(boiling range, 63° to 70° C.). The crude lipids from the first and sixth Skellysolve F extractions showed a variation of 17.5 units in iodine number and of 23.42 per cent in phosphatides. Those from the first and fifth Skellysolve B extractions showed a variation of 10.1 units in iodine number and of 17.33 per cent in phosphatides. With each solvent the series of intermittent extractions removed approximately 97 per cent as much oil as did an analytical quantitative extraction using that same solvent. The variation in percentages of the saturated and unsaturated acids was determined and found to be small. No preferential extraction of any glyceride was found. The Skellysolve B removed about the same amount of unsaponifiable matter, and slightly more than twice the weight of phosphatides, as was extracted by the Skellysolve F.

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Azo Dyes From Oleic Acid[1]

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Previous publications on the chemical conversion of oleic acid to useful products have described the arylstearic and sulfoarylstearic compounds (1, 2). The present report concerns the mononitration of the arylstearic compounds and the azo dyes which may then be prepared by the further application of typically aromatic reactions.

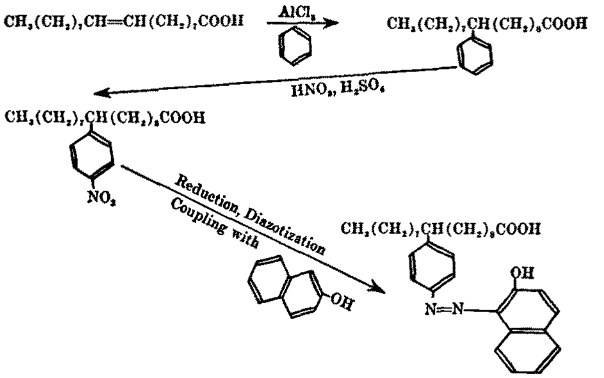
Phenylstearic acid, prepared by the Friedel and Crafts reaction between oleic acid and benzene in the presence of anhydrous aluminum chloride, is a viscous uncrystallizable oil. Nicolet and deMilt found that dinitrophenylstearic acid, which they prepared in an attempt to form a crystalline derivative, was likewise a viscous oil (3). The mononitroarylstearic compounds which we have now prepared also fail to be crystalline, presumably because they are a mixture of the 9- and 10-isomers (4).

The arylstearic compounds may be smoothly mononitrated in yields of about 90 per cent by means of a mixture of concentrated nitric and sulfuric acids. A molar ratio of nitric acid to sulfuric acid to compound to be nitrated of 2.2:2.7:1 gave satisfactory results. The following compounds were nitrated: phenylstearic acid, tolylstearic acid, ethoxyphenylstearic acid, phenoxyphenylstearic acid, phenylundecylic acid and ethyl phenylstearate. After isolation, the purity of the nitro compound was determined by titration with standard titanium trichloride solution (5) using a slightly modified method which was found to give accurate results for nitro compounds and for oil soluble azo dyes of known purity. The nitroarylstearic compounds could not be purified by distillation under reduced pressure because of extensive decomposition occurring at about 150° C.

The calcium, monoethanolamine, and triethanolamine soaps of nitrophenylstearic acid are insoluble in lubricating oil. This behavior is unexpected since calcium phenylstearate is readily dispersable and may be used to improve the properties of a Diesel lubricant (6). The insolubility of the soaps as well as the instability of the nitro compounds at higher temperatures indicate that these compounds cannot be used as addition agents to lubricants.

In the case of mononitrophenylstearic acid, the presence of the nitro group in the para position of the benzene nucleus was established by oxidative degradation with sodium dichromate and sulfuric acid. p-Nitrobenzoic acid was isolated in a yield of 60 per cent and identified by the method of mixed melting points.

From selected nitroarylstearic compounds, dyes were made by the reduction of the nitro compound to the amine, diazotization of the amine, and coupling of the diazonium compound with β-naphthol or β-naphthylamine. Using phenylstearic acid as a typical example, the equations representing the preparation of azo dyes from oleic acid are as follows:



β-Naphthol-azo-phenylstearic Acid

The dyes prepared in this manner were β-naphthol-azo-phenylstearic acid, β-naphthylamine-azo-phenylstearic acid, β-naphthol-azo-tolylstearic acid, β-naphthol-azo-ethoxyphenylstearic acid and ethyl β-naphthol-azo-phenylstearate. All of the dyes were viscous red oils ranging in purity from 45 per cent to 65 per cent as determined by titration with standard titanium trichloride solution. The colors of the dyes in alcoholic solution were quite similar and varied from a light yellow to a deep red depending upon the concentration of the dye. The dyes are not very soluble in cottonseed oil, but are readily soluble in alcohol, benzene and other organic solvents and completely insoluble in water.

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Two of the dyes, β-naphthol-azo-phenylstearic acid and β-naphthylamine-azo-phenylstearic acid were compared with Orange SS and Yellow OB (permitted food colors analagous in constitution) using a recording spectrophotometer.* The results of these measurements are shown in Fig. 1. The four dyes were compared as 0.0005 per cent solutions in 95 per cent ethanol.

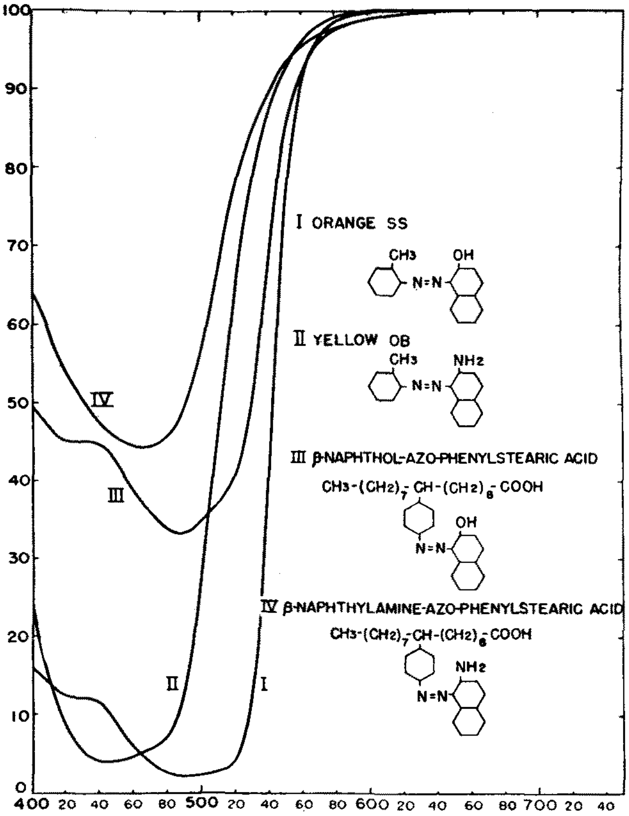

FIG. 1. Effect of length of side chain on transmittance.

It may be seen from the curves of Fig. 1 that the dyes from oleic acid furnish solutions less intense in color than do the corresponding simple aromatic dyes. The attachment of the long fatty acid chain on the benzene nucleus has had practically no effect on the hue. There is a marked resemblance between curves I and III (dyes made from β-naphthol) and between II and IV (dyes made from β-naphthylamine) which is to be expected.

In another series of experiments attempts were made to prepare dyes by coupling tetrazotized dianisidine with ethoxyphenylstearic acid, disodium sulfoethoxyphenylstearate and disodium sulfophenylstearate. Likewise, attempts were made to couple diazotized p-nitroaniline with p-aminophenylstearic acid. In all of these cases no dye formation was observed.

The dyes made from the arylstearic compounds do not appear to possess any obvious advantage over established commercial oil soluble dyes. They contain impurities, not readily removed, which would prohibit their certification as permitted food colors. Due to their high molecular weight and lower purity they furnish solutions less intense in color than solutions of equal weight concentrations of simpler and less expensive dyes.

The methods for the preparation of p-nitrophenylstearic acid and the dyes β-naphthol-azo-phenylstearic acid and β-naphthylamine-azo-phenylstearic acid are given in detail below. The other nitro compounds and azo dyes were prepared by similar methods.

Nitrophenylstearic acid. One mole (360 grams) of phenylstearic acid, b.p. 220-225°C./0.1 mm., was added dropwise to a well stirred mixture containing 198 grams of 70 per cent nitric acid and 278 grams of 95 per cent sulfuric acid (mole ratio $HNO_3:H_2SO_4:C_{24}H_{40}O_2 = 2.2:2.7:1$). During the addition, the temperature was kept below 60° C., after which the mixture was heated and agitated for one hour at 60° C. The cooled reaction mass was poured into ice water, the lower aqueous acid layer discarded, and the upper oily layer dissolved in ether. The ether solution was washed with water until acid free, dried over anhydrous calcium sulfate and filtered. The filtrate was treated with an activated carbon, filtered. and the ether evaporated under reduced pressure. The residue, 400 grams, was a pale yellow, viscous oil. Purity was estimated by titration for the nitro group. Weight of sample, 0.2276 g., 0.2302 g.; ml. 0.1035 N $TiCl_3$, 45.35, 45.65; ml. 0.1000 N $Fe_2(SO_4)_3 \cdot (NH_4)_2\ SO_4 \cdot 24\ H_20$, 16.93, 17.25. Calculated for $C_{24}H_{39}0_4$ N, 11.31 per cent—NO_2. Found, 10.11 per cent, 10.03 per cent. Purity of nitrophenylstearic acid preparation, 89 per cent. Yield, 88 per cent.

Aminophenylstearic acid. One mole (405 grams) of nitrophenylstearic acid was dissolved in 3.5 liters of glacial acetic acid and 528 ml. (6.0 moles) of concentrated hydrochloric acid. Zinc dust (216 grams, 3.3 moles) was added in small portions with occasional stirring, keeping the temperature at 95-100° C. during the addition, and for three hours afterward. Excess of zinc was filtered off. the solution was washed, dried, filtered, and the ether evaporated under reduced pressure. The residue, 380 grams, was a dark brown viscous oil which could not be distilled under reduced pressure. Calculated for $C_{24}H_{41}O_2$ N, 3.73 per cent N. Found, 3.40 per cent, 3.50 per cent.

β-Naphthol-azo-phenylstearic acid. One-half mole (188 grams) of aminophenylstearic acid was dissolved in a mixture of one liter of glacial acetic acid and 88 ml. (1.0 mole) of concentrated hydrochloric acid. The solution was cooled to 10° C. and a solution of 20 per cent sodium nitrite was slowly added until a starch iodide test indicated diazotization was complete. A solution was prepared containing one-half mole of β-naphthol (72 grams), 125 grams of sodium carbonate, 645 grams of sodium hydroxide and 3.5 liters of water, and then cooled to 10° C. The diazonium solution was slowly added with stirring to the solution containing β-naphthol. The mixture was stirred for one hour, allowed to come to room temperature, and extracted with ether. The ether solution was washed, dried, and the ether evaporated. The dye was obtained as a red, viscous oil (230 grams). Purity was estimated by titration. Weight of sample, 0.4202 g., 0.5760 g.: ml. 0.1035 N $TiCl_3$, 36.10, 36.00; ml. 0.1000 N $Fe_2(SO_4)_3 \cdot (NH_4)_2 \cdot SO_4 \cdot 24H_2O$, 17.40, 10.00. Dye purity, 63 per cent. Yield, 55 per cent (based on purity of dye).

β-Naphthylamine-azo-phenylstearic acid. One-half mole (72 grams) of β-naphthylamine in 750 ml. of 95 per cent ethanol was added, with stirring, to the

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* We are indebted to R. W. Stewart and S. H. Newburger, Federal Food and Drug Administration, for these measurements.

cold diazonium solution prepared as above. The mixture was stirred for 30 minutes, neutralized with a solution of 15 per cent sodium hydroxide, and the stirring continued for another 30 minutes. The dye was obtained by ether extraction in about the same yield and purity as for β-naphthol-azo-phenylstearic acid.

In the dyes made from the arylstearic compounds, the aromatic nucleus is in the middle of the fatty acid chain. It was of interest to compare these dyes with a dye similarly prepared from a compound having the aromatic nucleus at the end of a fatty acid chain. Compounds having such a structure are the alkyl aryl ketones described by Ralston and Christensen (7). For our purpose 4′-nitro-4-phenoxyphenyl heptadecyl ketone was selected, since it may be prepared directly from p-nitrodiphenyl ether and stearoyl chloride, by means of the Friedel and Crafts reaction.

We have followed the procedure described for preparing the ketone and have obtained a colorless crystalline product in a yield of 75 per cent, melting at 74-75° C. It is reported in the literature (7) that the compound resulting from this condensation melts at 177-178° C. The per cent of —NO_2 in the compound prepared in the present investigation was found to be 9.29 per cent (calculated for $C_{30}H_{43}O_4N$, 9.56 per cent) as determined by titration with standard titanium trichloride solution. This corresponds to a purity of 97.5 per cent. A control experiment using stearophenone showed that the carbonyl group consumed no titanium trichloride solution. The compound was also analyzed for nitrogen by a semi-micro Kjeldahl method with the following results: Calculated for $C_{30}H_{43}O_4N$, 2.91 per cent N. Found, 2.77 per cent, 2.87 per cent. To corroborate the point of attachment of the fatty acid part of the molecule to the aromatic part, the compound was oxidized by means of sodium dichromate and sulfuric acid. Pure p-nitrophenoxybenzoic acid was isolated in a yield of 10 per cent. It had a melting point of 235-236° C. (literature, 236° C. [8]) and a neutralization equivalent of 255 (calculated for $C_{13}H_9O_5N$, 259). From this nitro compound a dye was prepared by the procedure previously described, except that the amine was a solid and could be separated by filtration. β-Naphthol was used as the second component. The dye obtained was a red solid, soluble in organic solvents and readily soluble in cottonseed oil, on heating. The purity of the dye was found to be 64 per cent.

Summary

The preparation of mononitration products of arylstearic compounds derived from U.S.P. oleic acid has been described. Oil-soluble azo dyes have been prepared from the nitroarylstearic compounds by reduction, diazotization, and coupling with β-naphthol or β-naphthylamine.

4′-Nitro-4-phenoxyphenyl heptadecyl ketone has been prepared by the Friedel and Crafts reaction and an azo dye has been prepared from the ketone.

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Ceylon Candlenut Oil Aleurites moluccana (Linn.) Willd

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Barry (5), reporting on a sample of Candlenut or Lumbang oil and of the corresponding seeds from Malaya, stated that the iodine values of the oils (the original and that extracted from the seeds) were considerably lower than those recorded by Lewkowitsch (12) and Gardner (7) for Philippine oils. The present author, in connection with a survey of Ceylon vegetable oils, has examined a sample of seeds of *Aleurites moluccana* (Linn.) Willd. (known locally as "tel-kekuna"), grown at Peradeniya, Ceylon. The oil from this source had Iodine value (Wijs) of 160.0.

A fairly wide survey of the literature, summarized in Table I, has failed to reveal any significant difference in the range of the iodine value and other constants between oils from Malaya, the Philippines, and other sources. Certain earlier records have been omitted from the table since some doubt must attach to their reliability. Thus that of Lach, quoted by Mitchell (23), clearly refers to some other species, the iodine value of 118 being much below the usual range and the acids having the unusually high solidification point of 56°C. Fendler (24) again, referring to a sample of oil from the Cameroons, gives an iodine value of 114.2 and here, too, the reference is possibly to some other species, although the other particulars recorded (including the percentage oil in the kernels) are more normal; whilst Lespinasse (25) has reported the unusual saponification value of 175 and an iodine value of 137; and also states that 100 kilos of "nuts" give 7-10 kilos of kernels, though this percentage of 7-10 may be based on the weight of the fruits and not that of the seeds.

It is not thought that abnormally low iodine values are usually to be explained by assuming that the samples suffered deterioration from long storage, since a sample of oil I.V. 160.0, kept in an ordinary stoppered bottle without special precaution, had after two years I.V. 156.1.

Additional confusion has crept into the chemical literature concerning the botanical nomenclature of