Chemical Properties, Fatty Acid Composition, and Lipid Profiles of Picung (*Pangium edule* Reinw) Kernel Oil from Riau Province

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Abstract: A study on chemical properties, fatty acid composition, and lipid profiles of picung kernel oil (PKO) from Riau Province compared to palm olein (PO) and coconut oil (CO) was conducted. The chemical properties of PKO were examined by established methods, while fatty acids composition and lipid profiling were observed by GC-FID and FTIR. Picung kernel oil contains water, $30.26\pm0.06\%$; protein, $8.37\pm0.05\%$; fat, $8.91\pm0.08\%$; crude fiber, $36.88\pm0.08\%$; and carbohydrate, $14.50\pm0.10\%$. Acid, saponification, iodine, and peroxide values of PKO were 16.64; 126.44; 111.49; 8.53, respectively. Linoleic and oleic acids were the major fatty acids in PKO accounting $40.79\pm0.76\%$ and $38.31\pm1.28\%$, respectively. PKO has major unsaturated and saturated fatty acids similar to PO, especially olein, linoleic, palmitic, and stearic acids. FTIR spectra showed PKO resembled PO rather than CO. Meanwhile, CO didn't showed spectra at region at 3005.4/cm, 1655/cm, 1116 and 1097/cm, which were shown in PKO and PO.

1. Introduction

A large quantity of oils and fats, either for human consumption or industrial purposes, are presently derived from plant sources. In order to meet the increasing demand for oil, improvements are being made, with conventional crop, as well as with selected plant species, that have ability to produce unique and desirable oils. Plant seeds are important sources of oils in term of nutritional, industrial, and pharmaceutical perspectives. On the other hand, no oil from single sources has been found to be suitable for all purposes because oils from different sources generally differ in their composition. This necessitates the search for new sources of novel oils. Several plants are now grown, not only for food and fodder, but also for striking variety products with application in industry, including oils and pharmaceuticals.

Picung (*Pangium edule* Reinw), a member of Silacaceae family, is a tropical tree that grows in Malesia, Melanesia and Micronesia. The tree is wild and cultivated in Malaysia, Indonesia, Papua New Guinea, and Vanuatu. All parts of the plant are poisonous due to presence of cyanogenic glycoside, but the seed kernels are consumed after extensive processing to remove the toxic substance [1]. In Indonesia, seed kernels are known as vegetables and herbs after some treatments, also used as spices after 40 days fermentation in the ground. In Tanjung Belit Selatan Village (Riau Province, Indonesia), picung kernel oil (PKO) has been used as edible oil that can be stored for long time. PKO also has been used as ingredient of medicine and fuel. Some plant's root herbs which are poured in PKO and made into lotion or massage oil to cure rheumatic. Recently, research on physical and chemical properties of PKO methyl ester indicated that the oil can be considered as a future biodiesel source [2].

Chemical properties is very important to understand the usability of PKO in a wide range of edible or non-edible purposes. PKO is rich in saturated and unsaturated fatty acids, the major fatty acid are oleic and linoleic acid [3,4]. During picung seed germination, lipid content decreased, whereas the major fatty acids did not change significantly [3]. Phenolic and alkaloid extracts of picung seeds had antioxidant and

antibacterial activities [5,6], while picung leaf extract showed antifungal activitiy againt *Colletotrichum gleooporoides* [7]. Some biochemical changes during picung seed germination associated with antioxidant activity and the mobilization of lipids and phenolics [8].

   Literature of PKO are very limited and there are no reports about lipid profiles of PKO. The objective of this research was to study the chemical nature of PKO compared to palm olein (PO) and coconut oil (CO), as a basis for further chemical and nutrition investigation. The result can be used as indication of nutraceutical and economic potential of picung seeds as a new source of edible or non-edible oil.

2. Materials and Methodology
2.1.   Materials
   Fully ripened fruits from wildly grown picung plants were randomly collected from several plants grown in Tanjung Belit Selatan Village, Riau Province, Indonesia during December 2009. The hard seed coat was removed and kernels were washed in tap water and dried at room temperature. Picung kernel oil (PKO) was extracted by mechanical pressing the kernels at 500 kg/cm^2, after water soaking for 24 h and smoking for 24 h at 45°C. All chemicals used were analytical grade and purchased from J.T. Baker (Phillipsburg, NJ, USA).

2.2.   Method
Proximate Analysis
   Moisture, crude protein, crude oil, fiber, and ash content of picung seeds were determined using Ba 2a-38, Ba 4a-38, Ba 3-38, Ba 6-84 and Ba 54-49 methods, respectively [9]. Total carbohydrate was determined by difference. All determination were done in triplicate.

Chemical Analysis of Oil
   Iodine (Cd 1-25), saponification (Cd 3-25), peroxide (Cd 8b-90), and free fatty acid (Ca 5a-40) values of oils were determined according to AOCS methods [9].

Fatty Acid Composition
   Fatty acid composition was determined by converting the oil into fatty acid methyl esters (FAME). The FAME was prepared by adding 800 μl of hexane and 200 μl of sodium methoxide 30% (v/v) in methanol into 50 mg of oil. The mixture was vortexed for 5 sec and allowed to settled for 5 min. The top layer (1 μl) was injected into a gas chromatograph (Hewlett-Packard Model 5890, Palo Alto, CA, USA), equipped with a flame ionization detector (FID) and a Hewlett-Packard Model 3392A integrator. A polar capillary column BPX70 (0.32 mm internal diameter, 30 m length and 0.25 µm film thickness; SGE International Pty. Ltd., Victoria, Australia) was used at a column head pressure of 10 psi. Helium (99.995%) at approximately 23 ml/min (measured at oven temperature 150°C) was used as the carrier gas, and nitrogen (99.999%) at 20 ml/min was used as the made up gas. The FID and injector temperature were both maintained at 220°C. The initial column oven temperature was 115°C, temperature programmed to 180°C at 8°C/min and held at this temperature until the analysis was completed. FAME peaks were identified by comparing retention times to a Supelco 37 component FAME mix (Sigma-Aldrich, St. Louis, US) and quantified by the peak areas.

Lipid Profiling by FTIR
   FTIR spectrometer (Nicolet 6,700 fro, Thermo Nicolet Corp., Madison, WI) was equipped with deuterated triglycine sulfate as a detector and a KBr/Germanium as beam splitter, interfaced to a computer operating under Window-based, and connected to a software of the OMNIC operating system (Version 7.0 Thermo Nicolet Corp.). The instrument was maintained with automatic dehumidifier to diminish water vapor interference. A few drop of each sample were positioned in contact with attenuated total reflectance (ATR) on a multibounce crystal plate at a controlled ambient temperature (25°C). All FTIR spectra were recorded from 4,000 to 650 cm^{-1}, co-adding 32 interferograms at a resolution of 4/cm with strong apodization. These spectra were substracted against background air spectrum. After every scan, a new reference air background spectrum was taken. The ATR plate was carefully cleaned *in situ* by scrubbing with hexane twice and acetone, and dried with soft tissue before filling in with the next sample. Clean

lines was verified by collecting a background spectrum and comparing it to previous data. These spectra were recorded as absorbance value at each data point in triplicate [10].

3. Results and Discussion

3.1. Proximate Analysis of Picung Seed Kernels

Proximate analysis of picung seed kernels per 100 g (wet basis) is shown in Table 1. Picung seed kernels from Riau Province had water, lipid, and ash contents which were lower; while protein, crude fiber, and carbohydrate contents were higher than that of picung seed kernels from Sarawak, Malaysia [11] Picung seed kernels from Riau Province were collected from fruits which fell from the tree and probably oxidation process already happened before the fruits were collected. However, this study did not investigate the effect of oxidation process on picung seed kernels.

Picung seed kernels were relatively high as a source of oil with lipid content 8.91% (wb) or 20.53% (db). According to Andarwulan *et al,* [3], during seeds germination, the crude fat content of picung seeds decreased from 46.00 to 18.50% (db). In fact, for a plant to be suitable for oil production, it must meet the following two criteria : (i) the oil content must reach minimum for commercially viable exploitation, and (ii) the plant must be suitable for high acreage cultivation. The only exceptions are plant which contains unique lipids in their composition or with properties that can not be found elsewhere [12].

Table 1. Proximate Analysis Fresh Picung Kernel Seeds[a]

Component	Persen (wet basis)
Water	30.26 ± 0.06
Protein	8.37 ± 0.05
Lipid	8.91 ± 0.08
Ash	1.08 ± 0.00
Crude fiber	$36.88 + 0.08\%$
Carbohydrate[b]	$14.50 \pm 0.10\%$

[a] Mean $\pm$ standard deviation
[b] Carbohydrate obtained by difference

3.2 Chemical Analysis

Chemical analysis data of PKO are presented in Table 2. The peroxides value of a vegetable oil reflects its oxidative level and thus its tendency to become rancid. Peroxide value in PKO was 8.53 meq of O_2/kg of oil. According to Codex Standard [13], the maximum peroxide value for edible fats and oils is 10 meq of O_2/kg of oil, this means that the PKO still suitable to be used as edible oil. However, when picung kernel oil compared to PO or CO, the peroxide value was higher than PO or CO. The high content of unsaturated fatty acid, especially linoleic acid (C18:2) and oleic acid (C18:1) in PKO was the reason of peroxide value become high. Unsaturated fatty acids easily react with oxygen to form peroxides. Oil with high peroxide value are unstable and easily become rancid.

Iodine value is a measure of the degree of unsaturation of fats and oils. The iodine value of PKO was 111.49, higher than PO or CO which were 51-65 and 7.5–10.5, respectively [14]. The high of iodine value indicated that PKO has high degree of unsaturation. In this research, we found that ratio of unsaturated:saturated fatty acid in PKO was 79.76:20.24, PO and CO was 53.9:46.03 and 9.45:90.55, respectively.

Table 2. Chemical properties of picung kernel, palm, and coconut oil

Chemical properties	Picung kernel oil	Palm oil	Coconut oil
Peroxide value (meq of O_2/kg of oil)	8.53	max 10 [13]	max 10 [13]
Iodine value (g of I_2/100 g of oil)	111.49	51-65 [14]	7.5-10.5 [14]
Saponification value (mg of KOH/g of oil)	126.44	194-202 [13,14]	248-265 [13], 248-264 [14]
Acid value (mg of KOH/g of oil)	16.64	max 0.6 [13]	max 0.6 [13]

Saponification value is a measure of the average molecular weight of all the fatty acids present. The higher saponification value, the shorter the fatty acids on the glycerol backbond. As compared to PO and CO, PKO oil has low saponification value, which indicated that picung kernel oil contains a low amount of short chain fatty acids. According to Codex standard [13], specification for saponification value of edible

CO should be 248-265 mgKOH/g oil, and PO 194-202 mgKOH/g oil. The lower amount of short chain of fatty acid, the better quality of the oil producing soap and detergents. It was also stated that for soap making, the required percentage of free fatty acid values should be between 2-5%.

Free fatty acid are responsible for undesirable flavor and aromas in fats and oil. Free fatty acids are formed by hydrolytic rancidity, due to hydrolysis of an ester by lipase or moisture [15]. According Codex standard [13], the maximum acid value for refined oils was 0.6 mg KOH/g oil, PKO has acid value higher than standard. High presence of unsaturated fatty acid in PKO makes this oil easily oxidize by lipase or moisture. However, acid value analysis were done on crude PKO, which has not been purify. The relatively high acid value for oil makes the oil undesirable for nutritional application.

3.3 Fatty acid composition

Table 3. showed fatty acid compositions of PKO, PO and CO. Generally, PKO is rich in saturated and unsaturated fatty acid, same as PO and CO with difference ratio. Ratio of unsaturated:saturated fatty acid in PKO was 79.76:20.24, PO and CO was 53.97:46.03 and 9.45:90.55, respectively. Same as Andarwulan *et al,* [3] and Puspitasari-Nienaber [4], linoleic (C18:2) and oleic acids (C18:1) were the most dominant unsaturated fatty acids in PKO which was 40.79% and 38.31, respectively. PKO had the highest content of linoleic acid compared to PO and CO. In comparison to another seed oil, linoleic acid in PKO was lower than soybean, sunflower, sesame, safflower, poppy, and walnut seed, but higher than peanut, rapeseed, and linseed oil [16].

The presence of high amount of linoleic acid suggest that PKO could be used as a good source of essential fatty acid. The high percentage of oleic, make it suitable for use as edible cooking oil, similar to PO and desirable in terms of nutrition and high stability cooking and frying oil. The relatively high degree of unsaturated fatty acids allows PKO to be oxidize easily when used to deep-fat frying [17]. Therefore, edible oil industry has focused attention on high oleic vegetable oils.

The major saturated fatty acids in PKO were stearic acid, 12.91% and palmitic acid, 7.04%, relatively resemble PO rather than CO. Thus, the characteristic of saturated fatty acids seems to explained that the fat's suitability for formulation of margarine and cocoa butter substitutes, also in some cosmetic and pharmaceutical preparations. Besides, the higher content of stearic acid maybe an advantage to the paint industry and coating formulation.

Table 3. Fatty acids composition of picung kernel, palm, and coconut oil[a]

Fatty acids	Trivial name	Picung kernel oil	Palm olein	Coconut oil
C12:0	Lauric	0.01 ± 0.01	0.26 ± 0.02	46.22 ± 0.10
C14:0	Myristic	0.06 ± 0.01	1.01 ± 0.01	18.40 ± 0.03
C14:1	Myristoleic	0.01 ± 0.01	0.03 ± 0.00	0.01 ± 0.01
C16:0	Palmitic	7.04 ± 0.39	39.29 ± 0.17	9.56 ± 0.02
C16:1	Palmitoleic	0.06 ± 0.04	0.05 ± 0.04	0.02 ± 0.00
C18:0	Stearic	12.91 ± 2.14	5.23 ± 3.93	3.04 ± 0.02
C18:1	Oleic	38.31 ± 1.28	42.47 ± 3.92	9.26 ± 0.08
C18:2	Linoleic	40.79 ± 0.76	10.85 ± 0.08	0.03 ± 0.07
C18:3	Linolenic	0.31 ± 0.01	0.38 ± 0.00	0.03 ± 0.03
C20:0	Arachidic	0.12 ± 0.07	0.14 ± 0.00	0.06 ± 0.05
C22:1	Erucic	0.03 ± 0.02	0.06 ± 0.00	0.01 ± 0.01
C24:0	Lignoceric	0.05 ± 0.04	0.08 ± 0.00	0.04 ± 0.00

[a]Mean ± standard deviation

3.4 Lipid profilling

Fourier transform infrared (FTIR) spectroscopy is an excellent tool for quantitative analysis, as the intensities of the bands in the spectrum are proportional to the concentration of the corresponding samples according to Beer's Law [18]. The spectra of PKO, PO, and CO are shown in Figure 1. These spectra look very similar and showed a typical characteristic of absorption bands for common triacylglycerol [19]. The assignment of prominent peaks are compiled in Table 4.
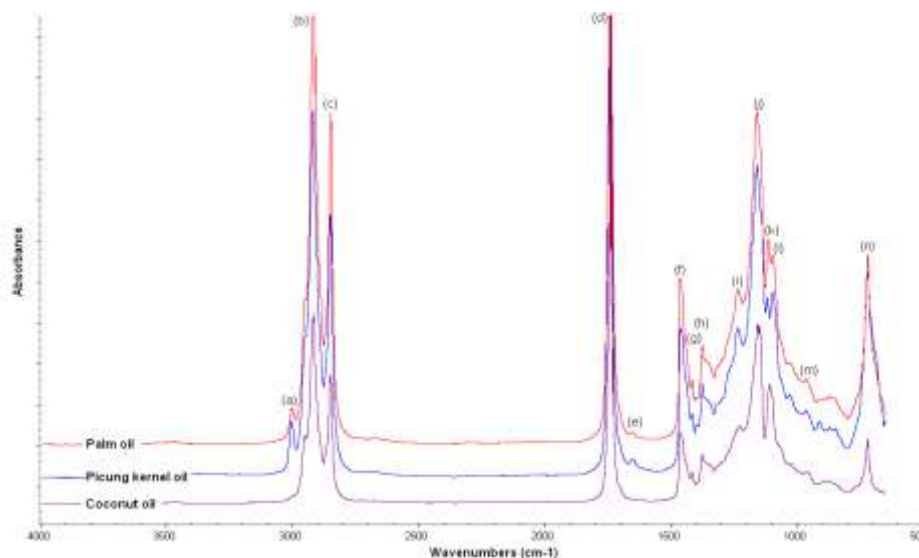
Figure 1. FTIR spectra of picung kernel, palm, and coconut oil

Upon a closer scrutiny, PKO is resemble PO rather than CO. PKO has major unsaturated and saturated fatty acids which are the same with PO, especially oleic (C18:1), linoleic (C18:2), palmitic (C16:0), and stearic acids (C18:0), as determined using gas chromatography (Table 3.). Differences between PKO and PO to CO are observed at several different spectra. CO didn't show spectrals at region at 3005.4/cm (a) which is due to the cis C=CH stretching, at 1655/cm (e) caused by cis C=C, and at 1116 and 1097/cm (k and l) corresponding to CH bending vibration and CH deformation vibration on fatty acids. This result is similar to Rohman and Che Man [10], differences spectra between palm and virgin coconut oil. PKO and PO contain more unsaturated fatty acids than CO, especially linoleic (C18:2) and oleic acid (C18:1). The presence of unsaturated fatty acid was observed in its FTIR spectrum at 3005.4/cm, which is absent in CO spectrum.

Table 4. Functional groups and modes of vibration in picung kernel, palm, and coconut oil spectra

Assigment	Frequency (/cm)	Functional group vibration
(a)	3005	*cis* C=CH stretching
(b)	2952	Asymmetric stretching vibration of methyl (-CH$_3$) group
(c)	2852	Asymmectric or symmetric stretching vibration of methylene (-CH$_2$) band
(d)	1747	Carbonyl (C=O) functional group from the ester linkage of triacylglycerol
(e)	1655	*Cis* C=C
(f)	1465	Bending vibrations of CH$_2$ group
(g)	1418	Rocking vibrations of CH bond of cis-disubsituted alkenes
(h)	1377	Symmetric bending vibrations of CH$_3$ groups
(i)	1236	Vibrations of stretching mode from the C-O group in esters
(j)	1160	Vibrations of stretching mode from the C-O group in esters
(k) and (l)	1116 and 1097	-CH bending and –CH deformation vibrations of fatty acids
(m)	962	Bending vibration of CH functional group of isolated trans-olefin
(n)	722	Overlapping of the methylene (-CH2) rocking vibration and to the out of plane vibration of cis-disubstituted olefins

Source : [10,18,20]

4. Conclusion

Crude PKO has chemical properties such as acid value 16.64, saponification value 126.44, iodine value 111.49, and peroxide value 8.539. This study showed that fatty acid composition of PKO is rich in oleic and linoleic acid, and the oil can be classified as unsaturated oil. The presence of high amount of linoleic acid suggest that these oil could be used as a good source of essential fatty acid. The high percentage of oleic, refined PKO might be used as edible cooking oil. Thus, the characteristic of saturated fatty acids

seems to explain the fat's suitability to the formulation of margarine and cocoa butter. FTIR spectra also showed that PKO resembled PO rather than CO.

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