

### Studies of food intakes of schoolchildren

By AILSA MELTON and BETTY Y. WINSTANLEY, *Department of Clinical Epidemiology and Social Medicine, St Thomas's Hospital Medical School, London, SE1*

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### Flavours of dairy products

By J. D. S. GOULDEN, *National Institute for Research in Dairying, Shinfield, Reading RG2 9AT*

#### *Introduction*

From the aspect of flavour, dairy products range from milk through mildly-flavoured butter and yoghurt to the highly-flavoured cheeses. Bland products such as milk and cream have little flavour of their own and most of the flavour problems associated with such products are those caused by the presence of undesirable off-flavours. These undesirable flavours can arise from feedstuffs eaten by the cow, be produced by staling or induced at various stages in the handling or processing. Since flavours are caused by trace components, sour milk will differ nutritionally very little from fresh milk, even though the flavour may be objectionable. The flavours of the various strong cheeses are produced as a result of a series of operations during manufacture, followed by storage under conditions which encourage the growth of bacteria. The importance of flavour is demonstrated by the differing prices of Cheddar cheeses with the same gross chemical composition and texture but with differing flavours.

As for other foods, flavour is a complex sensation with contributions from odour, taste and texture. Texture or 'mouth-feel' is relatively more important for bland products where the main flavour consideration is that there shall be practically no odour. Odour and taste are difficult to separate since they are linked together physiologically. Milk collected from a farm is rejected if any undesirable odour can be detected by the nose and a cheese grader assesses the flavour of cheese solely from its odour.

When we consider the possible use of physical and chemical methods for flavour assessment, we are impressed by both the sensitivity and the selectivity of the nose. A human nose can detect a few hundred molecules of an odorous compound which may be present only at the parts per million level in the presence of the major non-odorous constituents of the food. Table 1 shows the detectability limits for three different chemical compounds and demonstrates large differences between the values for the nose and for two different detectors frequently used in gas chromatographs. The gas-chromatograph data were obtained by Mrs H. Robinson in our

Table 1. *Limits (ng) of detectability by smell and gas chromatography for three compounds*

Compound	By human nose*	By gas chromatograph	
		Flame ionization detector†	Katharometer detector‡
Allyl mercaptan	$7 \times 10^{-6}$	0.14	900
Acetone	6	0.02	400
Water	—	—	1000

\*1 ml vapour (Stuiver, 1958).

†Pye 104.

‡LC-2 (helium carrier gas).

own laboratory and the values for the human nose were calculated from the odour threshold values listed by Stuiver (1958).

In view of the important contribution of odour to the flavour of both the bland and strongly flavoured dairy products, we have limited our initial study to the volatile constituents. This limitation has the practical advantage that it permits the removal and concentration of the volatile constituents so that the detection system is not swamped by its response to the main non-odorous components.

#### *Isolation of volatile flavour components*

There are two approaches to the removal and concentration of volatile flavour constituents of foods (Weurman, 1969). In the 'total volatiles' approach, an attempt is made to remove all volatile materials, irrespective of whether they contribute to the flavour or not. This is accomplished by prolonged vacuum distillation. The alternative approach of 'head-space analysis' is based on the assumption that the vapour in equilibrium with a product has the same composition as that entering the nose. We feel that the head-space approach is preferable when the concentration of flavour volatiles is sufficiently high, since this method is less liable to introduce artifacts. Distillates containing total volatiles are usually subjected to solvent extraction so that the relative concentrations in the final extract will be a function of their partition coefficients and are unlikely to be the same as those in the original vapour. In addition, there is always the possibility of reactions taking place with the solvent molecules or impurities so that the compound identified at the end of the analysis may not be the same one which was present in the starting material.

Head-space vapours contain many different components which must be separated by gas chromatography before presentation to the mass spectrometer for identification. Dairy products contain much water so that this will be the main constituent of head-space vapours. Apart from the more obvious difficulties caused by freezing and consequent blockage of cold traps, water presents several other problems to both the gas chromatographer and the mass spectroscopist. No completely satisfactory method has so far been found for removing water without removing some of the flavour volatiles. Since artifacts can be readily introduced, it is important to make full use of the human nose during the various stages of extraction and isolation.

We split the gas stream emerging from the column of our gas chromatograph so that only a portion is fed to the detector and the remainder can at the same time be subjected to olfactory assessment.

The work of Badings (1967) on the 'catty' off-flavour of certain cheeses is a good example of the application of gas chromatography to a flavour defect problem and shows how olfactory tests were able to demonstrate that the compound of interest had decomposed during its passage through the gas chromatograph. Vacuum distillates of fat from cheese with an offensive 'catty' off-flavour showed a gas-chromatographic peak additional to those obtained from normal Gouda cheese. The component responsible for this peak was trapped and identified by infrared spectroscopy as mesityl oxide. The odour of this compound is in no way reminiscent of the 'catty' odour but addition of hydrogen sulphide to mesityl oxide produced the offensive 'catty' odour, indicating that the original compound responsible for the cheese off-flavour was 2-mercapto-2-methyl-pentan-4-one, which had decomposed during passage through the gas chromatograph.

#### *Flavour components isolated from dairy products*

There seems to be little point in merely cataloguing all the hundreds of individual compounds which have already been reported as being responsible for particular flavours and off-flavours in dairy products. Most of the simple aliphatic alcohols, acids, esters, aldehydes and ketones have been found in dairy products, although it has not always been established which particular compounds contribute to the flavour.

Off-flavours are frequently caused by compounds which are present at concentrations greater than those present in the acceptable products. Dimethyl sulphide, for example, is present in small amounts in good-quality milk but produces an objectionable 'cowy' flavour if present at higher concentrations (Patton, Forss & Day, 1956). A particular compound can be objectionable in one product but highly desirable in another, e.g. the methyl ketones, which are considered to be key flavour components of Blue cheeses (e.g. Stilton, Danish Blue), are most objectionable when present at similar concentrations in butter. The free fatty acids in Cheddar cheese would make milk undrinkable if present at the same concentration (Kinsella, 1969).

Lipids seem to be particularly important in relation to flavour, since not only are they the source of many flavour compounds, but they also act as solvents for compounds produced from other components. Cheese made from skim milk has very little flavour whereas the odour of fat removed from Cheddar cheese suggests that most of the characteristic flavour resides in the fat. Thermal and enzymic reactions which produce flavour compounds from the fat are usually initiated at a double bond, free hydroxyl or carbonyl group along a fatty acid chain. Fatty acids, aldehydes, ketones and lactones can be formed by hydrolysis, autoxidation, decarboxylation or dehydration respectively. Other flavour constituents are formed by oxidative deamination of amino acids (Strecker degradation) which gives rise to branched-chain aldehydes of low molecular weight. For heat-treated products,

the Maillard reaction between sugars and amino acids can lead to the formation of compounds such as furfural which are soluble in the lipid phase.

Since fresh liquid milk has virtually no flavour of its own, off-flavours can be readily detected in milk. Over 100 years ago, it was appreciated that the feedstuffs consumed by the cow affected the flavour of the milk, and more recent work on this topic has been reviewed by Parks (1967). It has also been known for some time that rancidity in stale milk is due to fatty acids produced by the action of various lipases. Although pasteurization destroys the lipases in milk, rancidity can still be produced by non-enzymic hydrolysis of the fat. Hydrolytic rancidity has become an increasing problem in recent years owing to the increased degree of agitation produced by modern mechanized handling and processing techniques. Milk is also subject to 'oxidized' and 'sunlight' flavour defects which originate from the phospholipids of the fat-globule membrane and from the protein respectively.

The short shelf-life, and high transport-and delivery-costs of liquid milk have prompted much research into ways of producing milk concentrates, from which a liquid milk of acceptable flavour can be regenerated. Heat is required in all the concentration processes at present in commercial operation and this can lead direct to the production of off-flavours or to the formation of intermediate compounds which, although flavourless themselves, are converted during storage into compounds with undesirable flavours. Scanlan, Lindsay, Libbey & Day (1968) were able to show that the heating stage in the manufacture of ultra high temperature processed milk produced a series of methyl ketones, aldehydes and alcohols which were not present in the unheated milk. Their flavour-extraction techniques were so effective that they were able to demonstrate the presence of methyl iodide and various chlorinated benzenes in both the heated and unheated milk. These compounds were not introduced by the heat-treatment but by trace constituents from disinfectants used in the dairy and chlorinated insecticides used on the farms.

The flavour of butter is of considerable interest, especially to the margarine manufacturers. Forss (1969) has reviewed recent work on this topic and considers that the main components of butter flavour are: dimethyl sulphide,  $C_{2, 4, 6, 8, 10}$  n-alkanoic acids,  $C_{8, 10, 12}$ ,  $\delta$ -lactones and various phenolic and heterocyclic compounds.

The nature of the compounds responsible for the characteristic flavour of Cheddar cheese has so far eluded the efforts of many research workers (e.g. McGugan, Howsam, Elliott, Emmons, Reiter & Sharpe, 1968). Reiter, Fryer, Pickering, Chapman, Lawrence & Sharpe (1967) have, however, been able to demonstrate that the starter organisms play a vital role in determining the flavour of the cheese during the ripening stage. Although it was originally hoped that the characteristic Cheddar flavour might be attributed to a single chemical compound, the component-balance theory of Mulder (1952) is now becoming more attractive (Kosikowski & Mocquot, 1958). It seems likely that the flavour of Cheddar cheese will be describable only in terms of a series of contributions from different chemical compounds, each term having an appropriate weighting factor. Excess or deficiency of a particular component may produce an off-flavour. Not only are the ratios of the concentrations of the different components likely to be important, but also their absolute

concentrations. The importance of concentration is suggested by the work of Wiseblatt (1960) on the flavour of bread. From baking ovens, he was able to isolate a condensate which did not have the odour of bread until it was diluted by spraying into the atmosphere.

### Conclusions

Although it has been possible to identify the causes of some off-flavours in dairy products by use of gas chromatography and mass spectrometry, the components responsible for the characteristic flavours of the most important dairy products have still to be identified. The flavour of Cheddar cheese presents a particularly intriguing problem and the original hopes of attributing this characteristic flavour to a single compound have now faded.

The complex nature of food flavours may not be so surprising now that an insect sex pheromone has been found which consists of four components, all of which must be present in the correct concentration ratio.

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## The complex background to the sensory qualities of meat and fish

By J. A. LOVERN, 5 *Binghill Crescent, Milltimber, Aberdeen, AB1 0HP*

The sensory qualities by which a consumer judges a food include appearance and various eating qualities, of which I propose to cover three: taste, odour and texture. In most studies, taste and odour, which are often mingled in a composite sensation, are grouped together under the term 'flavour', and this concept will be used here. The chemistry of the flavourous components of meat (including chicken) and fish has been extensively reviewed in recent symposia and elsewhere (Doty, Batzer, Landmann & Santoro, 1961; Jones, 1961, 1967, 1969; Kazeniac, 1961;