Article

# The quality of New Zealand-produced olive oil compared with imported product

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## Introduction

The purpose of this study was to compare the quality of commercially available New Zealand and foreign olive oils. This was done not only by employing the standard regulatory measures of quality, but by the application of a Gas Chromatograph-Mass Spectrometry (GC-MS) Head-Space Solid Phase Micro Extraction (HS-SPME) analysis for determining the concentration of key volatile compounds known to be markers of quality in olive oil. The results of the volatiles analysis along with total polyphenol concentrations then were used to ascertain if the quality of the New Zealand product was significantly different from that of the imported products. The study also examined whether the levels of these compounds could be employed as an indicator of olive oil origin.

## The olive – an exceedingly brief history

The fruit of the evergreen olive tree *Olea europaea,* which originated from Asia Minor, has been cultivated for thousands of years in the Mediterranean area.[1] Olive oil has been produced from its fruit for at least 6000 years.[2] In ancient times, Crete was one of the earliest and largest centres of olive oil production. The olive was a highly beneficial crop for the Minoan civilisation, as olives could be grown on marginal agricultural land, opening up new areas to food production. From about 2000 B.C., the olive groves of Crete and elsewhere provided the Minoans and other Mediterranean peoples with fruit, oil for culinary purposes, lamp fuel, medicine, cosmetics, skin care and cleaning (later in soap), timber for roof construction and firewood for cooking and heating.[3] Today, olives are cultivated around the world, with Spain, Italy, Egypt and Greece in descending order being the major producers for approximately 90% of world production in 2010. Countries such as Australia, South Africa, America, Argentina, Chile and New Zealand are producing increasing quantities. Total world production of this important commodity has more than doubled in the last 20 years to more than 3 million tonnes annually.[4]

Given the usefulness of the olive it should come as no surprise that this tree made an early appearance in New Zealand. We know the olive existed here prior to 1835 since Charles Darwin, following his visit to the Bay of Islands, mentioned in a letter that he had found olives planted in Waimate North. Between 1860 and 1880, two prominent early settlers, Logan Campbell and Sir George Grey, independently attempted to establish an olive industry, but these attempts failed after a few years and were abandoned. It was not until the mid-1980s that the New Zealand olive oil industry began to develop, when Israeli-born, FAO Horticultural Representative, Gidon Blumenfeld retired to Marlborough and planted a grove, establishing a nursery of imported Barnea and other cultivars.[5] Most groves in New Zealand are located on the East coast from Canterbury to Hastings and around Auckland, with Northland and Nelson also important production regions.

## Olive oil – composition

The major components of olive oil are triglycerides accounting for more than 98% of olive oil by weight. Oleic acid (18:1 n-9) is the most abundant fatty acid with levels ranging from 56 to 84% of the total fatty acid content. It is the abundance of this monounsaturated fatty acid that sets olive oil apart from other vegetable oils. Olive oil also has high levels of the essential polyunsaturated fatty acid linoleic acid (18:2 n-6), with content ranging from 3 to 21%. Minor components account for approximately 2% of the total oil weight and include more than 230 compounds such as aliphatic and triterpenic alcohols, sterols, hydrocarbons, volatile compounds and antioxidants.[2]

### *Polyphenols*

Olive oils contain at least 30 different polyphenols which, in addition to their claimed health benefits, contribute to the oils' bitterness and pungency.

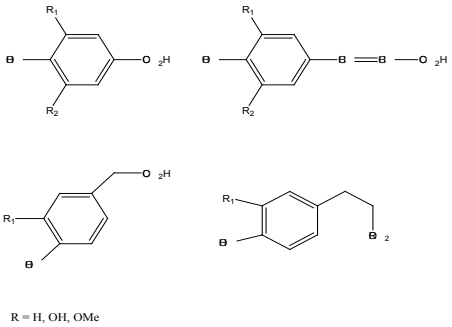


***Fig. 1.*** Generic structural formulae for olive oil polyphenols

According to Martin-Pelaes *et al*[6]: "The Mediterranean diet and consumption of olive oil has been connected in several studies with longevity and a reduced risk of morbidity and mortality… The benefits of consuming olive oil have been known since antiquity and were traditionally attributed to its high content of oleic acid. However, it is now well established that these effects must also be attributed to the phenolic fraction of olive oil with its antioxidant, anti-inflammatory and anti-microbial activities. The mechanism of these effects are varied and probably interconnected. For some activities of olive oil phenolic compounds, the evidence is already strong enough to enable the legal use of health claims on foods."

## Oil extraction and quality

Olive oil is produced by grinding the olives and extracting the oil mechanically or chemically. Traditionally, olives were ground to a paste using large millstones. The paste was spread on fibre disks which were stacked and placed in a press. Pressure on the stack squeezed out the oil and water which was allowed to separate. However, most olive oil currently is produced using hammer mills or disc crushers followed by centrifugal extraction. The paste left after mechanical extraction may contain 5-10% of the total oil which can be removed by chemical extraction.

### *Olive oil quality/grades*

From the first oil extracted from the centrifuge to the last portion bound to the paste, olive oil comes in various quality grades. The Codex Alimentarious Commission gives the classifications and criteria for each, as shown in Table 1.

## The Quality of New Zealand Produced and Foreign Oils – A Comparison

### *Aroma and quality*

Much work has been done investigating aroma-active compounds for evaluation of olive oil quality. Currently, this is determined by sensory evaluation via a "Panel Test", developed by the International Olive Council. While using well-trained panellists produces reproducible and reliable results, there remains the issues of a lack of stable, standardised reference oils and the large number of panellists required for statistically robust results.[10] Volatile compounds in olive oil are mainly produced by oxidation of fatty acids. It is generally agreed that endogenous plant enzymes are responsible for the positive aroma perceptions, while chemical oxidation and exogenous enzymes, usually from microbial activity, are associated with sensory defects. Both the processing and storage of the fruit and the oil contribute to the flavour and overall quality of olive oil.

The aroma of olive oil is attributed to a mixture of aldehydes, alcohols, esters, hydrocarbons, ketones and furans. Levels of these volatile compounds are highest in virgin olive oils. The phenolic content is also known to have a significant impact on the stability and sensory characteristics of olive oil, in addition to claimed health benefits. Evaluation of the sensory quality of virgin olive oils involves determination of the following favourable and unfavourable sensory attributes via the taste panel.[11]

### *Positive attributes*

(i) Fruity: characteristic of oil from healthy, fresh fruits either ripe or unripe.

***Table 1.*** Codex Alimentarious standards for olive oils and olive pomace oils[7,8]

| Grade[a] | FFA (%) as oleic acid[b] | Peroxide value (mEq/kg)[c] | Abs @ 270 nm[d] | $\Delta K$[e] | Median defect (odour and taste)[f] |
|---|---|---|---|---|---|
| Extra virgin olive oil | ≤0.8 | ≤20 | ≤0.22 | ≤0.01 | Me=0 (fruity Me>0) |
| Virgin olive oil | ≤2.0 | ≤20 | ≤0.25 | ≤0.01 | 0<Me≤2.5 (fruity Me >0) |
| Ordinary virgin olive oil | ≤3.3 | ≤20 | ≤0.3 | ≤0.01 | 2.5<Me≤6.0 |
| Refined olive oil | ≤0.3 | ≤5 | ≤1.10 | ≤0.16 | N/A |
| Olive oil (refined and virgin blend) | ≤1.0 | ≤15 | ≤0.90 | ≤0.15 | N/A |
| Refined olive oil pomace | ≤0.3 | ≤5 | ≤2.00 | ≤0.20 | N/A |
| Olive-pomace oil | ≤1.0 | ≤5 | ≤1.70 | ≤0.18 | N/A |

[a] Virgin oils must be produced by physical means, e.g. crushing, washing, decanting, centrifuging and filtering. Heat and chemicals are not permitted. Refined oils may be caustically refined, bleached and deodorised.

[b] Free Fatty Acid (FFA) is a crude indicator of the quality of the fruit and handling procedures prior to milling. It is a measurement of hydrolytic breakdown of the fatty acid chains from triglycerides into diglycerides and monoglycerides, liberating free fatty acids

[c] Peroxide value is a crude indicator of the amount of primary oxidation that has occurred to form peroxide compounds within the oil. A high value indicates that the olives or paste was likely handled improperly, the oil could be defective, and the oil might not keep well. A rancid taste may become noticeable between 30 and 40 mEq/kg.

[d] Absorbance at 270 nm is a more delicate indicator of oxidation, especially in oils that have been heated in the refining process. It measures the quantity of certain oxidized compounds that absorb at wavelengths of 232 and 270 nanometers (nm) in the ultraviolet spectrum.

[e] Delta ($\Delta$) *K* detects the use of colour removing substances and the presence of refined or pomace oil by measuring the difference between absorbance at 270 nm and the absorption difference between 266 nm and 274 nm.

[f] Taste Panel determination of quality. The volatile compounds formed during the processing of olive fruit contribute a combined sensation of smell and taste. Evaluation of the sensory quality of virgin olive oils involves perception of both favourable and unfavourable sensory attributes. Aroma and taste are very complex and cannot currently be determined in the laboratory. The tongue can also detect texture differences difficult to measure analytically. The first and primary objective in sensory evaluation of olive oil is to determine if oils contain one or more of the defects that commonly occur in oils from improper fruit storage, handling, pest infestation, oil storage, or processing.[9]

(ii) Bitter: primary taste produced by quinine, caffeine and other alkaloids.

(iii) Pungent: the biting tactile sensation characteristic of oils produced at the start of the crop year, primarily from unripe olives.

### *Negative attributes*

(i) Fusty: characteristic of oil produced from fruit stored for long periods before extraction undergoing anaerobic fermentation.

(ii) Musty-humid: a characteristic of oils from fruit infested with large numbers of fungi and yeast.

(iii) Muddy sediment: a characteristic of oil that has been left in contact with sediment for a long time.

(iv) Winey-vinegary: flavour due to fermentation of olives forming acetic acid, ethyl acetate and ethanol.

(v) Metallic: occurs in oils with prolonged contact with metallic surfaces.

(vi) Rancid: flavour of oils that have undergone oxidation.

Table 2 lists some of the key volatile compounds responsible for the positive and negative attributes of olive oils as determined by the taste panel.

### *Samples*

A total of 51 olive oil samples were purchased in Christchurch from various supermarkets and other outlets or submitted by olive growers "ready for sale". Of these, 39 were "extra virgin" oils and 12 were classed as "olive oil" or refined "extra light olive oil". Of the 39 extra virgin oils, 19 were produced in New Zealand. The remaining 20 imported oils were Italian (9), Spanish (5), Australian (4), Greek (1) and Palestinian (1).

All samples had their levels of free fatty acids, peroxide, absorbance at 270 nm and ΔK determined to ensure the label claim on each product was accurate. Results for free fatty acids and peroxide are summarised in Table 3. Two Italian oils were found to have a high absorption at 270 nm and low polyphenol levels which could indicate possible refining or mixing with refined oil. The results of all other samples conformed to the label claim.

### *Polyphenol analysis*

The total polyphenol content of olive oils in this study was determined using an adaption of the method of Gawel & Rogers 2006.[13] Briefly, weighed portions of olive oil were dissolved in hexane and extracted with aqueous methanol. The extract was diluted with water and an aliquot was treated with Folin-Ciocalteau reagent and saturated $Na_2CO_3$. The absorbance at 725nm was measured after 1

***Table 2.*** Key volatile compounds linked to positive and negative attributes investigated in this study. Volatiles considered undesirable in excess contributing to negative attributes are in bold italic[10,12]

| Volatile | Odour/taste | Volatile | Odour/taste |
|---|---|---|---|
| ethanol | fermented/musty | cis-***2-hexenyl acetate*** | end product of linolenic acid oxidation |
| penten-3-one | green | trans-***2-hexenyl acetate*** | end product of linolenic acid oxidation |
| ***ethyl butyrate*** | sweet, fruity, cheesy | hexanol | fruity, banana |
| ***ethyl-2-methyl butanoate*** | fruity | 2-nonanone | musty |
| ***ethyl-3-methyl butanoate*** | fruity | *cis*-3-hexenol | leafy |
| ***hexenal*** | green | nonanal | fatty, waxy, pungent |
| ***isoamyl acetate*** | pear, banana | *trans*-2-hexenol | grassy, green |
| 2-heptanone | sweet, fruity | trans-***2-nonenal*** | paper-like, fatty |
| *trans*-2-hexenal | green, astringent | ethyl salicilate | medicinal |
| ***3-methyl butanol*** | woody, whiskey, malty | t,t-***2,4-decadienal*** | deep-fried |
| ***2-phenyl ethanol*** | sweet, winey, musty | | |

***Table 3.*** Mean results for free fatty acid content, peroxide value, polyphenols and total volatile compounds of samples purchased locally

| Grade | FFA (%) Mean (range) | Peroxide (mEq/kg) Mean (range) | Total volatiles (mg/kg) mean (maximum) | Polyphenols (mg/kg) as gallic acid mean ± s.d. |
|---|---|---|---|---|
| Olive oil (n=7) | 0.145 (0.069-0.273) | 6.6 (5.6-9.0) | 1.5 (2.3) | 40 ± 7 |
| Extra light (n=5) | 0.067 (0.042-0.130) | 4.3 (0-7.5) | 0.4 (0.7) | 31 ± 5 |
| Extra virgin New Zealand (n=19) | 0.178 (0.072-0.371) | 12.7 (6.8-20.9) | 23.5 (42.0) | 295 ± 133[a] |
| Extra virgin imported (n=20) | 0.372 (0.174-0.742) | 12.2 (7.5-23.2) | 21.3 (42.1) | 188 ± 53[a] |

[a] Mean polyphenol levels in New Zealand products were higher than imported products, although the difference, given the wide range of levels found, could not be regarded as statistically different in the accepted sense, i.e. $p \leq 0.05$. The difference between these means only becomes "significant" at $p=0.2$ but given the very small sample set, this difference is tantalising indicating that the polyphenol levels of a larger olive oil sample set could be worth investigating.

***Table 4.*** Levels of key volatile compounds in New Zealand and imported extra virgin olive oils. Volatiles generally considered undesirable in excess are in bold italic.

| Volatile | New Zealand mg/kg (s.d.) n=19 | Imported mg/kg (s.d.) n=20 |
|---|---|---|
| ***ethyl butyrate*** | 0.003 (0.006) | 0.098 (0.071) |
| ***ethyl-2-methyl butanoate*** | 0.002 (0.002) | 0.019 (0.020) |
| ***ethyl-3-methyl butanoate*** | 0.000 (0.000) | 0.005 (0.005) |
| ***hexenal*** | 1.532 (0.633) | 2.011 (0.868) |
| ***isoamylalcohol*** | 0.009 (0.007) | 0.042 (0.026) |
| *trans*-2-hexenal | 11.111 (6.160) | 5.238 (2.986) |
| ***3-methy butanol*** | 3.931 (3.375) | 1.311 (1.102) |
| *cis*-3-hexenol | 1.388 (1.064) | 1.722 (0.842) |
| **trans-*2-nonenal*** | 0.122 (0.061) | 0.279 (0.165) |
| **t,t-*2,4-decadienal*** | 0.193 (0.153) | 1.490 (1.887) |
| ***2-phenylethanol*** | 0.196 (0.110) | 0.282 (0.150) |
| **cis-*2-hexenylacetate*** | 0.856 (0.786) | 2.260 (0.858) |
| **trans-*2-hexenylacetate*** | 0.610 (0.609) | 1.660 (0.789) |

hour. Total polyphenols were quantitated by comparison with a standard curve made up of gallic acid in concentrations of 5, 10, 25, 50 and 100 mg/L.

The refining process to which the non-virgin oils are subjected clearly reduced the FFA and peroxide values, but stripped virtually all those volatiles examined from the oil and almost completely eliminated the polyphenols.

### *Determination of key volatiles*

The key volatile compounds of extra virgin olive oils investigated in this study were quantitated using an adaption of the method of Vichi *et al*[14]. Briefly, one gram portions of olive oil were weighed into head space vials, 4-pentan-2-ol was added as an internal standard and the vial sealed. Volatiles were absorbed onto a divinylbenzene-carboxen-polydimethylsiloxane SPME fibre. Separation of volatiles was performed on a GC-MS equipped with a Supelcowax-10, 30 m x 0.25 mm I.D., 0.25 µm film thickness capillary column. Standard curves were prepared by spiking genuine olive oil with key volatiles in concentrations of 0.1, 0.25, 0.5, 1.0, 1.5, 2.5 and 5.0 mg/kg. Oil blanks were also included and the endogenous volatiles subtracted from the spiked levels. Results are shown in Table 4. Not all compounds of interest could be quantitated in part due to the great difference in relative concentration between some of the volatiles, e.g. ethanol, which could be present at high levels compared with the other volatiles resulting in a detector overload. These volatiles have been excluded from Table 4.

### *Multivariate analysis*

One of the aims of this investigation was to determine if the concentration of key volatiles in olive oils could be used to authenticate an olive oil as being of New Zealand origin. Dr Beverley Horn (ESR, Christchurch) undertook an exploratory multivariate analysis of the key volatile levels in 38 of the extra virgin oils (one sample was rejected as the results of the volatiles analysis were considered low and dubious). Principle component analysis (PCA) was conducted using scaled and centred measurements using the R statistical package.[15] The first two principle components provided the best differentiation between olive oils from New Zealand, Australia and other countries as illustrated in Fig. 2.

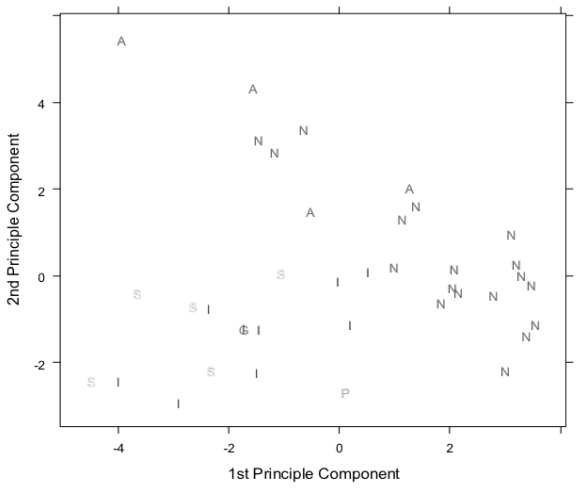


***Fig. 2***. Principle component analysis of olive oil volatiles with reference to country of origin."A" = Australia, "G" = Greece, "I" = Italy, "N" = New Zealand and "P" = Palestine.

Classification trees using binary recursive partitioning of the untransformed data from the tree package suggested oils of New Zealand origin could be separated from other oils on the basis of their isoamyl alcohol concentration, with most New Zealand oils containing < 0.0225 mg/kg. Dr Horn noted in reference to the results, "Both the principle component analysis and the classification tree approach indicate that segregation of extra virgin olive oils according to origin based on volatiles analysis is feasible. Allocations are not completely accurate, but from this small data set, the results are encouraging."

## Discussion

While it must be remembered that the number of samples in this study is very small, the differences between New Zealand and imported olive oils in regards to total

polyphenol and positive/negative volatile concentrations appear to tell a consistent story. While resistant to auto-oxidation, olive oil does undergo degradation with time. Polyphenol levels decrease, while undesirable volatiles increase, such as *trans*-2-hexenyl acetate, one of the final products of the linolenic acid oxidation pathway in olive oil. The New Zealand oils in this survey appear to contain lower levels of some undesirable volatiles than the imported product, although the differences may not be statistically significant in all instances given the wide range of concentrations found for some compounds. The slightly higher level of polyphenols in New Zealand product combined with lower levels of undesirable volatiles may simply indicate that the New Zealand olive oils are often fresher than imported oils that may have been in storage for longer periods or spent more time being shipped than the local product.

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