

# **Assessment of Bioactive Analytical Fractions of Destoned Virgin Olive Oils from Campania Region**

A. Ranalli, S. Contento, D. Marchegiani, Di. Pardi, F. Girardi, D. Pardi

CRA-Centro di Ricerca per l'Olivicoltura e l'Industria Olearia, Sede Scientifica di Città S. Angelo, Viale Petruzzi 75, 65013 Città S. Angelo (Pescara), Italy. Tel: 085/95294; Fax: 085/959518; E-mail: [alfonso.ranalli@entecra.it](mailto:alfonso.ranalli@entecra.it); Website: <http://alfonsoranalli.altervista.org>

**Keywords:** Pulp olive oils, physico-chemical traits, aroma, flavour, shelf-life, typicality

## **Abstract**

**This work reports on the sensory and analytical quality level of destoned virgin olive oils. Due to the non-mechanical/thermal stress of olive paste, related to the soft action of destoner, the above destoned oils stood out for their intense fragrance and their high levels of natural flavourings, aromas, antioxidants and vitamins.**

## **INTRODUCTION**

At present there is much interest, in Italy and other Mediterranean olive-growing countries, for destoned virgin olive oil (Patumi et al., 2003; Luaces et al., 2004; Lavelli and Bondesan, 2005; Servili et al., 2007). We, in the last few years, published several research papers reporting on the analytical data of many destoned oils taken during technological experiments, carried out in our experimental oil mill (Ranalli et al., 2007). Destoning led to obtain high-quality nutraceutical olive oil; however, addition to the oily pastes of food micronised talc and exogenous depolymerising enzyme processing aids was needed to obtain oil outputs comparable with those given by stoned olives. These

technological adjuvants were even useful when a bland finisher (disk or hammer crusher) was coupled to destoner. We also fully characterised destoned oils withdrawn from oil mills located in all Italian olive-growing regions. Generally, these oil mills do not produce the corresponding stoned oils. In order to obtain highest-quality destoned oils some producers collect only olives at the right maturation degree by repeating harvest more time in the same orchard during scalar ripening. Sometimes oil quality is further enhanced by coupling destoning to biological agricultural olive production techniques. Destoned oils, which have high production costs, are however often sold at a price as high as about € 80/kg. In this research paper we give the analytical pattern of destoned oils produced in Campania region from five cvs. of *Olea europaea* L. (Frantoio, Moraiolo, Carappellese, Leccino and Rotondella).

## **MATERIALS AND METHODS**

The composition of triglycerides was determined by HPLC using an LDC<sub>4</sub> 100 Ms model system equipped with a Shodex RF Se-61 differential refractometer and a chromoject integrator (Thermo Separation Products, Schaumburg, IL, USA). Volatiles, biophenols, fatty acids, phytosterols, triterpene dialcohols, superior triterpene alcohols, aliphatic long-chain alcohols, diterpene alcohols and waxes were determined by HRGC methods. Oxidised triglycerides, triglyceride oligopolymers, diglycerides and total polar compounds were determined by high-performance size exclusion chromatography (HPSEC). These analyses and others were performed as fully described in Ranalli et al. (2007). All oil samples came from olive batches processed by a two-phase decanter. They were stored frozen (-20° C) until analysed. The obtained analytical data

were processed using both univariate (ANOVA) and multivariate (PCA, CDA, HCA, SIMCA, KNN and CART) statistics.

## RESULTS AND DISCUSSION

Part of the analytical data is given in Tables 1, 2 and 3. In general, the examined destoned oil varieties from Campania region had a delicate and intense flavour and aroma and thus received high sensory scores. They in fact (noticeably *Carpellese*, *Rotondella* and *Leccino* oils) had high concentrations of pleasant volatiles, like (*E*)-2-hexenal and exanal (two major agreeable compounds of the aromatic oil head-space fraction). This circumstance is likely linked to the fact that the hydroperoxide-lyase (an enzyme making up the lipoxygenase system) is significantly inactivated at a temperatures as low as 15 °C. Thus, the biogenesis of green volatiles during the low temperatures of destoning-based processing, is higher (Ranalli et al., 2007).

Destoned oils had concentrations of biophenol antioxidants always over the 200 mg kg<sup>-1</sup> level. Among these, secoiridoid derivatives (free tyrosol and hydroxytyrosol and aglycon structures containing them), were significantly present. Consequently, their resistance to rancidity (and their potential shelf- life) was high (Table 1). This trend could be attributable to the soft action of destoner on olive drupes, which results in lower thermal quinonisation of phenols. Moreover, since the kernel tissues are richest in polyphenoloxidase and peroxidase enzymes, there was lower enzymatic oxidation of phenols (Ranalli et al., 2007). The usage of a soft destoner also leads to produce oils having always significant levels of tocopherols (Table 1).

By contrast the analysed destoned oils were not very rich in chlorophylls and carotenoids since destoner acts softly on the fruit hypoderm tissue (were these chloroplast

pigments are mostly located). The related values of CIE parameters (chroma and brightness) corroborated this circumstance. The other analytical parameters in Tables 1 and 2 were not or barely affected by destoning. Only the oil phytosterol compounds (Table 3) often tended to be low, owing to the absence in destoned oil of the sterol compounds from the olive seed (which has a plentiful sterol fraction).

## **ACKNOWLEDGEMENT**

This work was part of the special Projects VALOROLIO and RIOM funded by Ministero per le Politiche Agricole, Alimentari e Forestali, the latter by CIPE funds.

## **Literature cited**

- Lavelli, V. and Bondesan, L. 2005. Secoiridoids, tocopherol, and antioxidant activity of monovarietal virgin olive oil extracted from de-stoned fruits. *J. Agric. Food Chem.* 53: 1102-1107.
- Luaces, P., Pérez, A.G. and Sanz, C. 2004. Efecto del deshuesado de la aceituna sobre el aroma del aceite de oliva virgen. *Grasas y Aceites.* 55: 174-179.
- Patumi, M., Terenziani, S., Ridolfi, M. and Fontanazza, G. 2003. Effect of Fruit Stoning on Olive Oil Quality. *J. Amer. Oil Chem.Soc.* 80: 249-255.
- Ranalli, A., Benzi, M., Gomes, T., Del curatolo, D., Marchegiani, D. and Lucera, L. 2007. Concentration of natural pigments and other bioactive components in pulp oils from de-stoned olives. *Innov. Food Sci. & Emerg. Tech.* 8: 437-442.
- Servili, M., Taticchi, A., Esposito, S., Urbani, S., Selvaggini, R. and Montedoro, G.F. 2007. Effect of olive stoning on the volatile and phenolic composition of virgin olive oil. *J. Agric. Food Chem.* 55: 7028-7035.

## Tables

Table 1. Values of general analytical variables in five Italian destoned virgin olive oil varieties from Campania region. <sup>1</sup>

Analytical variables	Frantoio	Moraiolo	Carpellese	Leccino	Rotondella
Free acidity (% oleic acid)	0,3 <sup>a</sup>	0,2 <sup>a</sup>	0,2 <sup>a</sup>	0,4 <sup>a</sup>	0,3 <sup>a</sup>
Peroxide index (meq O <sub>2</sub> kg <sup>-1</sup> )	13,9 <sup>a</sup>	7,5 <sup>d</sup>	9,2 <sup>c</sup>	12 <sup>b</sup>	12,4 <sup>b</sup>
Carbonyl index-IWM (E/Y)	6,3 <sup>a</sup>	6,9 <sup>a</sup>	4,8 <sup>b</sup>	6,1 <sup>a</sup>	6,0 <sup>a</sup>
Total phenols (as caffeic acid, mg kg <sup>-1</sup> )	242 <sup>a</sup>	353 <sup>b</sup>	233 <sup>a</sup>	203 <sup>c</sup>	291 <sup>d</sup>
<i>o</i> -Diphenolics (as caffeic acid, mg kg <sup>-1</sup> )	123 <sup>a</sup>	194 <sup>b</sup>	111 <sup>c</sup>	118 <sup>c</sup>	166 <sup>d</sup>
Tyrosol (as resorcinol, mg kg <sup>-1</sup> )	16 <sup>a</sup>	22 <sup>b</sup>	10 <sup>c</sup>	5 <sup>d</sup>	13 <sup>c</sup>
Hydroxytyrosol (as resorcinol, mg kg <sup>-1</sup> )	23,8 <sup>a</sup>	27 <sup>b</sup>	14,1 <sup>c</sup>	7,3 <sup>d</sup>	22,6 <sup>a</sup>
Tyrosol-aglycons (as resorcinol, mg kg <sup>-1</sup> )	30 <sup>a</sup>	41 <sup>b</sup>	27 <sup>ac</sup>	25 <sup>c</sup>	35 <sup>d</sup>
Hydroxytyr-aglycons (as resorcinol, mg kg <sup>-1</sup> )	33 <sup>a</sup>	46 <sup>b</sup>	30 <sup>ac</sup>	27 <sup>c</sup>	41 <sup>d</sup>
Tocopherols (mg kg <sup>-1</sup> )	148 <sup>a</sup>	95 <sup>b</sup>	216 <sup>c</sup>	259 <sup>d</sup>	210 <sup>c</sup>
Swift's test (h) – Endurance to oxidation	11,6 <sup>a</sup>	23,1 <sup>b</sup>	13,8 <sup>c</sup>	20,8 <sup>d</sup>	15,6 <sup>e</sup>
Turbidity (NTU)	10,6 <sup>a</sup>	14,0 <sup>b</sup>	8,3 <sup>c</sup>	6,2 <sup>d</sup>	12,0 <sup>e</sup>
K <sub>232</sub>	2,16 <sup>a</sup>	1,50 <sup>b</sup>	2,11 <sup>a</sup>	1,89 <sup>b</sup>	2,02 <sup>a</sup>
K <sub>270</sub>	0,13 <sup>a</sup>	0,10 <sup>a</sup>	0,12 <sup>a</sup>	0,09 <sup>a</sup>	0,13 <sup>a</sup>
ΔKx10 <sup>3</sup>	-4	-1	-6	-4	-4
Sensory scoring (panel test)	8,3	8,5	9,1	8,8	9,0
Chlorophylls and pheophitins (mg kg <sup>-1</sup> )	80,1 <sup>a</sup>	150,5 <sup>b</sup>	73,9 <sup>c</sup>	65,9 <sup>d</sup>	105,7 <sup>e</sup>
Carotenoids (mg kg <sup>-1</sup> )	27,6 <sup>a</sup>	61,1 <sup>b</sup>	28,0 <sup>c</sup>	20,8 <sup>d</sup>	42,6 <sup>e</sup>
Brightness (%)	75,7 <sup>a</sup>	87,6 <sup>b</sup>	76,1 <sup>a</sup>	81,9 <sup>c</sup>	65,6 <sup>d</sup>
Chroma (%)	82,2 <sup>a</sup>	63,9 <sup>b</sup>	83,9 <sup>a</sup>	64,1 <sup>b</sup>	95,0 <sup>c</sup>
Hue (nm)	577 <sup>a</sup>	577 <sup>a</sup>	577 <sup>a</sup>	576 <sup>a</sup>	577 <sup>a</sup>
Integral colour index	10 <sup>a</sup>	25,7 <sup>b</sup>	9,9 <sup>a</sup>	5,5 <sup>c</sup>	17,4 <sup>a</sup>
Squalene (%)	0,5 <sup>a</sup>	0,6 <sup>ab</sup>	0,6 <sup>ab</sup>	0,7 <sup>b</sup>	0,9 <sup>c</sup>
Polyphenols/PUFA ratio	31,1 <sup>a</sup>	51,4 <sup>b</sup>	31,3 <sup>a</sup>	34,1 <sup>c</sup>	34,5 <sup>c</sup>
OOL+LnPP	13,6 <sup>a</sup>	7,9 <sup>b</sup>	15,1 <sup>c</sup>	11,1 <sup>d</sup>	11,5 <sup>d</sup>
OOO+PoPP	35,1 <sup>a</sup>	45,8 <sup>b</sup>	37,1 <sup>c</sup>	41,5 <sup>d</sup>	37,9 <sup>c</sup>
SOL+POO	23,65 <sup>a</sup>	26,5 <sup>b</sup>	22,7 <sup>c</sup>	31,9 <sup>d</sup>	25,1 <sup>e</sup>
MUFA/PUFA ratio	12,5 <sup>a</sup>	11,3 <sup>b</sup>	13,1 <sup>a</sup>	16,4 <sup>c</sup>	11,6 <sup>b</sup>
ω <sub>6</sub> /ω <sub>3</sub> ratio	10,8 <sup>a</sup>	12,1 <sup>b</sup>	8,9 <sup>c</sup>	9,8 <sup>d</sup>	9,6 <sup>d</sup>
( <i>E</i> )-2-hexenal (mg kg <sup>-1</sup> )	169 <sup>a</sup>	138 <sup>b</sup>	2155 <sup>c</sup>	666 <sup>d</sup>	926 <sup>e</sup>
Exanal (mg kg <sup>-1</sup> )	58 <sup>a</sup>	10 <sup>b</sup>	68 <sup>c</sup>	30 <sup>d</sup>	42 <sup>e</sup>
Waxes (C <sub>40</sub> -C <sub>46</sub> ) (mg kg <sup>-1</sup> )	46 <sup>a</sup>	42 <sup>a</sup>	48 <sup>a</sup>	38 <sup>b</sup>	66 <sup>c</sup>

<sup>1</sup> Data are means of three replicates (CVs ≤ 6,1%). Within each row, values without common superscript letters are significantly different (*Tukey's* HSD range test,  $p \leq 0.05$ ).

Table 2. Composition (mg kg<sup>-1</sup>) of the superior aliphatic and triterpene alcohol fractions in five Italian destoned virgin olive oil varieties from Campania region.<sup>1</sup>

	Frantoio	Moraiolo	Carpellese	Leccino	Rotondella
<b>Aliphatic alcohols</b>					
1-Docosanol (C <sub>22</sub> )	65,5 <sup>a</sup>	5,9 <sup>b</sup>	10,3 <sup>c</sup>	70,1 <sup>d</sup>	50,3 <sup>e</sup>
Tricosanol (C <sub>23</sub> )	4,4 <sup>a</sup>	3,3 <sup>b</sup>	1,8 <sup>c</sup>	2,4 <sup>d</sup>	2,1 <sup>d</sup>
1-Tetracosanol (C <sub>24</sub> )	81,3 <sup>a</sup>	16,4 <sup>b</sup>	28,3 <sup>c</sup>	38,9 <sup>d</sup>	54,6 <sup>e</sup>
Pentacosanol (C <sub>25</sub> )	13,9 <sup>a</sup>	5,5 <sup>b</sup>	7,0 <sup>c</sup>	6,8 <sup>c</sup>	4,7 <sup>b</sup>
1-Hexacosanol (C <sub>26</sub> )	139,3 <sup>a</sup>	37,7 <sup>b</sup>	72,7 <sup>c</sup>	48,7 <sup>d</sup>	63,6 <sup>e</sup>
Eptacosanol (C <sub>27</sub> )	9,0 <sup>a</sup>	4,3 <sup>b</sup>	4,9 <sup>b</sup>	3,3 <sup>c</sup>	3,9 <sup>bc</sup>
1-Octacosanol (C <sub>28</sub> )	62,9 <sup>a</sup>	5,9 <sup>b</sup>	34,0 <sup>c</sup>	25,6 <sup>d</sup>	29,4 <sup>cd</sup>
<b>Triterpene alcohols</b>					
β-Amyrin	121,0 <sup>a</sup>	35,5 <sup>b</sup>	44,1 <sup>c</sup>	19,6 <sup>d</sup>	63,6 <sup>e</sup>
Butyrospermol	156,7 <sup>a</sup>	84,4 <sup>b</sup>	95,4 <sup>c</sup>	97,7 <sup>c</sup>	98,3 <sup>c</sup>
Tirucallol	26,9 <sup>a</sup>	10,3 <sup>b</sup>	12,6 <sup>c</sup>	13,3 <sup>c</sup>	17,3 <sup>d</sup>
Dammaradienol	44,9 <sup>a</sup>	24,8 <sup>b</sup>	28,5 <sup>bc</sup>	29,5 <sup>c</sup>	36,0 <sup>d</sup>
α-Amyrin	12,2 <sup>a</sup>	6,7 <sup>b</sup>	7,9 <sup>b</sup>	18,19 <sup>c</sup>	44,7 <sup>d</sup>
Cycloartenol	483,3 <sup>a</sup>	312,0 <sup>b</sup>	268,8 <sup>c</sup>	471,7 <sup>a</sup>	437,7 <sup>d</sup>
24-Methylcycloartanol	548,2 <sup>a</sup>	250,7 <sup>b</sup>	296,3 <sup>c</sup>	634,0 <sup>d</sup>	313,7 <sup>c</sup>
Cyclobranol	0,2 <sup>a</sup>	1,6 <sup>b</sup>	5,1 <sup>c</sup>	7,9 <sup>d</sup>	2,0 <sup>e</sup>
Alcoholic index	0,14 <sup>a</sup>	0,01 <sup>b</sup>	0,04 <sup>c</sup>	0,62 <sup>d</sup>	0,61 <sup>d</sup>
<b>Diterpene alcohols</b>					
Phytol	235,4 <sup>a</sup>	81,4 <sup>b</sup>	322,0 <sup>c</sup>	322,0 <sup>c</sup>	125,4 <sup>d</sup>
Geranylgeraniol	126,5 <sup>a</sup>	13,3 <sup>b</sup>	58,6 <sup>c</sup>	58,6 <sup>c</sup>	44,8 <sup>d</sup>
<b>Methylsterols</b>					
Citrostadienol	502,8 <sup>a</sup>	64,0 <sup>b</sup>	351,7 <sup>c</sup>	351,7 <sup>c</sup>	141,6 <sup>d</sup>

<sup>1</sup> Data are means of three replicates (CVs ≤ 6,1%). Within each row, values without common superscript letters are significantly different (*Tukey's* HSD range test,  $p \leq 0.05$ ).

Table 3. Composition (mg kg<sup>-1</sup>) of the phytosterol and triterpene dialcohol fractions in five Italian destoned virgin olive oil varieties from Campania region. <sup>1</sup>

	Frantoio	Moraiolo	Carpellese	Leccino	Rotondella
<b>Phytosterols</b>					
Cholesterol	2,3 <sup>a</sup>	5,0 <sup>b</sup>	2,7 <sup>a</sup>	2,6 <sup>a</sup>	4,2 <sup>c</sup>
Brassicasterol	0,9 <sup>a</sup>	2,0 <sup>b</sup>	0,3 <sup>c</sup>	0,7 <sup>a</sup>	0,8 <sup>a</sup>
24-Methylencholesterol	4,3 <sup>a</sup>	7,0 <sup>b</sup>	3,0 <sup>c</sup>	3,0 <sup>c</sup>	5,7 <sup>d</sup>
Campesterol	83,0 <sup>a</sup>	82,0 <sup>a</sup>	90,8 <sup>b</sup>	60,2 <sup>c</sup>	87,3 <sup>ab</sup>
Campestanol	0,9 <sup>ab</sup>	1,0 <sup>a</sup>	0,7 <sup>a</sup>	1,5 <sup>b</sup>	1,5 <sup>b</sup>
Stigmasterol	41,3 <sup>a</sup>	27,0 <sup>b</sup>	20,9 <sup>c</sup>	31,3 <sup>b</sup>	43,4 <sup>a</sup>
Δ <sup>7</sup> -Campesterol	2,6 <sup>a</sup>	tr	0,6 <sup>b</sup>	0,9 <sup>b</sup>	4,9 <sup>b</sup>
Δ <sup>5</sup> -23-Stigmastadienol	tr	tr	tr	tr	tr
Chlerosterol	32,4 <sup>a</sup>	41,0 <sup>b</sup>	26,8 <sup>c</sup>	21,0 <sup>c</sup>	28,6 <sup>a</sup>
β-Sitosterol	2430,0 <sup>a</sup>	2872,0 <sup>a</sup>	2370,6 <sup>a</sup>	1853,7 <sup>b</sup>	2531,6 <sup>a</sup>
Sitostanol	15,6 <sup>a</sup>	9,0 <sup>b</sup>	16,4 <sup>a</sup>	13,9 <sup>c</sup>	8,6 <sup>d</sup>
Δ <sup>5</sup> -Avenasterol	337,6 <sup>a</sup>	575,0 <sup>b</sup>	223,5 <sup>c</sup>	366,7 <sup>a</sup>	270,8 <sup>d</sup>
Δ <sup>5</sup> -24-Stigmastadienol	30,6 <sup>a</sup>	46,0 <sup>b</sup>	16,9 <sup>c</sup>	22,7 <sup>d</sup>	22,2 <sup>d</sup>
Δ <sup>7</sup> -Stigmastenol	15,7 <sup>a</sup>	22,0 <sup>b</sup>	3,3 <sup>c</sup>	8,0 <sup>d</sup>	5,3 <sup>e</sup>
Δ <sup>7</sup> -Avenasterol	26,9 <sup>a</sup>	28,0 <sup>a</sup>	10,1 <sup>b</sup>	8,6 <sup>b</sup>	19,5 <sup>c</sup>
Total β-sitosterol	2846,2 <sup>a</sup>	3543 <sup>b</sup>	2654,2 <sup>a</sup>	2278,0 <sup>c</sup>	2861,8 <sup>a</sup>
<b>Triterpene dialcohols</b>					
Erythrodiol	23,0 <sup>a</sup>	46,0 <sup>b</sup>	8,8 <sup>c</sup>	19,0 <sup>d</sup>	19,5 <sup>d</sup>
Uvaol	3,6 <sup>a</sup>	13,0 <sup>b</sup>	0,7 <sup>c</sup>	4,3 <sup>d</sup>	0,8 <sup>c</sup>
Erythrodiol +uvaol	26,6 <sup>a</sup>	59,0 <sup>b</sup>	9,5 <sup>c</sup>	23,3 <sup>ac</sup>	20,3 <sup>c</sup>

<sup>1</sup> Data are means of three replicates (CVs ≤ 6,1%). Within each row, values without common superscript letters are significantly different (*Tukey's* HSD range test,  $p \leq 0.05$ ).

