ELSEVIER

PII: S0308-8146(97)00165-9

Food Chemistry, Vol. 62, No. 1, pp. 59–64, 1998

Printed in Great Britain
0308-8146/98 $19.00+0.00

A comparison of the vitamin C content of fresh and frozen vegetables

D. J. Favell

Unilever Research, Colworth Laboratory, Sharnbrook, Bedford, UK

(Received 23 December 1996; revised version received and accepted 17 July 1997)

This study, using vitamin C (ascorbic acid) as 'marker', allowed a direct comparison of the nutritional quality of fresh vegetables at various stages of distribution and storage, with the same vegetable commercially quick-frozen and stored deep frozen for up to 12 months. The nutrient status of frozen peas and broccoli was similar to that of the typical market-purchased vegetable and was superior to peas that have been stored in-home for several days. Fresh peas and broccoli retained their quality for up to 14 days when stored under chill conditions. The nutrient status of frozen whole green beans and frozen carrots, with no loss on freezing, was similar to the fresh vegetable at harvest. Frozen spinach also compared reasonably well with the harvested fresh vegetable and was clearly superior to all market produce. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Vegetables are an important component of the European diet, traditionally served alongside a protein food (e.g. meat, fish) or a carbohydrate food (e.g. pasta, rice, potato). They provide not only textural and colour variety to the main meal of the day but, importantly, often complementary nutrients such as dietary fibre, and certain vitamins and minerals. Vegetables are estimated to provide 30% of the vitamin C, 20% of the vitamin A (as carotenes), and 10% of the thiamine and iron of the average UK diet (Household Food Consumption and Expenditure, 1985, HMSO). Vegetables are also a rich source of folate (DoH Report 41, 1991).

The nutritional advice to 'eat less fat, more complex carbohydrate, more dietary fibre' has resulted in the current dietary advice to increase the consumption of vegetables (and fruit). Vegetables, as a group, are low fat, low energy, relatively low protein, but are high carbohydrate, high fibre foods which provide significant levels of certain micronutrients to the diet. These attributes are readily identified with fresh vegetables, but often are not accepted as appropriate to the commercially frozen vegetables, particularly with regard to the micronutrients. The consumer views 'fresh' as natural, wholesome, and hence full of nutrients, whilst 'processed', even the relatively mild process of 'quick-freezing', is seen as substantially reducing nutrient content.

Fresh vegetables available to the consumer have typically spent a period of 3–7 days in retail distribution and storage before consumption (Bushway *et al.*, 1989). Increasingly this transportation and storage is made at lower temperatures (i.e. refrigerated), but the traditional greengrocer and market trader and many householders continue to transport and store vegetables at ambient temperatures. Thus, fresh vegetables can be exposed to a variety of conditions which offer the potential for change in quality characteristics, including nutrient content (Perrin and Gaye, 1986; Shewfelt, 1990), before in-home cooking and consumption. On the other hand, vegetables for commercial freezing are frozen soon after harvest. Changes can occur, particularly during blanching (Lathrop and Leung, 1980)—necessary to inactivate natural enzymes (Guenes and Bayindirli, 1993)—but little further change can be expected thereafter during deep frozen storage (Bender, 1971). It is probable that the nutrient content of the fresh vegetable will, at some time during retail distribution and storage, be equal to that of the frozen vegetable, and will continue to fall to below that of frozen thereafter. This paper reports a study of the nutrient changes during the storage of fresh vegetables, over a period of days and weeks, and those of the corresponding frozen vegetables, post-process and stored for up to 12 months.

Ascorbic acid (vitamin C) is the micronutrient most readily associated with vegetables (and fruit). Vitamin C content varies considerably between different vegetables;

e.g. brassicas generally contain high levels (50–100 mg/100 g), and root crops relatively little (< 10 mg/100 g). Even within a particular vegetable type, vitamin C content can vary; i.e. peas can contain from 20 to 40 mg/100 g at harvest, depending upon variety, agronomy, etc. (Lee *et al.*, 1976). Thus, the level of vitamin C is not an indicator of quality per se, but, since the vitamin is vulnerable to chemical and enzymic oxidation, and is highly water soluble, it is a sensitive and appropriate marker for monitoring quality change during transportation, processing, and storage (Clegg, 1974; Morrison, 1974).

Nutritional quality comparisons of fresh or market vegetables with commercial frozen vegetables have often been inconclusive because of the 'unknown' differences in the source of the vegetables used (Hudson *et al.*, 1986; Bushway *et al.*, 1989), or because simulated (i.e. bench or pilot scale) processing has been used (Russell *et al.*, 1983; Ying Wu *et al.*, 1992). In the study reported here, five vegetables widely available in both fresh and frozen form to the European consumer—peas, green beans, spinach, broccoli, and carrots—are featured, and the study focuses on the changes in their vitamin C (mainly ascorbic acid) content over time. The work was done on location at commercial freezer plants, which allowed for study of the particular vegetable after conventional freezing, and the identical produce after storage at various temperatures to mimic transportation, marketing, and storage of fresh produce.

MATERIALS AND METHODS

Vegetable source

In each case the analytical study was made in the respective production sites as follows: peas, UK; green beans, Italy; spinach, Germany; broccoli, UK; carrots, Austria. Key commercial varieties of each vegetable were studied on two occasions (for most) during the normal growing season (e.g. early and late). 'Frozen' was defined as 'the conventionally quick-frozen vegetable'. 'Fresh' was defined as 'the harvested vegetables as they arrive at the factory', except peas when 24 kg of pods were hand picked (from various positions in the field being mechanically harvested) and brought to the factory with the mechanically harvested crop. 'Grab' samples of the fresh vegetables, to give a total of approx. 24 kg, were taken from various parts of the transporter, mixed to give homogeneity (without damage), and then divided into 24 portions of approx. 1 kg in mesh bags (nets).

Sample regime

For fresh vegetables, start of trial samples ($t = 0$) was analysed as soon after arrival at the factory as possible. For this, 4×1-kg bags were taken and the 'edible' portion analysed. Eight 1-kg bags were put on store at ambient temperature: 12×1-kg bags were put on store in chill temperature, four of which were transferred to ambient store on day 3.

The samples were taken for analysis according to the following scheme:

	Day 0	Day 1	Day 2	Day 3	Day 7	Day 14	Day 21
Ambient	4	1	1	2	1	1	2
Chill		1	1	2	1	1	2
ChillAmb					1	1	2

Where Ambient = 20°C; Chill = 4°C; and ChillAmb = chill storage for 3 days[a] then moved to Ambient for remainder of trial.

[a]Based on information on distribution/sales practice in major stores.

For the frozen vegetables, 24 packs (500 g–1 kg) produced from the same crop were put aside and held at −20°C. Eight packs were sampled on day 1, combined in 4×2 samples before analysis, then the remainder were similarly sampled and analysed after storage for 3, 6 and 12 months.

Analysis

All samples were analysed in duplicate for the following components. (1) Ascorbic acid: by the indophenol titration method (Association of Vitamin Chemists, 1966). In outline, ascorbic acid is extracted into metaphosphoric acid solution and titrated against 2,6-dichlorophenol-indophenol solution at pH 0.6 in the presence of formaldehyde, to a pink endpoint. (2) Dry matter content.

Each of the production sites was requested to follow the experimental design as closely as possible. However, the major variations were as follows: (i) peas—the three main varieties in current production, Avola, Bikini, and Novella were studied; (ii) spinach—leafy vegetables are reported (Blumenthal *et al.*, 1980) to contain significant levels of dehydroascorbic acid (DHAA), thus it was decided to use a variant of the indophenol method (titration before and after DHAA reduction with homocysteine) which enabled the measurement of ascorbic acid (AA), and total ascorbic acid (AA + DHAA).

Assay performance

The analyses were made in five different laboratories, and although each study was self-contained and essentially independent, a sample of potato powder was distributed to each laboratory as a check on performance. The data obtained for the potato powder from the participating laboratories were in the range 106–124 mg/100 g (i.e. 115 ± 10 mg/100 g), which was considered satisfactory.

A comparison of the two variants of the indophenol titration method (one measuring only AA, the other measuring total vitamin C) with an HPLC method measuring total vitamin C was made on frozen spinach samples. The results for four samples of spinach showed good agreement between methods (difference of < ±3 mg/100 g), demonstrating satisfactory performance of methods and also demonstrating the absence of any significant amount of DHAA in the frozen spinach samples.

Typical differences between the replicate samples on a single occasion for each of the vegetables were: peas and carrots < ±1 mg/100 g; spinach and green beans < ±2 mg/100 g; broccoli < ±3 mg/100 g.

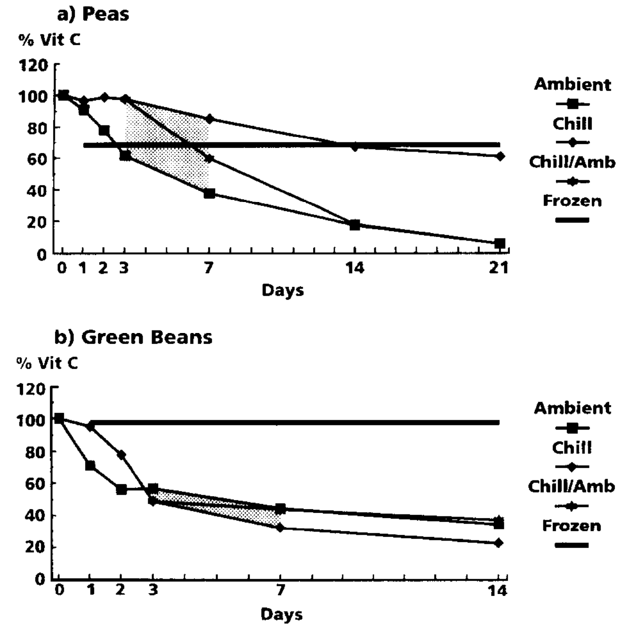

Fig. 1. Vitamin C retention in peas and green beans.

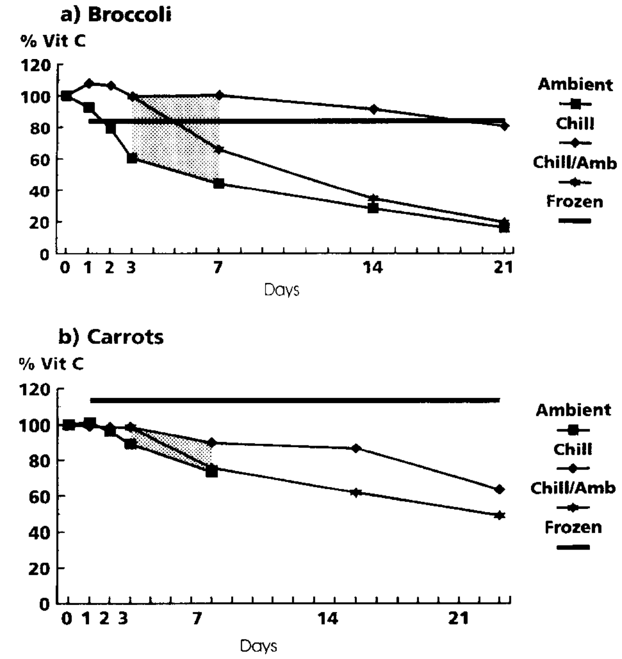

Fig. 2. Vitamin C retention in broccoli and carrots.

RESULTS

Peas

The average percentage retention of ascorbic acid in the three studies, expressed relative to day 0 sample dry matter, is shown in Fig. 1a. The three varieties, Avola (early season), Bikini (mid-season), and Novella (late season), had ascorbic acid contents of 31, 30, and 26 mg/100 g, respectively, immediately post-harvest, values typical for field-fresh peas. The frozen peas, analysed 1 day post-production, showed a loss on process of approximately 30% (range 26–37%), giving values in product of 20, 22, and 17 mg/100 g, again typical for commercially quick-frozen peas. Avola showed the greatest processing losses, Bikini the least. The frozen peas were re-examined after 3 and 6/7 months and 12 months storage; the ascorbic acid content decrease through the 12-month period was less than 10%.

Fresh peas in their pods were put on store in fine-mesh bags, stored under the specified conditions, and sampled for analysis as outlined in the Materials and methods. The samples stored at 4°C (Chill) showed little change in ascorbic acid content in the first 3 days, but deteriorated steadily at 2–3% per day thereafter. The rate of change was similar for each variety. The peas stored at ambient temperature (20°C) showed a much faster loss of ascorbic acid, the level deteriorating at about 10% per day over the first 7 days, and somewhat slower thereafter. The samples transferred from chill to ambient after day 3 showed the predicted profile; thus, after 3 days with little change, the loss of ascorbic acid increased to 10% per day, paralleling the ambient samples.

Whole green beans

The average percentage retention of ascorbic acid in the whole green bean samples is expressed relative to day 0 sample dry matter (Fig. 1b). The ascorbic acid contents of the initial samples of whole green beans were 15 and 12 mg/100 g and this level was almost fully retained in the blanched/frozen sample. Loss on subsequent frozen

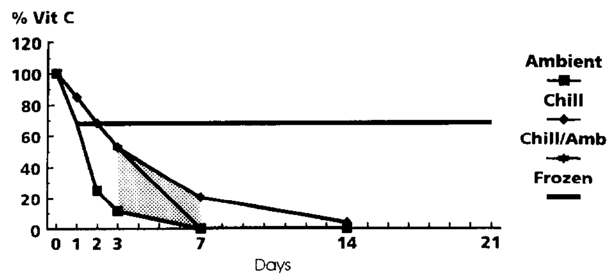

Fig. 3. Total vitamin C retention in spinach.

Table 1. Comparison of vitamin C in 'fresh' and frozen vegetables

	Garden fresh	Market fresh	Market fresh as used	Supermarket fresh	Supermarket fresh as used (1)	Supermarket fresh as used (2)	Frozen Product	
							Initial	Stored (12 months)
Peas	30.9	20.6	12.1	28.8	27.4	17.1	19.6	17.2
	29.6	16.6	11.1	30.4	23.8	17.1	21.8	19.5
	25.6	15.7	9.2	24.7	22.0	16.8	17.3	17.4
Broccoli	77.1	47.0	34.8	77.8	81.3	50.6	66.1	64.3
	93.1	55.7	40.4	91.5	88.4	61.6	76.7	73.7
Green beans	15.1	7.9	6.9	7.6	6.9	3.7	15.1	17.6
	11.8	7.2	5.1	5.6	4.7	5.1	11.2	n/a
Spinach	31.6	3.2	0	14.3	6.5	0	24.5	16.2
	21.6	2.6	0	12.8	4.2	0	12.6	n/a
Carrots	4.4	3.8	2.9	4.5	3.7	2.8	4.6	n/a
	3.7	3.4	3.0	3.5	3.5	3.2	4.4	n/a

All results are expressed as mg/100 g.

storage for 12 months was less than 20%. The fresh stored samples at ambient temperature initially lost ascorbic acid quickly, up to 30% after 1 day, but the rate of loss decreased thereafter and even after 14 days, when the product was totally inedible, nearly 40% of the ascorbic acid remained.

The samples stored at chill initially retained their ascorbic acid well, but this then declined steadily to a level below that in the ambient stored sample. The chill/ambient sample showed a similar stabilisation of ascorbic acid during the ambient storage phase.

Broccoli

The average percentage retention of ascorbic acid in the broccoli samples is expressed relative to day 0 dry matter (Fig. 2a). The levels of ascorbic acid in the freshly harvested broccoli were high at 77 and 93 mg/100 g, respectively, in the two trials, fairly typical values for broccoli. After the freezing/blanching process greater than 80% was retained, and there was little further loss (< 10%) during subsequent frozen storage.

On ambient storage of the fresh samples, when whole heads were put on store but 20-cm diameter florets analysed, a steady loss of ascorbic acid occurred with only 44% retained after 7 days and only 28% after 14 days. However, when stored at chill temperature, the retention of ascorbic acid was very good with no loss after 7 days; even after 21 days 80% of the vitamin remained. The chill/ambient stored samples showed no loss of the vitamin whilst in chill, but a rapid loss when moved to ambient, as had been observed in the samples stored at ambient from the outset.

Carrots

The data are expressed relative to day 0 dry matter (Fig. 2b). The level of ascorbic acid in the initial samples from both trials is approximately 4 mg/100 g, a typical value for carrots. There was no loss of ascorbic acid during the blanching/freezing process, indeed the levels found in both frozen samples were slightly higher than the initial values. It is most unlikely that processing is making ascorbic acid, rather it is an artefact of the analytical method, most probably the extraction stage. The ascorbic acid in the ambient stored samples held steady for 2 days then declined, falling after 7 days to 66% of the initial value in trial 1 but only to 81% in trial 2. Further sampling of the ambient stored samples was aborted due to severe moulding. The chilled stored samples showed much greater stability, the level of ascorbic acid remaining above 85% even after 14 days.

Spinach

The data are expressed relative to day 0 dry matter (Fig. 3). The initial samples had ascorbic acid (and total vitamin C) contents of 31 and 22 mg/100 g which reduced to 24 and 13 mg/100 g, respectively (78 and 58% retention), after the blanching/freezing process. A further 30% loss occurred during 12 months of deep frozen storage.

The ambient stored samples lost ascorbic acid very rapidly with only 10% remaining after 3 days. The chill sample lost ascorbic acid less rapidly, but even so only 20% remained after 7 days, falling to zero before day 14. The chill/ambient samples also rapidly lost ascorbic acid when transferred to the ambient conditions.

Table 2. The rate of loss of vitamin C at ambient and chill storage

	% Loss per day (averaged over 7 days)		Days to frozen value	
	Ambient	Chill	Ambient	Chill
Peas	8.9	2.1	< 3	14
Broccoli	8.0	0	< 2	18
Green beans	7.8	10.8	< 1	1
Spinach	> 14.2	10.7	< 1	< 2
Carrots	3.8	1.4	< 1	< 1

DISCUSSION

In any comparison of the quality aspects of fresh versus frozen vegetables it is important to define precisely the various terms that are used. Thus, it is clear that the freshest, and most probably the best quality is the immediate post-harvest 'garden fresh' produce. However, this is not commonly available to the consumer who purchases either from a greengrocer or, more commonly now, from the supermarket. Produce purchased from the greengrocer, 'market fresh', has traditionally been transported and stored pending sale at ambient temperature, whilst that purchased from the supermarket, 'supermarket fresh', has most probably been transported and stored at chill temperature. The purchased vegetables can be further stored at ambient or chill temperatures, by the consumer prior to use, giving further scope for quality changes. The quality of the final cooked vegetable is the most important of all, but because of the wide variety of cooking methods/times used by the consumer (Rognerud, 1972) and the already complex logistics of study on the 'raw' samples, the cooking stage has not been included in this study. The cooking time specified for the frozen vegetable is normally less than that specified for the fresh, and so losses during end cooking of frozen should be no greater than will be incurred in the cooking of the fresh.

The definition of the frozen vegetable is produce that has been harvested, prepared, blanched and quick frozen under the commercial conditions appropriate for each vegetable. However, the frozen produce is not immediately available to the consumer, and typically several months of low temperature storage can elapse before purchase and several more are possible during in-home storage.

The overall design of the study therefore sought to cover the various alternative modes of storage during transportation, retail and in-home prior to the ultimate point of use of the vegetables. The various storage temperatures and sampling times can be equated to the various 'fresh' definitions thus:

Garden fresh	Day 0 sample
Market fresh	Day 3 Ambient sample
Market fresh as used	Day 3 to day 7 Ambient sample
Supermarket fresh	Day 2/3 Chill sample
Supermarket fresh as used (1)	Day 3 Chill to day 7 chill sample
Supermarket fresh as used (2)	Day 3 Chill to day 7 Chill/Ambient sample

For frozen vegetables, samples were analysed initially on the day after production, and then after further storage at $-18°C$ for 3, 6/7, and 12 months. Changes observed thus far have been minimal.

The ascorbic acid levels in these various categories of fresh vegetables are compared with the levels in the corresponding frozen samples in Table 1.

For all vegetables studied, the vitamin C level in the commercially quick-frozen product is: (i) equal to or better than that in the 'market fresh'; (ii) much better than that in the 'market fresh as used'; or (iii) better than that in the 'supermarket fresh/ambient stored, i.e. as used (ii). The superior level of vitamin C in the quick-frozen product also applies to: (i) all market and supermarket whole green beans; (ii) all market and supermarket spinach; and (iii) all market and supermarket carrots. Further comparisons on the rate of loss of vitamin C from the fresh vegetables under ambient and chill storage conditions, and also the respective number of days storage needed to give a vitamin C level equal to that in the frozen, are given in Table 2.

The data show a rapid loss of ascorbic acid from all vegetables, except carrots, at ambient temperature, and this rapid loss is also seen at chill temperatures for spinach and whole green beans. The rate of loss of ascorbic acid from peas, carrots, and particularly broccoli, is slow at chill temperature. These observations on the rate of change during chill storage are in line with earlier studies (Albrecht *et al.*, 1990) who observed good stability of vitamin C in brassicas generally, moderate stability in peas, and poor stability in green beans. The postulated theory that sulphur or sulphydryl compounds are primarily responsible (Eheart and Odland, 1972) was not proven (Albrecht *et al.*, 1991), but such compounds may play a part.

The loss of ascorbic acid from all these vegetables is most probably dominated by enzyme-induced oxidation. The variation in the rate of loss demonstrates the differing vulnerabilities of the different vegetables, e.g. surface area, mechanical damage, sulphydryl content, as well as their differing enzyme activities. Peas, stored in their pods, clearly have an element of protection; broccoli, stored as whole florets, and carrots will not be unduly damaged at harvest. At the other extreme, spinach leaf is very vulnerable post-harvest. The green bean, harvested whole, should not suffer undue damage at harvest, but nevertheless seems particularly vulnerable presumably due to the high enzyme activity, and possibly also to low sulphydryl content.

ACKNOWLEDGEMENTS

Significant contributions to the work reported here were made by colleagues in Birds Eye Walls, Lowestoft, UK, in Sagit, Cisterna, Italy, in Langnese Iglo GmbH, Reken, Germany, in Unifrost GmbH, Gross-Enzersdorf, Austria, and in the Measurement Science Dept, Unilever Research, Colworth, UK.

REFERENCES

Albrecht, J. A., Schaffer, H. W. and Zottola, E. A. (1990) Relationship of total sulphur to initial and retained ascorbic acid in selected cruciferous and non-cruciferous vegetables. *Journal of Food Science* **55**, 181–183.

Albrecht, J. A., Schaffer, H. W. and Zottola, E. A. (1991) Sulphydryl and ascorbic acid relationships in selected vegetables and fruits. *Journal of Food Science* **56**, 427–430.

Association of Vitamin Chemists (1966) *Methods of Vitamin Assay* (3rd edn.) Wiley and Sons (London and New York).

Bender A. E. (1971) The fate of vitamins in food processing operations. *Vitamins*, ed. M. Stein. Churchill Livingstone (Edinburgh and London).

Blumenthal, A., Meier, M. and von Kaenel, B. (1980) The nutrient content of prepared foods I—vitamin C contents of fresh and industrially frozen leaf spinach before and after domestic and institutional preparation. *Alimenta* **19**, 95–97.

Bushway, R. J., Helper, P. R., King, J., Perkins, B. and Krishnan, M. (1989) Comparison of ascorbic acid content of supermarket versus roadside stand produce. *Journal of Food Quality* **12**, 99–105.

Clegg, K. M. (1974) Frozen vegetables. *Nutrition and Food Science* **36**, 6–8.

Dietary Reference Values for Food Energy and Nutrients for the United Kingdom (1991) DoH Report on Health and Social Subjects, No. 41 (HMSO).

Eheart, M. S. and Odland, D. (1972) Storage of fresh broccoli and green beans. *Journal of the American Dietetic Association* **60**, 402–406.

Guenes, B. and Bayindirli, A. (1993) Peroxidase and lipoxygenase inactivation during blanching of green beans, green peas and spinach. *Lebens. Wissenschaft u Technol.* **26**, 406–410.

Household Food Consumption and Expenditure (1985) Annual Report of the Food Survey Committee (HMSO).

Hudson, D. E., Cappellini, M. and Lachance, P. A. (1986) Ascorbic acid content of broccoli during blanching. *Journal of Food Quality* **9**, 31–37.

Lathrop, P. J. and Leung, H. K. (1980) Rates of ascorbic acid degradation during thermal processing of canned peas. *Journal of Food Science* **45**, 152–153.

Lee, C. Y., Downing, D. L., Tredale, H. D. and Chapman, J. A. (1976) The variations of ascorbic acid content in vegetable processing. *Food Chemistry* **1**, 15–22.

Morrison, M. H. (1974) The vitamin C and thiamine contents of quick frozen peas. *Journal of Food Technology* **9**, 491–500.

Perrin, P. W. and Gaye, M. M. (1986) Effects of simulated retail display and overnight storage treatments on quality maintenance in fresh broccoli. *Journal of Food Science* **51**, 146–149.

Rognerud, G. (1972) Content and retention of ascorbic acid in cooked frozen vegetables. *Tidskrift for Hermetikindustri* **58**, 130–135.

Russell, L. F., Mullin, W. J. and Wood, D. F. (1983) Vitamin C content of fresh spinach. *Nutrition Reports International* **28**, 1149–1158.

Shewfelt, R. L. (1990) Sources of variation in the nutrient content of agricultural commodities from the farm to the consumer. *Journal of Food Quality* **13**, 37–54.

Ying, Wu, Perry, A. W. and Klein, B. P. (1992) Vitamin C and β-carotene in fresh and frozen green beans and broccoli in a simulated system. *Journal of Food Quality* **15**, 87–96.