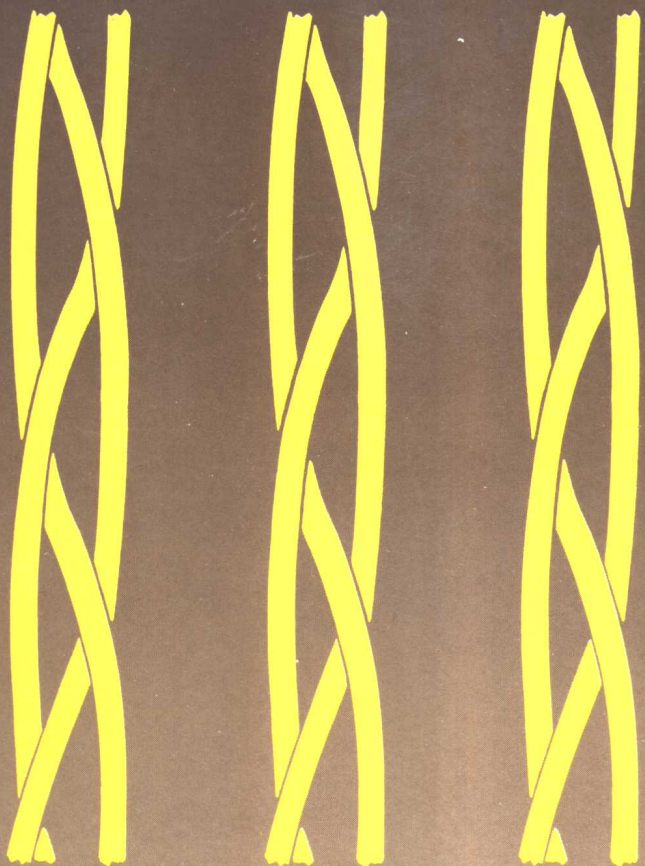
Food biochemistry & nutritional value



David S. Robinson

Food – biochemistry and nutritional value

David S. Robinson
Procter Professor of Food Science
Procter Department of Food Science
The University of Leeds

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Preface

This text has grown out of a need by an internationally broad based industry and its graduate employees to understand the action of enzymes in foods and the variable nature and nutritive value of food ingredients. While many long, but detailed specialist texts and review articles are now available on starch, sugars, lipids, oxidative enzymes, vitamins, etc., I have attempted to condense and distil the essential information into a critical and comprehensive text devoted to the biochemistry and nutritional value of food.

A considerable proportion of food ingredients are normally available at sources distant from the consuming populations. Such foods are harvested, moved and stored wherein the quality may deteriorate due to indigenous enzyme action and infestation. The cellular control of enzymatic activity is diminished in post-harvest foods so that substrates become more readily available for hydrolysis and oxidation. The increasing production of chilled fresh foods is increasing the awareness of the ability of enzymes to discolour and taint. While many of the effects of indigenous enzymes are negative, for example the decomposition of starch catalysed by α- and β-amylases and the production of off-flavours by lipases, enzymes may also be used as processing aids. For citrus fruits, microbial nomilin acetyl lyase and limonate dehydrogenase may be used to remove bitter compounds. For fermented foods various glycolytic pathways used by microorganisms are well known, but now pre-treatment with enzymes may be used to influence the availability of substrates for subsequent microbial growth. In the future the food biochemist may be able to define desirable pathways for the production of enhanced flavour and aroma in fresh foods, chilled foods and fermented foods.

There is an increased awareness by the consumer and government that the nutritive value and composition of the diet is important for health and well-being. The relationship of diet to health is an expanding, fascinating and controversial field. The food biochemist will be able to justify to the manufacturer and consumer the optimis-

ation of the nutrient content of foods. For example, it is now known that polyunsaturated fatty acids are required for the biosynthesis of prostaglandins, leucotrienes and thromboxanes. Linoleic and α-linolenic acids are essential dietary fatty acids, whereas the higher and more unsaturated fatty acids may all be essential metabolites. Likewise retinoic acids, which are also essential metabolites, are now known to control cell growth and cell division. The consumption of sucrose is falling and there is now dietary advice for total fat intake, cholesterol and common salt. Regulatory agencies are modifying their recommendations for the daily intake of protein, fats, mineral and vitamins by population groups and these aggregated pressures are leading the food manufacturer to re-examine his ingredients and re-evaluate his processes.

Conversely there are many misconceptions of the needs for so-called 'health foods'. However, the composition and mode of action of even dietary fibre, which is a heterogeneous mixture of polysaccharides not hydrolysed by human enzymes, is not fully understood. Furthermore, the presence of proteinase inhibitors and toxic haemagglutinins in most fresh plant foods is generally unrecognised. Digestive intolerances of substances like lactose and metabolic intolerance of galactose, as present in hydrolysed whey, are now recognisable diseases caused by deficiencies of human enzymes.

I have sought to produce a text which provides not only knowledge of the chemical structures of the main food components, but also a greater insight into the ways in which the action of enzymes change the composition, texture, nutritive values and acceptability of food. The text is suitable for B.Sc. Honours undergraduate food scientists, Mastership post-graduate taught course students who have first degrees in biological sciences, and as a reference text for research students, scientists carrying out research into the chemistry and biochemistry of food and industrialists. However, I have tried not to clutter the text with references but aimed to produce a readable but also authoritative presentation. Therefore references are given for factual data, and guidance is provided to recent review articles at the end of each chapter.

The book anticipates a basic knowledge of biochemistry. The text is wide ranging and sectionalised for carbohydrates, proteins, lipids, minor constituents and the post-harvest action of enzymes. Data for the nutritive value of foods is given where it is considered to be reliable. In the text there is no delineation into either food commodities or foods of plant and animal origin. Appendices are provided for quick reference and as an *aide-mémoire* to the well understood primary metabolic biochemical pathways; hence it has been possible to restrict the bulk of the text to the biochemistry and nutritive value of foods.

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Abbreviations and Glossary of Terms

ABBREVIATIONS

Å: 1 nm = 10 ångström units
A: antigen
AB: antibody
ADP: adenosine diphosphate
ADP: glucose: adenosyl diphosphoglucose
AMP: adenosine monophosphate
ATP: adenosine triphosphate
ATPase: adenosine triphosphatase
cAMP: cyclic AMP
DE: dextrose equivalent
DGDG: diglycosyl diglyceride
DiHETE: dihydroxyeicosatetranoic acid
DHSS: Department of Health and Social Security
DMA: dimethylamine
E_0': standard oxidation reduction potential at pH 7.0
FAD: flavin adenine dinucleotide (oxidised form)
$FADH_2$: flavin adenine dinucleotide (reduced form)
FAO: Food and Agricultural Organisation
Fru*f*: fructofuranose
F-1-P: fructose-1-phosphate
F-6-P: fructose-6-phosphate
ΔG^{01}: standard free energy change at pH 7.0
Gal*p*: galactopyranose
Gal*p*A: galacturonic acid in the pyranose form
gc/ms: gas chromatography–mass spectrometry
GDP: guanosine diphosphate
Glc*p*: glucopyranose
G-6-P: glucose-6-phosphate

GMP: guanosine monophosphate
GRAS: generally recommended as safe
GSH: reduced glutathione
GSSG: oxidised glutathione
HPETE: hydroperoxyeicosatetraenoic acid
GTP: guanosine triphosphate
HPLC: high performance liquid chromatography
Ile: isoleucine
IMP: inosine monophosphate
IUB: International Union of Biochemistry
IUPAC: International Union of Pure and Applied Chemistry
JECFA: Joint Expert FAO/WHO Committee on Food Additives
K_m: Michaelis constant
MAFF: Ministry of Agriculture, Fisheries and Foods
Mb: myoglobin
MbO_2: oxomyoglobin
MetMb: metmyoglobin
MGDG: monoglycosyl diglyceride
NAD^+: nicotinamide adenine dinucleotide (oxidised form)
NADH: nicotinamide adenine dinucleotide (reduced form)
$NADP^+$: nicotinamide adenine dinucleotide phosphate (oxidised form)
NADP: nicotinamide adenine dinucleotide phosphate (reduced form)
NAS: National Academy of Science
NOMb: nitric oxide myoglobin
NOMetMb: nitric oxide metmyoglobin
NRC: National Research Council
Pi: inorganic orthophosphate
PPi: inorganic pyrophosphate
ppm: parts per million
PQQ coenzyme: pyrroloquinoline coenzyme
RDA: recommended daily amount
Rha*p*: rhamnopyranose
R-6-P: ribose-6-phosphate
TCA: tricarboxylic acid cycle
TMA: trimethylamine
TMAO: trimethylaminoxolate
TPP: thiamin pyrophosphate
UDP: uridine diphosphate
UDP-galactose: uridine diphosphate galactose
UDP-glucose: uridine diphosphate glucose
UMP: uridine monophosphate
UTP: uridine triphosphate
WHO: World Health Organisation
Xly*p*: xylopyranose

GLOSSARY OF TERMS

acalins: cottonseed proteins.
actin: a globular protein (2S) which forms long linear polymers (F-actin). The globular units of F-actin interact with the myosin heads during the contraction of the muscle sarcomere.
amino acid score: ratio of the amount of amino acid in a food to that present in a reference protein.
annato: a yellow carotenoid pigment obtained from the seed pods of *Bixa orellana* used for the colouring of butter, margarine and cheese.
anomers: diastereomers differing in configuration at C-1 of the sugar pyranose and furanose rings.

carbonyl proteinase: contains carboxyl groups of Asp in the enzyme active site.
caseins: a group of phosphoproteins which interact to form suspended micelles in milk. The caseins are precipitated at acid pH values and by the action of chymosin.
cathepsins: proteinases which are contained within lysosomes.
chylomicrons: spherical droplets of emulsion with diameters 0.03 μm to 0.06 μm.
Coberine: a palm oil product that has been interesterified to produce a solid fat with melting characteristics which resemble cocoa butter.
cocoa butter: obtained from *Theobroma cacao* as the lipid with a sharp melting point used in the manufacture of chocolate.
colipase: a protein of approximately eighty-five amino acid residues which aids the action of pancreatic lipase by absorption to emulsified oil droplets.
cyclic AMP: adenosine 3′,5′-cyclic monophosphate.
cysteine proteinases: contain a cysteine residue in the enzyme active site.

desmosine: a natural cross-link formed by the condensation of lysyl aldehydes and lysyl ε-amino groups in elastin.
dietary essential: a substance which must be present in the diet as it cannot be synthesised by living tissues.

emulsifying agents: substances that aid the suspension of either oil drops in water or water droplets in oil.
endo-enzymes: catalyse the cleavage of covalent bonds linking the residues in the central parts of polymer chains.
erucic acid: a fatty acid containing twenty-two carbon atoms with one double bond at C-13 found in some *Brassica spp*.
essential metabolite: a substance which is synthesised by living tissues and is an essential component of metabolic processes, e.g. arachidonic acid (C20 : 4).

exo-enzymes: catalyse the cleavage of covalent bonds linking the terminal residues at the ends of polymer chains.

galactosamine: 2-aminogalactose.
gelatinisation: formation of a jelly-like semi-solid material imbibing substantial amounts of water, e.g. during the swelling of starch grains.
gliadins: wheat prolamins.
glucosamine: 2-aminoglucose.
glucosinolate: thioglucoside.
glutenins: the high molecular weight prolamine polymers which are insoluble in alcohol solvents. Glutenins are cross-linked by disulphide bonds.
glycolipids: glycosyldiacylglycerols.
goitrin: 5-vinyloxazolidine-2-thione is formed from some thioglucosides present in *Brassica spp.* and may cause goitre.

hairy zones: regions of linear polymers with a number of short side chains.
hordeins: barley prolamins.

Illipe butter: naturally occurring fat obtained from *Shorea stenoptera* and resembles cocoa butter with a relatively sharp melting point.
isodesmosine: an isomeric form of desmosine.

lectins: (haemagglutinins) proteins able to cause the agglutination of red blood cells, mainly found in plant foods.
legumins: the 11S storage protein of plant seeds.
limit dextrin: the branched polysaccharide residue remaining after hydrolysis of starch or glycogen catalysed by α- and β-amylases.
lingual lipases: lipases secreted by glands at the base of the tongue.
linoleic acid: an eighteen-carbon atom n : 6 fatty acid which contains two double bonds that are methylene interrupted by one–CH_2 group.
α-linolenic acid: an eighteen-carbon atom n : 3 fatty acid which contains three double bonds that are methylene interrupted.
γ-linolenic acid: an eighteen-carbon atom n : 6 fatty acid which contains three double bonds that are methylene interrupted.
lysophospholipid: the monoacyl derivatives of sn-glycerol-3-phosphate.

menaquinones: K-vitamers synthesised by microorganisms. Prenyl derivatives of naphthaquinones.
methylene interrupted double bonds: double bonds which are not conjugated and are separated by one–CH_2 group.
monenoic acids: fatty acids which contain only one double bond.
mycoprotein: a fibrous protein food derived from *Fusarium graminearum* (Schwabe).
myofibrillar sarcomere: the basic structural unit of muscle containing

the linear actin and myosin filaments.
myosin: the main multimeric linear muscle protein containing globular heads present in the muscle sarcomere. Complexes with the protein actin to form actomyosin as the main structural element of muscle.

ovoinhibitors: inhibitors of enzymes found in the eggs of avian species.

phytic acids: phosphate esters of myoinositol.
phytoquinones: K-vitamers found in plants. Phytyl derivatives of naphthaquinones.
polymorphic: a substance which crystallises in two or more distinct forms, each of which have a different physical appearance and different melting points.
polyols: sugar alcohols such as sorbitol, mannitol, inositol, and glycerol.
polyunsaturated fatty acids: fatty acids which contain more than one double bond in the alkane chain.
prolamins: proteins which are soluble in 70 per cent (v/v) ethanol generally obtained from seeds.

resistant starch: retrograded starch which is resistant to enzymatic hydrolysis.
retinoids: chemical derivatives of vitamin A, retinal or retinoic acids.
retrogradation: re-association of amylose polymers in a starch gel. Causes loss of gel structure and solubility to form a precipitate.
rigor mortis: a stiffening of muscle which occurs after death due to the increased association of the actin and myosin filaments.

secalins: rye prolamins.
serine proteinases: contain a serine residue in the enzyme active site.
sialic acid: N-acetylneuraminic acid, an aldol addition product formed from mannosamine and pyruvic acid.
smooth zones: regions of linear polymers without side chains.
stabiliser: substances which stabilise suspensions of colloidal particles and emulsions of oil-in-aqueous phases often by a thickening of the aqueous phase.
starch blockers: substances which inhibit the hydrolysis of starch by digestive enzymes, generally inhibitors of α-amylase.
syneresis: contraction of a gel due to the exudation of fluid and association of the polymer material from within a gel.

tropomyosin: a cable-like protein which lies within the grooves or between coiled linear actin polymers.

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vicilins: the 7S storage protein of plant seeds.
viscoelastic: a material which can flow like a liquid but recover its shape like a solid.
vitamers: different chemical derivatives of similar chemical composition that can substitute for a given vitamin.

water activity, a_w: the ratio between the vapour pressure of water in a solution or food and that of pure water at the same temperature.
whey: the liquid filtrate remaining after the removal of coagulated caseins during the manufacture of cheese.

zymogen: the inactive precursor of enzymes. Generally contains an extension peptide which blocks the active site of the enzyme.

Standard single letter notations and abbreviations for amino acids

A	Ala	Alanine
C	Cys	Cysteine
D	Asp	Aspartic acid
E	Glu	Glutamic acid
F	Phe	Phenylalanine
G	Gly	Glycine
H	His	Histidine
I	Ile	Isoleucine
K	Lys	Lysine
L	Leu	Leucine
M	Met	Methionine
N	Asn	Asparagine
P	Pro	Proline
Q	Gln	Glutamine
R	Arg	Arginine
S	Ser	Serine
T	Thr	Threonine
V	Val	Valine
W	Trp	Tryptophan
Y	Tyr	Tyrosine
Z	Glx	Glutamate or Glutamine
X		Undetermined

Contents

Part I
Food carbohydrates

INTRODUCTION

Historically the term 'carbohydrate' has been used to classify those substances with the empirical formula $C_n(H_2O)_n$, as the hydrates of carbon. This simple definition has been extended so that the class generally includes sugar alcohols, amino sugars, anhydro sugars and deoxy sugars. There are a substantial number of introductory texts in biochemistry, organic chemistry or food science, which list fully the very large number of structural isomers for carbohydrates that theoretically can be proposed and synthesised. However, the synthesis, properties and the chemical reactions of unusual monosaccharides are not of concern to the food scientist, the food industry, the public analyst or the consumer.

The number of naturally occurring free monosaccharides in foods is few, and is limited mainly to D-glucose, D-fructose and L-ascorbic acid. Only small amounts of D-galactose, sugar alcohols and myoinositol have been detected in foods. However, the sugar alcohols xylitol, sorbitol and mannitol, which strictly are not carbohydrates, are of increasing interest to the food scientist because of their use as humectants in intermediate moisture foods. Seeds and root crops contain a restricted number of di- and trisaccharides. The term 'oligosaccharide' is used for polymers containing less than ten monosaccharide units; polysaccharides are higher polymers and are complex gums, seaweed and bacterial mucilages, plant seed arabinans, mannans, starch, cellulose, pectins and animal glycogen. Glycoproteins which occur in plant cells and in animal foods such as milk and egg contain a small number of monosaccharide units including galactose, mannose, glucosamine and galactosomine as short oligosaccharide units. The best-known disaccharide is sucrose obtained from sugar-beet (*Beta vulgaris, var. rapa*), or from sugar-cane (*Saccharum officinarum*). The disaccharide lactose, found in animal milk, is synthesised in the mammary gland. Small amounts of maltose (the repeating disaccharide unit of

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