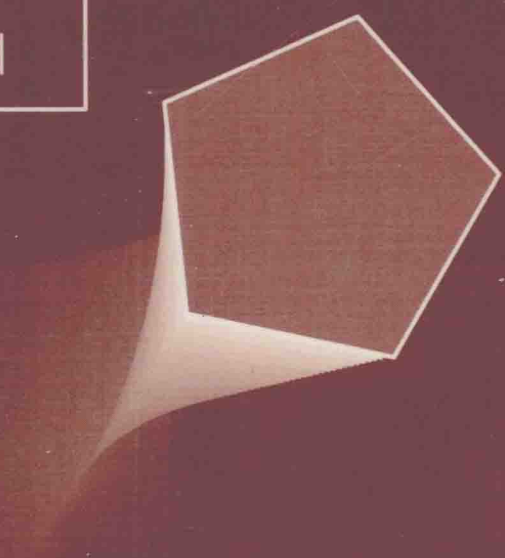
Free Radicals and Food Additives

Edited by
Okezie I. Aruoma
and
Barry Halliwell



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Preface

Everyone consumes food and drink. Food consumption is determined by the economic status of the consumer, life-style and the availability of foodstuffs. Food and drinks are composed of chemicals, both natural and synthetic. Most of the additives discussed in this book are those not normally present in unprocessed food material. The use of a variety of additives during the production of food and drinks by manufacturers is aimed at generating products that look good, maintain their nutritional quality, taste good and last for a long time on the shelves. The interaction of synthetic food additives with natural food components, whilst being important for the integrity of food, may have different implications *in vivo*. There is increasing public awareness of what the food and drink consumed actually contain.

The present volume is not a comprehensive text on food additives. Our purpose here is to consider the role of food additives in relation to a rapidly growing area of biomedical research: free-radical biochemistry. Free-radical reactions have been the concern of polymer chemists and food scientists for many years. In the past two decades, interest has grown in the biomedical importance of free radicals. It is difficult these days to open a medical journal without seeing some paper on the role of 'reactive oxygen species' or 'free radicals' in human diseases including, for example, cancer, atherosclerosis, rheumatoid arthritis, inflammatory bowel disease and malaria. The book begins with an examination of consumers' perception of food safety. Worldwide views on food safety are not readily available. This point becomes apparent when one considers that the attitude towards food and drinks is largely determined by the second sentence of this preface. Nevertheless, the first chapter serves as a representative illustration. This is followed by the core chapters of the book. A historical account of free radical chemistry (Chapter 2) is followed by a consideration of the biological toxicity of reactive oxygen species (Chapter 3).

The process of lipid peroxidation is of concern to biochemists and food chemists. There is a growing interest in the problems of lipid peroxidation as they relate to food deterioration and health status. The mechanism of lipid peroxidation and the biological aspects of the reaction are considered (Chapter 4).

Evidence linking a particular food or food constituent with a particular disease is often circumstantial and great care must be exercised in assessing its significance. However, this does not rule out the possibility that diet by itself is one of the factors involved in the multifactorial nature of a disease process. Dietary fat is believed to play an important role in heart disease. Chapter 5 on the potential health aspects of lipid oxidation products in food considers coronary heart disease (CHD). There is a wealth of information in the literature on CHD which is important because of its epidemic nature in most countries. Coronary heart disease is closely associated with advanced atherosclerosis which reflects several deteriorative phenomena leading to the narrowing of coronary arteries, and often causing thrombosis and coronary infarction.

Within the European Economic Community (EEC), France, West Germany, Italy, The Netherlands and the UK are the countries with the largest food-processing industries. Consumers are increasingly buying foodstuffs made possible by additives. In one of a series of comprehensive studies by Frost and Sullivan, it was suggested that the potential market for food chemicals will continue to rise gradually. For example, a perusal of Fig. 1 reveals the projected expenditure on food additives by EEC based countries. The list includes antioxidants. The use of antioxidants to retard the oxidative decomposition of lipid containing food is particularly important because, on the one hand, the end products of lipid oxidation are toxic (Chapter 5), and on the other hand, rancidity or 'off-flavour' in food is minimized. This then allows maintenance of nutritional quality and an increase in the shelf-life of a variety of lipid containing foods. Hence in Chapter 6, the use of antioxidants in foods is discussed.

The migration of trace amounts of additives, monomers and solvents from polymer barriers used in food and beverage packaging can adversely affect product quality. The recognition that the migration of residual monomers from plastics into food might represent a potential hazard is comparatively recent. For example, vinyl chloride, which was subsequently found to be a human carcinogen, was among the first monomers found to be capable of migrating into foods that had been packaged with polyvinyl chloride (PVC). Others include vinylidene chloride, styrene and acrylonitrile. The potential toxicity of substances such as the unpolymerized monomers antioxidants and/or stabilizers used to produce plastics that are in contact with food, must be exhaustively tested. It should be pointed out at this stage that the antioxidants used to stabilize plastics are not always the same as those added directly to food (Chapter 6). However, there is a strong similarity in the mechanism of action of antioxidants (Chapters 4 and 7).

The road ahead leads towards the development of polymer additives (antioxidants or stabilizers, plasticizers, lubricants, antistatic agents, for example) which are chemically bound to the polymer substrate and reduce the extent to which they are leached out. In the light of this challenge, 'the toxicological implications associated with loss of antioxidants from plastics for use in food-packaging application', is discussed (Chapter 7).

From a practical point of view, an attempt is made to describe assays for testing the ability of food additives and/or nutrient components to promote free-radical reactions (Chapter 8). In the case of antioxidants, most of those used in food are tested in lipid systems. It seems evident that, under certain conditions, such 'antioxidants' might promote the production of tissue damaging free radicals.

The growth of micro-organisms must be prevented if food is to be kept in good condition for any length of time. Unfortunately, it is not always possible to tell whether food has been attacked by micro-organisms. Eating contaminated foods may result in food poisoning. It is therefore ironic that some of the most prized food flavours are a consequence of microbial activity. The mould *Penicillium roqueforti*, for example, found in notable blue cheeses such as Stilton and Roquefort, is responsible for the flavour which ardent

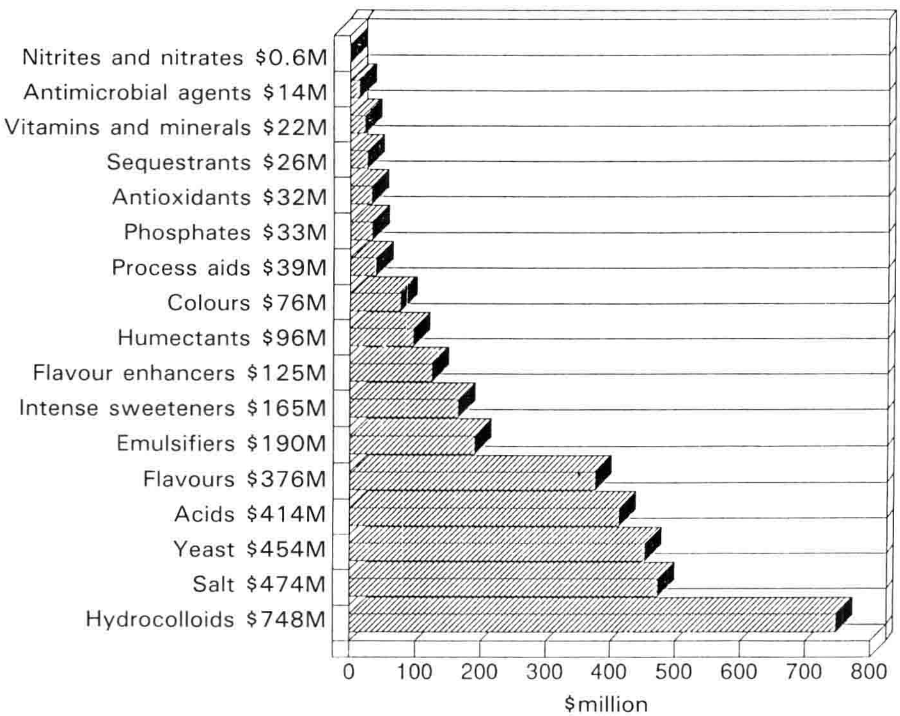

Figure 1. Food-additive market in the EEC, 1994.

Source: Report E903, Frost & Sullivan, Inc., Sullivan House, 4 Grosvenor Gardens, London SW14 0DH.

cheese eaters identify. The fermentation of grape juice by yeast is a fundamental stage in wine production. It could be regarded as food spoilage if the fermentation of the grape juice were not for the purpose of producing wine.

Protection of food against microbial attack may be achieved by treatment with chemicals, dehydration, heat, irradiation or storage at low temperatures. In suppressing the growth of micro-organisms, an effective method of food preservation must allow retention of the original characteristics of the food and should impair its nutritional quality as *little* as possible. A preservative may be defined as 'any substance which is capable of inhibiting or retarding the growth of micro-organisms or any deterioration of such food due to micro-organisms or of masking the evidence of any such deterioration'. In the early days, 'man' relied upon nature to provide 'fresh' food supplies in erratic quantities. This concept soon changed with industrialization coupled with population growth. As time went on, the consumer became more difficult to please. This subsequently led to a dramatic increase in the need for food preservation.

Food irradiation as a means of food preservation is of particular interest at the moment. Irradiation itself is not an additive by definition. The wealth of information on food irradiation (references on this subject in the suggested reading list, may be of use to the interested reader) cannot be adequately accommodated here. Some comments on food irradiation are worthwhile however. The consumer needs to be aware of the safety and the benefits of food irradiation. The use of irradiation is intended to act as an effective and versatile process of food preservation, disinfection and decontamination (Table 1).

A number of national programmes coordinated in part by the joint Food and Agricultural Organization/International Atomic Energy Agency division of the United Nations (FAO/IAEA), have conducted numerous studies that might facilitate the introduction of food irradiation technology. Irradiation involves bombarding batches of food with ionizing radiation such as γ rays (from ^{60}Co or ^{137}Cs sources), X-rays (generated from machine sources operated at a maximum energy of 5 MeV) and accelerated electrons (generated from machine sources operated at a maximum energy of 10 MeV). Due to the penetrating capabilities of X-rays, foods can be treated in final packaging or even in pallet loads. Electron beams have less penetrating power compared with γ rays or X-rays and their use is, therefore, limited to food items that can sustain a high dose of irradiation for a short time interval (for example, in the treatment of grains and spices). It has been suggested that treating food with ionizing radiation involves no significant change in the temperature of the food. This would mean that food irradiation is a cold process of preservation, able to kill insects or micro-organisms in foods which are sensitive to changes in temperature. When food materials are irradiated, short-lived, highly reactive free radicals are generated which kill the contaminating organisms. The effectiveness of food irradiation in this capacity is significant given that the incidence of food-borne diseases continues to affect adversely health and productivity in the populations of most countries, especially in developing ones. Illness due to contaminated food is perhaps the most widespread cause of illness in the contemporary world and, in a way, constitutes an important cause of reduced economic productivity. From the consumers' point of view, there remain reasons for concern. It is feared that some food producers may use irradiation to make unwholesome food appear fit for sale. Thus techniques for detecting irradiated food and measuring the dose of irradiation used are urgently required.

Food packaging materials contain chemicals that could conceivably come into contact with food (as discussed in Chapter 7). If the leached chemicals were to become transformed into reactive radical species upon irradiation, then there might be reasons for concern given that free radicals attack proteins, DNA and lipids (Chapter 3). Satisfactory assays to measure the components in foods modified by irradiation are not yet available. The identification of modified DNA bases is currently being considered by scientists as a

Table 1 Application of irradiation to food.[1]

Food products	Intended use	Recommended dose
High dose (10–50 kGy)[2]		
Meat, poultry, seafood, prepared foods, sterilized hospital diets	Commercial sterilization (in combination with mild heat)	30–50
Enzyme preparations, spices, natural gum	Decontamination of certain food additives and ingredients	10–50
Medium dose (1–10 kGy)		
Fresh fish, strawberries	Extension of food shelf-life	1.5–3.0
Fresh and frozen seafood, poultry and meat in raw or frozen state	Decontamination of pathogenic micro-organisms	2.0–5.0
Dehydrated vegetables (reduced cooking time), grapes (juice yield)	Improving the technological properties of food	2.0–7.0
Low dose (< 1 kGy)		
Potatoes, onion, garlic	Inhibition of sprouting	0.05–0.50
Fresh and dried fruit dried fish and meat, cereals and pulses, fresh pork	Insect disinfestation and parasite disinfection	0.15–0.50
Fresh fruits	Delay of ripening	0.50–1.0

[1] Adapted from Siburbjornsson and Loaharanu (1987).
[2] Gy = Gray, the unit used to measure absorbed dose. 1 Gy is the energy of 1 J absorbed by 1 kg of matter (1 Gy = 100 rad). 1 kGy = 1000 Gy.

possibility. The problem would centre on the ability to extract enough DNA from foods suspected of having been irradiated to enable characterization. In any case, it is known that free radicals generated in biologically relevant systems produce a series of modified bases in DNA which are detectable using gas chromatography/mass spectrometry/selected ion monitoring (GC/MS/SIM) (see Chapter 8).

In most cases, reactions involving free radicals lead to deterioration in food flavour and loss of food quality, but in some cases the products arising from such reactions appear to be an important part of the flavour. For example, consumers may appreciate the contribution of volatile compounds as desirable flavours in cheeses, fresh milk, dried potatoes and the 'creamy' flavour of cream. Some lipid oxidation products are also responsible for the rancid flavour of fats, peanuts, coconut, coffee and chocolate, for the stale flavour of dried potato baked goods and beer, as well as for the warmed-over meat flavour, etc. The extent to which the oxidation of fatty acids and esters contributes to the formation of volatile compounds in foods depends, at least in part, on both the chemical structure of the fatty acid, the process and/or the storage temperature.

Unsaturated and polyunsaturated lipids become oxidized under normal storage conditions. Certain products containing saturated acyl residues (in cooking oil for example) may degrade to form volatile compounds at the high temperatures normally achieved under frying conditions.

Flavouring agents (whether natural or synthetic) are used to increase the attractiveness of food and drinks. The concepts developed in Chapter 8, on the possible pro-oxidant properties of food additives and/or nutrient components might lead to new tests for proposed food and drink flavouring agents, colourants, emulsifiers and stabilizers and antioxidants.

It could be added that, with adequate knowledge, prudence in dietary choices and food habit offers the most reasonable approach to modifying the nutritional component of our food given the increasingly complex environment and pattern of life-style in any given society.

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Suggested reading

CHAN, H. W.-S. (Ed.), 1987, *Autoxidation of Unsaturated Lipids*, London: Academic Press.
FAO/WHO, (1984), Codex General Standard for the Irradiated Foods and Recommended Code of Practice for the Operation of Radiation Facilities Used in the Treatment of Foods, *Codex Alimentarius Commission*, Vol. XV, edition 1, Rome: FAO/WHO.
DIEHL, J. E., (1990), *Safety of Irradiated Foods*, New York: M. Dekker.
ELIAS, P. S. and COHEN, A. J., (1977), *Radiation Chemistry of Major Food Components*, Amsterdam: Elsevier.
GORMLEY, T. R., DOWNEY, G. and O'BEIRNE, D., (1987), *Food Health and the Consumer*, London: Elsevier Applied Science.
HALLIWELL, B. and GUTTERIDGE, J. M. C., (1989), *Free Radicals in Biology and Medicine*, 2nd edn, Oxford: Clarendon Press.
INTERNATIONAL CONSULTATIVE GROUP ON FOOD IRRADIATION, (1986), *Report of a Task Force Meeting on the use of Irradiation to Ensure Hygienic Quality of Food, 14–18 July 1986*, Vienna: IAEA.
LONDON FOOD COMMISSION, (1988), *Food Adulteration and How to Beat It*, London: Unwin Hyman.
MURRAY, D. R., (1990), *Biology of Food Irradiation*, Taunton: Research Studies Press Limited.
SIBURBJORNSSON, B. and LOAHARANU, P., (1987), *Irradiation and Food Processing, Symposium on Nutritional Impact of Food Processing*, 2–4 September 1987, Reykjavik, Iceland.
SIES, H., (Ed.), (1991), *Oxidative Stress II*, London: Academic Press.
TERANISH, R., FLATH, R. A. and SUGISAWA, H., (Eds), (1988), *Flavour Research 'Recent Advances'*, New York: M. Dekker.
THOMSON, D. M. H., (1988), *Food Acceptability*, London: Elsevier Applied Science.
TICE, P. A. and MCGUINESS, J. D., (1987), *Food Additives and Contaminants*, **4**, 267–76.

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Chapter 1

Consumers' perceptions of food safety

Melanie Miller

For the past year it has been difficult to open a newspaper without reading of some new scare connected with food. While consumers are getting punch-drunk from the media hype, irritated food technologists and toxicologists ask why concern is focused on the 'wrong' issues.

Changing food concerns

Levels of concern and issues of priority to consumers have of course changed over time. In 1983 a survey of 968 people by Consumers' Association found that 62% would decide against buying a food because of what they saw in the list of contents on the label. (For socio-economic groups A and B the figure was 74%.) When asked what would have to be in the food to stop them buying it: 59% referred to specific additives or additives in general; 35% said specific foods; 10% said soya or meat substitute; 8% said lots of fat or animal fat; and 6% said sugar.

Three years later, following a Government report on dietary fat and adverse media publicity about food additives, a survey by the Ministry of Agriculture Fisheries and Food (MAFF) showed nutrition and health had moved up the agenda. A total of 2000 adults were asked which of a list of eight food items they felt could cause damage to health. Two-thirds (66%) believed fat to be damaging to health, and 31% perceived fat to be the item most likely to cause damage. Just over half thought food additives, sugar and salt were damaging, but gave them a lower ranking than fat (Table 1.1). Table 1.2 shows that 24% of adults (34% of women) perceived additives as the item most likely to cause damage to health (MAFF, 1987).

Concern about additives primarily focused on the artificial colourings. The most common disadvantage cited was effects on health, with specific mention of allergic and intolerant reactions (MAFF, 1987).

Among the women who sometimes, usually or always looked at lists of ingredients (50% of women in the study) additives were primarily the item they looked out for, but sugar and salt were also mentioned (MAFF, 1987).

In the following year (1988) a Consumers' Association survey of 1107 adults found that 74% of people asked thought some chemical residues were

Table 1.1 Food items thought to damage health: 2000 respondents were asked which of a list of eight foods they felt could cause damage to health (MAFF, 1987).

Item	Responses (%)
Fat	66
Food additives	58
Sugar	57
Salt	52
Processed foods	35
Butter	32
Red meat	25
Bread	14
None	9

Table 1.2 Food items thought most likely to damage health: 2000 respondents were asked which food items they perceived to be *most* likely to cause damage to health (MAFF, 1987).

Item	Total, $n = 2000$ (%)	Women 25–34 years, $n = 216$ (%)
Fat	31	30
Food additives	24	34
Sugar	15	13
Salt	12	12
Processed foods	3	3
Butter	2	1
Red meat	3	2
Bread	—	—
None	9	4

dangerous to health, and 62% said they were prepared to pay more for food produced without chemical treatment (Consumers' Association, 1988).

A 1989 National Opinion Poll/Mintel survey of the attitudes of 933 adults to agrochemicals found 26% wanted to see all agrochemicals banned (30% of women), 45% wanted to see agrochemicals significantly reduced, 33% claimed they would be prepared to pay up to 10% more for organic produce, and 15% claimed to be prepared to pay premiums of more than 25% for organic produce (National Opinion Poll/Mintel, 1989).

A Consumers' Association survey of 1477 shoppers' views on organic food in 1989 found that of the 22% who had purposely bought organic food, 20% said that freedom from chemicals or residues was their main reason for buying (of the 78% who had never bought it, 27% were put off by its higher price and 19% were happy with conventional food) (Consumers' Association, 1990a).

A survey published in late 1989 showed that the topics of concern had shifted, and bacterial contamination had become the chief worry. Over three-quarters of respondents said that food-poisoning concerns influenced what they bought, 72% were influenced by artificial additives, 68% by cholesterol, 66% by salt and sugar, and 61% by pesticides. Despite massive publicity about food issues in recent years, there were also people who were relatively unconcerned about it all (*Food Magazine*, 1989).

Concerns in context

How do concerns about food compare with other health concerns? In a MAFF survey in 1986 respondents were asked to rank a list of six items, which were potentially damaging to health (Table 1.3). Men and women were equally highly concerned about smoking (40% ranked it highest). Environmental pollution and food were the next priorities. The groups who were more concerned about food than other issues were women aged 25–34 years and parents of children aged 0–5 years (MAFF, 1987).

A survey conducted by the Consumers' Association in December 1989 found that heart disease featured prominently, but food safety and nutrition were relatively low concerns. The possible health risks in this context are discussed further in Chapter 5. When 2204 people were asked which was currently the greatest cause of illness in the UK, their unprompted responses were as follows:

24% smoking, alcohol, drugs, solvent abuse;
17% heart disease;
14% colds and flu;
11% life-style, stress/tension, depression, mental health;

Table 1.3 Health concerns: 2000 people were asked to rank six items, which are potentially damaging to health, in order of their own concern, the figures listed indicate the issue which was of most concern (MAFF, 1987)

Item	Total, $n = 2000$ (%)
Smoking	40
Environmental pollution	28
Ingredients in food we eat	15
Amount of alcohol drunk	6
Obesity	4
Lack of exercise	4
None	4