

Physico-chemical Properties and Thermal Oxidative Stability of Seed Oil from *Camellia semiserrata* Chi.

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Abstract: In this paper, we reported the physicochemical characteristics and thermal oxidative stability of *Camellia semiserrata* Chi. seed oil. The oil content in *Camellia semiserrata* Chi. seed was 34.8% (wet weight). The extracted oil exhibited iodine value of 82.1 g I₂/100 g, saponification value of 215.3 mg KOH/100 g, acidity value of 1.51 g FFA/100 g, peroxide value of 2.98, and *p*-anisidine value of 0.96 g⁻¹. The K_{232nm} and K_{270nm} were 2.14 and 0.12, respectively. Differential scanning calorimetry analysis revealed that two characteristic peaks were detected in both crystallization and melting curves. Potassium, aluminium, potassium, magnesium and calcium were found at higher levels in the oil, which ranged from 9.7 to 26 mg/kg. The contents of other minerals were below 4.3 mg/kg. α -Tocopherol content in the oil was 5.6 mg/100 g, and the total content of β -tocopherol and γ -tocopherol were 0.79 mg/100 g. Oleic acid (74.74%) was the most predominant fatty acid followed by palmitic acid, linoleic acid and stearic acid and a small amount of other fatty acids. The scavenging activity toward DPPH radicals was also measured. The oil showed good thermal oxidative stability as evaluated based on K_{232nm} , K_{270nm} , POV and *p*-PAV values (microwave heating and 130 °C oven heating). These results suggest that *Camellia semiserrata* Chi. is a valuable special oilseed crop, providing highly nutritional oil.

Key words: physico-chemical properties; seed oil; *Camellia semiserrata* Chi.; oxidative stability

大果红花油茶种子油理化特性及热氧化稳定性

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摘 要: 研究大果红花油茶种子油的理化特性和热氧化稳定性, 其种子的含油量为 34.8%, 油的碘值 82.1g I₂/100g、皂化值 215.3mg KOH/100g、酸值 1.51g FFA/100g、过氧化值 2.98、对茴香胺值 0.96g⁻¹, 232nm 和 270nm 比紫外吸光度(K_{232nm} 和 K_{270nm})分别为 2.14 和 0.12; 示差扫描量热分析表明油的结晶和溶解曲线各有两个特征峰; 金属离子测定表明油中含有较高量的 K、Mg、Na、Al 金属离子(9.7~26mg/kg), 其他金属离子的含量在 4.3mg/kg 以下; HPLC 测定表明油中 α -生育酚含量 5.6mg/100g, β -生育酚和 γ -生育酚含量 0.79mg/100g; GC-MS 分析表明油酸是油中主要的脂肪酸, 含量占总脂肪酸的 74.74%, 其次为棕榈酸、亚油酸和硬脂酸; 并测定种子油的 DPPH 自由基清除能力。通过分别测定种子油热氧化过程中 K_{232nm} 、 K_{270nm} 、过氧化值、对茴香胺值, 分析了该种油脂的热氧化稳定性。结果表明: 大果红花油茶是一种非常有价值的高营养的特种油料作物。

关键词: 理化特性; 种子油; 大果红花油茶; 氧化稳定性

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The genus *Camellia*, which belongs to the Theaceae family, includes those of some important species such as *C. oleifera* Abel., *C. meiocarpa* Hu., *C. vietnamensis* Huang., *C. yuhshienensis* Hu., *C. chekiangoleosa* Hu., *C. reticulata* Lindl., *C. magniflora* Chang., *C. gigantocarapa* Hu., and *C.*

semiserrata Chi. They are mainly cultivated in China specifically for seeds. The *C. semiserrata* Chi. specie is a kind of arbor that produces esculent *Camellia* oil and widely distributed in the southern region of China including Guangdong and Guangxi provinces. It is a slow growing tree and can

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produce seeds for 100 years. The tree ranges in height from 4 — 8 m and the fruits are around 4 — 5 cm in diameter, 0.5 — 1.5 kg in weight per fruit, and 100 — 200 in fruit number per plant.

Seeds of *Camellia* have been utilized in China for a long time^[1], which contain *Camellia* saponin and *Camellia* oil. *Camellia* oil is a main cooking oil in China's southern provinces, especially Hunan and Jiangxi, which is generally recovered by pressing or solvent extraction from *Camellia oleifera* seeds. The high nutrition value of *Camellia* oil is mainly due to its high unsaturated fatty acid contents and high levels of natural antioxidants (phenols and tocopherols), which is very resistant to peroxidation forming few free radicals^[2].

To date only few investigations on physico-chemical properties of oil from *Camellia* plant seeds have been carried out^[3-4]. To our knowledge, few data have been reported on the compositions and characteristics of *C. serniserrata* Chi. seeds and seed oils. The main objective of the present study was to investigate the physico-chemical characteristics, compositions, and oxidative stability of oil from *Camellia serniserrata* Chi. seeds.

1 Materials and Methods

1.1 Material and Reagen

The seeds of *C. serniserrata* Chi. grown in the *Camellia* growing region of Guangdong, China, were procured. All chemicals and solvents used were of analytical grade.

1.2 Microstructural examination of seed

To get a better insight into seed structure, the samples were observed with light microscopy. The sections were mounted on glass slides and washed with distilled water until they presented a clear creamy colour. To differentiate the cell walls, the section were stained red by immersion for 1 min in safranin solution (10 g safranin in 145 mL distilled water and 155 mL 95% ethanol; this solution was diluted 1:1 with 50% ethanol before use). The cross-sections were rinsed with distilled water and stained for 3 min with Alcian Blue solution (0.1% — 0.5% in 3% acetic acid), rinsed again with distilled water and with 96% ethanol until the red colour disappeared, and finally dehydrated in absolute ethanol^[5].

1.3 Physical analysis of *C. serniserrata* Chi. seed

The seed kernels were separated by hand. The moisture content of seed was determined gravimetrically by placing samples in an oven at 105 °C for 10 h until constant weight was achieved and the oil content of seed kernel was found using hexane extraction.

1.4 Oil extraction

The extraction of seed oil was carried out by solvent extraction. The oil was extracted from the seed powder using hexane as solvent. The extracted oil was filtered and excess solvent was evaporated “in vacuo” leaving behind a yellowish oil. Finally, the seed oil was stored in a freezer and it was evaluated for its chemical properties.

1.5 Chemical analysis of seed oil

Acid value (% FFA): The acid value of seed oil was determined according to China Official Method GB/T 5530 — 2005 *Animal and Vegetable Fats and Oils: Determination of Acid Value and Acidity*. The percentages of free fatty acids (FFAs) were calculated using oleic acid as the factor.

Iodine value: The iodine value of seed oil was determined according to China Official Method GB/T 5532 — 2008 *Animal and Vegetable Fats and Oils: Determination of Iodine Value*.

Saponification value: The saponification value of seed oil was determined according to China Official Method GB/T 5534 — 2008 *Animal and Vegetable Fats and oils: Determination of Saponification Value*.

Peroxide value: The peroxide value of seed oil was determined according to China Official Method GB/T 5538 — 2005 *Animal and Vegetable Fats and Oils: Determination of Peroxide Value* and expressed as Milliequivalents (mequiv) of active oxygen per kilogram of oil.

Specific extinctions: The specific extinctions at 232 nm and 270 nm were determined using an UV spectrophotometer by measuring absorbance of 1% solution in cyclohexane at 232 nm and 270 nm with 1 cm of pass length.

p-Anisidine value: The oil samples dissolved in isooctane were allowed to react with *p*-anisidine for 10 min to produce colored complex and the absorbance values were noted at 350 nm using a spectrophotometer.

Chlorophyll and carotenoid contents: Following the procedures described by Minguez-Mosquera et al.^[6], a sample of *Camellia* oil (7.5 g) was placed in a volumetric flask and filled until 25 mL with cycle-hexane. The chlorophyll fraction was measured in a UV spectrophotometer at 670 nm and the carotenoid fraction at 470 nm. The contents of pigments were expressed using the following equations where the density was that of the oil (g/mL), respectively.

$$c(\text{Chlorophylls})/(\text{mg/kg}) = \frac{A_{670\text{nm}} \times 10^6}{613 \times 100 \times \rho_{\text{oil}}/(\text{g/mL})} \quad (1)$$

$$c(\text{Carotenoids})/\text{mg/kg} = \frac{A_{470\text{nm}} \times 10^6}{2000 \times 100 \times \rho_{\text{oil}}/(\text{g/mL})} \quad (2)$$

1.6 Differential scanning calorimetry (DSC) analysis

DSC analysis was performed according to the following conditions: Samples of oil (6.6mg) were analyzed with DSC Q200 V23.10 Build 79 (TA Instruments, New Castle, USA). Oil samples were equilibrated at 30 °C for 3 min and then DSC analysis were performed from -60 °C to 60 °C at a rate of 5 °C/min. Dry nitrogen was purged in the DSC cell at 40 mL/min. Cooling and melting thermograms were analyzed with Universal Analysis Software (Version 4.4A, TA Instruments) to obtain enthalpy (DH, J/g), onset temperature (t_{on} , °C) and offset temperature (t_{off} , °C) of the transitions (intersection of baseline and tangent at the transition). The range of transitions was calculated as temperature difference between t_{on} and t_{off} .

1.7 Semi-quantitative analysis of mineral contents

The sample solution for determination of mineral contents by dry ashing method was prepared. Determination of total copper (Cu), zinc (Zn), lithium (Li), boron (B), aluminium (Al), iron(Fe), manganese(Mn), sodium(Na), potassium(K), rubidium(Rb), magnesium(Mg), calcium(Ca) and barium(Ba) was carried out with a inductively coupled plasma mass spectrometry (7500A ICP-MS; Agilent, USA).

1.8 Tocopherol contents

Tocopherols were analyzed using an HPLC following China Official Method GB/T 5009.82 — 2003 *Determination of Retinol and Tocopherol in Foods*. Oil (1 g) and 30 mL ethanol were placed in a saponification flask. Five milliliters of 10% ascorbic acid and 10 mL of aqueous KOH solution (1:1) were added into the saponification flask and vortexed for 30 s. The saponification flask was refluxed in a water bath (100 °C) for 30 min. The saponification flasks were placed in an ice bath for 5 min, then 50 mL deionized water and 50 mL ethylether were added and vortexed for 30 s. The upper ethylether layer was transferred to another rotary evaporator flask. The aqueous layer and the residue were re-extracted by repeating the same procedures. The upper ethylether layers from both the extractions were pooled and dried with anhydrous sodium sulfate, then evaporated at 55 °C and finally dried under stream of nitrogen. Two milliliters of ethanol were added into the flask and vortexed 30 s to re-dissolve the extract and then transferred to an HPLC sample vial. 20 μ L sample was injected into ultrasphere ODS column (4.6 mm \times 25 cm, 5 μ m). Tocopherols were qualified using

standard UV spectrum analysis. Samples were analyzed in triplicate. The tocopherol to oil ratio was expressed as mg/100 g. Under the chromatographic conditions used, β - and γ -tocopherols did not separate fully, so the sum of β - and γ -tocopherols was determined.

1.9 Fatty acid compositions

Fatty acid compositions were analyzed by gas chromatography-mass spectrometry (GC-MS), using Agilent-Technologies 6890N Network GC system, equipped with an Agilent-Technologies 5973 inert XL Mass selective detector. Fames were separated on Agilent-Technologies DB-FFAP (30 m \times 0.32 mm, 0.50 μ m). About 0.1 mL of oil was converted to the methyl ester using 2 mL NaOMe (0.5 mol/L) in 1 mL hexane before being injected into GC. A sample of 1.0 μ L was injected in the split mode (split ratio 1:10). Helium was used as a carrier gas. Column oven temperature was programmed from 70 to 220 °C at 10 °C/min. For GC-MS detection, an electron ionization system was used. Injector and MS transfer line temperatures were set at 230 °C and 280 °C, respectively. Scanning mass range was m/z 29 — 450. The fames were expressed as relative area percentage by JY/T 003 — 1996 *General Principles of Organic Mass Spectrometry Method*.

1.10 Radical scavenging activity (RSA) toward DPPH radical

RSA toward DPPH radicals was examined by reduction of DPPH radicals in toluene. A toluenic solution of DPPH radicals was freshly prepared at a concentration of 10^{-4} mol/L according to Ramadan et al.^[49] with minor modifications. Oil samples (50 ± 1) mg, (100 ± 1) mg, (150 ± 1) mg were placed in test tubes, respectively, and then 4 mL aliquot of DPPH toluenic solution was added and vortexed for 20 s at ambient temperature. Against a blank of pure toluene without DPPH radicals, the decrease in the absorption at 515 nm was measured in 1 cm quartz cell after 1, 20 min and 50 min of mixing, using a UV-visible spectrophotometer (Ultrospec 2000 UV-VIS, Pharmacia Corporation, New Jersey, USA). RSA toward DPPH radicals was estimated from the differences in absorbance of toluenic DPPH solution with or without sample (control) and the inhibition percents were calculated using the following equation.

$$\text{Inhibition}/\% = \frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}} \times 100 \quad (3)$$

1.11 Thermal oxidative stability tests

The thermal oxidative stabilities of *Camellia* oil were tested under 130 °C oven heating for 8 h and microwave

heating conditions for a period of 70 min (800 W), respectively. Heating at 130 °C mimicked cooking and frying conditions. Oil samples were removed after heating treatments. The thermal oxidative stabilities of oil were evaluated by measuring K_{232nm} , K_{270nm} , peroxide, and p -anisidine values.

2 Results and Discussion

2.1 Chemical analysis of seed oil

Table 1 Compositional characteristics of *Camellia serniserrata* Chi. seed

Seed varieties	Oil content/%	Moisture/%	Solid/%
<i>Camellia serniserrata</i> Chi.	34.8	40	25.2
Olive Koroneiki ^[8]	24.3	52.5	23.2
Olive Mission ^[8]	13.1	70.2	16.7

Proximate compositions of *Camellia serniserrata* Chi., Olive koroneiki, and Olive mission seeds are shown in Table 1. Significant differences were observed among the seeds in their contents of moisture, oil and solid. *Camellia serniserrata* Chi. seed had higher level of oil (34.8 g/100 g) content compared to olive seeds^[7], which made the seeds suitable for the oil industry application. *Camellia serniserrata* Chi. seeds also had high amount of solids (25.2 g/100 g) which mainly contained proteins and carbohydrates. Therefore, the defatted *Camellia* seed meals should be applicable in animal feeds.

2.2 Cotyledonary structure

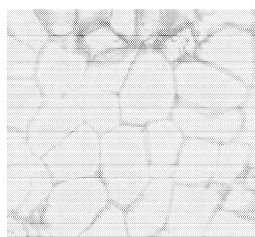


Fig.1 Light micrograph of *Camellia serniserrata* Chi. cotyledon stained by SAB($\times 40$)

The cell walls of cotyledonary cells can be observed in Fig. 1, which showed light micrograph of cotyledonary tissue structure of *Camellia serniserrata* Chi. seed stained by

Safranin-Alcian Blue (SAB). SAB stained sample showed the polygonal cells delimited by the cell wall.

2.3 Chemical analysis of seed oil

The chemical quality indices such as AV, SV, IV, POV, and p -anisidine value (p -AV) and so on give structural stability and quality information about oils and fats^[8]. The results of various physico-chemical characteristics of the extracted oil from *Camellia serniserrata* Chi. seed are reported in Table 2.

The saponification value is defined as the number of milligrams of potassium hydroxide that will react with one gram of sample. It is an indication of the average molecular mass of fatty acids present in oil. The high saponification value of seed oil of *C. serniserrata* Chi. (215.3 mg KOH/g) clearly suggested that it mainly contained fatty acids of medium-chain fatty acids (i.e. C_{16} and C_{18}). When compared with other oilseed crops, the saponification value of *C. serniserrata* Chi. seed oil was found to be superior to those of corn (187 – 195) mg KOH/g, cottonseed (189 – 198) mg KOH/g, olive (184 – 196) mg KOH/g, pumpkin (185 – 198 mg KOH/g), soybean (188 – 195) mg KOH/g, and rice bran (179 – 195) mg KOH/g oils^[9].

The iodine value is a measure of the unsaturation levels in fats and oils. A high iodine value is an indication of the presence of high unsaturation levels in oil. The determined iodine value of *C. serniserrata* Chi. seed oil was 82.1 g I₂/100 g oil. The iodine value (IV) of *C. serniserrata* Chi. seed oil, exceeded to that of palm oil (50 – 55 g I₂/100 g oil), was found to be within the range of olive oil (75 – 94 g I₂/100 g oil) and lower than the range of IV for soybean and sunflower oils (110 – 143 g I₂/100 g oil), reported in^[10-11]. The low iodine value of *C. serniserrata* Chi. oil was due to the presence of low content of polyunsaturated fatty acids (8.86%).

The quantity of free fatty acids, measured as oleic acid is used for oil quality assessment and classification index. The Codex Standard^[12] defines 0.8 g FFA/100 g, 2.0 g FFA/100 g, and 3.3 g FFA/100 g for extra virgin, virgin and ordinary virgin olive oils, respectively. 1.51 mg KOH/g oil of the acid value of *C. serniserrata* Chi. seed oil, fall well within the Codex standards for vegetable oils. The FFA had a positive correlation with

Table 2 Physico-chemical properties of *Camellia serniserrata* Chi. seed oil

Item	Peroxide value/ (meq/kg oil)	Free fatty acid/ (g FFA/100 g)	Saponification value/ (mg KOH/g)	Iodine value (g I ₂ /100 g)	p -Anisidine value/g ⁻¹	K_{232nm}	K_{270nm}	Carotenoids contents/(mg/kg)	Chlorophylls contents/(mg/kg)
<i>Camellia serniserrata</i> Chi. oil value	2.98	1.51	215.3	82.1	0.96	2.14	0.12	1.99	2.74

the presence of polyunsaturated fatty acids in oils^[13]. The *C. serniserrata* Chi. seed oil had a low content of polyunsaturated fatty acids and the observed FFA contents of *C. serniserrata* Chi. seed oil were found to be much lower, which indicated the amount of free fatty acids released by hydrolysis (generally deterioration) in *C. serniserrata* Chi. seed oil was lower than sunflower seed oil and soybean oil. It must be mentioned that refined oils have a less than acid value^[14].

The oxidative state of oil was determined using the peroxide value, specific extinction at 232 nm and 270 nm, and *p*-anisidine value, respectively. The peroxide value determines the formation of hydroperoxides (primary oxidation products)^[15]. The peroxide value obtained for *C. serniserrata* Chi. seed oil was 2.98 meq/kg that was significantly lower than those of Spanish Broom oil (15 meq/kg), linseed oil (11.28 meq/kg) and sunflower oil (12.87 meq/kg) as well as olive oil (5.98 meq/kg)^[16]. Spanish Broom, linseed, and sunflower oil as well as olive oil can be stored for a long time without deterioration, since oils become rancid when the peroxide value ranges from 20.0 to 40.0 meq O₂/kg oil^[17]. The low POV of *C. serniserrata* Chi. seed oil indicates that it is less prone to oxidative rancidity at room temperature.

The specific extinctions at 232 nm and 270 nm reveal the oxidative deterioration and purity of oil^[18-19]. Usually $K_{232\text{nm}}$ is accepted as an indicator of fat autoxidation, and $K_{270\text{nm}}$ is useful as a measure of the presence of conjugated dienes and trienes. The Codex Standard (2003) defines a maximum or equal values of 0.22, 0.25, and 0.30 of $K_{270\text{nm}}$ readings for extra virgin, virgin and ordinary olive oils, respectively. The results showed that $K_{232\text{nm}}$ and $K_{270\text{nm}}$ for *C. serniserrata* Chi. oil was 2.14 and 0.12, respectively, and the values were under the limit value of extra virgin olive oil indicating that *C. serniserrata* Chi. oil has higher oxidation stability than other oils.

The *p*-anisidine value (*p*-AV) measures the secondary oxidation products of oils, i.e. aldehydes, which the primary products of oxidation (peroxides) decompose and develop in the process of oil oxidation, and they are responsible for the rancid smell and taste^[20]. According to Rossell et al.^[21], oils with an anisidine value below 10 were considered as good quality, while Subramanian et al.^[22] considered good quality oils as having an anisidine value of less than two. The *p*-anisidine value of *C. serniserrata* Chi. seed oil presented in Table 2 was 0.96 g⁻¹, which indicated that the quality of the oil was relatively good.

The chlorophyll and carotenoid contents of oils are an important parameter because they are correlated with colour which influences the selection made by consumers. Moreover, pigments are also involved in auto-oxidation and photo-oxidation mechanisms^[6], which are effectively eliminated during the refining and bleaching processing of oils. The vegetables oils with minimum color are more acceptable for edible and domestic applications. In the studied *C. serniserrata* Chi. seed oil, the concentrations of chlorophyll and carotenoid pigments were 2.74 mg/kg and 1.99 mg/kg, respectively (Table 2). The oil colour was yellowish.

2.4 Differential scanning calorimetry (DSC) analysis

Since every oil has own unique fatty acid and triacylglycerol (TAG) profiles, which results in their different DSC cooling/melting thermograms, DSC that is a well-known calorimetric technique has been used for the characterization of the thermal behavior of pure edible oils^[23], heat of fusion and crystallization^[24], the fat liquid/solid ratio^[25] and polymorphic forms^[26-27] in lipid chemistry. Melting and crystallisation, two commonly used physical events to characterise thermal behaviour of oil samples, require intake or release of thermal enthalpy^[28].

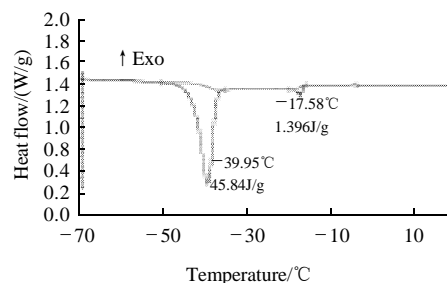
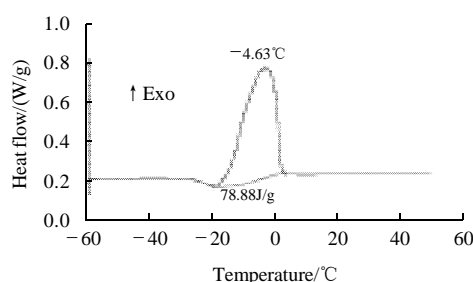


Fig.2 DSC crystallization curves of *C. serniserrata* Chi. seed oil

DSC cooling thermogram of *C. serniserrata* Chi. seed oil is shown in Fig. 2, which has two exothermic events, with the minor exotherm with maxima at -17.58°C and the major at -39.95°C where the minor exotherm peak depends on the saturation degree of the oil and the major exotherm peak relates to the unsaturated TG^[29]. As previously reported, that of extra virgin olive (EVOO) also exhibited two well distinguishable exothermic events, with the minor exotherm peaking at about -15°C and the major at about -37°C ^[30-31]. Two exothermic peaks of *C. serniserrata* Chi. seed oil were about 2°C lower than those of extra virgin olive, respectively, which may be related to a higher content of oleic acid (74.74%) in *C. serniserrata* Chi. seed oil.

Fig.3 DSC melting curves of *C. serniserrata* Chi. seed oil

DSC melting thermogram of *C. serniserrata* Chi. seed oil is shown in Fig. 3, which showed a melting profile different to that of extra virgin olive (EVOO) previously described where three events were found: a first exothermic event, occurring in the temperature range of -30 to -15 °C and two endotherm peaks at -6.0 °C and 8.5 °C^[31]. DSC melting thermogram of *C. serniserrata* Chi. seed oil had two typical events: the minor exothermic event occurring in the temperature range of -30 to -17 °C which was related to the transition/rearrangement of TAG polymorphic crystals into more stable forms in other vegetable oils^[32] and the major endothermic event peak occurring at -4.63 °C.

2.5 Mineral content semi-quantitative analysis

Table 3 Mineral contents of oil from *Camellia serniserrata* Chi. seed

Minerals	Li	B	Na	Mg	Al	K	Ca	Mn	Fe	Cu	Zn	Rb	Ba
Content/(mg/kg)	0.53	0.35	16	16	13	26	9.7	4.3	0.58	0.12	1.1	0.18	0.14

In *Camellia serniserrata* Chi. seed oil, the mineral elements that are Na, K, Ca, Mg, Fe, Mn, Cu, Al and so on (Table 3) were determined with a inductively coupled plasma mass spectrometry (7500A ICP-MS; Agilent, USA). Potassium, aluminium, potassium, magnesium and calcium were found in higher quantities in oil samples which ranged from 9.7 to 26 mg/kg. Other mineral contents were below 4.3 mg/kg. The order of nutritive elements depending on content/kg of oil was: $K > Mg = Na > Al > Ca > Mn > Zn > Fe > Cu$. Nevertheless, the toxic minerals such as As and Pb, for consumption^[33] were not detected in oil samples.

The highest content was recorded for potassium (K), a cardiac tonic and muscular tonic element and its salts may benefit bone health by providing an anion that can be metabolized completely to carbon dioxide, or influence Ca excretion directly^[34]. In addition, dietary K intake may exert a modest influence on markers of bone health, which may contribute to a reduced risk of osteoporosis^[51]. In human body, manganese is an important glandular regulator, which is involved in metabolism of glucydes, lipides and protides^[35]. Ca is necessary for many processes in the body including contraction of

muscles, nerve function, blood coagulation and cell division. Zinc (Zn) is a key element in cell division and growth. Copper (Cu) is a dynamic element, anti-infectious, antiviral, anti-inflammatory. Daily required amount of copper for an adult human is 2.5 mg^[35]. Besides, Cu and Fe have been known as the major catalysts for oxidation^[36]. Although the prooxidant Fe and Cu were found at very low concentrations, the oxidation of oil might take place via the induction of prooxidants.

2.6 Tocopherol contents

Table 4 Tocopherol contents in *Camellia serniserrata* Chi. seed oil

Sample	mg/100g			
	α -Tocopherol	$(\beta + \gamma)$ -Tocopherol	δ -Tocopherol	Total
<i>Camellia</i> oil	5.6	0.79	ND	6.39
Spanish Broom oil ^[16]	3.44	0.65	1.24	5.33
Linseed oil ^[16]	2.75	ND	ND	2.75
Sunflower oil ^[16]	0.09	0.49	0.14	0.72
Olive oil ^[16]	8.53	ND	ND	8.53

Tocopherols refer to a group of minor but important lipid-soluble compounds being involved in physiological and biochemical functions. Tocopherols are natural lipophilic antioxidants found, which are very important in vegetable oils^[37-38]. As shown in Table 4, tocopherols were detected in *Camellia serniserrata* Chi. seed oil among which α -tocopherol was the major tocopherol (5.6 mg/100 g), $(\beta + \gamma)$ -tocopherols was at lower amounts (0.79 mg/100 g) and δ -tocopherol was not detected. Of other seed oils previously investigated^[17], olive oil had the highest total tocopherol values (8.53 mg/100 g) followed by Spanish Broom oil (5.33 mg/100 g), linseed oil (2.75 mg/100 g) and sunflower oil (0.72 mg/100 g) where all tocopherols were detected in sunflower oil as well as Spanish Broom seed oil and α -tocopherol is the only tocopherol detected in linseed oil as well as olive oil.

Table 5 Fatty acid composition of *Camellia serniserrata* Chi. seed oil

Fatty acids	Content/%		
	<i>Camellia</i> seed oil	Olive Arbequina oil ^[50]	Olive Manzanilla oil ^[50]
Myristic acid(14:0)	0.07	ND	ND
Palmitic acid (16:0)	10.52	16.42	15.33
Hexadecenoic acid (16:1)	0.13	2.01	2.08
Heptadecanoic acid(17:0)	0.1	ND	ND
Stearic acid (18:0)	4.46	1.56	1.46
Oleic acid (18:1, <i>n</i> -9)	74.74	64.98	72.39
Linoleic acid (18:2, <i>n</i> -6)	8.65	14.3	7.9
Linolenic acid (18:3, <i>n</i> -3)	0.21	0.74	0.83
Arachidic acid (20:0)	0.2	ND	ND
Eicosanoic acid (20:1, <i>n</i> -9)	0.62	ND	ND
Erucic acid (22:1, <i>n</i> -9)	0.29	ND	ND
Σ Saturated fatty acid	15.35	17.98	16.79
Σ Monounsaturated fatty acids	75.78	66.99	74.47
Σ Polyunsaturated fatty acids	8.86	15.04	8.73

Table 5 shows the FA compositions of *Camellia serniserrata* Chi. seed oil as determined by GC-MS. The major saturated fatty acids in oil sample were palmitic and scamelliatic acids which accounted for 10.52% and 4.46% of the total FAs, respectively, with myristic acid (0.07%), heptadecanoic acid (0.1%), and arachidic acid (0.2%) present in small amounts. The main unsaturated fatty acids were oleic acid (74.74%) and linoleic acid (8.65%), with small amounts of hexadecenoic acid (0.13%), linolenic acid (0.21%), eicosanoic acid (0.62%), and erucic acid (0.29%). The mono-unsaturated fatty acids i.e. oleic acid are of great importance due to their high nutritional value and positive effect on the oxidative stability of oils^[39]. Oleic acid was present in higher concentrations in virgin olive oils, which was between 64.91% and 76.36%^[40]. Virgin olive oils have two types based on their fatty acid compositions. The first type of olive oil has low linoleic as well as palmitic and high oleic acid contents while the second type contains high linoleic as well as palmitic and low oleic acid contents. Turkish virgin olive oils (like Spanish, Italian and Greek) are of the first type and Tunisian oils are classified into the second type^[41]. As compared with olive oils already reported, *Camellia serniserrata* Chi. seed oil has a higher content of oleic acid indicating a good nutritional value of *Camellia serniserrata* Chi. seed oil.

2.7 Radical scavenging activity (RSA) toward DPPH radical

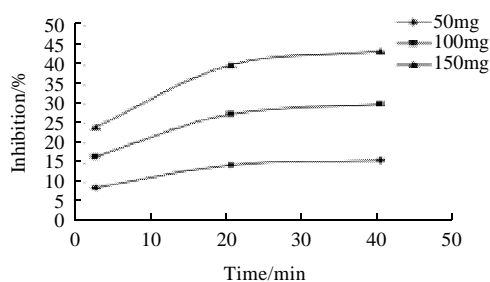


Fig.4 DPPH scavenging activity of *Camellia serniserrata* Chi. seed oil

The DPPH test has been widely used to evaluate antioxidant activity of different plant extracts and vegetable oils for free radical scavenging. The antioxidant activity increase with the increase in total tocopherol and phenolic contents was found^[42-45]. The results of free radical quenching capabilities of oil samples measured by the DPPH method are shown in Fig. 4. The DPPH radical quenching abilities of different amount oils were found to be in the order 150 mg > 100 mg > 50 mg, which were 43.6%, 29.9% and 15.6%,

respectively. These results exhibit a good DPPH scavenging activity of *Camellia serniserrata* Chi. seed oil.

2.8 Thermal oxidative stability tests

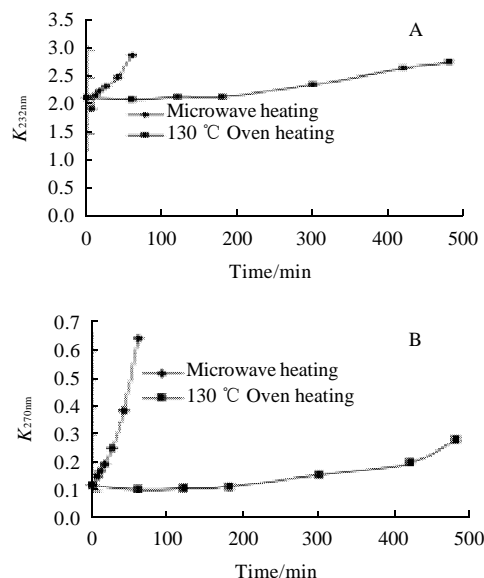


Fig.5 Evolution of K_{232nm} (A) and K_{270nm} (B) during microwave heating and 130 °C oven heating

As is well-known, K_{232nm} and K_{270nm} are used for monitoring the progress of oxidation^[46]. The changes in K_{232nm} and K_{270nm} versus heating time during microwave heating (800 W) and 130 °C oven heating were monitored. The results are shown in Fig. 5. After the K_{232nm} and K_{270nm} slow increases in initial stages, microwave heating oil showed a significant increase of K_{232nm} and K_{270nm} values after 25 min, while 130 °C oven heating oil after 5 h. After initial stage heatings, *Camellia serniserrata* Chi. seed oil had still a lower values of K_{232nm} and K_{270nm} indicating a good thermal oxidative stability because of the high percentage of oleic acid (74.74%).

The *p*-anisidine assay is used to quantify the carbonyl compounds present in oils as a means to assess the quality of oil^[47-48]. The *Camellia serniserrata* Chi. seed oil had very low PAV 1.0/g⁻¹. Its thermal oxidation stability was also evaluated by the measurement of PAV and peroxide value. The evolutions of PAVs and peroxide values versus heating time are shown in Fig.6. During heating at 130 °C after 5 h and microwave heating at 800 W after 25 min, a steep rise in the slope occurred indicating that the oxidation process speeded up, which might cause great damage on the quality of oil even during a short period. This behaviour was also confirmed by the evolution of the first and secondary oxidation products (K_{232nm} and K_{270nm}).

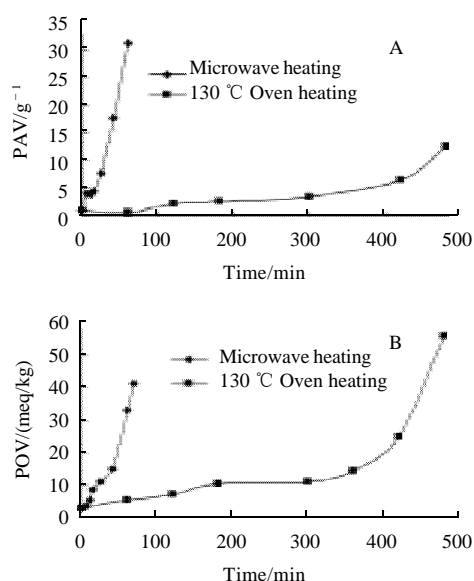


Fig. 6 Evolution of *p*-anisidine value (PAV) (A) and peroxide value (POV) (B) during microwave heating and 130 °C oven heating

3 Conclusions

This is the first report on the physico-chemical properties and thermal oxidative stability of oil from *Camellia serniserrata* Chi. seed that has a very high oil content (34.8%, wet weight) with high oleic acid content more than those of seeds from olive varieties. The results also show that *Camellia serniserrata* Chi. seed oil has good physico-chemical characteristics and thermal oxidative stability and it will be very suitable for it to be used into cosmetics, pharmaceuticals, and food. Thus, *Camellia serniserrata* Chi. seed oil has the potential to become a new source of high-oleic acid oil and its full potential should be exploited.

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