DEVELOPMENTS IN OILS AND FATS

Edited by R. J. Hamilton

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Developments in Oils and Fats

Preface

This first volume in a series is intended to provide up-to-date information on specific topics in oils and fats. The book will be especially valuable for any practising scientist or technologist who deals in any way with oils and fats whether from a nutritional, surfactant, cosmetic or analytical chemistry point of view. In addition there is sufficient depth in most of the articles to catch the imagination of many more senior managers in the industry.

The oils and fats industry is closely aligned with the food industry and it is no surprise to find that five of the chapters (1, 2, 3, 6 and 7) are written from a food perspective. The current arguments about diets and their fat content are well developed in Dr Enser's chapter on meat lipids. He has presented a very balanced picture explaining that there are many reports which contradict the fashionable 'saturated fatty acids are bad' theory. This chapter will do much to illustrate the dietary implications of meat lipids and should stimulate discussion and further research.

Professor Sargent and Dr Henderson have described in considerable detail the composition of marine oils. It is appropriate at present with the latest '*trans* fatty acid' theories in full swing to see the composition of 56% of the oils used in margarine. The authors consider the methods available for producing concentrates of (*n*-3) polyunsaturated fatty acids including fractional crystallisation in liquid nitrogen, supercritical fluid extraction and silver nitrate chromatography. They acknowledge the value of such concentrates in diet supplements with capsules, but indicate that increased consumption of naturally oily fish would be at least as good.

The prime importance of chocolate in confectionery fats is explained by Dr Shukla who has provided much valuable data on solidification of chocolate from different geographical regions of producer countries. He also highlights the advantages and disadvantages of cocoa butter substitutes and cocoa butter equivalents. Dr Shukla completes this chapter by explaining the importance of this fat in industry and commerce.

It is important to be reminded that oils and fats have an important role in the oleochemical industry. It was a great pleasure when Dr Watanabe agreed to describe his studies of fatty acids where he has outlined the importance of fatty acid derivatives in the production of lubricants for metal working and cutting. He has explained the test methods which are needed to measure corrosion resistance. There are full practical details of the preparation of additives for lubricants.

By contrast the next two chapters describe two very important oils – sunflowerseed oil and palm oil.

The chapter on sunflowerseed oil is essentially the work of Dr Morrison. There is a very clear description of how the fatty acid content of the sunflower plant can be altered by a careful breeding programme. The position of high oleic sunflowerseed oil is illustrated as well as attempts to produce hybrids which have less wax than the commercial varieties. This chapter also illustrates that there is more to oils and fats than as a raw material for foodstuffs with sections on alternative fuels and oleochemical uses.

Soya bean oil and palm oil are the two most important oils in commerce where they compete with one another on price and availability. Each oil has its own special characteristics and Dr Ong, Dr Choo and Dr Ooi have been especially successful in their explanation of the significance of palm oil. The care which is needed to ensure the highest quality of oil is very satisfactorily explained. Many physical characteristics e.g. slip point of solid fat content, as well as chemical characteristics e.g. fatty acid and triglyceride compositions are provided in the tables in this chapter.

The uses of palm oil as a frying medium, in margarine and as blends in confectionery fats are well illustrated. Equally palm oil can be used as an oleochemical feedstock and its use for metal soaps, in detergent manufacture, in candles and for the production of glycerine have been detailed. Finally the section on nutrition helps to re-emphasise the potential for good balanced diets which palm oil presents.

As Berger and Hamilton relate in their chapter on rancidity, the interaction between oxygen and lipids has always been with humankind. This chapter briefly outlines the mechanisms of the reactions involved in autoxidation and shows how the volatile components responsible for the off-flavours arise. Some very important guidelines on how to minimise the risk of rancidity development should prove especially useful to workers in the factory.

Dr Timms was the Lewkowitsch Lecturer of the Oils and Fats Group of the Society of Chemical Industry for 1992. He is a leading international expert on the topic of crystallisation and his lecture was well received by an appreciative audience in London. The shortened version of his lecture which appeared in *Chemistry & Industry* served to stimulate further international interest in this topic. Chapter 8 is therefore an updated and fuller version of his Lewkowitsch lecture. He deals with the science both physical and chemical which lie behind the successful growth of crystals in the oils and fats industry. The expansion of the β-polymorph of hardened rape seed oil is shown in Figure 8.15 and such an expansion can produce stresses in the containment vessel causing the vessel to crack.

Dr Cast provides the last chapter on infrared and Raman spectroscopy. This authoritative chapter starts with basic principles, explains the way in which spectra may be produced and then details many of the applications of the techniques to lipids. Dealing with internal reflection spectroscopy, internal reflection devices, diffuse reflectance spectroscopy, near infrared spectroscopy and Raman spectroscopy in turn, the instrumentation is covered and the advantages of each are detailed.

Finally very full tables of assignments for the important functional groups in lipids are provided.

The authors of the chapters are based in England, Scotland, Denmark, Japan, USA and Malaysia so that a truly international view of the oils and fats industry is presented.

I am pleased to acknowledge the help from the publishers who have worked hard to turn this concept of a development series into reality.

R.J.H.

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1 Meat lipids

M. ENSER

1.1 Introduction

The lipids of animals have structural, metabolic or storage functions. The structural lipids are present in membranes where they exist as a lipid bilayer. Specialized structural lipids also occur as the myelin sheath surrounding nerves and in the brain. Except for these, structural lipids are present in tissues in relatively small amounts, approximately 0.5% of the weight of muscle or fatty tissue, and are therefore consumed *in situ* as part of the meat. Despite their low concentration they are important contributors to the species-specific cooked meat flavour and also to the rancid odour and flavour of meat, both raw and cooked, which has been stored too long. Many of the components of the structural lipids in meat will be incorporated into the structural lipids in the body of the consumer.

The storage lipids are the triacylglycerols present in the fat cells or adipocytes which make up the fatty tissues of the animal. Adipocytes also occur between muscle fibres, giving rise to the 'marbling' of meat, and within the bone marrow. The lipid content of adipose tissue is affected by many factors such as the age of the animal, the site within the animal and the nutritional state of the animal, but in animals slaughtered for meat it is usually between 70% and 90% of the tissue by weight. The triacylglycerols contain a wide variety of fatty acids although only five or six are usually present in large amounts. It is the fatty acid composition and the combinations of these fatty acids in the triacylglycerol that determine the physical characteristics of the lipid. Lipid is a major component of the human diet, contributing up to 40% of the calories in the diet of the developed countries. In the UK, meat lipids *in situ* or after rendering and processing, contribute one-third of the total dietary lipid consumption. Over the last few years the nutritional advisability of such a high fat consumption has been questioned, particularly the consumption of fat from ruminant animals which contains a high proportion of saturated fatty acids and a low proportion of polyunsaturated fatty acids.

Under metabolic lipids are included those of the bile, which make possible the absorption of dietary fat, the plasma lipoproteins which act to transport lipid around the body, and the metabolites of the essential fatty acids such as prostaglandins, prostacyclins, thromboxanes and leucotrienes.

Since none of these are major components of meat they will not be considered further.

The main aim of this chapter is to discuss the changes which are taking place in the meat industry and how they affect the composition and characteristics of meat lipids. An attempt has been made to predict future changes and to identify areas which need further investigation. The relationship of lipids to the development of flavour and off-flavour in meats is discussed, since this represents a major research area and is most applicable to consumer appreciation of meat.

1.2 Coronary heart disease (CHD)

The Committee on the Medical Aspects of Food Policy (COMA) recommended that the consumption of fat and particularly saturated fatty acids should be decreased in the UK[1] in order to reduce mortality from cardiovascular disease, the major cause of death.[2] This followed similar recommendations by WHO[3] and the National Advisory Committee on Nutrition Education,[4] and in the United States an NIH Consensus Development Conference on Lowering Blood Cholesterol came to the same conclusion.[5] These recommendations are based on the 'lipid theory' of CHD although it is clear that other factors such as hypertension and smoking are important components of the complex aetiology of this disease, together with a considerable genetic contribution. Essentially the lipid theory may be stated as follows: high concentrations of plasma cholesterol are associated with an increased risk of CHD. The concentration of plasma cholesterol depends, in part, upon the quantity and type of fatty acids present in the diet. The saturated fatty acids, lauric, myristic and palmitic increase plasma cholesterol whereas polyunsaturated fatty acids (PUFA) decrease it. This hypothesis, stemming from the work of Keys and Ahrens and their colleagues in the 1950s, has provoked considerable controversy. However, a reassessment of 19 prospective trials, using meta-analysis has confirmed the relationship between plasma total cholesterol and mortality.[6]

The role of fatty acids in affecting the levels of plasma cholesterol and in the atherosclerotic process has been extensively clarified over the last 10 years (see review by Ulbricht and Southgate).[7] Oleic acid, the major dietary mono-unsaturated fatty acid is now known to decrease plasma LDL cholesterol like polyunsaturated fatty acids but without their decrease in HDL cholesterol, a form protecting against CHD.[8,9] Thus, the old ratio of polyunsaturated to saturated fatty acids (P:S ratio) is inappropriate as an index of diet atherogenicity. The formation of an atherosclerotic plaque is only the first part of the disease process. This narrows the arteries but a heart attack occurs when a clot forms in the narrow artery and blocks it. Saturated fatty acids, including stearic acid are thrombogenic. However, dietary stearate may have little effect *in vivo* as opposed to *in vitro* since it does not increase plasma stearate levels very much.[10] The effect of polyunsaturated fatty acids on thrombogenesis is more complex. They are precursors for the production of antithrombogenic prostacyclins and thrombogenic thromboxanes, the net effect depending upon the relative activity of the two products. Dihomogammalinolenic acid is antithrombogenic whereas arachidonic acid is thrombogenic although both are derived from linoleic acid, the former preceding the latter in the synthetic pathway of the *n*-6 fatty acids. Eicosapentaenoic acid (EPA), of the *n*-3 series derived from alpha-linolenic acid, is antithrombogenic.

Thus, there is a conflict between the positive hypocholesterolaemic effect of linoleic acid (*n*-6) and the greater thrombogenic risk caused by deposition of its metabolic product arachidonic acid. The *n*-3 PUFA derived from linolenic acid are more favourable in that they lower plasma triglycerides and are antithrombogenic. Although their precursor, alpha-linolenic acid is preferred over linoleic acid in the synthetic pathway, this is counteracted by the high consumption of linoleate compared with linolenate and the latter is not incorporated into tissue lipids as readily as the former. Furthermore, there is some doubt whether the synthetic pathway can produce longer chain products in humans at a sufficient rate.[11]

The need to balance *n*-6:*n*-3 fatty acid intake to cope with these conflicting actions of fatty acids in the two groups has long been recognised but has received little publicity. Taylor *et al.*[12] suggested that thrombogenesis rather than atherosclerosis was the main cause of the increase in CHD which started earlier this century and that it correlated with an increase in the *n*-6:*n*-3 ratio from 6:1 to 10:1 through increased consumption of high linoleate vegetable oils. Studies of early man suggest he consumed food with a ratio of 1:1 or 2:1.[13] The Eskimo diet has a ratio of 0.4:1 compared with 3.57 urban Danes who have a high incidence of CHD which is almost absent in the Eskimo.[14] The Japanese, with the greatest male life expectancy in the world have a diet with a ratio of 4:1, but like the Eskimo diet, it is high in seafood. As with the P:S ratio, the *n*-6:*n*-3 ratio is clearly a crude approximation and its meaning is interpreted in different ways. Some have only included the precursor essential fatty acids linoleic and alpha-linolenic[15] on the basis that they use the same metabolic pathway and compete with each other. Also the metabolic effects of their products are difficult to quantify comparatively. However, since the longer-chain fatty acid products consumed as fish can bypass the competition for delta-6-desaturase and are associated with decreased CHD, their inclusion appears justified if this ratio is to have a valid meaning. Currently recommended intakes of *n*-6, as percent of energy, range from 1% to 10% and for *n*-3 from 0.2% to 1.0%.[15]

The other important group of fatty acids relevant to meat are the *trans*-

unsaturates. The COMA report[1] suggested that they should be added to saturated fatty acids when considering the atherogenicity of the diet. However, although they are treated metabolically like saturated fatty acids for incorporation into complex lipids, they did not appear to increase plasma cholesterol.[16] More recently, it has been reported that they may increase the risk of CHD by lowering HDL and raising LDL and by raising levels of lipoprotein (a).[17,18] Furthermore, a prospective study has revealed a strong correlation between the consumption of *trans*-unsaturated fatty acid and the incidence of CHD.[19] However, the effect was related to products based on partially hydrogenated fats which contributed 60% of the *trans* isomers and not to the ruminant based products which contributed 40%; nor was it related to consumption of meat. This points to the importance of the particular *trans*-unsaturated fatty acids. Partially hydrogenated fats have double bonds in a whole range of positions and most studies of specific fatty acids have involved elaidic acid, the *trans* isomer of oleic acid.[17,18] However, the major fatty acid in beef and lamb and butter is the 11-isomer, *trans*-vaccenic acid.

1.2.1 Will dietary change decrease CHD?

There have been several 'Intervention Trials' aimed at demonstrating that lowering plasma cholesterol by diet and/or drug treatment will result in a decreased mortality from CHD. In the US Lipids Research Clinics study,[20,21] in which diet and cholestyramine were used, cholesterol was decreased by 8.5% and CHD was 19% less although overall mortality was unchanged. In the WHO clofibrate trial,[22] the fall in cholesterol only resulted in a 25% decrease in non-fatal myocardial infarction and overall mortality was increased. It appears, therefore, that lowering plasma cholesterol decreases CHD, but the effect on mortality is largely abolished by the drugs used.[23] In the Oslo trial,[24] dietary changes and a small decrease in smoking were much more effective, with a 33% decrease in total mortality, and further follow-up has shown that the results are now significant, using the more discriminating two-tailed *t*-test.[25] Analysis of the data indicate that 7.5% of the improvement resulted from the dietary changes which lowered total fat intake from 44.1% to 27.9% of calories and saturated fatty acids from 18.3% to 8.3% of calories.

These trials have been criticized in that they used patients in the high risk factor group with raised plasma cholesterol. However, studies on random populations have been less successful. In the North Karelia study,[26,27] the incidence of CHD and associated mortality was reduced, but a fall in the control population meant that the results were not significant. In the WHO collaborative trial involving four countries, the overall changes in CHD just failed to reach significance, although the changes which occurred were related to the degree of reduction in plasma cholesterol.[28] The latter was