Effect of Heat Treatments on the Volatile Composition of Coconut Oil

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ABSTRACT

Fresh coconut oil was heated under different conditions for 48 hr at 180 C. The heat treatments included heating in vacuo, heating in air and heating in air and water. The samples were distilled under high vacuum and the volatiles thus obtained were analyzed by combined gas chromatography-mass spectrometry. In all heated samples, a series of n-alkanes and 1-alkenes, n-alkanals, methyl alkanones, alkenals, gamma- and delta-lactones, methyl and ethyl esters and free fatty acids were identified. The relative amounts of these compounds varied with the type of heat treatment to which the coconut oil was subjected.

INTRODUCTION

Compared with other vegetable fats, coconut oil contains higher amounts of the shorter chain fatty acids and a lower concentration of the unsaturated fatty acids. This imparts characteristics of consistency and stability towards oxidation, which make it especially useful in the preparation of confectionary products and in some frying operations. The oil has its limitations since upon hydrolysis the liberated short chain fatty acids may cause undesirable flavor.

Two series of volatile components were identified in 1965 by Allen (1) in untreated coconut oil. These were the methyl ketones of odd carbon numbers from C_7 to C_{15} and even carbon numbered δ-lactones from C_6 to C_{14}. Kawada and Yamazaki analyzed the volatile compounds (2) and reported the identification of δ-lactones, n-alkanes, n-alkanals and 2-alkanones in hydrogenated coconut oil which was used for deep fat frying.

The present work was designed to investigate the effects of various heat treatments on the volatile composition of coconut oil under controlled conditions.

EXPERIMENTAL PROCEDURES

Materials

Refined, deodorized, unhydrogenated coconut oil was purchased from PVO International Inc., New Jersey. The specifications for this oil, as furnished by the supplier, were as follows: melting point 24.5 C, free fatty acid content 0.05%, iodine value 11.0, moisture content 0.05%. The fatty acids, analyzed as their methyl esters according to Metcalfe (3) were: C_8 4.6%, C_{10} 5.3%, C_{12} 47%, C_{14} 20%, C_{16} 9.8%, C_{18} 1%, $C_{18:1}$ 11%, $C_{18:2}$ 1.1%.

Heat Treatments

Samples, 25 g each, were heated in sealed glass tubes 8 in. long and 1 in. diameter. The tubes were placed in an oil bath maintained at 180 C for 48 hr. Three different heat treatments were used. Heating under vacuum (10^{-3} torr) was accomplished by evacuating the tubes prior to sealing. Heating in the presence of laboratory air was accomplished by sealing the tube after the addition of the oil. In the case of heating in air and moisture, oil plus 1% by weight of water were added to the tube before sealing. Unheated coconut oil served as the control.

Fractionation

The heated samples and the unheated controls were distilled under vacuum according to the techniques previously described by Nawar et al. (4). The distillations were carried out at 80 C for 1 hr. The distillate from each sample was dissolved in pentane and passed through a sodium bicarbonate reaction column which retained the free fatty acids. The column eluent, free of fatty acids, was treated with activated silica gel to separate the nonpolar compounds from the polar compounds. The polar fraction was then treated with 2,4-dinitrophenylhydrazine to separate carbonyl compounds from noncarbonyls. The free fatty acids were retrieved as sodium esters by passing water over the sodium bicarbonate column. Acidification of the eluent and subsequent ether extraction yielded the free fatty acid fraction. This technique of fractionation permitted the preparation of simpler samples for gas chromatographic and mass spectrometric analysis, minimized peak overlap for more accurate quantitative calculations, and provided information useful for chemical identification of compounds.

Identification

Each fraction isolated as described above was analyzed in a combination gas chromatograph (Aerograph 1200) – mass spectrometer (Hitachi Perkin-Elmer RMU-6A). A stainless steel 6 ft. x 1/8" column packed with 10% DEGS + 2% H_3PO_4 on Chromosorb WAW 60:80 mesh for free fatty acid analysis, and a stainless steel 500 ft. x .02" Carbowax 20M column for the other decomposition products. Retention times and mass spectra of the separated compounds were compared with those of authentic compounds purchased or synthesized in our laboratory. The ancillary techniques of hydrogenation, with platinum black as a catalyst, and reaction with 2,4-dinitsophenylhydrazine according to Schwartz and Parks (5) were employed to aid in the identification of unsaturated and carbonyl compounds, respectively.

Quantitative Analysis

The volatile decomposition products of the heated samples and the unheated controls were subjected to quantitative analysis by gas chromatography. A series of standard mixtures analogous to the identified volatile decomposition products was prepared and added to stripped, unheated coconut oil. These along with a nonpolar (6-dodecyne), a polar (5-decanol), and an acidic (n-nonanoic acid) internal standard were distilled, fractionated, and analyzed by gas chromatography as described above. This procedure permitted the calculation of recovery factors and response factors relative to the respective internal standards for each compound. The same internal standards were added to the heated samples and the controls before distillation for quantitative analysis and the appropriate correction factors were applied. The quantitative data presented in the tables represent the results of five experimental runs.

RESULTS AND DISCUSSION

The compounds identified in the unheated and heated samples as well as the quantitative amounts for each

TABLE I

Quantitative Analysis (mg Volatiles/100 ml Oil) of the Major Nonpolar Compounds Produced by Heating Coconut Oil at 180 C for 48 Hours

Compound	Unheated control	Heated in vacuo	Heated in air	Heated in air + H_2O
n-octane	N.D.[a]	0.07	6.2	6.0
l-octene	N.D.	tr[b]	tr	tr
n-nonane	N.D.	0.07	1.3	1.6
l-nonene	N.D.	tr	tr	tr
n-decane	tr	0.06	0.98	1.4
l-decene	tr	0.05	0.48	0.57
n-undecane	tr	0.07	1.7	1.6
l-undecene	tr	0.06	0.38	0.31
n-dodecane	0.01	0.06	0.53	0.35
l-dodecene	0.02	0.07	0.31	0.23
n-tridecane[c] butylbenzene[c]	tr	0.06	0.81	0.40
l-tridecene	0.04	0.04	0.21	0.13
n-tetradecane	tr	0.05	0.31	0.12
l-tetradecene	0.04	0.09	0.30	0.19
n-pentadecane	tr	0.05	0.39	0.11
Int. pentadecene[d]	N.D.	0.02	0.14	0.14
l-pentadecene	tr	0.02	0.31	N.D.
n-hexadecane	tr	0.03	0.25	0.04
Int. hexadecene	N.D.	0.03	0.15	0.09
l-hexadecene	0.02	0.06	0.24	0.08
n-heptadecane	tr	0.03	0.23	0.27
Int. heptadecene	N.D.	N.D.	0.15	0.09
Unidentified[e]	N.D.	N.D.	0.16	0.10
n-octadecane	tr	0.03	0.04	0.04
Int. octadecene	N.D.	N.D.	0.05	N.D.
l-octadecene	0.01	0.02	0.05	N.D.

[a] Not detectable under the experimental conditions used.

[b] Trace: less than 0.01 mg/100 ml oil

[c] Peaks not well resolved.

[d] Internally unsaturated: double bond not in terminal position.

[e] This component had a molecular ion at m/e 222 and exhibited a high m/e 96.

TABLE II

Quantitative Analysis (mg Volatiles/100 ml Oil) of the Major Free Fatty Acids Produced by Heating Coconut Oil at 180 C for 48 Hours

Compound	Unheated control	Heated in vacuo	Heated in air	Heated in air + H_2O
Acetic acid	N.D.[a]	N.D.	tr[b]	N.D.
Propanoic acid	N.D.	N.D.	tr	N.D.
Butanoic acid	N.D.	N.D.	0.19	tr
Pentanoic acid	N.D.	N.D.	0.33	tr
Hexanoic acid	0.03	0.38	1.9	82
Heptanoic acid	N.D.	N.D.	0.46	N.D.
Octanoic acid	0.25	4.4	13.	920
Decanoic acid	0.11	1.9	5.5	250
Dodecanoic acid	0.25	2.5	11.	460
Tetradecanoic acid	0.02	0.22	1.1	36

[a] Not detectable under the experimental conditions used.

[b] Trace: less than 0.01 mg/100 ml oil.

individual compound are presented in Tables I, II, and III. The pattern of volatile compounds produced by heating of coconut oil is, in general, similar to that reported for oxidized fats and oils, with hydrocarbons being the major nonpolar compounds and aldehydes the major polar components (6-12). In addition to hydrocarbons and aldehydes, heated coconut oil contains lactones and methylketones as major volatile components. It should be pointed out that other minor decomposition products found by other workers in oxidized fats such as alcohols and aromatic compounds were not detected in this study. These compounds are produced in trace quantities and their analysis requires the pooling of volatiles from repeated treatments of large amounts of oil samples.

Table I presents the major nonpolar compounds identified. The unheated control contained very few compounds, essentially saturated and unsaturated straight chain hydrocarbons. Heating in vacuo produced a series of n-alkanes and l-alkenes, with the shorter chain members produced in larger quantities than the longer chains, reflecting the high content of short chain fatty acids in coconut oil. It can also be seen that, at least for the hydrocarbons of less than C13, the alkanes were formed in greater amounts than the corresponding l-alkenes.

Heating in air and heating in air and water produced significantly larger amounts of all compounds than heating in vacuo. In both cases short chain n-alkanes and l-alkenes were again produced in higher amounts than the corresponding long chain compounds. In these samples, however, there were several predominant n-alkanes and one predominant l-alkene present. For example, octane was produced in the largest amount in both samples. This may be attributed to

TABLE III

Quantitative Analysis (mg Volatiles/100 ml Oil) of the Major Polar Compounds Produced by Heating Coconut Oil at 180 C for 48 Hours

Compound	Unheated control	Heated in vacuo	Heated in air	Heated in air + H_2O
2-pentanone	N.D.[a]	N.D.	0.18	C
pentanal	tr[b]	0.14	0.18	C
2-hexanone	tr	tr	0.07	0.03
hexanal	tr	0.30	1.4	0.52
2-heptanone	tr	tr	0.23	0.21
Heptanal	tr	0.20	0.38	0.28
2-hexenal[c]	N.D.	0.01	0.12	0.10
2-octanone	N.D.	tr	0.04	0.03
octanal	tr	0.03	0.14	0.14
2-heptenal	N.D.	0.07	0.85	0.32
2-nonanone	tr	0.01	0.35	0.20
Methyl Octanoate	0.01	0.01	tr	0.14
nonanal	tr	0.06	1.5	0.73
2-octenal	N.D.	0.04	0.26	0.15
Ethyl Octanoate	N.D.	tr	0.07	0.01
2-decanone	N.D.	0.01	0.24	0.34
decanal	tr	0.02	0.18	0.23
2-nonenal	N.D.	0.02	0.34	0.23
2-undecanone	0.01	0.04	0.45	0.45
Methyl decanoate	tr	tr	0.15	tr
undecanal	N.D.	0.06	0.27	0.64
2-decenal	N.D.	0.08	0.75	0.35
Ethyl decanoate	N.D.	tr	tr	tr
2-decanone	N.D.	N.D.	0.19	0.23
dodecanal	N.D.	0.07	0.17	0.25
undecenal	N.D.	0.07	0.84	0.36
Methyl dodecanoate	tr	0.03	0.41	0.56
tr, tr-2, 4-decadienal	N.D.	0.25	0.64	tr
2-tridecanone	tr	tr	tr	0.44
Ethyl dodecanoate	tr	0.01	0.10	0.10
γ-octalactone	N.D.	0.04	0.43	0.47
δ-octalactone	tr	0.02	0.17	0.23
Methyl tetradecanoate	tr	0.01	0.24	0.30
γ-nonalactone	N.D.	0.01	0.33	0.18
Ethyl tetradecanoate	tr	0.02	0.16	0.03
γ-decalactone	tr	0.01	0.45	0.47
δ-decalactone	tr	0.03	0.24	0.32
Methyl hexadecanoate	tr	.01	0.06	0.26
γ-undecalactone	N.D.	tr	.24	.22
Ethyl hexadecanoate	tr	tr	.05	N.D.
γ-dodecalactone	tr	0.02	0.49	0.98
δ-dodecalactone	0.01	0.04	0.28	0.55
Ethyl Octadecanoate	tr	tr	N.D.	N.D.

[a] Not detectable under the experimental conditions used.

[b] Trace: less than 0.01 mg/100 ml oil.

[c] This peak contained an undetermined amount of pentylfuran.

the breakdown of the 10-hydroperoxide of oleic acid, which accounts for 11% of the fatty acid content of coconut oil. Similarly, 1-decene, the predominant alkene in both samples, may be derived from the breakdown of the 9-hydroperoxide of oleic acid. The high amount of undecane formed can be explained by the decarboxylation of n-dodecanoic acid, the most abundant fatty acid of coconut oil, comprising 47% of the total acid.

Besides the n-alkanes and the 1-alkenes, several other compounds were detected in the nonpolar fraction. Pentylfuran was a major component of the nonpolar fraction and a minor component of the polar fraction. Since the pentylfuran partitioned between the two fractions and overlapped with a compound in the polar fraction, its quantitative amount could not be accurately determined under the experimental conditions employed. The only aromatic compound detected was butylbenzene. Unfortunately, its GC peak overlapped with that of tridecane, making its quantitation difficult. A series of long chain internally unsaturated alkenes, not detected in the control, were present in the heated samples. Heating in air and heating in air and water produced more of these compounds. Finally an unidentified compound with a molecular ion at m/e 222 with a high m/e 96 was detected when the coconut oil was heated in air and water. This compound was not detectable in the unheated control or the sample heated in vacuo.

It is difficult to explain the effect of water on the production of hydrocarbons. The amounts of short chain hydrocarbons produced in the presence of water were similar to those produced in its absence. However, a marked decrease in production of the majority of the longer chain hydrocarbons was observed when water was present. While the presence of moisture was reported by some workers to accelerate thermal oxidative deterioration of oils (13,14), contradictory observations have been made by others (12,15).

The addition of water to the coconut oil before heating does, however, markedly affect the production of free fatty acids as shown in Table II. The unheated control had small amounts of free fatty acids of the even carbon numbers C_6 to C_{14}. Heating *in vacuo* increased the amounts of all free fatty acids produced but did not change the qualitative pattern. Heating in air significantly increased the amounts of all free fatty acids produced and gave rise to five fatty acids not detected in the sample heated in vacuo. There was a 28-fold increase in decanoic acid production. Decanoic acid can arise from the decomposition of the 8-hydroperoxide of oleic acid. However, octanoic acid, which would be expected to arise by the decomposition of the 9-hydroperoxide of oleic acid, was formed in only minor quantities. The presence of water during heating resulted in substantial hydrolysis as shown by the remarkable increase in the amounts of all the C_6-C_{14} even-carbon-numbered free fatty acids. Octanoic acid production increased 70-fold while the others increased 30-40-fold.

Carbonyl compounds were found to be the major components in the polar fraction of most samples (Table III). The unheated controls had trace amounts of some n-alkanals, methyl alkanones, methyl and ethyl esters and lactones. It is of interest to note that one component identified as trichloroethylene was also detected. Allen (1) reported odd numbered methyl ketones and lactones of even-carbon-number as the major volatile components of unheated coconut oil.

Heating in vacuo increased the amounts of nearly all volatiles. In the polar fraction, alkanals were produced in larger amounts than the other compounds with hexanal being the predominant compound. It is possible that a small degree of oxidation took place even when the samples were heated under vacuum. Methyl ketones were also produced but in lesser quantities than the aldehydes. The predominant alkanone was 2-undecanone which could arise by the decarboxylation of the β-keto form of coconut oil's major fatty acid, dodecanoic acid.

Heating in air produced a substantial increase in the amounts of all volatiles. The two major compounds produced in the polar fraction were nonanal and hexanal, respectively. However, the unsaturated aldehydes were major components in this case. These were absent in the unheated control and present in unremarkable amounts when heating in vacuo. In general the alkanals were formed in greater amounts than their corresponding methyl ketones. This trend, however, was reversed for members of the series with chain lengths of ten or more carbon atoms.

Heating in air and water produced results similar to those obtained by heating in air. In addition to the marked increase in free fatty acids, the most outstanding difference is that the major compound formed in the presence of water was γ-dodecalactone. Nonanal, hexanal and δ-dodecalactone were also major compounds. However, in this case undecanal was produced in higher amounts than hexanal. Another notable difference when heating in air and water is the relatively decreased amounts of alkenals and the alkadienal. In this case the dienal decreased in amount significantly to the trace level. Heating in air and water generally appeared to produce an enrichment of certain alkanones, lactones and esters compared to heating in air. It can also be noted that when water was present, 2-tridecanone was formed in amounts equal to 2-undecanone, whereas in the other samples, 2-tridecanone had been produced in trace amounts.

Coconut oil is unique among vegetable oils in the high amounts of γ- and δ-lactones present both naturally and in heated samples. Lactones contribute significantly to flavor and aroma. The formation of γ- and δ- lactones probably arises by the cyclization and dehydration of γ- and δ-hydroxy acids as described by Kinsella et al. (16). Although the presence of odd-carbon-numbered lactones is not expected due to the absence of uneven-carbon-numbered fatty acids, the C9 and C11 γ-lactones were produced. The absence of the C14 γ- and δ-lactones is surprising. These are predicted on the basis of the high content (20%) of tetradecanoic acid. However, it is possible that the exceedingly long GC retention time of C14 γ- and δ-lactones on carbowax columns prevented their detection. Heating in vacuo increased the amounts of all the lactones except the γ-undecalactone. The C8 γ- and C12 δ-lactones were produced in the highest amounts. Heating in air and heating in air and water caused a large increase in the amounts of all lactones produced relative to heating in vacuo. In both cases all γ-lactones were produced in higher amounts than the corresponding δ-lactones. The C12 γ-lactone was the predominant lactone produced, which corresponds to the fact that dodecanoic acid comprises 47% of the coconut oil fatty acids. As expected, both the C12 γ- and the C12 δ-lactones were formed in larger quantities when water was present, since the hydrolytic release of the hydroxy acids from the triglyceride molecules facilitates the lactonization process.

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