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Chemical Preservatives in Foods in Australia

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The use of chemical preservatives in foods in Australia is governed in each State by a separate Pure Foods Act or its equivalent. In the past, individual States introduced amendments or new regulations to their State Act and did not attempt to secure uniform legislation by prior consultation with other States. This resulted on some occasions in significant differences in the regulations of the various States which complicated interstate marketing.

Such difficulties have been progressively overcome in recent years since all States have agreed to accept National Health and Medical Research Council recommendations concerning the use of food additives, including preservatives.

Regulations

The National Health and Medical Research Council relies on its Food Additives Committee for an evaluation of potential new additives and also of the advisability of the continued acceptance of permitted additives. Bottomley (1967) has given a concise account of the principles and machinery involved in current food additive legislation in Australia. Many interested parties seem to be largely unaware of these principles and the description by Bottomley is recommended as an introduction to this subject.

Although each Australian State has its own Pure Food Act, the definition of a preservative is essentially the same in each. As set down in the New South Wales Pure Foods Act, it is 'any substance which is capable of inhibiting, retarding, masking, or arresting the process of fermentation, putrefaction, acidification, or other decomposition of food, and includes for the purpose of these Regulations boric acid, borax or benzoic acid, sulphites, metabisulphites, formaldehyde, nisin, sorbic and propionic acids, or their salts and any peroxide, but does not include prescribed antioxidants, salt, saltpetre (sodium or potassium nitrate), nitrites, sugars, acetic acid or its sodium salts, vinegar, alcohol, or potable spirits, herbs, hop extract, spices or essential oils used for flavouring purposes or any substance added to food by the process of curing known as smoking'. Chemicals not included in this definition are prohibited from all foods and the preservatives listed are also prohibited unless their addition is specifically permitted in the appropriate Regulation. The table shows in condensed form the officially approved uses in Australia of the chemical preservatives considered in this paper.

Whenever a preservative is specifically permitted, the Regulation governing the addition of the preservative to a given foodstuff will include a maximum permitted concentration. The strict control of both the nature of the preservative and the quantity which may be used safeguards the consumer and the processor in two ways. The main consideration is whether the preservatives might be toxic to the consumer and comprehensive data on the acute and chronic toxic effects of all prospective chemical preservatives are carefully examined before a preservative is regarded as sufficiently free from hazard to be permitted. If further scientific evidence becomes available, a decision can be changed and a substance can be removed from the permitted list, or a previously rejected substance admitted. The second consideration is protection of the public from faulty processing techniques. The function of chemical preservatives is to extend the storage life of a foodstuff when there is no alternative practicable and economic means. The Regulations are so framed that irresponsible or inefficient processors cannot use preservatives to disguise the use of poor-quality raw materials or careless manufacturing methods.

Traditional 'Preservatives'

Of the food ingredients specifically excluded from the legislative definition of 'preservative' above, salt, nitrates, nitrite, and acetic acid (or vinegar) deserve some discussion. When speaking of the chemical preservation of foods today, the tendency is to except such well-established processes as curing of meats and pickling of vegetables. These processes, however, depend for their success on the preservative action of one or more specific, non-toxic chemicals that have become recognized as a part of the normal diet. This is probably because in the case of salt and acetic acid, the preserving agent contributes significantly to the flavour of the product and the consumer, if not the processor, no longer regards it in any other way. With other chemical preservatives, the use of quantities sufficient to be detected on the palate is considered a disadvantage. Similarly, any new preservative would have to be virtually tasteless to be accepted by the public, quite apart from any properties required by the National Health and Medical Research Council.

Application of Principal* Chemical Preservatives permitted in Australian Foods

S, sulphur dioxide; N, nitrite and nitrate
B, benzoic acid or benzoates; Sb, sorbic acid or sorbates
P, propionates; Ni, nisin

Food Product		Permitted
Beverages	Fruit drinks	S, B, Sb
	Fruit juices	S, B, Sb
	Fruit squash	S, B, Sb
	Fruit juice concentrates	S, B, Sb
	Fruit juice cordials	S, B, Sb
	Carbonated drinks	S, B, Sb
	Wines, sweet	S
	Wines, dry	S
	Beer	S, B
	Cider and perry	S
	Non-excisable fermented drinks	S, B, Sb
Dairy products	Cheese and cheese products	S, Sb, Ni
Baked goods	Pastry	Sb, P, A
	Flour	Sb, P, A
	Bread	Sb, P, A
Meat and fish products	Fish semi-preserves	B, Sb
	Uncooked sausage meat	S, N
	Gelatine	S
	Pickled and cured meats	N
	Canned meat	N
Canned foods	Tomato juice	Ni
	Tomato pulp	Ni
	Tomato paste	Ni
	Fruit	Ni
Miscellaneous	Maraschino cherries	S, B, Sb
	Dehydrated vegetables	S
	Pickled vegetables	S
	Dried fruit	S
	Imitation fruit flavours	S, B, Sb

*Boric acid and glycerine are permitted in some junket products; diethyl pyrocarbonate has been approved for use in many fruit products but has not yet been written into Regulations.

Salt

Salt concentrations formerly found in cured meats (5–20% in aqueous phase) selectively inhibited most pathogenic and putrefactive bacteria. At the same time organisms that could tolerate these concentrations were able to grow and formed an integral part of the finished product. With the continuing trend of public taste towards less strongly salted foods, the storage life of cured meats is being concurrently shortened. The types of organisms present in the product can also be expected to change and it is necessary for processors to give this aspect of their process due consideration with regard to both growth of spoilage organisms and possible food-poisoning strains.

There is, too, a definite need for a greater understanding of the preservative action of curing salts in canned meats, and recent work in England and the U.S.A. has contributed significantly to this (Roberts and Ingram 1966; Duncan and Foster 1968). This work was designed to explain the remarkable stability of these products which is achieved even though the curing ingredients by themselves are not sufficient to prevent spoilage of the meat, and the relatively mild heat treatment used is not nearly sufficient to destroy all the bacterial spores. The results obtained suggest that the effectiveness of sodium chloride in combination with heat lies in preventing outgrowth of sensitized spores after they have germinated. The concentra-

tions used in practice are not sufficient to prevent germination itself: approximately 15% sodium chloride is necessary to prevent germination while about 5% will suffice to prevent outgrowth of both *Bacillus* and *Clostridium* spores.

Nitrites

Nitrite is quite different from salt in its action. The main function of nitrite in the cure is to produce the typical pink colour of cured meat by combination with muscle pigments. At the low concentrations permitted, and at the pH of cured meat (approximately pH 6), the active preserving agent is probably undissociated nitrous acid. The pH is such that the nitrite is highly effective but it does not decompose rapidly. Roberts and Ingram (1966) point out that quite small changes in the pH of the meat, as from the addition of phosphates, may be bacteriologically significant. The function of nitrate is not clear although it is usually added as a continuing source of nitrite by microbiological reduction. There is a tendency, however, to omit nitrate from brine mixtures.

Acetic Acid

Acetic acid can still be classed as one of the major types of food preservatives but, as with salt, the emphasis is shifting from its long-term preservative effect towards its value as a flavour component. When acetic acid alone is used to preserve pickled products, an equilibrium concentration of at least 3·6% is necessary to ensure stability of the pack (Binsted, Devey, and Dakin 1962). This level is too high to be acceptable to most consumers and there is a trend towards heat-pasteurized pickled products containing about 1% acetic acid. The product then retains its pickled character and is also microbiologically stable because of the associated heat process at the existing pH.

Although acetic acid is non-toxic and specifically excluded from control, it does share many features with other acid preservatives such as sulphur dioxide and benzoic and sorbic acids. The most noteworthy of these is that its preservative action is probably one of enzyme inhibition (Wyss 1948) and that it is only the undissociated molecules of the acid which are capable of exerting an inhibiting effect. In general, acetic acid appears to be more effective against bacteria and yeasts than against moulds (Ingram, Ottaway, and Oppock 1956), while sodium diacetate when used in bakery products inhibits both *Bacillus mesentericus*, the bacterium that is the principal cause of the disorder known as 'rope', and also mould growth. Levels of 0·3% are usually satisfactory and this is the maximum level permitted by all the Australian States.

Preservatives Permitted in Australian Foods

The range of permitted preservatives in the Australian States is not great. In addition, the number of foodstuffs in which their use is allowed is comparatively small. Almost every approved preservative is acidic in nature and this markedly influences the efficiency of their use. Substances in this group are sulphur dioxide, benzoic acid, sorbic acid, propionic acid, and boric acid. The only exceptions are the polypeptide antibiotic nisin, which is permitted in some canned foods and cheese, and glycerine, which is permitted in some States in rennet and junket essence. Incidental absorption by some smoked products of formaldehyde is permitted to a stated maximum concentration while nitrite, which is specifically excluded from the definition of a preservative, may be used in cured meats to a maximum level of one grain per pound expressed as potassium nitrite. Similarly sodium diacetate, which is also excluded from the definition of a preservative, is permitted in flour, bread, and pastry to a maximum level of 0·3%.

Mode of Action of Preservatives

The mechanisms whereby chemical preservatives inhibit the growth of microorganisms are not fully understood. Most studies in this field have been directed towards determining the efficiency of a particular preservative in a given type of food product against a known trial population of microorganisms. These studies have revealed a number of factors that influence the activity of chemical preservatives but, in general, they have not been designed to determine how the metabolism of the microorganisms is affected. When this knowledge is obtained, it could lead to the use of more efficient techniques in chemical preservation. Comparatively recent studies by Bosund (1962), Wallnöfer and Rehm (1965), and York and Vaughn (1964) on the major

preservatives, benzoates, sulphur dioxide, and sorbates, have been inconclusive in elucidating the mode of action of these substances. Experimental evidence indicates that the preservatives interfere with many enzymatic processes, both aerobic and anaerobic, which affect the growth rate of both the aerobic and anaerobic microorganisms concerned. It must also be stressed that it is not known positively whether the molecules must actually pass into the microbial cells to produce the whole or part of their growth-inhibiting effect.

Empirical experiments have given valuable information on the factors that influence the efficiency of preservatives. The principal factors are:

- Concentration of the preservative
- Composition of the food
- Type of organism to be inhibited

Concentration of Preservative

In general, the quantities of preservative permitted by the Food Regulations are inhibitory rather than lethal to contaminating microorganisms. It is therefore essential that the microbiological population of the food to be treated is kept to a minimum by hygienic handling and processing. Permitted levels of preservative will preserve food with a normal microbial load for a useful period but will be ineffective when incorporated into spoiling or grossly contaminated foodstuffs.

Composition of the Food

This is important for two reasons: the pH of the product will determine the concentration of the acidic preservatives existing in the undissociated form, and the chemical constituents of the product will determine the proportion of the preservative that is rendered ineffective by chemical combination. This second point is particularly important when the use of sulphur dioxide is being considered.

Many workers (Ingram, Ottaway, and Oppock 1956; Bosund 1962; von Schelhorn 1953) have reported that the undissociated acid is the microbiologically active portion of the molecule of acidic preservatives. A high pH leads to a greater proportion of dissociated acid and this explains the greater effectiveness of the common preservatives at lower pH.

Type of Organism to be Inhibited

Perishable foods normally contain a mixed population of microorganisms and in some instances a combination of two preservatives may be more effective than either alone. Combinations of preservatives also are used when the necessary concentration for a single preservative would give an objectionable taste. The use of preservatives in this way is also governed by the various Pure Food Acts.

Properties of Specific Preservatives

Sulphur Dioxide and Sulphites

These are probably the most widely used chemical preservatives and find their main application in the preservation of fruit products, particularly in juices where they are used in concentrations up to 2 grains per pint or 230 p.p.m. Their use is permitted in all States in fruit products and juices and also in uncooked sausage meat, and in addition in South Australia sulphites may also be added to minced meat.

The active preserving agent is normally considered to be undissociated sulphurous acid; the concentration of undissociated acid is a function of pH so the efficiency of sulphurous acid as an anti-microbial agent is pH-dependent. For this reason, when sulphur dioxide is used as a preserving agent the pH of the product should be 3·5 or less. Sulphur dioxide inhibits yeasts, moulds, and bacteria but, as with other preservatives, its activity varies according to the organisms present. Wallnöfer and Rehm (1965) have tried to explain this from its effect on the metabolic cycles of each type of organism, the pathway with which the preservative interferes being more important in bacteria than in yeast.

Sulphur dioxide at concentrations of about 100 p.p.m. will successfully preserve fruit juices; at greater concentrations many people find the sharp taste objectionable. Sulphur dioxide is also an anti-oxidant and its use results in fruit juices retaining their ascorbic acid and colour better than when other preservatives are used, e.g. benzoic acid.

Reaction occurs readily between sulphur dioxide and carbonyl and aldehyde groups. Such reactions bind sulphur dioxide and the resultant bound sulphur dioxide has very little if any inhibitory effect on yeast (Ingram, Ottaway, and Oppock 1956). It does have

an effect on some bacteria, however, as reported by Fornachon (1963) in studies on the malo-lactic fermentation in Australian wines in which sulphur dioxide is extensively used. Acetaldehyde is the most important binding agent in wine while sugars and aldehydes are the main binding agents in fruit juices and more particularly juice concentrates. Due to this ineffectiveness of bound sulphur dioxide it is almost impossible to control yeast action in a juice that has begun to ferment by the addition of sulphur dioxide. Acetaldehyde is a product of the fermentation and quantitatively it has a greater binding efficiency than the sugar fraction of the fermenting juice; 44 parts by weight of acetaldehyde combine with 64 parts by weight of sulphur dioxide. This is many times the combining power of glucose with sulphur dioxide.

Sulphur dioxide prolongs the storage life of sausage meat by retarding the multiplication of contaminating bacteria, particularly when the meat is stored at a low temperature (32–34°F), which in itself considerably retards bacterial multiplication. The sulphur dioxide, with sulphurous acid probably the active agent again, selectively inhibits the Gram-negative putrefactive rods that normally spoil untreated meat. Gram-positive acid-producing rods are not inhibited to the same extent but the sour odour produced by them does not become objectionable until the bacterial population reaches a much higher level than is acceptable without sulphur dioxide (Christian 1963).

Benzoic Acid

Benzoic acid, usually as the sodium salt, is used in Australia almost exclusively for the preservation of fruit products, although N.S.W. Food Regulations also permit its use in fish semi-preserves. The sodium salt is commonly used because of the low solubility in water of the free acid. In fruit products the salt is converted to the acid and below pH 4·0 this exists in the undissociated form, when it is most effective as a preservative (Bosund 1962).

The use of benzoic acid is permitted in most compounded fruit products at a concentration of 7 grains/pint or 800 p.p.m. In fruit drinks and soft drinks, 400 p.p.m. is the maximum quantity permitted and this is quite effective, particularly when used in conjunction with some other preservative.* Sulphur dioxide and benzoic acid are often combined in fruit drinks while the carbonation of soft drinks also has a preservative action in these products. At concentrations of 400 p.p.m. and above, the taste of benzoate is quite noticeable, and many people find it objectionable at much lower concentrations.

Sorbic Acid and Its Salts

Sorbic acid, normally used in the form of its potassium salt because of its greater solubility, has a broad-spectrum activity against yeasts and moulds. It is not so effective against all bacterial species, lactobacilli and clostridia being two important groups not inhibited by sorbate, and once again this can be attributed to the metabolic pathways with which the preservative, a straight-chain monocarboxylic acid, interferes (Emard and Vaughn 1952; York and Vaughn 1964).

The pH range of optimum effectiveness of sorbates is somewhat higher than that of other acidic preservatives and thus sorbate can be used to advantage in a wide range of foodstuffs. In addition to their use in fruit products, sorbic acid or sorbates find application in the preservation of cheese, pastry, bread, and other baked products. In all States of Australia specified concentrations of sorbates are permitted in these products and in some other countries they may also be used in margarine, pickled products, and prepared salads.

Sorbates inhibit yeasts as well as moulds and therefore cannot be added directly to yeast-raised baked goods. With such products the surface can be sprayed after baking with potassium sorbate solution or alternatively a wrapper impregnated with sorbic acid may be used. The required levels of addition are of the order of 0·1% of dough weight, depending on the acidity of the product. Sorbates find their greatest use in this field in the protection of fruit cakes and fruit pies from mould growth.

The use of sorbates in cheese is restricted to the impregnation or coating of wrappers

*The addition of two preservatives is permitted providing each is permitted separately under the Regulations and providing that the total concentration of the mixed preservatives does not exceed the total of the proportionate amounts of each preservative permitted under the Regulations.

with no more than 5 g of sorbic acid per 1000 sq in and providing that the wrapped cheese contains no more than 0·1% of sorbic acid incidentally absorbed. Since mould growth on cheese, as with baked products, is a surface phenomenon this method of application is quite effective but incomplete contact between wrapper and food can result in incomplete protection.

Propionic Acid and Its Salts

Propionic acid is an aliphatic monocarboxylic acid and is used in the food industry as the sodium and calcium salts which are free-flowing powders. Food Regulations restrict its use to pastry, flour, and bread where it is used to control surface mould growth and also 'rope'. Because the propionates are less active against yeast than are sorbates, they are more suitable for use in yeast-raised baked goods although the use of more yeast may be necessary (Huitson 1968).

The calcium salt is preferred in bread while the sodium salt is used in cakes where the calcium ion can interfere with chemical leavening. These salts have a slight cheese-like flavour but this is not noticeable at the permitted concentrations. The maximum permitted addition is 0·2% and this is only necessary in warm humid weather when mould growth is a particular problem.

Nisin

The antibiotic nisin, which has no clinical application, is permitted in Australia in processed cheeses, canned tomato products (pH 4·5), and other canned fruit products (pH 4·5). While the presence of most antibiotics in foods would be objectionable from the public health point of view, nisin can be said to be in a different category for a number of reasons (Tramer 1966), and provided its inhibitory action is clearly understood, it can be a useful aid in certain circumstances.

Although there is still disagreement about the exact mode of action of nisin, all the work so far described emphasizes the importance of ensuring the presence of residual nisin throughout the expected shelf life of the product. It is the sporostatic property of nisin that makes it of interest to food processors and its use is restricted to spoilage problems that may exist when spore-forming bacteria survive the maximum heat process consistent with the highest quality of the final product. In some countries, nisin may be used in canned foods with a pH higher than 4·5 provided these cans have received a heat process with a minimum F_0 value of 3, i.e. a process regarded as sufficient to inactivate any spores of *Cl. botulinum* which may have been present in the pack. Use of nisin in this way is not approved by Australian authorities although the National Health and Medical Research Council (63rd session) recommended that its use be permitted in canned soups that had been heat processed to destroy any *Cl. botulinum* present.

Perhaps the most effective application of nisin is in the control of clostridial 'blowing' of processed cheese; the bacterial spores are not destroyed during processing and outgrowth and spoilage can readily occur under normal packaging conditions. Usually 100 units of nisin per gramme are used in such cheeses and this is equivalent to approximately 2·5 p.p.m. of pure nisin. One argument used to support the claim that nisin is quite safe when used as a food additive was that some lactic acid bacteria normally occurring in milk and cheese are capable of producing nisin. For this reason it could be safely assumed that for a very long time this antibiotic has been consumed by the public with no ill effects.

Diethyl Pyrocarbonate

Diethyl pyrocarbonate is not yet gazetted in State Pure Food Acts as a permitted preservative but the National Health and Medical Research Council has recommended its use in some products and State approval can be expected in the near future. The National Health and Medical Research Council (66th session) recommendation is 'that diethyl pyrocarbonate be permitted for use in cider, cider vinegar, and fruit juices, for which sulphur dioxide is at present permitted, in an amount not exceeding 200 p.p.m. provided that the final products do not contain more than 1 p.p.m. of diethyl carbonate'. The Council had earlier (65th session) made the same recommendation regarding the use of this preservative in wine.

Diethyl pyrocarbonate or diethyl dicarbonate is a colourless liquid which is not very soluble in water but is soluble in the common organic solvents. It has a fruity ester-like odour and when added to aqueous solutions

it rapidly hydrolyses to ethanol and carbon dioxide leaving only trace residues. For this reason, unlike most other preservatives, the taste of the product should not be affected. However, Seale (1965) did find some flavour effects when diethyl pyrocarbonate was used in soft drinks. It decomposes more rapidly in neutral than in acid solutions.

The fact that diethyl pyrocarbonate breaks down rapidly in juices and drinks means that to be of value in preservation it must be lethal to residual microorganisms. This is quite distinct from the action of the other preservatives which only inhibit microorganisms in the permitted concentrations. It also means that contamination must be at a fairly low level if the preservative is to be effective. As is often the case with chemical preservatives, the greater the number of microorganisms present the higher the concentration of preservative necessary to contain their growth.

Diethyl pyrocarbonate is especially active against a wide range of yeast (Chichester and Tanner 1968) and provided the population is less than about 1000 organisms per millilitre, a sterile final product can be obtained if the pyrocarbonate is added immediately before the filling operation. When the initial microbial load is significantly higher, it must be reduced to the suggested level before filling and this is usually accomplished by filtration. The diethyl pyrocarbonate then destroys the low number of remaining cells and thus the term 'cold sterilization' has been used to describe the combined action of filtration and use of this preservative.

Although diethyl pyrocarbonate does have some advantages over more widely used chemical preservatives, it is important to recognize that it has only a limited range of application. It is probably most useful with bottled fermented drinks, notably wine and cider, and also with bottled vinegar. Its presence in these products prevents the regrowth of the small numbers of organisms used in their manufacture which may remain after filtration. Its use, however, will not eliminate the prior need for treatment with sulphur dioxide in wine and cider manufacture, for this also helps to inhibit browning and clouding in fruit juices, while diethyl pyrocarbonate does not. Manufacturers intending to use diethyl pyrocarbonate should carry out small-scale trials under practical conditions to determine whether they will in fact obtain the results they are seeking.

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Product Quality in Freeze Drying

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The statement that 'Freeze drying is only as good as the quality of its products' is often interpreted to mean that product quality is entirely dependent on the drying process. Ancillary processes such as preparation, freezing, storage, and rehydration, however, are essential to freeze drying, but they may not be the only ones. It is becoming apparent that small amounts of an agent could be added to the fresh food before freeze drying to give better quality, which results from improved rehydration capacity, retention of volatile flavour compounds, and reduced non-enzymic browning or lipid oxidation.

The incorporation of agents to enhance the quality of freeze-dried food is being studied extensively. Goldblith and Karel (1966) in a comprehensive review recall the discovery of Wismer-Pedersen (1965) that a neutral solution of ethylenediaminetetraacetate increased the rehydration capacity of meat without affecting water removal during freeze drying. Retention of volatile flavour compounds in bananas has been found by Goldblith and Karel (1966) to be substantial in the presence of added sucrose. In sugar-free model systems, while Kallistratos and von Sengbusch (1964) found that there was very little retention of pure volatiles, Rey and Bastien (1962) showed that retention was better when glucose was present.

Non-enzymic browning of freeze-dried fruit has been investigated by Anet and Reynolds (1957), and Matheson (1962) has reviewed lipid oxidation in freeze-dried raw and cooked meat.

With freeze-dried specimens of micro-organisms, medical products, and other biological materials, protective agents have been used for some time. For example, Greaves (1964) recommends adding 5–10% sucrose to the suspending fluid Mist. Desiccans for optimum viability of freeze-dried micro-organisms. The sucrose protects by preventing the residual moisture content from falling below 1% and since it contains no carbonyl groups it does not react with components of bacterial membranes (Scott 1959). Greaves (1964) also considers that the addition of 1% sodium glutamate still further improves stability under high storage temperatures, and to aid reconstitution he recommends the addition of a neutral polymer: polyvinyl-pyrrolidine or dextran at a concentration of 5–10% to give structure to the freeze-dried suspension. Dimethyl sulphoxide has been found to afford better protection as unlike other agents it penetrates the cells so that the freezing rate is not so critical (Lovelock and Bishop 1959).

These agents which reduce irreversible changes during preparation, freezing, storage, and rehydration as well as during freeze drying itself might be considered in the broadest sense as the unifying step in freeze drying food for improving the quality of the product. The concept is due to Gheorghiu (1968) who pointed out that an agent could be introduced during preparation of the product for freeze drying, and that its role would be multiple and more important than other procedures for preparation except the freeze drying itself. She considers that agents protect during freezing as well as freeze drying by limiting osmotic shock resulting from the withdrawal of water.

The observations now being reported indicate the role of protective agents in freeze drying for improving the quality of food products. Examples include agents used in

the preparation of fruit for freeze drying to retain flavour and colour, in the storage of a freeze-dried vegetable, and in the rehydration of whole freeze-dried shellfish. Most of the experiments were only preliminary trials with the exception of the quality of freeze-dried peas which were studied in some detail by taste panels.

The products were freeze dried under cyclic vacuum pressures (Mellor 1967) giving faster rates of drying, especially during the approach to the end point, when the rate was more than double that obtained under constant vacuum pressures.

Treatments in Freeze Drying

Sulphite Treatment for Stored Peas

Part of the normal preparation of vegetables for dehydration is a dip in a solution of sodium metabisulphite. The vegetables absorb a certain amount of sulphite which protects vitamin C and plays a part in retarding the browning reaction, although in storage the treated vegetables gradually lose sulphite. Once freeze drying of vegetables became established, sulphite treatment of many vegetables was omitted, because of the lower moisture contents attainable (Gooding 1962). However, in recent storage trials the quality of peas freeze-dried without sulphite has deteriorated substantially, while sulphite treatment gave good quality when the peas were first punctured through the skin into the cotyledons to ensure uptake of the agent.

Preparation.—Two lots of mature peas were harvested, one lot was punctured in the CSIRO pea puncturing machine (Mitchell and Lynch 1967) with pins of 1·2-mm diameter, and the other lot left unpunctured. Both lots were blanched in water at 96°C for 80 sec, cooled in water for 60 sec, then drained, placed on trays, and frozen at −20°C. When sulphite treatments were included, blanched peas were dipped in a 0·3% solution of sodium metabisulphite for 30 to 60 sec. All the frozen peas were freeze-dried by the cyclic-pressure method with a sublimation temperature ranging from −4°C to −20°C, and with a heater temperature progressively lowered from 100°C to 40°C. The tray loading was 4·1 kg/m² and the drying time 5½ hr, the finish of drying being determined by the trapped-pressure method which involves sampling the gas space above the product and taking the ratio of the partial air pressure, after condensing the water vapour, to the absolute pressure. When the ratio approached a constant value the product was removed from the freeze dryer and the moisture content of the samples determined gravimetrically by oven drying to constant weight. Finally the peas were packed in tins, sealed under vacuum, and stored at 20°C and at 37°C for 7 months.

Tasting tests were carried out on all of these samples with the colour, texture, and

Table 1

Sulphur content, moisture content, and tasting test scores of punctured and unpunctured peas

Sample*	Sulphur Content		Moisture Content	Score for Colour		Score for Texture		Score for Flavour	
	Before Storage (p.p.m.)	After Storage (p.p.m.)	(%)	Mean	S.E.	Mean	S.E.	Mean	S.E.
20P			2·8	7·2	±0·2	5·9	±0·3	4·7	±0·3
20PS	—	413	1·9	7·3	±0·2	6·2	±0·3	6·1	±0·3
20SG	507	275	3·8	5·0	±0·2	4·1	±0·3	4·6	±0·3
20PSG	—	518	—	7·3	±0·3	6·4	±0·3	6·0	±0·2
37			3·6	2·4	—	2·3	—	1·9	—
37S	435	125	3·4	3·2	—	4·1	—	3·6	—
37PS	378	225	0·2	6·8	±0·3	6·4	±0·3	5·1	±0·3
37SG	691	—	3·0	4·4	—	4·5	—	3·8	—
37PSG	—	429	0·1	7·2	±0·2	6·2	±0·3	5·3	±0·3

*20P = 20°C storage, punctured; 20PS = 20°C storage, punctured, sulphited; 20SG = 20°C storage, sulphited, graded; 37S = 37°C storage, sulphited; 20PSG = 20°C storage, punctured, sulphited, graded.

Table 2
Differences in tasting test scores for frozen and freeze-dried peas

Sample	Colour				Texture				Flavour			
	F1*	20PSG	F2*	20PSG	F1	20PSG	F2	20PSG	F1	20PSG	F2	20PSG
Mean score	7·5	7·3	7·0	7·3	7·2	6·4	6·7	6·4	6·9	6·0	6·7	6·0
Difference significant	No		No		0·1%		No		0·1% High		No 1%	Yes 5%

*F1 = first-grade frozen peas; F2 = second-grade frozen peas.

flavour scored according to the hedonic scale (1–2 inedible, 3–4 poor, 5–6 fair, 7–8 good, 9 excellent) and the mean scores and standard errors evaluated. The results together with the moisture and sulphur contents of the products are tabulated in Table 1.

Results and Discussion.—The scores in Table 1 for the punctured peas are the most interesting, the sulphited samples giving fair scores for a stringent temperature test of 37°C for 7 months. Sulphiting is important for storage at high temperature providing the peas are punctured, but low moisture content (below 1%) could also be important. Unless the peas are punctured, moisture contents below 3% are much harder to obtain in freeze drying.

Scores for punctured and sulphited peas stored at 20°C and 37°C were compared by pooled statistics (equal to the difference of the means divided by the standard error of the difference) with 38 degrees of freedom and found to be not significantly different.

Grading seems to influence only colour scores, which is to be expected, but even here puncturing is just as important, since during freeze drying the cotyledons do not shrink if the skin of the pea is punctured to allow the water vapour to escape during drying. Reconstitution is better also and tasters tend to give weight to the shrunken appearance more often than to the green colour under such circumstances.

A comparison (Table 2) has also been made between two grades of commercial frozen peas and freeze-dried punctured, sulphited, and graded peas stored at 20°C by pooled statistics with 66 degrees of freedom. The colour and texture scores of second-grade frozen peas and the freeze-dried peas are not significantly different and the flavour scores, although significant at one level of significance, are not significant at a higher level. It could therefore be inferred that these freeze-dried peas are about as good as second-grade frozen peas.

A more sensitive tasting test, in which the theory of the analysis of variance for differences in score between two or more tasters is used, has been applied (Coote, personal communication) instead of the usual analysis of variance for absolute scores. No significant difference in the colour, texture, or flavour between punctured and sulphited peas stored at 20°C and 37°C was found.

Pronase Reconstitution of Oysters

Although oysters are relatively easy to freeze dry they are nevertheless one of the most difficult products to store when dried and, in addition, whole oysters are extremely difficult to reconstitute in water. Fresh oysters are composed of 87% water and 13% solid material of which 6·2% is protein and 1·2% is fat. Oxidation of fat in freeze-dried oysters is very rapid with off-flavours developing within a few hours. The protein, on the other hand, needs to be digested to a certain extent with a proteolytic enzyme before reconstitution in water can be successful. One such proteolytic enzyme from *Streptomyces griseus*, known as Pronase, has been studied by Nomoto and Narahashi (1959). A very small percentage of the enzyme added to the water is substantially more effective in aiding reconstitution of a dry oyster than is puncturing with a pin or prior evacuation of the air from the product to aid penetration of water.

Preparation.—One kg or more of chopped or whole oysters was freeze dried by the cyclic method: the chopped product in 8 hr at a drying temperature below −20°C and the whole product in 12 hr between −10 and −20°C. Heater temperatures were gradually lowered from between 50 and 70°C

in the first hour to between 30 and 35°C towards the end of the run. All oysters were carefully removed from the freeze dryer under an atmosphere of dry inert nitrogen gas, and were then packed in cans *in vacuo*.

Reconstitution of the chopped and whole oysters was carried out in shallow dishes containing water or 0·1% solution of Pronase P so that rehydration took place from the bottom up through the pieces. Some whole oysters were pricked before drying, others after drying, and some whole ones were rehydrated under vacuum.

Results and Discussion.—There was little difficulty in reconstituting chopped oysters in cold water provided that the pieces were small. Reconstitution took some minutes depending on size, but was generally rapid in boiling water. Whole oysters were extremely difficult to reconstitute in cold or warm water, sometimes taking up to 2 hr, during which time off-flavours developed. Pricking or rehydration under vacuum had little or no effect.

When a 0·1% solution of Pronase P was used whole oysters reconstituted completely in about 15 minutes. The slight digestion, resulting from hydrolysis of the peptide bonds in 0·5 g protein estimated for each oyster, was sufficient to allow the water to penetrate through the bottom and up to the top surface of the oyster where the apparent skin was tough and glass-like in appearance. This did not impair their structure or make them too soft for eating. Even when a longer time was allowed for reconstitution excessive digestion was not apparent. The oysters reconstituted under these conditions appeared similar to fresh ones and, provided they were eaten within a short time, appeared to have a reasonable texture and flavour.

2-Mercaptobenzothiazole Control of Browning in Pears

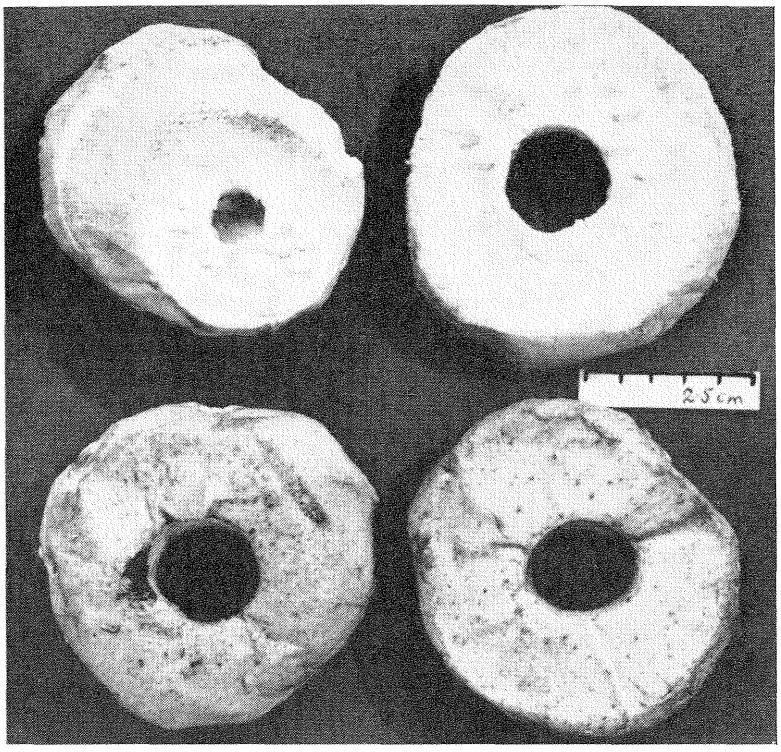
Enzymic browning appears rapidly during preparation of pears and other fruits for freeze drying and has been partially controlled by dipping freshly cut fruit in 0·5% solutions of ascorbic acid. A more powerful agent for this purpose was found to be sodium 2-mercaptobenzothiazole, which could be used in smaller concentrations. Moreover, this substance, while inhibiting non-enzymic browning in storage, did not, as did ascorbic acid, impart a pinkish colour to lighter-coloured dried fruits, especially bananas.

Preparation.—To test the effect of the agent, freshly picked pears were peeled, sliced into 10-mm disks, cored, and part dipped in 0·5% ascorbic acid, part in 0·025% mercaptobenzothiazole solutions, and part left untreated. Treated and untreated samples were frozen to below −20°C and freeze-dried at an average sublimation temperature of −30°C for 11 hr with heater temperatures reduced from 75°C to below 40°C. The products were stored for 22 months at ambient temperature in aluminium foil–plastic laminate pouches sealed under nitrogen gas and had a moisture content of about 4·5%. This figure for moisture content would have been lower had the drying time been extended or the trapped-pressure method used for end-point determination as it has been for freeze drying peas and oysters already described.

Results and Discussion.—The effect of the mercaptobenzothiazole treatment compared with the untreated product may be clearly seen from the photograph. In the treated disk on the top left of the photograph two small patches of darker colour can be observed which are pieces of the skin of the pear still retaining their original green colour against the very light yellowish green colour of the flesh. By contrast the patches in the bottom left untreated product were dark brown against the greyish and speckled coloured flesh. These colour effects were also retained in the freshly rehydrated products, with the untreated products deteriorating rapidly compared with the treated. The results for ascorbic acid treatments were little better than for the untreated samples.

Sucrose and Flavour Retention in Pineapple

Flavour retention in fruit juices and beverages in the course of freeze drying is a much discussed problem. Saravacos and Moyer (1968) have investigated factors that influence flavour retention in pectin, starch, gelatine, cellulose, pectin with added glucose, and apple, and they, as did earlier workers, found that sugars improve flavour retention by what they describe as 'locking-in' of the volatile flavour components rather than by sorption. Flink and Karel (unpublished) reported a critical moisture range below which flavour loss ceases while water removal continues, and Thijssen and Rulkens (1969) have examined flavour retention analytically by considering a model for the product being freeze dried composed of three phases: ice



Freeze-dried pear: *top*, treated with mercaptobenzothiazole; *bottom*, untreated.

phase, liquid phase, and gas phase, and they conclude that flavour retention increases with drying rate, increases with concentration, and increases inversely to the freezing rate.

Much more work will be required to elucidate the many interacting factors involved. However, it is not intended to discuss these in this article but to report that 10% sucrose added to pineapple pulp before freeze drying reduces the loss of the volatile esters making up pineapple flavour.

Such a product has been dried on a semi-industrial scale in under 12 hr using the cyclic method of freeze drying with sublimation temperatures below −25°C and heater temperatures ranging from 70 to 40°C. Final moisture content for the normal product was 1·8% and for the sweetened 2·8%. The normal product was found to have a fair to good colour, texture, and flavour, and the sweetened product could be described as good to excellent.

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News from the Division of Food Preservation

Mr. G. Fisher.

New Technical Secretary

Mr. George Fisher has been appointed to succeed Mr. R. B. Withers as Technical Secretary of the Division. After early training in physics, Mr. Fisher was for many years active in the field of non-destructive testing, first at the University of New South Wales and later in private industry, both in Australia and in England. For the past six years he has been assistant secretary of the Australian Institute of Nuclear Science and Engineering, Lucas Heights, N.S.W. The experience acquired in that capacity should be of value in his new position, which he took up on January 12.

Other Appointments

Dr. R. W. D. Rowe has been appointed to a post-doctoral fellowship in muscle science with the Division of Food Preservation. Dr. Rowe graduated B.Sc. with honours from the University of Hull in 1964 and Ph.D. from the same university in 1967. Since then he has been a research fellow in that University's Department of Zoology.

Three further appointments were made to the professional staff at the Division's Meat Research Laboratory at Cannon Hill, Qld., in October and November 1969 and January 1970, respectively.

Mr. J. C. Bensink, who obtained a diploma in tropical agriculture in Deventer, Holland, and a B.Sc. degree from McGill University in Canada, will carry out laboratory and field investigations of the technological problems in the Australian meat industry.

Dr. J. P. F. M. van Eerd has joined the Division of Food Preservation to study factors affecting the stability of emulsions based on meat proteins and the utilization of meat proteins in manufactured products. Dr. van Eerd graduated B.Sc. from the University of Nijmegen, Holland, in 1966 and Ph.D. from the same university in 1969.

Mr. R. K. Tume, who obtained his B.Sc. (Hons.) degree from the University of Adelaide in 1964, will investigate biochemical mechanisms in the metabolism of muscle and properties of muscle enzymes and subcellular structure.

Miss Carolyn Symmons has joined the group at Ryde studying the production of taint in live mullet, including the substances concerned and their metabolism. Miss Symmons obtained her B.Sc. degree in zoology and biochemistry from London University in 1967.

Overseas Travel

Dr. J. K. Raison, Senior Research Scientist in the Division's Plant Physiology Unit at Sydney University, has accepted a 12-months appointment to work as an assistant research biochemist at the University of California at Riverside, California. The visit will permit continuation of a joint study commenced with Professor J. Lyons, head of the Department of Vegetable Crops at Riverside, during sabbatical leave spent in this Division.

Research to date has defined the chilling sensitivity in plant tissues in terms of mitochondrial activity and further investigation of membrane permeability at low temperatures will have an important bearing on both the basic and applied aspects of plant physiology.

Dr. Raison departed on October 27, 1969, and will return in November 1970.

In *CSIRO Food Preservation Quarterly* Vol. 29 No. 4, the report of the visit by Dr. W. B. McGlasson of the Division's Plant Physiology Unit to the Gordon Research Conference on Post-harvest Physiology and to the Eleventh International Botanical Congress omitted to mention the financial support given by the Organising Committee of the Gordon Research Conference and the Banana Research Advisory Committee of the Commonwealth Department of Primary Industry.

Gas Flames in Food Processing

For some years the Division of Food Preservation has been interested in flame sterilization: the sterilization of canned foods by direct heating in gas flames. As a result of encouragement and assistance from the Division, an Australian company has built and is successfully operating a flame sterilizer processing dairy beverages at the rate of 120 cans per minute. Very high rates of heating, in excess of 4 degF/sec for 10-oz cans, have been achieved in liquid foods by this method.

There are now promising possibilities for other applications of gas flame heating in food processing, for instance in the pasteurization and evaporation of liquid foods such as fruit juices, tomato products, and dairy products.

The Executive of CSIRO has made available to the Division development funds to support a new project to develop a continuous heat exchanger for applications such as pasteurization, atmospheric concentration, and pre-heating for vacuum evaporation. The project will be under the direction of Mr. D. J. Casimir, and two positions are being advertised for a chemical, mechanical, or fuel engineer and an engineering tradesman. It is expected that the widespread availability of natural gas in Australia will greatly increase commercial interest in direct gas heating.

Retirement of F. E. Huelin

An appreciation by J. R. Vickery

Dr. F. E. Huelin retired from the Division of Food Preservation on March 12, after nearly 40 years' service with CSIRO and its predecessor, CSIR. Frank Huelin had acquired an international reputation in the fields of post-harvest physiology and the chemistry of fruits and vegetables. He was one of the small band of pioneers whose work conferred great economic benefits on Australia through the methods they defined for the prevention of wastage in stored fruit and for extending the storage life.

Frank Huelin graduated from the University of Western Australia with a Bachelor of Science degree with chemistry as a major subject. In 1928 he was appointed by CSIR to study the ripening of bananas with Professor L. S. Bagster at the Chemistry Department, University of Queensland. This work, together with complementary studies by Hicks and Young in Melbourne, quickly resulted in highly successful methods of ripening, using low concentrations of ethylene at regulated temperatures.

Huelin's interest in the mechanism of ethylene-assisted ripening was maintained when, in 1930, he was awarded a CSIR overseas studentship tenable at Cambridge University. With Dr. John Barker, at the Low Temperature Research Station, he studied the biochemical effects of ethylene on potato tubers, and he was awarded a Ph.D. degree in 1932. It has probably been a considerable disappointment to Huelin that neither he nor any other research worker has yet been able to define the mechanism of the action of ethylene on its biosynthetic pathway.

When Huelin returned to Australia in 1932, the country was still gripped by the great economic depression, and CSIR had no money to build laboratories. The Victorian Department of Agriculture, however, had useful facilities at the Victoria Dock Cool Stores, Melbourne, and they invited Huelin and his colleague, Dr. S. A. Trout, to join Mr. George Tindale in a team attack on some of the storage disorders in pome, stone, and citrus fruits. Their collaboration in the next few years was highly productive, and several outstanding advances were made, particularly in the study of the metabolism of pears after picking and in defining precisely the conditions necessary for their normal ripening after storage.

By 1941, the Division of Food Preservation, at its headquarters at Homebush, N.S.W., was deeply involved in war-time food technological problems in the supply of food to the armed services, and there was a pressing need for Huelin's help at Homebush. A long series of scientific papers on various aspects of food chemistry, arising from Huelin's war-time investigations, was published during and shortly after the war.

The coating of apples, pears, and other fruits with various materials dissolved or dispersed in water was proposed during the war as a substitute for cold storage, and the Homebush team conducted a large series of feasibility studies. These investigations aroused Huelin's interest in the natural oily or waxy coatings of fruit and in the volatile substances given off by apples after picking. With Mrs. Thompson and R. A. Gallop, he made many notable contributions on the chemical constitution of the volatiles and the oily and waxy components of the coatings.

In all this work, Huelin had in mind the causation of superficial scald, a serious disorder in several varieties of apples and pears, particularly Granny Smith apples. Circumstantial evidence pointed to a volatile substance produced by the fruit as being the

causal agent, but all attempts to identify it had failed. Success came nearer in 1964, when Murray, Huelin, and Davenport discovered α-farnesene in the natural coating of apples. While α-farnesene itself is not the cause of superficial scald, it is now almost certain, following further work by Huelin and his colleagues, that the oxidation products of this substance are responsible for the disorder.

The output of many research workers diminishes in volume and importance with age; in contrast, Huelin's career has been marked by a sustained effort over 40 years, with the output rate and relevance of his latest work probably exceeding that of 30 years ago, as is evident in the bibliography.

Because of his wide knowledge and gifts, Frank Huelin is going to be difficult to replace. His colleagues will miss his wise counsels, his kindliness, and that little touch of eccentricity which marks so many good scientists.

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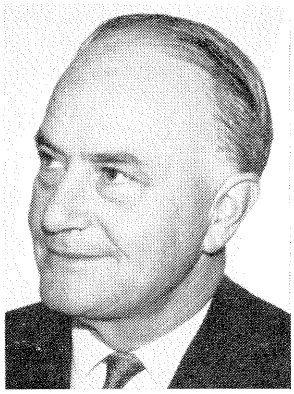
CORRIGENDA

CSIRO Food Preservation Quarterly Vol. 29, No. 3, September 1969

Page 46, column 2, line 26:
Delete 'per hr' *after* '1 kW'.

Page 47, Figure 4, right-hand view:
Delete 'k' *in* '500 kW'.

Stephen Myles Sykes, 1918-69



Mr. S. M. Sykes, universally known to his food technologist friends as 'Bill', died suddenly in Hobart on November 17, 1969.

After graduation in Agricultural Science at the University of Sydney, Bill Sykes worked for the CSIRO Division of Food Preservation, Homebush, N.S.W., for a short period in 1943–44 in fruit storage research. He then became a Fruit Research Officer of the N.S.W. Department of Agriculture although he continued to be stationed at Homebush. After an overseas tour in 1947 investigating the frozen food industry, he set up pioneering research programmes on the freezing of fruits and vegetables which greatly assisted the frozen food industry in Australia during its formative period.

In 1958 Sykes rejoined the staff of the Division of Food Preservation when he was appointed leader of the Food Research Unit at the CSIRO Tasmanian Regional Laboratory, Hobart. Here he swiftly gained the confidence of the Tasmanian food industry and was very frequently consulted on a wide range of local problems. At the same time he conducted research and development programmes on the canning and freezing of berry fruits and peas, the canning and drying of apples, and the processing and quality assessment of potatoes. He also supervised fish preservation research at the Hobart Laboratories embracing studies on Australian salmon, crayfish, and abalone.

In 1963 he was awarded the degree of M.Sc. from the University of Hobart for a thesis on 'A Kinetic Study of the Drying of Apples'.

Sykes was a foundation associate of A.I.F.S.T., having been a member of I.F.T. for many years. In the early stages of food technology education in Australia he was a part-time lecturer at Sydney Technical College and the University of New South Wales.

He is survived by his widow and three children. Mrs. Sykes is a graduate in Agricultural Science, and met her husband when they both worked in the Homebush laboratories. During 1969 she accompanied him on a tour of food laboratories and processing plants in America, Great Britain, and Europe.

In addition to his valued advice and assistance to the food industry in Tasmania, Sykes made a major contribution to community life in Hobart through his devotion to music and his self-effacing charitable work in the Society of St Vincent de Paul.

J. F. KEFFORD

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1962. Rapid estimation of moisture in dried apples. (With G. G. Coote.) CSIRO Aust. Div. Fd Preserv. tech. Pap. No. 29.

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1969. Kinetics of drying apple slices. (With F. H. C. Kelly.) *J. Sci. Fd Agric.* **20**, 654–9.

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Copies of most of these papers are available from the Librarian, CSIRO Division of Food Preservation, P.O. Box 43, Ryde, N.S.W. 2112 (Telephone 88 0233).

ANET, E. F. L. J. (1969).—Autoxidation of α-farnesene. *Aust. J. Chem.* **22**, 2403–10.

BOARD, P. W., and HOLLAND, R. V. (1969).—Inhibition of nitrate-induced corrosion of tinplate cans. *Br. Corrosion J.* **4**, 162–5.

BOARD, P. W. (1969).—Practical heat sterilization. *Proc. roy. Aust. chem. Inst.* **36**, 125–30.

CHRISTIE, ELIZABETH M., and ROPE, EILEEN (1969).—Application of testing methodology in the brewery. Proc. Inst. Brewing, Aust. & N.Z. Sect. Convention 10th. pp. 1789–91.*

DAVENPORT, J. B. (1969).—Chromatography of lipids on polystyrene gel column. *Lipids* **4**, 308.*

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* Copies not available for distribution.

† Not an officer of CSIRO.

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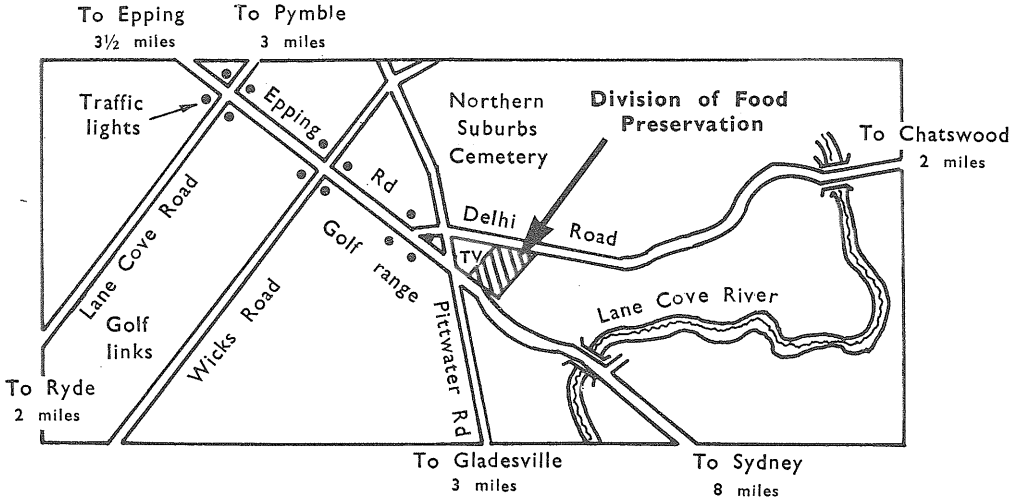

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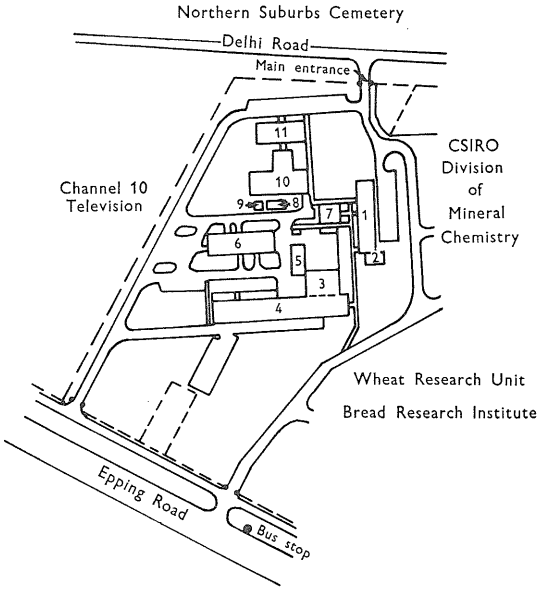

1 Administration and library
2 E. W. Hicks meeting room
3 Controlled-temperature rooms
4 Food science building
5 Boiler house and engine room
6 Workshops and store
7 Canteen and taste test room
8 Sulphuring room, liquid air plant
9 Refrigeration plant for blast freezer
10 Food processing building
11 Food technology building