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The Aromatization of Linoleic Acid with Palladium Catalyst[1]

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CERTAIN METALS are known to catalyze the isomerization of double bonds in unsaturated fatty acids. Since it has been postulated that isomerization and conjugation are preliminary steps in the polymerization of linoleic acid, attempts were made to polymerize linoleic acid and its methyl ester in the presence of palladium, one of the more active metal catalysts.

Very little polymerization took place at 270°C. Instead part of the linoleic acid cyclized, and the cyclic acid was dehydrogenated to give an aromatic ring. The hydrogen released was accepted by part of the unsaturated acids. It is likely that other hydrogen transfer catalysts would also be effective. Aromatization of hydrocarbons has been shown to occur in the presence of oxide catalysts, but at much higher temperatures (1).

The reaction product was separated (as methyl esters) into its various constituents by fractional distillation, and the fractions were examined. It was found that a very small part of the original fatty acids had been decarboxylated to give unsaponifiable matter and that linoleic acid had been converted to less unsaturated compounds. There was an increase in the contents of saturated and mono-olefinic acids although no hydrogen had been introduced into the system. A fraction amounting to about 15–16% of the total was found to have unusual properties—very low iodine number, very high refractive index, and a boiling point just above that of stearic acid.

Formation of cyclic monomer from linoleic acid has been suggested before in the literature (2–8) although it has never been identified or the ring size determined.

A cyclic monomer, containing an aromatic ring, formed by aromatization in the presence of palladium, would show the properties found in the unusual fraction obtained from the reaction mixture—low or negligible iodine number, high refractive index, and high boiling point. In addition, spectral analysis of this fraction would indicate the presence of an ortho dialkyl benzene.

Oxidation of the fraction rich in this material gave an oxidation product which, according to ultraviolet analysis, contained a polycarboxy benzene although in such small quantity that it could not be isolated.

This preliminary evidence was confirmed by experiments in which pure methyl linoleate was heated with a catalytic amount of palladium. From this reaction mixture was obtained stearic acid and a concentrate rich in aromatic content. Oxidation of this concentrate yielded phthalic acid, which was isolated and identified.

The findings are significant in that they give positive evidence of cyclization of linoleic acid and show that aromatic compounds can be formed by heating fatty materials with metal catalysts. This is accompanied by transfer of hydrogen to saturate olefinic double bonds.

Experimental

Reaction of Tall Oil Fatty Acids with Palladium Catalyst. A mixture of 300 g. of tall oil fatty acids (General Mills Aliphat 44A) and 15 g. of 10% Pd-C catalyst was charged into a 1-liter, stainless steel autoclave. The autoclave was flushed with nitrogen and then sealed. The mixture was agitated and heated to 270°C., then held at that temperature for 6 hrs. with constant agitation. It was cooled, removed from the autoclave, and diluted with 400 ml. of Skellysolve C. The catalyst was filtered off, and the solvent was distilled from the filtrate. There was obtained a semi-solid mass (completely fluid at 46° C.) in place of the original liquid acids.

Analytical data are given below.

Original Acids		Reaction Product	
Acid No.	194.9	Saponification No.	149.3
Saponification No.	196.5	Iodine No.	30.7
Unsaponifiable	2.4%	Conjugated linoleic acid	0
Saturated acids	7.1%	Trans C=C (on ester)	28.4%
Rosin	1.3%		
Iodine No.	125.5		
Total linoleic acid	44.2%		
Conjugated linoleic acid	6.6%		
Linolenic acid	0		
Trans C=C (on ester)	0		

Isolation of Ketone from Reaction Product. Forty grams of the product from the reaction described in the preceding paragraph were dissolved in 200 ml. of hot 95% ethanol, and the solution was allowed to cool at room temperature. The precipitate which formed was separated (m.p. 61–62°) and recrystallized from hot acetone. A very small amount of crystals (m.p. 80–82°) was obtained. A mixed melting point with authentic stearone showed no depression. Later distillation data show however that very little of the stearone or related ketones of similar molecular weight could be present.

Distillation of Reaction Product. Polymer formed by heating tall oil fatty acids with Pd-C catalyst was determined by distillation. A sample (200 g.) of the product from the reaction was distilled under reduced pressure, using an alembic still. The maximum pot temperature was 193°C.

Total distillate (B. P. 87/0.1 mm. to 176/.08 mm.)	183.2 g
Pot residue	8.9 g.
Trap (dry ice)	5.2 g.
Total	197.3 g.

Total polymer—not over 4.5% (including ketones)

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Preparation of Methyl Esters. The distillate obtained as described in the previous paragraph was esterified by refluxing with methanol (7.7 cc./g., with 2% concentrated sulfuric acid catalyst).

The esters were recovered in the usual manner.

Acid No. 2.7.

Fractional Distillation of Methyl Esters. A portion (140 g.) of the methyl esters of the reaction product, prepared as just described, was subjected to fractional distillation in a Podbielniak Hyper-Cal column. Distillation was conducted at a head pressure of 4.5–5 mm. and a reflux ratio of 10:1.

Fractions were collected and analyzed. An attempt was made to cut fractions at constant-boiling levels, whenever possible. The data for the distillation are shown in Table I.

TABLE I

Fractional Distillation of Monomeric Methyl Esters of Palladium-Treated Acids in Podbielniak Column

Fraction No.	Weight	B. P. °C./5 mm.	Iodine No.	Sap. No.	n_D^{45}
1	2.18	114–131	70.8	—	1.4453
2	10.32	131–125	72.7	3.2	1.4380
3	3.68	125–136	61.5	4.0	1.4350
4	8.84	136–140	37.0	2.0	1.4353
5	3.20	140–164	10.3	118.1	1.4440
6	5.44	164–170	13.5	186.0	1.4390
7	4.36	170–181	45.3	167.5	1.4550
8	5.85	181–187	42.4	176.8	1.4510
9	11.58	187–186	29.7	186.1	1.4482
10	10.82	187–187	25.3	188.4	1.4470
11	9.61	187–188	21.9	189.4	1.4472
12	11.08	188–186	19.3	190.2	1.4467
13	10.54	186–183	17.1	190.5	1.4471
14	7.69	183–146	13.9	189.5	1.4490
15	21.95—Pot residue; not enough to push through				

Then the pot residue was distilled through an alembic still to give 20.2 g. of distillate—B. P. 127–134/.03 mm., sap. no. 176.8, iodine no. 25.7, n_D^{45} 1.4771.

The analytical data for the fractions listed in Table I show that the first four fractions (about 18% of total) consist largely of low-boiling unsaponifiables. Fraction 5 is an intermediate fraction while fraction 6 seems to be largely methyl palmitate. Fractions 7 and 8, again, are intermediate fractions, probably containing methyl palmitate, mono-olefinic esters, and unsaponifiables. Fractions 9 to 14 appear to be mixtures of mono-olefinic esters and methyl stearate, with the ratio of stearate to mono-olefins increasing in the later fractions. Fraction 14 probably also contains a little of the material later found concentrated in fraction 15 (as the refractive index indicates). The mono-olefin stearate mixtures accounted for about 43.5% of the total.

Fraction 15 amounted to 15–16% of the total. It had very unusual properties — low iodine number, very high refractive index, and boiling point just higher than methyl stearate.

About 9% of the material subjected to fractional distillation was not accounted for and must have been lost during the manipulations.

Purification of Final Fraction from Distillation. It was clear that one of the important changes which took place during the treatment of the tall oil fatty acids with palladium was the disappearance of linoleic acid. The data also indicated a pronounced drop in total unsaturation (as measured by iodine number) and a suggested increase in saturated acid content. Since the polymer formation was almost negligible and since no hydrogen had been introduced into the reaction system, the disappearance of linoleic acid and the drop in iodine value were difficult to explain. Cyclic monomer formation followed by disproportionation offered one possible explanation. The situation has a parallel in the disproportionation of rosin acids in the presence of fatty acids with palladium or nickel catalysts (9).

The drop in iodine number would be explained by a) the fact that aromatic substances show little or no unsaturation as measured by iodine number and b) part of the original unsaturated acids were partially or completely reduced by hydrogen released during aromatization.

The key to the whole question seemed to lie in the composition of the final fraction from the distillation of the methyl esters of the reaction mixture. Attempts therefore were made to purify the fraction. A solution of 12.96 g. of the distilled product was dissolved in 130 g. of methyl isobutyl ketone, and the soluton was passed through a column (wetted with the ketone) of 44.6 g. of urea. The column measured 2½ feet long by ¾ in. diameter. Then 130 g. more of methyl isobutyl ketone were passed through the column. The eluates were combined and washed four times with warm water to remove urea. Distillation of the solvent left a cloudy oil, which was clarified by dissolving in chloroform and filtering. The yield of clear oil was 9.8 g. This process should have removed all the methyl oleate and methyl stearate which may have been present.

Unsaponifiable matter was removed by heating a mixture of 5.9 g. of the product from the urea treatment, 1.3 g. of potassium hydroxide, and 25 ml. of 95% ethanol under reflux for 1½ hrs., diluting with 50 ml. of water, and extracting with five 15-ml. portions of ether. The soap solution which was left was acidified and the acids isolated by ether extraction.

Unsaponifiables removed	0.65 g.
Acids recovered	4.7 g.

Preparation of Methyl Ester. The acids (4.7 g.) freed of unsaponifiable matter as just described were heated under reflux for 1 hr. with a solution of 6 drops of concentrated sulfuric acid in 40 g. of methanol. The ester was separated by means of Skellysolve C, washed, dried, and isolated from the solvent. The yield was 4.4 g. This sample was expected to contain aromatized cyclic monomer methyl ester. It was virtually free of methyl linolenate, methyl linoleate, methyl oleate, methyl palmitate, methyl stearate, and unsaponifiable matter. Analytical data are given below:

Saponification No.	192.8
Iodine No.	9.4
n_D^{20}	1.4862[a]
Ultraviolet analysis	No linoleic acid; evidence for aromatic ring in benzene region.
Infrared analysis	No *trans* double bonds; evidence for aromatic ring and probable ortho substitution at 14.3, 13.3, and 6.7 microns.

[a] The cyclized and aromatized monomer of methyl eleostearate is reported (10) to have n_D^{20} of 1.4946.

Oxidation of Methyl Ester. A solution containing 3.2 g. of potassium permanganate and 0.3 g. of potassium hydroxide in 100 ml. of water was prepared. To it was added 0.7 g. of the purified methyl ester prepared from the unsaponifiable free-acids just reported. The mixture was stirred and heated under reflux for 6 hrs. Very little change was observed. The methyl ester was still unsaponified. In order to bring the ester into solution so that it could be saponified and oxidized enough acetone (75 ml.) was added to give a clear solution. The mixture was stirred, and the acetone was distilled out. Disappearance of the oily layer showed that the ester had been saponified during this treatment while the permanganate color also disappeared and a brown precipitate of manganese dioxide formed. Portions of 3.2% permanganate solution were added from time to time to the refluxing mixture as the oxidizing agent was gradually used up. From then on powdered potassium permanganate was added as needed. A total of 32 g. of potassium permanganate was required before permanent purple color persisted. This is much more than the theoretical 9.6 g. needed to oxidize the suspected aromatic ester to phthalic acid, and the excess is partly accounted for through oxidation of acetone left in the reaction mixture. A few drops of 1% sodium bisulfite solution were added to destroy the remaining permanganate, and the mixture was filtered while hot. The precipitate of manganese dioxide was washed with three 100-ml. portions of hot water. The filtrate and washings were combined and treated with 0.7 g. of barium hydroxide. No precipitate formed. The mixture was concentrated on the steam bath, under reduced pressure, to about 50 ml. and then acidified to litmus with dilute hydrochloric acid. The concentrate was taken to dryness on a steam bath in an evaporating dish.

Identification of Phthalic Acid. The dry residue from the oxidation just described was extracted in a Soxhlet apparatus with 80 g. of glacial acetic acid for 7 hrs. The extract was taken to dryness, and the residue was examined. The burning of a small portion indicated that it contained both organic and inorganic (KCl) matter. A few attempts at crystallization were unsuccessful. Therefore all of the residue was dissolved in 95% ethanol, the solution was diluted to known volume, and the ultraviolet absorption characteristics were determined alongside those of a known sample of phthalic acid. Extinction coefficients reported for the oxidation product are not absolute values since the concentration of active principle in the residue was not known. However the curve shape and the general relationships are correct as given. The ultraviolet absorption data are shown graphically in Figure 1.

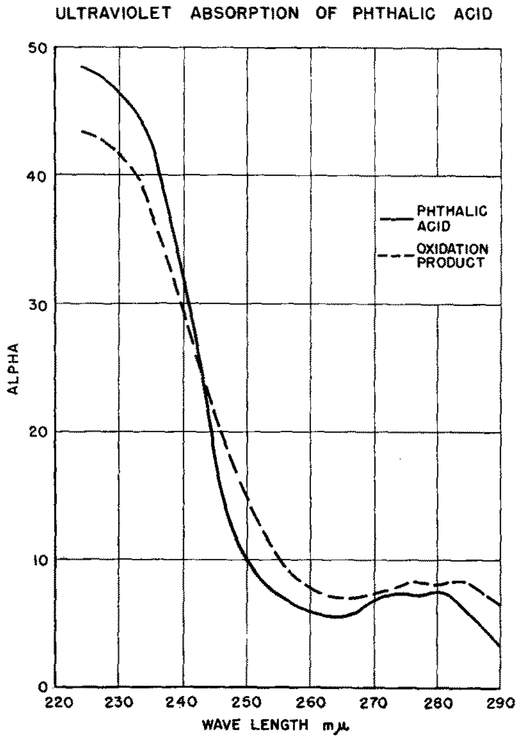

Fig. 1

The absorption data suggest the presence of polycarboxybenzene.

An attempt to prepare phthalic anhydride by heating the residue and to isolate the anhydride by sublimation was not successful. Charring and decomposition occurred without sublimation.

In view of these findings it was decided to repeat the work, using methyl linoleate in place of mixed fatty acids.

Starting Materials. Methyl linoleate was prepared from the methyl esters of safflower oil by exhaustive treatment with urea in methanol. The crude ester was distilled in a cyclic molecular still. The product showed: $n_D^{30} = 1.4571$; I. V. (refs.) 170.5 (Theoj. 172.4); oc [1 mg./l., 1 cm. KOH glycol 25 min. 180° (ref. 1)] = 87.5 at 2.33 mμ. The 10% palladium on charcoal was obtained from Baker and Company. The reagents used were of reagent grade.

Reaction of Methyl Linoleate with Palladium Catalyst. Methyl linoleate (200 g.) was heated at 270° ±5 for 6 hrs. with 5% (10 g.) of catalyst (10% Pd on charcoal). Ester, catalyst, and thermometer were placed in a one-liter ampule, degassed finally at 150° under high vacuum, and sealed. Insulation and protection from explosion hazard were afforded by glass wool.

The recovered ester showed: $n_D^{30} = 1.4625$; I. V. (refs.) = 43.9; α 233 after isomerization = 1.5 (no peak) (11). It was recovered by suction filtration (clear filtrate) and washed with methanol (cloudy, colored filtrate). The combined filtrates were stripped of solvent, treated with 10–20 g. of Celite, filtered, and washed with hexane. Removal of solvent gave 170 g. of clear light-colored ester.

Segregation of Methyl Linoleate Product by Urea. The ester was separated into an adduct-forming fraction of 58% (40% mono-olefinic, 18% methyl stearate) and a non-adducting fraction of 37% (30% monomeric, 7% polymeric). Loss was 5% (probably in aqueous urea).

First Urea Fraction. The ester (160 g.) was dissolved in 2,400 ml. of warm methanol containing 800 g. of urea. More urea or less alcohol caused oiling out. After over-night crystallization at room temperature the adduct was filtered with suction and washed with methanol saturated with urea. The wet crystals (330 g.) were dissolved in 1,500 ml. of methanol and recrystallized at −12°. The filtered, dried, crystals weighed 266 g. The adduct was dissolved in 750 ml. of warm water, and the ester layer was separated. The water layer was treated with 100 ml. of concentrated HCl in 250 ml. of water and extracted with four 200-ml. portions of hexane at 60–65°. The combined extracts and ester layer were twice washed with dilute HCl and then with water. The recovered ester weighed 65 g. It was flash-distilled *in vacuo* to yield 63.5 g. of colorless distillate, which showed: $n_D^{20} = 1.4450$; I. V. = 51.4, no normal linoleate or conjugated linoleate by spectral analysis. Infrared indicated considerable *trans* double bonds.

Fifty grams were crystallized at +15°C. from 250 ml. of methanol and again from 100 ml. of methanol. The dried crystals weighed 14 g. (m.p. 36–37°C., iodine value 9.4, trace of *trans* double bonds).

This ester was identified as mostly methyl stearate by conversion to the hydrazide. Yield of purified hydrazide was 87% (m. p. = 115–116°, m. p. of authentic stearic hydrazide = 115.5–116.5, m. p. 1–1 mixture = 115.3–116.5).

The combined ester filtrates yielded liquid esters weighing 35.5 g. ($n_D^{20} = 1.4466$, iodine value 68.4, much *trans* double bonds). It is concluded that this fraction contained about 79% mono-olefins (mostly *trans*) and 21% of saturates.

Second Urea Fraction. The combined filtrates from the first urea fraction were warmed to give a clear solution which was stored over-night at —20°C. The filtered crystals were recrystallized at —20° from 600 ml. of methanol containing 100 g. of added urea. The esters were recovered from the 162 g. of dry crystals as before and weighed 21 g. [$n_D^{20} = 1.4512$, iodine value 82.3, both *trans* (10.31 μ) and *cis* (3.31 μ) double bonds by infrared]. It is concluded that this fraction was largely mono-olefin.

Third Urea Fraction. The combined filtrates from the second urea fraction were added to 1,600 ml. of methanol containing 900 g. of urea. The solution was crystallized at 23°C., filtered, air-dried, and then washed three times with 800-ml. portions of hexane. The 875 g. of dry crystals yielded 7 g. of liquid ester ($n_D^{20} = 1.4552$, iodine value 74.9, % conjugated linoleate = 2.1, no normal linoleate). Infrared showed little *trans* but considerable *cis* double bonds plus unusual bands at 13.3 and 14.3 μ.

Fourth Urea Fraction. The filtrate, but not washings, from the third urea fraction was evaporated to dryness under high vacuum. The dry crystals were washed with the hexane washings from the third fraction and then several more times with fresh hexane. The dry crystals weighed approximately 264 g. The recovered esters weighed 1 g. ($n_D^{20} = 1.4885$); no conjugated linoleate; iodine value 20.7; infrared shows very little *trans,* less 3.31 μ band, new bands at 3.23, 6.23, 6.68 μ, very strong 13.3 μ band, some absorption at 14.3 μ (as for the third fraction).

Fifth Urea Fraction. The combined washings were washed free of urea and stripped of solvent. This non-urea-adduct-forming fraction of esters weighed 58 g. ($n_D^{20} = 1.4868$). These were flash-distilled at 0.1 mm. to a pot temperature of 235°C. The distillate[2] weighed 46 g. ($n_D^{20} = 1.4874$). The residue weighed 12 g. ($n_D^{20} = 1.4852$). It is interesting to note that the distillate had a higher refractive index than the distillation residue.

From examination of iodine values and n_D^{20} of the urea fractions it was estimated that the linoleate was converted 30% to aromatic compounds, 40% to mono-olefins, 18% to stearate, and 7% to polymer (5% handling loss).

Podbielniak Distillation of Cyclic Methyl Esters. The above distillate was fractionated in a Podbielniak miniature Hypercal column at 15-mm. pressure (for log see Figure 2). Conjugated diene was present in traces (slight inflection near 230 mμ on a steep slope due to end-absorption, in early fractions). A new band at 255 mμ appeared in fraction 15, reached a maximum in fraction 17 (a = 1.75), and then decreased in fractions 18 and 19. It may be due to an alkene conjugated with a benzene ring or due to tetrahydronaphthalenes. A band, sharp and well separated, is prominent at 273 mμ in all fractions and is characteristic of ortho-dialkyl benzenes (Figure 3).

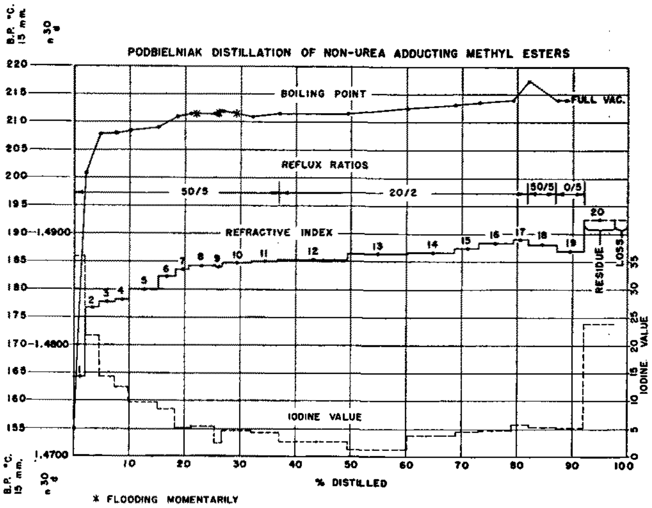

FIG. 2

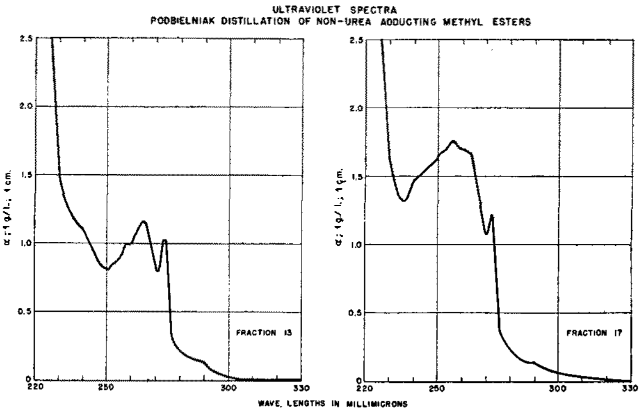

FIG. 3

The infrared spectra indicate that the first fraction which contains considerable low-boiling material differs from the others, that fractons 2 to 16 are similar, that 17 and 18 are transitional, and that 19 (Figure 4) is quite different (strong band at 13.5 μ instead of at 13.3 μ as in 2 to 16). The 13.3 μ band may be characteristic of the dialkyl benzene since it was found previously in the spectrum of aromatized, cyclic eleostearate. No assignment is made for the 13.5 band. Another band of unknown origin at 14.16 μ is present in fractions 1, 2, 18, 19, and 20.

Oxidation of Non-Urea-Adducting Methyl Ester. Since the 13.3 μ band was very strong in fraction 13 (Figure 3), this was oxidized, using a procedure similar to that used previously for aromatized cyclic eleo-

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[2] Sap. no. 192.7 (theory 193.2); I. V. 3.2; unsap. 1.75%; a-233 = 2.1 (after isomerization 1.5), a-268 = 1.1 (after isomerization 0.8), no peaks.

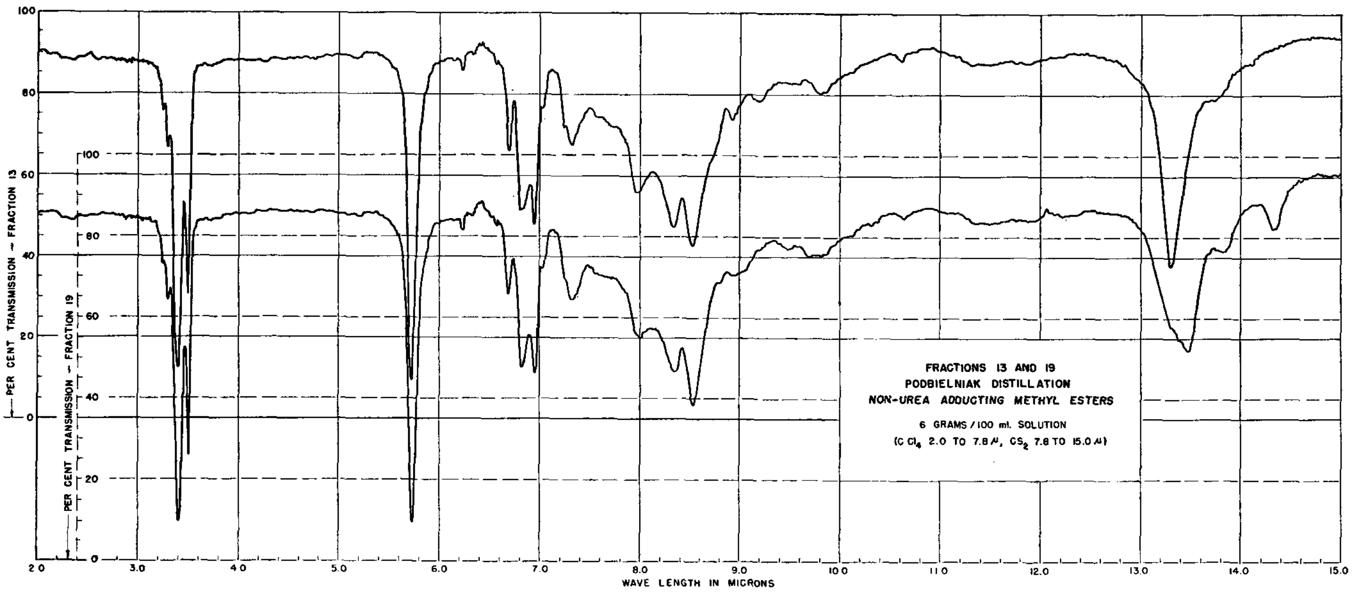

Fig. 4

stearate (ref. 4); 0.59 g. (0.002 moles) was brominated in 40 ml. of benzene by refluxing 3 hrs. with 0.712 g. N-bromosuccinimide (0.004 moles). The solvent-free residue (1.33 g.) was extracted 5 times with warm pentane (10 ml. each). (Wt. succinimide residue = 0.39 g.) The extracted dibromide was heated 17 hrs. at reflux in 50 ml. of 5% Na_2CO_3. The hydroxy acids were recovered from the acidified soap with three 20-ml. portions of ethyl ether. The ether was washed free of mineral acid and stripped off, to give 0.62 g. of pentane insoluble residue (theory = 0.65). Powdered $KMnO_4$ (1.68 g.) was added to a 100-ml. refluxing acetone solution of this residue in 3 hrs. The solution was refluxed another 2 hrs. and stripped of solvent. The MnO_2 was decolorized by adding 25 ml. of H_2O containing 2 ml. of concentrated H_2SO_4 and 1.44 g. of $NaHSO_3$. The solution was frozen, and the volatiles were removed over-night by high vacuum. The organic matter was extracted from the dry salts with several 10- to 15-ml. portions of ethyl ether. The ether was washed free of H_2SO_4, the washings were extracted with more ether, and this last was also washed. The residue from the combined ether solutions weighed 0.33 g.

This residue was sublimed in a 250-ml. beaker to a cold H_2O condenser (Pyrex 91,540, A.S.T.M. D-939) in an aluminum block air bath to 215°C. The sublimate consisted of an oil and characteristic phthalic anhydride crystals. This was crystallized from 1 ml. of CCl_4 and washed with 0.5 ml. CCl_4. Residue from the filtrate weighed 0.03 g. The crystals weighed 0.02 g. (6.8% theoretical) and melted 129–130°C. A mixture with pure phthalic anhydride (m.p. 131.0–131.6) melted 130.0–130.8.

Approximately 5 mg. of the crystals were heated on the steam bath with 1 ml. of concentrated NH_4OH. After 15 min. the last traces of volatiles were removed at room temperature by high vacuum. The residue melted 225–230°C. A mixture with pure phthalimide (m.p. 233–234°C.) melted 228–233°C. The residue was heated in 2 ml. of boiling toluene and cooled to 0; the solvent was removed with a medicine dropper capillary. The dry residue melted 230–232°C. A mixture with pure phthalimide melted 232.0–233.5°C. It is concluded that the methyl linoleate was cyclized and aromatized by the hydrogenation catalyst.

Because of the low yield of phthalic anhydride all residues were recovered and resubjected to $KMnO_4$ oxidation. An additional 0.07 g. of crude (or 0.03 g. of purified) anhydride was obtained (total yield 16.8% of theory).

Since the above oxidation had been one on only one fraction of the Podbielniak distillation, it was repeated on the material used for the distillation charge. The procedure was the same except that 50% more $KMnO_4$ (2.52 g.) was used. The recrystallized phthalic anhydride weighed 0.034 g. (11.5% of theory) and melted 127.0–128.0. A mixture with pure anhydride (m.p. 131.0–131.5°) melted 127.0–129.0°C.

The product obtained by treatment with NH_4OH melted at 232.5–233.5. A mixture with pure phthalimide melted 233.5–234.2.

It is concluded that the non-urea-adducting esters consist largely of ortho dialkyl benzenes or of the material such as polycyclics, which would give phthalic acid by $KMnO_4$ oxidation.

Discussion

No simple mechanism for the cyclization and aromatization of linoleic acid is apparent. One possible pathway is dehydrogenation to a conjugated triene followed by an eleostearate type cyclization to a cyclohexadiene. This could then be readily dehydrogenated to the dialkyl benzene. On the other hand, the ease with which 6 carbon rings undergo dehydrogenation, as compared with linear compounds, suggests that cyclization may precede any dehydrogenation. It is conspicuous that disproportionation of unsaturated fatty acids, without accompanying cyclization, is not known although under the conditions of these experiments the life of any triene might be so short that detection of it as an intermediate would be very difficult.

Conjugated trienes conceivably could arise by 1,4-dehydrogenation of 2 active methylenes of normal linoleate or 1,6-dehydrogenation of a conjugated linoleate.

Summary

Hydrogen transfer catalysts are known to promote the elaidinization and conjugation of unsaturated fatty acid derivatives. More extensive reactions were indicated when palladium was tried as a polymerization catalyst. A subsequent study showed that methyl linoleate could be readily cyclized and aromatized in the presence of palladium.

Methyl linoleate was heated in an evacuated ampule for 6 hrs. at 270°C. with 5% of a 10% palladium on charcoal. The iodine value was lowered to 43.9 and the apparent linoleate content to less than 2%. The products were separated by urea segregation and distillation. They consisted of approximately 7% polymer, 18% methyl stearate, 40% monoolefins, and 30% of a methyl ester of an aromatic fatty acid (handling loss 5%). The aromatic material was readily oxidized to orthophthalic acid.

The mechanism by which aromatics, mono-olefins, and saturates are produced through cyclization and hydrogen transfer is not known, but possible routes are suggested.

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An Investigation of the Adsorption of Detergent and Builders Onto Cotton and Soil by Radiotracer Methods

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THE FACT THAT ANIONIC DETERGENTS are adsorbed onto textile fibers from aqueous solutions has been demonstrated by many studies, such as those of Neville and Harris (1), Neville and Jeanson (2), Gardiner and Smith (3), Aickin (4), Swanston and Palmer (5), and Flett, Hoyt, and Walter (6). Harris has published an excellent review of the adsorption of surface-active agents by fibers (7). That adsorption onto fibers does take place is not surprising since adsorption at interfaces is a manifestation of the surface-active properties of long-chain ions. Thus the lowering of surface tension, wetting and spreading action, foaming, emulsification, and peptization all involve adsorption of long-chain ions or aggregates of these ions at interfaces.

The effect of alkaline builders on the surface-active properties of typical detergents has been the subject of much research activity; for example, Harris (8), Merrill and Getty (9), Niven and Gadberry (10), and Morrisoe and Newhall (11) have shown that builders markedly enhance the surface activity of dilute synthetic detergent solutions and also improve detergent action, in a synergistic fashion, especially with polyphosphates. In order to utilize this synergistic behavior, commercial laundry materials are heavily built with alkaline salts. Molecularly dehydrated phosphates are widely used in formulations designed as cotton detergents. In view of the known adsorption of detergents onto textile fabrics and synergistic effects of builders in detergency, an exploratory study was made on the effect of various builders on the adsorption of a long-chain alkylbenzene sulfonate on cotton and soils. A study was also made of the adsorption of builders on cotton and soils. With one exception the adsorption was determined by means of radioactive techniques. The purpose of this study was to obtain data which might help explain the mechanism by which builders improve detergent action.

Materials and Reagents

Preparation of Radioactive Dodecyl Benzene Sulfonate. Radioactive dodecyl benzene sodium sulfonate, containing S^{35}, was synthesized in the following manner. Some 29 ml. of technical dodecyl benzene, b.p. 60–160°C. (0.3 mm.) were placed in a 3-neck flask fitted with thermometer, stirrer, and dropping funnel. The contents were cooled by partially immersing in ice water. Five ml. of freshly fumed sulfuric acid, containing the desired activity of S^{35} as sulfuric acid, was added to a mixture of 15 ml. of sulfuric acid (100%) and 4 ml. of fuming sulfuric acid (30%). The acid mixture, after being cooled in an ice bath, was added dropwise with continuous stirring over a half-hour period to the dodecyl benzene in the cooled flask. The ice water was replaced by a constant temperature bath at 40 ± 1°C., and stirring was continued for 2 to 2½ hours. The sulfonation mixture was transferred to an 800-ml. beaker, the flask was rinsed twice with 10 ml. of water, and rinsing was completed with 300 ml. of 95% ethanol. The alcoholic sulfonation mixture was then neutralized to a pH of 7–7.2 with sodium hydroxide solution (40%). The neutralized mixture was allowed to stand for 1 hr. to permit salts to settle and then was filtered through a Buchner funnel, using No. 40 Whatman paper. The residue was washed twice with 50-ml. portions of 95% ethanol. The filtrate was extracted three times with 50-ml. portions of petroleum ether to remove unreacted dodecyl benzene and then was evaporated on a steam bath. The residue was transferred to an oven and dried for 3–4 hrs. at 105°C. The residue was dissolved in absolute alcohol, and the solution was filtered and evaporated on a steam bath. The residue was dried for 3–4 hrs. at 105°C. and overnight over phosphorus pentoxide. The detergent had a specific activity of 0.1 microcurie/mg. Its sulfur content was 9.05% compared to the calculated value of 9.19% for dodecyl benzene sodium sulfonate. A stock solution

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