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# Some Chemical Changes in Heated Crude Palm Oil

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## *ABSTRACT*

*Palm oil was heated for 2 h at a time at 100°, 150° or 200°C and then allowed to cool for 10 or 58 h. This was repeated twelve times. For the chemical monitoring of deterioration, the following parameters were measured: iodine value, free fatty acids, peroxide, anisidine, oxidation and thiobarbituric acid values, as well as the carotenes and fatty acid composition. Destruction of carotenes and linoleic acid (C18:2) contributed significantly to increases in peroxide value, p-anisidine value and thiobarbituric acid value at 452 nm. Oleic acid (C18:1) did not contribute significantly to these oxidation parameters. Hydrolysis and polymerisation, as indicated, respectively, by the free fatty acids and iodine value, did not play any significant rôle in the deterioration of the heated samples of palm oil.*

## INTRODUCTION

Crude palm oil is a complex mixture consisting of over 99% glycerides and about 0·5% non-glyceride materials on which the organoleptic, physical and chemical properties depend. The fundamental fatty acids in all samples of palm oil are myristic (C14:0), palmitic (C16:0), stearic (C18:0), oleic (C18:1) and linoleic (C18:2), but the amounts vary according to the variety of tree (Macfarlane *et al.*, 1975). The non-glyceridic components are carotenoids, tocopherols, sterols, phosphatides and alcohols (Jacini *et al.*, 1967; Loncin, 1974; Okiy, 1974) and their amounts depend on the state of maturation of the fruit, the variety of palm fruit and the geographical and climatological circumstances of the cultivation, as well as the state of health and nutrition of the palm.

When crude palm oil is heated, the components oxidize and may fragment to various compounds which alter the organoleptic, chemical and physical properties of the oil. The most labile components are the carotenoids and unsaturated fatty acids. Some of the decomposition products can be estimated by the *p*-anisidine (*p*-AV) or thiobarbituric acid (TBA) value, while peroxide value measures primary oxidation.

This paper reports on the contribution of the component oleic and linoleic acids, as well as carotenes, to some indices of deterioration of heated crude palm oil.

## MATERIALS AND METHODS

Fresh crude palm oil was obtained from the mill at the Nigerian Institute for Oil Palm Research, Benin City. One-litre samples were heated in open two-litre Pyrex beakers at 100°, 150° or 200°C for 2 h at a time and allowed to cool to room temperature overnight and during a weekend. Samples were withdrawn for analysis after every heating and cooling cycle. The total time of heating was 24 h.

Fatty acid methyl esters were separated on a column of diethylene glycol adipate (10% on 80–120 mesh celite) at 180°C, in a Pye Unicam Series 104 gas–liquid chromatograph. Carotene was determined according to the method of Brubacher (1968). The method of Tsoukalas & Grosch (1977) was used for *p*-anisidine value whilst thiobarbituric acid values were run by a modification of the procedure of Jacobson *et al.*, (1964), as described by Fioriti *et al.*, (1974). Oxidation value is 2 × peroxide value + *p*-anisidine value. Iodine value was determined by Wij's method while free fatty acids were determined by the method of Cocks & van Rede (1966).

## RESULTS

Table 1 shows the effect of heat of the characteristics of the samples of palm oil. The percentage increases in the deterioration indices are presented in Table 2. The oxidation indices showed significant increases but changes in iodine value and free fatty acids were not significant.

**TABLE 1**
Effect of Heat on the Characteristics of Crude Palm Oil

| | *Fresh sample* | *100°* | *150°* | *200°* |
|---|---|---|---|---|
| Carotene (ppm) | 710 | 544 | 116 | 56 |
| Linoleic acid (%) | 8·4 | 5·8 | 4·2 | 3·5 |
| Oleic acid (%) | 36·5 | 33·9 | 29·7 | 27·0 |
| Iodine value | 55·0 | 56·5 | 54·6 | 52·8 |
| Free fatty acids (%) | 4·7 | 5·6 | 5·5 | 3·6 |
| Peroxide value (Meq/kg) | 1·9 | 4·1 | 4·2 | 2·6 |
| β-Anisidine value | 1·7 | 4·4 | 5·3 | 6·3 |
| Oxidation value | 5·4 | 12·5 | 13·7 | 11·5 |
| TBA (452 nm) | 36·5 | 30·0 | 67·1 | 115 |
| TBA (532 nm) | 18·0 | 12·0 | 12·7 | 15·7 |

TBA, Thiobarbituric acid value. All samples heated twelve times for 2 h each time.

The correlation coefficients between the amounts of carotenes, linoleic and oleic acids destroyed and the formation of *p*-anisidine, peroxide and TBA values are given in Table 3. The destruction products of carotenes contributed significantly to *p*-anisidine reactions at 100°, 150° and 200°C, peroxide values at 100° and 150° and TBA (452 nm) reactions at 150° and 200°.

**TABLE 2**
Per cent Increase in Deterioration Indices

| | *100°* | *150°* | *200°* |
|---|---|---|---|
| Iodine value | 0·7 | −0·1 | −0·7 |
| Free fatty acids | 5·1 | 3·0 | −3·9 |
| Peroxide value | 30·7 | 21·7 | 6·2 |
| *p*-Anisidine value | 42·1 | 38·0 | 45·4 |
| Oxidation value | 34·9 | 27·6 | 19·0 |
| TBA (452 nm) | −4·7 | 15·0 | 36·2 |
| TBA (532 nm) | −8·8 | −5·3 | −2·1 |

**TABLE 3**

Correlation Coefficient (*r*) Between the Amounts of Carotenes, C18:2 and C18:1 Destroyed and P–AV, PV, TBA (452 nm) and TBA (532 nm) Formed after Heating 24 h

| *Carotene* | *P-AV* | *PV* | *TBA 452* | *TBA 532* |
|---|---|---|---|---|
| 100° | 0·83*** | 0·89*** | −0·27 | −0·36 |
| 150° | 0·77** | 0·84*** | 0·65* | −0·26 |
| 200° | 0·66** | 0·39 | 0·61* | −0·15 |
| C18:2 | | | | |
| 100° | 0·28 | 0·26 | −0·45 | −0·46 |
| 150° | 0·47* | 0·28 | 0·45 | −0·22 |
| 200° | 0·65* | 0·12 | 0·64* | −0·01 |
| C18:1 | | | | |
| 100° | 0·37 | 0·5 | −0·26 | −0·31 |
| 150° | 0·10 | 0·09 | 0·15 | −0·22 |
| 200° | 0·03 | 0·26 | 0·05 | −0·24 |

*** $p < 0{\cdot}001$. ** $p < 0{\cdot}01$. * $p < 0{\cdot}1$.

Linoleic acid destruction leads to significant reactions of only *p*-anisidine at 150° and 200°C and TBA (452 nm) at 200°C. The amounts of oleic acid destroyed did not contribute significantly to any of the indices of deterioration measured. The destruction of carotene, linoleic acid or oleic acid gave no significant TBA 532 nm reactions. Similarly, linoleic acid destruction did not significantly affect peroxide value under the conditions of this experiment.

## DISCUSSION

The results of this work indicate that secondary oxidation products formed during thermal deterioration of crude palm oil yield significant *p*-anisidine-reacting materials at all temperatures and TBA-reacting materials at the higher temperatures. TBA chromophores were more sensitive at 452 nm than at 532 nm. As modified by Jacobson *et al.* (1964), TBA reacts with saturated and mono-unsaturated aldehydes to give a yellow colour absorbing at 532 nm. Marcuse & Johansson (1973) also studied the reaction of TBA with various classes of aldehydes and found that alkanals, 2-alkenals and 2,4-alkadienals produced a yellow 452 nm pigment with TBA, while only 2,4-alkadienals and, to a lesser extent, 2-alkenals, produced the red 532 nm pigment.

The TBA results of this study would seem to indicate that the compounds present in oxidized crude palm oil were preponderantly saturated and mono-unsaturated aldehydes. Crude palm oil contains carotenes and fatty acids. Walter *et al.*, (1970) found that saturated carbonyl content was greater than unsaturated carbonyls during fragmentation of $\beta$-carotene in autoxidizing dehydrated sweet potato flakes. Also, the results of the work of Frankel *et al.*, (1981) showed that thermally decomposed methyl oleate and linoleate, respectively, produced about 77% and 67% saturated compounds.

A systematic analysis of the breakdown products of oxidized crude palm oil has not been carried out. However, some of the breakdown products of carotenes and fatty acids identified by Walter *et al.*, (1970) and Frankel *et al.*, (1981) would be consistent with the significant TBA (452 nm) reactions in this work. In addition, products of co-oxidation between carotene and residues of fatty acids such as oleic and linoleic acids would be present (Wong, 1977). The stable yellow pigments of heated palm oil, which are difficult to bleach, were identified by Wong (1977) to be some of the products of co-oxidation between carotene and linoleate residues. Carotenes contributed more than linoleic acid to *p*-anisidine, peroxide and thiobarbituric acid reactions. This is because carotene is less stable than linoleic acid (Baloch *et al.*, 1977). In addition, the concentrations of the breakdown products of carotenes were more than those of linoleic acids in the oxidized samples of crude palm oil.

The effects of breakdown products of linoleic and oleic acids on the formation of peroxide value were insignificant (Table 3) because carotenes protect these fatty acids against thermal oxidation (Oboh, 1983).

## CONCLUSION

The compounds which give positive *p*-anisidine and TBA reactions are mostly saturated and unsaturated carbonyl compounds. Saturated and unsaturated carbonyl compounds are off-flavour determinants (Jacobson, *et al.*, 1964; Marcuse & Johansson, 1973). In heated crude palm oil, the compounds responsible for significant *p*-anisidine and TBA reactions were found to be breakdown products of carotenoids which also gave significant peroxide values.

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