Pigment Composition and Color of Frozen and Canned Kiwi Fruit Slices

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Qualitative pigment differences between fresh (unripe and ripe), frozen, and canned kiwi fruit slices were determined. Pigments present in fresh and frozen kiwi fruit slices were xanthophylls, chlorophylls and their derivatives, and only one hydrocarbon carotenoid (β-carotene). The xanthophylls were identified as violaxanthin, neoxanthin, neochrome, auroxanthin, lutein epoxide, and lutein. Neo A and neo B, mono cis isomers of lutein, were observed in the extracts of fresh and frozen slices. The chlorophylls were identified as chlorophyll *b* and chlorophyll *a*, and the decomposition product as pheophytin *a*. The pigment pattern of the canned product showed the formation of zinc complexes, specifically the formation of the metallochlorophyll complexes, Zn–pheophytin *a* and Zn–pyropheophytin *a*. Thermal treatment induced the degradation of some xanthophylls, violaxanthin and neoxanthin, to afford neochromes, luteoxanthin and auroxanthin. *all-trans*-Lutein was accompanied by considerable amount of its 15,15′-isomer in canned kiwi fruit extracts. Large differences in Hunter color value −*a* (green) were observed between fresh or frozen and canned kiwi fruit slices. Hunter color values of frozen slices approached the color of fresh kiwi fruit.

INTRODUCTION

Kiwi fruit (*Actinidia chinensis* Planch) is grown extensively in New Zealand with 129 000 tons of fresh fruit being exported in the year ending June 1987 and with a 2-fold increase in production expected between 1987 and 1992 (New Zealand Kiwifruit Authority, 1986). In Spain, kiwi fruit is a relatively new crop, mainly harvested in the North of the country. Fruit which does not meet export standard and is not sold on the domestic fresh fruit market is processed into various products, primarily canned slices in syrup, frozen pulp and slices, juices, and wines. Changes in product quality after processing and prolonged storage of these commercial products have been suggested as being responsible for some of its marketing difficulties.

As long as the quantity of kiwi fruit available for processing rises, it becomes increasingly important to have a comprehensive knowledge of the composition of the fruit and the changes that it undergoes during processing. Changes in the composition and organoleptic properties on canning and freezing of kiwi fruit were reported by Beutel et al. (1976). Simmons (1978) investigated the drying of kiwi fruit with particular reference to color retention and gave a qualitative assessment of the candied product.

The biochemical, sensory, and quality changes that occur during processing and prolonged frozen storage of kiwi fruit pulp were studied by Venning et al. (1989). This work indicate that the temperature and processing time during pulp manufacture and freezing are critical factors in determining the percent total chlorophylls and ascorbic acid content of the product.

The retention of the bright green color of vegetables during heat processing has long been the goal of research in the canning industry. The degradation of chlorophylls involved a number of reactions. In the past years it has been shown that not only is the formation of pheophytins involved in the formation of the olive green color of canned vegetables, but also in the formation of pyropheophytins (Schwartz et al., 1981; Schwartz and Elbe, 1983).

A number of attempts have been made to preserve chlorophylls during heat processing through the application of different technics (pH control, high-temperature short-time processing, or a combination of these two factors) (Buckle and Edwards, 1970; Malecki, 1978). Regreening of vegetables has been observed and attributed to the formation of metallochlorophyll complexes. Elbe et al. (1986) reported the formation of zinc complexes, specifically the formation of the metallochlorophyll complexes, Zn–pheophytin *a* and Zn–pyropheophytin *a*, in Veri-Green canned beans. The application of high-performance liquid chromatography to separate zinc and copper complexes of pheophytin has been demonstrated by Schwartz (1984), and the pigment pattern of kiwi fruit flesh of the four major varieties (Hayward, Bruno, Monty, and Abbott) has been recently reported by Cano (1991).

The present investigation was made to determine qualitative pigment differences between fresh (unripe and ripe fruit), frozen, and conventional canned slices of kiwi fruit (cv. Hayward) in order to establish the pigment degradation due to freezing and canning preservation.

EXPERIMENTAL PROCEDURES

Reagents and Materials. The reference samples of chlorophyll *a* and *b* (Sigma–Aldrich, S.A.) were used without further purification. Lutein, zeaxanthin, and *all-trans*-β-carotene were provided by Hoffman-La Roche, Basel, Switzerland. HPLC-grade solvents, methanol and ethyl acetate (Promochem, W. Germany), were used without further purification. Pheophytins *a* and *b* were prepared by acidifying ether solutions of the chlorophylls with 13% HCl. The acid was removed by washing the ether layer twice with an equal volume of 5% Na_2SO_4. The pheophytin/ether mixture was dried over anhydrous Na_2SO_4 and evaporated under stream of N_2.

Canned samples of kiwi fruit slices (cv. Hayward) in syrup (17–19 °Brix) processed by conventional methods were supplied by Grower Cannaries Ltd., Hastings (New Zealand). Fresh kiwi fruits (cv. Hayward) cultivated in New Zealand were obtained from commercial sources (unripe stage) and stored at 1–2 °C under 90% relative humidity for near 2 months until the best maturity (ripe stage) for freezing preservation was reached.

Kiwi fruits were hand-peeled, sliced (6–8 mm), and frozen at −40 °C and 5.5 m/s air rate in an air blast freezer until the temperature of the product was raised to −20 °C. Frozen slices were packed in polyethylene bags, vacuum sealed, and stored at −18 °C for 6 months.

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Table I. TLC Bands Separated in the Order of Chromatographic Elution of Kiwi Fruit Extracts

fresh and frozen samples				canned samples		
band	color	R_f	chemical class	band	color	R_f
1	yellow	0.96	carotenes	1	yellow	0.96
2	gray-green	0.79	chlorophylls	2	gray-green	0.79
3	green	0.68	chlorophylls	3	green	0.68
4	light-green	0.65	chlorophylls	4	light-green	0.65
5	yellow-green	0.60	chlorophyll	5	yellow-green	0.60
6			xanthophylls	6	orange-yellow	0.58
7	orange-yellow	0.55	xanthophylls	7	orange-yellow	0.55
8	yellow	0.34	xanthophylls	8	yellow	0.34
9	light-yellow	0.32	xanthophylls	9	light-yellow	0.32
10			metallochlorophyll complexes	10	green	0.10
11			metallochlorophyll complexes	11	green	0.08
12	yellow	0.05	xanthophylls	12	yellow	0.05

Determination of Color Data. Triplicate samples (approximately 50 g) were pureed and placed in a 5-cm-diameter plastic dish to depth of not less than 2 cm. The sample dish was placed on the light port of a Hunter Lab Model D25-9 colorimeter. The instrument was standardized on a white plate, and accuracy was checked with standard green ($Y = 43.2$, $X = 36.4$, $Z = 44.1$). The sample dish was covered to avoid stray light. The L, a, and b values were recorded, and derived functions for hue (h), saturation (C), and total color differences (ΔE) were calculated: $h = \arctan(b/a)$; $C = (a^2 + b^2)^{1/2}$; $\Delta E = (L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2)^{1/2}$.

Pigment Analysis. Duplicates of all samples were extracted and analyzed for pigment composition by using high-performance liquid chromatography as follow.

Apparatus. A Hewlett-Packard Model 1040 quaternary solvent delivery system equipped with a Hewlett-Packard 1040A rapi-scanning UV/visible photodiode array detector was employed. The data were stored and processed by means of a Hewlett-Packard Model 9000/300 computing system and Color Pro plotter. The absorption spectra of the pigments were recorded between 300 and 600 nm at the rate of 12 spectra/min. The HP-9000 computer with a built-in integration program was used to evaluate the peak area and peak height. Absorption spectra of isolated components in various solvents were recorded on a Perkin-Elmer Lambda 15 UV/visible spectrophotometer.

Column. Separations were performed on a stainless-steel (10-cm × 4.6-mm-i.d.) Hypersil ODS (5-μm spherical particles) column (Hewlett-Packard), which was protected with a Hibar guard cartridge (3-cm length × 4.6-mm i.d.) packed with Spherisorp-C18 (5-μm particle size).

Chromatographic Procedure. The analytical separations were carried out according to a modified procedure of Schwartz et al. (1981). Gradient chromatography separated different components of the pigment pattern (xanthophylls, chlorophylls, and hydrocarbon carotenoids). A gradient mixture of methanol/water (75:25), eluent A, and ethyl acetate, eluent B, was used, beginning at time zero until time 10 (min) with a semifinal composition of eluent B (70%). The gradient eluent composition was followed at time 10 until time 14 (min) with the final composition of eluent B (100%). The flow rate employed was 1.7 mL/min, and the chromatographic runs were monitored at 430 nm. At the end of the gradient the column was reequilibrated under the initial conditions by a new gradient condition beginning at time 14 until time 20 (min) with a final composition of eluent B (0%) at the same flow rate (1.7 mL/min) (Cano, 1991).

Preparation of Fruit Samples for Extraction. Kiwi fruits were prepared for analysis in the same way they are prepared for consumption, i.e. inedible parts removed. The frozen samples were thawed in a refrigerator until the pigment extraction, and the canned ones were drained before this operation.

Extraction. The extraction procedure was similar to that employed by Fuke et al. (1985). Sodium carbonate, 1–2 g, was added to 50 g of kiwi fruit paste (made for homogenization of small pieces of kiwi fruit with seeds and core removed)) to adjust the pH to 8–9 to prevent conversion of chlorophyll to pheophytin. Chilled acetone (200 mL) was then added to the sample to produce an approximately 80% solution. This was mixed in a homogenizer and centrifuged at 4000g for 10 min (0–5 °C); this operation was repeated until the green color was completely removed from the residue. The supernatants were collected and transferred to a separatory funnel, and diethyl ether (75 mL) and cold deionized water (100 mL) were added. After vigorous shaking and standing, the aqueous layer was discarded. The washing procedure was repeated 5–10 times to remove acetone. The diethyl ether layer was dehydrated with fluorimetric analytical-grade sodium sulfate anhydride. This solution was transferred to a beaker and evaporated under a stream of nitrogen. The residue was dissolved and diluted to 5 mL with chromatographic-grade acetone. Duplicate 20-μL samples were injected for each extract for the HPLC analysis.

Separation of Pigments by Semipreparative TLC. A concentrated solution of each sample extract in acetone was chromatographed on semipreparative thin-layer plates (20 × 20 cm, layer thickness 200 μm; Kieselgel 60F 254, Merck, Darmstadt, W. Germany) under continuous stream of nitrogen using a solution containing petroleum ether (bp 30–60 °C) (50%) and acetone (50%) and allowed to condition for 30 min. The plate was then lowered into the solvent and the chromatogram developed for 1.5 h in darkness at room temperature. The resulting bands were scraped from the plate in the appropriate solvent for HPLC and spectrophotometric analysis. The bands exposed in Table I were separated in this procedure. This preparative TLC was employed to separate the individual kiwi fruit pigments in a relatively pure form so that standards were available for subsequent optimization of HPLC conditions.

Identification of the Pigments. Identification was based on chromatographic behavior on HPLC and TLC, visible absorption spectra, and specific chemical reactions.

RESULTS AND DISCUSSION

Figures 1 and 2 are typical chromatograms of pigment compounds found in fresh unripe and ripe kiwi fruit (cv. Hayward). In order of chromatographic elution on a C-18 reversed-phase column these are (a) xanthophylls (oxygenated carotenoids), (b) chlorophylls and their derivatives, and (c) hydrocarbon carotenoids (β-carotene). The chromatograms show the presence of the typical components of these various classes of compounds which are identified by spectroscopy and chromatography as well as chemical methods. The details of the identification and the chemistry of these compounds are previously reported by Cano (1991). Table II shows the different components of pigment pattern of fresh (unripe and ripe), frozen, and canned kiwi fruit slices and the absorption maxima of each compound compared with the standard and literature data.

The major xanthophylls found in fresh and frozen kiwi fruits were 9′-*cis*-neoxanthin (natural neoxanthin) (λ_{max} 438 nm) identified from its UV/vis light absorption and the hypsochromic shift of 4 nm in comparison to its all-trans compound; *trans*- and *cis*-violaxanthin identified from its light absorption and chemical transformations with retention times of 4.90 and 5.32 min, respectively; auroxanthin (λ_{max} 402 nm) and *all-trans*-lutein epoxide (λ_{max} 442 nm)—this last compound showed an 20-nm hypsochromic shift by treatment with trace amounts of acid; lutein (λ_{max} 446), the most abundant xanthophyll in fresh and frozen kiwi fruit, was shown to be accompanied

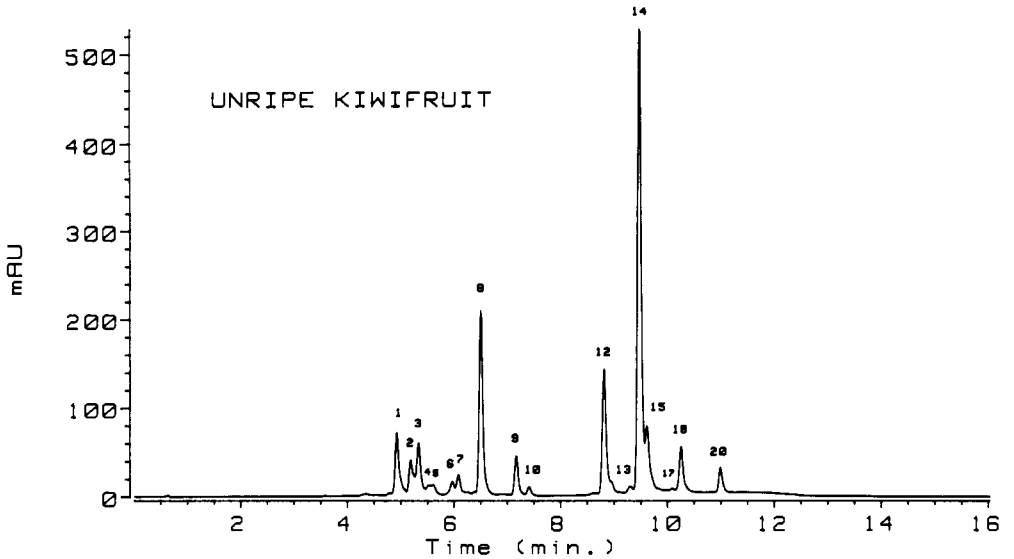

Figure 1. HPLC chromatogram of unripe Hayward kiwi fruit extract. Peak identifications are given in Table II.

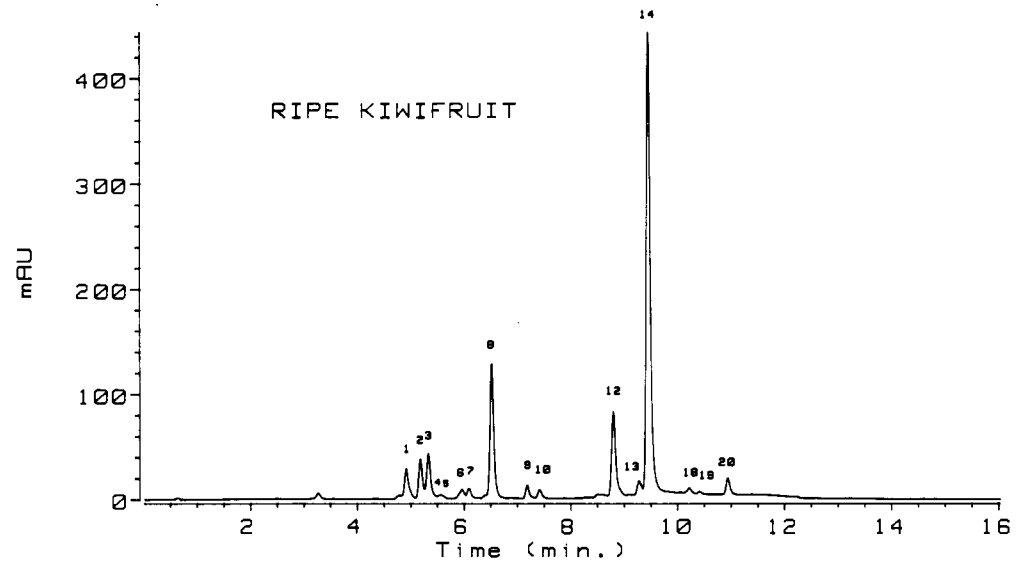

Figure 2. HPLC chromatogram of ripe Hayward kiwi fruit extract. Peak identifications are given in Table II.

by two minor cis isomers, neolutein B (λ_{max} 442 nm) and neolutein A (λ_{max} 438 nm).

The major chlorophylls in fresh kiwi fruit extracts were identified as chlorophyll *a* and *b* and several chlorophyll derivatives. Pheophytin *a*, the most common derivative of chlorophyll *a*, was present in all extracts of unripe and ripe kiwi fruits whereas pheophytin *b* was not detected in fresh fruits.

In unripe fruits chlorophyll a was accompanied by a minor quantity of its C-10 epimeric isomer, chlorophyll *a'*, while pheophytin *a'* was only present in ripe fresh fruits. Both unripe and ripe kiwi fruit pigment patterns showed the presence of an unknown chlorophyll a derivative with a retention time of 9.29 min and spectral characteristics like chlorophyll *a*. This compound have been previously reported in the literature (Kost, 1988). The chromatogram of the pigment pattern of unripe fruits showed a peak at 9.57 min identified as pyropheophytin *b*. The presence in trace amounts of this chlorophyll *b* derivative, with a similar spectral characteristics to those pheophytin *b*, could be explained by the low pH of unripe fresh kiwi fruit (pH 2.3) that could propitiate an intense pigment degradation (Schwartz and Elbe, 1983).

Frozen kiwi fruit slices stored at −18 °C during 6 months showed a similar pigment pattern to the fresh kiwi fruit ones (Figure 3). Antheraxanthin, a structurally related isomer of lutein epoxide, could be observed in the correspondent HPLC chromatogram (Figure 3). All remainder xanthophylls were the same as those observed in fresh kiwi fruit extracts. Chlorophylls *a* and *b* were accompanied by their most commun derivatives, pheophytin *a* and pheophytin *b*. This last compound, pheophytin *b*, was not observed in the chromatograms of the fresh kiwi fruit extracts. Some authors have previously reported that, even at −18 °C, chlorophyll degradation occurs (Robertson, 1985). Frozen purees of kiwi fruit showed within 36 days of storage that the chlorophyll concentrations had been reduced to less than one-third of their initial concentrations. Factors likely having a significant effect on the rate of chlorophyll degradation include pH, temperature, water activity, and time. The chlorophyll *a* derivative with an unknown structure reported by Kost (1988) was also present in the extracts of frozen kiwi fruit slices.

Figure 4 is a typical HPLC chromatogram of pigment pattern found in conventional canned kiwi fruit slices. The pigments were identified as xanthophylls, metallochlorophyll complexes, chlorophylls, and hydrocarbon carotenoids (Table II). The oxygenated carotenoids, xanthophylls, observed in canned kiwi fruit extracts showed a very complicated pattern due to the thermal processing. *cis*-Neochrome and *trans*-neochrome with a

Table II. Peak Identification of the Various Components of the Fresh, Frozen (Not Heated), and Canned (Heated) Kiwi Fruit Extracts Separated by HPLC

component	published max (ethanol)	author's standard ref max (ethanol)	HPLC solvent system: not heated peak	not heated max	heated peak	heated max
neochrome (cis)	398, 421, 449	398, 422, 449	4	398, 422, 449	1	398, 422, 448
violaxanthin (trans)	417, 440, 471	419, 440, 470	1	418, 442, 470	none	
neochrome (trans)	398, 421, 449	398, 422, 449	5	398, 422, 449	2	398, 422, 448
luteoxanthin	396, 420, 446	397, 420, 447	none		3	398, 422, 448
9′-*cis*-neoxanthin	417, 438, 467	415, 436, 465	2	412, 436, 464	none	
violaxanthin	417, 442, 471	418, 443, 471	3	418, 442, 470	none	
Zn–pheophytin *a*	408	408	none		4	408
Zn–pyropheophytin *a*	402	403	none		5	402
auroxanthin (cis)	375, 400, 425	377, 402, 423	none		7	380, 402, 425
auroxanthin	382, 403, 428	380, 402, 426	6	380, 402, 426	6	380, 402, 424
lutein epoxido	417, 440, 469	418, 440, 469	7	418, 440, 468	none	
flavoxanthin	400, 423, 448	400, 422, 448	none		8	402, 422, 448
all-trans-lutein	423, 446, 474	422, 446, 473	8	422, 446, 474	9	422, 446, 474
lutein (cis)	422, 445, 473	422, 445, 472	none		10	422, 446, 474
neolutein B	421, 445, 476	420, 442, 473	9	420, 438, 466	11	418, 440, 470
neolutein B′	421, 445, 476	420, 443, 472	none		12	418, 440, 470
neolutein A	421, 445, 476	420, 442, 473	10	420, 438, 466	13	422, 438, 462
antheraxanthin (trans)	421, 443, 473	421, 445, 473	none		14	422, 446, 474
antheraxanthin (cis)	419, 443, 469	420, 442, 467	11	422, 442, 466	15	422, 442, 466
chlorophyll *b*	(430), 464	(430), 464	12	(438), 462	none	
pheophytin *b* + pyropheophorbide *a*			none		16[a]	(412), 430
chlorophyll *a* derivative	432	432	13	430	none	
chlorophyll *a*	432	432	14	430	none	
chlorophyll *a*′	432	432	15	430	none	
pyropheophorbide *b* + chlorophyll *a* derivative			none		18[a]	(414), 436
pheophytin *b*	436	434	16	434	none	
pyropheophytin *b*	435	434	17	432	17	434
pheophytin *a*	409	408	18	408	19	408
pheophytin *a*′	409	408	19	408	20	408
pyropheophytin *a*	409	409	none		21	408
all-trans-carotene	426, 451, 478	424, 448, 476	20	422, 446, 474	22	430, 450, 476

[a] Impure peaks.

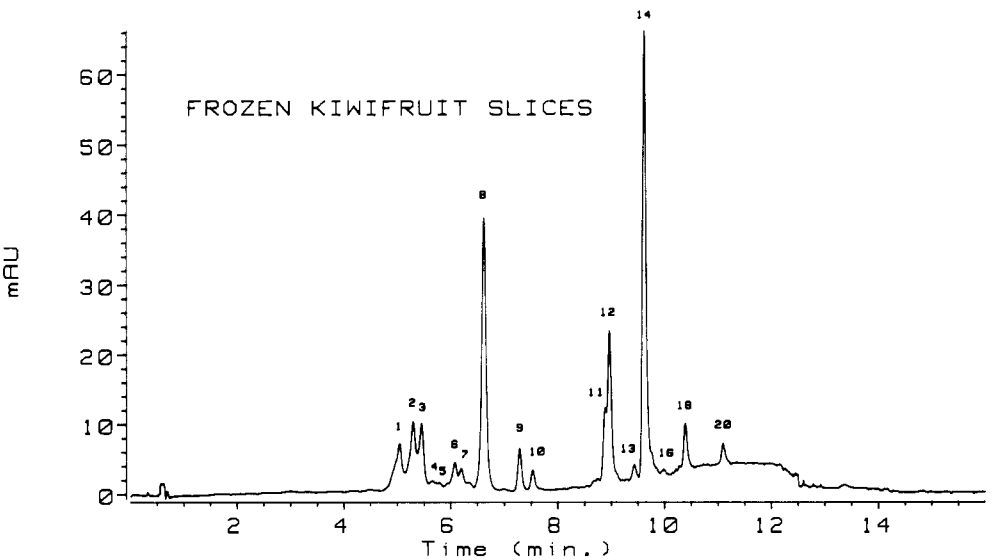

Figure 3. HPLC chromatogram of frozen kiwi fruit extract. Peak identifications are given in Table II.

retention times of 4.78 and 4.94 min, respectively, were the firt oxygenated carotenoids. These compounds were also observed in the chromatograms of fresh and frozen kiwi fruit slices but, in these last extracts, they appeared only in trace quantities. Thermal treatment of kiwi fruit slices appears to induce the degradation of some xanthophylls like neoxanthin and violaxanthin, observed in fresh and frozen product, by a epoxide furanoxide rearrangement to afford neochromes (λ_{max} 422 nm). In the same way, the chemical transformation of violaxanthin could result in the formation of luteoxanthin (λ_{max} 422 nm), 5.08-min retention time, and auroxanthin (trans and cis) (λ_{max} 402 nm), 5.84 and 5.95 min respectively. This behavior was also confirmed by isolation by TLC of violaxanthin that was thermally treated in acid solution to afford luteoxanthin.

Flavoxanthin, λ_{max} 422 nm, was also observed in the HPLC chromatogram of canned kiwi fruit extracts; this xanthophyll was not present in fresh and frozen products. Lutein, the most abundant xanthophyll in the green vegetables, was shown to be accompanied by four cis isomers, which were identified from their absorption spectra and chemical modifications. The peak at 6.77-min retention time and λ_{max} 446-nm absorption maxima was identified as *cis*-lutein, 15,15′-cis isomer (Figure 4). TLC isolation of these isomers permitted the verification

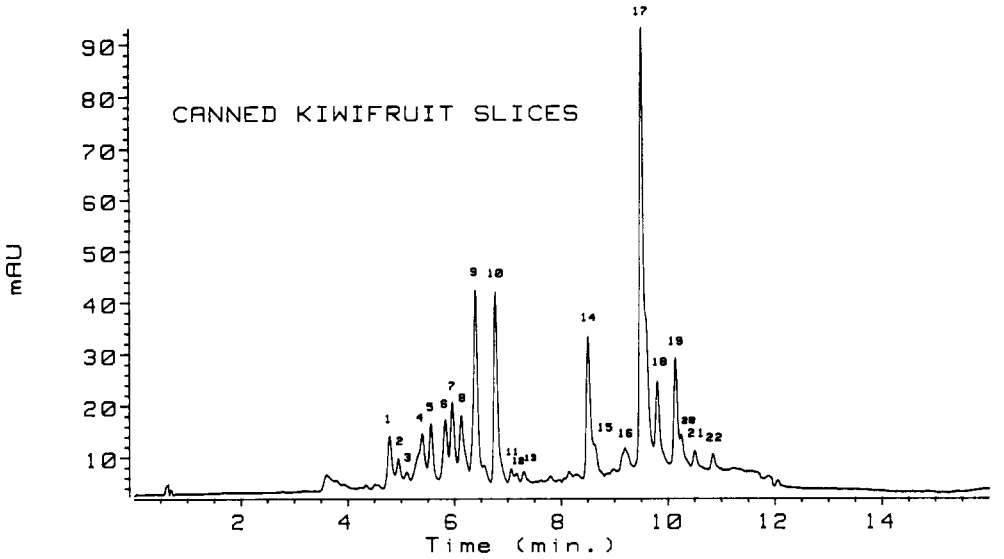

Figure 4. HPLC chromatogram of canned kiwi fruit extract. Peak identifications are given in Table II.

Table III. Hunter Color Values[a] of Kiwi Fruit Slices

sample	L	a	b	h	C	ΔE^a
fresh kiwi fruit						
unripe	43.38 a	−11.53 a	21.66 ac	61.97 a	24.53 a	
ripe	41.94 b	−12.26 a	21.73 a	60.56 b	24.95 a	
frozen kiwi fruit	42.53 b	−9.02 b	22.24 b	67.92 c	24.00 a	3.33 a
canned kiwi fruit	44.70 c	−1.47 c	21.19 c	86.03 d	21.24 b	11.15 b

[a] Values in the same column with the same letter are not statistically different ($p \leq 0.05$). h = arctan (b/a) (hue). $C = (a^2 + b^2)^{1/2}$ (calculated saturation value). $E = ((L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2)^{1/2}$ (total color difference). [b] Determined from ripe kiwi fruit values.

of their UV/vis maxima which were coincident with the previous reported values for theses compounds (Kost, 1988). The 15,15′-cis isomer of lutein resulted from the boiling of a benzene solution of *all-trans*-lutein; therefore it was not surprising that the extracts of canned kiwi fruit slices showed this oxygenated carotenoid.

The three minor isomers of *all-trans*-lutein observed in the chromatograms were neolutein B, neolutein B′, and neolutein A, 7.04-, 7.10-, and 7.22-min retention times, respectively. The absorption maxima of these compounds are compiled in Table III. Absorption maxima of neolutein B, in various solvents, showed a hypsochromic shift of 7–8 nm with respect to lutein, while such a hypsochromic shift for neolutein B′ was 5–6 nm. This last lutein isomer, neolutein B′, was not present in the fresh and frozen kiwi fruit extracts (Figures 1–3). Khachick et al. (1986, 1991b,c) reported the tentative identification by UV–visible absorption and the confirmation of the definitive geometry of the cis isomers of lutein by NMR evidences. In these studies, an isolated fraction of lutein and its various geometrical forms from raw and cooked vegetables were chromatographed on a nitrile-bonded column (Khachik et al., 1991a,b). It was confirmed that *all-trans*-lutein was accompanied by substantial levels of 9-*cis*-, 9′-*cis*-, 13-*cis*-, and 13′-*cis*-lutein as well as minute levels of 15- and 15′-*cis*-lutein.

Chlorophylls *a* and *b* were not present in the extracts of canned kiwi fruit slices (Figure 4). This result was not surprising because the standard commercial procedure for canning sliced kiwi fruit utilizes a processing time of 15 min at 100 °C (often preceded by passage of the cans through an exhaust box up to 20 min), and this process produces a canned kiwi fruit slices with a yellow-brown appearance. Robertson (1985) reported that reducing the processing time does not result in an improvement in the color since the fruit acids released on slicing, in combination with the elevated temperature, lead to rapid conversion of chlorophylls to pheophytins. Pheophytin *a* and pheophytin *b*, 10.16 and 9.18 min, respectively, were observed in the HPLC chromatogram (Figure 4) but they were not the most important chlorophyll degradative compounds. Peak 16 at 9.18 min, identified as pheophytin *b* (λ_{max} 412 nm), was an impure peak with 20% of other chlorophyll derivative with a 430-nm spectral absorption maximum and identified as pyropheophorbide *a*. Pyropheophytin *b* was the most important product of chlorophyll degradation. This compound, λ_{max} 414 nm, appeared at 9.57 min and was shown to be accompanied by a minor quantity of pyropheophytin *a* (λ_{max} 408 nm) at 10.54 min. This is in agreement with the results previously reported by Schwartz et al. (1981) and Schwartz and Elbe (1983) about the studies of the concentrations of pheophytins *a* and *b* and pyropheophytins *a* and *b* found in commercially canned products of spinach, peas, asparagus, and beans. These findings indicate that pyropheophytins *a* and *b* are major chlorophyll derivatives responsible for the olive-green color of canned vegetables.

Moreover in the extracts of canned kiwi fruit slices the amount of pyropheophytin a was very low in comparison with the correspondent pyropheophytin *b*. This fact could suggest that other degradative reactions must be taking place in the vegetable product.

Figure 4 shows two peaks at 5.42 and 5.54 min with spectral characteristics like chlorophyll derivatives (λ_{max} 408 nm and λ_{max} 402 nm, respectively). These compounds were identified as metallochlorophyll complexes of chlorophyll *a*, specifically Zn–pheophytin *a* and Zn–pyropheophytin *a*. Elbe et al. (1986) have previously reported the formation of these zinc chlorophyll complexes in canned green beans and suggested that the formation of Zn–pheophytin a and Zn–phyropheophytin *a* was the most efficient degradative reaction over time when a minimum of 25 ppm of Zn was present. In the extracts of canned kiwi fruit slices the amounts of pheophytin *a*, peak 19, and pyropheophytin *a*, peak 21, were lower than the pyropheophytin *b* one, peak 17. Schwartz and Elbe (1983)

demonstrated that the degradation of pheophytin *b* to pyropheophytin *b* takes place at a rate approximately 25–40% faster than the pheophytin a degradation depending upon temperature. However the formation of Zn complexes of pheophytin *b* and pyropheophytin *b* appeared to be less favorable than the formation of Zn complexes of chlorophyll *a* derivatives, and for this reason Zn complexes of chlorophyll *b* derivatives were not observed in the extracts.

Pyropheophorbides *a* and *b* were also present in the canned kiwi fruit slices. These compounds were produced by thermal treatment, favored by the acid medium, and shown to have similar spectral characteristics, with a 2-nm shift, to pheophytins *a* and *b*. HPLC chromatogram (Figure 4) showed that these pheophytin derivatives appeared overlapped to other compounds; therefore pyropheophorbide *a* was observed at 9.18 min together with pheophytin *b*, and pyropheophytin *b* appeared at 9.82 min together with the chlorophyll *a* derivative with an unknown structure.

β-Carotene, the only hydrocarbon carotenoid present in kiwi fruit, was not seriously affected by processing. Freezing and storage of kiwi fruit slices or canning in syrup did not produce important changes in its concentration. However, freezing preservation was the best process in order to retain this carotenoid.

TLC separation of pigments extracts (Table I) of fresh and frozen kiwi fruit produced nine bands using petroleum ether (50%) and acetone (50%) as eluent. In the same conditions, TLC separation of canned kiwi fruit extracts showed the presence of 12 bands where the principal characteristic was the two bands correspondent to the Zn–metallo complexes of pheophytina *a* and pyropheophytin *a*, R_f 0.08 and 0.10.

The color of fresh, unripe and ripe, frozen and canned kiwi fruit slices in terms of Hunter color values is given in Table II. There was little difference among fresh unripe and ripe samples in *b*, *h* (hue), and *C* (the calculated saturation value). Large differences were notted in the *L* (lightness) and $-a$ (greenness); the unripe fruits turned more green and dark on ripening. Frozen kiwi fruit slices showed very similar Hunter color values *L*, *b*, and calculation saturation values (*C*) to the fresh ripe fruits before freezing process. However, $-a$ (greenness), −9.02, *h* (hue), 67.92, and ΔE (total color difference), 3.33, values were significantly different, showing that the frozen and thawed product was slightly less green and more yellow. Canned products showed larger differences (statistically significant $p \geq 0.05$) in the Hunter color parameters *L*, $-a$, *h* (hue), calculated saturation value (*C*), and ΔE (total color difference). This sample turned to a brown yellow color characterized by the lower $-a$ value (−1.47) and the larger total color difference (11.15) when compared with fresh kiwi fruit sample values.

Canning of kiwi fruit slices in syrup by conventional processes produced important and dramatic changes in the color and pigment pattern, resulting in a commercial product with a yellow brown appearance very different from that of the fresh fruit. However, the freezing preservation of kiwi fruit slices in the assayed conditions led to a kiwi fruit product with similar color characteristics and appearance to fresh fruit and with no significant changes in its pigment pattern.

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Registry No. *cis*-Neochrome, 136521-16-9; *trans*-violaxanthin, 126-29-4; *trans*-neochrome, 25548-02-1; luteoxanthin, 1912-50-1; 9′-*cis*-neoxanthin, 14660-91-4; Zn-pheophytin *a*, 15739-11-4; Zn-pyropheophytin *a*, 15333-64-9; auroxanthin, 27785-15-5; lutein epoxide, 28368-08-3; flavoxanthin, 512-29-8; *all-trans*-lutein, 127-40-2; *cis*-lutein, 38327-39-8; neolutein B, 29414-89-9; neolutein B′, 79516-56-6; neolutein A, 32449-88-0; *trans*-antheraxanthin, 640-03-9; *cis*-antheraxanthin, 2086-88-6; chlorophyll *b*, 519-62-0; pheophytin *b*, 3147-18-0; pyropheophorbide *a*, 24533-72-0; chlorophyll *a*, 479-61-8; chlorophyll *a*, 22309-13-3; pyropheophorbide *b*, 82040-65-1; pyropheophytin *b*, 77331-75-0; pheophytin *a*, 603-17-8; pheophytin *a*′, 75598-38-8; pyropheophytin *a*, 14409-87-1; *all-trans*-carotene, 7235-40-7.