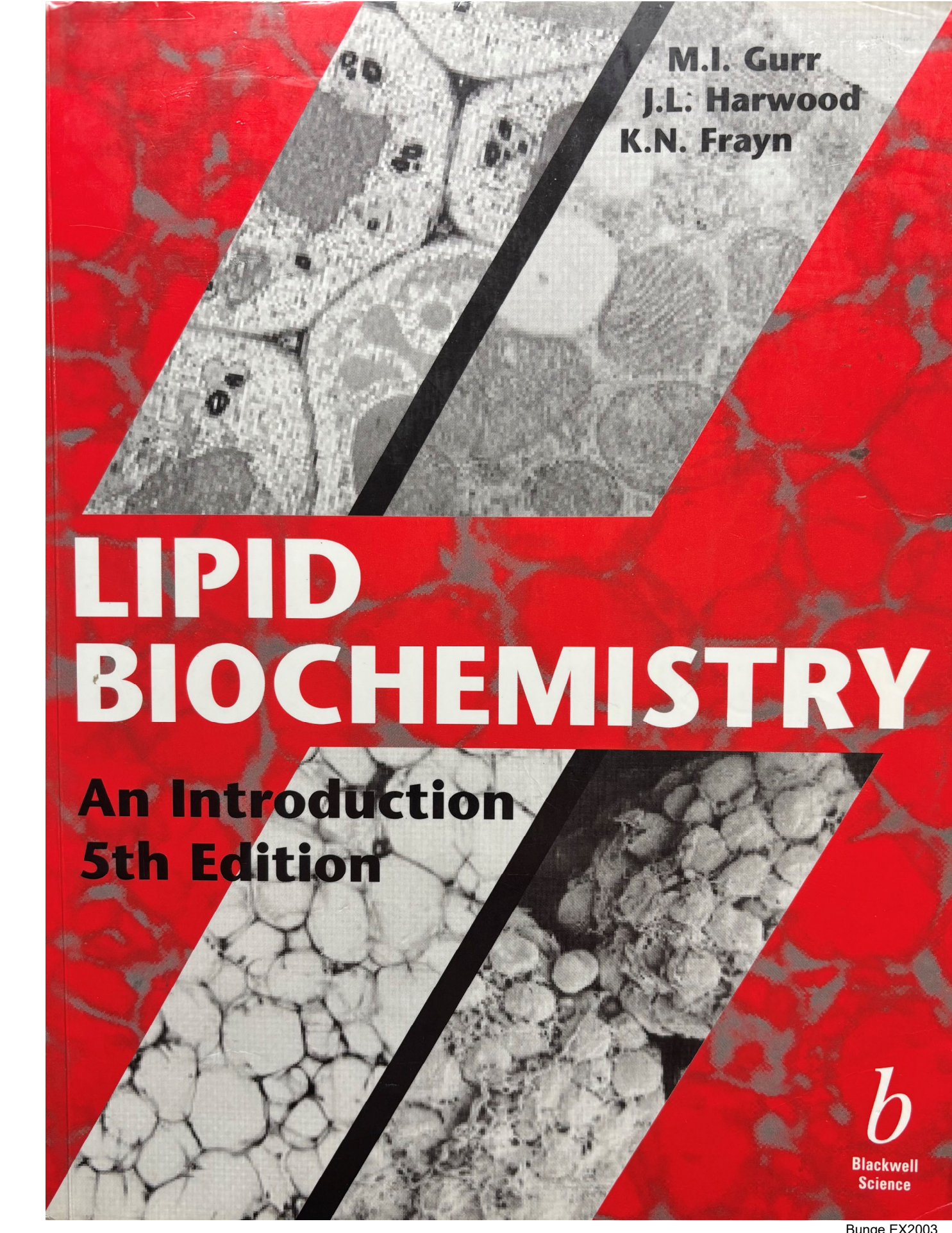




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LIPID BIOCHEMISTRY

**An Introduction
5th Edition**

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Lipid Biochemistry

5th Edition

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It is important to note that *trans* double bonds do occur in natural fats, as well as in industrially processed fats, but generally much less abundantly than *cis* bonds. Thus some seed oils have a significant content of fatty acids with *trans* unsaturation (see Table 2.3) although these are not important sources of fat in the human diet. All green plants contain small quantities of *trans*-3-hexadecenoic acid (see Table 2.2). The most important naturally occurring isomeric fatty acids in human foods are those in ruminant fats. In principle, the chemical outcome of rumen biohydrogenation (Section 2.2.6) is similar to that of industrial hydrogenation. However, whereas in ruminant fats there is a preponderance of the monoene with the *trans* bond at position 11 (*trans*-vaccenic acid), in industrially hydrogenated fats, monoenes with double bonds at positions 8, 9, 10, 11 and 12 make similar contributions (Fig. 4.1). Whereas *trans*-monoenes usually predominate, PUFA with *trans* unsaturation also occur in both natural and processed fats and these can have *cis* and *trans* bonds within the same molecule. Since the early 1990s, interest has been growing in a group of such isomers given the general description 'conjugated linoleic acid' (CLA). It was discovered that some components of the mixture, notably the *cis*-9, *trans*-11 isomer, could inhibit the growth of cancer cells *in vivo* or *in vitro* (Sections 4.4 and 5.4.2).

The fatty acid structural changes that occur as a result of industrial hydrogenation may have nutritional significance as discussed in Sections 4.1.4.3 and 5.4.2.

4.1.3.2 Heating

Either industrially or in the home, heating may be used to make food palatable and to make it safe by killing micro-organisms. Risk of reduction of heat-labile and oxygen-sensitive nutrients requires a balance to be struck between microbiological safety and nutritive value. Heating fat that has little contact with air (e.g. in a deep fat fryer) gives rise to gradual accumulation of polymeric products. The first substances to be formed are cyclic monomers of triacylglycerols followed by polymeric products. As long as oils are not reused excessively, such

polymeric material does not significantly reduce the functional properties of the oil, nor is it digested and absorbed.

More important changes in fats are brought about by heating in the presence of oxygen and trace metal catalysts (e.g. iron, copper). The major pathway is attack by reactive oxygen radicals at the double bonds of unsaturated fatty acids with the initial formation of a lipid peroxide (Section 2.3.4). The more highly unsaturated the fatty acid, the greater the susceptibility to oxidation. If allowed to go too far, lipid peroxidation can significantly reduce concentrations of essential fatty acids, vitamin A and vitamin E in foods and may also result in damage to proteins (including enzymes) and DNA. Some products may be carcinogenic. Lipid peroxidation may be held in check by the presence of lipid-soluble antioxidants, either natural (e.g. vitamin E, carotenoids) or synthetic (butylated hydroxytoluene, BHT, or butylated hydroxyanisole, BHA). Cholesterol in foods can also auto-oxidize, a process that is accelerated in heating or drying. Thus, 25-dihydroxycholesterol, 7-ketcholesterol, 7-hydroxycholesterol, 5- and 7-hydroperoxycholesterol and cholesterol-3,5,6-triol have been detected in products such as dried egg powder. These components are known to initiate arterial disease in rabbits when they are given in low quantities in the diet, where cholesterol itself has no effect.

4.1.3.3 Irradiation

Irradiation, used to kill pathogens in some types of foods, may generate lipid radicals and thus cause peroxidative damage. Vitamins E and K are particularly susceptible to irradiation damage but not, surprisingly, carotenes. In practice, however, very little direct nutritional damage occurs as a result of food irradiation because of its limited applications.

4.1.3.4 Interesterification

The process of interesterification involves treatment of a fat or fat blend with a catalyst (e.g. sodium methoxide) at an elevated temperature so as to randomize the fatty acids among the

triacylglycerol molecules, as distinct from their natural stereo-specific distribution (Section 3.2.2). Interesterification is used to change physical properties of lipids (crystal structure, melting point) resulting in a changed food texture. The process is now being used more extensively as an alternative to catalytic hydrogenation because of concerns about potential adverse metabolic effects of over-consuming *trans*-unsaturated fatty acids (Sections 4.1.3.1 and 5.4.2). Some evidence has been presented that interesterified fats are metabolized differently from their natural counterparts. For example, work in the 1960s showed that butter that had been subjected to interesterification to randomize its fatty acids had little influence on the concentration of cholesterol in plasma when given in the diet, in contrast to the generally observed cholesterol-raising effect of natural butter. However, these and other similar observations have not been confirmed by more recent research.

4.1.3.5 Fractionation

All natural fats and oils are mixtures of triacylglycerols with different fatty acid distributions (Section 3.2.2) and it is possible to effect partial or almost complete separations (fractionation) with various physical methods. Thus fractions enriched in more highly saturated or unsaturated molecular species can be obtained, yielding products with desirable physical, textural and metabolic properties. For example, fractions of triacylglycerols enriched in medium-chain fatty acids (8:0, 10:0) can be obtained from coconut oil (Table 3.2). These find clinical use for patients with fat malabsorption (Section 5.1.4). A recent development has been the production of spreadable butters by selective removal of higher melting triacylglycerols. Reduced cholesterol foods can now be produced by differential extraction with, for example, carbon dioxide. (Alternatively, the same result has also been achieved by treatment with cholesterol degrading enzymes.)

4.1.3.6 Structured fats

'Structured fats' is the name now generally given to

semi-synthetic mixed-acid triacylglycerols containing both very long and very short chain fatty acids. It is proposed that they may find applications in reduced energy foods. There are two main principles here. First, the short-chain acids have an intrinsically lower energy value than the longer chain fatty acids and are, in any case, metabolized in the liver in such a way that they are not deposited in adipose tissue (Section 5.1.3). Second, the very long chain acids are less efficiently absorbed. The combination of reduced gross energy and poorer absorption reduces the overall metabolizable energy of the fat. This is a relatively new concept and there is as yet no convincing evidence that such products contribute effectively to weight-reducing diets in the long term. Another type of structured triacylglycerol, which contains palmitic acid at position *sn*-2 to mimic the structure of a major molecular species in human milk triacylglycerols, has been introduced commercially for use in infant feeds. Molecules with this structure are digested and absorbed more efficiently by the human infant (Section 5.1.1).

Other products that are aimed at reducing dietary energy, including sucrose polyesters, are also now approved in the USA for limited food use. These are not triacylglycerols, but have fat-like texture. They are not attacked by pancreatic lipase (Section 5.1.1) and so are not absorbed and contribute no energy value to the diet. Other applications of such products are discussed in Section 5.1.4. Much discussion has taken place about potentially harmful effects of ingesting such compounds. These may include significant reductions in the absorption of fat-soluble vitamins (which can be overcome by fortification) or gastrointestinal discomfort and fatty stools.

4.1.4 A few dietary lipids may be toxic

Much of the discussion in this chapter is concerned with the positive contributions made by dietary lipids, especially fatty acids, to nutrition and health. It is equally important to consider whether dietary lipids can also have adverse or toxic effects.