ONE HUNDRED AND FIFTY-SEVENTH SCIENTIFIC MEETING
SIXTY-SEVENTH OF THE SCOTTISH GROUP
DEPARTMENT OF FOOD SCIENCE, ROYAL COLLEGE OF SCIENCE
AND TECHNOLOGY, GLASGOW

20 APRIL 1963

# ASPECTS OF CHEMICAL CHANGE DURING THE PROCESSING AND STORAGE OF FOOD

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## Foodstuffs as unstable chemical systems

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The subject matter of this symposium is too large to be encompassed in a group of five short papers, and the planning dilemma lay in the selection of a few illustrative topics from a great deal of material. The papers to be considered are therefore to be regarded as examples of topics of interest to those engaged in food research and not as an attempt to define the range of the subject.

Derived as they are from biological material, foodstuffs partake of its properties. They are chemically unstable substances generally found in a microbial environment which renders them still less stable. Since the food scientist is primarily interested in the utilization of foodstuffs, his greatest problems stem from this inherent lack of stability. The food technologist takes advantage of the studies of scientists in attempting to make the greatest possible practical use of such conditions as tend towards stability. M. Ingram of the Low Temperature Research Station, Cambridge put the problem neatly by saying something like this, 'Kill the bacteria and the enzymes take over. Destroy the enzymes and chemical change takes over. With luck you can reduce the rate of chemical change but it cannot be eliminated in a world above $0°$ K.' We are therefore concerned with rapid chemical change brought about by microbial invasion of food, with rather less rapid change catalysed by enzymes and other catalytic systems which may be present in food, and with what are often comparatively slow chemical interchanges which arise from the fact that the majority of foodstuffs are of a complex chemical constitution.

The scientist who would seek to employ his efforts in improving food utilization can approach his problem in two ways. He may attempt to arrest change by deployment of knowledge of the conditions under which rate of change is minimal, or he may encourage change in a specific and predetermined direction tending towards an altered and more stable state. In the first instance, an attempt is made to retain the characteristics of what is known colloquially as 'fresh' food. In the second, he alters the food to produce a new kind of product which can no longer be called 'fresh' but which has an extended storage life.

The idea of 'freshness' in food combines imprecision of meaning with implications of something inherently beneficial. The public desire for freshness has resulted in the

first approach to chemical change, the approach based on the wish to arrest it completely; in the verbiage of advertising 'to lock the golden days of high summer in the heart of a frozen strawberry'. It is a remarkable tribute to determined advance over difficult ground that a few processed foods do go far towards achieving this aim. But freshness in this sense can only be achieved in a limited number of foods whose chemical and physical nature bears a fortunate relationship to the process employed.

The second approach, that of admitting the inevitability of chemical change but directing it towards a situation of greater stability, has given us bacon and pickled meats, pickled vegetables, a whole variety of milk products including butter and cheese, wines, spirits and other fermented drinks, and has made important contributions towards products such as tea, cocoa and even jam and margarine. This approach results in new kinds of products which add variety to diet and may even enhance its nutritive desirability. I suspect that we shall see increasing scientific attention paid to this second approach in the future.

The pattern of chemical change to be found in food is complex. Most foodstuffs can be placed in one or another of five commodity groups: cereals, fruits and vegetables, dairy products, meat and meat products, and fish and fish products. Each member of each of these groups contains one or all of the following four groups of substances: protein, fat, carbohydrate and minor constituents (such as vitamins and minerals). Each of these groups of substances is subject (with minor reservations and additions) to five main types of chemical change which can be described for our present purposes as (1) thermal decomposition, (2) hydrolysis, (3) oxidation and reduction, (4) random interaction, (5) metabolic action and the production of metabolites. Simple combination gives us $5 \times 5 \times 4$ or 100 situations or types of situation which may arise from these factors.

Since the types of reaction mentioned may occur singly or together, simultaneously or in sequence, since each group of commodities represents dozens or hundreds of individual foodstuffs and since each of the four chemical classes represents a large number of different substances, the total number of reactions we have to consider is very large indeed and must run into millions. Nevertheless, the fact that the majority of them fall into one or another of about one hundred basic situations gives a perimeter to our thoughts.

Though I suppose it would be possible to give examples of most of these basic situations that I have indicated, we have to infer a great deal from the comparatively small number of reactions that have been investigated in detail. Moreover, as soon as we look closely at the course of a reaction we realize that practical situations involve interrelated phenomenons which cannot be placed neatly in one or another of the hundred convenient boxes which I have suggested.

The types of chemical reactions listed need no further explanation but comment must be made on the influence of metabolic action. When living fruits or vegetables are placed in temperature-controlled rooms to hasten ripening or to extend their marketable life it is easy enough to appreciate that a relatively crude attempt to increase or reduce metabolic activity is being made. When an animal is slaughtered for meat, metabolic activity continues after death but the reactions grind to a halt

with the formation of lactic acid in the muscle as ATP becomes exhausted and cannot be resynthesized. In this instance we are interested in chemical change of a metabolic nature but in abnormal circumstances. When a cereal such as wheat is ground to flour, the identity of microscopic structures is not lost and many of the flour particles are recognizable histological entities. When the flour is subsequently mixed with water to form a dough, chemical changes take place, some of which may be catalysed by systems of metabolic interest. Thus we can consider metabolic activity at the three levels of the living material, post-mortem 'metabolism' and residual reactions in partially disorganized material. Many reactions of interest to food science take place in material of the last sort. Unfortunately there is no adequate word to describe it. I have toyed with the thought that 'disorganate' may come to be understood as disorganized biological material which still retains some of the biochemical characteristics of the original specimen from which it is derived.

Any consideration of food chemistry that did not mention the nutritional implications of chemical change would be incomplete. The most important questions concern loss of nutritive value through chemical change and the possible formation of toxic by-products as a result of chemical change. Losses of vitamins, and in particular of vitamins A, B and C, have been the subjects of many studies, and it is probably true to say that good industrial processing methods are often less damaging than domestic cooking. In recent years, food science has been indebted to nutritional work on limiting amino acids and in particular on the effects of the Maillard reaction on lysine availability. Until comparatively recently, workers in this field have tended to argue that since chemical changes in domestic cooking are similar to those introduced by processing, and since man has been cooking food for thousands of years, and through many generations, without obvious harm, processing methods are not likely to involve chemical reactions producing toxic end-products.

Though this viewpoint is of attractive simplicity and has served its purpose in the past, its assumptions can no longer be supported. Fried potato products such as crisps and the ubiquitous fish supper raise points on the re-use of cooking oils which may partially decompose to potentially toxic substances. Newer methods of processing such as the use of ionizing radiations to reduce bacterial load result in randomized chemical reactions in the foodstuffs, the effects of which are of a different nature from those induced by previously well-tried methods of heat processing. The use of additives of one sort or another as technical aids to processing may be difficult to avoid but may also lead to the production of toxic substances in the food even if the additive itself has no demonstrable toxicity at the levels used. The fact that the onus for demonstrating the safety of a particular additive does not necessarily fall squarely on the shoulders of the user may be understood when the difficulties of such a demonstration are considered. For this reason the recent establishment of the British Industrial Biological Research Association is an event of some importance in relation to our considerations today, and is to be greatly welcomed both by nutritionists and food technologists.

I have only indicated the range of possible chemical change in food during processing and storage. Perhaps the complexity of the situation can best be indicated

from recent publications on flavouring constituents in foods. Coffee aroma rates high with sixty known constituents; the score for Cheddar cheese is thirty-seven, chicken twenty-six, white bread twenty-two, garlic a mere half dozen, whereas strawberry goes to the other extreme with forty-nine. Many of these are reactive substances such as aldehydes and terpenes. The numbers of these minor constituents, often present in quantities below the limits of conventional chemical detection, yet wholly important to our pleasure in eating, offer the most direct example of the complexity of chemical possibilities with which we are concerned in this symposium.

The papers which follow are therefore not to be taken as defining the range of today's topic (which can be interpreted to mean a major part of that branch of study now known as food science), but rather as examples that have been chosen in the hope that they may be of interest to the nutritionist as well as to the food scientist.

## Catalytic destruction of vitamin A and carotene

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### Introduction

Early studies on vitamin A stability were complicated by the natural association of the vitamin with the highly unsaturated fats of fish oils, and indeed as far back as 1920 it was possible to associate vitamin A deficiency in animals with the destructive effect of dietary fatty peroxides (Hopkins, 1920; Drummond & Coward, 1920). The lability of the principal provitamin, $\beta$-carotene, has also been linked to unsaturated-fat oxidation in vegetable materials, and the unsaturated-fat oxidizing enzyme, lipoxidase, was first studied as a carotene-destroying enzyme (Haas & Bohn, 1934). Though in some circumstances the stability of vitamin A and carotene in foods and feeding-stuffs may be dissociated from fat oxidation, it would, on the whole, be artificial to divorce the two topics.

The earlier literature on vitamin A stability has been reviewed by Olsen, Harvey, Hill & Branion (1959) and by Privett (1962).

Details of the oxidative destruction of the vitamin are as yet unknown. Some of the products of enzymically oxidized $\beta$-carotene have been identified by Friend (1961) who also discussed possible effects of oxidation on biological potency. The general belief that oxidation takes place through the propagation of free-radical chains would appear to be based on the inhibitory action of antioxidants and detection of peroxides in the autoxidizing vitamin (Budowski & Bondi, 1960).

When vitamin A is added to, or exists in, biological material, its stability will depend in part on physical contact with catalysts present, which in turn will depend on the nature of the dispersion. In animal feeding-stuffs, which have been the subject of most studies, three main types of dispersion may be distinguished: (1) as the intrinsic provitamin, as in lucerne or dried grasses, in the form of carotene within the chloroplasts; (2) as the vitamin A of added fish oils or concentrates; (3) as dry