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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Normal C=O vibration cm$^{-1}$</th>
<th>Hydrogen-bonded C=O vibration cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl (o-p-hydroxyphenyl) stearate (liquid)</td>
<td>1741-1735</td>
<td>1720-1712</td>
</tr>
<tr>
<td>Methyl (o-p-hydroxyphenyl) stearate (liquid)</td>
<td>1742</td>
<td>1722</td>
</tr>
<tr>
<td>Methyl (2,3-dihydroxy-5[6]-tert.-butylphenyl) stearate (liquid)</td>
<td>1744-1740</td>
<td>1718-1713</td>
</tr>
<tr>
<td>Methyl stearate (solid)</td>
<td>1750</td>
<td>1730</td>
</tr>
<tr>
<td>Mixture of methyl stearate and phenol</td>
<td>1750</td>
<td>1730</td>
</tr>
</tbody>
</table>

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 intramolecular 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 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 confirmed 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 ion 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.

**References**

2. Niederl, J. B., and co-workers, J. Am. Chem. Soc., 55, 3205 (1933); ibid., 56, 1063 (1934); ibid., 56, 284 (1934).

The Cyanoethylation and Infrared Spectra of Some Ricinoleic Acid Derivatives

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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 Brunson'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 (esterification of the hydroxyl and carboxyl groups of ricinoleic acid) took place.

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trihydroxyoctadecane. 1,12-Bis(β-cyanoethoxy)octadecane has previously been reported by Bruson, but it was not purified (2). 1,12-Bis(β-cyanoethoxy)-cis-9-octadecene was isomerized with nitrogen oxides to the trans isomer by the general procedure of McCutcheon et al. (5).

The infrared spectra for all these compounds were determined. The absorptivities in the 4.44 micron region (characteristic of the C==N group) for the trans isomer were studied and used as a basis for quantitative determination of these groups.

Experimental

Materials. 4-Ricinoleoylmorpholine, 4-ricinelaidoylmorpholine, and 4-(12-hydroxysestearoyl)morpholine were prepared by the general procedure of Dupuy, O'Connor, and Goldblatt (4). Commercial ricinoleyl alcohol (1,12-di-hydroxy-9-octadecene) and 12-hydroxysestearoyl alcohol (1,12-di-hydroxyoctadecane) were fractionally distilled under high vacuum. The ricinoleyl alcohol was crystallized from 15 volumes of acetone-hexane mixture (1:2) at 5°C. Eastman's practical grade of acrylonitrile and dioxane and commercial 35-40% benzyltrimethylammonium hydroxide (Triton B) in methanol were used without further purification.

4-(12-β-Cyanoethoxysestearoyl)morpholine. 4-Ricinoleoylmorpholine was cyanoethylated, employing 100% excess acrylonitrile. In a 2-liter, three-necked flask, equipped with a reflux condenser, a dropping funnel, a thermometer, and a magnetic stirrer, 365 g. of 4-ricinoleoylmorpholine (1 mole) and 365 g. of dioxane were added. Then 37 ml. of water and 37 ml. of Triton B were added, and the mixture was stirred and heated to 50°C. Two moles of acrylonitrile (106 g.) were added dropwise in about 30 min. During the addition of acrylonitrile the temperature rose from 50 to 85°C. The reaction was then continued for 3 hrs. The temperature was maintained between 60 and 70°C. The hot mixture was poured slowly into 3 liters of diethyl ether during the last 15-20 min. period and allowed to stand for several hrs. When the polyacrylonitrile precipitated out of solution, the ether solution was decanted, filtered, extracted three times with 300-ml. portions of 1 N hydrochloric acid, and washed twice with distilled water. After the ether was evaporated from the reaction product under reduced pressure, the hydroxyl content was determined. This indicated about 60% conversion. The crude cyanoethylated product was distilled rapidly (ca. 200 g./hr.) under high vacuum. Distillate fractions, b.p. 248-254°C./0.02 mm., were crystallized overnight from 15 volumes of methanol at -7°C.

Anal. Caled. for C₂₂H₄₅N₂O₈: C, 73.79; H, 10.54; N, 7.17; OH, 0. Found: C, 73.79; H, 10.54; N, 7.17; OH, 0.

4-(12-β-Cyanoethoxysestearoyl)morpholine. 4-(12-Hydroxysestearoyl)morpholine was cyanoethylated, employing 100% excess acrylonitrile as described above. Distillate fractions, b.p. 246-252°C./0.02 mm., were crystallized overnight from 10 volumes of acetone at -25°C. to precipitate the noncyanoethylated morpholide. After the acetone filtrate was evaporated under reduced pressure, the cyanoethylated morpholide was crystallized overnight from 15 volumes of methanol at -7°C, m.p. 35.2-36.2°C.

Anal. Caled. for C₂₄H₄₄N₂O₈: C, 71.04; H, 9.79; N, 6.63. Found: C, 70.85; H, 10.55; N, 6.55; n₀/₀°D 1.4864.

4-(12-β-Cyanoethoxyelaidoyl)morpholine. 4-Ricinelaidoylmorpholine was cyanoethylated by employing 100% excess acrylonitrile, as described above. Distillate fractions, b.p. 247-255°C./0.02 mm., were crystallized overnight from 3 volumes of acetone at -70°C. to precipitate the noncyanoethylated morpholide. After the acetone filtrate was evaporated under reduced pressure, the cyanoethylated morpholide was crystallized overnight from 15 volumes of methanol at -7°C.

Anal. Caled. for C₂₄H₄₄N₂O₈: C, 71.78; H, 10.54; N, 6.66; OH, 0. Found: C, 71.45; H, 10.55; N, 6.55; n₀/₀°D 1.4868.

4-(12-β-Cyanoethoxyelaidoyl)morpholine. 4-Ricinelaidoylmorpholine was cyanoethylated by employing 100% excess acrylonitrile, as described above. Distillate fractions, b.p. 247-255°C./0.02 mm., were crystallized overnight from 3 volumes of acetone at -70°C. to precipitate the noncyanoethylated morpholide. After the acetone filtrate was evaporated under reduced pressure, the cyanoethylated morpholide was crystallized overnight from 15 volumes of methanol at -7°C.

Anal. Caled. for C₂₅H₄₅N₂O₉: C, 73.79; H, 10.84; N, 7.17; OH, 0. Found: C, 73.79; H, 10.84; N, 7.08; OH, 0; n₀/₀°D 1.4632; c₂₅/₁₀° cm. 14.30.

1,12-Bis(β-cyanoethoxy)octadecane. 1,12-Dihydroxyoctadecane was cyanoethylated in dioxane solution, employing 100% excess acrylonitrile as described above except that the mixture had to be heated to 55°C. to dissolve the diol. While adding acrylonitrile,