M. E. Dreyfus

The Synthesis of Spiral Compounds

# THE SYNTHESIS OF SPIRAL COMPOUNDS

BY

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# THESIS

FOR THE

## DEGREE OF BACHELOR OF SCIENCE

IN

## CHEMICAL ENGINEERING

———

COLLEGE OF LIBERAL ARTS AND SCIENCES

## UNIVERSITY OF ILLINOIS

1920

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED THE SYNTHESIS OF SPIRAL COMPOUNDS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN CHEMICAL ENGINEERING

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# INTRODUCTION

There is a compound known to the manufacturers of synthetic
flavors and perfumes as "peach-lactone", which has been used com-
mercially for years, but which has received only scant attention
in the literature. As the name implies, it imitates the natural
peach flavor and odor and is used for that purpose. Its prepar-
ation from undecenoic acid by treatment with sulphuric acid sug-
gests that the lactone has an extremely unusual structure or is the
product of a unique reaction. Either it is a closed ring con-
sisting of eleven atoms, or the double bond of undecenoic acid has
shifted past six carbon atoms to close a ring of more usual dimen-
sions. If the first is true, a ring has been formed that is larg-
er than any heretofore known, and which on the basis of Baeyer's
famous strain theory would be considered almost impossible of
formation. If the shift of the double bond has occurred, we have
a rearrangement that is likewise extraordinary. The small amount
of work recorded on the compound indicates that the latter is the
correct explanation; but the possibility of the former having
taken place, in part at least, with its stereo-chemical signifi-
cance, is of sufficient interest to warrant the investigation here
recorded.

HISTORICAL PART

Upon investigating Schmidt's process for the conversion of oleic acid into solid fatty acids by heating with $ZnCl_2$, Benedikt (1) found that these solid products consisted chiefly of a mixture of iso-oleic acid and stearolactone. Shukoff and Schestakoff (2) prepared this stearolactone, $CH_3-(CH_2)_{13}-\underset{\underset{\rule{2.5cm}{0.4pt}}{O}}{CH}-CH_2-CH_2-C=O$, likewise by heating oleic acid, $CH_3-(CH_2)_7-CH=CH-(CH_2)_7-CO_2H$ with anhydrous $ZnCl_2$ at 185°, getting a yield of 8 to 9%. The stearolactone was then oxidized by chromic acid to the corresponding keto-acid, and the oxime of the latter was prepared. By the Beckman rearrangement the oxime gave the tetradecylamide of succinic acid upon treatment with sulphuric acid, and this was converted by concentrated hydrochloric acid to succinic acid and tetradecylamine. These reactions seem to indicate that the keto group was in the 1,4 position, and that stearolactone is a gamma-lactone, regardless of the fact that oleic acid has its double bond in the 9,10 position.

In 1904 Shukoff (20) obtained a German patent on the preparation of stearolactone by the action of concentrated $H_2SO_4$ on oleic, iso-oleic, elaidic, sulfostearic and hydroxystearic acids.

Four years later, Shukoff and Schestakoff (3) investigated the formation of gamma-lactones from oleic and other unsaturated acids in which the double bond is not in the gamma position. They found that saturated hydroxy acids may also yield lactones, the OH group wandering to the gamma position, giving first a gamma-hydroxy acid and then a gamma-lactone. Thus, by heating with anhydrous $ZnCl_2$ or concentrated $H_2SO_4$, they obtained gamma-stearolactone

from oleic, elaidic, iso-oleic, theta-hydroxystearic, and iota-hydroxy stearic acids; gamma-beheno-lactone from erucic acid; and gamma-undecenolactone from undecenoic acid. Crotonic and alpha-hydroxy butyric acids, however, gave no lactone, indicating, apparently, that lactones are formed only when the double linking or hydroxyl group  is at least four carbon atoms removed from the carboxyl group.

The above investigators prepared undecenolactone by the action of 8 parts $H_2SO_4$ on 10 parts undecenoic acid at 80° for 6 hours. The product boiled at 286° without decomposition and was converted by acids or alkali to gamma-hydroxy undecenoic acid, having a melting point of 34° and reverting to the lactone on standing at room temperature.

THEORETICAL PART

## Spiral Compounds

The well known "Strain Theory" of Baeyer (4) states that "the four valences of the carbon atom act parallel to lines joining the center with the corners of a tetrahedron, making an angle of 109° 28' with each other. The direction of the valences can be varied, but any such variation produces a strain, the magnitude of which is proportional to the angle through which the valences are diverted". Stewart (5) gives the following formula for calculating the deviation for a ring compound containing $\underline{n}$ carbon atoms: $1/2 \left[ 109° \ 28' - \frac{2(n - 2)}{n} \cdot 90° \right]$. The least deviation is therefore 0° 44', that of a five atom ring. For a six atom ring, it is -5° 16'. Consequently, the angle of no deviation is between these two; and rings containing five and six atoms should be the most stable, the stability decreasing as the number of atoms increases or decreases. The intended application of the strain theory was to rings only of carbon atoms, but in most cases heterocyclic compounds behave in the manner which the theory predicts for carbon rings. In general, the theory is supported by the heats of combustion of ring compounds and by other data. The largest cyclic compound that has been synthesized is probably cyclononane, a ring of nine carbon atoms.

Baeyer assumed that all the carbon atoms lay in the same plane, as otherwise it would not be possible to calculate the strain by the above formula. It is conceivable, however, that a

closed chain might have three dimensions. Instead of closing in
a single plane, it might describe two superimposed loops, each of
which is stable according to Baeyer's theory; while the whole forms
a continuous closed chain far exceeding in the number of its atoms
the limit of stability which the strain theory predicts. This is
the conception of "spiral compounds". The name should not be
confused with that of "spirocyclic compounds", by which Baeyer
designated two complete rings having one atom in common.

A spiral compound might consist of the superimposed loops
mentioned above, or it might resemble the figure "8". The actual
configuration would be most difficult to determine. But, if it
were proved that a ring having an extraordinarily large number of
atoms were stable, such an assumption would have to be made.

It was with this end in view that the present investigation
of the structure of undecenolactone was undertaken. Previous work
tended to show, as already pointed out, that the lactone was not
an eleven atom ring, as it would have to be in order to be consider-
ed a spiral compound. Instead, through an unusual rearrangement
a gamma-lactone apparently resulted. Nevertheless, there was the
possibility that the spiral compound was formed, in part at least;
especially as a ring of eleven atoms would be of the magnitude to
make two loops, each of which, according to Baeyer's theory, would
have the maximum stability.

### The Structure of Undecenoic Acid

The literature contains much controversy over the structure
of undecenoic acid, the disputed point being the location of the

double bond.   Krafft (6) asserted that it has the formula
$CH_2=CH-(CH_2)_8-CO_2H$, basing his proof on the oxidation of undecen-
oic acid to sebacic acid by fuming nitric.   He also cited this
structure in support of his formula for ricinoleic acid (7)
$CH_3-(CH_2)_5-CHOH-CH=CH-(CH_2)_8-CO_2H$, from which the undecenoic acid
is obtained by destructive distillation.   Goldsobel (8), however,
attacked Krafft's formula for ricinoleic acid, maintaining it to
be $CH_3-(CH_2)_5-CHOH-CH_2-CH=CH-(CH_2)_7-CO_2H$ on the basis of his in-
vestigation of ricinstearolic acid.   He furthermore drew the con-
clusion that undecenoic acid has, therefore, the corresponding
formula  $CH_3-CH=CH-(CH_2)_7-CO_2H$.   Two years later, Krafft (9)
presented additional evidence in favor of his theory, in his study
of dehydro-undecenoic acid, $CH\equiv C-(CH_2)_8-CO_2H$.   Others who have
entered the controversy are Perkin (10), who supported Krafft's
view after determining the magnetic rotation, and Eykman (11), who
found that the refractometric properties tended to confirm Gold-
sobel's theory.

A piece of work that proves without doubt that Krafft's form-
ula for undecenoic acid is correct was performed by Walker and
Lumsden (12).   By treating undecenoic acid with hydrobromic acid,
they obtained two hydrobromides with melting points of $35°$ and $50°$.
The hydrobromide of higher melting point is converted to the
corresponding hydroxy acid by sodium hydroxide, and this is oxi-
dized with chromium trioxide.   The compound thus obtained is a
dicarboxylic acid of eleven carbon atoms, thus proving that the
hydroxyl and consequently the bromine were on the end carbon,

and that therefore the double bond is adjacent to it, as Krafft claims.

Notwithstanding this fact, Goldsobel's and not Krafft's formula for ricinoleic acid has been shown to be correct by Kasansky (14), who studied its bromine addition products, and by Jegorow (13), who split it at the double bond by the action of nitrogen peroxide and concentrated hydrochloric acid. This apparent inconsistency has recently been explained by Mlle. Norduyn (15). By converting the unsaturated compounds into their ozonides and decomposing these with water, she confirmed Goldsobel's formula for ricinoleic acid and Krafft's formula for undecenoic acid, drawing the logical conclusion that in the destructive distillation by which undecenoic acid is obtained from castor oil, the double bond of ricinoleic acid is transposed.

## The Structure of Undecenolactone

If undecenolactone were an eleven atom ring, its formation from undecenoic acid would be through the addition of $H_2SO_4$ to the double bond, afterwards splitting off thus:

$$CH_2=CH-(CH_2)_8-\underset{OH}{C}=O + H_2SO_4 \longrightarrow CH_3-\underset{OSO_3H}{CH}-(CH_2)_8-\underset{OH}{C}=O \longrightarrow$$

$$CH_3-\underset{\lfloor_____O\rfloor}{CH}-(CH_2)_8-C=O + H_2SO_4$$
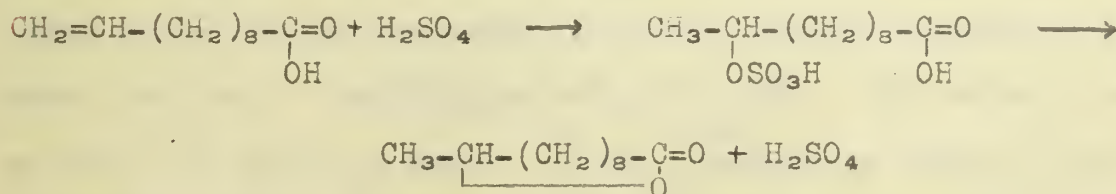
That a true lactone has been formed is proved by the nonacidity of the compound, its saturation, and its molecular weight, which is the same as that of undecenoic acid. The hydroxy acid was prepared from the lactone by saponification with NaOH. It

is a solid melting at 50° to 51°. Shukoff and Schestakoff (3),
who recorded the melting point as 34°, undoubtedly were working
with impure material; especially since their hydroxy acid reverted
to the lactone on standing. The writer found that an impure
sample did so revert, but that the recrystallized hydroxy acid of
the melting point above given was stable during a period of several
weeks.

By oxidizing the hydroxy acid with chromic acid, the corres-
ponding keto-acid, melting at 78° to 79°, was prepared. Tests
made on this compound to determine the presence of the group
$CH_3-\underset{O}{\overset{..}{C}}-$ were in general negative though not conclusive. This
same keto-acid was also obtained by the direct oxidation of un-
decenolactone by chromic acid.

The final proof of the structure of undecenolactone was based
on the products of the oxidation of the hydroxy acid by fuming
nitric. Chiefly caprylic, but also some succinic acid, was thus
obtained. This shows that the breaking of the hydroxy acid
occurred for the most part between the gamma and delta positions,
but also between the beta and gamma carbons. Therefore, the hyd-
roxyl group was in the gamma position, and undecenolactone is a
gamma lactone: $CH_3-(CH_2)_6-CH-CH_2-CH_2-C=O$. The malonic acid form-
ed with the caprylic would, in the presence of fuming nitric, de-
compose to acetic acid and carbon dioxide. The small amount of
heptylic acid that resulted along with the succinic, remained in
the caprylic acid as an impurity.

The rearrangement whereby a gamma lactone is formed from undecenoic acid must have taken place, and the conclusion of Shukoff and Schestakoff is thus confirmed. Consequently, undecenolactone is not a spiral compound as the latter was above defined.

EXPERIMENTAL PART

## The Preparation of Undecenoic Acid

The undecenoic acid used was prepared according to the method of Krafft (16).   One kilogram of commercial cold-pressed castor oil was placed in a two-liter flask and distilled on a lead bath at 95 mm. pressure.   380 grams of a distillate consisting of heptaldehyde, undecenoic acid and a small quantity of water passed over.   At this point the residue foamed so badly that the distillation had to be discontinued, whereupon the residue solidified almost instantly to a rubbery solid.   The water was separated from the distillate, and the latter was fractionated on an oil bath at  16 mm. pressure.   The undecenoic acid fraction was taken between 168° and 181°, most of it passing over at 172°.   105 grams of a high boiling residue remained.   The yield of undecenoic acid was 91 grams, or 16.5% of the theoretical, the theoretical amount of undecenoic acid in castor oil being 55.0%.   The average yield for four runs was 14.3%.   Krafft reports a yield of only 10%.

The lead bath was found to be superior to an oil bath, sand bath or bare flame for maintaining the necessary constant high temperature during the destructive distillation without local superheating.

The rubbery solid, the formation of which terminated the destructive distillation, is a polymer, polyundecenoic acid (17). Its formation chiefly is responsible for the low yield of undecenoic acid.   Heating it on a steam bath for 24 hours with alcoholic potash depolymerized it to some degree (18).   The undecenoic

acid distilled from the residue so treated was, however, not of sufficient purity or quantity to make this a practicable method for increasing the yield. The foaming and solidification occurred very quickly in this redistillation.

The purest undecenoic acid obtained had a neutral equivalent of 195 (theoretical 184), melting point, 20°-22° (Krafft, 24.5°) and boiling point, 173° at 17 mm. (Krafft, 165° at 15 mm.). The impurity present was probably biundecenoic acid, a polymerization product of two molecules of undecenoic acid to form a mono-basic acid of twice the molecular weight (17):

$$2\ CH_2=CH-(CH_2)_8-\overset{/\!/O}{C}-OH \longrightarrow CH_2=CH-(CH_2)_8-\overset{/\!/O}{C}-O-CH_2-(CH_2)_9-\overset{/\!/O}{C}-OH$$
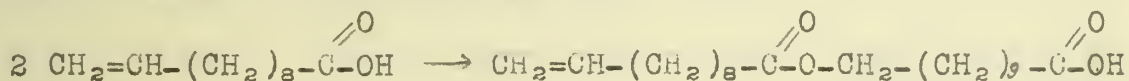
It boils at 265° to 275° at 15 mm. Since the polymerization is accelerated by heat and since biundecenoic acid has a melting point of 29°-30°, purification of the undecenoic acid could not be effected, either by fractional distillation or crystallization. The amount of biundecenoic acid present calculated from the neutral equivalent of 195 was 5.9%.

The high boiling residue remaining after the removal of the undecenoic acid fraction consisted chiefly of biundecenoic acid. 130 grams of this residue was refluxed on the steam bath for 24 hours with 40 grams KOH and 100 cc. alcohol. The alcohol was then boiled off; the acids were precipitated with HCl, washed, and distilled on the oil bath under 27 mm. pressure. 33 grams of un-decenoic acid came over between 183° and 193°, most at 187°. The total yield of undecenoic acid was thus increased to 22.5% of the theoretical.

## Preparation and Properties of Undecenolactone

The undecenolactone was prepared from undecenoic acid by treat-
ment with sulphuric acid.   To determine the proper conditions, the
following runs were made:

| Run No. | Conc. of $H_2SO_4$ % by vol. | Temp. ° C. | Time Hours | Undec. Acid Grams | $H_2SO_4$ cc. | Result |
|---------|---------|------|-----|-----|------|--------|
| 1 | 10 | 100 | 2.5 | 5 | 100 | No conversion |
| 2 | 30 | 100 | 2.5 | 5 | 125 | No conversion |
| 3 | 40 | 100 | 2.5 | 5 | 100 | No conversion |
| 4 | 50 | 100 | 2.0 | 10 | 100 | Charring. 2.5 gr. insoluble in $Na_2CO_3$ solution. Distilled, giving 2.3 grams lactone |
| 5 | 65 | 100 | 2.0 | 10 | 100 | Excessive charring. Solid carbon residue |
| 6 | 100 | 0 | 3.5 | 5 | 5 | No conversion |
| 7 | 100 | 20 | 20 | 15 | 5 | Slight conversion |
| 8 | 100 | 60 | 6 | 10 | 10 | Charring. 4.4 gr. insoluble in $Na_2CO_3$ solution. Distilled, giving 2.1 grams lactone |
| 9 | 100 | 100 | 1 | 5 | 25 | Excessive charring |

This data shows that the lactone can be obtained both by re-
fluxing with 50% $H_2SO_4$ and by treating with concentrated $H_2SO_4$ at
60°, with a slightly better yield by the former method.  Accordingly
50 grams undecenoic acid was refluxed with 300 cc.of 50% (by volume)
$H_2SO_4$ for 2.5 hours.   The oil was then separated from the reaction
mixture, washed twice with $Na_2CO_3$ solution and once with water.

The alkali insoluble portion, which was extracted with ether, weighed 20.4 grams. This was subjected to distillation under reduced pressure, 15 grams of undecenolactone coming over between 143° and 146° at 8 mm. pressure. Yield, 30% of the undecenoic acid.

The lactone thus obtained was a colorless liquid having a boiling point of 145.5° at 8 mm. pressure. It boiled at about 270° with some decomposition under atmospheric pressure. At -15° it was still liquid. The specific gravity of the lactone was 0.9358 at 24°. Its index of refraction was 1.4525 $[n]^{22}$. The odor resembled that of peaches and was much intensified when a drop was taken up in a large quantity of water.

## Investigation of the Structure of Undecenolactone

The molecular weight of the undecenolactone was determined from its saponification equivalent. 1.2190 grams was refluxed with 25 cc. 0.73 N alcoholic potash for 2 hrs. The excess alkali was titrated with 0.2665 N HCl; which, subtracted from a blank run, showed 24.42 cc. HCl difference. This gave a saponification equivalent of 187.3, the theoretical value of the molecular weight of the lactone and of undecenoic acid being 184.

The absence of the carboxyl group from the lactone was proved by the determination of its acidity. 0.211 grams required only 0.01 cc. of 0.2 n alkali for an end point with phenolphthalein, showing it to be neutral in reaction.

The determination of the iodine number of undecenoic acid and

undecenolactone proved the latter to be saturated, the double bond
of the acid being removed by the formation of the lactone. The
method employed was that of Wijs (19), the following results being
obtained:

| | Undecenoic Acid | | Undecenolactone | |
|---|---|---|---|---|
| | 1 | 2 | 1 | 2 |
| Sample, grams | 0.2169 | 0.2181 | 0.2534 | 0.2473 |
| $Na_2S_2O_3$, sol. cc. | 21.35 | 21.47 | 1.35 | 1.30 |
| Iodine Number | 135.4 | 135.5 | 7.3 | 7.2 |

1 cc. $Na_2S_2O_3$ solution = 0.01376 grams $I_2$

The theoretical value for undecenoic acid is 137.9. The very low
iodine number obtained for the lactone may be due to a small amount
of unsaturated impurity or to iodine substitution.

The saponification product of undecenolactone was prepared by
refluxing 2.5 grams with 100 cc. of 10% NaOH for 4.5 hours. Any
unchanged lactone was then extracted with ether. The hydroxy acid
formed was precipitated with HCl, separated, and dried. This oil
on cooling to 0° solidified completely, remaining solid at room
temperature. The hydroxy acid was purified by crystallizing
from petroleum ether, yielding 0.9 gram of white crystals having a
melting point of 50°-51°. The neutral equivalent was 205.6 as
determined by titration with 0.2 N alkali, the theoretical molecular
weight of the hydroxy acid being 202.

1.5 grams of the hydroxy acid in the form of the crude oil
from which any unsaponified lactone had been removed, was distilled
under reduced pressure. 0.5 gram of the colorless distillate

which came over at 158° required only 0.5 cc. of 0.2 N alkali for neutralization. This low value indicated that the distillate consisted chiefly of a neutral compound and that the hydroxy acid probably reverted to the lactone with the eleminiation of water upon heating.

The pure hydroxy acid was subjected to the iodoform test to determine the presence of the group $CH_3-CHOH-$. Although the characteristic odor of $CHI_3$ was faintly detected, no precipitate could be observed.

2.5 grams hydroxy acid, as the crude oil obtained by saponification of the lactone, was treated with 5 grams $K_2Cr_2O_7$ dissolved in 50 cc. of 10% $H_2SO_4$. The mixture was heated on the steam bath with stirring for two hours. After standing over night, the oil was separated, washed with water, dissolved in NaOH, and re-precipitated with HCl. The keto-acid thus prepared was crystallized from hot water, giving 1.6 grams of a white solid melting at 78° to 79° and having a neutral equivalent of 203. The theoretical neutral equivalent of the keto-acid is 200.

The keto-acid when given the iodoform test for the group $CH_3-CO-$ yielded no precipitate. Neither was any chloroform detected after treatment with NaClO. Sodium nitroprusside, however, appeared to give a positive reaction for the group, though this was not definite.

The keto-acid was also prepared by the direct oxidation of the lactone. 1.0 gram of the latter was refluxed for one hour with 15 cc. of a solution containing 5 grams $CrO_3$ and 4 cc. con-

centrated $H_2SO_4$ in 30 cc.water. After cooling, the solid was
filtered off and crystallized from hot water, yielding 0.3 grams
of the keto-acid, melting at 77° to 79°.

Oxidation of the hydroxy acid by alkaline permanganate yielded
an oil having a neutral equivalent of 201. The oxidation was
incomplete, the oil probably consisting of a mixture of the keto
and hydroxy acids. On cooling, it deposited a few white crystals,
but these could not be isolated.

2.0 grams of crude hydroxy acid was heated on the steam bath
with 10 cc. fuming $HNO_3$ till $NO_2$ ceased to be evolved. On cooling
the reaction mixture, white crystals were deposited. 100 cc. of
water was added, and from this an oil was separated. This was
taken up with ether, washed three times with water, evaporated, and
dried. The product was 0.72 grams of an oil having a neutral
equivalent of 142.5, indicating it to be caprylic acid, which has
a theoretical neutral equivalent of 144. The caprylic acid was
treated with $PCl_3$ to prepare capryl chloride, which gave capryl
amide on the addition of $NH_4OH$. The amide, after crystallizing
from hot water, melted at 103°. The literature gives 105° to
106° as the melting point of capryl amide. The identity of the
caprylic acid was thus confirmed. The slightly low value of its
neutral equivalent was due to the presence of a small quantity of
heptylic acid.

The solution from which the caprylic acid was first separated
was partly neutralized with NaOH and evaporated to dryness on the
steam bath. The residue was extracted three times with ether,

which deposited a white solid on evaporation. The latter was purified by crystallization from ether, yielding 0.15 grams of a solid acid with a melting point of 184° and a neutral equivalent of 60.7. Succinic acid melts at 185° and has a theoretical neutral equivalent of 59. The solid was thus identified as slightly impure succinic acid.

## SUMMARY

1. The term "spiral compound" was defined and the possibility of undecenolactone having such a structure was discussed.

2. Undecenoic acid was prepared from castor oil by the method of Krafft.

3. Undecenoic acid was converted to undecenolactone by treatment with $H_2SO_4$.

4. Undecenolactone was saponified to the corresponding hydroxy acid by NaOH.

5. The hydroxy acid was oxidized to the keto-acid by chromic acid.

6. The hydroxy acid was oxidized to caprylic and succinic acids by fuming $HNO_3$.

7. Undecenolactone was thus proved to be a gamma lactone, confirming the results of Shukoff and Schestakoff and showing that it is not a spiral compound.

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