

## Short communication

# Comparison of olive oil (*Olea europaea*) quality extracted by stonemill and hammermill

RODNEY J. MAILER

JAMIE AYTON

NSW Department of Primary Industries  
Wagga Wagga Agricultural Institute  
Private Mail Bag, Wagga Wagga  
NSW 2650, Australia  
email: mailerr@agric.nsw.gov.au

**Abstract** This study compared two olive oil extraction processes used in New Zealand to assess the influence of processing on oil quality. The extraction systems included an Enrossi stonemill and an Oliomio 50 hammermill, malaxing basin, and centrifuge. Olives (*Olea europaea*) from individual harvests were found to show significantly higher polyphenol and chlorophyll content from the hammermill process. Slightly higher free fatty acids resulted from the hammermill. Fatty acid profiles did not show significant differences between the methods of extraction. Storage over 17 months resulted in increased peroxide values for both oils but no change in chlorophyll, free fatty acids, or polyphenols.

**Keywords** olive oil; *Olea europaea*; fatty acids; polyphenol; induction time; peroxide; chlorophyll

## INTRODUCTION

The high quality of olive oils produced in Australia and New Zealand has been previously described (Mailer et al. 2002). Evaluation of olive oil production in Australia and New Zealand has revealed that quality components vary considerably between environmentally different areas and the range of cultivars grown. Additionally, the maturity of the olives (*Olea europaea* L.) and the method of processing have been shown to contribute to a wide range of quality aspects in oil produced within individual olive groves. Despite the success of the industry in achieving this quality, many factors play a role in determining the chemical and sensory characteristics of individual oils. Besides the influence of the olive (*O. europaea*) cultivar, environmental conditions (Paz Romero et al. 2003) and fruit maturity (Garcia et al. 1996) play a role in determining the degree of polyunsaturation of the fatty acids as well as the polyphenol and chlorophyll concentration of the oil. These factors relate to the nutritional value of the oil as well as the organoleptic characteristics. Together with the combination of agronomic and genetic effects, the oil extraction process can also significantly influence the final product.

Polyphenols have been attributed with many influences in the oil including oxidative stability as well as the sensory characteristics of pungency and bitterness. High levels of polyphenols have been correlated closely with long shelf life and induction time studies such as the rancimat test (Salvador et al. 1998). High polyphenol levels can result from early harvest timing which produces olive oil with a more pungent character than that of mature fruit. High polyphenols may also relate to the level of moisture available to the trees during fruit development.

The method of extracting olive oil in ancient times involved various modifications of a stone wheel revolving in a mortar (*mortarium*) (Chabour 2003). Other developments of oil extractors are reported by Chabour (2003), including various hydraulic

pressing mats and hammer mills. Today there are many modifications to these early types of mills, with technological advances allowing continuous extraction processes. As a result of the new developments, there are now many alternative olive processing methods and these machines can have a major influence on oil chemical quality and its characteristics (Di Giovacchino 2000).

Two methods currently used in New Zealand for oil extraction include the Oliomio hammermill and the Enorossi stonemill. Both are continuous extraction machines with the major difference being the method in which the olives are milled. The former method uses rapidly rotating hammers to break up the fruit and force it by centrifugal force through the holes of a revolving punched steel anulus. The stonemill however uses two rotating stainless steel covered concrete wheels to crush the fruit as they track around the floor of a stainless steel bowl. The stonemill therefore uses a squashing process to release the inter- and intracellular fluids whilst leaving much of the skin intact.

This study has used these two processes to extract oil from homogenous batches of olives which were divided into equal parts. The olives were processed within 24 h of harvesting and all conditions kept the same to ensure only the milling process was different. In this way, any differences in composition can be attributed directly to the milling method.

The oil from each milling method was considerably different in appearance, with that from the hammermill being bright green and the oil from the stonemill light green to straw coloured. There was a stronger degree of pungency observed in the oil from the hammermill, although this was not analysed by a sensory panel. Chemical analysis indicated that the hammermilled oil was higher in chlorophyll and polyphenols and had a longer rancimat induction time compared with that of the stonemill. Oil from the hammermill had a slightly higher free fatty acid level although it was well within the International

Olive Oil Council (IOOC) limit of <0.8% for extra virgin olive oil (EVOO). Fatty acid profiles showed no significant differences between the processes. Shelf life studies on the oil over 17 months indicated an increase in peroxide value as well as increases in  $K_{232}$  values of the oil. All of the oils were within the limits of IOOC EVOO for the entire analysis period.

## MATERIALS AND METHODS

### Processing mills

Two mills were used to compare the effects of each on oil quality. The first was an Enorossi stonemill plant consisting of a washer/deleaser unit, hopper/feeder, stonemill, malaxer, and centrifugal decanter. The second was an Oliomio 50 unit including a hopper, leaf blower, enclosed hammermill, malaxing basin, and centrifuge.

The stonemill has two concrete-filled wheels which rotate in a stainless steel bowl, all of which is covered with a Perspex dome. Olives are converted to paste by a bursting and squashing process rupturing the cell membrane to release inter- and intracellular fluids while leaving much of the skin intact. The Oliomio hammermill however, grinds the olives with high speed rotating hammers which force the olives as paste through holes in a revolving steel anulus. The main difference therefore between the two operations is the method of grinding to obtain olive paste.

### Olive samples

Three separate batches of olives were utilised in the study. The first was a batch of 'Frantoio' olives, harvested from Waiheke Island on 11 April 2002. The fruit were a mixture of green, straw, and black olives. The batch of 126 kg was put through a washer/deleaser unit, split into two equal batches of 63 kg, and milled within 22 h. The second batch were also 'Frantoio' olives, from Waiheke Island, harvested on 23 April 2002. A total of 130 kg was harvested and divided into two batches. The third batch was mixed cultivars, harvested on 18 May 2002 with a total of 124 kg which were separated into two batches of equivalent colour. The oil was visually different to that from the Oliomio mill, being bright green with a distinct pungent flavour. The oil extracted by stonemill was pale green with a mild flavour. Samples were received at NSW Agriculture, Australia in commercially packed bottles. The samples were stored in the dark in air-conditioned laboratories (20–25°C) during testing.

**Table 1** Date and percentage oil extracted at each harvest using two alternative mill types, stonemill and hammermill.

Harvest date	% oil	
	Stonemill	Hammermill
11 April 2002	12.26	12.01
23 April 2002	16.24	17.35
18 May 2002	14.78	12.58

## Analyses

### *Free fatty acids (FFA)*

Free fatty acids were determined by a modified method of the American Oilseed Chemists' Society (Aa 6-38) (AOCS 1998). Modification involved replacement of 0.25*N* sodium hydroxide (NaOH) with 0.1*N* NaOH. Fresh 0.1*N* NaOH was prepared daily.

### *Peroxide value (PV)*

Peroxide value was determined using the International Union of Pure and Applied Chemistry (IUPAC 1992) method 2-501.

### *Total polyphenols*

A modification of the Gutfinger (1981) method, using caffeic acid as the standard, was used to determine polyphenol content. Oil (10 g) was dissolved in hexane (50 ml), extracted with 80% aqueous methanol, and mixed with Folin-Ciocalteu reagent, as previously described (Mailer et al. 2002). A standard calibration curve was produced using caffeic acid. Standards were prepared and analysed in the same way as the sample solutions.

### *Induction time*

A Metrohm 679 Rancimat was utilised to measure induction time of the oil. A block temperature of 130°C was used with airflow of 20 litre air/h.

### *Chlorophyll content*

Chlorophyll content was determined using the American Oilseed Chemists' Societies method Ch 4-91 (AOCS 1998).

### *UV absorbance*

UV absorbance was determined using the IOOC method COI/T.20/ Doc 19 (IOOC 2003). Delta K is calculated from the extinction coefficient at 270 nm.

### *Fatty acid profile*

The fatty acid profile was determined as fatty acid methyl esters by gas chromatography as described previously (Mailer et al. 2002). Separation of the fatty acid methyl esters was performed on a Varian 3800 Gas Chromatograph using a Supelco BPX 70 chromatography column (30 m by 0.22 mm; 0.25 µm film) and flame ionisation detector (FID). The column temperature was programmed at 185°C for 8 min, and then increased at 10°C per min up to 220°C. It was held for 3 min before cooling. The injector (split mode) temperature was set at 240°C

with a split ratio of 1:50. Detector temperature was 250°C. Data was analysed using Star Workstation Chromatography software (Version 4.51).

## Statistical analysis

Statistical analysis was carried out using S-Plus for Windows provided by Insightful Corporation.

## RESULTS

### Analyses

#### *Olive oil yield*

Olive oil yield was similar for both methods with no consistent outcome for either method of extraction (Table 1). The yield was consistently higher for the second harvest which is similar to previous studies.

#### *Free fatty acids*

Free fatty acids in all batches of olives were ≤0.18%, well under the standard of ≤0.8% required to meet EVOO status (Table 2). The three batches of oil were similar for each method of extraction. However there was a significant difference ( $P < 0.01\%$ ) between the two systems with the hammermill producing higher levels of FFAs. There was no difference between oils tested when received or after standing for 8 and 17 months.

#### *Peroxide value*

Peroxide value was also within the IOOC standard of 20 meq/kg for EVOO with the maximum level at initial time of 7 to 11 meq/kg (Table 2). Although there was no difference between the oil from the different mills, there was a significant difference between oils after standing for 8 and 17 months. The average PV had risen from 8.6 to 13.7 after 8 months and to 18.8 after 17 months.

#### *Chlorophyll content*

The average chlorophyll content at harvest was also significantly higher in oil from the hammermill (8.9 g/kg) than that from the stonemill (3.6 g/kg) ( $P < 0.05\%$ ) (Table 2). The chlorophyll levels remained high in storage in the dark.

#### *Induction time*

Rancimat results showed the oil from the hammermill to be significantly more stable than oil from the stonemill with initial induction times of 5.5 and 2.0 h respectively (Table 2). Although the stability of the oil declined with age, the stability of the hammermill product remained comparatively higher throughout the study.

### Total polyphenols

Polyphenols showed significant differences between the two methods of processing with the stonemill extracting considerably less polyphenols than the hammermill. The average value at the initial analysis time was 126 g/kg for the stonemill and 278 g/kg for the hammermill which was almost double the concentration (Table 2). There was no significant difference between the oil at receipt and after 17 months.

### UV absorbance

The UV absorbance was only measured once oils had been stored for 8 and 17 months (Table 3). The oils were initially within IOOC specification for EVOO but in all instances continued to increase once oils had been stored for 8 to 17 months. At that time one oil had exceeded the standard for  $K_{232}$ .

### Fatty acid profile

Fatty acid profiles were only measured at the time of receipt and again after 17 months (Table 4). They were all consistent with IOOC standards for EVOO. There was no significant difference between batches of olives, methods of extraction, or times of storage.

## DISCUSSION

As the fruit were harvested and processed within the same time period, the fruit quality can be presumed to be identical for both methods of extraction. Therefore, as shown in this study, processing times and temperatures may be expected to be the major influence on the level of free fatty acids. Both processes were similar in timing (c. 2 h) from hopper to centrifuge. No heat or additional water was added

**Table 2** Chemical components of olives (*Olea europaea*) harvested and processed at three dates using two alternative mill types and analysed 2, 8, and 17 months after the final harvest (NS, not significant).

Sample	% Free fatty acids (as oleic acid)	Peroxide value meq/kg oil	Chlorophyll (mg/kg)	Induction (h)	Polyphenols (mg/kg as caffeic acid)
<b>Initial analysis 18 Jul 2002</b>					
Mean for stonemill	0.11	10	3.6	1.97	126
Mean for hammermill	0.16	7	8.9	5.47	278
<b>2nd analysis 8 Jan 2002</b>					
Mean for stonemill	0.14	15	3.1	1.41	206
Mean for hammermill	0.19	12	8.2	4.35	290
<b>3rd analysis 30 Oct 2003</b>					
Mean for stonemill	0.13	17	3.0	1.03	139
Mean for hammermill	0.18	21	8.2	3.43	239
<b>Analysis of variance</b>					
Mill	$P < 0.001$	NS	$P < 0.001$	$P < 0.001$	$P = 0.011$
Date of analysis	NS	$P < 0.001$	NS	$P = 0.0425$	NS
Mill $\times$ date	NS	NS	NS	NS	NS

**Table 3** Extinction coefficient at 232 and 270 nm of olive oil harvested and processed at three dates using two alternative mill types, stonemill and hammermill. Samples were tested at 8 and 17 months after final harvest.

Sample	$K_{1\text{ cm}}^{1\%}$	232 nm	K270 nm	$\Delta K$
<b>2nd analysis period 8 Jan 2003</b>				
Stonemill, mean of three harvests	1.943	0.105	0.00	0.00
Hammermill, mean of three harvests	1.762	0.123	0.00	0.00
<b>3rd analysis period 30 Oct 2003</b>				
Stonemill, mean of three harvests	2.192	0.119	0.00	0.00
Hammermill, mean of three harvests	1.914	0.141	0.00	0.00

**Table 4** Average fatty acid profiles (as % of total fatty acids) of three olive oil samples extracted by two alternative mills, at two months and 17 months after final harvest.

	C14:0	C16:0	C16:1	C17:0	C17:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C24:0
<b>Initial analysis 18 Jul 2002</b>													
Stonemill, mean of three harvests	0.0	11.7	0.8	0.1	0.1	1.8	78.6	5.5	0.6	0.3	0.3	0.1	0.0
Hammermill, mean of three harvests	0.0	11.2	0.7	0.1	0.1	2.0	78.9	5.5	0.6	0.4	0.3	0.1	0.0
<b>3rd analysis 30 Oct 2003</b>													
Stonemill, mean of three harvests	0.0	11.1	0.7	0.1	0.1	1.9	79.3	5.4	0.6	0.3	0.3	0.1	0.1
Hammermill, mean of three harvests	0.0	10.9	0.7	0.1	0.1	2.1	79.2	5.5	0.6	0.4	0.3	0.1	0.0

to either process. It is therefore not clear why the hammermill produced higher levels of free fatty acid on average. Sifi et al. (2001) found pressed oils were higher in acidity because of the increased contact with the vegetable water than centrifuged oils which encourage hydrolysis of triacylglycerols. However, both methods produced very low FFA within acceptable levels.

Peroxide value may also be related to temperature and exposure to oxygen in processing and storage. Clearly there was no influence from either system in increasing peroxide and the initial results were the same. However with time, peroxide values increased in all samples in storage to the extent that one sample had exceeded IOOC standards for EVOO.

Chlorophyll content was significantly higher in oil from the hammermill which was consistent with observations of the bright green colour at the time of processing. As a large proportion of the chlorophyll is contained in the epicarp, or skin, it appears the stonemill process was not as efficient at breaking up the epicarp to release more chlorophyll. Chlorophyll is considered an advantage in providing an aesthetic appearance to the oil but can also have negative attributes. Chlorophyll is known to promote oxidation when the oil is exposed to light, although it can also work as an antioxidant when stored in the dark (Boskou 1996). The maintenance of the chlorophyll levels in the oil over 17 months is indicative of its stability if kept in the dark. The lack of a treatment effect on peroxide value suggests that it has not played a significant role in contributing to stability in oils with considerably different levels of chlorophyll.

The Rancimat test is considered useful in predicting the stability and shelf life of oil. However the accelerated oxidation of the oil by holding it at an elevated temperature whilst passing oxygen through the sample is not closely related to oil stored in real-life situations. It has shown consistency in this study where stonemill oils had significantly lower Rancimat times throughout the study.

Polyphenols have long been considered a benefit to the stability of oil because of their antioxidant effect (Sifi et al. 2001). This can be seen from these results in which the polyphenol content has a direct relationship to the Rancimat test ( $R^2 = 0.66$ ). Considering the effect of other variables such as peroxide value and fatty acid profiles, this relationship indicates a major influence of polyphenols in providing stability. The high levels of polyphenols from the hammermill process showed clearly that polyphenols are extracted more efficiently by that

method. Very high levels of polyphenols are not necessarily ideal and the influence on sensory qualities needs to be considered. Immature fruit with high polyphenols content may be better extracted with a less vigorous system to avoid highly pungent flavours whereas more mature fruit may benefit from a system that can more efficiently extract those components.

Measurement of the UV absorbance of the oil is used to highlight aging of the oil and increases in primary oxidative products. The oils did not show a significant change in the UV absorbance over time (Table 3).

The fatty acid profile is generally cultivar dependant although environmental conditions can influence this (Paz Romero et al. 2003). As these olives were harvested from similar sites and the cultivar 'Frantoio' was prominent, a similarity in the fatty acid profile may be expected. Despite harvest timing being spread over 5 weeks, this period would not be expected to have a significant influence on fatty acid composition, based on previous studies (unpubl. data).

The influence of processing has been shown in previous studies to have a major relationship to oil quality, sensory characteristics, and shelf life. Using two common extraction methods and controlled evaluation of olives grown and processed in New Zealand, the extent of this relationship has been described. Both processes provide benefits to growers—they can choose the best method to process olives of varying characteristics to produced optimum oil quality.

#### ACKNOWLEDGMENTS

Ms Jeryl Aldred of Waiheke Wild Limited, Waiheke Island, provided the olives and details of harvest and processing procedures. NSW Agriculture funded the research.

#### REFERENCES

- AOCS 1998: Official methods and recommended practices of the American Oil Chemists Society. 5th ed. Champaign, Illinois, AOCS Press.
- Boskou, D. 1996: Olive oil: chemistry and technology. Champaign, Illinois, AOCS Press. p. 115.
- Chabour, M. 2003: Olive oil extraction methods in Algeria: changes and surviving traditions. *Olivae* 99: 50–55.
- Di Giovacchino, L. 2000: Technological aspects. In: Harwood, J.; Aparicio, R. ed Handbook of olive oil: analysis and properties. Gaithersburg, Maryland, Aspen Publishers. Pp.17–60.
- Gutfinger, T. 1981: Polyphenols in olive oils. *Journal of the American Oil Chemists' Society* 62: 895–898.
- IOOC 2003: International Olive Oil Council Trade Standard applying to olive oil and olive-pomace oil. Madrid, Spain, International Olive Oil Council.
- IUPAC 1992: Standard Methods for the Analysis of Oils, Fats and Derivatives. 7th ed. Oxford, United Kingdom, Blackwell Scientific Publications.
- Mailer, R. J.; Ayton, J.; Conlan, D. 2002: Comparison and evaluation of the quality of thirty eight commercial Australian and New Zealand olive oils. *Advances in Horticultural Science* 16(3–4): 259–266.
- Paz Romero, M.; Jesus Tovar, M.; Ramo, T.; Jose Moltiva, M. 2003: Effect of crop season on the composition of virgin olive oil with protected designation of origin "Les Garrigues". *Journal of the American Oil Chemists Society* 80(5): 423–430.
- Salvador, M.; Aranda, F.; Fregapane, G. 1998: Chemical composition of commercial Coormicabra virgin olive oil from 1995/1996 and 1996/1997 crops. *Journal of the American Oil Chemists Society* 75(10): 1305–1311.
- Sifi, S.; Ben Hamida, J.; Amamou, T. 2001: Impact of processing methods on oil quality. *Olivae* 87: 33–38.