ADVANCED DAIRY CHEMISTRY

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ADVANCED DAIRY CHEMISTRY–2: LIPIDS

Second edition

Edited by

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PREFACE

Advanced Dairy Chemistry can be regarded as the second edition of *Developments in Dairy Chemistry*. The first volume in the series, on Milk Proteins, was published in 1992; this, the second volume, is devoted to Milk Lipids. Considerable progress has been made in several aspects of milk lipids during the past 11 years which is reflected in revised versions of seven of the eight chapters included in *Developments in Dairy Chemistry – 2*, most of them by the same authors. The theme of one chapter has been changed from physical properties and modification of milk fat to the crystallization of milk fat. Two new chapters have been added, i.e. chemistry and technology aspects of low-fat spreads and the significance of fat in consumer perception of food quality, which reflect the continuing consumer awareness of a healthy diet. Low-fat spreads have become increasingly significant during the past decade and are now the major type of spread in many countries. However, reducing the fat content of foods generally results in a concomitant decrease in the organoleptic quality of the food; consumer attitudes to reduced-fat dairy products are discussed in one of the new chapters.

Like its predecessor, the book is intended for lecturers, senior students and research personnel and each chapter is extensively referenced.

I would like to thank all the authors who contributed to this book and whose cooperation made my task as editor a pleasure.

P. F. Fox

PREFACE TO THE FIRST EDITION

Many of the desirable flavour and textural attributes of dairy products are due to their lipid components; consequently, milk lipids have, traditionally, been highly valued, in fact to the exclusion of other milk components in many cases. Today, milk is a major source of dietary lipids in western diets and although consumption of milk fat in the form of butter has declined in some countries, this has been offset in many cases by increasing consumption of cheese and fermented liquid dairy products.

This text on milk lipids is the second in a series entitled *Developments in Dairy Chemistry*, the first being devoted to milk proteins. The series is produced as a co-ordinated treatise on dairy chemistry with the objective of providing an authoritative reference source for lecturers, researchers and advanced students. The biosynthesis, chemical, physical and nutritional properties of milk lipids have been reviewed in eight chapters by world experts. However, space does not permit consideration of the more product-related aspects of milk lipids which play major functional roles in several dairy products, especially cheese, dehydrated milks and butter.

Arising from the mechanism of fatty acid biosynthesis and export of fat globules from the secretory cells, the fat of ruminant milks is particularly complex, containing members of all the major lipid classes and as many as 400 distinct fatty acids. The composition and structure of the lipids of bovine milk are described in Chapter 1, with limited comparison with non-bovine milk fats. Since the fatty acid profile of milk fat, especially in monogastric animals, may be modified by diet and other environmental factors, the biosynthesis of milk lipids is reviewed in Chapter 2 with the objective of indicating means by which the fatty acid profile, and hence the functional properties of the lipids, might be modified. Lipids in foods are normally present as an emulsion, stabilized by a layer of protein adsorbed at the oil-water interface. The fat in milk and cream exists as an oil-in-water emulsion with a unique stabilizing lipoprotein membrane, referred to as the milk fat globule membrane (MFGM). The inner layers of the MFGM are formed within the secretory cell and are relatively stable; however, the outer layers, which are acquired as the fat globule is exported through the apical membrane of the secretory cells, are unstable. Damage to the MFGM leads to chemical and physical instability of the fat phase in milk and hence the structure of the membrane has been the subject of considerable research, the results of which are reviewed in Chapter 3.

Lipids strongly influence, for good or evil, the flavour and texture of foods, especially high-fat products such as butter. The influence of various colloidal features of milk fat on the properties of milk and cream is considered in Chapter 4, while the crystallization of milk fat and how this may be controlled, modified and measured are reviewed in Chapter 5. Unfortunately, lipids are subject to chemical and enzymatic alterations which can cause flavour defects referred to as oxidative and hydrolytic rancidity, respectively. The storage stability of high-fat foods, especially midly flavoured foods like milk, cream and butter, is strongly influenced by these changes which have been reviewed in Chapters 6 and 7.

Dietary lipids play many diverse nutritional roles, some of which are essential. However, dietary lipids, especially saturated lipids of animal origin, have been the subject of much controversy in recent years, particularly in regard to their possible role in atherosclerosis. Various aspects of the nutritional significance of lipids are discussed in Chapter 8.

Finally, I wish to thank sincerely the 14 authors who have contributed to this text and whose co-operation has made my task as editor a pleasure.

P. F. Fox

CONTENTS

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COMPOSITION AND STRUCTURE OF MILK LIPIDS

W. W. CHRISTIE

1.1 INTRODUCTION

Lipids in milk provide a major source of energy and essential structural components for the cell membranes of the newborn in all mammalian species. They confer distinctive properties on dairy foods that affect processing. In consequence, the composition, structure and chemistry of milk lipids have probably been studied more intensively than those from any other natural source. Milk lipids from the cow have received most attention because of their commercial importance, but human milk lipids have also been investigated in great detail, and those from many other species have been sampled for comparative biochemical purposes. The content and composition of lipids from milks from different species vary with such factors as diet, stage of lactation, number of lactations, breed and season, and these data are not always recorded by authors. As far as is possible, this review is concerned with milk from animals on an 'average' diet for the species, and in mid-lactation; other factors are discussed elsewhere in this volume. Published results can sometimes be misleading because of errors in sampling, sample handling or analytical methodology and the author has tended to ignore data that appear doubtful.

The lipid compositions of milks in general have been reviewed many times (Morrison, 1970; Patton and Jensen, 1975; Jensen and Clark, 1988; Jensen *et al.*, 1990, 1991) and reviews dealing with lipids of ruminant (Jensen, 1973; Christie, 1978) and human (Jensen *et al.*, 1978, 1980; Jensen, 1988) milk, in particular, have appeared. The reviews by Morrison (1970) and Patton and Jensen (1975) are especially comprehensive. Although this chapter is intended to be a complete review of the subject within the space available, there has been

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some concentration on more recent publications and the reader is referred to the earlier reviews for a historical perspective and for the older literature. In recent years, the pace of new work on milk composition appears to have slackened.

Most authors have tended to stress the complexity of milk lipids, but this is an aspect which can be exaggerated. A very high proportion (about 98%) of the lipids consist of a single lipid class, triacylglycerols, with all other components being present at relatively low concentrations, although the latter may have appreciable nutritional or technological importance. Although many more fatty acids have been characterized as present in milk fat than in any other tissue, this is in part because no other lipid material has been investigated with such intensity. On the other hand, fatty acids with a wider range of chain lengths tend to be found in esterified form in milk fat than in other tissues of the same species.

1.2 Content and physical form of fat in milk

Milk fat is secreted in the form of globules surrounded initially by a membrane, the milk fat globule membrane, which maintains the integrity of the globules and renders them compatible with their aqueous environment (Mulder and Walstra, 1974; Patton and Jensen, 1975; Keenan and Dylewski, 1985; Keenan *et al.*, 1988). A mild method for preparation of the globules, and thence their membranes, has recently been described (Patton and Huston, 1986). The fat globules themselves consist almost entirely of triacylglycerols, whereas the membranes contain most of the complex lipids. After secretion, parts of the membrane detach and are found, together with their phospholipid constituents, with fragments of other mammary epithelial cell membranes in the skim milk phase. In bovine milk, the skim milk phospholipids are identical in composition and structure to those of the milk fat globule membrane, confirming their common origin (Patton and Keenan, 1971) (Section 1.3.2). The same is likely to be true for other species, assuming similar mechanisms for milk fat secretion. In human milk, for example, most of the membraneous material (80%), and thence the phospholipids and cholesterol, are in the milk fat globule membrane (Huston and Patton, 1986). The fat globules in bovine milk can vary somewhat in their size distribution but average 2–4 μm in diameter (Mulder and Walstra, 1974), and the same has been found to be true for the human and for the few other species that have been examined (Ruegg and Blanc, 1981). In fact, there are populations of milk fat globules of different sizes, the compositions of which differ in a manner that appears to be related to fluidity (Timmen and Patton, 1988).

The ratio of fat to water in milk from different species can vary markedly, and is highly dependent on the stage of lactation. Some typical average values are listed in Table 1.1. Data for many more species are available in the review by Jenness and Sloan (1970). The content of fat in bovine milk is dependent on the breed and is highest in those from the Channel Islands, but 37 g l^{-1} is a reasonable average value. The milks of other ruminants have a comparable or slightly higher content of fat, and the same is true of those of the human, other primates, pig and guinea-pig. Higher values have been recorded for some rodents and rabbits (100–200 g l^{-1}), but the highest values of all (300–520 g l^{-1}) are for marine mammals, especially those from colder waters such as seals and whales. Presumably, this is an evolutionary adaptation which ensures that the young of these species can rapidly build up their stores of fat for energy and insulation to protect against the harsh environment. It has been pointed out that differences in the calorific values of milks from various species are due almost entirely to differences in the fat content (Jenness and Sloan, 1970). The young of each species can vary appreciably in their dependence on milk as a source of nutrients, for example from the human which is totally dependent to the hare which appears to have a very limited requirement. Yet, no correlation between stage of maturity of the young and milk fat content has been observed (Jenness and Sloan, 1970).

1.3 Lipid class composition of milks

1.3.1 Main lipid classes

In the milks of all species studied to date, triacylglycerols are by far the major lipid class, always accounting for 97–98% of the total lipids (Table 1.2). The triacylglycerols are almost invariably accompanied by small amounts of di- and monoacylglycerols, free cholesterol and cholesterol esters (commonly in the ratio 10 : 1), unesterified (free) fatty acids and phospholipids (Section 1.3.2). In addition to these, a number of minor simple lipids (Section 1.3.3) and glycolipids (Section 1.3.4) have been found. Comparatively high proportions of partial glycerides and unesterified fatty acids have been recorded in some published papers, but this usually indicates that faulty handling of the milk has led to some lipolysis. For example, the data for rat milk recorded in Table 1.2 must be regarded with some suspicion. In an analysis in which the lipids of bovine milk were isolated with particular care, it was demonstrated that the small proportion of diacylglycerols present were mainly of the *sn*-1, 2-configuration and were therefore probably intermediates in the biosynthesis of triacylglycerols rather than degradation products (Lok, 1979). This would not be true of milk in which some lipolysis had occurred. Although relatively few species have been examined to date, the compositional data are sufficiently similar to suggest comparable mechanisms of synthesis and secretion. Phospholipids were reported to comprise 15·3% of the total lipids of mink milk, a figure 10-fold higher than expected,

TABLE 1.1
Fat content of milks from various species

Species	*Fat content* ($g\ l^{-1}$)	*Reference*	*Species*	*Fat content* ($g\ l^{-1}$)	*Reference*
Cow	33–47	Christie (1978)	Marmoset	77	Turton *et al.* (1978)
Buffalo	47	Jenness and Sloan (1970)	Rabbit	183	Jenness and Sloan (1970)
Sheep	40–99	Christie (1978)	Guinea-pig	39	Jenness and Sloan (1970)
Goat	41–45	Christie (1978)	Snowshoe hare	71	Baker *et al.* (1970*a*)
Musk-ox	109	Baker *et al.* (1970*b*)	Mink	134	Kinsella (1971)
Dall-sheep	32–206	Cook *et al.* (1970)	Chinchilla	117	Volcani *et al.* (1973)
Moose	39–105	Jenness and Sloan (1970)	Rat	103	Jenness and Sloan (1970)
Antelope sp.	93	Dill *et al.* (1972)	Red kangaroo	9–119	Griffiths *et al.* (1972)
Elephant	85–190	Peters *et al.* (1972)	Dolphin	62–330	Ackman *et al.* (1971)
Human	38	Jensen (1988)	Manatee	55–215	Bachman and Irvine (1979)
Horse	19	Jenness and Sloan (1970)	Pygmy sperm whale	153	Jenness and Odell (1978)
Monkeys	22–85	Smith and Hardjo (1970)	Harp seal	502–532	Cook and Baker (1969)
Lemurs	8–33	Buss *et al.* (1976)	Bear (four species)	108–331	Jenness *et al.* (1972)
Pig	68	Mellies *et al.* (1978)			