Influence of Processing and Palm Oil on the Carbonyls and Fatty Acids in Nigerian Cassava Foods

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ABSTRACT

Monocarbonyls, free fatty acids and total fatty acids were determined for traditionally and mechanically processed gari, lafun, and crude palm oil. n-Alkanals and 2-alkanones were most abundant in the cassava foods, and unsaturated aldehydes contributed by palm oil to yellow gari were observed to a limited extent. 2-Alkanones were not found in the palm oil, which indicated that they arise through the fermentation processes. Mechanically processed gari exhibited a total fatty acid profile generally similar to traditionally processed gari.

INTRODUCTION

Fermented cassava root (*Manihot esculenta* Crantz) foods contain little protein (<3%), but are important carbohydrate sources in Nigeria and other West African countries (1-3). Natural acidic fermentations are an integral part of the processing of many of these products, and lowered pH conditions, enzymatic activity of linase, and heating during drying combine to remove linamarin, a toxic cyanogenic glyoside contained in most cassava (1,4-6). During gari manufacture, lactic acid is produced early in the fermentation by lactic acid bacteria which grow associatively with *Cornyebacterium manihot,* and later an overgrowth of *Geotrichum candidum* occurs in the cassava mash (7,8).

Variations in the finished product occur as the result of mechanization of the process (9), and the optional addition of small amounts of crude palm oil prior to frying to a reduced moisture content (ca. 15%) to yield either white (without palm oil) or yellow gari. Yellow gari is preferred by some populations because of improved flavor presumably derived from carbonyls originating in the oil. The bulk of the palm oil produced in Nigeria is presently used locally (10) for a variety of food uses, but because of its relatively low cost, larger amounts are being exported for food uses in developed countries (11,12).

The objectives of this study were to determine the monocarbonyls and fatty acids that could influence the quality and flavor of traditional and mechanically processed gari and lafun, a less extensively fermented cassava paste food (3). Further, it was an objective to examine the potential contribution of crude palm oil to similar properties of yellow gari.

EXPERIMENTAL PROCEDURES

Materials

All chemicals and solvents were reagent grade. Carbonyl-free hexane was prepared by the method of Hornstein and Crowe (13). The method of Schwartz and Parks (14) was used for rendering benzene and chloroform carbonyl-free. Ethanol and methanol were purified by the methods of Tripp et al. (15) and Schwartz et al. (16), respectively. Ethylene dichloride and nitromethane were distilled over excess boric acid (17). Celite 545 (Johns Manville, Denver, CO and Alumina F20 (Aluminum Co. of America, Pittsburg, PA, were dried at 150 C (17). The Alumina was rehydrated with 6% water before use. Seasorb 43 (Fisher Scientific, Pittsburg, PA was heated for activation at 400 C in a muffle furnace for 48 hr.

White gari (traditionally processed), yellow gari (containing crude palm oil), lafun, and crude palm oil were obtained from a market in Ile-Ife, Western Nigeria. Mechanically processed gari was obtained from the Federal Institute of Industrial Research, Oshodi, Nigeria. The gari and lafun samples were packed in polyethylene bags, and the crude palm oil was sealed in a tinned steel can and sent to the U.S.

Isolation and Separation of Monocarbonyls

Carbonyl compounds in the gari and lafun samples were converted to 2,4-dinitrophenylhydrazones (2,4-DNPH) by grinding dry samples (100 g) with excess (6 g) reagent grade 2,4-dinitrophenylhydrazine (2,4-DNP) in a mortar. These mixtures were each added to 200 ml of carbonyl-free methanol which contained 20 ml of 5N HCl, mixed, and held overnight at 5 C. Monocarbonyls were extracted with carbonyl-free hexane, and remaining 2,4-DNP reagent was removed from the extract by the cation-exchange column of Schwartz et al. (16).

Carbonyls in palm oil were converted to 2,4-DHPH by the reaction column of Schwartz and Parks (14). Fat was removed from the 2,4-DNPH of palm oil and yellow gari containing palm oil by the Seasorb 43-Celite 545 column procedure of Schwartz et al. (16).

For each of the products, 2,4-DNPH derivatives of dicarbonyls, ketoglycerides and sugars were separated from monocarbonyls by using the weak alumina column of Schwartz and Parks (14). The monocarbonyl derivatives were separated into alkanal, 2-alkanone, 2-alkenal and 2,4-alkadienal classes by chromatography on a Celite 545-Seasorb 43 column (17). Individual compounds within a class were separated by chromatography on preparative thin layer plates of Kieselguhr G impregnated with Carbowax-400 (18,19).

Identification and Quantification of Carbonyl Compounds

2,4-DNPHs of carbonyl compounds were identified by comparing R_f values of unknown and authentic 2,4-DNPHs, and characteristic colors of the derivatives on Carbowax-400 impregnated Kieselguhr G plates after spraying with KOH. The quantity of each isolated carbonyl derivative was determined spectrometrically by measuring absorbance in chloroform at the wavelength of maximum absorbance (20). Based on data for selected compounds in each class, corrections for recoveries of the 2,4-DNPH during column and thin layer chromatography (alkanals, 80%; methyl ketones, 70%; 2-alkenals, 55%; 2,4-alkadienals, 50%) were made, and concentrations were calculated as parts per billion.

Fatty Acid Analyses

Lipids from gari and lafun samples were extracted with anhydrous diethyl ether in Soxhlet extractors using Whatman cellulose single thickness extraction thimbles (33 x 94 mm), while palm oil was analyzed without further prepara-

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TABLE I

Monocarbonyl Compounds in Cassava Products and Palm Oil

Carbonyl	Traditionally processed white gari	Mechanically processed white gari	Lafun	Traditionally processed yellow gari	Crude palm oil
	(ppb)				
n-Alkanals					
Methanal	tr[a]	—[b]	tr	—	—
Ethanal	35.0	65.0	—	—	—
Propanal	tr	23.0	—	—	—
Hexanal	20.0	—	52.0	5.0	tr
Heptanal	tr	—	10.0	1.0	—
Octanal	15.0	—	10.0	35.0	68.0
Nonanal	17.0	2.0	30.0	91.0	420.0
Decanal	tr	tr	tr	920.0	1,005.0
2-Alkanones					
Propanone	920.0	350.0	1,700.0	900.0	—
2-Butanone	40.0	2.0	100.0	tr	—
2-Pentanone	1.0	tr	50.0	—	—
2-Hexanone	750.0	50.0	1,900.0	820.0	—
2-Heptanone	510.0	1,080.0	320.0	950.0	—
2-Decanone	—	—	tr	—	—
2-Undecanone	—	—	tr	—	—
3-Hydroxy-2-butanone	tr	tr	tr	—	—
2-Alkenals					
2-Propenal	tr	tr	tr	70.0	121.0
2-Octenal	—	—	—	—	73.0
2-Decenal	—	—	—	1.0	85.0
2,4-Alkadienals					
2,4-Heptadienal	—	—	—	tr	tr
2,4-Decadienal	—	—	—	tr	1,275.0

[a]Trace detected.
[b]Not detected.

tion. Free fatty acids (FFA) were isolated from unsaponified lipids by the method of Hornstein et al. (21). FFA were first absorbed on a strong anion exchange resin (Amberlite IRA-400), and the resin was washed free of fat with petroleum ether. Free fatty acids were then converted directly on the resin to methyl esters using methanolic KOH.

Total fatty acids were obtained by esterifying total lipid fracitons with BF_3-methanol (22). Approximately 150 mg of the fat and 25 mg of hepatdecanoic acid internal standard were weighed into a 25 x 150 m m screw cap (Teflon-coated) test tube. After adding 4 ml of 0.5 N methanolic sodium hydroxide, the mixture was heated in a water bath until the fat droplets were completely dispersed in the solution. After cooling, 5 ml of BF_3-methanol (Perco Supplies, No. 72803) was added. The mixture was then boiled for ca. 2 min, cooled, and transferred quantitatively to a Babcock skimmilk test bottle. Saturated sodium chloride was added to the test bottle until the methyl ester layer was apparent in the graduated column. The test bottle was then placed in a Babcock dairy centrifuge for 30 min, and the resulting methyl ester fraction was used directly for G.C. analysis.

Gas chromatography of methyl esters was carried out with a stainless steel column (3 m x 2 mm i.d.) packed with 15% (wt/wt) of diethyleneglycol succinate on 80-100 mesh Chromosorb G, AW-DMCS. An isothermal column temperature of 185 C was maintained with a F & M model 810 gas chromatograph equipped with a hydrogen flame detector. The injector temperature was maintained at 235 C and the detector at 240 C. The flow rate of nitrogen carrier gas was 25 ml/min measured at ambient temperature. Fatty acid methyl esters were identified by coincidence of retention times with those of authentic methyl esters of fatty acids (Analabs, North Haven, CT).

Hydrogenation of Palm Oil

Five g of palm oil were dissolved in a minimal quantity of isopropyl alcohol, and then was diluted to about 25 ml with absolute ethanol. The solution was then placed in a test tube (2 cm i.d. x 17 cm), and ca. 1.5 g of moist, activated Raney nickel catalyst was placed in the test tube. Hydrogen gas was slowly bubbled through the mixture with stirring for 2 hr. The mixture was then filtered, and the filtrate was evaporated to dryness with a rotary evaporator. The white residue was collected, saponified and methylated by the previously described methods for gas liquid chromatographic analysis of total fatty acids.

RESULTS AND DISCUSSION

Monocarbonyl Analysis

The results of the analysis of the cassava products and crude palm oil for monocarbonyls are presented in Table I. The fermented cassava products each contained substantial amounts of n-alkanals and 2-alkanones while only the traditionally processed yellow gari with added palm oil also contained 2-alkenals. However, it is notable that only limited amounts of unsaturated aldehydes were observed in the yellow gari. Apparently the levels of 2-alkenals and 2,4-alkadienals provided by palm oil added to yellow gari (<0.5%) were generally below the level of detection or had been depleted by further oxidative reactions. It can also be noted that the crude palm oil did not contain methyl ketones which might have been anticipated from advantitious mold activity during fermentative processing of palm oil. Gaddis et al. (23) also did not detect methyl ketones in palm oil using 2,4-DNP derivatization procedures. However, very recently Dirinck et al. (24) have reported the observation of notable levels of both 2-heptanone and 2-nonanone,

TABLE II

Extractable Lipid and Free Fatty Acid Content of Cassava Products and Palm Oil

Product	Percent composition (wt/wt)	
	Ether extractable lipids	Total free fatty acids by GC
Traditional white gari	0.25	0.05
Mechanically processed white gari	0.05	0.01
Traditional yellow gari	0.65	0.04
Lafun	0.45	0.04
Cassava flour	0.11[a]	--[b]
Crude palm oil	(100)	1.97

[a]From Harris (36).

[b]Not available.

as well as 2-methyl-2-hepten-6-one, in crude palm oil using G.C.-M.S. analysis.

The 2-alkanones observed in the cassava products would appear to be derived from the activity of organisms present during fermentation. The high levels of propanone have also been observed in fermenting cassava samples (7), and propanone may be derived from lactic-acid-producing *Streptococci* (25). The fermentation of gari involves the initial development of populations of *Streptococcus faecium* that produce lactic acid, and this is paralleled by the growth of nonacid-producing *Corynebacterium manihot* (4,5,8) whose exact role in the fermentation is not known as yet. After 3-4 days the fermented cassava mash then supports a luxuriant growth of *Geotrichum candidum* (8), but this organism apparently is not capable of producing methyl ketones from fatty acids (26). However, other molds, particularly *Penicillium sp.*, are well known for their capability of converting fatty acids to methyl ketones (27-29). It would appear that unrecognized mold activity in the ferment could account for methyl ketone formation in the traditionally fermented cassava products. A similar case has been documented for fermenting cocoa beans where greater levels of methyl ketones were found in moldy beans than in nonmoldy beans (30).

The data show that both of the traditionally processed gari samples contained comparable levels of the methyl ketones that were found commonly in each product. However, mechanical processing of gari yielded less propanone, but more 2-heptanone than traditional processing. Traces of 3-hydroxy-2-butanone were detected in some of the samples, and its presence probably reflects streptococcal metabolic development of diacetyl during the fermentation. Variations in levels of methyl ketones noted among the fermented cassava products probably reflect the occurrence of the uncontrolled, mixed culture fermentations. However, it is probable that the combined effects of the methyl ketones are contributory to the flavor of fermented cassava products.

The observations for aldehydes in the 2,4-DNPH derivatives from crude palm oil were in general agreement with those reported by Gaddis et al. (23) for a presumably refined palm oil sample and Dirinck et al. (24) for crude palm oil. Inconsistencies in data between studies could be anticipated because of different crude palm oil recovery practices (10) and the resulting variable oil quality (12). The most abundant monocarbonyl found in the crude palm oil was 2,4-decadienal. The ratio of the *trans-cis* to *trans-trans* isomers of this compound (24,31), however, was not discernible using 2,4-DNP methods. Addition of palm oil to fermented cassava mash to give yellow gari probably contributes volatile flavors to the product, especially through alkanals. Additions of larger amounts of palm oil (>0.5%) would provide additional energy and flavor although decreased oxidative stability of products from centralized processing plants could lead to reduced consumer acceptances. Shelf instability of cassava products has already been noted (32).

Fatty Acid Analyses

Data for total ether extractable lipids for the cassava products are shown in Table II. Each of the products contained only small quantities of lipid materials, and even the palm oil-containing yellow gari sample had only 0.65% lipids. Comparing the lipid content of the white gari to that of the yellow gari, it appears that less than 0.5% palm oil was added to the yellow gari sample. Only the mechanically processed white gari appeared to differ from the other fermented cassava products in regards to FFA levels (Table II), and this sample exhibited the lowest level of FFA of the group.

The palm oil sample had a total FFA content of ca. 2% (Table II), which placed it in the category of a relatively high quality palm oil (12). The high oleic acid content of the palm oil (Table III) placed it in the category of that from the more easternly portion of West Africa (Ghana to Nigeria) (33) or that of a hybrid of *Elaeis guineensis* and *Elaesis oleifera*(12). The FFA distribution in the palm oil was similar to that of the total fatty acid pattern, and indicated that selective lipolysis had not occurred during oil recovery.

During G.C. analysis of the samples, a fatty acid component was consistently noted between myristic and palmitic acids. Exhaustive hydrogenation of palm oil with Raney nickel catalyst failed to alter the size of the unknown fatty acid peak while the C_{18} unsaturated fatty acid peaks were virtually eliminated. Based on this observation, and the report of Knight (34) who used g.c.-m.s. to identify a similar peak in palm kernel oil, the peak was assigned the tentative identity of pentadecanoic acid. Hexadecenoic acid which has been reported in palm oil (35) and cassava flour (36) was not detected in any of the products analyzed in this study.

The fatty acid and FFA patterns for the fermented cassava products were generally similar (Table III). However, some selectivity in FFA occurrence was observed, particularly in the white gari samples where higher percentages of free pentadecanoic and/or palmitic acids were found generally at the expense of oleic acid. Compared to the composition of cassava flour, gari manufacture resulted in reduced amounts of linolenic acid while this fatty acid was not altered in lafun. The fermentation of cassava also appeared to slightly increase the relative amounts of shorter chain fatty acids over that found in cassava flour. Considering the amounts of FFA found in the fermented products (Table II), a direct role for fatty acids in the flavor of these cassava food items is not readily apparent. The total unsaturated lipid content could be expected, however, to play a flavor precursor role in the quality and acceptance

TABLE III

Relative Fatty Acid Composition of Lipid Fractions from Cassava Products and Palm Oil

	Percentage of fatty acids in fractions (wt/wt)										
	Traditionally processed white gari		Mechanically processed white gari		Traditionally processed yellow gari		Crude palm oil		Lafun		Commercial cassava flour (36)
Fatty acids	Total FA	FFA	Total FA	FFA	Total FA	FAA	Total FA	FFA	Total FA	FFA	Total FA
Lauric (12:0)	0.2	tr[a]	0.2	—[b]	—	—	—	—	tr	3.12	tr
Myristic (14:0)	1.0	0.5	0.2	—	0.8	tr	0.1	tr	0.3	0.3	tr
Pentadecanoic (15:0)[c]	9.6	37.5	6.5	18.4	3.2	2.9	0.4	6.6	0.7	1.7	tr
Palmitic (16:0)	37.0	25.9	25.6	52.9	39.0	33.9	32.7	30.4	31.8	30.9	32.7
Stearic (18:0)	4.6	5.2	3.8	—	5.4	5.5	5.6	3.9	1.6	5.0	1.5
Oleic (18:1)	38.1	20.9	41.0	28.6	38.6	40.0	47.4	45.4	43.2	36.9	43.7
Linoleic (18:2)	18.3	8.9	20.3	tr	11.2	15.5	14.2	13.8	16.9	18.9	16.6
Linolenic (18:3)	0.4	1.3	1.7	—	1.9	2.2	tr	tr	5.6	5.2	5.5

[a]Trace detected.

[b]Not detected.

[c]Tentative identification.

of both fresh and stored products. Therefore, it probably should be anticipated that flavor stability problems similar to those encountered with dehydrated potato *(Solanum tuberosum)* products may be encountered in the industrialization of fermented and dehydrated cassava products.

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REFERENCES

1. Akinrele, I.A., A.S. Cook, and R.A. Holgate, "The Manufacture of Gari from Cassava in Nigeria," Research Report No. 12, Federal Institute of Industrial Research, Lagos, Nigeria, 1962.
2. Ayres, J.C., Food Technol. 26:128 (1972).
3. Stanton, W.R., and A. Wallbridge, Process Biochem. 4:45 (1969).
4. Akinrele, I.A., "Further Studies on the Fermentation of Cassava," Research Report No. 20, Federal Institute of Industrial Research, Lagos, Nigeria, 1963.
5. Akinrele, I.A., J. Sci. Food Agric. 15:589 (1964).
6. Oke, O.L., Nature 212:1055 (1966).
7. Abe, M.O., and R.C. Lindsay, "Evidence for a Lactic Streptococcal Role in Nigerian Acidic Cassava (Manihot esculenta Crantz) Fermentations," J. Food Protect. 41:781 (1978).
8. Collard, P., and S. Levi, Nature, 183:620 (1959).
9. Akinrele, I.A., M.I.O. Ero, and F.O. Olatunji, "Industrial Specifications for Mechanized Processing of Cassava into Gari," Tech. Memorandum No. 26, Federal Institute of Industrial Research, Oshodi, Nigeria, 1971.
10. Banigo, E.O.I., A. Ogunlesi, and O. Ofi, JAOCS 54:593 (1977).
11. Robertson, J.A., W.H. Morrison, B.G. Lyon, and R.L. Shaw, J. Food Sci. 43:420 (1978).
12. Cornelius, J.A., JAOCS 54:943A (1977).
13. Hornstein, I., and P. Crowe, Anal. Chem. 34:1037 (1962).
14. Schwartz, D.P., and O. Parks, Ibid. 33:13960 (1961).
15. Tripp, R.C., B. Trimm, M. Iyer, T. Tichardson, and C.H. Amundson, Proc. Am. Soc. Brewing Chem., p. 65, 1968.
16. Schwartz, D.P., A.R. Johnson, and O. Parks, Microchem. J. 6:37 (1962).
17. Lillard, D.A., "The Autoxidative Degradation of Some Secondary Products of Autoxidizing Lipids," Ph.D. Thesis, Oregon State University, Corvallis, OR, 1964.
18. Badings, H.T., and J.G. Wassink, Neth. Milk Dairy J. 17:132 (1963).
19. Urbach, G., J. Chromatogr. 12:196 (1963).
20. Day, E.A., R. Bassett, and M. Keeney, J. Dairy Sci. 43:463 (1960).
21. Hornstein, I., J.A. Alford, L.E. Elliot, and P.E. Crowe, Anal. Chem. 32:540 (1960).
22. Metcalfe, L.D., and A.A. Schmitz, Ibid. 33:363 (1961).
23. Gaddis, A.M., R. Ellis, and G.T. Currie, JAOCS 38:371 (1961).
24. Dirinck, P., L. Schreyen, L. DeSchoenmacker, F. Wychuyse, and N. Schamp, J. Food Sci. 42:645 (1977).
25. Keenan, T.W., D.D. Bills, and R.C. Lindsay, Can. J. Microbiol. 13:1118 (1967).
26. Stokoe, W.N., Biochem. J. 22:80 (1928).
27. Gehrig, R.G., and S.G. Knight, Nature. 182:1937 (1958).
28. Gehrig, R.G., and S.G. Knight, Ibid. 192:1185 (1961).
29. Gehrig, R.G., and S.G. Knight, Appl. Microbiol. 11:166 (1963).
30. Hansen, A.P., and P.G. Keeney, J. Food Sci. 35:37 (1970).
31. Hoffmann, G., and J.G. Keppler, Nature 185:310 (1960).
32. Strasser, J., and R. Olivas, Abstr. No. 162 of the 32nd Annual Meeting of the Institute of Food Technologists, Minneapolis, MN, p. 114, 1972.
33. Hilditch, T.P., and P.N. Williams, "The Chemical Constituents of Natural Fats," 4th Edition, John Wiley, 1964.
34. Knight, J.B., "Computerized GC/MS Analysis of Some Triglycerides," Application Tips – No. 39, Finnigan Instruments Corp., CA, 1972.
35. Eckey, E.W., "Vegetable Fats and Oils," Reinhold, 1964.
36. Harris, R.V., J. Sci. Food Agric. 21:626 (1970).

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