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☆A Study of the Cause of Rapid Color Development of Heated Refined Palm Oil

Y.A. TAN, S.H. ONG, K.G. BERGER, H.H. OON and B.L. POH, Palm Oil Research Institute of Malaysia, No. 6, Persiaran Institusi B.B. Bangi, P.O. Box 10620, Selangor, Malaysia

ABSTRACT

One of the most obvious changes when oils are heated is color darkening. Palm oil darkens very rapidly compared to other oils. The cause of this rapid color development was investigated. Various methods used to pretreat Lotox crude palm oil (CPO) to retard darkening during heating were by agitation with activated carbon S511, by water and water/isopropyl alcohol (95:5) washing of neutralized and unneutralized oil, and by liquid/liquid extraction of oil using water and water/isopropyl (95:5). Pretreatment of CPO did succeed in retarding color development. Retardation was especially evident in oils previously neutralized with sodium hydroxide before washing with water and water/isopropyl alcohol. The UV spectra of the liquid/liquid extracts showed strong absorption maxima at 256 nm. The addition of a base resulted in darkening of the extracts accompanied by shifts to longer wavelengths (288 nm). Reaction with freshly diluted 1-2% ferric chloride solution gave a brown color. The development of paper chromatography in butanol: acetic acid:water (6:1:2) revealed a blue fluorescence near the solvent front, with the same relative retention time as that of tannic acid. This evidence indicates that phenolic compounds were responsible for color darkening in palm oil.

INTRODUCTION

The color of refined oils is a good indication of their quality, inasmuch as bad quality oils are difficult to process into acceptable, light-colored products. While carotenoids are responsible for the dark orange-red color of crude palm oil, the final color of refined palm oil and its subsequent color on storing and/or heating is attributed to the process of oxidation and inherent color precursors in the oil itself. Although oxidation bleaches the carotenoid pigments, it also develops the color of other types of coloring materials and may even produce colored compounds of a quinoid nature (1). The partial oxidation of vegetable oils is known to increase this red and yellow color as a result of the formation of the chroman-5,6-quinones (2). In a study of the bleaching of cottonseed and soybean oils, there is evidence that oxidation develops new pigments and stabilizes existing pigments against adsorption, with the adsorbent itself strongly catalyzing the oxidation reaction (3). Traces of iron and some other metallic contaminants

greatly favor color development in some fats, and certain pigments are very refractory to ordinary refining and bleaching treatment but may be removed effectively by liquid-liquid extraction.

When oils are heated as in the frying process, they rapidly change from a light yellow to an orange brown color. This is the combined results of oxidation, polymerization and other chemical changes. Darkening is considered a useful phenomenon in that it prevents the continual use of edible oils which have undergone excessive deterioration.

Palm oil darkens very rapidly on heating. While it has been reported that high molecular weight compounds are responsible for the color of refined palm oil (4) as well as for difficulties associated with decolorization of certain crude palm oils, the cause of rapid color development of heated refined palm oil is not fully understood.

Color changes on heating are primarily the result of oxidation but the responsible compounds formed in palm oil are not known. Red color development in soybean oil is attributed to α, β- and α, α'-unsaturated carbonyls (5). The appearance of a visible color in the oil is indicative of its ability to absorb visible light, and this is associated with the presence of certain unsaturated molecular groups (6). This report outlines the investigation into the cause of darkening in refined palm oil and the effort to isolate and identify the color causing compounds.

EXPERIMENTAL PROCEDURES

Apparatus

Ordinary laboratory apparatus were used. Instruments used included a Hewlett-Packard 8450A UV-visible spectrophotometer coupled to a H.P. 7225B plotter, a JOEL FX 100FT NMR and a Perkin Elmer Model 1330 IR spectrophotometer.

Reagents

All reagents were of analytical or spectroscopic grade.

Starting Materials

A total of seven types of pretreatment were carried out on Lotox grade crude palm oil (CPO). The seven pretreatments were as follows:

(a) A 1:1 mixture of CPO in hexane was agitated with activated carbon S511 for 30 min (7). The carbon was activated at 120 C for one day prior to use. The ratio of carbon to oil used was 5:1. After agitation, the carbon was filtered off under vacuum and the above procedure was repeated three times on the oil with a fresh batch of activated carbon each time. An oil (S511. PO) registering zero absorption at 446 nm (carotene free) was thus recovered.

(b) Neutralized oil was washed with a 95:5 water/isopropyl alcohol (IPA) solution by shaking in a separating funnel. A 1:1 ratio of oil to washing solution was used. On separation of the two phases, the oil *[n. RPO (95:5)] was taken out for refining.

(c) Procedure (b) was repeated with water as the washing solution. The final oil after refining *[n. RPO (100)] was heat tested for color darkening.

(d) Procedure (b) was repeated on an unneutralized CPO *[un. RPO (95:5)].

(e) Same treatment as (c), but an unneutralized CPO was used *[un. RPO (100)].

(f) A liquid-liquid extraction procedure in a downward displacement apparatus was carried out on CPO with a solvent consisting of 95:5 water/IPA. Oil to solvent ratio was 1:1 *[e. RPO (95:5)].

(g) Same treatment as (f), but with water as the solvent *[e. RPO (100)].

Nb: *Code of oils after refining.

Oil Refining Methods

All pretreated oils from (b)-(g) were separated from the aqueous phase and bleached according to the SCOPA Method (8). A sample of untreated CPO was similarly bleached to act as control *[RPO]. The earth used for bleaching was Galleon V_2 super.

Aqueous Extracts from CPO Treatment

After separation from the oil, the aqueous extracts from (e) and (g) were centrifuged and filtered to separate remaining oil droplets from the extracts. The extracts were then concentrated or evaporated (depending upon the analyses to be carried out) using a rotary evaporator. Appropriate solvents were then used to test the solubility of the evaporated extracts and to prepare them for further analytical and instrumental analyses.

Heat Tests

Sixty-five ml of each oil were then heated in 100-ml beakers for a total of 49 hr (7 hr daily). The test temperature was kept at 180 C ± 5 C, and a Stuart Hotplate was the heat source.

Analytical Methods

The fresh oil colors and colors developed on heating at the end of the day were read in a 1″ cell in a Lovibond Tintometer Type D.

The solubility of the extracts from (e) and (g) were tested in water, chloroform and a 1:1 mixture of iso-octane/ethanol. Their reactions with freshly diluted 1-2% ferric chloride solution were observed.

The extracts as solutions in iso-octane/ethanol (1:1) were applied on chromatography paper. Development was by ascending technique in a closed tank at room temperature in a developing solvent of butanol:acetic acid:water (6:1:2). The developed chromatogram was viewed in UV light.

Thin-layer-chromatography of the extracts was carried out. HPLC plates pre-coated with silica gel 60 F_{254} were used. Development was carried out in chloroform:acetic acid (9:1), and the developed chromatogram was visualized in UV_{254} light and by the universal detection reagent iodine.

UV-visible spectra of the extracts in iso-octane/ethanol (1:1) solvent were obtained using a Hewlett Packard 8450A UV-visible spectrophotometer coupled to a H.P. 7225B plotter. Another UV-visible scan was run after addition of a base (1 drop of 1 M sodium methoxide solution) to the two extract solutions.

IR analysis was carried out on the extracts in deuterated chloroform $(CDCl_3)$ in a 0.5 mm sodium chloride cell with a 12-min scan time.

For NMR analysis, the extracts first were dissolved in $CDCl_3$, and the remaining $CDCl_3$ insoluble portion was dissolved in D_2O. Then both solutions were analyzed in 5 mm tubes at 28 C.

RESULTS AND DISCUSSION

Effect of Heat and Time of Heating upon the Color Development of Test Oils

As expected, darkening was observed in all the oils. However, the rates of darkening were different. Figure 1 illustrated the difference in oil color between RPO, S511.PO, n. RPO (95:5) and n. RPO (100). The control, RPO, was seen to darken very rapidly compared to the other three oils. Figure 2 again emphasizes the point that untreated CPO resulted in a refined oil which developed color at a much faster rate than CPO which had undergone pretreatment before refining.

Activated carbon S511 was found to be very successful in retarding darkening (Fig. 1) in heated palm oil. Oils treated with S511 required no subsequent refining. This was because carbon was a powerful adsorbent and most color causing precursors and pigment in the oil would have been removed by adsorption onto carbon. As far as treatment by washing with the two solvents water and water/IPA was concerned, color darkening was reduced more effectively if the Lotox CPO was neutralized previously with an appropriate dose of sodium hydroxide solution (Figs. 1 and 2). This suggested that the color causing materials or precursors in CPO were affected by reaction with a base. Figure 2 indicates that the solvent mixture water/IPA was more effective than water alone in removing color causing materials from neutralized CPO; the effect was reversed in the case of unneutralized CPO.

Liquid-liquid extraction procedure was found to be able to retard color darkening to some extent, as shown in Figure 2. The darker end color as compared to the other pretreatments was the result of overheating to over 200 C on the fourth heating day, i.e. 28 hr.

Figures 1 and 2 indicate that ordinary untreated palm oil (RPO) itself differs in the rate of heat darkening. This could be explained by the fact that different batches of Lotox CPO were used in the studies.

Analysis of Aqueous Extracts Obtained from Washing and Liquid-Liquid Extract of Lotox CPO with Water

The light yellow water soluble extracts were found to be soluble in a mixture of iso-octane/ethanol (1:1) and partially soluble in chloroform. Reaction with freshly diluted 1-2% ferric chloride solution resulted in a brown color. On the addition of a base (sodium methoxide solution), a dark yellow color was observed. This, in turn, reverted to a light yellow color on addition of an acid.
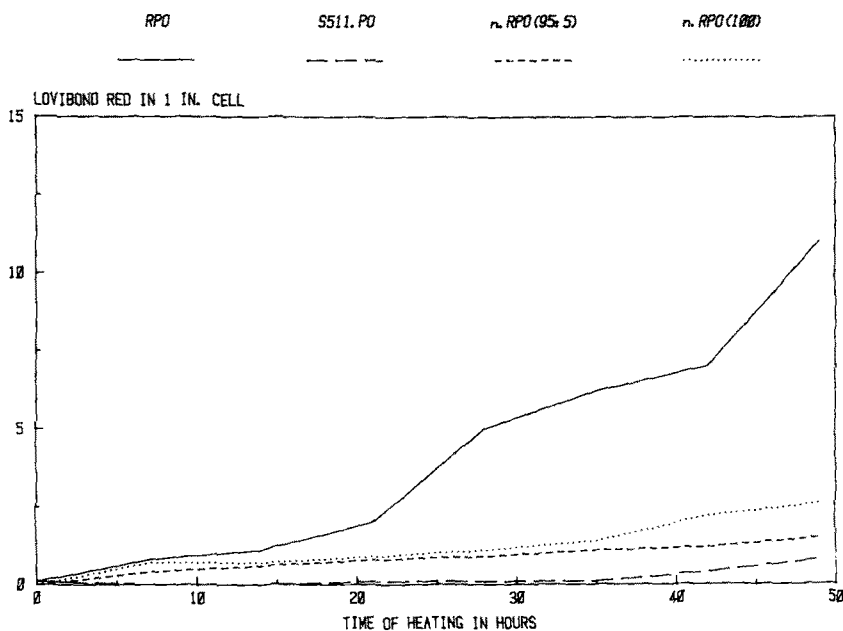
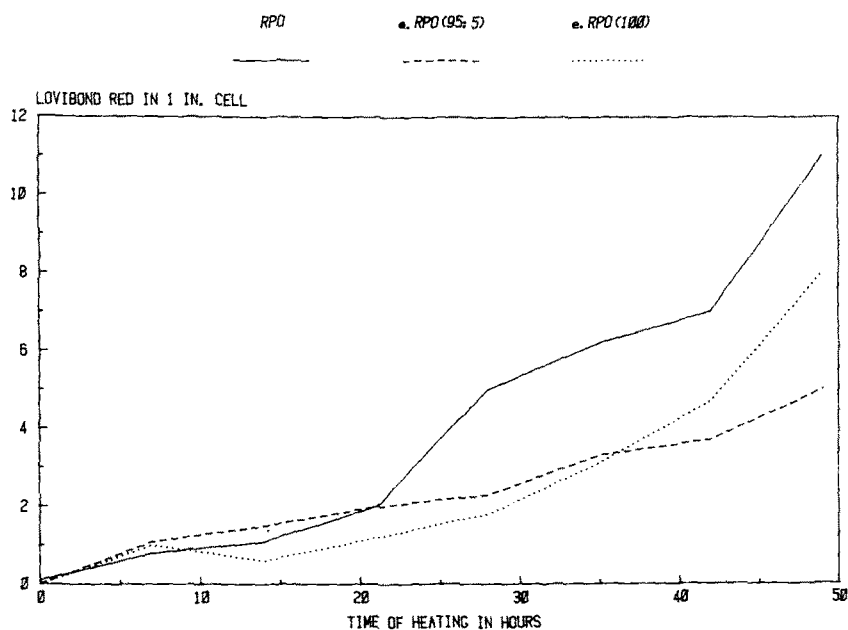FIG. 1. Effect of heat on oil color. Heated oil at 180 C.

FIG. 2. Effect of heat on oil color. Heated oil at 180 C.

A fully developed paper chromatogram of the extracts revealed blue fluorescent spots when viewed under UV light.

When viewed in UV light (254 nm), the developed TLC revealed three bands having Rf values of 0.58, 0.42 and 0.31. An addition of three more bands with Rf values of 0.54, 0.09 and 0.05 was detected when the plate was placed in a closed tank containing iodine crystals. The band with Rf value of 0.31 was identified as parahydroxybenzoic acid.

A UV-visible scan of the extracts in iso-octane/ethanol gave the spectra in Figures 3 and 4. Absorption was observed in the UV region at around 256 nm. This was shifted to longer wavelengths of about 288 nm on the addition of a base (sodium methoxide).

All the above test results indicated the presence of phenolic compounds in the extracts. The polyphenol tannic

acid was used as a reference for the above tests (Fig. 5).

The NMR spectra of the extracts showed a crude, four-line spectrum in the region of 7-7σ and 6-9σ (Figs. 6-9) which was typical of a para-disubstituted aromatic system.

A study of the IR spectra of the extracts (Figs. 10 and 11) showed absorptions at 3530, 3534, 1730 and 1600 cm^{-1}. These bands indicated the possible presence of $-NH_2$, $-OH$, C = O groups and C = C aromatic ring.

The chemical and instrumental analyses carried out on the extracts strongly indicated the presence of phenolic compounds perhaps coupled to $-NH_2$ groupings.

Current studies carried out by Azis et al. in PORIM indicate that tannin is one of the few stable compounds found in the palm fruit. It is therefore highly probable that the compound slipped through into the pressed oil and finally into refined palm oil, thereby causing the rapid heat
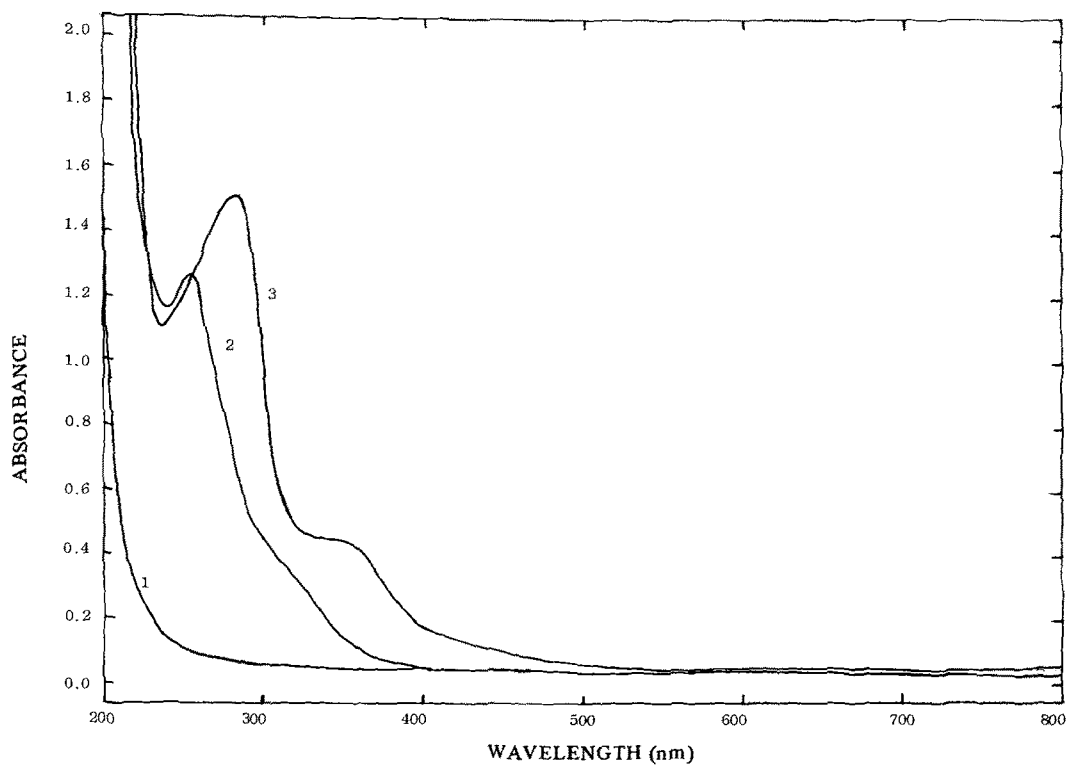
FIG. 3. Ultraviolet-visible spectra of un.RPO (100). 1, solvent: iso-octane/ethanol (1:1); 2, extract, and 3, extract + alkali.
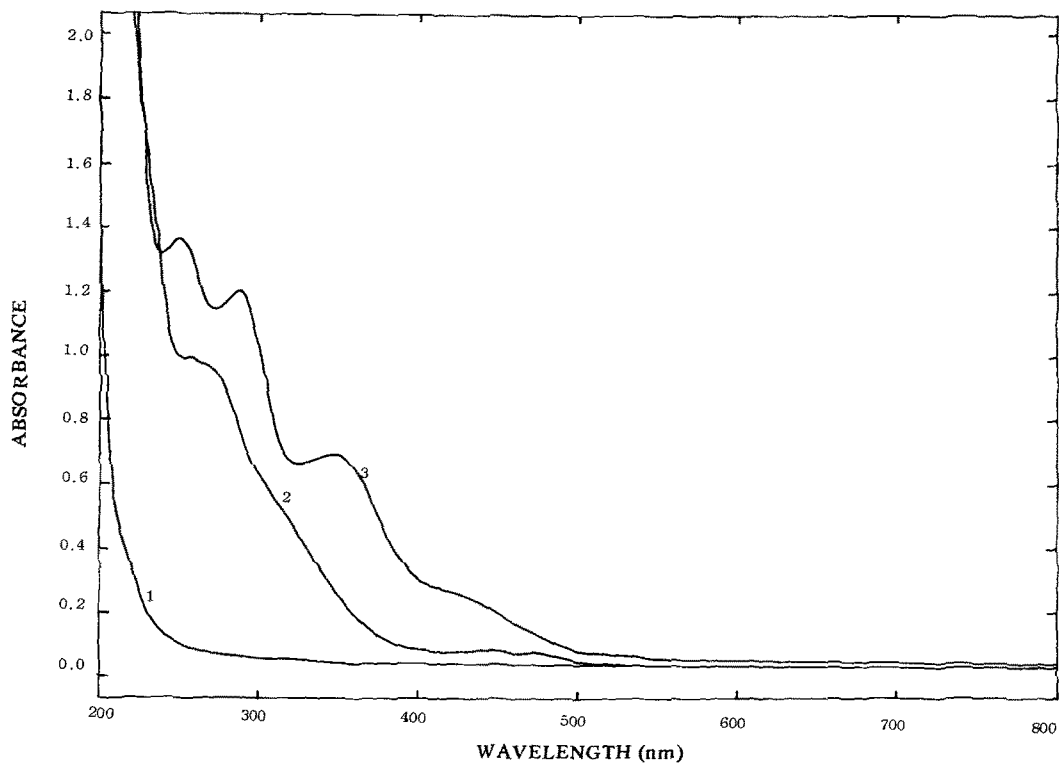

FIG. 4. Ultraviolet-visible spectra of e.RPO (100). 1, solvent: iso-octane ethanol (1:1); 2, extract, and 3, extract + alkali.
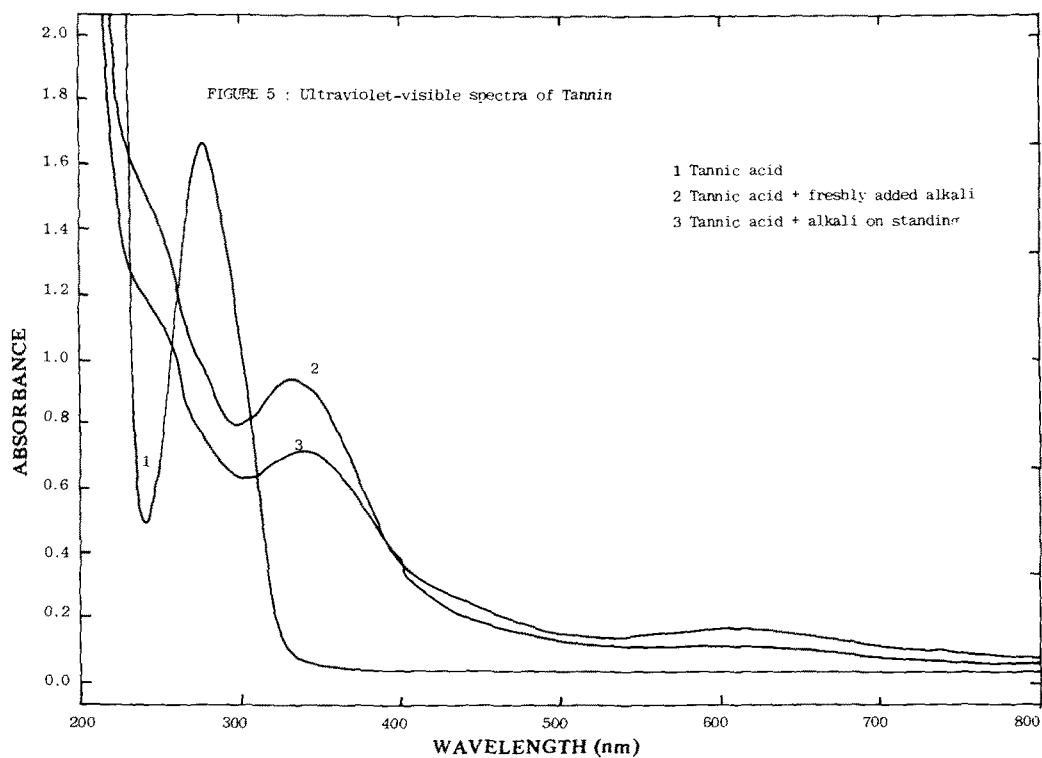
FIGURE 5 : Ultraviolet-visible spectra of Tannin

1 Tannic acid
2 Tannic acid + freshly added alkali
3 Tannic acid + alkali on standing

FIG. 5. Ultraviolet-visible spectra of tannin. 1, tannic acid; 2, tannic acid + freshly added alkali, and 3, tannic acid + alkali on standing.
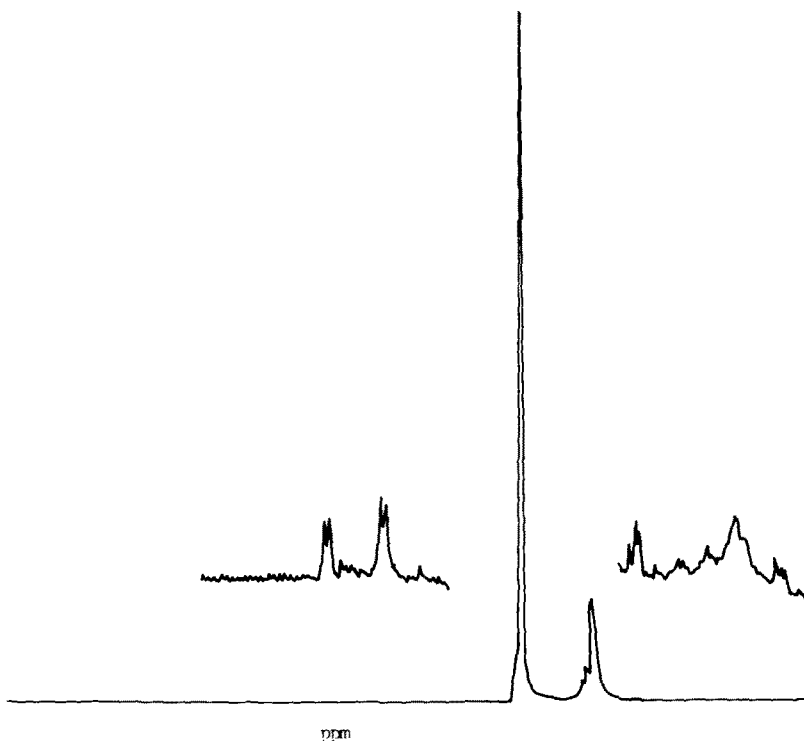
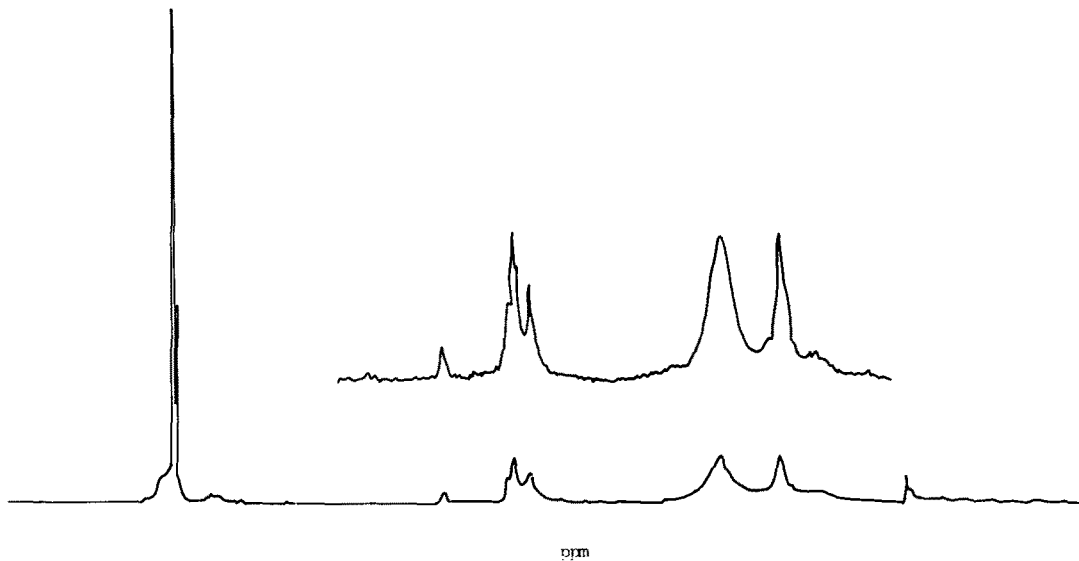**FIG. 6. The NMR spectrum of un.RPO in D_2O.**

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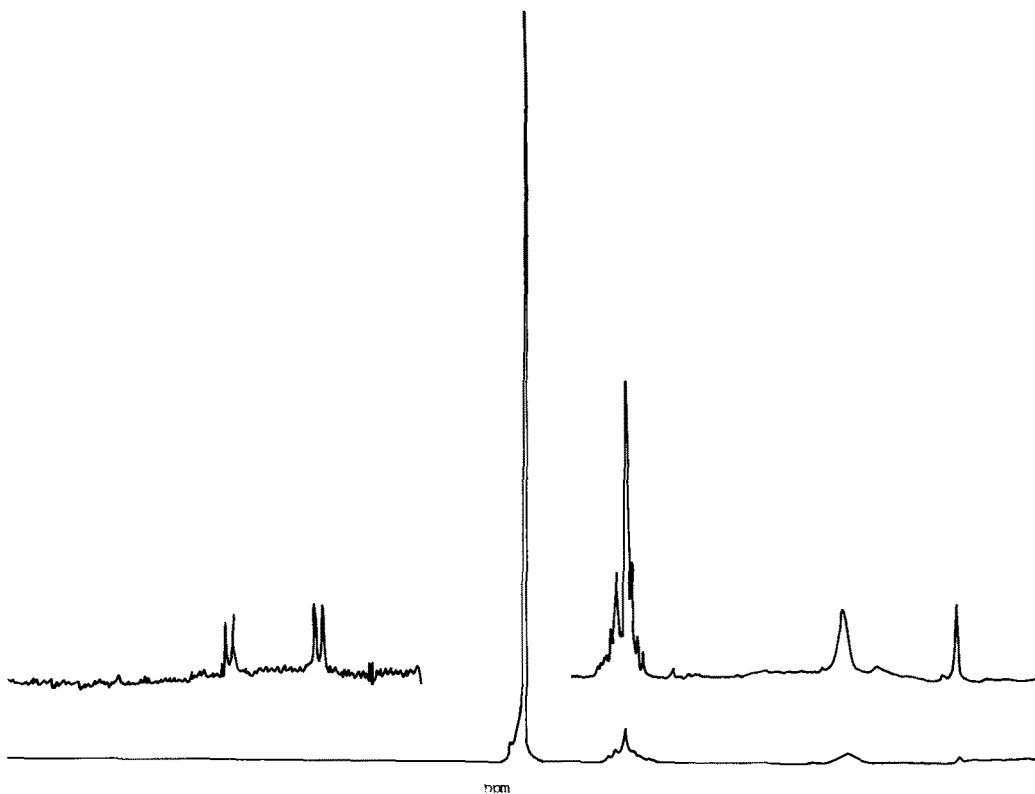
FIG. 7. The NMR spectrum of un.RPO in CDCl₃.

FIG. 8. The NMR spectrum of e.RPO (100) in D₂O.

darkening of palm oil as compared to other edible oils.

The extracts could be tannin or precursors of tannin. If these precursors were present in the palm fruit and subsequently in the oil, they could have been converted into tannin during the refining process. Further heating of the oil might have caused progressive polymerization into larger molecular weight tannin and therefore darker colored oils.

The principal findings of the investigation were that color darkening in refined palm oil was caused by com-

pounds present in the crude oil. These compounds were not removed during the refining process and when heated underwent changes which resulted in rapid heat darkening. Pretreatment of the crude oil was necessary to remove the color precursors and to retard darkening. Analyses showed that the compounds responsible were phenolic in nature and were probably associated with tannin present in palm fruit itself. One of the compounds was identified as para-hydroxybenzoic acid. The exact structure of the other
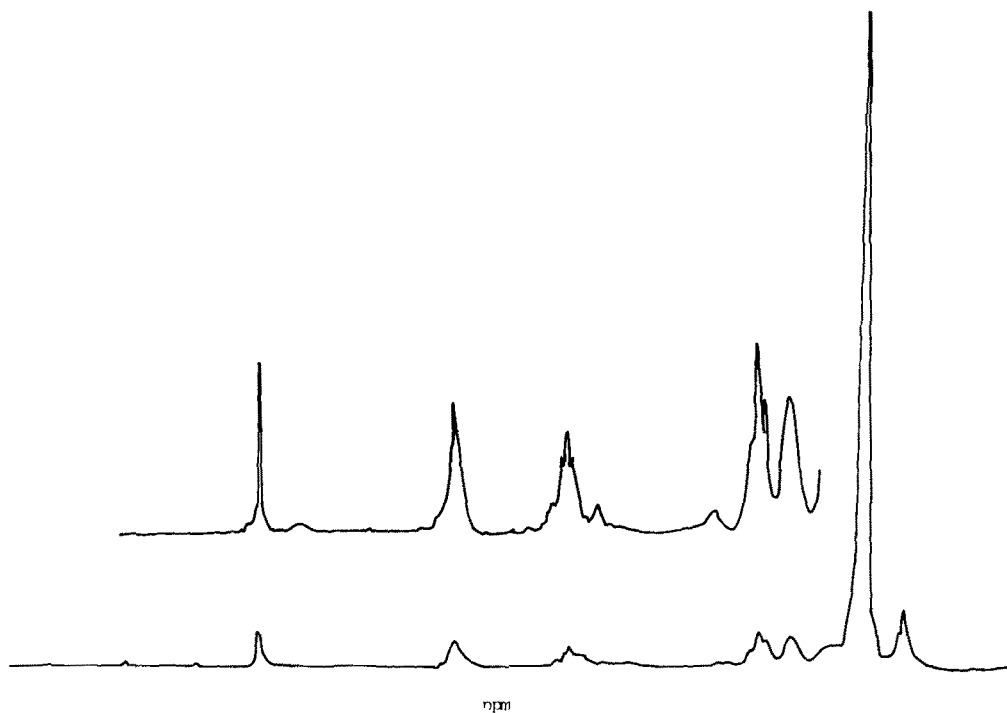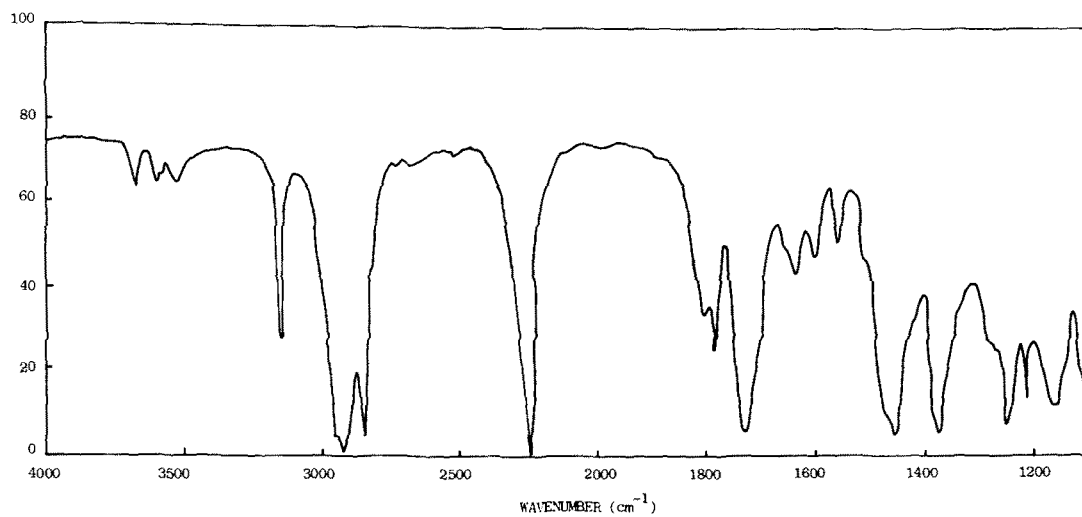
npm

FIG. 9. The NMR spectrum of e.RPO (100) in CDCl$_3$.

WAVENUMBER (cm^{-1})

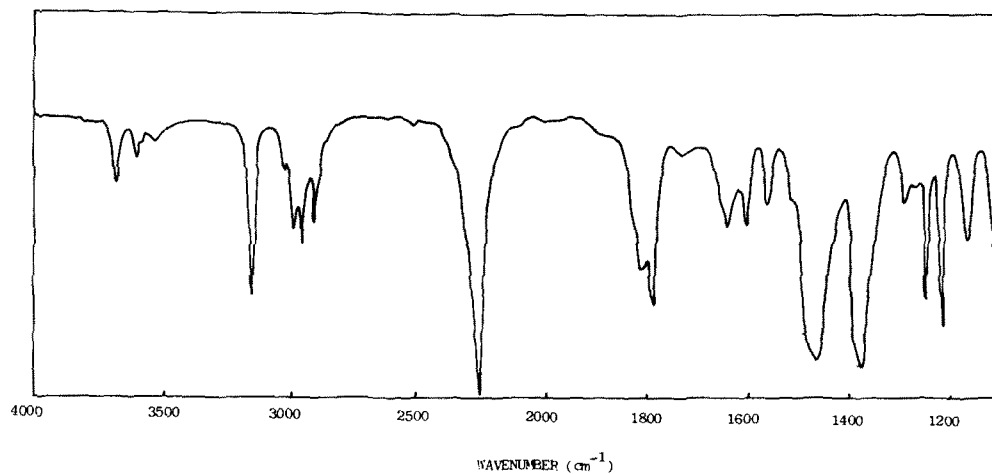FIG. 10. The IR spectrum of e.RPO (100).

WAVENUMBER (cm^{-1})

FIG. 11. The IR spectrum of un.RPO (100).

compounds is still being studied, but preliminary tests indicate the presence of a para-disubstituted aromatic system with possible presence of $-NH_2$ groups.

One of the major uses of oils is for frying. According to Lantz and Carlin (9), frying oils often are discarded when their Lovibond red color increases from 1.5-3.5 to 20-30 units. One of the problems with palm oil is that it darkens rather quickly during frying, although this does not indicate rapid oxidation and should not be used as a guide to the oil quality (10). The study of the cause of this rapid heat darkening and its prevention is important because of this.

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✺The "Hard" and "Soft" Surfactant Profile of Israel Municipal Wastewaters

URI ZOLLER, Division of Chemical Studies, Haifa University - Oranim, The School of Education of the Kibbutz Movement, P.O. Kiryat Tivon 36910, Israel

ABSTRACT

A study of mapping and field monitoring of Israel's municipal sewage wastewaters in respect to the content, distribution and the initial nonbiodegradable-biodegradable ratio of surfactants in them has been undertaken over the central and northern parts of the country under in vivo conditions.

Typical concentrations of nonionics (mainly "hard" alkylphenol-based ethoxylates) and anionics (mainly the "soft" LABS) in influents were found to be within the range of 1.1-2.2 and 9.6-10.6 mg/liter respectively. In (treated) effluents, the corresponding concentrations are 0.3-0.45 and 0.3-4.3 mg/liter.

The above is in accordance with current world trends following the switch to biodegradable surfactants. However, the concentrations of nonionic surfactants in the municipal wastewaters are surprisingly low in view of the preferred consumption of "hard" nonionic surfactants in the local market.

It is concluded that 20-40% of all nonionic surfactants discharged into municipal sewage, additional amounts of their metabolites and some of the anionic surfactants, too, find their way into receiving waters, because they resist substantial removal via only primary and secondary treatment.

INTRODUCTION

The annual world production of all kinds of surfactants mainly for household and industrial cleaning formulations already has passed the 17 million ton mark (1,2). The extent, mechanism and rate of biodegradation of the various synthetic anionic and nonionic surface active agents (3,4) under aerobic and anaerobic conditions are critical to the pollution of water resources, with the plethora of technological and environmental consequences involved (5-7).

The increase in environmental concerns is worldwide, and the urgent need to use more reclaimed wastewaters of various sources will undoubtedly affect the future development, use and economics of the detergent industry. All kinds of surfactants (anionic, nonionic and cationic), ultimately find their way into either man-made sewage systems or natural surface and ground water bodies. Consequently, surfactants are a significant factor in the municipal sewage profile (8) which, in turn, determines both the possibility of the sewage water's reuse after appropriate

purification processes and the efficiency of the latter (5). Currently, the main uses of reclaimed municipal wastewater are agricultural irrigation (restricted and unrestricted), industrial recycling (mainly for cooling and washing purposes) and ground water recharge (8-10).

In Israel, which is a model of efficient water utilization (11), natural water resources have reached almost the limit of practical exploitation. Within two years, about two-thirds the total volume of sewage collected by sewers will be used for agricultural purposes (12).

Alongside the biodegradable anionic LABS, "hard" (nonbiodegradable) nonionic surfactants of the ethoxylated alkylphenol type currently are the most commonly used nonionics in the country (13). The situation concerning household detergent formulations has no parallel in other Western industrial countries (14). Furthermore, a substantial portion of the country's municipal wastewaters is dumped directly into the Mediterranean Sea without any treatment, while the remaining portion reaches other surface water bodies after only a very brief preliminary treatment. The above facts make the determination of the surfactant content of our wastewaters imperative.

Mapping and monitoring of Israel's municipal sewage influents (15) as outlined in the Abstract would enable appropriate action on a national scale in terms of surfactant production and formulation, regulation, water resources management, future planning of the use of reclaimed treated wastewater and the protection of the environment.

RESULTS AND DISCUSSION

The concentrations of anionic (mainly LABS) and nonionic surfactants found in some representative municipal influents in the central and northern parts of the country are given in Table I. The determinations are based on the classical MBAS (16) method and the modified SDA-CTAS (17) method for the anionic and nonionic surfactants, respectively.

Since the given data represent about 60% of the collected municipal sewage, including different categories of