Lipid Science and Lipid Commerce

Frank Gunstone

Scottish Crop Research, Invergowrie, Dundee DD2 5DA, Scotland
E-mail: fdg1@st-and.ac.uk

Tribute to Douglas Lloyd on the occasion of his 80th birthday

Douglas was appointed to a post in the Chemistry Department (now School of Chemistry) in 1947 and continued until his retirement in 1988 when an honorary appointment was conferred on him. I joined him in 1954 and left only in 1996 when (post-retirement) I took an honorary appointment at The Scottish Crop Research Institute in Dundee. We were colleagues under three Professors (John Read, John Cadogan, and John Tedder) and worked in two different buildings with the change coming in 1968. During these many years – almost 100 between us – we shared a loyalty to the university, to our profession as university teachers, and to appropriate professional associations, even if we expressed these in different ways. Because of our long shared experience I am pleased to be associated with others in this tribute to Douglas and to mark my recognition of his qualities as a teacher, researcher, colleague, wide-traveler, and organist. I remember him saying to me on one occasion "We all have the right to choose how we waste our own time". I am sure that the word waste carried inverted commas for his "wasted" time has been spent at the organ, traveling, and keeping up with his many and ever-growing circle of friends. In all of these activities he has brought much pleasure to many people and we all salute him.

Abstract

Lipid science is now an important and respected field of endeavour involving many individual sciences though this was not always true for organic chemists. The reasons for this change are discussed. Some current topics of interest are described including dietary recommendations, transgenic genetic modification of oilseeds, developments in analytical methods, and conjugated linoleic acid. Finally some significant features of the production and consumption of these materials are outlined.

Keywords: Lipids, science, commerce

This essay-review describes some significant features in today's science and commerce related to lipids (oils and fats) and places them in a historical context. Topics to be covered include the recent acceptance of lipid science as an important and respected field of endeavor involving many individual sciences, dietary recommendations, transgenic genetic modification of oilseeds, developments in analytical methods, and conjugated linoleic acid. Finally, some significant features of the production and consumption of these materials are outlined.

1. Lipid chemistry was not highly rated by organic chemists in the mid-20th century

Up to about 1950 organic chemistry was dominated by the isolation, identification, and synthesis of natural products. Since isolation of a pure compound was a necessary part of this process organic chemists worked mainly with volatile liquids, which could be distilled, crystalline solids, which could be crystallised, and coloured compounds which could be separated by the primitive forms of adsorption chromatography then practised. Oils and fats (lipids), as they were then known, did not meet these requirements.

Apart from a few saturated acids, lipids and their derivatives were oily liquids or low-melting solids and the difference between one natural fat and another was mainly quantitative. Their study called for tedious and unexciting analytical procedures. The differences between one fat another seemed insignificant. On the few occasions when a novel fatty acid was discovered its structure was either unexciting, as with 9-hexadecenoic acid[1], or too difficult to identify by the limited procedures then available. In a lecture given in 1948 by Hilditch[2] the structure of eicosapentaenoic acid (20:5) was incorrectly formulated and the correct structure for docosahexaenoic acid (22:6) was not included among the five possibilities listed. Symbols such as 20:5 and 22:6 are used by lipid scientists to describe the structure of fatty acids with 20 or 22 carbon atoms and 5 or 6 unsaturated centres. Further symbols may be added to indicate the position and configuration of the unsaturated centres, which are almost always double bonds with cis configuration. In the absence of other information the carbon atoms form a straight chain.

A further problem was the belief that fats served only one purpose. They were considered to be an efficient source of calories providing fuel for the biological machine. All that has now changed and lipids are accepted for their vital importance in human health even though the current consensus is under challenge.

The seeds of a different outlook had been planted in the 1920s and 1930s but it took two or three decades before these ideas became widely known and accepted and began to influence wider areas of thought. I cite two seminal papers:

- Burr and his wife[3] introduced the concept of essential fatty acids. These acids, required for animal and human health, can be biosynthesised by plants but not by animals. They are therefore essential dietary requirements. Burr and Burr demonstrated that linoleic acid (18:2) was one such acid.
- A decade later von Euler[4] described materials derived from C_{20} fatty acids that we now know as prostaglandins or more generally as eicosanoids. In 1982 the Nobel Prize in

medicine or physiology was awarded to JR Vane, SK Bergstrom, and BI Samuelsson for research on prostaglandins.

2. Lipids in health and disease – an active topic of debate

Ideas developed in the 1950s onward concerning a relationship between dietary fat and health/disease. The lipid hypothesis attracted the attention of dieticians, health commissars, government committees, and politicians all of whom found it convenient to relate the problems of multifactor coronary heart disease to one simple cause viz "-saturated" fat. No thought seems to have been give, for example, to the fact that saturated fatty acids are a group of fatty acids with four to eighteen carbon atoms per molecule, not all of which are metabolised in the same way. Some have argued that the evidence does not fully support the conclusions that have been drawn[5.6] but they have been enjoined, "not to rock the boat" now that the general public is beginning to get the message. Those accepting the current views have not adequately refuted these criticisms nor do the dietary recommendations distinguish adequately between persons who show the symptoms of coronary heart disease and those who are healthy. A lot of expensive research in seed breeding is being carried out today to produce seed oils with changed fatty acid composition (see section 3) to match the best dietary requirements based on what some consider to be a flawed theory.

In producing margarines and other spreads, frying oils, and the shortenings and cooking fats that go into baked goods it is often necessary to submit unsaturated liquid oil to partial hydrogenation. This is done to obtain a semi-solid product with the required melting behaviour. Unfortunately, at the same time, this process reduces the level of essential fatty acids and produces monoene acids with *trans* unsaturation (the natural unsaturated acids are almost entirely of *cis* configuration). These are now considered to be as nutritionally undesirable as saturated acids. New technologies now make it possible to produce fat blends with appropriate melting behaviour without partial hydrogenation and in Europe, at least, material is available that is "virtually *trans* free".

The requirement to ingest appropriate levels of essential fatty acids is now generally accepted but debate continues on the optimum ratio of n-6 acids based on linoleic acid (18:2) and of n-3 acids based on α-linolenic acid (18:3). The n-6 acids are readily available from (non-hydrogenated) vegetable oils and the n-3 acids from some vegetable oils and from fish oils. Most of these valuable acids are changed during partial hydrogenation.

3. Lipids from genetically modified oilseeds

Oil seed plants have been bred by traditional methods over many years leading to improved yields and modified fatty acid composition. When the range of natural germplasm was insufficient then this was extended by irradiation or by the use of chemicals. With developments in biotechnology new tools are available and products have been obtained by transgenic modification.

The first examples of these included soybean, rapeseed/canola, corn, and cotton plants developed for agronomic reasons with in-built resistance to herbicides and to insect attack. The benefits accrued mainly to the farmer and to the environment in terms of a reduced need for herbicide and pesticide and a lessened need for tillage, which in turn diminishes the loss of soil and of moisture. These may have little significance for the final consumer and the proteins, oils, and by-products from these genetically modified crops caused concern on several counts, particularly in Europe. Arguments were based on claims concerning animal and human health, the environment, and producers in the developing world. Coming on stream now is a second group of seeds containing oils with modified ("healthier") fatty acid composition. Some, but not all of these, have been obtained by transgenic modification[7]. When produced in quantity these modified oils will have to be kept separate from botanically related material of different fatty acid composition (identity preserved) and will be harvested, transported, stored, and processed in smaller quantities than the traditional commodity materials. This will result in some extra cost. Seed oils will then be available with:

- Lower levels of saturated acids on nutritional grounds
- Higher levels of saturated acids to avoid partial hydrogenation and consequent formation of *trans* acids
- Higher levels of mid-chain saturated acids (C_{10}-C_{14}) required for oleochemical purposes
- Higher levels of oleic acid on nutritional grounds
- Lower levels of linolenic acid to avoid partial hydrogenation and extend shelf life
- Oils with uncommon hydroxy and epoxy acids for industrial use

Lipid science now covers much more than chemistry and lipid scientists have to be aware of developments in many different sciences including physics, biochemistry, surface science, catalysis, nutrition, enzymology, and many others. I no longer describe myself as a fat chemist: the term lipid scientist is more appropriate.

4. Developments in analytical methods

The tedious analytical procedures of the first half of the 20th century have been revolutionised since the advent of gas chromatography, which is now widely used but was developed in the first instance for fatty acid analysis by Martin and James[8, 9]. Today's lipid analyst uses a wide range of chromatographic and spectroscopic techniques. These allow quicker analyses, give more accurate results, and can provide quantitative and qualitative information leading to a deeper insight into the physical and chemical composition of lipid mixtures including those obtained in small quantities from biological systems. Plant breeders, for example, carry out hundreds of analyses each day by gas chromatography and have developed robots to assist in these large tasks. In most of these analytical procedures the disciplines of chemistry have been largely replaced by those of physics and engineering.

5. Conjugated linoleic acid (CLA)

Lipid science like most areas of science generates, from time to time, novel topics, which suddenly arouse a lot of interest reflected in research papers, books, and international conferences. Conjugated linoleic acid (CLA) falls into this category[10].

It has been known for many years that ruminant fats, in both meat and milk, contain up to 1% of a group of isomeric acids with a straight chain of 18 carbon atoms and a *cis trans* conjugated diene. The major member of this group is rumenic acid (9*c*11*t*-18: 2). These acids are produced from dietary linoleic acid (9*c*12*c*-18: 2) by metabolism in the animal rumen.

Since the quantity of material available from the ruminant sources is limited a similar product is being produced commercially from linoleic acid or from seed oils containing over 80% of this acid. By heating with alkali the natural 9*c*12*c* acid is converted to a mixture of the 9*c*11*t* and 10*t*12*c* isomers. Because it is important to make studies with single isomers this mixture has been separated into individual components using appropriate lipase preparations.

It is now believed that these acids or selected members of the group have a range of important biological properties including, among others, their ability to inhibit breast cancer and to modulate the protein/fat ratio. This latter may be of interest to body builders but is likely to be of greater significance in the formulation of animal feed to promote protein formation and inhibit fat production.

Many of these significant properties have been demonstrated only in animal experiments or with cell lines and much needs to be done to demonstrate their potency in humans.

6. Oils and fats in commerce

Forty years ago fat production was at a level of about 29 million tonnes per anuum and dominated by animal fats with butter (4.2 million tonnes), tallow (3.4 million tonnes), and lard (3.2 million tonnes) occupying the first three places. Today (2000-2001) annual production is about 117 million tonnes. The three major animal fats have now fallen to ranking positions 5-7 and today's list is dominated by four vegetable oils: soybean (26.6 million tonnes), palm (23.0 million tonnes), rape/canola (14.3 million tonnes), and sunflower (8.8 million tonnes)[11]. Oils and fats are used for food (80%), animal feed (6%), and as the basic raw material for the oleochemical industry.

At present this last is dominated by production of soap and the more sophisticated anionic cationic, and non-ionic surface-active compounds, all of which depend on the amphiphilic properties of fatty acids and their derivatives. Other industrial uses as lubricants, solvents, and bio diesel are expected to become more significant. Compounds based on lipids are claimed to have superior environmental properties over similar compounds of petrochemical origin, both in terms of production from a renewable resource and disposal after use.

Biodiesel, which is usually the methyl esters of almost any oil or fat, can be used as a complete or partial replacement of mineral oil in diesel engines. The recent increase in the cost of crude (mineral) oil and the fall in the price of most vegetable oils have aroused an interest in producing increasing amounts of rapeseed methyl esters (RME) in Europe, particularly in Germany. These esters can also be used as an environmentally friendly solvent and as a heating fuel. The recently built new Reichstag building in Germany has the facility to burn RME in addition to the normal mineral fuel. Because of environmental concerns rapeseed and other vegetable oils are being used as a lubricant especially in the "total loss" situations such as chain saws and powerboats and as hydraulic fluid in situations where loss of fluid would cause environmental embarrassment. Lipid-based products can never completely replace mineral oil and petrochemicals because the annual production of mineral oil is about 30 times greater than that of lipid most of which must be used as food and feed. Nevertheless lipids have much to offer in the move towards greater use of renewable resources.

At least one organisation studying agricultural products has suggested that by 2100 world production of oils and fats has will have risen to close on a billion tonnes and that up to 50% of this will be available for oleochemical use[12]. This is expected to be particularly true in the second half of the century when population will probably level off at about 10 billion, up from the present level of 6 billion.

References

1. Armstrong, E.F.; Hilditch, T.P. *J. Soc. Chem. Ind.* **1925**, *44*, 202.
2. Hilditch, T.P. *J. Chem. Soc.* **1948**, 243.
3. Burr, G.O.; Burr, M.M. *J. Biol. Chem.* **1929**, *82*, 345.
4. Von Euler, U.S. *J. Physiol*. **1936**, *88*, 213.
5. Gurr, M.I. In *Lipids in Nutrition and Health;* The Oily Press: Bridgwater, UK, 1999; p 49.
6. Taubes, G. *Science* **2001**, *291*, 2536.
7. Gunstone, F.D. *J. Oleo Science* **2001**, *50*, 269.
8. Martin, A.J.P.; Synge, R.L.M. *Biochem. J.* **1941**, *35*, 1358.
9. James, A.T.; Martin, A.J.P. *Biochem. J.* **1952**, *50*, 679.
10. Yurawecz M.P. Ed. A*dvances in Conjugated Linoleic Acid Research*; Huang,Y-S; Ziboh, A., Eds.; AOCS: Champaign Illinois, 1998; Vol. 1 and Vol. 2, 2001.
11. *Oil World* 1958-2007, ISTA Mielke GmbH, 1989, and Oil World Weekly (March 30, 2001).
12. Fry, J, Lecture to a meeting of the Oils and Fats Group of the Society of Chemical Industry, Hull, April 2001.