Titration of sample in cm^3
W = Weight of sample in g

3.2.9 Acid Value

The acid value of free fatty acids was determined by the method described by Devine and Williams (1961). About 1.0g of accurately weighed lipid was dissolved in a neutral mixture of diethyl ether:methanol (25 cm^3 : 25 cm^3 neutralised with 0.1N sodium hydroxide) and titrated with 0.1N sodium hydroxide with phenolphthalein as indicator.

The determination was carried out in duplicate.

The acid value was calculated from the formula:

$$\text{Acid Value} = \frac{5.61 \times S}{W}$$

Where: S = Titration of sample in cm^3

W = Weight of lipid in g.

3.2.10 Saponification Value

The saponification value was determined by the method 5.3 described by Pearson (1973). Approximately 2.0g of lipid was accurately weighed into a 250 cm^3 ground glass jointed flat-bottomed flask, 25 cm^3 of 0.5N alcoholic potassium hydroxide was added and the contents were gently mixed by rotating the flask. An air condenser was attached to the flask and the contents refluxed for 60 minutes using a boiling water bath. The air condenser was removed after cooling and the contents of the flask were titrated with 0.5N hydrochloric acid, using 0.5 cm^3 of phenolphthalein as an indicator.

The determination of the saponification value was carried out in duplicate and a blank was also determined.

The saponification value was calculated from the formula:

$$\text{Saponification Value} = \frac{28.05\ (B-S)}{W}$$

Where: B = Titration of blank in cm^3

S = Titration of sample in cm^3

W = Weight of lipid in g.

3.2.11 Conjugable oxidation products (COP) Value

The conjugable oxidation products value was determined by the method described by Fishwick and Swoboda (1976). About 0.25g of accurately weighed lipid was dissolved in 5 cm^3 of iso-octane:ethanol (1:1, v/v) and 1 cm^3 aliquots were pipetted into each of three 25 cm^3 stoppered flasks (thereafter referred to as "O", "R" and "D"). To the flask "O", 1 cm^3 of isopropanol was added and the volume made up to 25 cm^3 with ethanol. To the flask "R", 1 cm^3 of sodium borohydride saturated solution in isopropanol (prepared by dissolving 0.5g of sodium borohydride in 100 cm^3 isopropanol and filtering) was added and the flask was placed in a water bath at 60°C for 30 minutes, after which it was cooled and the volume made up to 25 cm^3 with ethanol. Flask "D" was treated as "R", but before making up the volume to 25 cm^3, 5 cm^3 of 20% sulphuric acid in ethanol (5.4 cm^3 sulphuric acid, specific gravity 1.84 made up to 50 cm^3 with ethanol) was added. The absorption of the contents of each flask was determined using an ultraviolet spectrophotometer over the range 200 to 450 nm using 1 cm cells and ethanol as a reference.

The conjugate oxidation products value was determined from the formula:

$$\text{COP Value} = \frac{\left(A_{268}\,D - A_{268}R\right) + \left(A_{301}\,D - A_{301}R\right)}{0.8\ W}$$

$$\text{Oxodiene value} = \frac{A_{275}O - A_{275}R}{0.8\ W}$$

$$\text{COP ratio} = \left(A_{301}D - A_{301}R\right) \div \left(A_{269}D - A_{268}R\right)$$

Where: W = weight of lipid in g.

A_{268} = absorbance of solution "D" at 268 nm, etc.

The Oxodiene value and COP value are expressed in units of absorbance measured in a 1 cm cell for a 1% w/v lipid solution.

3.2.12 Fatty acid analysis by gas chromatography

The methyl esters were prepared by a method based on that of Metcalfe, Schmitz and Pelka (1966). About 150 mg of mackerel lipid was weighed into a 50 cm^3 round-bottomed flask and 1 crystal of BHT (butylated hydroxy toluene), 2 cm^3 toluene and 4 cm^3 of 0.5N methanolic sodium hydroxide was added. The contents of the flask were refluxed over a water bath for 30 minutes, allowed to cool and transferred to a 100 cm^3 separating funnel and 20 cm^3 of water were added. The round-bottomed flask was rinsed with 35 cm^3 of hexane and the rinsings added to the separating funnel, which was shaken for about 1 minute and the layers were allowed to separate. The water/methanol (bottom) layer was run off into a second separating funnel and 35 cm^3 of hexane was added. The mixture was shaken and allowed to settle. The bottom aqueous layer was run off and discarded. The hexane layers from both separating funnels were combined, 20 cm^3 of water was added, the mixture was shaken vigorously for about 1 minute and the layers were allowed to separate. The aqueous (bottom) layer was discarded and the hexane layer, containing the fatty acid methyl esters was dried with 5g anhydrous sodium sulphate. One microlitre of this fatty acid methyl esters solution was injected into a Perkin Elmer F-11 flame ionisation gas chromatograph, fitted with a 2 m (length), $^1/_8$ in (internal diameter) stainless steel column, packed with 10% SP2330 supported on 80 to 100 mesh chromosorb W-AW (acid wash). The operating conditions in the chromatograph were: hydrogen pressure 18 lb/in^2, air pressure 20 lb/in^2, nitrogen flow rate 35 cm^3/min, initial temperature 155°C, temperature programme 155°C to 230°C at a rate of 2°C/min and initial period at 115°C for 5 minutes. The peaks observed on the chromatograms of the fatty acid methyl esters were identified by comparison with standard

peaks obtained from two methyl esters standards: Chromopack GLC reference mixture No. 3 (AOCS) Cat. No. 32246 and "PUFA I" supplied by Chromatography Services, Carr Lane Industrial Estate, Hoylake Wirral.

The area of each chromatographic peak, representing the amount of a fatty acid methyl ester present, was calculated by cutting out and weighing the peak.

The triangulation method, which involves calculating the area by multiplying the peak height by the width at half the height was also employed and results compared to the cutting out method. It was found that the cutting out method gave more reproducible and therefore these are the only results quoted.

4. RESULTS

4.1 List of tables

4.2 Tables

Table 13 Biometric data for Batch A (caught in December 1980)

Sample No.	Length (cm)	Total weight (g)	Eviscerated weight (g)	Fillet weight (g) Left	Fillet weight (g) Right	Fillet (a) processed	Wt. gained on brining (g)
1	33	322	304	105.8	89.9	Right	1.5
2	36	407	388	125.9	105.9	"	1.8
3	36	359	338	109.2	102.8	"	6.3
4	35	350	328	100.1	102.8	Left	4.1
5	37	377	355	109.7	111.4	"	3.7
6	35	374	352	100.2	105.9	"	4.7
7	37	352	337	96.3	100.6	"	4.9
8	35	321	319	89.7	95.3	"	3.9
9	35	356	337	103.5	96.8	Right	3.5
10	36	349	333	100.2	100.2	"	4.4
11	38	400	380	113.7	103.7	Left	1.8
12	35	348	328	100.0	101.5	"	3.7
13	34	321	308	89.9	101.9	"	3.7
14	34	320	302	93.1	96.1	"	1.7
15	34	302	389	82.8	91.6	Right	2.7
16	34	304	292	82.7	91.7	"	2.7
17	36	322	302	85.7	91.4	"	1.8

(Table 13 continued)

18	36	318	299	92.0	92.8	Right	3.3
19	38	351	378	120.0	112.7	"	1.2
20	36	398	364	114.4	114.2	"	3.6
21	35	340	321	98.0	80.0	"	3.6
22	37	387	340	107.2	98.9	"	3.3
23	35	354	349	106.8	110.8	"	3.4
24	36	356	361	111.2	115.9	"	2.6
25	36	369	349	111.0	109.0	Left	1.3
26	36	341	331	89.3	102.2	"	2.3
27	35	341	323	101.6	97.3	"	2.7
28	35	353	269	112.4	103.1	"	3.0
29	36	364	320	104.1	100.3	"	1.2
30	37	380	322	102.3	95.2	"	2.7
31	37	368	296	96.8	92.0	"	3.3
32	35	335	294	105.9	110.4	"	4.0
Mean[b]	35.6	351.2	331.5	101.9	100.8		3.1
Std. Dev.	1.2	27.1	29.8	10.5	8.2		1.2

(a) The fillet used for processing (brining, heat processing etc.) is given in the table. The other fillet from each fish was not processed and is referred to as "raw" in subsequent tables.

(b) The Mean and Standard Deviation (Std. Dev.) values are for the 32 fish in Batch A.

Table 14 Biometric data for Batch B (caught in April 1981)

Sample No.	Length (cm)	Total weight (g)	Sex	Eviscerated weight (g)	Fillet weight (g) Left	Right	Fillet processed (g)
33	39	550	F	420	147.1	145.7	Right
34	39	500	F	400	158.3	163.0	"
35	41	590	M	480	142.3	144.6	"
36	41	540	F	430	110.1	114.7	"
37	41	430	F	340	116.5	117.2	Left
38	38	450	M	360	123.9	120.0	"
39	40	490	M	400	116.0	110.1	"
40	37	420	F	340	107.3	105.2	"
41	37	390	F	320	136.0	137.0	"
Mean	39.2	484.4		387.7	128.6	128.6	
Std. Dev.	1.6	67.1		51.9	18.0	19.7	

Table 15 Biometric data for Batch C (caught in April 1981

Sample No.	Length (cm)	Total weight (g)	Sex	Eviscerated weight (g)	Fillet weight (g) Left	Right	Fillet processed(1)	Wt. gained on brining (g)
42	41	590	M	470	138.3	148.8	Right	4.7
43	42	600	F	470	148.0	157.3	"	4.9
44	41	550	F	450	142.0	142.8	"	3.9
45	43	680	F	510	160.1	163.4	"	4.8
46	44	680	F	560	179.9	181.3	Left	5.2
47	40	530	F	420	126.9	137.7	"	3.0
48	38	470	M	380	115.2	120.5	"	2.9
49	40	440	M	370	112.3	112.7	"	3.2
Mean	41.1	567.5		453.8	140.3	145.6		4.1
Std. Dev.	1.8	88.1		63.9	22.7	22.4		0.9

(1) The fillet used for processing (brining, heat processing etc.) is given in the table. The other fillet from each fish was not processed and is referred to as "raw" in subsequent tables.

Table 16 Biometric data for Batch D (caught in August 1981)

Sample No.	Length (cm)	Total weight (g)	Eviscerated weight (g)	Fillet weight (g) Left	Fillet weight (g) Right	Fillet processed(1)	Wt. gained on brining
50	40	550	440	137.1	145.6	Right	2.5
51	38	600	520	183.6	178.4	"	6.1
52	36	450	380	122.4	126.2	"	3.2
53	36	450	380	128.1	124.2	"	2.8
54	34	430	370	129.0	133.2	"	3.5
55	36	440	365	109.4	116.4	Left	2.6
56	37	445	375	123.1	125.4	"	2.9
57	35	390	380	106.8	112.1	"	2.4
58	35	430	355	120.3	120.6	"	2.4
59	35	390	375	100.3	104.5	"	1.8
Mean	36.2	457.5	394	126.0	128.7		3.0
Std. Dev.	1.8	66.7	49.7	23.1	20.8		1.2

(1) The fillet used for processing (brining, heat processing etc.) is given in the table. The other fillet from each fish was not processed and is referred to as "raw" in subsequent tables.

Table 17 Biometric data for Batch E (caught in August 1981)

Sample No.	Length (cm)	Total weight (g)	Eviscerated weight (g)	Fillet weight (g) Left	Fillet weight (g) Right	Fillet processed[1]	Wt. gained on brining (g)
60	42	780	670	231.6	223.1	Right	5.5
61	41	740	640	215.5	206.1	"	6.5
62	40	700	610	185.7	193.3	"	6.7
63	41	750	660	191.5	209.2	"	7.9
64	41	780	690	198.3	225.2	"	4.4
65	41	790	680	201.2	216.5	Left	5.8
66	39	680	600	176.3	186.0	"	4.3
67	41	800	690	228.6	223.0	"	6.5
68	43	830	720	230.3	231.3	"	7.0
69	40	700	610	207.7	196.5	"	5.2
Mean	40.9	755	657	206.7	211.0		6.0
Std. Dev.	1.1	49.5	40.6	19.5	15.3		1.2

(1) The fillet used for processing (brining, heat processing etc.) is given in the table. The other fillet from each fish was not processed and is referred to as "raw" in subsequent tables.

Table 18 Analytical data for raw mackerel fillets[1]

Batch	A	B	C		D	E
Month caught	Dec.	Apr.	Apr.	Apr.	Aug.	Aug.
No. of samples	3	6	3	3	3	6
	without skin	without skin	without skin	with skin	with skin	with skin
Total lipids wet basis	16.7 (5.6)	10,3 (3.5)	11.0 (3.7)	9.1 (2.4)	20.1 (1.1)	30.1 (2.8)
Total lipids dry basis	-	32.4 (8.3)	36.5 (10.5)	32.5 (2.6)	52.7 (2.1)	62.9 (4.4)
Iodine Value	139 (7.5)	122 (12.7)	-	121 (14.6)	153 (5.0)	162 (9.0)
Peroxide Value	6.9 (3.0)	20.3(6.2)	23.4 (2.4)	18.7(10.0)	6.5 (1.9)	13.4 (2.0)
Acid Value	2.0 (0.9)	3.2 (0.9)	2.2 (0.7)	3.2 (1.5)	2.3 (0.2)	2.0 (0.7)
Saponification Value	202 (17)	170 (21.5)	-	176 (9.3)	200 (2.6)	188 (1.8)

(1) These figures are the means (standard deviations in parentheses) of data taken from subsequent tables for raw mackerel fillets i.e. mackerel fillets that were analysed after only a few days storage at $-25^{o}C$ without brining or heat processing.

Table 19 Effect of brining on mackerel fillets (Batch C)[1]

SAMPLE No / ANALYSIS	42		43		44	
	Raw	Brined	Raw	Brined	Raw	Brined
Total Lipids wet basis (%)	11.2	12.2	9.6	11.2	6.5	8.3
Total Lipids dry basis (%)	34.9	34.5	32.8	35.2	24.7	28.7
Iodine Value	138	138	111	112	115	131
Peroxide Value (meq/Kg)	10.0	16.1	16.4	30.2	29.6	33.7
Acid Value	2.3	1.8	2.2	2.0	5.0	2.9
Saponification Value	184	184	179	190	166	179

(1) The brining was in saturated brine for 10 minutes at 15°C. The analyses were carried out on mackerel fillets with skin.

Table 20 Effect of brining on mackerel fillets (Batch D)[1]

SAMPLE No. / ANALYSIS	53		57		59	
	Raw	Brined	Raw	Brined	Raw	Brined
Total Lipids wet basis (%)	21.1	21.8	18.9	20.1	20.3	21.7
Total Lipids dry basis (%)	54.1	54.4	50.3	49.9	53.8	53.7
Iodine Value	152	150	153	150	148	144
Peroxide Value (meq/kg)	4.7	6.7	6.3	9.5	8.5	10.0
Acid Value	2.2	2.3	2.5	2.5	2.1	2.2
Saponification Value	203	211	119	204	198	193

(1) The brining was in saturated brine for 10 minutes at 15°C. The analyses were carried out on mackerel fillets with skin.

Table 21 Effect of brining and refrigerated storage on mackerel fillets (Batch C)(1)

SAMPLE No. / ANALYSIS	46		47		48	
	Raw	Brined	Raw	Brined	Raw	Brined
Total Lipids wet basis (%)	7.6	7.2	15.0	17.2	10.3	15.2
Total Lipids dry basis (%)	27.3	25,3	47.9	55.4	34.4	42.4
Peroxide Value (meq/Kg)	23.5	27.2	21.0	27.0	25.8	27.0
Acid Value	3.0	3.3	1.8	2.5	1.8	2.0

(1) The brining was in saturated brine for 10 minutes at 15°C; the refrigerated storage was at 4°C for 96 hours. The analyses were carried out on mackerel fillets without skin.

Table 22 Effect of brining and frozen storage on mackerel fillets (Batch A)(1)

SAMPLE No. / ANALYSIS	21		26		30	
	Frozen raw	Frozen brined	Frozen raw	Frozen brined	Frozen raw	Frozen brined
Total Lipids wet basis (%)	16.2	14.8	14.5	16.6	8.7	9.8
Total Lipids dry basis (%)	43.2	40.9	39.5	43.1	22.2	30.2
Iodine Value	154	150	151	150	161	164
Peroxide Value (meq/Kg)	28.1	38.5	24.2	37.8	26.7	52.1
Acid Value	2.3	2.2	2.4	1.8	4.4	3.9
Saponification Value	212	224	197	194	212	198

(1) The brining was in saturated brine for 20 minutes at 15°C and the frozen storage was for 3 months at -25°C. The analyses were carried out on mackerel fillets without skin.

Table 23 Effect of heat processing on mackerel fillets canned in 2% brine (Batch B)(1)

SAMPLE No. / ANALYSIS	33		34		37	
	Raw	Canned	Raw	Canned	Raw	Canned
Total Lipids wet basis (%)	15.9	22.4	12.1	17.3	9.1	12.0
Total Lipids dry basis (%)	45.5	53.1	36.3	43.0	30.5	32.2
Iodine Value	132	119	119	122	123	120
Peroxide Value (meq/Kg)	24.5	26.7	10.1	10.0	19.0	7.4
Acid Value	2.3	2.9	2.5	2.1	3.5	2.8
Saponification Value	180	172	145	188	176	210

(1) The analyses were carried out on mackerel fillets without skin.

Table 24 Effect of heat processing on mackerel fillets canned in simulated tomato sauce (Batch B)(1)

SAMPLE No. / ANALYSIS	35		36		39	
	Raw	Canned	Raw	Canned	Raw	Canned
Total Lipids wet basis (%)	5.4	10.9	9.8	17.5	9.4	10.4
Total Lipids dry basis (%)	20.3	35.9	31.9	49.0	29.6	35.8
Iodine Value	115	108	103	148	139	113
Peroxide Value (meq/Kg)	28.4	17.3	20.6	16.4	19.3	9.6
Acid Value	4.8	3.7	3.5	2.2	2.8	5.4
Saponification Value	187	201	189	172	140	187

(1) The simulated tomato sauce was a buffer solution pH 4.7. The analyses were carried out on mackerel fillets without skin.

Table 25 Effect of heat processing on mackerel fillets canned in 2% brine (Batch E)(1)

SAMPLE No. / ANALYSIS	60		66		68	
	Raw	Canned	Raw	Canned	Raw	Canned
Total Lipids wet basis (%)	27.1	28.0	34.2	30.0	27.0	32.0
Total Lipids dry basis (%)	56.9	57.1	65.1	62.6	58.1	66.1
Iodine Value	163	165	157	157	179	179
Peroxide Value (meq/Kg)	12.6	7.8	15.1	5.1	13.7	9.5
Acid Value	1.7	2.1	1.6	2.0	1.6	1.9
Saponification Value	187	187	190	187	189	189

(1) The analyses were carried out on mackerel fillets with skin.

Table 26 Effect of heat processing on mackerel fillets canned in simulated tomato sauce (Batch E)[1]

SAMPLE No. / ANALYSIS	62 Raw	62 Canned	64 Raw	64 Canned	65 Raw	65 Canned
Total Lipids wet basis (%)	30.9	27.6	32.0	28.1	29.8	29.7
Total Lipids dry basis (%)	67.3	60.1	66.1	59.7	64.0	61.7
Iodine Value	159	159	155	153	156	154
Peroxide Value (meq/Kg)	16.0	9.0	10.5	7.0	12.5	4.2
Acid Value	1.7	2.1	3.4	3.6	1.9	2.4
Saponification Value	187	186	185	186	189	192

(1) The simulated tomato sauce was a buffer solution pH 4.7. The analyses were carried out on mackerel fillets with skin.

Table 27 Effect of storage on canned mackerel fillets (Batch A)[1]

SAMPLE No. / ANALYSIS	3		7		11	
	Raw	Canned	Raw	Canned	Raw	Canned
Total Lipids wet basis (%)	21.9	25.8	17.4	19.7	10.7	13.2
Iodine Value	140	144	132	131	147	160
Peroxide Value (Meq/Kg)	3.9	11.1	9.9	11.7	6.8	10.9
Acid Value	1.4	1.7	1.6	1.8	3.0	3.7
Saponification Value	185	193	203	197	219	222

(1) The storage for the canned fillets was at room temperature (about 20°C) for 1 month. The analyses were carried out on mackerel fillets without skin.

Table 28 Effect of storage on canned mackerel fillets (Batch A)(1)

SAMPLE No. / ANALYSIS	8		10		12	
	Frozen	Canned	Frozen	Canned	Frozen	Canned
Total Lipids wet basis (%)	11.7	16.6	15.6	19.9	16.4	20.3
Total Lipids dry basis (%)	35.2	47.0	41.1	51.5	41.6	52.0
Iodine Value	144	139	141	140	137	138
Peroxide Value (Meq/Kg)	20.8	13.9	23.1	14.8	23.1	18.1
Acid Value	3.3	2.5	3.3	2.0	3.7	3.1
Saponification Value	176	199	194	207	137	138

(1) The storage for the canned fillets was at room temperature (about 20°C) and the frozen fillets at -25°C for 6 months. The analyses were carried out on mackerel fillets without skin.

Table 29 Mean values on the effect of storage on mackerel fillets (Batch A)(1)

STORAGE PERIOD / ANALYSIS	Raw	1 Month	6 Months	
		Canned	Frozen	Canned
Total Lipids wet basis (%)	16.7 (5.6)	19.6 (6.3)	14.6 (2.5)	18.9 (2.0)
Total lipids dry basis (%)	-	-	39.3 (3.5)	50.2 (2.7)
Iodine Value	139 (7.5)	145 (14.5)	141 (3.5)	139 (1.0)
Peroxide Value (meq/Kg)	6.9 (3.0)	11.2 (0.4)	22.3 (1.3)	15.6 (2.2)
Acid Value	2.0 (0.9)	2.4 (1.1)	3.4 (0.2)	2.5 (0.5)
Saponification Value	202 (17.0)	204 (15.7)	169 (23.8)	181 (37.7)

(1) The storage for the canned fillets was at room temperature (about 20°C) and the frozen fillets at -25°C for 6 months. The analyses were carried out on mackerel fillets without skin.

Table 30 Paired differences "t" test on the effects of brining, heat processing and storage on mackerel fillets

Process	Batch	Table	Total Lipids dry basis	Significance level	Iodine Value	Peroxide Value	Significance level	Acid Value	Significance level	Saponification Value
BRINING	A	22	NS		NS	R < B	p < 5%	NS		NS
	C	19	NS		NS	NS		NS		NS
	C	21	NS		-	NS		NS		-
	D	20	NS		NS	R < B	p < 2.5%	NS		NS
HEAT PROCESSING	A	27	-		NS	NS		R < C_b	p < 5%	NS
	A	28	F < Cb	p < 0.1%	NS	F > Cb	p < 1%	F > Cb	p < 2.5%	NS
	B	23	NS		NS	NS		NS		NS
	B	24	R < Ca	p < 5%	NS	R > Ca	p < 5%	NS		NS
	E	25	NS		NS	R > Cb	p < 5%	R < Cb	p < 0.5%	NS
	E	26	NS		NS	R > Ca	p < 2.5%	R < Ca	p < 2.5%	NS

R = raw, F = frozen, B = brined, Ca = canned in simulated tomato sauce,
Cb = canned in brine, NS = not significant.

Table 31 Fatty acid composition of raw and canned mackerel fillets in brine (Batch A)(1)

SAMPLE No. / Fatty Acid	3		7		11		Mean			
	Raw	Canned	Raw	Canned	Raw	Canned	Raw	S.D.	Canned	S.D.
14:0	9.54	9.37	6.59	5.70	6.50	6.21	7.54	1.73	7.09	1.98
16:0	13.48	13.44	20.87	21.43	15.85	15.68	16.73	3.77	16.85	4.12
16:1	5.24	5.20	6.02	5.48	5.00	4.94	5.42	0.53	5.20	0.27
18:0	1.73	1.85	3.32	3.51	3.10	2.68	2.71	0.86	2.68	0.83
18:1	14.03	14.01	20.35	20.53	24.35	24.43	19.57	5.20	19.65	5.26
18:2	2.94	3.09	2.13	2.18	2.40	2.02	2.49	0.41	2.43	0.57
20:1 18:3 18:4	13.15	11.74	4.60	4.45	8.00	8.00	8.58	4.30	8.06	3.64
22:1 20:4	16.31	16.02	9.15	9.26	12.15	11.63	12.53	3.59	12.30	3.43
20:5	4.64	4.48	5.31	5.05	4.75	4.61	4.90	0.36	4.71	0.29
24:1	1.76	1.70	1.70	2.05	1.50	1.69	1.65	0.13	1.81	0.20
22:5	0.73	0.67	0.90	1.07	0.65	0.75	0.76	0.12	0.83	0.21
22:6	10.24	10.20	12.33	12.38	9.45	10.07	10.67	1.48	10.88	1.29
others	6.11	8.23	6.73	6.91	6.30	7.29	6.38	0.31	7.47	0.68

(1) The analyses were carried out on mackerel fillets without skin. Each figure is the mean of two determinations.

Table 32 Conjugable oxidation products (COP) Value on mackerel fillets (Batch A)(1)

SAMPLE No. 3	Oxodiene Value	COP Value	COP Ratio
Raw fillet	0.06	3.78	1.23
Canned fillet	0.12	4.50	1.26

(1) The storage of the canned fillet was at room temperature for 1 month. The analyses were carried out on mackerel fillets without skin.

Table 33 Fatty acid composition of raw, brined, and canned mackerel fillets (Batch E)[1]

SAMPLE No. / Fatty Acid	53				64				68			
	Raw		Brined		Raw		Canned in tomato sauce		Raw		Canned in brine	
14:0	9.21	9.26	10.50	10.43	10.06	9.92	10.63	10.69	9.20	9.23	8.99	8.95
16:0	16.23	16.14	16.77	16.71	9.64	9.70	9.94	9.87	13.05	13.01	13.09	13.05
16:1	6.95	6.89	6.01	6.09	3.93	3.87	4.36	4.39	4.96	5.01	4.62	4.64
18:0	2.19	2.23	2.15	2.11	0.95	0.91	1.09	1.11	1.43	1.45	1.85	1.84
18:1	12.17	12.22	12.16	12.10	6.92	6.97	6.99	6.95	9.84	9.79	10.26	10.21
18:2	2.37	2.33	1.93	1.98	1.62	1.64	2.17	2.14	1.29	1.28	1.54	1.56
20:1	8.17	8.21	7.30	7.22	11.56	11.61	10.00	10.04	10.25	10.23	10.95	11.01
18:3	5.76	5.81	6.15	6.12	7.43	7.38	8.33	8.37	5.93	5.97	4.12	4.09
18:4	1.10	1.03	0.68	0.68	1.37	1.39	1.35	1.32	0.64	0.66	0.62	0.59
22:1	12.95	12.92	12.58	12.52	20.11	20.16	16.98	17.03	15.15	15.19	15.82	15.79
20:5	6.55	6.49	5.81	5.89	6.87	6.92	6.55	6.50	9.56	9.51	9.24	9.27
24:1	1.35	1.40	0.94	0.97	1.59	1.57	1.23	1.29	1.29	1.28	1.31	1.29
22:5	0.51	0.54	0.53	0.56	0.78	0.76	0.71	0.75	0.93	0.90	1.01	1.02
22:6	8.95	8.91	8.14	8.09	10.06	10.01	9.15	9.11	10.27	10.31	10.17	10.22
Others	5.54	5.62	8.35	8.53	7.11	7.19	10.52	10.44	6.21	6.18	6.41	6.47

(1) The analyses were carried out on mackerel fillets with skin.

5. DISCUSSION

A difficulty inherent in working with a fatty fish such as mackerel is the wide seasonal and individual variation in composition, in particular in the lipid content (see Sections 2.1.3.2 and 2.2.3). In order to avoid problems associated with seasonal variation it is advantageous to take a large batch from a single catch,so that most of the fish would be likely to have a similar lipid content,and then store them until required for experiments. However the lipids of fish stored even at -30°C have been shown to undergo significant lipid changes (oxidation and lipolysis) after only a few weeks storage (see Section 2.1.3.5). Hence only a very limited number of experiments could be carried out on a single batch.

In this investigation five batches of fish were used, caught in December 1980 and in April and August 1981 (two batches in each of the latter months). Detailed biometric data and lipid analytical data were obtained for each batch, in order to be able to take into account the seasonal variation between the batches, when interpreting the data for the processing experiments.

In order to compensate for individual variations one fillet of each fish was processed whilst the other fillet was used as a control (referred to as raw fillet). No significant differences have ever been reported in the composition of the left and right fillets of fish (see Section 2.1.3.2).

5.1 Biometric data

Organoleptic assessment indicated that the fish in all of the five batches used in this investigation were about 2 to 3 days

post-mortem (stored in ice). The biometric data for each of the batches are given in Tables 13, 14, 15, 16 and 17. The fish varied in length between 33 and 44 cm with the Batch A fish being in general shortest (average length 35.6 cm) and the Batch C longest (average length 41.1 cm). These lengths correspond to adult mackerel in each case (Bolster, 1974; Keay, 1979). The total weights do not correlate directly with length, the variation probably being due to the feeding behaviour of the fish directly before capture. The eviscerated weights which relate to sexual maturity were 94%, 80%, 80%, 86% and 87% of the total weights for Batches A, B, C, D and E respectively. Only Batches B and C had gonads large enough to be visually sexed.

The mackerel were hand-filleted following commercial practice. There was no significant difference in weights between the left and right fillets in any of the batches. The fillets were randomized as far as possible with respect to side and sex in the processing experiments.

After brining, the fillets showed an increase in weight (about 3%). This is due to diffusion of brine into the flesh faster than the extraction of water, during the short period of immersion (10 minutes), as also noted by Voskresensky (1965).

5.2 Analytical data for raw fillets

The analytical data for raw fillets for each of the Batches A, B, C, D and E are given in Table 18. The fillets of Batches A and B and half of Batch C were analysed without skin. Whereas

Batch D, Batch E and the other half of Batch C where analysed with skin. The initial experiments were carried out on fillets without skin since, in general for mackerel fillets, the skin is not eaten. However, during the course of these experiments, it was observed that significant lipid migration occurred from the skin to the flesh during heat processing, leading to difficulties in comparing the raw with the processed fillets. Later the experiments were carried out on the fillets with skin, and thus they are not directly comparable with the earlier experiments. However, it should be noted that for the Batch C raw fillets analysed (see Table 18), no significant difference was found between the fillets without skin and with skin for total lipids, Peroxide Values and Acid Values.

The total lipids in the fillets is related to the season (see Section 2.2.3). The lowest values for Cornish mackerel are normally found between April and July and the highest values between October and February. The values given in Table 18 for Batches A, B and C are in agreement with this; the values for Batches D and E are rather higher than normally found at that time of year, but this may be due to the inclusion of skin in the analyses.

The Iodine Values range from 121 (Batch C) to 162 (Batch E), and are in general high for fillets with high lipid content. This was noted also by Hardy and Keay (1972), and indicates that the lipid is more unsaturated when the lipid content in the mackerel is high. The Peroxide Values range from 6.5 (Batch D) to 23.4 (Batch C) and are in general low when the lipid content is high. This was observed also by Smith *et al.* (1980) for mackerel and indicates that the lipid oxidation is more rapid when the lipid content is low. No satisfactory explanation can at present be put forward to explain these correlations.

The Acid Values are all in the range 2.0 to 3.2 and no statistical correlation with the total lipid content is observed. The Saponification Values range widely (170 to 202), but again no correlation with the total lipid content is observed.

5.3 Brining

Changes in the mackerel lipids during the pre-canning brining process were investigated using standard brining conditions of 10 minutes at 15°C with saturated brine. Four sets of results were obtained. The results in Tables 19 and 20 are for analyses performed directly after brining for Batches C and D respectively. The results in Table 21 are for analyses carried out after storing the brined fillets for 96 hours at 4°C. This was done in order to access the effect of a delay between brining and heat processing. The results in Table 22 are for analyses carried out after storing the brined fillets at -25°C for 3 months. This was done in order to assess the effect on the brined fillets of frozen storage before canning. The raw fillets were in each case frozen directly after filleting and stored at -25°C until analysed. This storage was less than four days, except in the case of the Batch A fillets, which were stored frozen for 3 months (see Table 22).

The results in Tables 19 and 20 are for lipid changes on brining for mackerel fillets containing low total lipid content (Batch C approx. 10%), and high total lipid content (Batch D approx. 20%), respectively.

The Peroxide Values for the brined fillets are higher than those for raw fillets for both batches, but the difference is significant only for Batch D ($p < 5\%$). It appears that the brining process has an accelerating effect in the lipid oxidation. This has also been reported by Nair *et al.* (1974) and Ahn *et al.* (1978), although the

mechanisms involved are not fully understood (see Section 2.1.2.1). The Iodine Values do not differ significantly between raw and brined for either batch.

The brining does not appear to affect significantly the Acid Values, indicating that the rate of lipolysis is not affected by the brining operation. The Saponification Values between the raw and brined fillets in Batches C and D are not significantly different.

The results in Table 21 shows the effect on the brined fillets of refrigerated storage. Both samples, raw and brined fillets, were kept for the same period of time, 96 hours at $4^{o}C$, before analysis. The total lipid content for the raw and brined fillets, is not significantly different even though in this case the analyses were carried out on mackerel fillets without skin.

The mean Peroxide Value for the brined fillets is higher than for the raw fillets (27.1 compared with 23.4), however the difference is not statistically significant. Therefore refrigerated storage of brined mackerel fillets for 96 hours at $4^{o}C$ has not been shown to increase significantly the lipid oxidation.

The mean Acid Value was higher for the brined fillets than for the raw fillets (2.9 compared with 2.2), however the difference is not statistically significant.

The Iodine Values and Saponification Values were not determined due to lack of sample.

The effect of brining, followed by frozen storage at $-25^{o}C$ for 3 months, on the mackerel fillets, was assessed and results are given in Table 22. The raw fillets are designated in the table as "frozen raw" since they also were stored frozen for 3 months. Comparing the analytical results for the frozen fillets in this table with those for the raw fillets of the same batch (Batch A) in Table 18, it is seen that the Peroxide Values have increased on

frozen storage from a mean value of 6.9 to a mean value of 26.3; this increase is significant at $p < 2.5\%$. This is in agreement with results previously reported for frozen storage of fatty fish (Hardy, 1980).

The Acid Values are also slightly higher in the frozen samples (mean value 3.1 compared with 2.0) but this increase is not significant.

The Peroxide Values for the "frozen brined" fillets are higher than for the "frozen raw" fillets ($p < 5\%$) (see Table 22) which indicates that the brine is behaving as a pro-oxidant under these conditions (Lea, 1962b). Nair et al. (1974) suggested that the salt in the fillet might increase the amount of unfrozen water, thus allowing greater interplay between the reacting entities. The Iodine Values, Acid Values and Saponification Values are not significantly different for the "frozen raw" and "frozen brined" fillets.

5.4 Heat processing

In order to determine the effect of heat processing on the lipids in the mackerel fillets, four experiments were carried out, the results being given in Tables 23, 24, 25 and 26. Two filling liquids were used, 2% brine and simulated tomato sauce, since besides oil these fillings are the most commonly used for mackerel fillets. The processing time was 115°C for about 90 minutes, until an Fo value of 14 was achieved. This process is typical of that used for canned mackerel fillets (see Section 2.3.2). In each case the analyses for the processed fillets were performed within a few days of processing.

In Table 23 are the results for the Batch B fillets canned in

2% brine and analysed without skin, and in Table 24 the results for Batch B fillets canned in simulated tomato sauce and also analysed without skin.

The total lipids are higher on both a wet weight and dry weight basis for the canned fillets than for the raw fillets, although the difference is only significant ($p < 5\%$) for the fillets canned in simulated tomato sauce. The most likely explanation of these results is that diffusion of lipids from the skin to the flesh has occurred during the heat processing.

The mean Peroxide Values were lower for the canned than the raw fillets, but the difference was significant ($p < 5\%$) only for the fillets canned in simulated tomato sauce (see Table 24). An explanation of these results is that some of the hydroperoxides have broken down on heat processing. Biggar et al. (1975) reported that the heat processing inhibits lipid oxidation since in canning oxygen from the air is eliminated and avoided by vacuum seaming and air-tight containers. However there have been no previous reports of peroxide values decreasing during heat processing, although very little work has been carried out in this area (see Section 2.1.3.5).

The Iodine Values, Saponification Values and Acid Values do not differ significantly between the raw and canned fillets for either treatment (see Tables 23 and 24).

The differences in the total lipids in the raw and canned fillets when analysed without skin introduces uncertainties when assessing the lipid changes on processing, therefore further batches of fillets were analysed with skin.

In Table 25 are the results for Batch E fillets canned in 2% brine, and Table 26 lists results for Batch E fillets canned in simulated tomato sauce, and in both cases the fillets were analysed

with skin. The figures for total lipids between raw and canned fillets are not significantly different, however the values are relatively high (average 30%). This is due to the inclusion of skin (see Section 2.2.3).

The mean Peroxide Values in the raw fillets are higher than the canned fillets ($p < 5\%$) for both canning in brine and in simulated tomato sauce, indicating that during canning the hydroperoxides have broken down, as discussed above.

The mean Acid Values are higher in the canned fillets than the raw fillets ($p < 2.5\%$) for both canning in brine and simulated tomato sauce. This is probably due to hydrolysis of some lipids because of the high process temperature, as noted also by Strokova and Smirnova (1978), and Andrade and Lima (1980). It is not clear why similar results were not obtained for the Batch B fillets although it is possible that the lipid which diffused from the skin to the flesh had a relatively low Acid Value so distorting the comparison between raw and canned. It was also observed that there was no difference in Acid Values between the fillets canned in simulated tomato sauce and brine even though the pH of the brine was 7.2 compared to 4.7 for the tomato sauce.

The Iodine Values and Saponification Values do not differ significantly between the raw and the canned for the Batch E fillets.

5.5 Storage

Tables 27 and 28 (Batch A) show the result of the analyses carried out to assess the effect of storage of canned mackerel for 1 and 6 months at room temperature and frozen storage of mackerel for the same period. Table 29 gives the mean values.

The total lipids in the canned fillets are significantly higher than in the frozen fillets in Table 28. This again is due to the migration of the lipid from the skin to the flesh, since the skin was not included in the analyses.

The Iodine Values of the raw and frozen fillets and the canned fillets are not significantly different from each other, after storage for 1 or 6 months.

The Peroxide Values after 1 month do not differ significantly between the raw and canned fillets (see Table 27). However in Table 28, in which the fillets were stored for 6 months, the frozen fillets show higher values than the canned fillets ($p < 1\%$) which is an indication that frozen storage for long periods of time is less effective in slowing down the rate of lipid oxidation than canning. This was also quoted by Bail'ozov and Ilieva (1975). Fatty fish such as mackerel are subject to lipid oxidation and lipolysis even at a very low temperature storage (see Section 2.1.2).

The Acid Values for canned fillets after 1 month storage are significantly higher ($p < 5\%$) than the raw fillets, which again indicates that the breakdown of some lipids during heat processing has increased the free fatty acids. After 6 months however, the Acid Values in the frozen fillets are higher than the canned fillets ($p < 2.5\%$). This shows that lipolysis has occurred in the frozen fillets, since the mean Acid Values for the canned fillets after 1 month and 6 months storage are similar (see Table 29). The occurrence has been reported to be not only in the phospholipid fraction (Lovern and Olley, 1962; Viswanathan Nair *et al.*, 1976), but also in the triglyceride fraction (Botta *et al.*, 1973 a, b).

The Saponification Values, although variable, are not significantly different for frozen and canned fillets either after 1 month or 6 months storage.

5.6 Effect of brining and heat processing on the fatty acid composition

The fatty acid profiles, by gas chromatography, for the canned fillets stored for 1 month (Samples 3, 7 and 11 of Batch A) were determined and results are given in Table 31. The mean and standard deviation for each fatty acid from three different fish are given. Paired differences "t" distribution test (Harper, 1979), and the level of significance was calculated from tables (Murdoch and Barnes, 1979). The fatty acid profiles compare reasonably well with similar results in mackerel (S. scombrus) reported by Stansby (1969), also with the fatty acid profile in neutral lipid, reported by Hardy and Keay (1972), and in light flesh by Ackman and Eaton (1971).

The separation of linolenic acid (18:3 ω 3) and arachidonic acid (20:4 ω 6) was not achieved in this batch, possibly due to the column or the operating conditions. However these fatty acids were not separated, either, by Hardy and Keay (1972). In Table 31, these peaks are calculated as composite peaks. The areas of peaks not identified by comparison with the standards (see Fig. 13 in the appendix) were summed and appear as "others" in the table.

The main fatty acids are oleic acid (18:1 ω 9), palmitic acid (16:0), docosaenoic acid (22:1 ω 11), whose peak in the chromatogram is combined with that of arachidonic acid (20:4 ω 6), and docosahexaenoic acid (22:6 ω 3). The "t" test revealed a significant change only in the thymnodonic acid (20:5 ω 3) which has decreased on canning ($p < 2.5\%$). This might have been caused by oxidation since this fatty acid is highly unsaturated and thus more liable to oxidation. However the Peroxide Values did not show a significant increase on canning (see Table 27) although as mentioned above hydroperoxide breakdown may have occurred on canning.

In addition the conjugable oxidation products (COP) Value for sample 3 (Batch A) were also determined.

All absorbance readings were divided by 4 since a 4 cm cell was used and the formula calls per 1 cm cell. The canned fillet shows a slighly higher COP Value than the raw fillet (see Table 32 and Fig. 14 in the appendix) but this difference is probably not significant, which is in agreement with the Peroxide Values and gas chromatography.

Results of the fatty acid profile of mackerel fillets 53, 64 and 68 (Batch E) brined, canned in simulated tomato sauce and canned in brine respectively are shown in Table 33. Although the results are in duplicate and statistical analysis is therefore difficult, it is apparent that no major changes in fatty acid composition have occurred on brining or heat processing.

6. CONCLUSIONS

The commercial processing of canned mackerel fillets involves various steps in which the fish is filleted, brined, packed into cans and sterilized at a high temperature (115 to 121°C) for a relatively long period of time (90 to 100 minutes). Thus degradation of higher unsaturated fatty acids might be anticipated. However this study shows only very slight changes in these fatty acids.

The pre-process operation of brining, where the fillets are soaked or immersed in saturated brine for 10 minutes, increases the Peroxide Values an average of 28%. Refrigerated storage for 96 hours at 4°C after brining, does not affect significantly the lipid oxidation. However, frozen storage for 3 months at -25°C increases the Peroxide Values by an average of 38%.

The heat processing decreases the Peroxide Values an average of 38%.

The Iodine, Acid and Saponification Values are not significantly affected by the operations of brining or heat processing.

The storage of cans after heat processing for periods ranging from 30 to 180 days does not significantly increase the Peroxide or Acid Values.

It appears that a migration of lipid from the skin to the flesh occurs during heat processing, although it does not substantially affect the lipid oxidation.

The fatty acid composition of the total lipids of mackerel is not significantly affected by the brining or heat processing except for the thymnodonic acid (20:5) which decreases on heat processing an average of 4%.

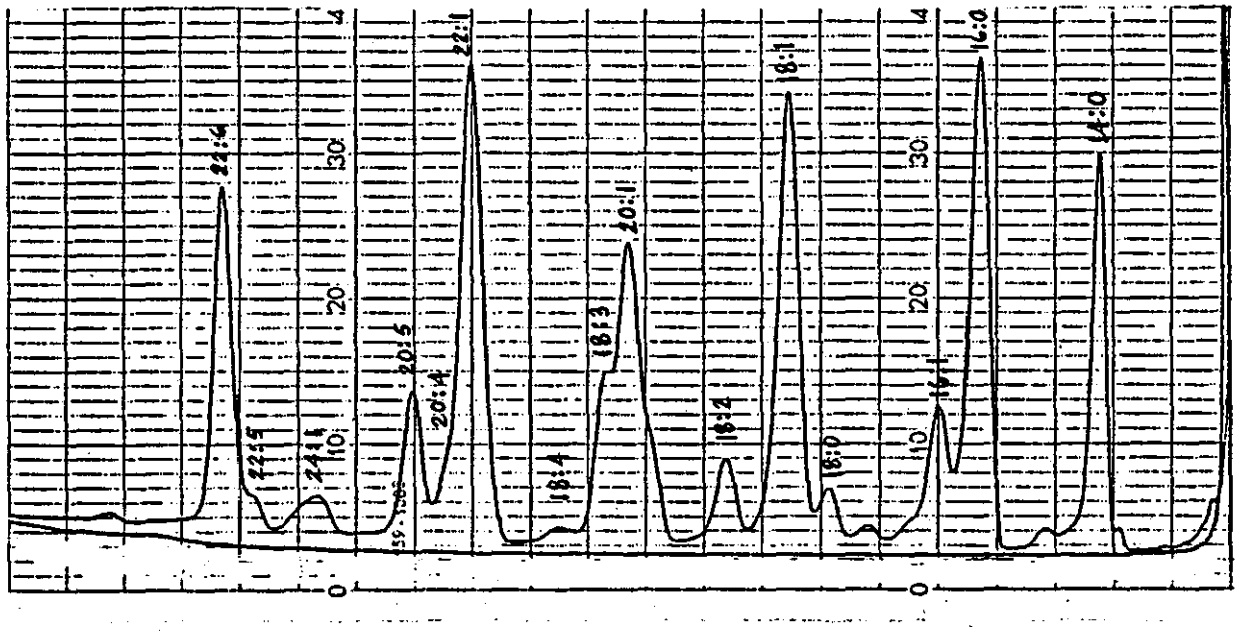
7. SUGGESTIONS FOR FURTHER WORK

1) Separation of the total lipids into lipid classes, that is phospholipids, neutral lipids and free fatty acids might help in the identification of changes occurring in the fatty acid composition during processing and storage, since most changes appear to be very small and statistically not significant. Moreover the use of a capillary column in the gas chromatograph is recommended for improved separation.

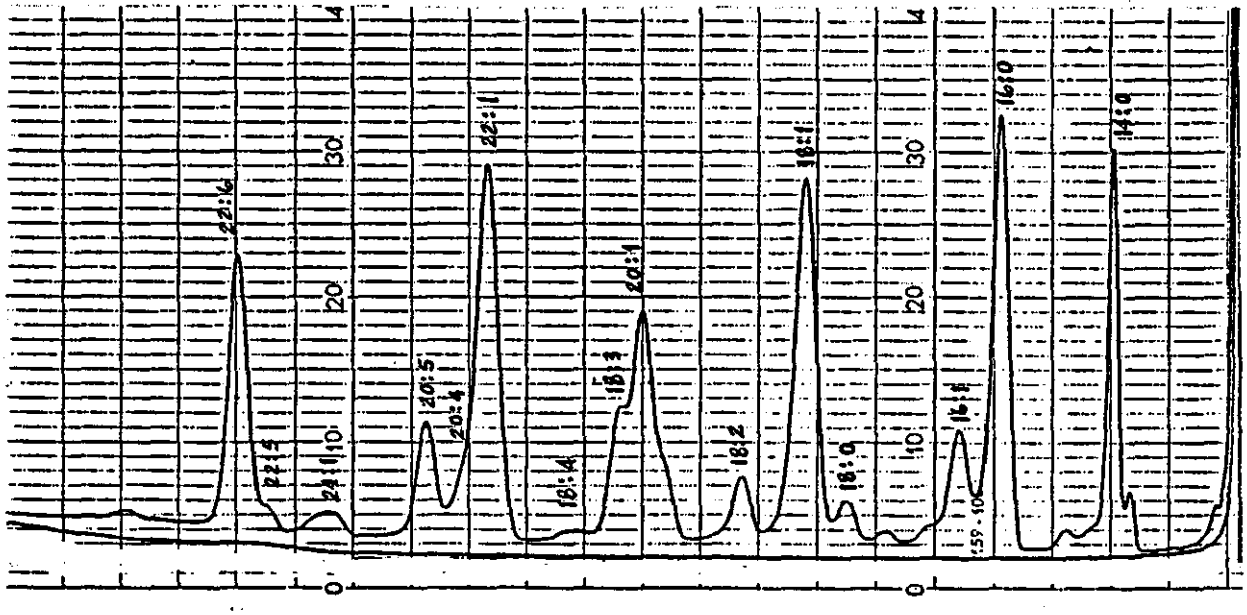
2) Organoleptic assessment of the canned as well as the "raw" fillets in addition to the chemical analyses (Peroxide, Acid, Iodine and Saponification Values) might be incorporated.

APPENDIX

Figure 13 Chromatograms of fatty acid methyl esters from raw and canned mackerel fillets

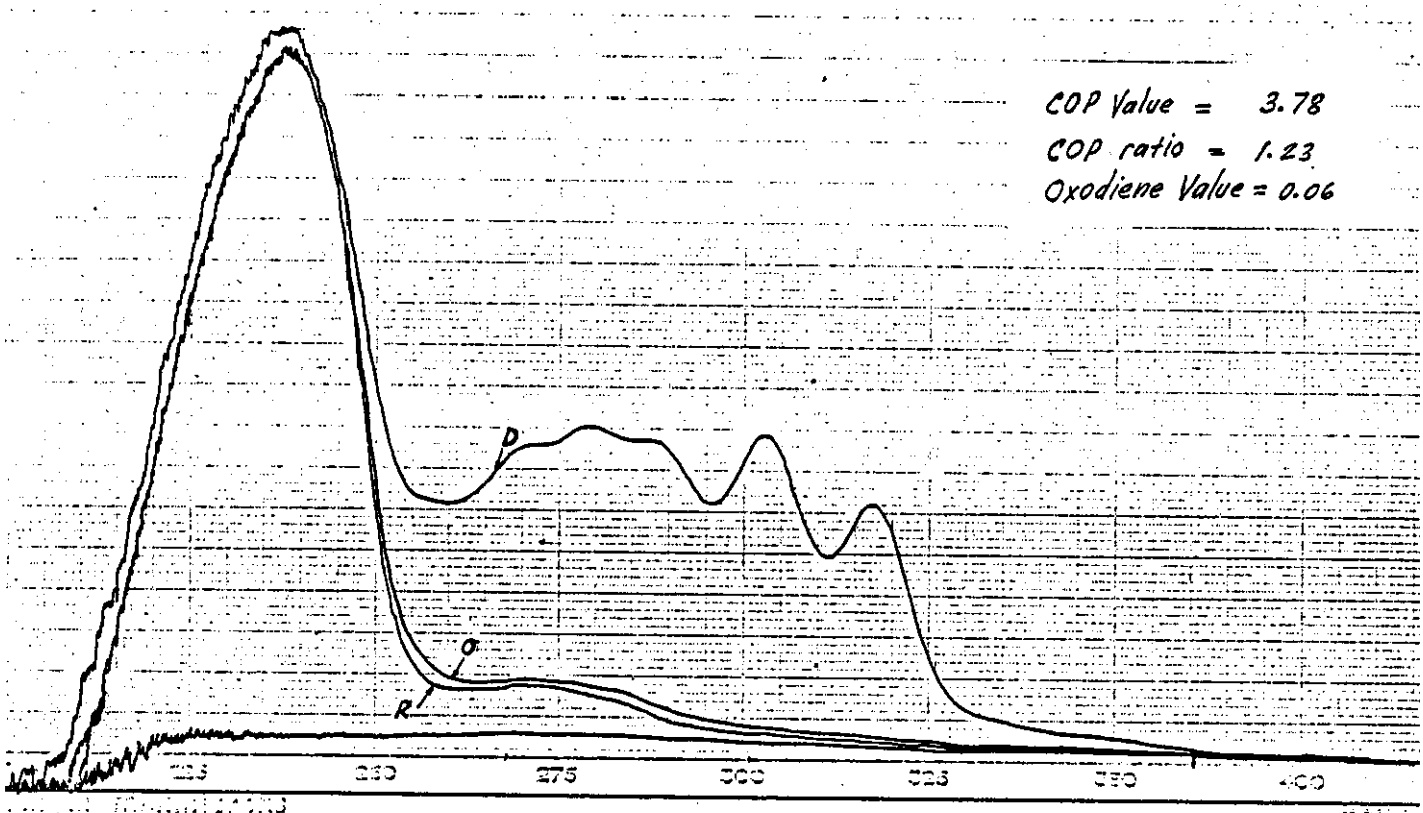


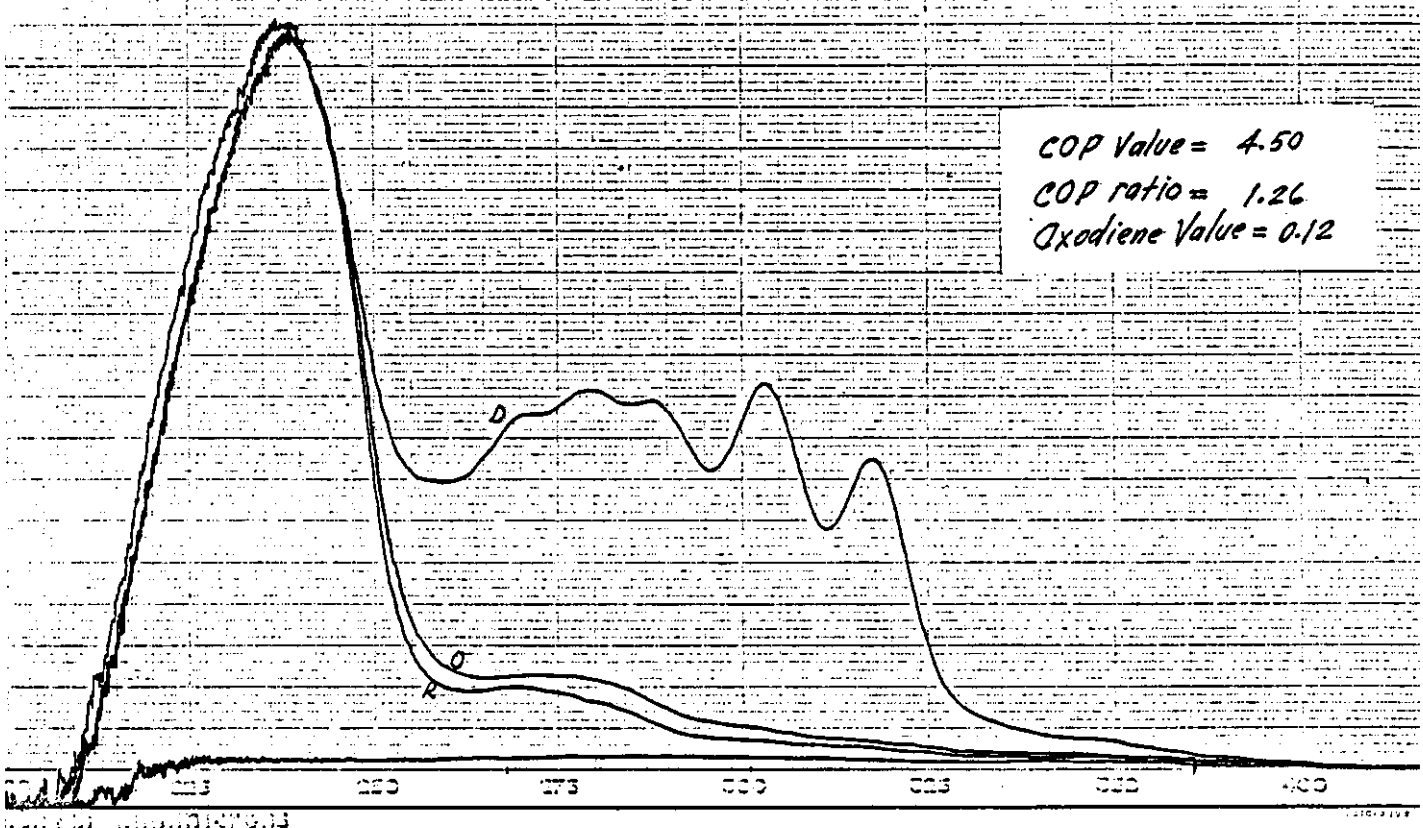
Sample No. 3 (Batch A) raw fillet



Sample No. 3 (Batch A) canned fillet

Figure 14 Spectra for COP analysis in raw and canned mackerel fillets





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