

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

STUDIES ON THE PROCESSING OF NEW ZEALAND

GRAPEFRUIT JUICE

A thesis presented in partial fulfilment
of the requirements for the degree
of Master of Technology in
Food Technology at
Massey University

GORDON LINDSAY ROBERTSON

1974

"The safest position is somewhere between
arrogance based on unrecognised ignorance,
and arrogance based on unwarranted
certainty."

Professor John Yudkin

"Pure, White and Deadly", 1972

ABSTRACT

The likely origin of the New Zealand grapefruit (NZGF) is discussed and present and future trends in its production and utilisation presented. Early and late season samples of NZGF juice were analysed for the presence of the enzymes pectinesterase, polygalacturonase and ascorbic acid oxidase, no trace of the latter two being found. Samples of juice from NZGF harvested at regular intervals from July until December 1973 were analysed for yield, total soluble solids, titratable acidity, pH, pectinesterase activity, and ascorbic acid content.

The average yield of juice obtained (35.6% w/w) was significantly lower than that reported from overseas for true grapefruit. The level of total soluble solids remained fairly constant in the range 12.0 to 12.6%, while the pH of the juice increased throughout the season from 2.95 to 3.40. The titratable acidity was within the range 1.0 to 2.0 grams of citric acid per 100 ml of juice, while the Brix : acid ratio varied from 5.02 to 10.03. The level of pectinesterase in the juice (which increased as the season progressed) was comparable with that found in overseas citrus juices, while the level of ascorbic acid in the juice declined over the season from 32.4 to 23.2 mg/100 ml, in agreement with overseas trends. With the exception of yield, the compositional characteristics of NZGF juice reported here do not differ markedly from overseas grapefruit juices.

The important role which pectinesterase plays in the destabilisation of citrus juice cloud is outlined and possible methods for inactivating the enzyme are described. As the application of heat is the only method in commercial use, factors affecting and methods for studying the thermal inactivation of enzymes are discussed. As the major objection to most of these methods is the way in which the heating and cooling lags are evaluated, a new method which adequately describes these thermal lags has been developed for determining the thermal resistance of pectinesterase in NZGF juice.

A digital computer was programmed to determine (using a trial and error technique) the constants in two expressions which relate the equivalent effect of unsteady-state heating and cooling of NZGF juice to the inactivation of pectinesterase. One expression assumed that the rate of inactivation was exponentially related to temperature; in this case the constant was the z value. The other expression assumed that the rate was related to temperature according to the Arrhenius equation, in which case the constant was the activation energy. The two constants were evaluated for both low and high pH juice. It was found that the latter expression using the Arrhenius equation described the change in rate of inactivation with temperature more adequately than the former expression. From these expressions the times required at different temperatures to inactivate pectinesterase in NZGF juice of varying pH were calculated. The application of these results to the industrial processing of NZGF juice is discussed.

ACKNOWLEDGEMENTS

I wish to thank the following people:

My supervisor, Professor E.L. Richards, for his assistance in the preparation of this thesis.

Mr. A.W. Nelson of Tiki Orchards Ltd., Te Puke, for providing the grapefruit used in this study.

Mr. M.J. Reeves, for helpful discussions on aspects of the work in Chapter Three.

Messrs. T.M. Gracie, E.J. Baxter and J.J. Wellington, for technical assistance.

My wife Brenda for typing this thesis and providing help in numerous other ways during the past two years.

Gordon L. Robertson

July, 1974.

TABLE OF CONTENTS

	<u>PAGE</u>
Acknowledgements	v
List of Figures	ix
List of Tables	xi
<u>Chapter 1</u> "The Development of the Citrus Fruit Industry in New Zealand with particular reference to Grapefruit"	1
<u>Section I</u> "The Origin of New Zealand Grapefruit"	2
<u>Section II</u> "Production of Citrus Fruits"	8
<u>Section III</u> "Future Trends in New Zealand Grapefruit Production and Utilisation"	13
<u>Chapter 2</u> "Seasonal Changes in the Compositional Characteristics of New Zealand Grapefruit Juice of Importance to Citrus Processors"	18
<u>Section I</u> "Compositional Characteristics of New Zealand Grapefruit Juice of Importance to Citrus Processors"	19
<u>Section II</u> "Analysis of New Zealand Grapefruit Juice for Enzymes"	31
<u>A. Pectic Enzymes</u>	
1. Introduction	31
2. Experimental	36
3. Results	38
4. Discussion	39
5. Conclusion	41
<u>B. Ascorbic Acid Oxidase</u>	
1. Introduction	41
2. Experimental	42
3. Results	43
4. Discussion	43
5. Conclusion	43
<u>Section III</u> "Seasonal Changes in the Compositional Characteristics of New Zealand Grapefruit Juice of Importance to Citrus Processors"	44

	<u>PAGE</u>
1. Introduction	44
2. Experimental	45
3. Results	49
4. Discussion	68
5. Summary	85
6. Conclusions	87
<u>Chapter 3</u> "Cloud Stabilisation in New Zealand Grapefruit Juice"	88
 <u>Section I</u>	
1. The Nature of the Cloud in Citrus Juices	89
2. Stabilisation of the Cloud in Citrus Juices	93
 <u>Section II</u>	
1. The Heat Inactivation (Denaturation) of Enzymes	98
2. Factors Affecting the Heat Inactivation of Enzymes	102
3. Methods for Determining the Thermal Inactivation Conditions for Enzymes	105
 <u>Section III</u>	
1. Development of a Method for Studying the Thermal Inactivation of Enzymes	110
(i) Introduction	110
(ii) Methods for Determining the Lethality of a Thermal Process	110
(iii) A Method for Studying the Thermal Inactivation of PE	123
2. Experimental	129
(i) Inactivation of PE	129
(ii) Calculation of Results	131
3. Results	135
4. Discussion	146
5. Conclusion	160
 <u>Section IV</u> "Cloud Stability in Heat Treated New Zealand Grapefruit Juice"	 162

	<u>PAGE</u>
1. Introduction	162
2. Experimental	163
3. Results	164
4. Discussion	166
5. Conclusion	168
<u>Chapter 4</u> "Application of these Studies to the Industrial Processing of New Zealand Grapefruit"	169
Appendix I Computer programmes 'A' and 'B' to calculate optimum z and M values	176
Appendix II Computer programmes 'C' and 'D' to calculate regression equations and standard errors of estimates for relationship between F_{180} value and D value using optimum z and M values	182
Appendix III Sample data from one run showing time- temperature (in millivolts) readings	188
Appendix IV Sample printout from programmes 'A' and 'B' showing F_{180} values at different z and M values	189
Bibliography	191

LIST OF FIGURES

<u>FIGURE</u>	<u>TITLE</u>	<u>PAGE</u>
1	Seasonal variation in yield of NZGF juice.	55
2	Seasonal variation in TSS and yield of NZGF juice.	56
3	Seasonal variation in pH of NZGF juice.	57
4	Seasonal variation in titratable acidity of NZGF juice.	58
5	Relationship between titratable acidity and TSS of NZGF juice.	59
6	Seasonal variation in Brix : acid ratio of NZGF juice.	60
7	Relationship between Brix : acid ratio and pH of NZGF juice.	61
8	Relationship between Brix : acid ratio and TSS of NZGF juice.	62
9	Relationship between Brix : acid ratio and titratable acidity of NZGF juice.	63
10	Seasonal variation in pectinesterase activity of NZGF juice.	64
11	Seasonal variation in ascorbic acid content of NZGF juice.	65
12	Relationship between pH and titratable acidity of NZGF juice.	66
13	Seasonal variation in ascorbic acid content of NZGF.	67
14	Possible pathways for enzymic breakdown of pectin by pectinesterase, polygalacturonase, and polymethygalacturonase.	96
15	Hypothetical thermal destruction curve passing through 1 minute at 180 F.	113
16	Diagrammatic plot of the logarithm of the decimal reduction time as a function of the absolute temperature.	121

<u>FIGURE</u>	<u>TITLE</u>	<u>PAGE</u>
17	Typical time-temperature (in millivolts) profile of the thermal process to which the juice samples were subjected.	136
18	Time for a 5D reduction in PE concentration in Valencia orange juice at various temperatures.	151
19	Logarithm of the time for a 5D reduction in PE concentration as a function of temperature for low and high pH NZGF juice.	156
20	Equivalent times at 180 F for a 5D reduction in PE in NZGF juice as a function of pH.	159
21	Calibration curve for UNICAM Colorimeter and bentonite suspensions.	165
22	Turbidity of NZGF juice with varying levels of PE as a function of time.	167

LIST OF TABLES

<u>TABLE</u>	<u>TITLE</u>	<u>PAGE</u>
I	Classification of Citrus Fruits	3
II	World Production of Citrus Fruits	8
III	Main Producers of Citrus Fruits in 1972	9
IV	Main Areas of Grapefruit Production in 1972	9
V	Growth in New Zealand Citrus Production	11
VI	Relative Importance of Four Main Citrus Growing Regions in New Zealand in 1972	11
VII	Projections of Supply of NZGF	13
VIII	Estimated Annual Consumption of Fresh Citrus Fruits	15
IX	Estimated Consumption of Citrus Juice in Kilograms per Head	16
X	Effect of rootstock on composition of NZGF juice	22
XI	Pectinesterase Activity in NZGF Juice	38
XII	Polygalacturonase Activity in Early Season (July) NZGF Juice	38
XIII	Polygalacturonase Activity in Late Season (December) NZGF Juice	39
XIV	Seasonal Changes in NZGF Juice in 1973	50
XV	Relationships Between Various Compositional Characteristics of NZGF Juice	51
XVI	Juice Yield and TSS in Concentration of Juice to 42 deg. Brix	71
XVII	Required Ratios of TSS to Acid	77
XVIII	PE Activity in Various Citrus Juices	81
XIX	Composition of Orange Juice Cloud and Component Parts of Oranges	91
XX	Correlation coefficients between calculated F_{180} values and decimal reductions of PE inactivation in low pH (3.05) juice for varying values of z	137

<u>TABLE</u>	<u>TITLE</u>	<u>PAGE</u>
XXI	Correlation coefficients between calculated F_{180} values and decimal reductions of PE inactivation of high pH (3.40) juice for varying values of z	138
XXII	Correlation coefficients between calculated F_{180} values and decimal reductions of PE inactivation in low pH (3.05) juice for varying values of M	139
XXIII	Correlation coefficients between calculated F_{180} values and decimal reductions of PE inactivation in high pH (3.40) juice for varying values of M	140
XXIV	Optimum z and M values for PE inactivation	141
XXV	Regression Equations for Predicting F_{180} from D	142
XXVI	F_{180} values for 1D and 5D Reductions in PE Concentration	143
XXVII	Values of z calculated from M	145
XXVIII	Published Energies of Inactivation (E 's) for Protein Denaturations	146
XXIX	Times for 5D reduction in concentration and 100% inactivation of PE in Valencia Orange Juice at pH 4.1	150
XXX	Equivalent times at different temperatures to achieve a 5D reduction in PE concentration	157

CHAPTER ONE

THE DEVELOPMENT OF THE CITRUS FRUIT INDUSTRY IN

NEW ZEALAND WITH PARTICULAR REFERENCE TO GRAPEFRUIT

SECTION I

THE ORIGIN OF NEW ZEALAND GRAPEFRUIT VARIETIES

It was not with an apple that Eve tempted Adam, according to one tradition, but with a citrus fruit - a primitive citron called etrog or Adam's apples. (Kefford, 1966). Citrus fruits with their attractive colours and distinctive flavours continue to tempt the appetites of men, and as the richest natural sources of vitamin C, they are important to human nutrition. More citrus fruits are consumed directly as human food than any other kind of fruit, and the world crop of citrus fruits is second only to the grape crop, much of which, however, is utilised in fermented liquors.

New Zealand is a signatory to the Codex Alimentarius Commission Standards on fruit juices which are likely to become accepted internationally within the next three years. Once this happens, any grapefruit products exported from New Zealand will have to meet the Codex standards. Therefore it is important to the citrus processor to know how New Zealand grapefruit compare with overseas species and varieties.

The botanical or horticultural names of the major citrus fruits, together with the taxonomic relationships between them, are summarised in Table I, after Swingle and Reece (1967) and Hodgson (1967).

Table I
Classification of Citrus Fruits

General Name	Botanical Name	Varietal Groups
Sweet orange	<u>Citrus sinensis</u>	Normal oranges Naval oranges Blood oranges Low-acid oranges
Bitter or sour orange	<u>Citrus aurantium</u>	Bitter (Seville) oranges Bittersweet oranges
Mandarin	<u>Citrus reticulata</u>	Common mandarins Tangerines Satsuma mandarins Mediterranean mandarins Small-fruited mandarins
Grapefruit	<u>Citrus paradisi</u>	Pale-fleshed grapefruits Red-fleshed grapefruits
Pummelo or Shaddock	<u>Citrus grandis</u>	Common pummelos Pigmented pummelos Low-acid pummelos
Lemon	<u>Citrus limon</u>	Acid lemons Low-acid lemons
Lime	<u>Citrus aurantifolia</u>	Small-fruited acid limes Large-fruited acid limes Low-acid limes

The origin and significance of the name "grapefruit" are obscure. According to Webber (1943), who made a comprehensive search of the literature, the earliest recognisable mention of grapefruit occurred in Barbados (West Indies) in 1750 under the name "forbidden fruit", from which the species designation paradisi was assigned in 1830. The first known use of the term grapefruit occurred in 1814 in Jamaica, in which it was referred to as a special and smaller kind of

shaddock whose flavour somewhat resembled that of the grape. It seems more likely, however, that the name was derived from the fact that the fruits commonly occur in small clusters rather than singly, as with most shaddocks (pummelos). Early in the present century, the name pomelo was proposed and for a time was used by American horticulturists. It was not accepted by the industry, however, and has now virtually disappeared.

According to Hodgson (1967), the grapefruit almost certainly originated in the West Indies, for it is not described in the old literature and was not known in Europe or in the Orient until after its discovery in the Western Hemisphere. That it was derived from the pummelo is certain, but whether by somatic mutation or natural hybridisation is not known. However, it is the opinion of Hodgson (*ibid.*), based on observations of numerous natural hybrids of the pummelo in northeastern India, Sikkim, and eastern Nepal, that the grapefruit originated as a natural hybrid.

Although the grapefruit was said to be common in Jamaica and probably throughout the West Indies, it remained for Florida to introduce the grapefruit to the American consumer and to develop a commercial industry. This fact explains why, with the sole exception of Redblush (Ruby), all the grapefruit varieties of commercial importance have originated in Florida and apparently trace back to the original introduction.

The so-called New Zealand grapefruit is not a true

grapefruit but is a natural hybrid of obscure origin with tangelo characteristics. That it originated in the Orient is suggested by Bowman's statement (1956) that it was brought to Australia (presumably the fruit) from Shanghai by a Captain Simpson early in the 19th Century. The earliest description of the Poorman orange (as the variety was then called by the Australians), given in a New South Wales nursery catalogue of 1820, indicates that the original introduction might have been a shaddock (pummelo).

According to Bowman (ibid.) the Poorman was taken to New Zealand by Sir George Grey, who established his home on Kawau Island in the Hauraki Gulf about 1855. About 1861, Grey provided propagation materials to John Morrison of Warkworth, and for many years the most commonly grown strain of this fruit was known as Morrison's seedless. The name 'New Zealand Grapefruit' (hereafter referred to as NZGF) was later given to this and other thin-skinned high quality strains of Poorman oranges. A popular strain being planted at present is known as 'Golden Special' and is probably a variation of Morrison's strain. 'Lippiatts' is another strain which has been grown and which arose as a seedling of the Poorman orange.

The earlier plantings of NZGF were of trees propagated on either sweet orange or rough lemon rootstocks which grew to a very large size, and although these trees were heavy bearers, harvesting costs were high. The trend with recent plantings has been to propagate trees on trifoliata rootstocks, and this is resulting in smaller trees

which are easier to handle and which can also be planted closer together to maintain yields per acre. In fact, double planting at about 230 trees per acre is now not uncommon, but the average density of trees over all plantings is at present only about 145 trees per acre (Fletcher, 1971).

The NZGF is medium-large, oblate to broadly obovate to nearly globose. Despite having numerous seeds, it is monoembryonic. It has a pale orange-yellow colour at maturity, with a medium-thick rind. The flesh colour is yellowish orange, coarse-textured and juicy, the flavour being pleasantly subacid with a trace of bitterness. Compared with true grapefruits, it matures very early, but holds on the tree exceptionally well without loss in colour. The tree is vigorous, large and prolific, with dark green leaves, and the petioles are suggestive of mandarin or bitter orange rather than grapefruit (Hodgson, *ibid.*).

The only other kind of grapefruit which is grown in New Zealand is the Wheeny grapefruit. This is a late variety, ripening from November to March. It originated as a chance seedling at Wheeny Creek near Kurrajong, New South Wales, Australia, and was first introduced into New Zealand about 1935. The fruit is pale yellow, large, thin skinned, and very juicy, somewhat similar in appearance to American and Jamaican grapefruit varieties. It is not a true grapefruit, however, but a natural hybrid, probably with a Seville orange parent. Interest in Wheeny grapefruit has waned in recent years, and production of this variety is not important in New Zealand at present.

As mentioned earlier in this section, New Zealand is a signatory to the Codex Alimentarius Commission Standards on fruit juices. The draft Codex Standards on citrus juices (Codex Alimentarius Commission, 1971) require that grapefruit juice be extracted from the species Citrus paradisi Macfadyen, the true West Indian grapefruit. The New Zealand Food and Drug Regulations (1973) regulation 197, state that grapefruit juice shall be the expressed juice of mature grapefruit of the species Citrus paradisi, or of hybrids of that species, or of hybrids of the species Citrus grandis.

However, the above discussion has indicated that New Zealand grapefruit is unique, belonging to neither of the above-mentioned species. Therefore, at this point in time, all NZGF juice sold in New Zealand fails to meet the Food and Drug Regulations. Furthermore, NZGF juice could never meet the Codex Alimentarius Commission Standards from a species point of view. The proper course would seem to be to have a special designation in both the Codex Standards and the New Zealand Food and Drug Regulations for NZGF juice. Because of the recent increases in NZGF juice processing, there would appear to be some urgency in this matter.