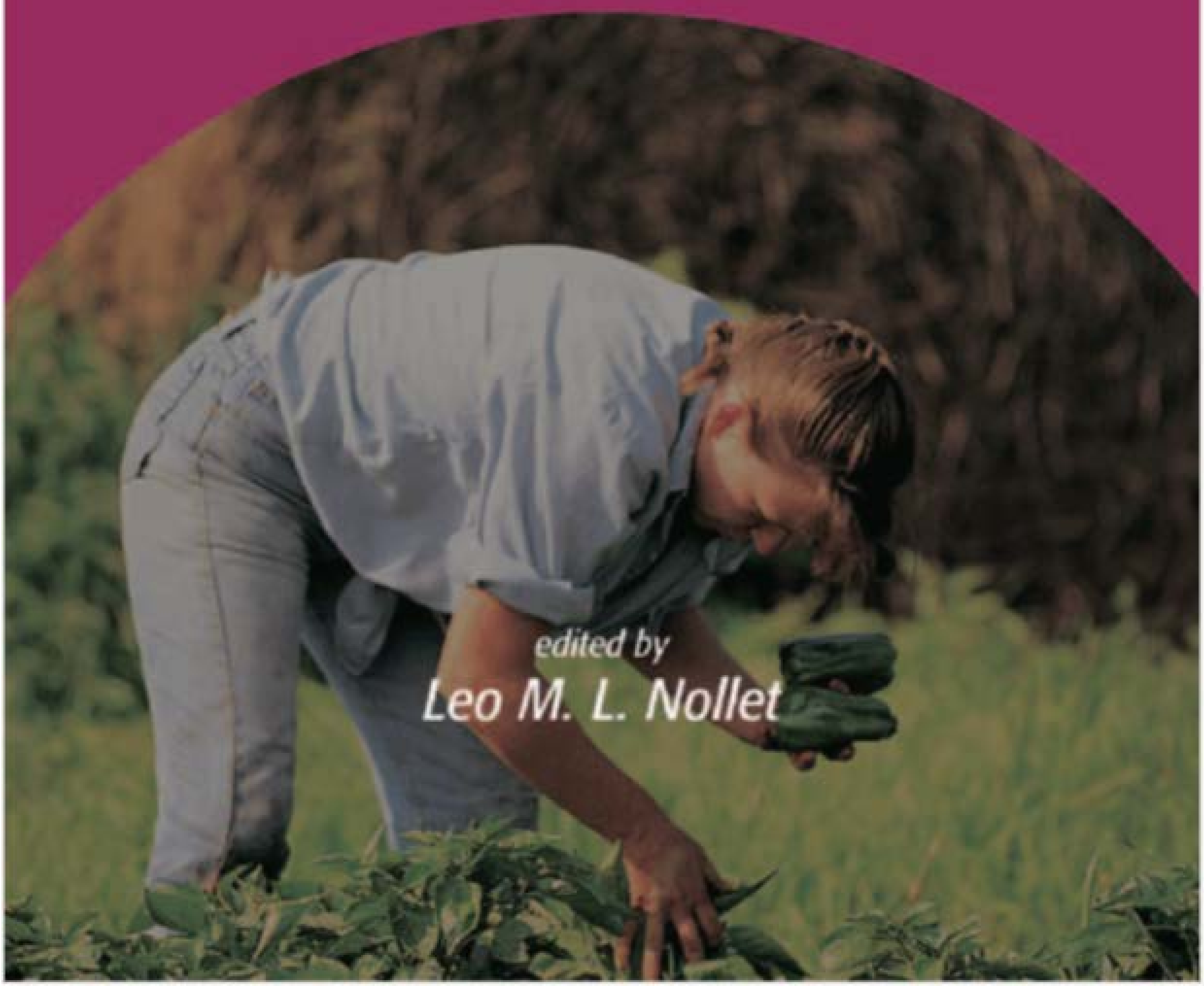
Volume 1 thru 3

Handbook of Food Analysis

Second Edition, Revised and Expanded

Physical Characterization and Nutrient Analysis



edited by
Leo M. L. Nollet

Volume 1

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Fatty Acids

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I. INTRODUCTION

Lipids consist of a broad group of compounds that are generally soluble in organic solvents but only sparingly soluble in water. They are major constituents of adipose tissue, and together with proteins and carbohydrates, they constitute the principal structural components of all living cells. Glycerol esters of fatty acids, which account for about 98% of the lipids in our foods and over 90% of the fat in the body, have been traditionally called fats and oils, based solely on whether the material is solid or liquid at room temperature (1–4).

Food lipids are either consumed in the form of isolated fats or as constituents of basic foods. Worldwide, food lipids' intake varies considerably from some countries to others. In general, the consumption of food lipids increases with increasing per capita income. Thus, in developing countries food lipids' intake is, and has been for many generations, 10 to 20% of the energy intake, while in developed countries dietary food lipids' intake ranges from 35 to 45% of the total energy intake (5–8).

Fatty acids are key components of lipids. They are the aliphatic monocarboxylic acids that can be liberated by hydrolysis from naturally occurring fats. Although more than 1000 acids have been identified, the number occurring frequently in most common lipids is much fewer than this and most food analysts will probably encounter not more than a few tens of different acids.

II. STRUCTURE, OCCURRENCE, AND PROPERTIES

A. Chemical Structure

Because fatty acids are made biosynthetically from a limited number of substrates by a limited number of pathways certain structural features recur frequently. Thus, most fatty acids are straight-chain compounds with an even number of carbon atoms in each molecule. This chain may have double bonds, which has commonly Z (*cis*) configuration, and, in the case of several double bonds, these are usually separated by one methylene group. All these general conclusions have exceptions and branched, *trans*, and conjugated fatty acids may be found to some extent in most foods. In addition, substituted acids are rare, but natural hydroxy, epoxy, and oxo acids have been described.

Fatty acids are classified according to their chain length, the existence and the number of double bonds, and the presence of branches, cycles, or other groups. There is not a generally accepted division of fatty acids according to chain length, although short-chain fatty acids are usually considered having from 4 to 10 carbon atoms; medium-chain fatty acids, 12 or 14 carbon atoms; and long chain fatty acids, 16 or more carbon atoms.

The following sections will give an overview of the most significant characteristics of the different types of fatty acids that can be found in foods. It is out of the scope of this chapter to present an exhaustive review of the different classes of fatty acids. It can be found elsewhere (see, for example, Ref. 8–14).

1. Unbranched Saturated Fatty Acids

Unbranched, straight-chain molecules with an even number of carbon atoms are dominant among the saturated fatty acids (Table 1). These acids are present in a high content in animal fats and in some vegetable fats such as palm and coconut oils. Medium- and short-chain fatty acids are triacylglycerol constituents in the fat and oil of milk, coconut, and palmseed. Fatty acids with odd numbers of carbon atoms are present in food only in traces (Table 2).

2. Unbranched Unsaturated Fatty Acids

The unsaturated fatty acids, which are major constituents of lipids, contain one or more allyl groups in their chains. The naturally occurring unsaturated fatty acids in fats are almost exclusively in the *cis*-form, although *trans*-acids are abundant in ruminant milk fats and in the catalytically hydrogenated fats (17,18). In ruminant milk fats, these *trans* bonds, which may constitute about 10% of total unsaturated fatty acids, result from microbial action in the rumen where polyunsaturated fatty acids of the feed are partially hydrogenated.

In the monounsaturated fatty acids, one double bond is present in the aliphatic chain (Table 3). Its position is determined from the carboxyl end (systematic and Δ numbering) or from the methyl end (*n* or *ω* numbering). Thus, for example, palmitoleic acid or 9(*Z*)-hexadecenoic acid, according to the systematic name, is represented by the numeric symbol 16:1 Δ9 or 16:1 *n*-7. Unless otherwise indicated, the double bond has *cis* configuration.

The structural relationship that exists among unsaturated fatty acids derived from a common biosynthetic pathway is better understood when fatty acids with the same methyl ends are combined into groups. This is because organisms lengthen fatty acid chains by adding carbons at the acid end of the chain. Using the *n* or *ω* system, four family groups of unsaturated fatty acids can be distinguished: *n*-3, *n*-6, *n*-7, and *n*-9 (Table 4). In plants the most widespread methylene-interrupted polyene fatty acids are linoleic acid (18:2 Δ9,12) and α-linolenic acid (18:3 Δ9,12,15), which are the origin of the *n*-6 and *n*-3 families, respectively. The presence of these two fatty acids in foods is of great importance since they cannot be synthesized de novo by human and animal tissues and should thereby be provided with the diet. On the other hand, polyenes of the *n*-7 and *n*-9 families, derived from palmitoleic (16:1 Δ9) and oleic (18:1 Δ9) acids, respectively, are rarely encountered in animal food, except when animals are deficient in essential fatty acids (presence of 20:3 Δ5,8,11).

3. Other Fatty Acids

In plant and animal food, less common fatty acids may be present. Thus, short-chain, odd-numbered, and branched-chain fatty acids are present in ruminant milks and their derivatives. The most common type of branching is a single methyl group at the positions *n*-2 (*iso* acids) or *n*-3 (*anteiso* acids). Acids with more than one methyl group generally have them attached to even carbon atoms. Hydroxylated fatty acids can be found principally in plant lipids. Other oxygenated fatty acids, epoxy and keto fatty acids, are usual components of several seed oils. Conjugated, allenic, and acetylenic fatty acids do not occur to any significant extent in food lipids. Cyclic fatty acids are usual components of several seed oils. Thus, the cyclopropene fatty acids, malvalic and sterculic, are found in noticeable amounts in baobab and kapok seed oils and in trace amounts in cottonseed oil. They are frequently accompanied by cyclopropane fatty acids. Other oxygenated and cyclic acids are formed in certain amounts when polyunsaturated fatty acids are oxidized or heated at relatively high temperature (19). More detailed information regarding these unusual dietary fatty acids can be obtained from specialized books (9,10,12).

B. Occurrence

In general, the following outline of fatty acid composition can be given:

- Depot fats of higher land animals consist mainly of palmitic, oleic, and stearic acids and are high in saturated fatty acids (Table 5). The total content of acids with 18 carbon atoms is about 70%. Nevertheless, the kind of feed consumed by the animals may greatly influence the composition of the depot fats.
- Ruminant milk fats are characterized by a much greater variety of component fatty acids (Table 5). Many fatty acids have been identified in different studies, and about 15 of the fatty acids occur in quantities of 1% or more of the total fatty acids. Short saturated acids with 4 to 10 carbon atoms are present in relatively large amounts. The major fatty acids are palmitic,

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