GRASAS Y ACEITES, 63 (2),
ABRIL-JUNIO, 143-151, 2012,
ISSN: 0017-3495
DOI: 10.3989/gya.083811

INVESTIGACIÓN

Lipid components and oxidative status of selected specialty oils

By **S.R.P. Madawala**[a]*, **S.P. Kochhar**[b] and **P.C. Dutta**[a]

[a]Department of Food Science, Division of Food Chemistry, Swedish University of Agricultural Sciences, SLU, Uppsala BioCenter, Box 7051, SE-75007, Uppsala, Sweden
[b]SPK Consultancy Services, 14 Holmemoor Drive, Sonning, Reading RG4 6TE, UK.
*Corresponding author: samanthi.madawala@slu.se

RESUMEN

Componentes lipídicos y estado oxidativo de una selección de aceites especiales.

Muchos aceites vegetales se venden como aceites especiales debido a su flavor, gusto y características distintas. Muestras de aceites especiales de almendra, avellana, nuez, nuez de macadamia, argán, aguacate, semillas de uva, de sésamo tostadas, salvado de arroz, y aceites orgánico de semillas de colza prensado en frío y, prensado caliente, y refinados que se producen y comercializan al por menor, se obtuvieron en comercios de grandes superficies en Reading, Reino Unido, y Uppsala, Suecia, y se les determinó su composición detallada de lípidos y su estado oxidativo. Los niveles de peróxidos (PV) fueron bastante bajos (0,5 a 1,3 mEq O_2/kg), pero la acidez (AV) y los valores de la estabilidad oxidativa Rancimat a 100 °C (excepto los aceites de colza) variaron considerablemente (0,5-15,5%) y (4,2 a 37,0 h), respectivamente. El aceite de nuez de macadamia se encontró que fue el aceite más estable, seguido por el aceite de argán, mientras que el aceite de nuez fue el menos estable. Entre los aceites especiales, el aceite de nuez de macadamia, presentó el menor nivel de ácidos grasos poliinsaturados (AGPI) (4%) y aceite de nuez el más alto (71%). El aceite ecológico de colza prensado en frío tenía un contenido considerablemente menor de AGPI (27%) en comparación con otros aceites de colza (28-35%). En todas las muestras, α-y γ- fueron los principales tocoferoles, y el aceite de nuez presentó los niveles más bajos. Los esteroles totales variaron desde 889 hasta 15.106 mg/g de aceite. Los principales esteroles fueron: β-sitosterol (61-85%) y el campesterol (6-20%). El aceite de argán contenía schottenol (35%) y espinasterol (32%). En comparación con los valores de la literatura, no se observaron diferencias significativas entre los aceites de colza procesados de manera diferente, cultivado ecológicamente y prensado en frío y otros aceites especiales de este estudio.

PALABRAS CLAVE: Aceite de colza ecológico – Aceites de colza de diferentes procesados – Aceites de nuez – Aceites especiales – Estado oxidativo – Lípidos – Rancimat.

SUMMARY

Lipid components and oxidative status of selected specialty oils.

Many vegetable oils are marketed as specialty oils because of their retained flavors, tastes and distinct characteristics. Specialty oil samples which were commercially produced and retailed were purchased from local superstores in Reading, UK, and Uppsala, Sweden and profiled for detailed lipid composition and oxidative status. These oil samples include: almond, hazelnut, walnut, macadamia nut, argan, avocado, grape seed, roasted sesame, rice bran, cold pressed, organic and cold pressed, warm pressed and refined rapeseed oils. The levels of PV were quite low (0.5-1.3mEq O_2/kg) but AV and Rancimat values at 100 °C (except for rapeseed oils) varied considerably at (0.5-15.5) and (4.2-37.0 h) respectively. Macadamia nut oil was found to be the most stable oil followed by argan oil, while walnut oil was the least stable. Among the specialty oils, macadamia nut oil had the lowest (4%) and walnut oil had the highest (71%) level of total PUFA. The organic cold pressed rapeseed oil had considerably lower PUFA (27%) compared with other rapeseed oils (28-35%). In all the samples, α- and γ- tocopherols were the major tocopherols; nut oils had generally lower levels. Total sterols ranged from 889 to 15,106 μg/g oil. The major sterols were β-sitosterol (61-85%) and campesterol (6-20%). Argan oil contained schottenol (35%) and spinasterol (32%). Compared with literature values, no marked differences were observed among the differently processed, organically grown or cold pressed rapeseed oils and other specialty oils in this study.

KEY-WORDS: Differently processed rapeseed oils – Organic rapeseed oil – Lipids – Nut oils – Oxidative status – Rancimat – Specialty oils.

1. INTRODUCTION

Among edible fats and oils, a considerable number of products are sold as specialty oils which have undergone minimum or no processing. Examples of such products, commonly known as specialty oils, include extra virgin olive oils, oils extracted from different nuts, cold pressed rapeseed oils, etc. Many specialty oils are unique in flavor, odor and special characteristics which suggest their specific use for cosmetic, therapeutic and dietary purposes. Rapeseed oil represents the most common vegetable oil consumed in Sweden along with other Nordic countries. Among the different commercially available rapeseed oils, cold pressed oils generally claim higher quality. They are extracted without applying heat and promoted as specialty oils, sold at a higher price. The cold

pressed oil products may contain both pro- and antioxidative compounds and that would affect the quality of these oils (Pekkarinen *et al.*, 1998).

The general perception of consumers is that foods grown organically and subjected to less processing are better and healthier and thus cold pressed oil is an appealing choice since no solvents and no further processing other than filtering are involved (Koski *et al.*, 2002). Studies reveal that organic crops tend to contain higher dry matter, certain minerals, antioxidants (phenols, resveratrol) and lower amounts of nitrates, residues of toxic chemical pesticides, fungicides and herbicides compared with conventionally grown crops (Lairon, 2010). In order to comply with these trends and environmental concerns, the edible fats and oils industries are also developing milder processing conditions (Jung *et al.*, 2009).

Extensive studies have shown that plant sterols and stanols reduce total- and LDL- cholesterol levels in humans (Normen *et al.*, 2004). Through a study with home prepared foods in real-life conditions, it has been found that part of the beneficial effects of the enhanced Mediterranean diet on the lipid profile is due to an increased consumption of phytosterols and other constituents which might be bioactive even in small amounts in their natural food matrix (Escurriol *et al.*, 2009). Natural oils are also preferred due to higher levels of other bioactive components such as squalene, tocopherols and tocotrienols compared with their processed counterparts. Beyond the active role of α-tocopherol, it has been found that γ-and δ-tocopherols and tocotrienols have a specific pharmaco dynamic profile due to their different metabolic patterns (Franke *et al.*, 2007). For studying the overall quality of oil, the parameters such as detailed fatty acid composition, content and composition of unsaponifiables (sterols, tocopherols, etc.) and oxidative status and stability are generally assessed. The stability of oil is important for nutritional and functional quality as well as for its organoleptic properties.

Studies on the effects of minor oil components on oxidative status for differently processed rapeseed oils are scarce (Pekkarinen *et al.*, 1998, Koski *et al.*, 2002). To our knowledge, no published data on minor lipid components is available for commercially available, organically grown, cold pressed rapeseed oil. The main objective of this study was to evaluate the oxidative status and stability of selected specialty oils commercially available in the UK, commercial samples of differently processed rapeseed oils, and organic and cold pressed rapeseed oils collected in Sweden in relation to their fatty acid profiles and minor antioxidant components.

2. MATERIALS AND METHODS

2.1. Materials

Five different cold pressed, one ecological and cold pressed, one warm pressed and one fully refined commercial rapeseed oil were purchased from a retail market in Uppsala, Sweden. They are marketed under the following brand names and producers:. extra fine cold pressed rapeseed oil (cold-pressed 1), Arvid Nordquist, Solna, Sweden; Swedish cold pressed rapeseed oil (cold pressed 2), ICA AB, Solna, Sweden; cold pressed extra virgin rapeseed oil (cold pressed 3), Druvan, Eslöv, Sweden; ZETA (Fyllig & Nötig) Swedish cold pressed rapeseed oil (cold pressed 4), Luca & Di Luca AB, Stockholm, Sweden; ZETA (mild & blommig) Swedish cold pressed rapeseed oil (cold pressed 5), Luca & Di Luca AB, Stockholm, Sweden; ICA Rapeseed oil (fully refined), ICA Handlarnas AB, Solna, Sweden; ICA organic Swedish cold pressed rapeseed oil (organic), Ektek Oil AB, Järfälla, Sweden; warm pressed rapeseed oil (warm pressed), Druvan, Eslöv, Sweden. Specialty oil samples of almond, hazelnut, walnut, macadamia nut, argan, avocado, grape seed, roasted sesame and rice bran oils were purchased from local retail superstores in Reading, UK, and were provided by SPK Consultancy Services, Reading, UK.

2.2. Determination of peroxide value (PV)

Approximately 0.02g of lipid sample in triplicate were used to analyze PV following the IDF standard method 7A (1991).

2.3. Determination of *p*-anisidine value (AV)

AV was determined using 2.5 g oil in triplicate according to the published method of the IUPAC (1987).

2.4. Determination of oxidation stability by Rancimat

The Oxidation stability of the oils was measured using 2.5 g oil sample in duplicate as described previously by Savage *et al.* (1997), except that accelerated oxidation was performed at 100 °C and 20L/h air flow rate using a Rancimat 679 (Metrohm, Herisau, Switzerland).

2.5. Analysis of fatty acid methyl esters (FAME)

Preparation of FAME was done using 10 mg oil samples and analyzed by capillary column GC according to the published method (Azadmard-Damirchi and Dutta, 2008).

2.6. Analysis of tocopherols and tocotrienols

Tocopherols and tocotrienols were analyed by direct injection of the oil samples dissolved in HPLC grade heptane (ca.10mg/ml) using an HPLC coupled to a fluorescence detector according to the method published previously (Azadmard-Damirchiand Dutta, 2008).

2.7. Analysis of sterols by GC and GC-MS

The Trimethylsilylether derivatives of sterols after saponification of the oil samples (ca. 20 mg) were determined by capillary column GC using 5α-cholestane as internal standard according to the published method (Azadmard-Damirchi and Dutta, 2008). Confirmation of the sterol structures was made with GC-MS using a GC 8000 Top Series GC and an AS800 auto sampler (CE Instruments, Thermo Quest Italia S.P.A., MI, Italy) coupled to a Voyager mass spectrometer with Xcalibur version 1.2 (Finnigan, Thermo Quest, Manchester, UK). The column and conditions used were the same as for the GC.

3. RESULTS AND DISCUSSION

3.1. Fatty acid composition

The fatty acid profile of the different specialty oils is presented in Table 1. The high polyunsaturated fatty acid (PUFA) contents (71 and 69% respectively) observed in walnut and grape seed oil explained the low oxidative stability of these oils. Oleic acid (18:1) was the predominant fatty acid in all the oils except for the walnut and grape seed oils in which linoleic acid (18:2) was observed at higher levels. Walnut oil had a significantly high amount of linolenic acid (18:3) which was 10.4% compared with 0.3% in grape seed oil. Macadamia nut, hazelnut, avocado, almond and rapeseed oils showed the highest levels of monounsaturated fatty acids (MUFA). Macadamia nut oil contained 18% palmitoleic acid (16:1) which was not common in many specialty oils. According to the published literature (Charrouf and Guillaume, 2008; Crews *et al*., 2005, 2005, 2006; Dubois *et al*., 2007; Kochhar, 2002; Lu *et al*., 2009; Maguire *et al*., 2004; Rubio *et al*., 2009; Savage *et al*., 1997, 1999), in all the oils tested, SFA (saturated fatty acid) levels were comparatively low except for rice bran and argan oil. Among differently processed rapeseed oils, the level of SFA was very similar 6-7%. MUFA varied from 59-66% with oleic acid being the dominant one. The PUFA contents in these samples varied from 28-35% and linoleic acid was observed as the dominant fatty acid (18-22%), and the linolenic acid content varied from 8-12%. Organic cold pressed rapeseed oil had a bit higher level at 18:1 (62%) compared with the other rapeseed oils (54-61%). This higher level of oleic acid was compensated by the lower levels of 18:2 (18%) and 18:3 (8%). The ranges of these fatty acids in the other rapeseed oil samples were (18 -22%) and (8-12%), respectively. All the rapeseed oil samples had relatively higher levels of vaccenic acid (3-4%) compared with other specialty oils, as shown in Table 1. The fatty acid profiles observed for different brands of rapeseed oils were generally uniform and concur with the published data (Dubois *et al*., 2007; Koski *et al*., 2002). No data is known to our knowledge on fatty acids in organic rapeseed oil, however, a previous study has shown that the level of oleic acid was higher in organic virgin olive oil (Gutiérrez *et al*., 1999). We did not make any effort to identify *trans* fatty acids in the samples. If there were any *trans* fatty acids present in some samples those are presented under the column "Others" in Table 1. It has been reported that minor amounts of *trans* fatty acids are present in commercially refined edible oils. The authors have cautioned that deodorization temperature is critical to minimize the formation of *trans* fatty acids in oils containing high amounts of polyunsaturated fatty acids (Tasan *et al*., 2011).

3.2. Tocopherol (Tp) and tocotrienol (Tt_3) content

The contents of different isomers of tocopherol (Tp) and tocotrienol (Tt_3) in the different specialty oil samples showed wide variations (Table 2). α-Tp and γ- Tp were the main isomers present in all the specialty oil samples. In almond, hazelnut, avocado and grape seed oils, the predominant isomer was α-Tp, while γ-Tp was predominant in all the other samples. Among the different tree nut oils, macadamia nut oil showed the lowest Tp and Tt_3 and the total tocopherol level was only 54 μg/g oil. This was comparable with the data published by Kaijser *et al.* (2000).

In accordance with the data published by Crews *et al.* (2006), only γ-Tp could be detected in roasted sesame oil. According to Kochhar (2002), the Tp in crude sesame oils can vary from 400-700 μg/g of which γ-Tp is predominant along with a small proportion of δ-Tp. The roasting of sesame seeds improves the oxidation stability of its oil and thereby protects antioxidant compounds like tocopherols in the oil.

The highest Tt_3 levels were observed in rice bran and grape seed oil. The different levels of different Tp observed in argan oil were well in accordance with the data published previously by Khallouki *et al.* (2003). The relatively high stability of rice bran oil is most likely due to the combined effect of oryzanol, phytosterols, squalene, tocopherols and tocotrienols, while the stability of roasted sesame oil is due to the higher antioxidant activity of the sesamol formed from sesamolin during roasting and the high level of potent γ-tocopherol antioxidants (Kochhar, 2002).

Among the specialty samples investigated, hazelnut oil and macadamia nut oil contained α-Tt_3, whereas ricebran oil and roasted sesame oils contained high amounts of both α-Tt_3 and γ-Tt_3 (Table 2). The literature values concerning total tocopherols in sesame oils vary widely ranging from 88-1609 μg/g oil (Kochhar, 2002). The total tocol content in ricebran oil in our study (567 μg/g) is in good agreement with this data and Abidi (2003). In walnut oil, γ- and δ-Tp contents were in accordance with the data published by Crews *et al.* (2005) except for α-Tp. The predominant isomer γ-Tp represents 69% of the total tocol contents (373 μg/g) which is a similar finding to published data (Crews *et al*., 2005; Miraliakbari and Shahidi, 2008).

Table 1
Composition of fatty acids (% ± SD) in different specialty oils

Sample	14: 0	16: 0	18: 0	20: 0	Total SFA[a]	16: 1	18: 1 (Oleic)	18: 1 (Vaccenic)	20:1	Total MUFA[b]	18: 2	18: 3	Total PUFA[c]	Others
Almond oil	tr	4.4 ± 0.0	2.3 ± 0.0	0.5 ± 0.0	7.2 ± 0.0	tr	64.3 ± 0.1	1.5 ± 0.0	0.3 ± 0.1	66.1 ± 0.1	25.1 ± 0.1	0.5 ± 0.0	25.6 ± 0.1	1.1 ± 0.1
Hazelnut oil	tr	5.3 ± 0.1	2.4 ± 0.0	tr	7.7 ± 0.1	0.3 ± 0.0	75.7 ± 0.1	1.7 ± 0.0	0.2 ± 0.0	77.9 ± 0.1	13.2 ± 0.0	0.4 ± 0.0	13.6 ± 0.0	0.8 ± 0.0
Walnut oil	nd	7.0 ± 0.0	3.0 ± 0.0	tr	10.0 ± 0.0	nd	14.8 ± 0.1	0.9 ± 0.0	tr	15.7 ± 0.1	60.1 ± 0.1	10.4 ± 0.0	70.5 ± 0.1	3.8 ± 0.1
Macadamia nut oil	0.7 ± 0.2	8.1 ± 0.1	3.6 ± 0.0	2.7 ± 0.1	15.1 ± 0.1	18.1 ± 0.2	54.6 ± 0.1	3.7 ± 0.1	2.4 ± 0.1	78.8 ± 0.1	3.3 ± 0.0	0.4 ± 0.0	3.7 ± 0.0	2.4 ± 0.0
Argan oil	tr	11.9 ± 0.1	5.8 ± 0.0	0.4 ± 0.0	18.1 ± 0.1	nd	44.8 ± 0.1	0.2 ± 0.0	0.4 ± 0.0	45.4 ± 0.1	35.6 ± 0.1	0.1 ± 0.0	35.7 ± 0.1	0.8 ± 0.1
Avocado oil	nd	12.6 ± 0.2	0.5 ± 0.0	nd	13.1 ± 0.1	4.3 ± 0.1	65.3 ± 0.2	6.9 ± 0.1	tr	76.5 ± 0.2	9.7 ± 0.1	0.6 ± 0.1	10.3 ± 0.1	0.1 ± 0.0
Grapeseed oil	nd	6.9 ± 0.1	4.1 ± 0.0	0.2 ± 0.0	11.2 ± 0.1	tr	18.3 ± 0.1	0.8 ± 0.0	0.2 ± 0.0	19.3 ± 0.1	68.4 ± 0.2	0.3 ± 0.0	68.7 ± 0.1	0.8 ± 0.1
Sesame oil, roasted	tr	8.7 ± 0.1	4.0 ± 0.0	0.5 ± 0.0	13.3 ± 0.1	nd	40.7 ± 0.1	0.8 ± 0.0	0.2 ± 0.0	41.7 ± 0.1	43.4 ± 0.1	0.4 ± 0.1	43.8 ± 0.1	1.2 ± 0.1
Ricebran oil	0.4 ± 0.0	18.2 ± 0.2	2.2 ± 0.0	0.9 ± 0.0	21.7 ± 0.1	tr	41.3 ± 0.1	0.9 ± 0.0	0.5 ± 0.1	42.7 ± 0.1	32.4 ± 0.1	1.0 ± 0.0	33.4 ± 0.1	2.2 ± 0.1
Rapeseed oil, cold-pressed 1	nd	4.3 ± 0.0	1.6 ± 0.0	0.5 ± 0.0	6.4 ± 0.0	tr	58.0 ± 0.0	3.5 ± 0.1	1.7 ± 0.0	63.2 ± 0.1	18.7 ± 0.1	9.8 ± 0.1	28.5 ± 0.1	1.9 ± 0.1
Rapeseed oil, cold-pressed 2	nd	3.9 ± 0.0	1.6 ± 0.0	0.5 ± 0.0	6.0 ± 0.0	tr	54.0 ± 0.1	3.4 ± 0.1	1.4 ± 0.0	58.8 ± 0.1	22.2 ± 0.0	12.3 ± 0.1	34.5 ± 0.1	0.7 ± 0.1
Rapeseed oil, cold-pressed 3	nd	4.5 ± 0.0	1.7 ± 0.0	0.5 ± 0.0	6.7 ± 0.0	tr	60.6 ± 0.0	3.2 ± 0.2	1.3 ± 0.1	65.1 ± 0.2	18.4 ± 0.1	9.1 ± 0.0	27.5 ± 0.2	0.7 ± 0.2
Rapeseed oil, cold-pressed 4	nd	3.9 ± 0.0	1.6 ± 0.0	0.5 ± 0.0	6.0 ± 0.0	tr	54.1 ± 0.1	3.3 ± 0.0	1.2 ± 0.1	58.6 ± 0.1	22.2 ± 0.1	12.4 ± 0.0	34.6 ± 0.1	0.8 ± 0.1
Rapeseed oil, cold-pressed 5	nd	3.9 ± 0.0	1.6 ± 0.0	0.5 ± 0.0	6.0 ± 0.0	tr	54.1 ± 0.1	3.3 ± 0.0	1.2 ± 0.1	58.6 ± 0.1	22.2 ± 0.1	12.4 ± 0.0	34.6 ± 0.1	0.8 ± 0.1
Rape seed oil, cold-pressed (organic)	nd	4.2 ± 0.0	2.0 ± 0.0	0.5 ± 0.0	6.7 ± 0.0	tr	61.5 ± 0.1	3.5 ± 0.1	1.2 ± 0.0	66.2 ± 0.1	18.4 ± 0.1	8.2 ± 0.1	26.6 ± 0.1	0.5 ± 0.2
Rapeseed oil, warm-pressed	nd	4.3 ± 0.0	1.7 ± 0.0	0.5 ± 0.0	6.5 ± 0.0	tr	60.0 ± 0.1	3.8 ± 0.1	1.1 ± 0.2	64.9 ± 0.2	19.4 ± 0.1	8.7 ± 0.1	28.1 ± 0.2	0.5 ± 0.1
Rapeseed oil (fully refined)	nd	4.7 ± 0.0	1.7 ± 0.0	0.5 ± 0.0	6.9 ± 0.0	tr	57.7 ± 0.0	3.7 ± 0.2	1.4 ± 0.0	62.8 ± 0.1	20.2 ± 0.1	8.4 ± 0.1	28.6 ± 0.1	1.7 ± 0.2

[a], saturated fatty acids; [b], mono-unsaturated fatty acids; [c], poly-unsaturated fatty acids; SD, standard deviation; tr, detected in amounts <0.1%; nd, not detected; Others, unidentified fatty acids.

Table 2
Content of tocopherols (Tp) and tocotrienols (Tt_3) (μg/g oil) in different specialty oils

Sample	α-Tp ± SD	α-Tt_3 ± SD	β-Tp ± SD	γ-Tp ± SD	γ-Tp_3 ± SD	δ-Tp ± SD	Total ± SD
Almond oil	174 ± 5	nd	16 ± 6	57 ± 6	tr	17 ± 4	264 ± 21
Hazelnut oil	87 ± 3	28 ± 2	nd	nd	nd	nd	115 ± 5
Walnut oil	71 ± 2	nd	nd	259 ± 19	nd	43 ± 2	373 ± 12
Mac. nut oil	8 ± 0	20 ± 1	nd	15 ± 0	tr	11 ± 1	54 ± 2
Argan oil	90 ± 3	nd	nd	463 ± 20	nd	71 ± 6	624 ± 29
Avocado oil	89 ± 2	nd	8 ± 1	38 ± 2	nd	14 ± 3	149 ± 8
Grapeseed oil	216 ± 3	137 ± 5	nd	111 ± 8	191 ± 9	nd	655 ± 25
Sesame oil, roasted	251 ± 8	nd	nd	521 ± 22	nd	nd	772 ± 30
Ricebran oil	108 ± 2	63 ± 3	nd	112 ± 3	284 ± 13	nd	567 ± 21
Rapeseed oil, cold-pressed 1	211 ± 6	nd	nd	396 ± 10	nd	tr	607 ± 16
Rapeseed oil, cold-pressed 2	153 ± 6	nd	nd	469 ± 14	nd	tr	622 ± 20
Rapeseed oil, cold-pressed 3	239 ± 6	nd	nd	474 ± 12	nd	tr	713 ± 18
Rapeseed oil, cold-pressed 4	213 ± 2	nd	nd	433 ± 3	nd	tr	646 ± 5
Rapeseed oil, cold-pressed 5	181 ± 6	nd	nd	460 ± 5	nd	tr	641 ± 11
Rapeseed oil, cold-pressed (organic)	245 ± 3	nd	nd	399 ± 13	nd	tr	644 ± 16
Rapeseed oil, warm-pressed	255 ± 3	nd	nd	467 ± 8	nd	tr	722 ± 11
Rapeseed oil (fully refined)	256 ± 4	nd	nd	433 ± 9	nd	tr	689 ± 13

SD, standard deviation; tr, detected in amounts <0.5 μg/g oil; nd, not detected.

Crews *et al.* (2005) observed α-Tp in different varieties of hazelnut oil varying in the range of 314-548 μg/g except for one Italian variety which had 118 μg/g. A lower level, such as 94 μg/g, has been reported by Parcerisa *et al.* (1998) and it was comparable to the 87 μg/g observed in our study.

The level of γ-Tp in the rapeseed oil samples was generally higher (396 -474 μg/g oil) compared with other oils except for argan and sesame oil samples which contained 463 and 521 μg/g oil, respectively. The highest level of α-Tp was observed in fully refined and warm pressed rapeseed oil samples followed by the organic cold pressed rapeseed oil sample. The high total Tp observed in the warm pressed sample may suggest better extraction of the tocopherols from the structural components of seeds (Falk and Munné-Bosch, 2010). Alpha and γ-Tp in rapeseed oil samples were comparable with the published data (Koski *et al.*, 2002, Schwartz *et al.*, 2008). In the latter study, it was shown that organic rapeseed oil had a generally lower content of α-Tp but slightly higher level of γ-Tp, compared with refined and cold pressed rapeseed oils.

3.3. Sterol content

The content and composition of sterols in different specialty oil samples are presented in Table 3. The total sterol content of the oil samples varied in a range between 889-6204 μg/g oil, except for the rice bran oil. The predominant sterol was β-sitosterol followed by other common desmethyl sterols such as campe-, stigma- and Δ5-avenasterol in all the samples except in argan oil. Individual as well as total sterol contents in hazelnut oil were in good agreement with the published data (Crews *et al.*, 2005). A rather similar sterol profile was found in the avocado oil sample but the total sterol content was twice the amount observed in nut oils.

Argan oil showed a characteristically different sterol profile compared to all the other oil samples. The major sterols identified were schottenol which represents 51% and spinasterol with 46% of the total identified sterols. The observed sterol profile of argan oil was comparable with the data published by Khallouki *et al.* (2003). However, the content of each type of sterol observed in our study was much

Table 3
Content (μg sterols/g oil) and composition (%)[1] of different sterols in different specialty oils

Sample	Brassica[a] ± SD (%)	Campe[b] ± SD (%)	Stigma[c] ± SD (%)	β-Sito[d] ± SD (%)	Δ5-Avena[e] ± SD (%)	Cholesterol ± SD (%)	Total ID ± SD	Total UN ± SD	Total sterol ± SD
Almond oil	tr	134 ± 64 (16.7)	55 ± 3 (6.9)	580 ± 23 (72.4)	32 ± 6 (4.0)	nd	801 ± 31	421 ± 27	1222 ± 58
Hazelnut oil	nd	44 ± 1 (5.5)	10 ± 0 (1.3)	681 ± 9 (85.3)	63 ± 1 (7.9)	nd	798 ± 11	91 ± 1	889 ± 11
Walnut oil	nd	68 ± 1 (5.0)	9 ± 1 (0.7)	1191 ± 12 (88.0)	86 ± 0 (6.3)	nd	1354 ± 13	298 ± 4	1652 ± 11
Mac. nut oil	nd	116 ± 2 (7.0)	22 ± 1 (1.3)	1353 ± 40 (82.0)	160 ± 9 (9.7)	nd	1651 ± 47	189 ± 13	1840 ± 60
Argan oil[f]	nd	nd	nd	nd	nd	nd	1217 ± 31[§]	447 ± 62	1664 ± 103
Avocado oil	nd	187 ± 6 (5.5)	7 ± 0 (0.2)	3023 ± 58 (88.1)	215 ± 6 (6.2)	nd	3432 ± 70	910 ± 23	4342 ± 72
Grapeseed oil	9 ± 0 (0.5)	184 ± 7 (10.3)	164 ± 6 (9.2)	1336 ± 20 (74.9)	91 ± 7 (5.1)	nd	1784 ± 37	881 ± 27	2665 ± 10
Sesame oil, Roasted	tr	916 ± 15 (18.2)	355 ± 5 (7.1)	3337 ± 38 (66.5)	413 ± 8 (8.2)	nd	5021 ± 36	1183 ± 26	6204 ± 46
Ricebran oil	14 ± 0 (0.2)	1448 ± 23 (19.7)	943 ± 13 (12.9)	4449 ± 78 (60.6)	487 ± 16 (6.6)	nd	7341 ± 127	7765 ± 109	15106 ± 161
Rapeseed oil, cold-pressed1	537 ± 9 (9.7)	2155 ± 41 (38.8)	13 ± 2 (0.2)	2451 ± 34 (44.1)	382 ± 5 (6.9)	19 ± 1 (0.3)	5557 ± 87	140 ± 8	5697 ± 94
Rapeseed oil, cold-pressed 2	282 ± 15 (9.0)	1145 ± 45 (36.7)	9 ± 1 (0.3)	1489 ± 66 (47.8)	163 ± 13 (5.2)	32 ± 3 (1.0)	3120 ± 131	147 ± 12	3267 ± 143
Rapeseed oil, cold-pressed 3	874 ± 9 (13.0)	2605 ± 23 (38.9)	25 ± 1 (0.4)	3029 ± 27 (45.2)	145 ± 2 (2.2)	24 ± 0 (0.3)	6702 ± 59	146 ± 2	6848 ± 127
Rapeseed oil, cold-pressed 4	532 ± 27 (9.5)	2239 ± 57 (40.2)	23 ± 5 (0.4)	2604 ± 72 (46.6)	164 ± 4 (2.9)	22 ± 2 (0.4)	5584 ± 162	134 ± 10	5718 ± 167
Rapeseed oil, cold-pressed 5	629 ± 11 (9.2)	2610 ± 19 (38.0)	11 ± 1 (0.2)	3199 ± 51 (46.6)	352 ± 7 (5.1)	65 ± 4 (0.9)	6866 ± 63	228 ± 7	7094 ± 57
Rapeseed oil, cold-pressed, (organic)	342 ± 13 (6.8)	2114 ± 48 (42.4)	9 ± 2 (0.2)	2299 ± 76 (46.1)	200 ± 11 (4.0)	27 ± 1 (0.5)	4991 ± 150	173 ± 8	5164 ± 156
Rapeseed oil, warm-pressed	446 ± 15 (10.2)	1647 ± 22 (37.5)	12 ± 2 (0.2)	2163 ± 24 (49.3)	101 ± 1 (2.3)	21 ± 1 (0.5)	4390 ± 28	135 ± 7	4525 ± 64
Rapeseed oil (fully refined)	750 ± 3 (10.6)	2655 ± 43 (37.7)	38 ± 4 (0.5)	3340 ± 12 (47.5)	229 ± 1 (3.3)	26 ± 2 (0.4)	7038 ± 33	175 ± 15	7213 ± 72

[1], Values given in parenthesis are individual sterol as a% of total identified sterols; [a], Brassicasterol; [b], campesterol; [c], stigmasterol; [d], β-sitosterol, [e], Δ5-avenasterol; ID, identified sterols; UN, unidentified sterols; SD, standard deviation; tr, detected in amounts < 0.5 μg/g oil; nd, not detected; [f], Argan oil contained mainly stigmastadiene, spinasterol and schottenol (40 ± 1, 557 ± 15, and 620 ± 15 μg /g oil, respectively, included in total ID.

lower than their values. The total sterol content of grape seed oil was in agreement with the Codex range (1999) and for Italian varieties (Crews *et al.*, 2006). Though the origin of the grape seed oil in our study is not known, the relative proportion of the individual sterols identified as% total identified were similar to the Italian varieties rather than the French and Spanish varieties analyzed in their study.

The individual and total sterol contents observed in our study for roasted sesame oil were in the range mentioned by Crews *et al.* (2006). Rice bran oil contained the highest amount of sterols in this study, which concurs with the published literature (Kochhar, 2002, Piironen *et al.*, 2000). In addition to the highest total sterol levels, a considerably high level of stigmasterol (13%) was observed in the rice bran oil sample compared with the other oil samples analyzed.

The content of sitosterol greatly varied from 1489-3340 μg/g in the rapeseed oil samples. Sitosterol was the predominant sterol (44-49%) but as an individual sterol, sitosterol was lower when compared with the other specialty oil or nut oil samples analyzed in this study (Table 3). The lower proportion of sitosterol was compensated by a higher percentage of campesterol. The brassicasterol content varied from 282-874 μg/g while it was 1145-2655 μg/g for campesterol, and Δ5-avenasterol was present in moderate levels. Despite the variation in individual sterol contents among the different rapeseed oil samples, their relative proportions remained uniform. The content of different sterols observed were in line with previously published data (Schauss, 2008; Schwartz *et al.*, 2008). The authors observed no clear relationship regarding their origin such as organic rapeseed oil or the processing method. However, the relative proportion of brassicasterol in organic rapeseed oil sample (7%) was considerably lower compared to other rapeseed oil samples. The authors also confirmed that sterol contents were roughly the same in crude and refined rapeseed oil or cold pressed organic rapeseed oils.

Variations in individual and total sterol contents in the oil can be due to genetic factors among varieties, growing and storage conditions, refining, etc., but the relative percentage composition of individual sterols generally remains similar. Some plant sterols are partly removed during industrial oil refining depending on the extent of refining conditions (Piironen *et al.*, 2000). In our study, the lowest level of Δ5-avenasterol (101 μg/ g oil) was observed in the warm pressed rapeseed oil sample compared with the other rapeseed oil samples and ranged from 145-382μg/ g oil. In addition, the lowest total sterol content was observed in the warm pressed rape seed oil sample, with the exception of one sample (cold pressed 2 rapeseed oil).

3.4. Oxidative stability

The results of the oxidative stability tests for specialty oils are given in Table 4. The peroxide value (PV) of the different oils was in the range of 0.5-1.3 meq O_2/kg oil, indicating freshly produced oils with their characteristic flavors. Peroxides are

Table 4
Oxidative status parameters of different specialty oils

Sample	PV[a](± SD)	AV[b](± SD)	T V[c] (± SD)	Rancimat[d]
Almond oil	1.1 ± 0.1	12.6 ± 0.3	14.8 ± 0.2	10.2
Hazelnut oil	1.1 ± 0.0	7.5 ± 0.0	9.7 ± 0.1	16.0
Walnut oil	0.9 ± 0.0	3.9 ± 0.1	5.7 ± 0.1	4.2
Macadamia nut oil	0.5 ± 0.0	0.8 ± 0.0	1.8 ± 0.0	37.0
Argan oil	1.1 ± 0.0	1.0 ± 0.0	3.2 ± 0.1	27.6
Avocado oil	1.2 ± 0.1	1.2 ± 0.1	3.6 ± 0.3	16.9
Grapeseed oil	1.0 ± 0.0	15.5 ± 0.1	17.5 ± 0.1	8.9
Sesame oil (roasted)	0.6 ± 0.0	10.9 ± 0.1	12.1 ± 0.1	18.0
Rice bran oil	1.1 ± 0.1	4.2 ± 0.0	6.4 ± 0.1	18.7
Rapeseed oil, cold-pressed 1	1.0 ± 0.0	1.2 ± 0.1	3.2 ± 0.1	
Rapeseed oil, cold-pressed 2	1.1 ± 0.0	1.6 ± 0.0	3.8 ± 0.1	
Rapeseed oil, cold-pressed 3	1.3 ± 0.1	0.5 ± 0.0	3.1 ± 0.2	
Rapeseed oil, cold-pressed 4	1.1 ± 0.0	0.7 ± 0.1	2.9 ± 0.1	
Rapeseed oil, cold-pressed 5	1.0 ± 0.0	2.1 ± 0.1	4.1 ± 0.1	
Rapeseed oil, cold-pressed (organic)	1.1 ± 0.0	1.2 ± 0.1	3.4 ± 0.1	
Rapeseed oil, warm-pressed	1.2 ± 0.0	1.8 ± 0.0	4.2 ± 0.1	
Rapeseed oil (fully refined)	1.1 ± 0.1	1.7 ± 0.1	3.9 ± 0.1	

[a] PV, Peroxide value (mEq O_2/kg oil); [b]AV, Anisidine value; [c] TV,Totox value = 2 (Peroxide value) + (Anisidine value); [d], Rancimat value (hours) at 100 °C; SD, standard deviation.

formed during early/initial stages of oil oxidation, and the PV was very low in all the oil samples, compared with the values of the Codex standard for vegetable oils (1999). Secondary oxidation products in the oils such as high molecular weight saturated and unsaturated carbonyl compounds were measured as anisidine value (AV), and were in the range of 0.5-15.5 for all the analyzed samples. The totox value (TV), a measurement of the total oxidation status of oil, was calculated as $2 \times PV + AV$ and ranged from 1.9-17.5. Secondary oxidation products, measured as AV and TV, were considerably higher in the oil samples from grape seed, almond and roasted sesame. However, underlying reasons could not be explained from the lipid composition without accurate background information on the samples. There were no remarkable differences in the lipid oxidation parameters tested for different rapeseed oil samples. The PV values in differently processed rapeseed oils were considerably lower than previously published results from cold pressed rapeseed samples in Finland (Pekkarinen *et al*., 1998; Koski *et al*., 2002).

Rancimat induction time at 100 °C varied from 4.2-37 hours in the specialty oil samples, except for the rapeseed oils. Among the oils tested, walnut oil was the least heat stable oil. On the other hand, macadamia nut oil was the most stable oil followed by argan, rice bran and roasted sesame oil. The relatively high stability of rice bran oil is most likely due to the combined effect of oryzanol, phytosterols, squalene, tocopherols and tocotrienols; while the stability of roasted sesame oil is due to the high antioxidant activity of sesamol formed from sesamolin during roasting and the high level of the potent antioxidant γ-tocopherol (Kochhar, 2002).

According to Savage *et al.* (1999), who did a study on walnut oil, Rancimat value had a negative correlation with 18:2, 20:1, and 18:1n-9 contents but 18:3 did not show a strong relationship with Rancimat value. Similarly, macadamia nut oil, which contained only 3.7% PUFA, showed high oxidative stability despite low levels of tocopherols and tocotrienols. This can be a reason for the comparatively lower Rancimat value of walnut oil than grape seed oil even though they had close levels of total PUFA, MUFA and SFA. Miraliakbari and Shahidi (2008) also noted walnut oil as the least stable and most unsaturated while almond and hazelnut exhibited intermediate stability in a study on the oxidative stability of tree nut oils. Also, grape seed oil contained 216 μg/g α-tocopherol compared to walnut oil which contained only 71 μg/g oil.

Rice bran and argan oil showed comparable fatty acid profiles although argan oil showed a comparatively higher stability against heat induced oxidation. On the other hand, argan, rice bran and toasted sesame oil, which had moderate levels of PUFA (33-44%) and MUFA (42-45%), showed comparatively higher Rancimat values. It appears that the association of high levels of tocopherols (especially γ- and δ-, above 400 μg) with some unknown minor potent components might contribute significantly towards the high oxidative stability of argan oil, which warrants further investigation.

4. CONCLUSIONS

This paper adds to and updates the available compositional data for several commercially available specialty oils along with some cold pressed and organic cold pressed rapeseed oils. It seems that the oxidative stability of many specialty oils tested in our study was affected mainly by their fatty acid profiles and tocopherol and tocotrienol contents of the oil. The different specialty oils tested showed unique profiles and vary among each other in fatty acid, tocol and sterol profiles. Macadamia nut oil was found to be the most stable oil followed by argan oil: while walnut oil was the least stable among all the oils examined. It is thought that the high oxidative stability of argan oil is probably due to the combined effect of potent tocopherols (γ- and δ-) and other potent antioxidative components. Rapeseed oil represents one of the major oils which is naturally rich in tocopherols and sterols with a unique fatty acid composition (with good ratio of ω-6 and ω-3 fatty acid, 2:1). There were no clear differences among the different commercially available brands of cold pressed, organically produced cold pressed, warm pressed or refined (general purpose) rapeseed oils.

ACKNOWLEDGEMENTS

We would like to thank Dr. Kumari Ubhayasekera at Food Chemistry Lab, SLU, for technical support during laboratory analysis.

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Recibido: 18/8/11
Aceptado: 4/10/11