of palmitic and a smaller amount of stearic acid. In other group the quantity of palmitic and stearic acids is higher (nearly 15%) and the amount of higher saturated acids is almost negligible in as much as that only one and in some cases two of the three C20, C22 and C24 acids are present. However, there seems to be no sharply defined boundary between them. These variations may possibly be due to the biological variations as suggested by Hilditch.57.

A further point of interest in the work on the Leguminosae seed fats arose from the fact that their seeds were being investigated in these laboratories for their saponin contents.

**NEW WORK**

*Family Umbelliferae (Seseli indicum and Anethum Trifoliatum)*

The results of the fatty acid composition of these fats are given below:

**TABLE I.**

<table>
<thead>
<tr>
<th>Acids</th>
<th>Seseli indicum</th>
<th>Anethum trifoliatum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic</td>
<td>6.18</td>
<td>9.37</td>
</tr>
<tr>
<td>Petroselinic</td>
<td>46.06</td>
<td>48.85</td>
</tr>
<tr>
<td>Oleic</td>
<td>30.96</td>
<td>33.90</td>
</tr>
<tr>
<td>Linoleic</td>
<td>13.80</td>
<td>7.88</td>
</tr>
</tbody>
</table>
The conclusions based on these results are summarised below:

These results on Anethum trifoliatum and Seseli indicum are in line with the findings of all other investigators on the seed fats of the members of the family Umbelliferae i.e. the presence of petroselinic acid as a major component acid, appreciable amount of resinous matter, low saponification value, high contents of unsaponifiable matter and the presence of palmitic acid as the only saturated acid.

Family Leguminosae (Albizia Odoratissima, Albizia Procera and Leucaena glauca).

The fatty acid composition of these seed fats examined by the author are summarised in Table II.

<table>
<thead>
<tr>
<th>Acids</th>
<th>Albizia odoratissima</th>
<th>Albizia procera</th>
<th>Leucaena glauca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palmitic</td>
<td>14.33</td>
<td>7.23</td>
<td>12.74</td>
</tr>
<tr>
<td>Stearic</td>
<td>6.88</td>
<td>14.26</td>
<td>5.01</td>
</tr>
<tr>
<td>Arachidic</td>
<td>0.81</td>
<td>12.21</td>
<td></td>
</tr>
<tr>
<td>Behenic</td>
<td>-</td>
<td>-</td>
<td>3.64</td>
</tr>
<tr>
<td>Lignoceric</td>
<td>-</td>
<td>-</td>
<td>0.67</td>
</tr>
<tr>
<td>Unsaturated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oleic</td>
<td>26.56</td>
<td>50.39</td>
<td>23.63</td>
</tr>
<tr>
<td>Linoleic</td>
<td>51.42</td>
<td>15.41</td>
<td>54.31</td>
</tr>
</tbody>
</table>
The result of the above work leads to the following points:

(i) The presence of specific saturated acids in these fats confirm the generalisations regarding the Leguminosae seed fats in which one or more of the higher fatty acids are usually present.

(ii) The main components of the total fatty acids are the C₁₈ unsaturated acids, oleic and linoleic. The preponderant occurrence of these acids to the extent of 60–80% of the total fatty acids corroborates Hilditch's generalisation that Leguminosae seed fats in this respect resemble the simple 'linoleic-oleic-palmitic' type of fats.

(iii) The absence of linolenic acid in these fats is in conformity with the earlier findings that this acid is not at all present in the Leguminosae seed fats so far examined.

Fatty acid composition of the seed fat of *Haloptela integrifolia* (U. Urticaceae).

During the course of the above work on indigenous seed fats the attention of the author was drawn to the
seed fat of *Haloptela integrifolia*. The seed fat of this plant is used for edible purposes. Even the seeds as such are cherished by children and cattle.

Well powdered, air-dried seeds, on petrol extraction gave 50% of fat. The fat very much resembles the cow milk fat in appearance. The fatty acid composition by the procedure earlier recorded was estimated as under:

**Saturated acids.**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic</td>
<td>37.64</td>
</tr>
<tr>
<td>Stearic</td>
<td>10.04</td>
</tr>
<tr>
<td>Arachidic</td>
<td>2.03</td>
</tr>
</tbody>
</table>

**Unsaturated acids.**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic</td>
<td>46.66</td>
</tr>
<tr>
<td>Linoleic</td>
<td>3.63</td>
</tr>
</tbody>
</table>

It is of interest to note here that a few seed fats of the family Urticaceae earlier examined contain fatty acids where the ratio of saturated to unsaturated is 1:12 while in this seed fat the ratio is about 1:56. Further the extraordinary high palmitic acid content (37.64%) of this seed fat is remarkable and accounts for its consistency in which it resembles the cow milk fat. However, the high fat content of the seeds and the consistency of this fat attracts attention for its utilisation as an edible fat.
Studies on the Hypohalogenation of the isomeric 6:7-Octadecenoic acids.

Hypochlorination:

The hypochlorination of petroselinic and petroselaidic acids was carried out,
(a) by sodium hypochlorite solution and,
(b) by chlorine water

6(7):7(6)-chlorohydroxystearic acids from petroselinic acid.

Petroselinic acid on hypochlorination with a solution of sodium hypochlorite in presence of potassium hydroxide yielded 50-55% of a mixture of the two isomeric (6(7):7(6)-chlorohydroxystearic acids m.p. 50-55°. This melting point on twice recrystallisation from methyl alcohol was raised to 59-60°.

When the hypochlorination was carried out with chlorine water, it was found that a small amount (15-20%) of 6(7):7(6)-chlorohydroxystearic acids was easily isolable which on further purification from aqueous methyl alcohol melted sharply at 59-60.
A determination of the mixed melting point of the 6(7):7(6)-chlorohydroxystearic acids obtained through the action of sodium hypochlorite with those prepared by using chlorine water, showed no depression thus confirming the identity of the two products.

The chlorohydroxy acids on dehydro-halogenation by treatment with alkali readily afforded a nearly theoretical yield of 6:7-epoxystearic acid m.p. and mixed melting point with a genuine sample 59-60°.

Petroselinic acid m.p. 30° \[\xrightarrow{\text{HCl}}\] 6(7):7(6)-chlorohydroxystearic acid m.p. 59-60° \[\xrightarrow{\text{Alkali}}\] 6:7-epoxystearic acid m.p. 59-60°

6(7):7(6)-chlorohydroxystearic acids from 6:7-epoxystearic acid.

6:7-epoxystearic acid (petroselinic acid epoxide) in ether solution readily reacted with concentrated hydrochloric acid to give a mixture of 6(7):7(6)-chlorohydroxystearic acids m.p. 53-56°. On repeated crystallisations a fairly pure mixture of chlorohydroxy acids melting at 59-60° was obtained. It showed no depression.
when mixed with samples of acids obtained by the use of either sodium hypochlorite solution or chlorine water.

The treatment of these chlorohydroxy acids with alkali yielded the original epoxide from which they were prepared as represented below:

\[ \text{cis-epoxy acid} \xrightarrow{\text{HCl in ether}} \text{ether} \xrightarrow{\text{OH} \rightleftharpoons \text{Cl (ring closure)}} \text{cis-epoxy acid} \]

It has been earlier pointed out that the reactions of hypohalous acids proceed by a trans-addition to the double bonds of ethylenic acids and that the epoxidation reaction is stereospecific in nature. In the light of these reaction mechanisms the foregoing results may be systematically represented as below:
Thus, the chlorohydroxy acids, obtained from the cis-acid (petroselinic acid) with hypochlorous acid and those obtained by the epoxidation of the cis-acid and subsequent treatment of the epoxide with hydrochloric acid, are identical. The identity of the chlorohydroxy acids is of considerable importance from the point of view of configurational relationships in the formation of halohydrins and their conversion to epoxides.

The fact leads at once to the conclusion that inversion in the configuration does occur during the reaction of the epoxide with hydrochloric acid (i.e., on the opening of the epoxide ring on hydrohalogenation)
and negates the suggestion of Nicolet and Poulter, and supports the findings of King. Further, this also goes contrary to the conclusion of Hilditch and Atherton, who postulated no inversion during either the opening or the closure of the epoxy ring.

Finally, this fact provides additional experimental evidence in support of Swern's general reaction scheme described earlier (page 43).

The identity of the two epoxides could only be explained if the inversion during the closure of the ring is allowed for. This means that the inversion takes place both during the opening as well as of the closing of the epoxy ring.

6(7):7(6)-chlorohydroxystearic acids from petroselaidic acid.

It has been found that hypochlorous acid in aqueous solution adds on to petroselaidic acid and gives 55-60%

* The authors having earlier suggested that these chlorohydroxyacids differ, one of them possibly being the 9-hydroxy-10-chloro and the other 9-chloro-10-hydroxy-stearic acid.

** King suggested the possibility of inversion both in the opening and the closing of the epoxy ring.
yield of 6(7):7(6)-chlorohydroxystearic acids melting at 47-52°. The product on repeated crystallisations yielded a pure mixture of 6(7):7(6)-chlorohydroxystearic acids m.p. 55-56°. These are stereoisomeric with those prepared from the petroselinic acid or its epoxide.

The same 6(7):7(6)-chlorohydroxystearic acids m.p. 55-56° were obtained when petroselaidic acid was treated with chlorine water.

The treatment of these chlorohydroxy acids with alkali resulted in the formation, in quantitative yields, of the trans-petroselaidic epoxide m.p. 66-67°.

The hydrohalogenation of the petroselaidic acid epoxide thus formed, readily yielded 6(7):7(6)-chlorohydroxystearic acids identical with those obtained either by the action of hypochlorous acid solution or of chlorine water on petroselaidic acid.

The results are summarised below:

\[
\begin{align*}
\text{a-CH}=\text{CH}-\text{b} & \quad \text{HOCl} & \quad \text{a-CH}=\text{CH}-\text{b} + \quad \text{a-CH}=\text{CH}-\text{b} \\
\text{Trans-acid} & \quad \rightarrow & \quad \text{OH} \quad \text{Cl} & \quad \text{Cl} \quad \text{OH} \\
\text{Per-acids} & \quad \rightarrow & \quad \text{Hydrohalogenation} \\
\text{a-CH}=\text{CH}-\text{b} & \quad \rightarrow & \quad \text{Hydrohalogenation}
\end{align*}
\]
Preparation of the 6:7-Dihydroxystearic Acids.

The low and high melting 6:7-dihydroxystearic acids, (threo-isomer, m.p. 115-116° and erythro-isomer, m.p. 122°) were prepared in good yields from petroselinic and petroselaidic acids respectively through the use of performic acid (cf. Swern)⁵⁷.

Conversion of Erythro-6:7-Dihydroxystearic Acid m.p. 122° into Threo-Isomer, m.p. 115-116°.

6:7-dihydroxystearic acid m.p. 122° was converted primarily to a cis-epoxide m.p. 59-60° by the action of dry hydrogen chloride gas and the subsequent hot saponification of the viscous oily product. A small quantity of the low melting 6:7-dihydroxystearic acid m.p. 115-116° was also obtained from the hydrolysed product. This indicated the possibility of progressive hydrolysis of the epoxide formed as a main product by the action of alkali.

The cis-epoxy acid m.p. 59-60° on saponification either in a sealed tube at 170° or on simple refluxing, readily yielded the threo-6:7-dihydroxystearic acid m.p. 115-116°.
On acid hydrolysis of the epoxide a solid was obtained which after crystallisation yielded low melting 6:7-dihydroxy stearic acid m.p. 115-116°.

The melting point was not depressed when a mixed melt was taken with the acid prepared by the oxidation of petroselaidic acid with alkaline potassium permanganate. The course of the above reactions may be represented as under:

\[ \text{6:7-dihydroxy stearic acid m.p. 122°} \xrightarrow{\text{HCl gas}} \text{Chlorohydring alcoholic alkali} \xrightarrow{\text{Hydrolysis}} \text{6:7-dihydroxy stearic acid m.p. 115-116°} \]

Conversion of three-6:7-dihydroxy stearic acid m.p. 115-116° to erythro-isomer m.p. 122°.

Under conditions similar to those described above the low melting 6:7-dihydroxy stearic acid m.p. 115-116° on treatment with dry hydrogen chloride gas afforded a viscous oil which on saponification yielded the trans-epoxide m.p. 66-67°.
This epoxide on hydrolysis gave the high melting 6:7-dihydroyxystearic acid m.p. 122°.

\[
\begin{align*}
\text{Hydrolysis} & \quad \xrightarrow{\text{HCl}} \quad \xrightarrow{\text{alcoholic alkali}} \\
\text{a-CH} - \text{CH-b} & \quad \text{OH} \quad \text{OH} \quad \text{Cl} \\
\text{OH} & \quad \text{OH} \quad \text{a-CH} - \text{CH-b} \\
\text{m.p. 115-116°} & \quad \text{m.p. 122°}
\end{align*}
\]

These interconversions of the dihydroyxystearic acids of 6:7-octadecenoic acid are in line with the earlier findings of King and Hilditch on the isomeric 9:10-dihydroyxystearic acids obtained from oleic and elaidic acids. These authors have formulated the stereochemical course of the transformations on assumptions which differ from each other in some fundamental respects. Their experimental evidence was based on almost similar findings in the interconversions of isomeric 9:10-hydroxy- stearic acids as under:
9:10-dihydroxy-stearic acid $\xrightarrow{\text{HCl, gas}}$ Chloro-hydrins $\xrightarrow{\text{dil NaOH}}$ Oxido-stearic acid m.p. 132°

Conc. NaOH $\xrightarrow{}$ 9:10-dihydroxy-stearic acid, m.p. 95°

King concluding that the inversion occurs only during the opening of the epoxide ring (stage III), while Hilditch and Atherton on the other hand suggesting that the inversion takes place during the replacement of hydroxy group by the chlorine atom (stage I). These latter authors at the same time assumed that the closure and the opening of the epoxy ring (stage II and III) takes place without inversion.

These results about the mutual transformations of the isomeric 6:7-dihydroxystearic acids m.p. 115-116° and
m.p. 122° show that the inversions of configurations occur in all the three stages as under:

(i) during the replacement of the hydroxyl group by chlorine atom
(ii) at the time of the closing of the epoxy ring and,
(iii) at the time of the opening of the epoxy ring.

King, from his work on the stereochemistry of the halogenohydroxystearic acids from oleic and elaidic acids, has already suggested this 3-stage inversion. This also supports Swern’s assumption of the three fold inversions made on theoretical grounds.

6(7):7(6)-Bromohydroxystearic acids from petroselinic acid and its epoxide.

A 25-35% yield of a mixture of pure 6(7):7(6)-bromohydroxystearic acids m.p. 36-37° was readily obtained when a solution of petroselinic acid was treated with sodium hypobromite solution in presence of an alkali. These acids were easily crystallisable from n-hexane or a mixture of low boiling petrol and benzene.

When the mixture of the bromohydroxystearic acids was treated with a dilute aqueous solution of an alkali, petroselinic epoxide m.p. 59-60° was obtained.
The action of aqueous hypobromous acid on petroselinic acid in ether gave an oil which finally crystallised yielding 6(7):7(6)-bromohydroxystearic acids m.p. 36-37°. These acids were the same as those obtained by the action of sodium hydrobromite on petroselinic acid. On saponification with aqueous alkali these acids gave petroselinic epoxide m.p. 59-60°.

The treatment of the epoxide with hydrobromic acid yielded a product which on repeated crystallisations gave 6(7):7(6)-bromohydroxystearic acid m.p. 56-37° (in good yields). The action of dilute alkali on these acids regenerated the original epoxide.

6(7):7(6)-Bromohydroxystearic acids from petroselaidic acid and its epoxide.

Petroselaidic acid on hypobromination with sodium hypobromite gave crystalline 6(7):7(6)-bromohydroxystearic acids m.p. 55-56°. The action of hypobromous acid on petroselaidic acid also reproduced the same acids. These bromohydroxy acids readily hydrolysed to trans-6:7-epoxy-stearic acid m.p. 66-67°. The epoxy-acid on treatment with hydrobromic acid readily gave 6(7):7(6)-bromohydroxy-stearic acids m.p. 55-56°.
The identity of these acids with the ones obtained on hypobromination of petroselaidic acid was established by a mix melt and a regeneration of the same epoxide on dehydrohalogenation of either mixture of acids.

The results of the hypobromination are summarised below:

\[ \text{HOBr or NaOBr} \rightarrow \text{Petroselenic acid m.p. 30°} \]
\[ \text{Bromohydroxystearic acids m.p. 36-37°} \]
\[ \text{HBr} \uparrow \quad \text{alkali} \]
\[ \text{Per-acetic acid} \rightarrow \text{6:7-epoxystearic acid m.p. 59-60°} \]

\[ \text{HOBr or NaOBr} \rightarrow \text{Petroselaidic acid m.p. 52-53°} \]
\[ \text{Bromohydroxystearic acids m.p. 55-56°} \]
\[ \text{HBr} \uparrow \quad \text{alkali} \]
\[ \text{Per-acetic acid} \rightarrow \text{6:7-epoxystearic acid m.p. 66-67°} \]
6(7):7(6)-Iodohydroxy stearic acids from petroselic acid and its epoxide.

Petroselic acid in moist ether reacted with iodine in presence of mercuric oxide to yield the corresponding 6(7):7(6)-iodohydroxy stearic acids m.p. 69-70°. These acids when treated with cold aqueous alkali furnished the petroselanic acid epoxide m.p. 59-60°.

The same 6(7):7(6)-iodohydroxy stearic acids were conveniently prepared by the action of hydroiodic acid on petroselanic acid epoxide m.p. 59-60°. The latter was regenerated by the treatment of the 6(7):7(6)-iodohydroxy stearic acids with cold alkali.

Under conditions similar to those described above a pure mixture of 6(7):7(6)-iodohydroxy stearic acids m.p. 56-57° was obtained both by the action of iodine in presence of mercuric oxide on petroselaidic acid and by the action of hydroiodic acid on petroselaidic acid epoxide. These acids in each case yielded the same epoxy acids on hydrolysis.
The following diagram gives all these reactions at a glance.

- Iodine in presence of Mercuric oxide
  - Petroselinic acid m.p. 30° → Iodohydroxystearic acids m.p. 69-70°
    - HI → alkali
  - Peracetic acid → 6:7-epoxystearic acid m.p. 59-60°

- Iodine in presence of Mercuric oxide
  - Petroselaidic acid m.p. 52-53° → Iodohydroxystearic acids m.p. 56-57°
    - HI → alkali
  - Peracetic acid → 6:7-epoxystearic acids m.p. 56-57°

The foregoing results on bromo- and iodo-hydrins which are exactly the same in details as in the case of chlorohydrins lend further support to the earlier observation of the changes of configuration during hypohalogenation, hydrohalogenation and dehydrohalogenation of 6:7-octadecenoic acids and their epoxides respectively.
6(7):7(6)-Hydroxyacetoxystearic acids were prepared in two different ways (i) by the action of hydrogen peroxide on petroselinic acid in acetic acid medium; and (b) by the action of glacial acetic acid on petroselinic acid epoxide.

Both the procedures readily yielded a mixture of monoacetyl derivatives m.p.53-54º of the 6:7-dihydroxy-stearic acid m.p.115-116º. The hydroxyacetates obtained from two different sources were found to be identical on the basis of their mixed melting point. It has been found that the hydroxyacetoxy derivatives could only be obtained if the duration of reaction is reduced from that reported by King in his studies on the oxidation of oleic and elaidic acids. A longer reaction time resulted only in the formation of 6:7-dihydroxystearic acid m.p.115-16º.

The oxidation of petroselaidio acid with hydrogen peroxide or of its epoxide with glacial acetic acid under conditions similar to those mentioned above, yielded the 6(7):7(6)-hydroxyacetoxystearic acids m.p.65-66º. The
results are summarised below:

\[
\text{Petroselinic acid} \quad \text{H}_2\text{O}_2 + \text{HAc} \quad \text{6:7-Hydroxyacetoxystearic acids m.p. 53-54}\degree C
\]

\[
\text{Per-acetic acid}
\]

\[
\text{cis-6:7-epoxystearic acid} \quad \text{m.p. 59-60}\degree C
\]

\[
\text{Petroselaidic acid} \quad \text{H}_2\text{O}_2 + \text{HAc} \quad \text{6:7-Hydroxyacetoxystearic acid m.p. 65-66}\degree C
\]

\[
\text{Peracetic acid}
\]

\[
\text{Trans-6:7-epoxystearic acid} \quad \text{m.p. 66-67}\degree C
\]

The fact that the epoxy acids united readily with acetic acid to give the 6(7):7(6)-hydroxyacetoxystearic acids, suggested that these compounds are intermediates in the conversions of the epoxides to the corresponding dihydroxystearic acids. It is, however, difficult to find appropriate reaction conditions (particularly the time factor and the reaction temperature) which will be
specific for the preparation of these compounds from mono-unsaturated acids. However, the present results indicate that most probably the following course of reactions, as suggested by Boeseken and Elsen\textsuperscript{59}, takes place during hydrogen peroxide oxidation.

\[ R\text{-CH} = CH - R' \xrightarrow{\text{AcO}_2\text{H}} R\text{-CH} - CH - R' \xrightarrow{\text{AcOH}} \]

\[ R\text{-CH(OAc)} - CH(OH) - R' \quad \text{and} \quad R\text{-CH(OH)} - CH(OAc) - R' \xrightarrow{\text{H}_2\text{O}} R\text{-CH(OH)} - CH(OH) - R' \]