are unsaturated, or the fractions in question contain some other unsaturated components.

Data and characteristics concerning Fraction I are inconsistent. It seems that if only the molecular weight and the carbon content are taken into consideration, Fraction II could be the methyl ester of an aliphatic monocarboxylic acid C_{20}H_{40}O_2, and Fraction III some methyl ester of the acids C_{19}H_{39}O_2-C_{22}H_{44}O_2. The hydrogen content however is smaller than in the molecules mentioned above, which can be explained by the unsaturated character of the fractions in question.

If the molecular size of Fraction IV is calculated on the basis of its hydroxyl number, 122.5, and if the presence of an aliphatic monohydroxy acid is assumed, the resultant molecule will be C_{25}H_{52}O_3. On the basis of the molecular weight and carbon content our result will be a methyl ester C_{20}-C_{21}, which is also indicated by Beilstein’s (11) report about the melting point 70-71°C of the methyl ester of 20-hydroxyecosan-carboxylic acid. Since the hydroxy acid contained in Fraction IV evidently is not pure, the number 122.5 is too small and the molecular weight calculated on the basis of it is too large. Thus the real molecular size would be nearer to the latter alternative, C_{20}-C_{21}. Fractions V and VI have an ash content which obviously is Al_{2}O_{3} carried over from the column.

**Acknowledgment**

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**References**

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We have now studied this same reaction, but under pressure. Yields of 80 to 90% have been obtained. Optimum conditions for this reaction have been applied to the reaction of dimethyl maleate with linseed and soybean oils. Use of dimethyl fumarate and di-\(n\)-butyl maleate with safflower oil has been explored. Anthraquinone and nickel catalysts have been examined.

Experimental

Reactions were run in a Parr pressure reaction apparatus. In a typical run the bomb was cooled with solid carbon dioxide and then charged with 150 g. of safflower oil (77.5% linoleate, equivalent to 0.133 mole trilinolein), 117.2 g. (0.8 mole, 100% excess) of dimethyl maleate, 0.75 g. (0.5% based on linoleate) of liquid sulfur dioxide, and 1 g. of hydroquinone. The bomb was sealed and heated to 296-302 °C. The optimum conditions for this reaction have been applied to the reaction of dimethyl maleate with linseed and soybean oils. Use of dimethyl fumarate and di-\(n\)-butyl maleate with safflower oil has been explored. Anthraquinone and nickel catalysts have been examined.

Results and Discussion

The optimum conditions for the reaction of dimethyl maleate with safflower oil were found to be 100% excess maleate (based on linoleate), 0.5% sulfur dioxide catalyst, and 0.69% hydroquinone inhibitor (both based on oil); the mixture was heated at 290 °C for 1 hr., transesterified, and distilled.

Under these conditions, consistent yields of 80 to 90% were readily obtained. In one experiment a 99% yield of adduct fraction was achieved, with a 10% residue. This yield could not be exactly duplicated, probably because of the sensitivity to any minor variations in conditions. When only an equivalent quantity of maleate was used, the maximum yield was 65%. Increasing the sulfur dioxide ratio to 10% had no favorable effect. Lower temperatures gave lower yields, and extended reaction times did not improve them. With benzene as a solvent, yield is reduced. Benzene as a solvent plus water to inhibit polymer formation (1) resulted in a 59% yield with 17% residue. Elimination of the sulfur dioxide causes a small decrease in residue but a more-than-corresponding loss in yield. Calculations based on forerun and residue suggest that the function of the hydroquinone is to inhibit copolymerization of the maleate with the isomerized oil.

After optimum conditions for the dimethyl maleate-safflower oil reaction were established, these conditions were used with other oils, dienophiles, and catalysts. Linseed oil differs from safflower oil in that the major constituent is linoleic acid rather than linoleic acid. This difference had little effect on the reaction as a 78% yield of adduct fraction, based on linoleate plus linolenate, was obtained. With soybean oil, which contains linoleate and linolenate in about 10:1 ratio, the yield was 80%.

The foreruns from the distillation of the transesterified reaction products was analyzed by gas-liquid chromatography (Table I). From these data it appears that, when there is a possibility for competitive reactions, the linolenate reacts preferentially. Because of the complex nature of the adduct fraction, the exact course of the reaction cannot be elucidated at this time.


<table>
<thead>
<tr>
<th>Oil</th>
<th>Linoleate, %</th>
<th>Linolenate, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linseed</td>
<td>In oil</td>
<td>In forerun</td>
</tr>
<tr>
<td></td>
<td>15.6</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>51.0</td>
<td>12.6</td>
</tr>
<tr>
<td>Soybean</td>
<td>48.5</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>4.7</td>
<td>12.6</td>
</tr>
<tr>
<td>Safflower</td>
<td>77.3</td>
<td>9%</td>
</tr>
<tr>
<td></td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

\(^a\) Unknown including linoleate.

To extend the reaction to other dienophiles, dimethyl fumarate and di-\(n\)-butyl maleate were used. With the fumarate the yield of adduct fraction was 71%. This yield was unexpected as our previous work had shown no appreciable differences in the reactivity of maleate and fumarate. Possibly in the present reaction some of the fumarate sublimed from the reaction zone, thereby lowering the yield somewhat. It should also be emphasized that the conditions used were those found best for the dimethyl maleate-safflower oil reaction and that relatively minor variations have significant effect on yields. Slight modifications for different reactants would very probably effect improvement in yields.

Use of di-\(n\)-butyl maleate at atmospheric pressure had been found to be complicated by a previously unrecognized decomposition (6). It was thought that, since decomposition products include two gases, operation under pressure might suppress this decomposition. If there were any such suppression, it was more than counterbalanced by other reactions. Yield was 55% with 39% residue.

Two other isomerization-elaidinization catalysts were investigated. With anthraquinone (4) (5% based on oil) the yield of adduct fraction was 53% with 37% residue. With Unilever nickel catalyst (2) the yield was 64%, residue 23%.

As indicated above and in Part I of this series, the adduct fractions are considered to be mixtures of equimolar adducts of dienophile with linoleate or linolenate with virtually no oleate-derived adducts. Conditions were chosen to form a trans,trans conjugated system in the linoleate (and linolenate) portion of the oil. Therefore we assume that the Diels-Alder-type adduct (I) is formed in preference to, and probably to the exclusion of, the substituted succinate (II) (8):

\[
\begin{align*}
\text{I:} & \quad - \overset{\text{C=C}}{\text{C}} - \overset{\text{C}}{\text{C}} - \overset{\text{C}}{\text{C}} - \overset{\text{C}}{\text{C}} \\
\text{II:} & \quad - \overset{\text{C=C}}{\text{C}} - \overset{\text{C}}{\text{C}} - \overset{\text{C}}{\text{C}} - \overset{\text{C}}{\text{C}} \\
\end{align*}
\]

Nevertheless, because of the complex nature of the distillable adduct fraction and the virtual impossibility of separating a Diels-Alder adduct from a succinate adduct, the possibility of some oleate reaction cannot be categorically eliminated.

Efforts to force reaction with the oleate portion of safflower oil by increasing the reaction time were unsuccessful. When the reaction was run for 3 hrs, the