Essential quality parameters of commercial virgin coconut oil

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Abstract

Chemical analysis conducted on commercial samples of virgin coconut oil (VCO) produced by four different methods gave the following ranges of values. % Fatty acid composition :- C6 : 0.24 to 0.49%; C8 : 4.15 to 8.30%; C10 : 4.27 to 5.75%; C12: 46.0 to 52.6%; C14: 16.0 to 19.7%; C16: 7.65 to 10.1%; C18: 2.86 to 4:63%; C18:1: 5.93 to 8.53%, C18:2: 1.00 to 2.16%; % moisture by Karl Fischer and % matter volatile at 120°C can be used to differentiate VCO from and refined, bleached and deodorized coconut oil (RBD CNO). No trans-fatty acid was detected in both VCO and RBD CNO down to 0.01% (w/w) detection limit.

Becasue of the increasing commercial importance of VCO, it is imperative to develop quality criteria which can differentiate VCO from RBD CNO. Currently, there are two standards which are used : the Codex standard for coconut oil and the APCC standard for virgin coconut oil. The Philippines has promulgated a provisional set of standards designated PNS/BAFPS 22:2004.

Introduction

'Virgin oils' are defined by Codex Alimentarius (2006) and APCC (2006) as vegetable oils which undergo minimal processing in order to preserve the original components of the oil. In particular, both Codex and APCC specify that virgin oils should be prepared 'without altering the nature of the oil by mechanical or natural means with or without the application of heat. They may have been purified by washing with water, settling, filtering and centrifuging only.' However, there is a need for a standard that enables differentiation of VCO from refined, bleached and deodorized coconut oil (RBD CNO).

Dia and co-workers (2005) conducted a comparative physicochemical study on VCO using three methods (desiccated coconut meat with incubation, coconut milk with incubation, and coconut milk-freeze-and-thaw) and three types of coconut meat (two varieties and one hybrid), together with six commercial VCO products and one commercial RBD CNO product. They found that all of the VCO samples were within the Codex standards for coconut oil, and that although differences in chemical and quality properties were noted, these were not large enough to affect their overall quality.

Becasue of the increasing commercial importance of VCO, it is imperative to develop quality criteria which can differentiate VCO from RBD CNO. Currently, there are two standards which are used : the Codex standard for coconut oil and the APCC standard for virgin coconut oil (Table 2). The Philippines has promulgated a provisional set of standards designated PNS/BAFPS 22:2004.

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Table 1. Quality parameters from existing standards: Codex Alimentarius for coconut oil and APCC for virgin coconut oil

Parameters	Codex Alimentarius	APCC
% Fatty acid composition	ND - 0.7	0.4 - 0.6
C6:0	4.6 - 10.0	5.0 - 10.0
C10:0	5.0 - 8.0	4.5 - 8.0
C12:0	45.1 - 53.2	43.0 - 53.0
C14.0	16.8 - 21.0	16.0 - 21.0
C16:0	7.5 - 10.2	7.5 - 10.0
C18:0	2.0 - 4.0	2.0 - 4.0
C18:1	5.0-10.0	5.0-10.0
C18:2	1.0-2.5	1.0-10.0
C18:3	ND-0.2	<0.5
C20:0	ND-0.2	
C20:1	ND-0.2	
C20:2 - C24:1	ND	
Iodine valuc	6.3-10.6	4.1-11.00
Free fatty acid	None	≤0.4%
Moisture, % weight, max	-	01.-0.5
Matter volatile at 105 °C, m/m	0.2%	0.2%
Peroxide value	<15 meq active oxygen/kg oil	< 3 meq/kg oil
Microbiological contamination	-	<10 cfu

Objectives

This work sought to study methods that can differentiate between RBD CNO and VCO. In order to attain this objective, the standard methods from Codex Alimentarius were reassessed using appropriate reference compounds and internal standards, spikes and % recoveries, % fatty acid profile, % moisture by gravimetric method and by Karl Fischer method, iodine value, % free fatty acid (as lauric acid), peroxide value, and microbial contamination (by colony forming units, CFU). Determination of *tans*-fatty acids was also carried out by GC analysis (IFST 2005. US FDA 2007).

Methodology

A) Coconut oil samples

Samples of virgin coconut oil were provided by members of the Virgin Coconut Oil Producers and Marketers Association. Inc. (VCO Association) or were purchased from commercial outlets. Copra oil samples were supplied by the Philippine Coconut Authority. Samples of RBD coconut oil were purchased from supermarkets and were provided by Spring Oil Co.

Twenty samples were analyzed, commercial VCO (n=13), copra oil (n=3) and RBD edible oil (n=4) . The 13 commercial methyl undecanoate (CIIME 99%) VCO samples are broken down into the following types: expeller process (n=4), enzymatic (n=2), fermentation with heating (n=2), fermentation without heat (n=2), and centrifuge (n=3).

B) Determination of % Fatty Acid Composition and trans-Fatty Acids in Coconut Oil by Gas Chromatography

The fatty acid and fatty acid methyl ester standards used in this analysis were obtained from Sigma-Aldrich: octanoic acid (C8, 99 + %), methyl octanoate (C8ME, 99%). undecanoic acid (C11, 99%), lauric acid (C12, 98%), methyl laurate (C12ME, 99.5%), stearic acid (C18,

Table 2. % FA and trans-FA using internal standard and molecular weight correction, and comparison with Codex Alimentarius and APCC standards

	Fatty acid, %								
	C6:0	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1c9	C18:2c9,12
Standard									
Codex Alimentarius	ND ~ 0.7	4.6 ~ 10.0	5.0 ~ 8.0	45.1 ~ 53.2	16.8 ~ 21.0	7.5 ~ 10.2	2.0 ~ 4.0	5.0 ~ 10.0	1.0 ~ 2.5
APCC	0.4 ~ 0.6	5.0 ~ 10.0	4.5 ~ 8.0	43.0 ~ 53.0	16.0 ~ 21.0	7.5 ~ 10.0	2.0 ~ 4.0	5.0 ~ 10.0	1.0 ~ 2.5
Samples									
All CNO samples									
Average	0.35	6.70	4.97	48.82	18.06	8.66	3.40	7.27	1.77
Range	0.23 ~ 0.49	4.15 ~ 8.30	4.17 ~ 5.75	46.0 ~ 52.6	16.0 ~ 19.7	7.65 ~ 10.1	2.86 ~ 4.63	5.93 ~ 8.53	1.00 ~ 2.16
VCO samples only									
Average	0.35	6.89	5.12	48.95	18.06	8.55	3.48	7.09	1.51
Range	0.24 ~ 0.49	4.15 ~ 8.30	4.27 ~ 5.75	46.0 ~ 52.6	16.0 ~ 19.7	7.65 ~ 10.1	2.86 ~ 4.63	5.93 ~ 8.53	1.00 ~ 2.16
RBD samples only									
Average	0.37	6.05	4.75	48.13	18.29	9.15	3.29	7.71	2.28
Range	0.32 ~ 0.43	5.32 ~ 6.82	4.56 ~ 4.90	46.7 ~ 49.4	17.6 ~ 19.6	8.82 ~ 9.73	2.94 ~ 3.69	7.24 ~ 8.04	2.14 ~ 2.36

99%), methyl stearate (C18ME, 99%), oleic acid (C18:1*c*9, 99%), linoleic acid (C18:2*c*9,12, 99+%), and *trans*-13-octadecenoic acid (C18:1*t*13, 99%).

The % fatty acid composition of the coconut oil samples was determined by methylation of fatty acids using the boron trifluoride method to produce the fatty acid methyl esters (FAME), followed by GC analysis (AOAC Official Method 969.33/963.22). One μL of FAME extract was then injected into a Shimadzu GC-14B gas chromatograph equipped with flame ionization detector (FID). Sepearation was done on a DB-1 capillary column (J&W Scientific, polydime thylsiloxane, 60m x 0.25 mm i.d. x 0.25 μm film thickness) with the following oven temperature programme: initial temperature at 60 ^{0}C, hold for 6 minutes; increase to 180 ^{0}C/ at-5^{0}Cmin. hold for 2 min; increase to 210 ^{0}C at 5 ^{0}C/min, and increase to 230 ^{0}C at 1 ^{0}C/min, hold for 5 min. The total run time was 63 min. The injector and detector temperatures were set at 210^{0}C and 230 ^{0}C. respectively.

The GC response factors for C8ME, C12ME, C18:oME, C18:1*c*9ME, C18:2*c*9, 12ME and C18:1*t*13ME versus the C11ME internal standard (IS) were obtained by taking the average response factor from five separate solutions which were prepared within the expected concentration range for each fatty acid. The response factors for the other saturated FAMEs were obtained by extrapolation. The % FAME composition for each sample was converted to %FA composition (w/w) by molecular weight correction. GC analysis of coconut oil samples was done in duplicate.

Confirmation of the identities of the FAME compounds, as well as the presence or absence of *trans*-fatty acids was done by GC-MS using a Hewlett Packard 5890 Series, II gas chromatograph coupled to a Finnigan MAT95 mass spectrometer, using an identical GD capillary column and oven program parameters. MS analysis was carried out by electron ionization at 70 eV. scanning from m/z 35 to 350.

C) Iodine Value

This procedure is based on AOAC Official Method 920-158. The measured % recovery using oleic acid and linoleic acid were 92% and 85%, repspectively. Analysis of samples was done in duplicate.

D) Moisture content by Karl Fischer Titration

This pocedure is based on AOAC Official Method 984.20. The moisture content was determined using a Metrohm 785 DMP Titrino Karl Fischer titrator. This method gave a recovery of 102%. Analysis of samples was done in duplicate.

Table 3. Summary of results of analysis for quality parameters and comparison with Codex and APCC standards (ND : none detected)

	% Moisutere, Karl Fischer	Volatile matter at 120^{0}C, %	% FFA, as Lauric acid (w/w)	Iodine value	Microbial contamination, cfu	Peroxide value, meq/kg oil
Standard						
Codex Alimentarius	-	0.2*	-	6.3 - 10.6	-	15
APCC	-	0.2*	<0.5%	4.1 - 11.0	≤10	≤3
Samples						
All CNO smaples						
Average	0.081	0.399	0.304	7.24		0.74
Range	0.017 ~ 0.144	ND ~ 1.911	0.011 ~ 2.502	5.64 ~ 10.34	< 10 - <250	ND ~ 2.80
VCO samples only						
Average	0.080	0.147	0.134	7.10		0.55
Range	0.049 ~ 0.121	0.124 ~ 0.178	0.042 ~ 0.329	5.64 ~ 10.34	< 10 - <250	ND ~ 1.40
RBD samples only						
Average	0.058	ND	0.029	7.92		0.78
Range	0.017 ~ 0.014	0.0	0.011 ~ 0.074	6.81 ~ 8.91	<10 - <250	0.30 ~ 1.19
Copra oil samples only						
Average	0.114	1.911	1.405	6.94	<250	1.49
Range	0.079 ~ 0.144	1.911	0.645 ~ 2.502	6.61 ~ 7.31	<250	0.72 ~ 2.80

*Codex Alimentarius and APCC specifiy that % matter volatile should be determined at 105^{0}C

E) Moisture content by Gravimetric Analysis

Codex (2006) stipulates a gravimetric procedure using oven drying at 105°C. However, comparision of results from Karl Fishcer determination indicated that a higher temperature may be required for some samples. Therefore, a parallel determination using oven drying was performed at 120°C. Coconut oil matrix spiked with known amounts of water gave an average recovery of 108%. Analysis of samples was done in duplicate.

F) % Free Fatty Acids as Lauric Acid

This procedure is based on AOAC Official Method 940.28. Recovery of the method was 83%, which corresponds to the difference of one drop of titrant. Analysis of samples was done in duplicate.

G) Peroxide Value

This procedure is based on AOAC official Method 965.33. The minimum detectable amount was 0.1 meq/kg. Analysis was done in duplicate.

H) Microbial Contamination

The determination of microbial contamination was carried out by the Microbiology Section, Natural Science Research Institute, University of the Philippines. Diliman. The colonies appearing per plate were counted and the number of colony-forming units (CFU) per ml.

Results and Discussion

A) % Fatty acid composition

The % fatty acid composition is the most important parameter used to differentiate the various vegetable oils. The GC response factor for each FAME standard was obtained versus the IS at the expected composition level. For example, the response factor for C12ME was determined by averaging the response factors of 5 solutions within the range 40 to 60% while the response factor for methyl stearate was determined within the range 0 to 5%. The response factors for the various FAME standards were plotted versus carbon number. From the plot, the response factors for the other saturated FAMEs were obtained.

The % FAME profile for each sample was determined against the IS, and the %FA composition was calcualted by molecular weight correction. The % FA composition of the coconut samples generally fell within the Codex and APCC standards (Table 2). Except for one sample, the key fatty acid of interest - C12 - fell within the standards, along with C14, C18:1*c*9 and C18-2*c*9,12. However, there were slight variances for C6, C8. and C10 FAs.

For the analysis of *trans*-fatty acids, C18 : 1*t*13 was selected as the reference compound. Calibration solutions were prepared down to the 0.01% level. Analysis of the coconut oil samples by GC-MS did not detect the presence of C18:1*t*13 or any other monounsaturated C18 fatty acid, apart from C18:1*c*9. down to the 0.01 % level.

B) Iodine value

The iodine values obtained for

Table 4. Number of milliequivalent double bond / gram of coconut oil from GC and Iodine value

	% FA from Gas Chromatography meq double bond/g				Iodine value method	
Samples	C18:1	C18:2	Total meq double bond/g (exptl.)	Iodine value (theoretical from total meq. double bond)	Iodine value (exptl.)	Meq. double bond/g (calc. from iodine value)
All CNO samples						
Average	0.23	0.11	0.34	8.58	7.24	0.29
Range	0.18 ~ 0.28	0.08 ~ 01.5	0.26 ~ 0.44	6.33 ~ 11.05	5.64 ~ 10.34	0.22 ~ 0.41
VCO samples only						
Average	0.22	0.09	0.32	8.04	7.10	0.28
Range	0.18 ~ 0.27	0.8 ~ 0.13	0.26 ~ 0.34	6.33 ~ 9.97	5.64 ~ 10.34	0.22 ~ 0.41
RBD samples only						
Average	0.24	0.14	0.38	9.59	7.92	0.31
Range	0.22 ~ 0.25	0.13 ~ 0.15	0.35 ~ 0.44	8.99 ~ 10.24	6.81 ~ 8.91	0.27 ~ 0.35
Copra oil samples only						
Average	0.24	0.14	0.38	9.53	6.94	0.27
Range	0.21 ~ 0.28	0.13 ~ 0.15	0.34 ~ 0.44	8.68 ~ 11.05	6.61 ~ 7.31	0.26 ~ 0.29

the various coconut samples in this study ranged from 5.64 to 10.34 (Table 3). Commercial Minola oil gave a higher iodine value of 8.91 because it is fortified with Vitamin A while VCO sample D, gave the highest iodine value at 10.34. Thus, for coconut oil products as a whole, the APCC Standard for iodine value is more appropriate than Codex.

Table 4 compares the resutls of the Iodine value test with the concentration of C18:1 and C18:2 from GC analysis. Since the iodine value is a measure of total double bonds in an oil sample, the iodine value should be comparable with the GC results in the absence of other olefinic compounds. The total milliequivalents of double bonds can be converted into a theoretical Iodine value assuming complete conversion using the conversion: 0.10 milliequivalents of double bond = 2.54 Iodine value.

It should be noted that the % recovery for the iodine value method was determined to be 92% and 85% for oleic acid and linoleic acid, respectively, which indicates that the addition of iodine is incomplete. Thus the iodine value underestimates the number of double bonds present in the fatty acids present.

C) Peroxide value

Codex gives a peroxide value limit of 15 meq/kg for virgin oils in general, while APCC specifies 3 meq/kg oil for VCO. All of the VCO samples in this study were well below the APCC limit giving a range of values from none detected to 1.4 (Table 3). This indicates that VCO is stable to oxidative rancidity and that oxidation is not a signficant cause of degradation.

D) Moisture content

The Codex standard specifies the gravimetric method and stipulates a maximum loss of 0.2% upon heating at 105 ^{0}C. Initial trials with some VCO and copra samples at 105^{0}C gave lower values when compared with Karl Fischer titration (Hahn 2006). The gravimetric method was repeated at 120 ^{0}C, with better results. This suggests that for some samples, heating at 105 ^{0}C may be insufficient to remove all water or volatile organic compounds.

The data from Karl Fischer titration and the gravimetric method at 120^{0}C are summarized in Table 3. By Karl Fischer, the moisture content of the VCO samples ranged from 0.05 to 0.12%. In comparison, the weight loss of VCO samples upon heating to 120^{0}C ranged from 0.124 to 0.178%. All of the VCO samples complied with the Codex and APCC standard for volatile matter.

By difference, the weight loss due to volatile organic compounds in VCO samples can be estimated to range from 0.02 to 0.08%, while in RBD CNO samples, the weight loss due to volatile organic compounds was negligible. This can be used to differentiate VCO from RBD CNO.

E) % Free fatty acids, as Lauric acid

The range of values obtained for VCO was 0.042 to 0.329%, while for RBD CNO samples the FFAs were lower as would be expected (0.011 to 0.074%). All of the copra oil samples exceeded the APCC limit of 0.5% (Table 3). However, based on studies conducted by the Philippine Coconut Authority, a 0.2% FFA limit is suggested (Gonzales 2004).

F) Microbial contamination

The APCC standard is <10 colony forming units. Failure to meet this standard indicates poor product quality, and is a potential health hazard. Three VCO samples and all of the copra oil samples exceeded this limit. The APCC standard is cleraly desirable and attainable.

Conclusions and Recommendations

This paper sought to address the question of whether the VCO products fall within the Codex and APCC standards for coconut oil. It should be pointed out, however, that the Codex and APCC standards are not identical in all respects.

While the % FA composition of all the coconut oil samples analyzed genrally fell with the Codex and APCC standards, some minor variances were noted, which should be addressed in a proposed VCO standard. The % FA composition cannot differentiate VCO from RBD CNO. However, it should be anticiaptd that if coconut varieties with higher lauric acid content are developed, an adjustment of the fatty acid profile may be needed.

The analysis for *trans*-fatty acids by GC using C18:1*t*13 as a reference compound gave a negative result down to a detection level of 0.01%.

In terms of the other analytical parameters which were measured (% volatile matter, % FFA, idoine number and peroxide value), the VCO products were generally within the standards.

For the iodine number, the APCC standard was found to be more appropriate than the Codex standard. However, the iodine value method gives an incomplete determination of fatty acid double bonds by an averge of 15%. GC analysis using an internal standard is suggested as an alternative to the iodine value method with the following values ; oleic acid : 5.9~ 8.6% and linoleic acid : 1.0 ~ 2.4 %.

The inclusion of the Karl Fischer analysis for direct moisture analysis is suggested with the standard to be set at ≤ 0.15% moistre, and a change in the temperature for determining volatile matter of 120 ^{0}C instead of 105 ^{0}C, with an allowable loss of 0.12 - 0.20% w/w which will account for both moisture and volatile organic compounds. Taken together with the volatile matter, this means that the VCO sample should have 0.02 - 0.10% volatile orgnaic compounds, which is characteristic of VCO. RBD CNO gives very low values for this test, while copra oil gives higher values. The use of both methods in combination is the simplest strategy for differentiating VCO from RBD CNO and copra oil.

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