corn or pure ethyl linoleate autoxidized to a peroxide value of 78, when heated in t-butanol without added potassium, did not form an absorption maximum at 268 mμ (Table V). Furthermore the 20 hours of heat treatment did not produce any oxidation-conjugation in fresh extracts of corn. The samples from corn showed a maximum at 268 mμ only after heat treatment with alkali.

Gas-liquid chromatography of the methyl esters prepared from Corn C extract separated an amount of linolenic acid ester in agreement with the alkaline isomerization treatments. The experimental conditions were: flow rate, 70 ml. of helium/min.; temperature, 218°; sensitivity, 250 milliamperes; column (5 ft., ½ in. in diam.), Craig butanediol succinate. However this procedure did not clearly define a peak for methyl linolenate in the esters prepared from Corn A extract.

Summary

Potassium tertiary butoxide (1.1 M, 15.5%) in t-butanol readily isomerized linoleic and linolenic acids at 60°C. The absorptivity value for linoleic acid during isomerization rose rapidly, then slowly reached a maximum (88.5) after three days. Maximum absorptivity values for linolenic acid at both 233 mμ (68.5) and at 268 mμ (65.0) were attained at 12 hrs.; thereafter absorptivity at both wavelengths decreased with time.

Glycerol also reacted with potassium-t-butoxide under the experimental conditions to produce an absorption maximum at 267 mμ; however this absorbance was easily destroyed by treatment with hydrochloric acid.

A simple procedure has been described for isomerization with the alkoxide in a reagent bottle at 60° for 20 hrs. Analyses for linoleic and linolenic acids in five seed oils isomerized by the "bottle method" agreed well with results obtained by the A.O.C.S. KOH-glycol method.

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Acid-Catalyzed Addition of Phenols and Phenyl Ethers to Oleic Acid[1]

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OUR WORK on the addition of nitriles to unsaturated compounds (1, 2) suggested that other nucleophilic substances should add to the reactive center of oleic acid in strong acid media, that is, in the presence of carbonium ion-producing substances. In this paper we are reporting the addition of phenols and phenyl ethers to oleic acid in a sulfuric acid medium and also in the presence of an acid ion-exchange resin catalyst. We are also reporting on the structure of the reaction products based on infrared absorption spectra.

Although isolated instances of reactions between phenols and unsaturated compounds have been known for a long time, Niederl and co-workers (3) examined the reaction more closely and applied it to several types of unsaturated compounds. Later m-cresol (4) and phenol (5) were added to oleic acid in the presence of concentrated sulfuric acid. Stirton and co-workers (6) have reported the addition of aryl ethers to oleic acid, using aluminum chloride as the condensing agent. More recently Gisser and co-workers (7) published their work on the preparation of hydroxyarylstearic acid. In one instance, with sulfuric acid as the condensing agent, p-tert.-butylcatechol added to oleic acid to form 9(10)-(2,3,-dihydroxy-5-tert.-butyl)phenylstearic acid. Inasmuch as derivatives of this type are of interest as lubricant additives, we hoped to broaden the scope of the reaction to include other phenolic materials and, in the cases reported, to increase the yields.

By adaptation of the methods found successful in our earlier work with nitriles (1, 2), other phenolic materials than were previously reported have now been added to oleic acid in a sulfuric acid medium. When it became apparent that the limiting factor in the yields of products was by-product formation owing to polymerization or other reaction, different condensing agents were sought. Recently Loev and Massengale (8) used sulfonic acid cation-exchange resins as catalysts for the alkylation of phenol with olefins. While their investigations were with the relatively more reactive olefins, such as isobutylene and 1-nonene, we were able to obtain condensations with oleic acid, provided sufficient reaction time was allowed and a sufficient quantity of the appropriate resin catalyst was used. No attempt was made to examine a wide variety of resins.

Experimental

Starting Materials. Oleic acid (93.3%) essentially free of polyunsaturated acids was prepared from commercial oleic acid by one low-temperature crystallization and fractional distillation. The phenols and phenyl ethers were the best commercial grades and were used as received.

Infrared Spectra. Infrared spectra were obtained on a Perkin Elmer Model 21 double beam recording spectrophotometer. For general spectra a demountable cell consisting of sodium chloride prisms (one

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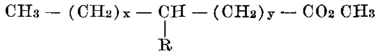
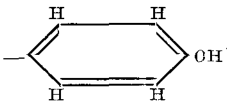
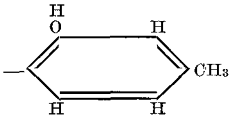
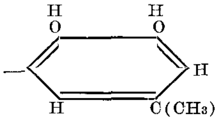
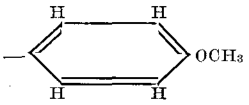
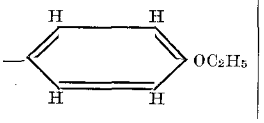
TABLE I

Methyl Esters of Substituted Phenylstearic Acids



$$CH_3-(CH_2)_x-\underset{\displaystyle R}{\underset{|}{CH}}-(CH_2)_y-CO_2CH_3$$

$(x+y=15)$

R[a]	Method[b]	Times Dist.	Boiling point		Yield, %	$n^{30/D}$	Saponification equivalent		Carbon, %		Hydrogen, %		Hydroxyl, %	
			°C.	mm.			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
	A	1	225–255[c]	0.5	15	1.4904	391	381	76.9	77.2	10.8	10.6	4.35	4.07
	B	2	183–186	0.2	31	1.4858	391	380	76.9	76.3	10.8	10.8	4.35	3.37
	A	2	179–185	0.2	14	1.4912	405	387	77.2	77.4	11.0	10.6	4.20	3.64
	A	3	200	0.1	23	1.4920	463	......[e]	75.3	75.4	10.9	11.0	3.68	......[e]
	B	3	......[d]	......	11	1.4702	463	......[e]	75.3	75.8	10.9	11.0	3.68	......[e]
	A	2	171–175	0.1	19	1.4820	405	399	77.2	75.8	11.0	10.8	......	......
	A	2	189–190	0.1	49	1.4818	419	412	77.5	76.8	11.1	10.6	0	......
	B	1	172–176	0.3	39	1.4833	419	395	77.5	77.8	11.1	11.1	0	1.72[f]

[a] The formulas shown are only intended to indicate the radical attached and not necessarily the point of attachment.
[b] See Experimental.
[c] Probably high; infrared heating lamp used on small volume of liquid.
[d] An unusually low boiling point was obtained. This may be caused in part by the small amount of material distilled.
[e] Could not be determined either colorimetrically or potentiometrically.
[f] Infrared spectra showed OH bands; confirmed by OH determination.

window with a moat type of channel) (9), and 0.025- and 0.03-mm. spacers was used since all samples were liquid.

Dilution studies were made in the hydroxyl region on methyl hydroxyphenylstearate and a mixture of phenol and methyl stearate with initial concentrations of 0.070 molar in carbon tetrachloride. The proportion of phenol to methyl stearate closely approximated the amount contributed by each to a single molecule, such as methyl hydroxyphenylstearate. Concentrations of 0.007, 0.0014, and 0.00028 molar, corresponding to dilutions of 1:10:50:250 were studied by using 10- and 25-mm. thick quartz cells.

Dilution studies were also made in the carbonyl region on methyl hydroxyphenylstearate with an initial concentration of 0.050 molar in carbon tetrachloride, using sodium chloride cells (0.5- and 3-mm. thick). Other concentrations studied were 0.010, 0.002, and 0.001 molar, corresponding to 1:5:25:50. The band from the final solution (0.001 molar) could be investigated only by expanding it five times and by using a 3-mm. cell.

Preparation of Methyl Esters of Substituted Phenylstearic Acids. Method A. Sulfuric Acid Method. The preparation of methyl methoxyphenylstearate is typical. A homogeneous mixture of 32.4 g. (0.115 mole) of oleic acid and 48.7 g. (0.45 mole) of anisole was added in 40 min. to 51 ml. (0.9 mole) of 95% sulfuric acid with rapid stirring. The temperature was maintained between 18 and 22° by external cooling. After the reactants were mixed, stirring was continued for 80 more minutes at room temperature. At the end of this time the mixture was poured into approximately one liter of crushed ice and water. The product was extracted with ether and washed free of sulfuric acid with 20% aqueous sodium sulfate solution. The ether solution was dried over anhydrous sodium sulfate and filtered, and the ether was then evaporated. The reaction products were converted to methyl esters, and the excess anisole was removed by vacuum distillation. (In other experiments the excess phenolic material was removed before preparation of the methyl esters. Good results were obtained by either method.) Distillation of the methyl esters from an alembic flask gave 15 g. (32% yield) of pale yellow liquid, b.p. 183–193 (0.7 mm.). Redistillation of 12 g. gave 7 g. (19% yield) of almost colorless liquid, b.p. 171–175° (0.1 mm.) (Table I).

Method B. Resin Catalyst Method. The preparation of methyl hydroxyphenylstearate is typical. A mixture of 28.3 g. (0.1 mole) of oleic acid and 28.3 g. (0.3 mole) of phenol were stirred together with 2.83 g. of Permutit QH fine mesh (acid-treated) (9) for 72 hrs. at 75°. (With experiments using phenetole and p-tert.-butylcatechol, 168 hrs. at 135° ± 10° were necessary.) The methyl esters were prepared simply by adding 142 ml. of anhydrous methanol to the reaction mixture and refluxing for 12 hrs. with stirring to prevent bumping. After removal of the catalyst by filtration, the mixture was distilled from an alembic flask. The apparatus was cleaned out after distillation of the phenol to prevent contamination of the following fractions. The main fraction consisted of 25 g. (63% yield) of pale yellow liquid, b.p. 189–196° (0.2 mm.). Redistillation of 22 g. gave 10.5 g. (31% yield) of pale yellow liquid, b.p. 183–186° (0.2 mm.) (Table I).

Results and Discussion

This work clarifies and elaborates earlier work in which phenols were condensed with oleic acid in the presence of sulfuric acid. It further shows that phenyl ethers can also be added to oleic acid by using sulfuric acid as the condensing agent. For the first time the use of acid cation exchange resins to condense phenols and a phenyl ether with oleic acid are reported, and the results have been compared with those obtained with sulfuric acid as catalyst.

From our experience in the addition of nitriles to olefins (1, 2) we expected to increase the yields of addition products substantially by application of these same methods. Apparently, competing side-reactions could not be avoided, with a consequent reduction in yield. In the earlier literature no yields were reported when m-cresol (4) and phenol (5) were added to oleic acid. We have obtained 14 and 15% yields, respectively, using sulfuric acid as the condensing agent. With phenol and oleic acid, using a cation exchange resin, a 31% yield of product was obtained.

Gisser and co-workers (7) reported a 17.5% yield of 9(10)-(2,3-dihydroxy-5-tert.-butyl)phenylstearic acid by reaction of p-tert.-butylcatechol with oleic acid, using sulfuric acid as the condensing agent. The yield of distilled methyl ester obtained by us was only 23%.

The yield of methyl methoxyphenylstearate we obtained was only 19% when sulfuric acid was used as condensing agent; we obtained a 49% yield of methyl ethoxyphenylstearate under identical conditions. No clear-cut advantage between the two types of condensing agents can be shown from the data, taking the distillation residues as a measure of by-product formation. Experiments in which phenol was condensed with oleic acid in the presence of sulfuric acid yielded from 50 to 100% residues on distillation of the methyl esters of the reaction products. Where the cation-exchange resin was used, the distillation residue was only about 7%. With phenetole the distillation residues were essentially the same, 18% from the sulfuric acid process and 15% from the cation exchange process. The distillation residues obtained when p-tert.-butylcatechol was condensed with oleic acid were 18% with sulfuric acid and 60% with the cation exchange resin.

An attempt to prepare methyl 9(10)-phenylthiostearate by the reaction of oleic acid and thiophenol was made, using the sulfuric acid method. Distillation of the methyl esters yielded a product which had an unaccountably high sulfur content (found, 10.17%; calcd., 7.88%) for methyl phenylthiostearate, but information on the structure of this compound will be found in the section on Infrared.

Infrared Absorption Spectra. Because of the thickness of the cells used and the interference of the carbonyl absorption between 1800–1700 cm.$^{-1}$, the absorption pattern the region between 2000–1600 cm.$^{-1}$ could not be utilized in determining the type of substitution on the aromatic ring. The substitution bands however appear when a 0.05 molar solution of the sample in carbon tetrachloride and a 3-mm. cell are used. The out-of-plane C-H deformation vibrations in the 1000–650 cm.$^{-1}$ region were relied upon almost exclusively to give the type of substitution on the aromatic ring with confirmation being sought in the 1250–950 cm.$^{-1}$ region. The upper part of this region (1250–1150 cm.$^{-1}$) could not be relied upon because of the very strong absorptions (1250, 1200, 1175 cm.$^{-1}$) of methyl esters (10, 11).

Methyl(o[p]-hydroxyphenyl)stearate, prepared in sulfuric acid or with an ion-exchange resin, is a mixture of both the *ortho* and *para* derivatives as shown by the strong, sharp bands at 750 cm.$^{-1}$ and 830 cm.$^{-1}$, respectively. Loev and Massengale (8) generally found no *ortho* isomer when phenol was alkylated with isobutylene by using a cation exchange resin. The product made by the ion-exchange method however also contains a monosubstituted compound, as indicated by a band of medium intensity at 688 cm.$^{-1}$ (12). This compound is probably methyl phenoxystearate. This would account for the low percentage of hydroxyl obtained on this product.

Methyl (2[4]-hydroxy-4[2]-methylphenyl)stearate shows absorption bands at 881, 856 cm.$^{-1}$ (weak-medium intensity), 810 cm.$^{-1}$ (strong and sharp), 775 cm.$^{-1}$ (weak and sharp), and at 1040 cm.$^{-1}$ (weak), suggesting that the ring is 1,2,4-substituted.

Methyl (2,3-dihydroxy-5[6]-tert.-butylphenyl)stearate shows sharp bands of medium intensity at 873 and 810 cm.$^{-1}$, indicating that substitution on the aromatic ring is 1,2,3,5- and 1,2,3,4-, respectively. The amount of 1,2,3,5-substituted compound produced in concentrated sulfuric acid is much larger than that produced with the ion-exchange resin based on the relative heights of the 873 and 810 cm.$^{-1}$ bands in each spectrum. With the ion-exchange resin the isomers are produced more nearly in equal amounts. Support is given to this conclusion by bands at 1094 cm.$^{-1}$ and 974 cm.$^{-1}$. Other bands believed to be C-H out-of-plane deformation vibrations are sharp bands of medium intensity at 930 and 785 cm.$^{-1}$.

Methyl o(p)-methoxyphenylstearate has absorption bands at 751 (medium-sharp) and 830 cm.$^{-1}$ (strong-sharp), indicating that *ortho* and *para* substituted forms are present. This is partially substantiated by a strong band at 1042 cm.$^{-1}$ (very strong). A weak band is also found at 680 cm.$^{-1}$ (sharp), indicating some anisole contamination probably as a result of decomposition during distillation.

Methyl o(p)-ethoxyphenylstearate has sharp bands of medium intensity at 754 and 1052 cm.$^{-1}$, indicating *ortho* substitution, and bands at 833 (medium-sharp), 1097 (shoulder) and 1052 cm.$^{-1}$, indicating *para* substitution. Surprisingly the product prepared in concentrated sulfuric acid was purer than that prepared with the ion-exchange resin. The latter product was also contaminated with an hydroxy derivative as shown by an absorption at 3410 cm.$^{-1}$ and by the appearance of shoulders on the carbonyl band. Confirmation of this is shown by the hydroxyl analysis of 1.72%.

The methyl ester of the reaction product of thiophenol and oleic acid has very intense bands at 738 and 684 cm.$^{-1}$, indicating that the aromatic ring is monosubstituted. Bands of medium to weak intensity at 1090 and 1066 cm.$^{-1}$ support this conclusion. The product therefore is predominantly a thio-ether. The C-S band, a very weak band, appears at 657 cm.$^{-1}$.

Carbonyl Absorption. Two strong bands of approximately equal intensity appear in the carbonyl region, as opposed to one in methyl stearate, in all cases where the aromatic ring contains an hydroxyl group.

Compound	Normal C=O vibration cm.$^{-1}$	Hydrogen-bonded C=O vibration cm.$^{-1}$
Methyl (o[p]-hydroxyphenyl) stearate (liquid)	1741–1735	1720–1712
Methyl (2[4]-hydroxy-4[2]-methylphenyl) stearate (liquid)	1742	1722
Methyl (2,3-dihydroxy-5[6]-t-butylphenyl) stearate (liquid)	1744–1740	1718–1713
Methyl stearate (soln.)	1750	....
Mixture of methyl stearate and phenol	1750	1730

Dilution studies were run in the carbonyl and hydroxyl regions on methyl (o[p]-hydroxyphenyl) stearate and on a mixture of methyl stearate and phenol in an effort to find an explanation for the appearance of the second carbonyl band. The mixture, in carbon tetrachloride, also produced a spectrum in which two carbonyl bands appeared, indicating that intermolecular hydrogen bonding occurs between the hydroxyl group in phenol and the carbonyl group in the ester. The second carbonyl was less intense than the ester carbonyl. The spectrum also showed free hydroxyl (3650 cm.$^{-1}$, sharp) and bonded hydroxyl (3500 cm.$^{-1}$).

When methyl (o[p]-hydroxyphenyl)stearate is diluted, the carbonyl band at 1720 cm.$^{-1}$ appears as a shoulder at a concentration of 0.010 molar. This shoulder does not disappear however at lower concentrations (0.001 molar). At higher concentrations two distinct bands appear although the second carbonyl band is smaller. In the hydroxyl region, methyl (o[p]-hydroxyphenyl)stearate in solution has a spectrum showing both free hydroxyl and bonded hydroxyl whereas in the neat liquid only the bonded hydroxyl band appears.

The ester carbonyl band in the methyl (2,3-dihydroxy-5[6]-tert.-butylphenyl)stearate spectrum is smaller than the bonded carbonyl band when the compound is prepared in sulfuric acid. The predominance of the 1,2,3,5-substituted compound was concluded from bands at 873 and 810 cm.$^{-1}$. Consistent with this are the carbonyl bands if the 1,2,3,5-substituted compound is capable of bonding and the 1,2,3,4-substituted compound is not. This is in agreement with the observation made in the C-H out-of-plane deformation vibration region. Two bands are of approximately the same intensity in the compound prepared with an ion exchange resin catalyst.

Summary

Phenols and phenyl ethers have been added to oleic acid, using both sulfuric acid and a strong acid cation exchange resin as condensing agents. By-product formation during the condensations resulted in low yields and products which were difficult to purify. Infrared spectra were used to identify the various products and to show that ring isomers form. Infrared spectra also assisted in identifying by-products and permitted differentiation between the two strong acid condensing agents.

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The Cyanoethylation and Infrared Spectra of Some Ricinoleic Acid Derivatives[1]

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THE CYANOETHYLATION of ricinoleic acid derivatives was undertaken to provide compounds from castor oil which would have potential utility, such as plasticizers or organic intermediates. According to Bruson's review (3), cyanoethylation, the addition of acrylonitrile, occurs with a variety of compounds possessing labile hydrogen atoms, such as amines, oximes, and alcohols. The esters of hydroxy acids however resisted cyanoethylation (3). Attempts in this laboratory to cyanoethylate methyl ricinoleate (methyl 12-hydroxy-9-octadecenoate) by conventional procedures were likewise unsuccessful. When potassium, sodium, or sodium methoxide was employed as the cyanoethylation catalyst, an increase in optical rotation and a decrease in hydroxyl content were observed while dissolving the catalyst in methyl ricinoleate. Very little cyanoethylation occurred while slowly adding the acrylonitrile; instead a considerable amount of polyacrylonitrile was formed, accompanied by a further increase in optical rotation and decrease in hydroxyl content. Apparently estolide formation (interesterification of the hydroxyl and carboxyl groups of ricinoleic acid) took place. When benzyl-

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