



Chemical characterization of seeds and seed oils from mature *Terminalia catappa* fruits harvested in Côte d'Ivoire

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Abstract

The seeds of mature *Terminalia catappa* ripe (MTCRF) and unripe fruits (MTCUF) from Côte d'Ivoire were analysed for their main chemical compositions. Studies were also conducted on properties of oils extracted from the same seeds. The following values (on a dry-weight basis) were obtained for seeds of MTCUF and MTCRF, respectively: moisture 5.10 ± 0.75 and $4.80 \pm 0.34\%$, crude protein 29.77 ± 1.12 and $29.89 \pm 0.41\%$, oil 58.61 ± 0.13 and $63.65 \pm 0.04\%$, total sugars 3.02 ± 0.05 and $3.53 \pm 0.10\%$, reducing sugars 0.08 ± 0.01 and $0.06 \pm 0.01\%$, total carbohydrate 5.38 ± 0.02 and $5.09 \pm 0.12\%$, total ash 5.10 ± 0.20 and $4.60 \pm 0.14\%$ and calorific value 573.79 ± 1.02 and 567.75 ± 0.84 kcal/100 g. Within these seeds, the potassium concentration was the highest, followed by phosphorus and calcium. The major saturated fatty acid was palmitic acid, while the main unsaturated fatty acid was oleic acid for the MTCRF and linoleic acid for the MTCUF seed oils. These seed oils had characteristically low acidity and peroxide values and showed some absorbance in the UV-B and UV-C ranges. MTCUF and MTCRF seeds and seed oils originated from Côte d'Ivoire were a good quality and could be used in cosmetic, pharmaceutical and food products.

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Introduction

Terminalia catappa (TC) tree belongs to the Combretaceae family, with a Meridional Asia origin (Cavalcante *et al.*, 1986). It is a large, spreading tree distributed throughout the tropics in coastal environments. The tree grows principally in freely drained, well aerated and sandy soils. It is widely planted for shade, ornamental purposes and edible nuts (dos Santos *et al.*, 2008). In fact, there is hardly any public quarter where the tree is not found in Abidjan (Côte d'Ivoire). Several species of the genus *Terminalia* have long been used in the traditional medicine in both East and West African countries to treat infectious diseases (Fabry *et al.*, 1996). In Asian countries, the extract of the leaves have been used in folk medicine for treating dermatitis and hepatitis (Kinoshita *et al.*, 2006). It has shown anti-oxidative, anti-inflammatory and hepatoprotective actions (Gao *et al.*, 2004). Several tannins of this extract have shown inhibiting HIV replication in infected H9 lymphocytes with little cytotoxicity (Nonaka *et al.*, 1990).

TC fruit contains a very hard kernel with an edible almond (Thomson and Evans, 2006). The nuts may be consumed fresh shortly after extraction from the shell or else preserved by smoking. In some areas, the nuts are mainly a snack food consumed by children, with the fleshy fruit also sometimes being consumed. In other areas, tropical almond nuts are highly regarded as a human food source. Proximate analyse of TC seed shows that it has high amounts of protein and oil (Oliveira *et al.*, 2000). Ezeokonkwo and Dodson (2004) reported that the proteins of this seed have a good pattern of the essential amino acids and are highly digestible. They can support growth and positive nitrogen balance and thus have a high dietary protein quality. These findings are in contrast with those reported by Oliveira *et al.* (2000) for the same seeds. The authors concluded that the proteins of TC seed are deficient in various essential amino acids. They are severely deficient in lysine for 2-5 and 10-12 year old children and have histidine as the second limiting amino acid. According to

Abdullahi and Anneli (1980), Ajayi *et al.* (2008) and dos Santos *et al.* (2008), the fatty acid composition of TC seed oil shows high amount of unsaturated fatty acids with linoleic and oleic acids as the major ones. This seed oil contains palmitic and stearic acids as the main saturated fatty acids. Ajayi *et al.* (2008) reported the presence of linolenic acid in TC seed oil. This finding deviated from the result obtained by Oliveira *et al.* (2000), reporting absence of linolenic acid in this seed oil. dos Santos *et al.* (2008) have reported the chemical constituents of TC seed oil. Whereas, the values obtained by Ajayi *et al.* (2008) and Abdullahi and Anneli (1980) for most of these parameters were different. The TC seed analysed by Ajayi *et al.* (2008), dos Santos *et al.* (2008), Ezeokonkwo and Dodson (2004), Oliveira *et al.* (2000) and Abdullahi and Anneli (1980) were from Ibadan (Nigeria), Alagoas (Brazil), Nsukka (Nigeria), Ceara (Brazil) and Somalia respectively. This pattern seems that chemical composition and profile characteristics of seed and seed oil from TC fruit vary with species, geographical location, season and temperature (Kaehler and Kennish, 1996; Dawes *et al.*, 1993). In addition, most studies on the chemical composition and physico-chemical properties of this seed neglected the effect of physiological maturity of the fruit.

The objective of this study is to evaluate the chemical composition and profile characteristics of seeds and seed oils from mature *Terminalia catappa* ripe (MTCRF) and unripe fruits (MTCUF) harvested in Côte d'Ivoire (West Africa). This is done in order to compare these characteristics to those obtained earliest by different authors on the same seeds and improve its quality.

Materials and methods

Materials

Mature fruits of TC were harvested from the trees at the University of Abobo-Adjamé (Abidjan, Côte d'Ivoire) in May 2009. The climate in this area is characterised by high humidity, precipitation up to 4,000 mm per annum and relatively high

temperatures, averaging 28°C. All the chemicals, reagents and solvents used in the experiments were of analytical grade and were products of Sigma Chemical Co. (St. Louis, MO).

Preparation of powdered seeds

The powdered seeds were prepared using Ezeokonkwo and Dodson (2004) method. The fresh fruits were carefully cracked and the seeds were removed, cleaned and washed of any adhering residue. Then, they were hand-picked to eliminate damaged ones. The selected seeds were dried to a constant weight using an oven preset at 60°C for 24 h. The whole seeds were finely milled using a laboratory hammer mill and screened through a mesh of 0.5 mm dia. The meal obtained was stored in an airtight container at 4°C until required for analyses.

Proximate composition analysis

The dry matters contents were determined by drying in an oven at 105°C during 24 h to constant weight (AOAC, 1990). The crude protein contents were calculated from nitrogen contents ($N \times 6.25$) obtained using the Kjeldahl method by AOAC (1990). The oil yields were determined by continuous extraction in a Soxhlet apparatus for 8 h using hexane as solvent (AOAC, 1990). The total ash contents were determined by incinerating in a furnace at 550°C (AOAC, 1990). The method described by Dubois *et al.* (1956) was used for the total sugar contents analysis. The reducing sugar contents were determined according to the method of Bernfeld (1955) using 3,5 dinitrosalicylic acids. The carbohydrate contents were determined by difference that is by deducting the mean values of other parameters that were determined from 100. Therefore % carbohydrate = $100 - (\% \text{ moisture} + \% \text{ crude protein} + \% \text{ crude fat} + \% \text{ crude fibre} + \% \text{ ash})$ (Al-Hooti *et al.*, 1998). The energy value of the seeds were estimated in kilojoules by multiplying the protein, fat and carbohydrate percentages by the factors 16.7, 37.7 and 16.7, respectively according to Eknayake *et al.* (1999) method.

Mineral composition analysis

The minerals, such as calcium, copper, iron, magnesium, sodium, potassium and zinc were analysed after first wet-ashing according to the method prescribed by Onwuliri and Anekwe (1992) with an atomic absorption spectrophotometer (Pye-Unicam 969, Cambridge, UK). Phosphorus contents were estimated colorimetrically (UV-visible spectrophotometer, JASCO V-530, MODEL TUDC 12 B4, Japan Servo CO. LTD Indonesia), using potassium dihydrogen phosphate as the standard (AOAC, 1980).

Determination of the seed oil colour

The seed oil colour was measured using the CIE (Commission Internationale de l'Eclairage) L*, a*, and b* colour system. The CieLab coordinates (L*, a*, b*) were directly read with a spectrophotocolorimeter MS/Y-2500 (Hunterlab, In., Reston, VA, USA), calibrated with a white tile. In this coordinate system, the L* value is a measure of lightness, ranging from 0 (black) to 100 (white), the a* value ranges from -100 (greenness) to +100 (redness) and the b* value ranges from -100 (blueness) to +100 (yellowness).

Chemical analysis of the seed oil

Standards ISO (International Organisation for Standardisation) were used for the determination of the peroxide value (ISO, 3960), acidity (percentage of free fatty acid was calculated as oleic acid) (ISO, 660), iodine value (ISO, 3596) and saponification value (ISO, 3657) of oil. Refractive index was determined by AOAC method 41.1.07 (AOAC, 2000) using an Abbe' refractometer (Bausch & Lomb, Salt Lake, UT). The viscosity was followed at 25°C with a Stress Tech Rheologica Rheometer (Rheologica Instruments AB, Lund, Sweden) conducted with a steel cone-plate (C40/4) under a constant shear rate of 100 s^{-1} according to Besbes *et al.* (2004) method. Analyses of fatty acid methyl esters were carried out with a Hewlett Packard Gas Chromatograph (Model, 439), equipped with a hydrogen flame ionisation detector and a capillary column, Supelcowax Tm, fused silica (60 m x 0.25 mm i.d., of 0.2 µm particle diameter). Temperatures of injector,

column and detector were 260, 180 and 250°C, respectively. Hydrogen was used as carrier gas at a flow rate of 30 ml/min. Identification and quantification of fatty acid methyl esters was accomplished by comparing the retention times of the peaks with those of standards. Absorptivity of oil solutions (1%, v/v) in hexane were measured using a spectrophotometer (JASCO V-530, WITEG Labortechnik., Gmbh).

Statistical analyses

The mean values and standard deviations of each analysis are reported. Analysis of variance (ANOVA) was performed as part of the data analyses (SAS, 1988). When F-values were significant ($p < 0.05$) in ANOVA, then least significant differences were calculated to compare treatment means.

Results and discussion

Chemical composition of seed

The proximate compositions of seeds from MTCRF and MTCUF harvested in Côte d'Ivoire are shown in Table 1. The ripening led to a significant ($P < 0.05$) reduction in the moisture, total carbohydrate and total ash levels, whereas the total sugar and oil contents increased significantly ($p < 0.05$). The crude protein and reducing sugars contents were not affected by the ripening. Moisture contents of the seeds from MTCRF and MTCUF were below 6%, thereby giving the seeds a better shelf life (Aryee *et al.*, 2006). The total carbohydrate contents obtained for seeds from MTCRF ($5.09 \pm 0.12\%$) and MTCUF ($5.38 \pm 0.02\%$) collected in Côte d'Ivoire were lower when compared to those of seeds from *Terminalia catappa* fruits (TCF) originated to Brazil (9.9%, Oliveira *et al.*, 2000), Nigeria (6.5%, Omeje *et al.*, 2008) and Congo (16.02%, Kimbonguila *et al.*, 2010). The decrease in carbohydrate content of seeds from ripe fruits as compared to that from unripe fruits had earlier been attributed to the transformation of starch into soluble sugars under the action of phosphorylase enzyme during ripening (Germain and Linden, 1981). This enzymatic behavior leached high total sugar contents occurred into the seeds from ripe fruits. Similar findings were

reported for banana (Ibrahim *et al.*, 1994), mango (Abu- Kansci *et al.*, 2003; Goukh and Abu-Sarra, 1993) and date (Dowson and Aten, 1962). The result showed that oil is the most important chemical component in the seeds of MTCRF ($63.65 \pm 0.04\%$) and MTCUF ($58.61 \pm 0.13\%$) harvested in Côte d'Ivoire. This finding corroborated well with those reported for castor (57.33 %), dikanut (62.80 %), melon (53.04 %), bean (52.07 %), palm kernal (54.18 %, Onyeike and Acheru, 2002) and seeds of TCF grown in Ceara, Alagoas (58.3 %, Oliveira *et al.*, 2000), Enugu (56.71 %, Omeje *et al.*, 2008) and Brazzaville (51.80 %, Kimbonguila *et al.*, 2010). In addition, the seed oil contents of MTCRF and MTCUF were found to be higher than those reported for grapeseed, corn (15.8 %, Wang *et al.*, 1996), coconut seed (42.00 %, Onyeike and Acheru, 2002), groundnut seed (40.83 %, Onyeike and Acheru, 2002), Chinese chive seed (15.8%, Hu *et al.*, 2006) and various soybean cultivars (18.3-21.5 %, Vasconcelos *et al.*, 1997). This indicated that the seeds of TCF are a cheap source of edible oils that can be used in cooking and in the manufacture of soap. The oils can also find use in cosmetic industries. The oil content increased during ripening as shown in Table 1. Similar observation was recorded by Salvador *et al.* (2001), Gutierrez *et al.* (1999) and Chimi and Atouati (1994) when using olive fruits. The result also showed that besides oil, protein and ash are another important group of component in seeds of MTCF originated to Côte d'Ivoire. This pattern was in good accordance with those published by Kimbonguila *et al.* (2010), Omeje *et al.* (2008) and Oliveira *et al.* (2000) for the same seeds cultivated in Ceara, Enugu and Brazzaville respectively. The crude protein content ($29.89 \pm 0.41\%$ for ripe fruit seed and $29.77 \pm 1.12\%$ unripe fruit seed) was not affected significantly ($p < 0.05$) by ripening. This result was contrary to those obtained by Bashir and Abu-Goukh (1984) who reported that total protein in pulp and peel of the white and pink guava types increased systematically up to the full-ripe stage (fruit firmness 0.61 kg/cm) and suddenly decreased. Also, Abu-Goukh and Abu-Sarra (1993) described that

proteins of three different mango cultivars increased up to the full-ripe stage and then decreased at the over-ripe stage, due to enzymatic activity. Total protein contents of seeds from MTCF grown in Côte d'Ivoire were higher than those reported for the seeds of cereal such as corn, triticale and wheat (8.4. to 14.8 %, Heger and Eggum, 1991), important grain legumes (18.0 to 25.0 %, Singh and Singh, 1992) and TCF cultivated in Nsukka (25.81%, Ezeokonkwo and Dodson, 2004), Enugu (26.3%, Omeje *et al.*, 2008) and Brazzaville (23.78%, Kimbonguila *et al.*, 2010). However, these values were comparable to the seed protein content of TCF from Ceara, (29.4%, Oliveira *et al.*, 2000). The total ash contents of the seeds from Ivorian MTCF (4.60 ± 0.14 % for ripe fruit seed and 5.10 ± 0.20 % unripe fruit seed) were higher than those reported for the seeds from the same fruits cultivated in Ceara (2.4%, Oliveira *et al.*, 2000). However, these values were comparable to the seed ash contents of TCF grown in Enugu (4.55 %, Omeje *et al.*, 2008) and Brazzaville (4.27%, Kimbonguila *et al.*, 2010). This suggested that the seeds from Ivorian MTCF could be a source of mineral elements having nutritional importance. The decrease of total ash contents of seeds from Ivorian MTCF during ripening could be attributed to the fact that during maturation inorganic ions migrate from different parts of the plant to the region of active growth (Sanchez *et al.*, 1991). The result presented in Table 2 showed the mineral composition of the seeds from MTCF harvested in Côte d'Ivoire. The magnesium, manganese and iron contents of the seeds kept decreasing with ripening, while increase in zinc and cooper, potassium, sodium, phosphorus and calcium. The seeds of MTCF harvested in Côte d'Ivoire contained significant amount (on dry weight basis) of important minerals. The potassium concentration (3068.96 ± 1.70 and 4116.30 ± 0.85 mg/100g) was the highest, followed by phosphorus (2128.03 ± 1.80 and 2048.50 ± 2.37 mg/100g) and calcium (587.72 ± 2.56 and 380.70 ± 1.22 mg/100g). Similar observations were recorded by Takruri and Dameh (1998) when using five varieties of black cumin

seeds (Iranian, two Syrian, Turkish and Jordanian). The other elements, in descending order by quantity, were sodium (66.40 ± 0.85 and 61.40 ± 0.99 mg/100g), magnesium (19.73 ± 1.43 and 21.02 ± 0.12 mg/100g), iron (5.32 ± 0.03 and 5.65 ± 0.07 mg/100g), manganese (2.60 ± 0.19 and 4.66 ± 0.91 mg/100g), cooper (1.75 ± 0.03 and 1.43 ± 0.35 mg/100g) and zinc (0.77 ± 0.09 and 0.62 ± 0.04 mg/100g). This order was different to those reported by Al-Hooti *et al.* (1998) and Devshony *et al.* (1992) for the seeds of date fruit (cultivars of United Arab Emirates) and date palm respectively. The K:Na ratios (67.04 and 46.21) were close to the recommended 5.0 (Szentmihalyi *et al.*, 1998). Dietary changes leading to reduced consumption of potassium than sodium have health implications. Diets with higher ratio K:Na are recommended and these are found usually in whole foods (Arbeit *et al.*, 1992). The high K:Na suggested that the seed from Ivorian MTCF could be suitable in helping to ameliorate sodium-related health risk (Appiah *et al.*, 2011). The Ca:P ratio of the seeds from MTCF grown in Côte d'Ivoire was below 1. However, according to SCSG (2007) a good menu should have a Ca:P ratio over 1. Foods high in phosphorus and low in calcium tend to make the body over acid deplete it of calcium and other minerals and increase the tendency towards inflammations (Appiah *et al.*, 2011). In order to avoid this problem, these seeds need supplementation with calcium to prevent mineral and osmotic imbalance (Appiah *et al.*, 2011). The chemical composition of the seeds from MTCRF and MTCUF harvested in Côte d'Ivoire revealed their nutritional value for human and/or animal consumption. Such variation in nutrient concentrations among varieties of seeds from TCF may be related to the variations of cultivated regions, storage conditions and maturity stage. It may also be due to geographical and climatic differences where TC had been grown (Atta, 2003). These conditions may affect the qualitative and quantitative composition of the seeds by altering the activity of the enzymes involved in synthesis and breakdown process (Lingle and dunlap, 1987).

Seed oil colour and UV-visible profile

CieLab coordinates (L^* , a^* , b^*) of seed oils from MTCRF and MTCUF harvested in Côte d'Ivoire are shown in Table 3. Compared to the oil of seed from MTCUF, seed oil from MTCRF showed a higher L^* and a lower a^* and b^* values. This indicated that the ripening had caused an increase in the bright and a decrease in the red and yellow units of colour. The CieLab coordinates (L^* , a^* , b^*) values of other vegetable oils, such as palm, soybean, sunflower, olive and corn ranged from 63.4 to 69.5, 3.8 to 4.4 and 9.2 to 10.4, respectively (Hsu and Yu, 2002). This showed that the MTCF seed oils b^* values were higher than those of other vegetable oils, indicating that these oils were more yellow-coloured than vegetable oils studied by Hsu and Yu (2002). This suggested the presence of more yellow pigments (carotenoids) in TCF seed oils.

The difference in the crude oil absorbances between the MTCRF and MTCUF seeds was not significant in the UV-C (100-290 nm), UV-B (290-320 nm) and UV-A (320-400 nm) range. However, in the 400-800 nm range, there was significant difference ($p < 0.05$) between seed oil absorbances from MTCUF and MTCRF. These seed oils showed a high absorbance in the UV-C and UV-A range at low concentration (10 g/l) (Fig. 1). In the UV-B range, the wavelengths of ultraviolet light responsible for most cellular damage, TCF seed oils can shield against UV-A induced damage by scattering (high transmission), as well as by absorption. The shielding power in the UV-A range depends mostly on the scattering effect. Thus, TCF seed oils may act as a broad spectrum UV protectant and provide protection against both UV-A, an exogenous origin of oxidative stress to the skin, and UV-B. The optical transmissions of TCF seed oils, especially in the UV range (290-400 nm) were comparable to those of seed oils from raspberry (Oomah *et al.*, 2000), *Maclura pomifera* (Fatnassi *et al.*, 2009) and *Washingtonia filifera* (Nehdi, 2011). The absorbance at 232 nm (1.9) can be explained by the presence of hydroperoxides of the linoleic acid and other products resulting from their decomposition.

However, the low absorbance at 268 nm (0.14) indicated the presence of weak quantity of secondary products of oxidation and specially alpha-diketones or alpha unsaturated ketones (Karleskind, 1992). These results were in agreement with the low values of the peroxide values (Table 4). Green pigments, particularly chlorophyll content, usually measured at 630, 670 and 730 nm, were high as indicated by very strong absorbance in the 600-750 nm range for TCF seed oils. Also, the strong absorbance in the 418-470 nm range indicated the presence of an important quantity of carotenoids (typical of beta-carotene absorption at 425, 450 and 477 nm) which explained the intense yellow colour of the TCF seed oils. TCF seed oils contained more yellow colouring than raspberry seed oil which was characterised by an absorbance ranging from 0.08 to 0.11 at 440-460 nm, studied by Oomah *et al.* (2000) under the same conditions. This confirmed the results obtained with the CieLab Miniscan instrument. This yellow colour, which included carotenoids, is beneficial, since it stimulates the appearance of butter without the use of primary colorants such as carotenes, annatto, and apocarotenals commonly used in the oil and fat industry (Oomah *et al.*, 2000).

Seed oil physicochemical characteristics

From Table 4, the seed oil from MTCUF was light golden yellow in colour, liquid at room temperature (25°C) with pleasant odour while seed oil from MTCRF was pale yellow, liquid at room temperature with pleasant odour. The colour of seed oil from MTCRF was different to that obtained from TCF seed oil originated to Nigeria (golden yellow, Omeje *et al.*, 2008). There was significant difference ($p < 0.05$) between seed oils from MTCUF and MTCRF harvested in Côte d'Ivoire in terms of their saponification and acid values. The saponification value was higher in the seed oil from MTCRF (188.40 ± 1.87 mg KOH/g of oil) than that of the seed oil from MTCUF (185.44 ± 0.62 mg KOH/g of oil). These data were higher compared to that of seed oil from the same fruit originated to Nigeria (166.2 mg KOH/g of oil, Omeje *et al.*, 2008), but

lower than those observed for the oils of TCF seed collected in Congo (Kimbonguila *et al.*, 2010), safflower, sunflower and corn (O'Brien, 2004) with average saponification values ranging between 191 and 250 mg KOH/g of oil (Gunstone *et al.*, 1994). The values of saponification indicated the presence of many fatty acids of low molecular weight, making possible the utilization of these oils in the manufacture of soaps and lather shaving creams. The increase in acid value indicated that free fatty acids were formed during ripening in the seed showing the presence of the lipase activity in the seed. These data were lower compared to those of seed oils from the same fruits originated to Brazil (0.5%, dos Santos *et al.*, 2008) and Nigeria (3.53%, Omeje *et al.*, 2008). The lower acid values of the seed oils from MTCF (0.31 ± 0.09 and $0.38 \pm 0.08\%$) compared to palm oil showed a possible low free fatty acid composition which suggested lesser susceptible rancidity (having a disagreeable odour), long shelf lives (Dosunmu and Ochu, 1995; Li *et al.*, 2007) and direct use in industries without further neutralization as described by Arogba (1997). In addition, oil of low acidity has been considered acceptable for edible application. There was no statistically significant ($P < 0.05$) difference in the viscosity, refractive index, peroxide and iodine values of seed oils from MTCRF and MTCUF harvested in Côte d'Ivoire. This pattern is an indication that ripening did not greatly affect these physico-chemical properties in the seed oils from MTCF. Peroxide value (< 0.02 mEq O₂/kg of oil) which is a function of unsaturation, time and type of storage fairly was lower compared to that of palm oil (13.40 mMol kg⁻¹) and seed oils from TCF originated to Nigeria (8.59 mEq O₂/kg of oil, Omeje *et al.*, 2008) and Congo (0.51 mEq O₂/kg of oil, Kimbonguila *et al.*, 2010). This implied that the seed oils from MTCRF and MTCUF may be more stable to oxidative degradation (Manzoor *et al.*, 2007). In addition, the peroxide values are lower than 10 mEq O₂/kg of oil, which characterize the majority of conventional oils (Codex Alimentarius Commission, 1993). The iodine value in seed oils was 70.41 ± 0.16 g/100 g of oil. This value compared

to those of the palm oil (Eka, 1980) and seed oil from TCF collected in Congo (82.43 g/100 g of oil, Kimbonguila *et al.*, 2010) suggested that the seed oils of MTCF from Côte d'Ivoire may have a lower unsaturated fatty acid and hence low susceptibility to oxidative rancidity than the palm oil and seed oil from TCF originated to Congo. However, the iodine values of seed oils from MTCRF and MTCUF grown in Côte d'Ivoire were higher than that of the seed oil from the same fruits harvested in Nigeria (38.59 g/100 g of oil, Omeje *et al.*, 2008) but lower than those of TCF seed oils originated to Brazil (83.92 g/100 g of oil, dos Santos *et al.*, 2008). Table 4 showed that the viscosity of seed oil from MTCF (20 ± 0.21) grown in Côte d'Ivoire was lower than those of the same oil originated to Nigeria (40.79 mPa .s, Omeje *et al.*, 2008), Congo (32.92 mPa .s, Kimbonguila *et al.*, 2010) and most vegetable oils, but this value was similar to the oleic acid and raspberry seed oil studied by Oomah *et al.* (2000). This difference is likely due to the fatty acid chain length (Geller and Goodrum, 2000; Gustone *et al.*, 1986) and presence of double bonds (Besbes *et al.*, 2004). Refractive index of MTCF (1.45) seed oil was similar to those of the same oil originated to Nigeria (Omeje *et al.*, 2008) and rapeseed oil (Karlesind and Wolff, 1992). Most of the physico-chemical characteristics of MTCF grown in Côte d'Ivoire were considerably different from those reported for the same oils originated to Nigeria (Ibadan and Enugu) (Ajayi *et al.*, 2008; Omeje *et al.*, 2008) and Brazil (dos Santos *et al.*, 2008), indicating that variations in these characteristics could be attributed both to environmental and genetic differences (Nelson *et al.*, 2002).

Seed oil mineral and fatty acid compositions

Mineral compositions and concentrations of the seed oils from MTCRF and MTCUF are shown in Table 5. The result revealed potassium to be the prevalent mineral element in these seed oils, followed in descending order by phosphorus, sodium, calcium, magnesium, iron and copper. The most abundant fatty acid in seed oil from MTCRF was palmitic acid ($37.26 \pm 0.05\%$) followed by oleic

(32.40 ± 0.02%) and linoleic (C18:2 ω 6, 24.65 ± 0.09%) acids, with smaller amounts of stearic (5.55 ± 0.04%), linolenic (C18:3 ω 3, 0.55 ± 0.02%), palmitoleic (0.41 ± 0.01%), myristic (0.17 ± 0.01%) and lauric (trace) acids (Table 6). However, the main fatty acids of the seed oil from MTCUF were palmitic (36.20 ± 0.02%), linoleic (31.67 ± 0.01%), oleic (27.97 ± 0.08%) acids. Negligible amounts of stearic (4.02 ± 0.05%), linolenic (0.50 ± 0.01%), myristic (trace), lauric (trace) acids were obtained. Comparing the fatty acid compositions of the seed oils from MTCUF and MTCRF with the seed oils of TCF from different varieties and locations, it could be observed that 4 and 8 fatty acids had been earlier reported in the seed oils of the TCF grown in other geographical regions (Kimbonguila *et al.*, 2010, Ajayi *et al.*, 2008, dos Santos *et al.*, 2008), while 7 and 8 fatty acids were identified in the MTCUF and MTCRF seed oils, respectively. In addition, a wide variation had been observed in the quantitative composition of the fatty acids in seed oils from TCF of different varieties and locations. The seed oil of TCF from Nigeria contained fatty acids with long-chain like 11,14,17-eicosatrienoic acid (C20:3), eicosadienoic acid (C20:2), 11-eicosenoic acid (C20:1), eicosanoic acid (C20:0) (Ajayi *et al.*, 2008). The consumption of diets containing high levels of polyunsaturated fatty acids has been reported to be immensely correlated to mortality from certain systematic diseases (Thompson *et al.*, 1993). In this work, relative saturated fatty acid contents were higher in the seed oil of MTCRF (42.98 ± 0.42%) than in the seed oil of the MTCUF (40.22 ± 0.05%), and vice versa for relative total polyunsaturated fatty acid contents. When TCF seed and soybean oils (15%, Campbell, 1999) are compared, one can observe that the former presents a higher grade of saturation. It is important also to remark that polyunsaturated fatty acid contents of TCF seed oils were lower than that obtained with soybean (61%, Campbell, 1999) oil, but higher than that of palm oil (10%, Campbell, 1999). The fatty acid compositions of the TCF seed oils examined in this study (Table 5) revealed that oleic (32.40 ± 0.02 and 27.97 ± 0.08 %) and linoleic (24.65 ± 0.09 and 31.67 ± 0.01%)

acids were the predominant unsaturated fatty acids. This particular finding is encouraging because it is a desirable feature in human food (Vijayakumari *et al.*, 1997). The ratio of linoleic acid to oleic acid was 76% in seed oil of the MTCRF and 113% in the seed oil of the MTCUF. These values were lower than those reported in oils of soybean (C18:2 = 52%, C18:1 = 25%), corn (C18:2 = 58.7%, C18:1 = 26.6%) (Ramadan and Mörsel, 2002) and TCF seed originated to Congo (C18:2 = 29.40%, C18:1 = 31.65%) (Kimbonguila *et al.*, 2010). The ratio of saturated to unsaturated fatty acids was 74% in the seed oil of the MTCRF and 66% in the seed oil of the MTCUF. These ratios were lower than those reported by Campbell (1999) for palm oil (85%), but were higher when compared to those of soybean oil (17%, Campbell, 1999) and black cumin seed oil (25.7%, Ramadan and Mörsel (2003). Ajayi *et al.* (2008) and dos Santos *et al.* (2008) reported that the ratios of linoleic acid to oleic acid were 78% and 66% in TCF seed oil originated to Nigeria and Brazil respectively. The source of this variability may be genetic (plant cultivar and variety grown), seed quality (maturity, harvesting-caused damage and handling/storage conditions), oil processing variables, or accuracy of detection, lipid extraction method and quantitative techniques (Ramadan and Mörsel, 2002). Recent studies have demonstrated that monounsaturated fatty acids are better contributors to plasma cholesterol lowering effects than saturated fatty acids. The high linoleic acid content of the seed oils, is significant since linoleic acid is undoubtedly one of the most important polyunsaturated fatty acids in human food due to its prevention of distinct cardiovascular disease. According to Vles and Gottenbos (1989) and Dagne and Johnson (1997), cardiovascular disorders such as coronary heart diseases, atherosclerosis and high blood pressure are prevented by dietary fats rich in linoleic acid.

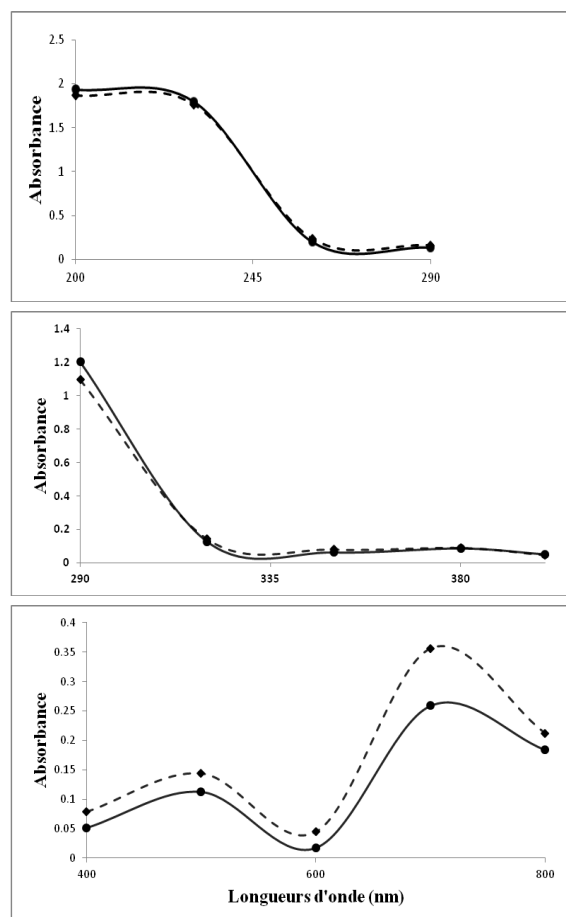


Fig. 1. Ultra violet/visible spectra of seed oils from mature *Terminalia catappa* ripe (●) and unripe (◆) fruits harvested in Côte d'Ivoire

Table 1. Proximate composition of seeds from mature *Terminalia catappa* ripe and unripe fruits harvested in Côte d'Ivoire.

Proximate composition	Values of seed proximate composition from	
	ripe fruits	unripe fruits
Moisture (%)	4.80 ± 0.34 ^b	5.10 ± 0.75 ^a
Crude protein (%)	29.89 ± 0.41 ^a	29.77 ± 1.12 ^a
Crude fat (%)	63.65 ± 0.04 ^b	58.61 ± 0.13 ^a
Total sugars (%)	3.53 ± 0.10 ^b	3.02 ± 0.05 ^a
Reducing sugars (%)	0.06 ± 0.01 ^a	0.08 ± 0.01 ^a
Total carbohydrate (%)	5.09 ± 0.12 ^b	5.38 ± 0.02 ^a
Total ash (%)	4.60 ± 0.14 ^b	5.10 ± 0.20 ^a
Caloric value (kcal/100 g)	567.75 ± 0.84 ^a	573.79 ± 1.02 ^b

Averages of three replicates (n = 3). Superscripts with different letters within the column show significant differences at $\alpha = 0.05$; using Duncan's multiple range test.

Table 2. Mineral composition of seeds from mature *Terminalia catappa* ripe and unripe fruits harvested in Côte d'Ivoire.

Mineral composition	Values of seed mineral composition from	
	ripe fruits	unripe fruits
Calcium (mg/100g dry weight)	587.72 ± 2.56 ^b	380.70 ± 1.22 ^a
Phosphorus (mg/100g dry weight)	2128.03 ± 1.80 ^b	2048.50 ± 2.37 ^a
Magnesium (mg/100g dry weight)	19.73 ± 1.43 ^b	21.02 ± 0.12 ^a
Sodium (mg/100g dry weight)	66.40 ± 0.85 ^b	61.40 ± 0.99 ^a
Potassium (mg/100g dry weight)	3068.96 ± 1.70 ^b	4116.30 ± 0.85 ^a
Iron (mg/100g dry weight)	5.32 ± 0.03 ^b	5.65 ± 0.07 ^a
Manganese (mg/100g dry weight)	2.60 ± 0.19 ^b	4.66 ± 0.91 ^a
Zinc (mg/100g dry weight)	0.77 ± 0.09 ^b	0.62 ± 0.04 ^a
Cooper (mg/100g dry weight)	1.75 ± 0.03 ^b	1.43 ± 0.35 ^a
K/Na	46.21	67.04
Ca/P	0.27	0.18

Averages of three replicates (n = 3). Superscripts with different letters within the column show significant differences at $\alpha = 0.05$; using Duncan's multiple range test.

Table 3. Colour parameters L* (brightness), a* (redness) and b* (yellowness) of seed oils from mature *Terminalia catappa* ripe and unripe fruits harvested in Côte d'Ivoire.

Colour parameters	Values of seed crude oils from	
	ripe fruits	unripe fruits
L*	81.05 ± 0.02 ^b	78.92 ± 0.02 ^a
b*	+ 18.14 ± 0.02 ^b	+ 20.07 ± 0.02 ^a
a*	-3.96 ± 0.04 ^b	+ 0.06 ± 0.04 ^a

Averages of three replicates (n = 3). Superscripts with different letters within the column show significant differences at $\alpha = 0.05$; using Duncan's multiple range test.

Table 4. Physicochemical characteristics of seed oils from mature *Terminalia catappa* ripe and unripe fruits harvested in Côte d'Ivoire.

Physicochemical parameters	Values of seed crude oils from	
	ripe fruits	unripe fruits
Physical state at room temperature (25°C)	liquid	liquid
Colour	Pale yellow	Golden/yellow
Odour	Pleasant	Pleasant
Refractive index (25°C)	1.45 ± 0.03 ^a	1.45 ± 0.05 ^a
Viscosity (mPas.s)	20 ± 0.32 ^a	20 ± 0.21 ^a
Acid value (% as oleic acid)	0.38 ± 0.08 ^a	0.31 ± 0.09 ^b
Peroxide value (mEq O ₂ /kg of oil)	< 0.02 ^a	< 0.02 ^a
Saponification value (mg KOH/g of oil)	188.40 ± 1.87 ^b	185.44 ± 0.62 ^a
Iodine value (g/100 g of oil)	70.41 ± 0.16 ^a	70.88 ± 0.21 ^a

Averages of three replicates (n = 3). Superscripts with different letters within the column show significant differences at $\alpha = 0.05$; using Duncan's multiple range test.

Table 5. Mineral composition of seed oils from mature *Terminalia catappa* ripe and unripe fruits harvested in Côte d'Ivoire.

Mineral composition	Values of oil mineral composition from	
	ripe fruit seed	unripe fruit seed
Calcium (mg/100g dry weight)	3.26 ± 0.02 ^b	2.87 ± 0.02 ^a
Phosphorus (mg/100g dry weight)	8.40 ± 0.03 ^b	8.62 ± 0.01 ^a
Magnesium (mg/100g dry weight)	1.66 ± 0.03 ^a	1.61 ± 0.02 ^a
Sodium (mg/100g dry weight)	3.59 ± 0.03 ^a	3.59 ± 0.03 ^a
Potassium (mg/100g dry weight)	17.92 ± 0.04 ^b	16.73 ± 0.02 ^a
Iron (mg/100g dry weight)	0.29 ± 0.03 ^a	0.34 ± 0.02 ^a
Zinc (mg/100g dry weight)	0	0
Cooper (mg/100g dry weight)	0.10 ± 0.01 ^a	0.09 ± 0.01 ^a

Averages of three replicates (n = 3). Superscripts with different letters within the column show

significant differences at $\alpha = 0.05$; using Duncan's multiple range test.

Table 6. Fatty acid composition of seed oils from mature *Terminalia catappa* ripe and unripe fruits harvested in Côte d'Ivoire.

Physicochemical parameters	Values (%) of seed crude oils from	
	ripe fruits	unripe fruits
Lauric acid (C12:0)	Trace ^a	Trace ^a
Myristic acid (C14:0)	0.17 ± 0.01 ^b	Trace ^a
Palmitic acid (C16:0)	37.26 ± 0.05 ^b	36.20 ± 0.02 ^a
Palmitoleic acid (C16:1n7)	0.41 ± 0.01 ^b	00 ^a
Stearic acid (C18:0)	5.55 ± 0.04 ^b	4.02 ± 0.05 ^a
Oleic acid (C18:1n9)	32.40 ± 0.02 ^b	27.97 ± 0.08 ^a
Linoleic acid (C18:2n6)	24.65 ± 0.09 ^b	31.67 ± 0.01 ^a
Linolenic acid (C18:3n3)	0.55 ± 0.02 ^a	0.50 ± 0.01 ^a
Saturated fatty acids	42.98 ± 0.42 ^b	40.22 ± 0.05 ^a
Monounsaturated fatty acids	32.81 ± 0.02 ^b	27.97 ± 0.08 ^a
Polyunsaturated fatty acids	25.20 ± 0.02 ^b	32.17 ± 0.01 ^a

Averages of three replicates (n = 3). Superscripts with different letters within the column show significant differences at $\alpha = 0.05$; using Duncan's multiple range test. Tr., trace amounts (less than 0.15%).

Conclusion

The ripening of MTCF led to a significant ($P < 0.05$) reduction in the moisture, total carbohydrate and total ash levels, whereas the total sugar and crude fat contents increased significantly ($p < 0.05$). The crude protein and reducing sugars contents were not affected by this physiological parameter. The seeds from Ivorian MTCF are a cheap source of edible oil, protein and mineral elements having nutritional importance. Within these seeds, the

potassium concentration was the highest, followed by phosphorus and calcium. In the seed oil, the ripening had caused an increase in the bright and a decrease in the red and yellow units of colour. There was significant difference ($p < 0.05$) between seed oils from MTCUF and MTCRF in terms of their saponification and acid values. There was no statistically significant ($P < 0.05$) difference in the viscosity, refractive index, peroxide and iodine values of seed oils from MTCRF and MTCUF. The major saturated fatty acid was palmitic acid, while the main unsaturated fatty acid was oleic acid for the MTCRF and linoleic acid for the MTCUF seed oils. These seed oils showed some absorbance in the UV-B and UV-C ranges with potential use as a broad spectrum UV protectant. The seed of MTCF harvested in Côte d'Ivoire has its unique characteristics, indicating that such variation in nutrient concentrations among varieties of seeds from TCF may be related to the variations of cultivated regions, storage conditions and maturity stage. It may also be due to geographical and climatic differences where TC had been grown. MTCUF and MTCRF seeds and seed oils originated from Côte d'Ivoire were a good quality and could be used in cosmetic, pharmaceutical and food products.

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