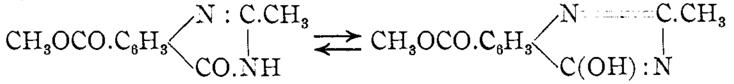
needles, melting with decomposition at 342° (corr.). It is soluble in alkalies and reprecipitated on acidification.

Found: C, 58.9; H, 4.0; N, 13.95. Calulated for $C_{10}H_8O_3N_2$: C, 58.8; H, 3.9; N, 13.72.

It is difficultly soluble in boiling water and crystallizes therefrom with a molecule and a half of water of crystallization, which is driven off at 110°.

Methyl Ester,



$$CH_3OCO.C_6H_3\left\langle\begin{array}{l}N:C.CH_3\\ \quad\ \ |\\ CO.NH\end{array}\right. \rightleftarrows CH_3OCO.C_6H_3\left\langle\begin{array}{l}N=C.CH_3\\ \qquad\ \ |\\ C(OH):N\end{array}\right.$$

This ester was prepared from the sodium or potassium salt of the above acid with the calculated amount of dimethyl sulphate. It crystallizes from alcohol in colorless silky needles, very light and bulky, m. p. 273-4° (cor.).

Found: N, 12.9. Calculated for $C_{11}H_{10}O_3N_2$: N, 12.8.

INVESTIGATION OF THE ESSENTIAL CONSTITUENT OF TURKEY-RED OIL AND ITS DERIVATIVES.

BY AD. GRÜN AND M. WOLDENBERG.

Received July 10, 1909.

Turkey-red oil, obtained by the action of concentrated sulphuric acid on castor oil, and dissolving the resulting product in ammonia or soda solution, is a very complicated mixture of derivatives of ricinoleic acid, $C_{17}H_{32}(OH)COOH$.

It contains (in the form of salts): free ricinoleic acid, the sulphuric ester and the sulphuric ester of castor oil;[1] perhaps also a mixed diricinoleic-acid-sulphuric glyceride,[2] sulphuric ester of dioxystearic acid,[3] ricinoleic acid anhydride,[4] polyricinoleic acids,[5] and other complicated compounds.

The reaction of sulphuric acid on ricinoleic acid or its glyceride has been often investigated. Regardless of this fact, however, the course of the reaction in relation to time is still very uncertain; the most important product of this reaction, the ricinoleic-acid-sulphuric ester, has not been thoroughly investigated (not even isolated in pure form) and has never been characterized through its derivatives.

The following research has been undertaken with the object of joining the numerous bits of information on this subject, which are at hand, and filling in such gaps as may present themselves, so as to leave the problem, if possible, conclusively solved. The reaction of gram-molec-

---

[1] Benedikt and Ulzer, *Monatsh. Chem.*, 8, 208 (1887). Scheurer-Kestner, *Bull. soc. ind. Mulhouse* (1891). See also Wilson, *J. Soc. Chem. Ind.*, 26 (1891).

[2] Bogajewski, *Chem. Centrbl.*, 1897, II, 335. See also Liechti, *Ber.*, 16, 2453 (1883).

[3] Fuillard, *Bull. soc. chim.*, 1891, 6; 1894, 280. Fuillard, *Bull. soc. ind. Mulhouse*, 1892, 415.

[4] Fuillard, *Loc. cit.*

[5] Scheurer-Kestner, *Loc. cit.* Fuillard, *Loc. cit.*

ular equivalents of sulphuric acid and ricinoleic acid was investigated first, then the reaction between sulphuric acid and the methyl ester of ricinoleic acid was studied. (In place of the glyceride [castor oil] we used the methyl ester, as this reduces the difficulties to a minimum, and at the same time gives a similar reaction to that of the glyceride.) As the isolation of the sulphuric ester of the ricinoleic acid from the other products of this reaction did not seem worth while, we worked out another method for its direct preparation. This new method was adapted to saturated and unsaturated derivatives of ricinoleic acid, so that in this way derivatives of the sulphuric ester of ricinoleic acid could be obtained and compared.

The following is an outline of the experiments undertaken: 1. Action of sulphuric acid on ricinoleic acid and on its methyl ester. 2. Action of chlorsulphonic acid on ricinoleic acid and on its methyl ester (preparation of the sulphuric ester, $C_{17}H_{32}(OSO_3H)COOH$). 3. Preparation of ricinstearoleic acid and its sulphuric ester. 4. Synthesis of the sulphuric ester of ricinoleic acid dibromide. 5. Direct conversion of ricinoleic acid methyl ester into 12-hydroxystearic acid methyl ester. 6. Preparation of 12-hydroxystearic acid and conversion into its sulphuric ester. 7. Preparation of polyricinoleic acids.

Sulphuric acid reacts violently with ricinoleic acid; at room temperature there follows an instantaneous black coloring, due to oxidation of the organic compound and generation of sulphur dioxide. It is necessary, therefore, to mix the components of the reaction at a temperature of at least 0°. Even with this precaution, an increase of temperature is noticeable after the addition of each drop of sulphuric acid.

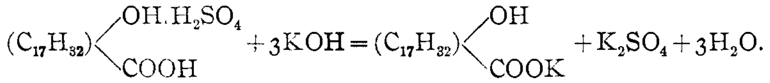
The first series of tests showed somewhat surprising results. These showed that the esterification is much slower than expected, on judging by sight. Numerous checks always gave similar results, namely, that —as was analytically determined through the acid number[1] and the Hübl number[2] of the reaction mixture—only small amounts of the ricinoleic acid sulphuric ester were formed, and that also in the first few hours of the reaction there followed no addition on the double bond of ricinoleic acid with formation of dihydroxystearic acid monosulphuric ester.

The reaction mixture is, regardless of the above observations, a wholly homogeneous, clear liquid, in which neither free ricinoleic acid nor sulphuric acid can be directly detected. This phenomenon is explainable on the assumption that first an addition of sulphuric acid takes place not on the double bond, but on the alcoholic hydroxy group of the ricinoleic acid (or rather on its hydrogen atom), and a salt is formed, which by virtue of its nature is unstable and decomposes when titrated:

---

[1] Acid number = mg. KOH per 1 gram substance.

[2] Hübl number = per cent. iodine, which could be added.



$$(C_{17}H_{32})\left\langle\begin{matrix}OH.H_2SO_4\\COOH\end{matrix}\right. + 3KOH = (C_{17}H_{32})\left\langle\begin{matrix}OH\\COOK\end{matrix}\right. + K_2SO_4 + 3H_2O.$$

Other observations show also that the hydroxy group of the ricinoleic acid possesses a weak basic character.

A primary formation of salts during the esterification of alcohols through sulphuric acid is possible. Hantzsch[1] found, that methyl alcohol dissolved in concentrated sulphuric acid showed two-thirds its normal value by the cryoscopic determination of its molecular weight. This proves, according to Hantzsch, that there appears to be a primary addition, and that there follows on splitting off of water, the formation of the ester. Also in the case of ricinoleic acid, the reaction resolves itself principally into a splitting off of water and an ester formation.

The addition on the double bond proceeds more slowly. However, if we let the reaction mixture stand until the first reaction (esterification) has quantitatively taken place (determined by acid number), then the Hübl number of the mixture shows that the addition on the double bond has also taken place to a decidedly noticeable degree.

From the decrease of the Hübl number (= 15.6) it may be calculated that the reaction mixture contains approximately 18 per cent. of a saturated acid, 9,12-dihydroxystearic acid,

$$CH_3(CH_2)_5—CH(OH)—(CH_2)_2—CH(OH)—(CH_2)_7—COOH;^2$$

it follows, therefore, that about one-fourth of the quantity of ricinoleic acid reacted in this sense (see Plate I). As the dihydroxystearic acid does not exist here free, but in the form of its mono- and perhaps also its disulphuric ester, so the observed decrease in the acid number is not traceable exclusively to the esterification of ricinoleic acid.

The acid number determined after the reaction of the mixture for 115 hours coincides with that calculated for a quantitative formation of ricinoleic-acid-sulphuric ester, but the side reaction, which also consumes sulphuric acid, shows that even after such a long space of time the first reaction is *not* complete.

Besides the two reactions mentioned, there remains a third still to be considered, namely, that of the formation of anhydrides of ricinoleic acid (by removal of water), which would also tend to decrease the acid number. It is easily seen that the analytical results are not sufficiently decisive to give an entirely clear picture of the course of the reaction. Nevertheless, these results suffice to show the investigator that the reaction is indeed complicated, and that this method for the preparation of ricinoleic acid sulphuric ester is not suitable.

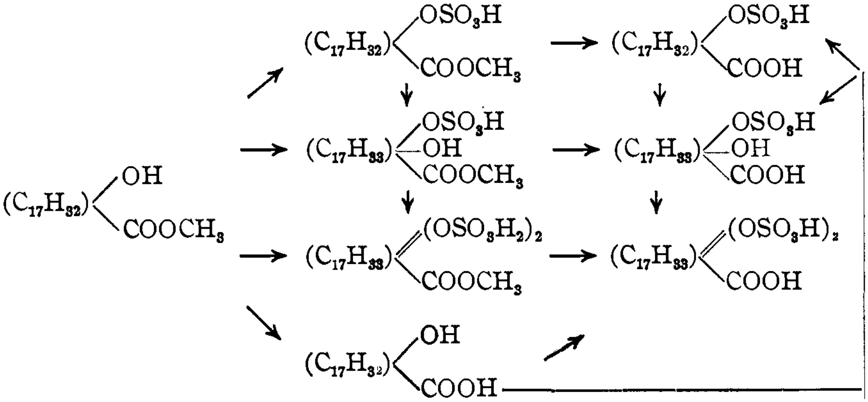
Still more complicated are the circumstances in the reaction of ricin-

---

[1] *Z. physik. Chem.*, 61, 267 (1907).

[2] Ad. Grün, *Ber.*, 39, 4400 (1906).

oleic-acid-methyl ester, because in this case there follows, on the one hand, a decrease in the acidity of the mixture by the esterification of the alcoholic hydroxy group (through addition on the double bond), and on the other hand, there is also the possibility of an increase in the acidity due to saponification, in that the primarily formed compound, $CH_3—OSO_3H$, decomposes:



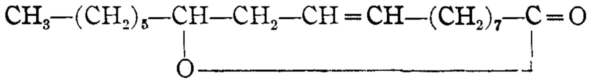
Nevertheless, this series of tests shows a continual decrease of the acid number (also the Hübl number), consequently a simultaneous progress of the substitution- and addition-reactions (see Table II). The reaction mixture, after about 118 hours, contains 14 per cent. saturated acid (calculated as ester, from the decrease in the Hübl number). Therefore, about 18.5 per cent. of the ricinoleic acid ester originally used, added sulphuric acid on the double bond. It follows that a new method is necessary for the preparation of ricinoleic acid sulphuric ester. From a great number of tests, it became evident that the most appropriate method is with chlorsulphonic acid in a neutral medium. After trying chloroform, carbon tetrachloride, and several other solvents, ether was tried and found to give the best results.

The pure ester obtained in this manner:

$$CH_3(CH_2)_5—CH(OH)—CH_2—CH=CH—(CH_2)_7—COOH + ClSO_3H =$$
$$ClH + CH_3(CH_2)_5—CH(OSO_3H)—CH_2—CH=CH—(CH_2)_7—COOH$$

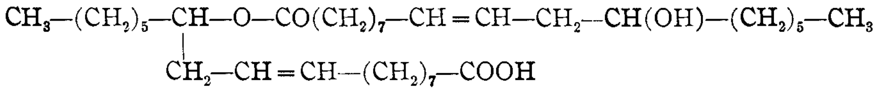
was investigated and the results coincided partly with those which have been already reported of the technical product. The compound is very stable in alkaline solution, to a certain degree in cold water, but is unstable in acid solution. By boiling a diluted solution of the ester, there appeared to be a quantitative splitting off of sulphuric acid.

Up to the present it has been overlooked that by this process the ricinoleic acid is not wholly regenerated. A large portion of the acid is converted into an anhydride. As yet, it is not decided which compound is formed. The simplest suggestions are as follows:

I. 

$$CH_3-(CH_2)_5-\underset{\underset{O}{|}}{CH}-CH_2-CH=CH-(CH_2)_7-\underset{|}{C}=O$$

Lactone of ricinoleic acid.

II. 

$$CH_3-(CH_2)_5-\underset{\underset{CH_2-CH=CH-(CH_2)_7-COOH}{|}}{CH}-O-CO(CH_2)_7-CH=CH-CH_2-CH(OH)-(CH_2)_5-CH_3$$

Ricinoleic-acid-ester of ricinoleic acid.

It is also possible that a lactide of ricinoleic acid could be formed. This point requires special investigation, however, and time does not permit of its treatment in this work.[1]

It was found to be impossible to prepare the sulphuric ester of ricinoleic acid methyl ester by a direct method. This was due to the fact that the methyl ester saponified partially, regardless of all precautions. In this case the resulting product is also principally the sulphuric ester of the *free* acid. It was characterized in the form of its barium salt.

The reaction of chlorsulphonic acid on the other derivatives of ricinoleic acid were carried out without many difficulties.

The greatest difficulties were encountered while working with the original compounds. This is especially true of the 12-hydroxystearic acid, which was finally prepared by means of catalytic reduction of the methyl ricinoleate in ethereal solution (analogous to Fokin's splendid method for reducing unsaturated compounds), and saponification of the saturated ester thus obtained. The sulphuric ester of the 12-hydroxystearic acid is more stable than the ricinoleic acid derivative, which fact is to be expected, as this compound is less liable to intramolecular reactions.

The derivative of the ricinstearoleic acid proved to be quite stable. It occupies about the middle position, as regards stability, between the sulphuric ester of ricinoleic acid and that of 12-hydroxystearic acid.

In the case of the sulphuric ester of ricinoleic acid dibromide the tendency to form an anhydride through the splitting off of water, or rather sulphuric acid, was likewise observed; in fact, the property of "closing of the ring" (intramolecular reaction) is *more* marked with this compound than even with ricinoleic acid itself. It was necessary to prove this very point with a saturated derivative of ricinoleic acid, which showed that the condensation is *independent* of the configuration of the ricinoleic acid and its unsaturated derivatives. The sulphuric ester of the dibromide, $C_{17}H_{32}Br_2(OSO_3H)COOH$, is more unstable than the rest of the analogous compounds, but this characteristic may be put down

---

[1] From the report of an investigation still in progress under Ad. Grün and H. Wetterkamp, it has been determined, that first the compound II is formed, and then after long heating of the ester in water the lactide of ricinoleic acid is formed. See *Z. Farben-Industrie*, 7, Heft 22 (1908).

to the instability of the bromine atom, which fact was already demonstrated in the case of ricinoleic acid dibromide.

The numerous observations of the formation of anhydrides or inner esters created a desire for a method of preparing these compounds directly. This desire was made keener when it was learned that the closing of "molecular rings," such as the formation of a 1,12-lactone or lactide had been heretofore never ascertained.

The action of phosphorus pentoxide on ricinoleic acid was investigated with this end in view. These experiments led to peculiar results, namely, that polymerization products were formed and not anhydrides, as was expected. Two distinctly different polymerized ricinoleic acids were isolated. One compound is, as might be concluded from its properties, a product of the union of a lesser number of molecules, $[(C_{18}H_{34}O_3)_2?]$, which is soluble in ether and can be reconverted into ricinoleic acid. The other compound shows no properties of a fatty acid but has a more rubber-like consistency, is insoluble in all organic solvents, and does not allow itself to be reconverted into ricinoleic acid (at least not by the same conditions as the first polymerization product).

Action of Sulphuric Acid on Ricinoleic Acid.—Fifteen grams ricinoleic acid were mixed with an equimolecular quantity (= 4.888 gram) of sulphuric acid, which was added drop by drop. The ricinoleic acid was immersed in a cooling mixture and was constantly stirred during the operation. The addition of the sulphuric acid lasted ½ hour. The viscous, dark brown product was homogeneous, but nevertheless contained a mixture of different reaction products, which fact was shown by its partial insolubility in water.

The above operation was repeated with slightly larger quantities of the components. The acid number of the reaction product was determined so as to decide whether or not any ester was formed.

1.1511 g. substance required 29.40 cc. KOH solution for neutralization (1 cc. = 0.01320 g. KOH).

Acid number found	337.2
Calculated acid number of an equimolecular mixture of free ricinoleic acid and free H_2SO_4	425.0
Calculated acid number of ricinoleic-acid-sulphuric ester and 1 molecule water	283.3

It is seen that the alcoholic hydroxy group of the ricinoleic acid reacts with the formation of ester, but that this reaction is not quantitative. The determination of the acid number and the Hübl number, as well as that of free sulphuric acid, of the reaction product, were repeated at certain intervals of time, so as to ascertain whether an addition of sulphuric acid on the double bond of ricinoleic acid follows instead of the formation of ester, by the reaction of the hydroxy group with sulphuric acid.

Progress of the Reaction in Relation to Time.—The quantities used in reaction were 26.8956 g. ricinoleic acid and 8.7880 g. sulphuric acid. The sulphuric acid was added drop by drop to the ricinoleic acid, which was cooled to 0° by means of a freezing mixture. The reaction mixture did not appear homogeneous at this stage. The addition of the sulphuric acid required about 1½ hours. The mixture was allowed to stand at room temperature about two hours after the addition was completed, after which period the solution was obtained in a perfectly homogeneous condition. By this time the reaction had taken place and samples were weighed for the various determinations, as by longer standing the mixture decomposes. The weighed samples were kept in a desiccator until the time for their respective working-up became due.

[By means of a special test it was determined that the presence of sulphuric acid has no effect upon the reaction of the mixture with Hubl's iodine solution.]

The following results were obtained for the samples:

TABLE I.

Time.	Acid number.	Hübl number.	Free sulphuric acid. Per cent.	Sulphuric acid (not free) out of the difference. Per cent.	Free ricinoleic acid. Per cent.
Mixture of free ricinoleic acid and sulphuric acid, 1 : 1	425.0	64.04	24.62	...	75.38
After 2 hours	365.55	66.72	15.99	8.63	5.93
" 18 "	335.20	58.44	...	...	...
" 27 "	327.20	59.31	18.52	6.10	7.41
" 42 "	314.84	54.89	20.73	3.89	0
" 50 "	311.80	54.98	21.03	3.59	0
" 68 "	306.23	51.53	14.10	10.52	0
" 74 "	303.78	51.77	...	...	...
" 80 "	302.78	50.54	15.75	8.87	0
" 98 "	300.13	49.59	...	...	...
" 115 "	279.79	48.38	18.36	6.26	0

Action of Sulphuric Acid on Ricinoleic-acid-methyl Ester (Progress of the reaction in relation to time).—The quantities used in the reaction were 19.1849 g. methyl ricinoleate and 6.0237 g. sulphuric acid. This reaction was carried out in exactly the same manner as the one just described with free ricinoleic acid. After the mixture was homogeneous, the samples for the various determinations were weighed out and worked up as the time for their analysis fell due.

The free sulphuric acid was determined in the first series of tests. The reaction mixture contained no free ricinoleic acid.

Following is a tabulated form of results obtained for this series of tests:

TABLE II.

Time.	Acid number.	Hübl number.	Free sulphuric acid. Per cent.	Sulphuric acid (not free) out of the difference. Per cent.
Mixture of free ricinoleic acid methyl ester and free sulphuric acid, 1 : 1	273.6	61.86	23.9	...
After 2 hours	250.02	57.90	22.89	1.01
" 8 "	245.69	52.83	19.66	4.24
" 22 "	233.99	57.46	...	...
" 31 "	231.47	57.91	14.41	9.48
" 46 "	225.62	50.71	10.73	13.17
" 55 "	225.63	53.90	12.13	11.73
" 70 "	225.92	51.20	13.51	10.38
" 79 "	227.52	53.24	...	...
" 94 "	232.51	49.09	17.02	6.88
" 103 "	231.08	48.28	...	...
" 118 "	236.83	50.36	21.78	2.12

Action of Chlorsulphonic Acid on Ricinoleic Acid, CH_3—$(CH_2)_5$—$CH(OSO_3H)CH_2$—$CH=CH$—$(CH_2)_7$—$COOH$.—After we had tried several series of tests under various conditions, and were satisfied that the ricinoleic-acid-sulphuric ester could not be obtained by the direct addition of sulphuric acid, we turned to chlorsulphonic acid, which finally gave us favorable results. It became evident that operating in absolute ether solutions was most advantageous; ligroin could not be used, as ricinoleic acid is insoluble therein, chloroform offered certain advantages, for example, on account of its small hygroscopicity, and because of its small capability of entering into side-reactions, but ether had the great advantage of being easily vaporized.

The reactions were carried out in a thick-walled bottle, which was closed with a double-bored cork stopper, through one hole of which a dropping funnel protruded, and an exhaust tube through the other. A calcium chloride tube was attached to the exhaust to insure against moisture entering the bottle. The reaction took place at a temperature of about —5°, obtained by a freezing-mixture. The ricinoleic acid was weighed into the bottle, and about 3 times the volume of absolute ether was added. After cooling the whole to the desired temperature, the calculated quantity of chlorsulphonic acid was allowed to drop into the bottle. The addition required ordinarily about 1½ hours.

The following quantities were used for the reaction at successive trials:

13 gm. ricinoleic acid and 5.2 gm. $ClSO_3H$.
13.68 gm. ricinoleic acid and 5.47 gm. $ClSO_3H$.
24.27 gm. ricinoleic acid and 9.71 gm. $ClSO_3H$.

After the reaction was completed, the ethereal solution was placed in a desiccator over sulphuric acid and moist sticks of potassium hydroxide, so that the ether and hydrochloric acid could be removed. (We tried to remove the hydrochloric gas by shaking the ethereal solution with freshly precipitated, dry silver oxide or silver carbonate, but the results were not favorable and the idea was given up.)

After several hours the preparation is obtained in pure form, free from ether and hydrochloric acid. The ester is a brown, thick, weakly fluorescent liquid, soluble in ether, alcohol or chloroform. It is also soluble in water; saturated solutions contain about 10 per cent. of the ester. The compound in water is light yellow, and lathers considerably on being shaken.

On long standing it begins to decompose, which may be concluded from the change in color to dark brown or even black and the reaction for free sulphuric acid, either of which is *not* a property of the freshly prepared ester:

Calculated for $C_{18}H_{34}SO_6 + H_2O$:	Acid number, 283.3;	SO_4, 24.23.
Found:	Acid number, 282.44;	SO_4, 24.44.

It was formerly difficult to prepare the free sulphuric ester in perfectly pure form, as the removal of the hydrochloric acid required several hours, and during this time decomposition of the ester had already started. On the other hand, the salts of the ester are more easily obtained in pure form. We may start from the barium or ammonium salt to obtain these.

A solution of the ester in water is precipitated with one-third the calculated amount of barium chloride, so that, if sulphuric and dihydroxystearic acids are present, they can be removed with a little of the barium salt of the ester. The filtrate from this precipitation is neutralized with ammonium hydroxide and precipitated with an excess of barium chloride. The barium salt is washed with water, then with hot alcohol and finally with ether. The compound obtained by this treatment is identical with that prepared from ricinoleic-acid-methyl ester (see below).

It is perhaps easier, as was later discovered, to start from the ammonium salt. The sulphuric ester was dissolved in absolute alcohol, cooled in ice, and supersaturated with ice-cold, alcoholic ammonium hydroxide. At this stage, if there is a small precipitation of ammonium sulphate (and ammonium dihydroxystearate) it can be separated from the mother-liquor by filtration. The filtrate is placed in a desiccator and allowed to stand over sulphuric acid until the excess of ammonia has disappeared. The alcoholic solution of the ammonium salt gives no precipitation with alcoholic solutions of calcium chloride, sodium acetate, or lead acetate, but gives gelatinous separations on addition of water. Solutions of the ammonium salt in water give precipitates with solutions of calcium chloride, barium chloride, alum, and lead acetate. These precipitates are yellow-white, amorphous, slimy and insoluble in ether, alcohol, or water. The silver salt is the only one of a harder consistency; it is a white, cheesy substance, similar to silver chloride.

Other Reactions of the Ester.—A fresh solution of the ester in water gives no precipitate with barium chloride in the presence of mineral acids, which fact shows that it is free from sulphuric acid. On the other hand, if a solution, upon standing some length of time, is shaken with ether, allowed to rest and the two layers separated, it is noticed that the water layer now contains a considerable amount of free sulphuric acid. Coinciding with this is the fact that the ether layer now showed a decrease of 90.77 in its acid number, which was now 191.67.

Action of Alkalies.—Pure sulphuric acid was dissolved in an excess of potassium hydroxide solution and allowed to stand for 48 hours. There followed absolutely no splitting off of sulphuric acid, which was proved by the fact that the solution of ester upon addition of a solution of barium chloride gave a precipitate which dissolved clear in mineral acids. The alkaline solution was then supersaturated with hydrochloric acid and the precipitated acid was taken up in ether. After vaporizing the ether, there remained *unchanged* ricinoleic-acid-sulphuric ester in the form of a light yellow, clear oil. The ester is, according to this, very stable when treated in the presence of alkali, coinciding with the relation of many analogous compounds (when treated under the same conditions).

Action of Pyridine.—A solution of the ester in dry pyridine was heated for 6 hours at 100°-110°; the pyridine was then removed by shaking the whole with hydrochloric acid. The investigation of the hydrochloric acid extraction, on the one hand and the oil residue on the other showed that a considerable portion of the sulphuric acid was split off, but at the same time the decomposition of the ester was not quantitative.

Action of Heat.—The older references on this subject say that through heat, the solution of the ester is decomposed into its components, ricinoleic acid and sulphuric acid. There has been always a very interesting reaction overlooked in this regard, namely, the simultaneous production of a ricinoleic-acid anhydride, whose origin was decidedly proved by the following quantitative test:

Two g. ester were dissolved in 150 cc. water and boiled 4 hours, at the same time keeping the water at the same volume. After some time the separation of oil drops became noticeable; this oil was taken up in ether, and separated from the water. It was then washed with potassium chloride solution, dried and the ether distilled off. The isolated product was wholly free from sulphuric acid, its acid number being 130.65.

It follows from the relation between the ricinoleic-acid number *calculated*, and then *found* (assuming that ricinoleic-acid-ricinoleic ester was formed), that the composition of the above analyzed product is:

Free ricinoleic acid, $C_{18}H_{34}O_{31}$	38 per cent.
Anhydride, $(C_{18}H_{32}O_2)_2$	62 per cent.

Further tests (see later) showed that on sufficient heating this intramolecular esterification follows quantitatively.

Action of Chlorsulphonic Acid on Methyl Ricinoleate.—The methyl ester was prepared by saturating a solution of 250 g. ricinoleic acid in 500 g. methyl alcohol immersed in a cooling mixture, with hydrochloric gas, washing several times with water until neutral reaction of the ester, taking up in ether, drying with sodium sulphate, and vaporizing of the ester.

According to the reactions and analysis the ester was found to be pure, the saponification number found being 179.74; calculated for $C_{19}H_{36}O_3$, 179.76.

The quantities used in the reaction were 16.784 g. methyl ester, and 6.5135 g. chlorsulphonic acid. The addition of the chlorsulphonic acid was made in the same manner as in the esterification of the free ricinoleic acid, but in a solution of chloroform. It required 40 minutes. The reaction-product was poured into 500 cc. of water and thoroughly shaken in a separating funnel, whereby a semi-solid, white emulsion was produced. This emulsion contained but a small amount of free sulphuric acid and was soluble in hot water, alcohol or ether. It divided itself into two parts by standing overnight. Under the clear, watery layer, which contained free sulphuric acid and methyl alcohol, there existed a clear, brown, chloroform solution of the reaction-product. The latter was separated from the water layer and the chloroform was allowed to vaporize from a crystallizing dish. The residue of the chloroform layer was transferred to a thick-walled tube, in which, while warming slightly, a vacuum was obtained. There resulted a brown, clear oil, which proved to be a mixture of the ester and the free acid. Although numerous variations of the above-described experiment were tested, a direct method for the production of the sulphuric ester of the ricinoleic acid methyl ester [$C_{17}H_{32}(OSO_3H)COOCH_3$] was not obtained. Several products always result, among which neutral anhydrides form an important part.

A solution of 12 g. potassium hydroxide in 250 cc. water was added to the preparation resulting from the addition of 8.04 g. chlorsulphonic acid to 20.68 g. methyl ester, dissolved in 40 g. chloroform, whereby a semi-solid mass was produced. This was shaken on a shaking-machine for 4 hours, then allowed to stand for 48 hours, whereby the chloroform layer separated from the water layer. The whole of the organic substance was contained in the chloroform layer, from which the chloroform was vaporized by placing in a vacuum over paraffin-wax. The residue was dissolved in water and barium chloride was added, whereby a liquid substance fell to the bottom of the vessel. This was washed with water, then shaken with sulphuric acid (1: 10) (in order to decompose any potassium salt which may have been mixed with it), and taken up in ether. After drying with calcium chloride, and distilling off the ether, there remained a light-yellow, solid mass, which gave an acid number almost 0; Hübl number, 52.25.

It follows that the substance is of a neutral character, but from the Hübl number it can be seen that it is not composed of one compound (the theoretical Hübl number for an anhydride of ricinoleic acid being 90.58). There is, doubtless, also a saturated anhydride (a derivative of dihydroxystearic acid) present.

[A fruitless attempt to separate these two compounds was made by the following method: The substance was dissolved in the smallest amount of ether possible and precipitated by the addition of ligroin; the larger portion of the substance remained in solution and could not be precipitated in this manner. (From what is already known about the solubility of similar compounds, it could be foreseen, that the insoluble substance in the ligroin is the saturated compound, the derivative of a hydroxy acid with a free hydroxy group.) The powdery precipitate was filtered through a filter paper moistened with ligroin, and the solution freed from ligroin and ether by placing the same over paraffin-wax, in a vacuum. The resulting oil was neutral (acid-number = 0) and gave a Hübl number of 60.86.

The unsaturated anhydride had, according to the above results, been enriched in the soluble fraction. Attempts to separate the mixture into its components through further precipitations proved worthless; chemically pure substances could not be isolated. Nevertheless, the experiment showed beyond doubt that a formation of anhydrides of the acid (set free out of the methyl ester) took place; also from the ricinoleic acid as well as from a saturated compound (dihydroxystearic acid) formed through primarily addition of sulphuric acid or chlorsulphonic acid on ricinoleic acid].

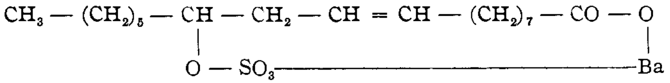
For the main reaction of chlorsulphonic acid on ricinoleic acid methyl ester there still remains to be decided whether there is simply a saponification of the ester, or a primary formation of the sulphuric ester and then a decomposition of the same.

A separation of the primary reaction-products before the formation of the emulsion looked very unlikely, so that it was necessary to find another method to isolate the ricinoleic-acid-sulphuric ester. For this object, conversion into the barium salt appeared most beneficial. (Barium ricinoleate is insoluble in water, but soluble in alcohol. The barium salt of the reaction products is soluble in water, while the barium salt of ricinoleic-acid-sulphuric ester is insoluble in both solvents.) A freshly prepared reaction mixture was dissolved in water after standing over night. The solution was then allowed to stand for 12 hours at 0°, filtered, ammonia added, and precipitated with a barium-acetate solution. The precipitate was collected on a filter, dried by means of the suction-pump, washed with hot water, then hot alcohol, and finally with ether. The precipitate was then placed upon a watch-glass in a vacuum desiccator over P_2O_5 in order to get thoroughly dry. The following results were obtained on analysis:

$C_{18}H_{32}SO_6Ba$.	Calculated. Per cent.	Found. Per cent.	
Barium	26.74	25.73	26.13
Sulphuric acid	16.75	16.27	16.33

[For ricinoleic-acid-methyl-ester-sulphuric ester = $(C_{19}H_{35}SO_6)_2Ba$, the theoretical results would be: Sulphuric acid, 14.95 and barium, 20.88].

It follows that the salt we have is the barium salt of the ricinoleic-acid-sulphuric ester:

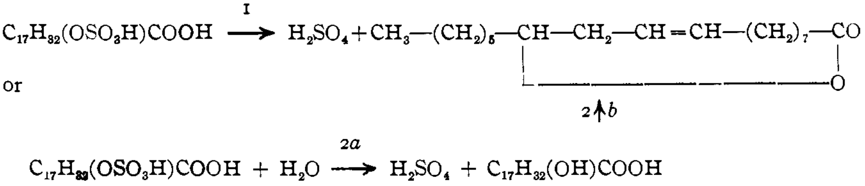


$$CH_3 - (CH_2)_5 - \underset{\displaystyle O - SO_3 - Ba}{CH} - CH_2 - CH = CH - (CH_2)_7 - CO - O$$

We see from the above, that by the reaction of chlorsulphonic acid on ricinoleic-acid-methyl ester there is first a splitting off of the methyl group from the carboxyl group and then an esterification of the alcoholic hydroxy-group

$$C_{17}H_{32}(OH)COOCH_3 + ClSO_3H = C_{17}H_{32}(OSO_3H)COOH + CH_3Cl$$

The way in which the anhydride is formed is as yet uncertain. It occurs, most likely similarly to the formation of anhydride by heating a solution of ricinoleic-acid-sulphuric ester. It still remains to be proved whether here a direct splitting off of one molecule of sulphuric acid takes place, (1) or first saponification with addition of water (2*a*) and then the formation of a normal lactone or lactide with the splitting off of water takes place (2*b*).



$$C_{17}H_{32}(OSO_3H)COOH \xrightarrow{1} H_2SO_4 + CH_3-(CH_2)_5-\underset{\displaystyle \llcorner\!- O}{CH}-CH_2-CH=CH-(CH_2)_7-CO$$

or $\qquad 2\uparrow b$

$$C_{17}H_{32}(OSO_3H)COOH + H_2O \xrightarrow{2a} H_2SO_4 + C_{17}H_{32}(OH)COOH$$

Ricinstearoleic-acid-sulphuric Ester, $CH_3 - (CH_2)_5 - CH(OSO_3H) - CH_2 - C \equiv C - (CH_2)_7 - COOH$.—The acid is prepared according to the process of Ulrich[1] by heating ricinoleic-acid dibromide with alcoholic potassium hydroxide solution. According to Ulrich's report, 8 hours of heating should suffice; we found this to be wrong, as we had to heat for 20 hours even with a much stronger alkali than that which Ulrich originally used.

The raw product was purified by dissolving in a small quantity of ether, and then precipitating with a quantity of ligroin equal to 5 times the amount of ether used. The precipitated oil solidifies quickly, and crystallizes in yellow-white needles which melt at 52° C. Analysis, $C_{18}H_{32}O_3$.

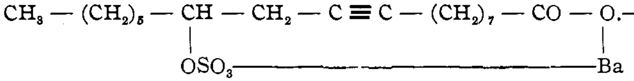
	Calculated.	Found.
C	73.49	73.60
H	11.00	11.33

The transformation of this acid into its sulphuric ester was carried out according to the same general method heretofore used in preparing the ricinoleic acid derivative.

The quantities used for the reaction were 12.0620 g. ricinstearoleic acid and 4.446 g. chlorsulphonic acid. The reaction was carried out in ether solution, the addition of the mineral acid requiring about 30 minutes. The reaction took place at room-temperature because at a lower temperature the ricinstearoleic acid was recrystallized out of the ether. The reaction-product was freed from ether and hydrochloric acid in the usual manner, the sulphuric ester remaining as a clear, yellow-brown oil. The compound is easily soluble in water, the solution reacting strongly acidic but containing no free sulphuric acid. The compound remains unchanged for several days, then in the presence of air a deposit of crystals is observed; this phenomenon is most likely due to decomposition, through the action of water, which the compound diligently draws out of its surroundings. But it appears to be very stable when kept in a sealed tube. Analysis, $C_{18}H_{32}SO_6$.

	Calculated.	Found.
C	57.34	57.12
H	8.63	8.5
Acid number	298.73	302.623–07.48

Barium Salt,



$$CH_3 - (CH_2)_5 - \underset{OSO_3\text{———————————————————}}{\overset{}{\underset{|}{CH}}} - CH_2 - C \equiv C - (CH_2)_7 - CO - \underset{Ba}{\underset{|}{O}}$$

.—After the sulphuric ester had been freed from hydrochloric acid and ether, it was dissolved in a small quantity of absolute alcohol, and then alcoholic ammonia was added (until the solution smelled of ammonia). The ammonium sulphate which was precipitated was filtered off, the filtrate was then placed in a desiccator over concentrated sulphuric acid in order to drive off the excess of ammonia present. The solution was then diluted and precipitated with barium acetate. The precipitate was filtered off, washed with alcohol, then with water and finally spread upon drying plates, and put into the desiccator. The salt is a light yellow powder, which is insoluble in water and alcohol, but easily soluble in chloroform. Analysis, $C_{18}H_{30}SO_6Ba$.

	Calculated.	Found.
C	41.91	42.18
H	6.22	5.98
Ba	26.07	26.64

Ricinoleic-acid-dibromide-sulphuric Ester, $C_{17}H_{32}(OH)COOH + Br_2 \longrightarrow C_{17}H_{32}Br_2(OH)COOH + ClSO_3H \longrightarrow C_{17}H_{32}Br_2(OSO_3H)COOH + HCl$.—23.57 g. ricinoleic-

---

[1] **Ulrich**, *Ztschr. Chemie*, 3, 545 (1867).

acid dibromide were dissolved in 30 cc. absolute ether, and the equimolecular quantity (= 4.109 g.) chlorsulphonic acid added drop by drop. The liquid was kept mixed by constant agitation. After the mineral acid had been added, the reaction-mixture was freed from hydrochloric acid and ether in the usual manner.

When the hydrochloric acid gas was entirely gone (which, by the way, required several hours), there remained a clear, brown liquid, which upon long standing decomposed. This substance dissolves clear in water, alcohol and ether. Freshly prepared solutions of the oil contain no free sulphuric acid. Upon analysis, this oil proved to be dibromo-ricinoleic-acid-sulphuric ester, $C_{18}H_{34}Br_2SO_6$.

Acid number....... calculated 209.76, found 227.27.

The acid number came out too high, because it is very difficult to free the reaction product wholly of hydrochloric acid. If we allow the substance to stand over caustic potash and sulphuric acid for a long time, in order to free it entirely from its impurities, a partial decomposition takes place, and the sulphuric acid split off increases the acid number. To prove this, we allowed one sample to stand several days before determining its acid number, and found 237.6.

In order to determine the acid number, a weighed portion of the freshly prepared product is dissolved in about 30 cc. of neutralized alcohol and titrated as fast as possible, so that the alcoholic solution does not form any ester. The tendency to form ester was shown nicely by a specially prepared sample, which was titrated two days after being dissolved in alcohol, giving the acid number 186.79 instead of 208.76 calculated. It follows that 10 per cent. of the acid was already converted into ester.

Conduct of Ricinoleic-acid-dibromide-sulphuric Ester in Cold Water Solution, Hot Water Solution and Hot Pyridine Solution.—Cold water solutions of the ester split off sulphuric acid upon standing; however, there follows no separation of ricinoleic-acid dibromide. If we shake the solution with ether, then the dibromide and the unchanged portion of its sulphuric ester are dissolved in the ether. The ethereal solution when dried with sodium sulphate and freed from ether, leaves a liquid acid which on analysis gave an acid number of 148.46. Theoretical acid number for ricinoleic-acid dibromide, 122.5, for sulphuric ester 208.76.

Accordingly there was about 70 per cent. of the ester partially decomposed. A coinciding result was obtained with another sample by means of a gravimetric determination of the sulphuric acid in the ether solution and that in the water solution.

For this purpose a portion of the sulphuric ester was placed over phosphorus pentoxide for 3 days, then dissolved in water, shaken with ether, "salted out" with ammonium chloride, and the sulphuric acid in the water solution and ether solution determined; 1.4042 g. substance were used for the analysis:

	$BaSO_4$. Gram.	Found. Per cent.
H_2SO_4 in the water solution............	0.3563	10.41
H_2SO_4 in the ether portion..............	0.2436	7.12
Total...........................	....	17.53–17.83

Five g. ricinoleic-acid-dibromide-sulphuric ester were dissolved in 40 cc. water, and heated on the water-bath for 6 hours. The water solution, which contained the total free sulphuric acid was decanted off, the organic residue washed with water until the latter showed a neutral reaction, then taken up with ether, dried and freed from ether. The remaining substance gave acid number 71.07.

After the sulphuric acid was split off, the substance should, as ricinoleic-acid dibromide, have an acid number of 122.5. If monobromo-ricinoleic acid ($C_{17}H_{37}BrOH.COOH$) were present, the result on account of its lower molecular weight would give a higher acid number. The observed acid number proved that there exists a mixture of free acid and another substance, an anhydride of ricinoleic-acid dibromide.

Assuming that no essential loss of bromine has occurred, then it is found that the percentages of free acid and anhydride come to 58 per cent. free acid and 42 per cent. *neutral* anhydride, that is, 16 per cent. free acid and 84 per cent. *acidic* anhydride (or acid ester).

By heating a solution of ricinoleic-acid-dibromide-sulphuric ester in pyridine for several hours on the water-bath, it was likewise observed that a considerable quantity of sulphuric acid is split off. Whether or not an anhydride was formed in this case was not investigated.

Experiments on the Preparation of the Sulphuric Ester of Methyl-recinoleate Dibromide.—Methyl-ricinoleate dibromide was first prepared. This was done by treating 30 g. methyl ricinoleate suspended in about 100 cc. of water, with 20 g. bromine. The vessel containing the methyl ester was shaken constantly and the bromine added in small portions. The formation of the new compound was observed by the appearance of a new substance at the bottom of the flask. After the whole of the bromine had been added, the contents of the flask were washed with water, then several times with sodium carbonate solution. The heavy oil was taken up in ether and transferred to a large separating-funnel, then dried by the addition of finely ground, water-free sodium sulphate, filtered and freed from the ether.

For the preparation of the sulphuric ester, 20.215 g. of the substance were dissolved in twice its volume of absolute ether, and the calculated theoretical amount of chlorsulphonic acid (= 4.529 g.) was added drop by drop in the usual manner, the addition requiring about 30 minutes. After the hydrochloric gas and ether were driven off, the reaction product gave the following results on analysis:

	Found:	Theoretical for the sulphuric ester of the methyl-recinoleate dibromide [$C_{19}H_{36}Br_2SO_6$].	Theoretical for the sulphuric ester of the free resinoleic-acid dibromide [$C_{18}H_{34}Br_2SO_6$].
Acid number.........	187.63	101.6	208.76
Saponification number	285.04	203.2	208.76

The acid number shows that through the action of chlorsulphonic acid, saponification of the methyl ester takes place for the greater part here also, and a mixture of the ester and free acid is the result instead of the pure ester as was expected. The large saponification number is the result of a partial splitting off of bromine, due to the treating with dilute potassium hydroxide solution, which shows conclusively that this method of analysis is not applicable to the above compound.

The following process was applied to convert the methyl ester, which is still contained in the substance (as was shown by the analysis), into its free acid: 15 g. of the substance were treated with 125 cc. potassium hydroxide solution of known strength (about $N/2$) and shaken thoroughly on the shaking-machine until a sample of the shaken mixture gave on titration a percentage of free alkali which corresponded with the small excess of potassium hydroxide solution originally used. (Mixture shaken about 4 hours in all.) The mixture was then treated with a small excess of $N/2$ HCl until it showed an acid reaction, and the organic acid dissolved in ether, dried and isolated by distilling off the ether.

The substance isolated proved to be (through qualitative reactions) identical with the sulphuric ester of the ricinoleic-acid dibromide.

$$[C_{17}H_{32}Br_2(OH)COOCH_3 + ClSO_3H = CH_3Cl + C_{17}H_{32}Br_2(OSO_3H)COOH].$$

12-Hydroxystearic-acid-methyl Ester, $CH_3 — (CH_2)_5 — CH.OH — (CH_2)_{10} — COOCH_3$.—This compound was prepared by reduction of ricinoleic-acid-methyl ester.

Fokin[1] reduced oleic-acid ester to stearic acid in the cold, using ethereal solution, and colloidal platinum as a catalysor. This excellent method, which is a worthy addition to the material already existing on reduction methods, proved itself applicable to the reduction of ricinoleic-acid ester. The latter is far more difficult to reduce, and also the purification of the hydrogen offered at first many difficulties. The colloidal platinum was repeatedly "poisoned," permitting of its use only for short periods. Only after many fruitless attempts was the following method found and then favorable results obtained.

The hydrogen was made to pass first through 3 flasks containing respectively very concentrated potassium hydroxide solution (2 : 1), a saturated solution of potassium permanganate, concentrated sulphuric acid, and then through a specially arranged flask containing phosphorus pentoxide. From here it passed through a tube (about 10 inches long) containing previously strongly heated asbestos filaments, and finally through a tube containing a reduced copper-gauze spiral. The hydrogen was obtained in a very pure condition by this system.

The colloidal platinum was prepared by dissolving $H_2PtCl_6 + 6aq$ in 1 g. quantities in as little water as possible and reducing under the application of heat, with 40 per cent. formaldehyde and potassium hydroxide solution. A very finely divided platinum was obtained, which was washed a number of times with water, alcohol, and ether.

Five g. portions of methyl ricinoleate were dissolved in 30 cc. absolute ether and poured into a flask with the platinum. The hydrogen passed through this ethereal solution in a very slow stream. During the first 15 hours after the hydrogen is allowed to react on this solution, the separation of a white, crystalline substance is noticeable. This separation is complete at the end of 60 hours. The crystalline substance was dissolved in ether, filtered from the adhering platinum and allowed to crystallize out of the ether until a constant melting point was obtained. The ester crystallizes in clean, white plates with silky luster, which melt at 58°. It is easily soluble in all the common organic solvents and in warm water. Analysis, $C_{19}H_{38}O_3$.

	Calculated. Per cent.	Found. Per cent.
C	72.44	72.81
H	12.37	12.65
Saponification number	178.78	177.30 177.77

12-Hydroxy-stearic Acid, $CH_3 — (CH_2)_5 — CHOH — (CH_2)_{10} — COOH$.—The free acid was prepared from the methyl ester, as the direct reduction was not successful in the case of the free ricinoleic acid. The methyl ester was saponified by means of alcoholic potassium hydroxide solution. The potassium salt thus produced was dissolved in water and hydrochloric acid added.

The precipitated acid was filtered off, washed with water, then boiled with alcohol and bone charcoal and filtered. The filtrate was precipitated by the addition of water, the solution filtered by means of suction, the precipitate dissolved in alcohol and again precipitated, this process being continued until a pure product was obtained. The substance was then placed on drying plates and put into the desiccator. The compound separates in white, minute crystals, which melt at 78°. It is soluble in alcohol, ether and chloroform but insoluble in ligroin. Analysis, $C_{18}H_{36}O_3$.

	Calculated. Per cent.	Found. Per cent.
C	71.83	71.00
H	12.21	12.62

---

[1] *Chem. Centralbl.*, 1907, II, 1324.

12-Hydroxystearic-acid-sulphuric Ester, $CH_3 — (CH_2)_5 — CH(OSO_3H) — (CH_2)_{10} — COOH$.—The quantities used for the reaction were 3.1952 g. 12-hydroxystearic acid and 1.2373 g. chlorsulphonic acid. The addition of the mineral acid took place in an ethereal solution and was carried out in the manner adopted for the preparation of the other sulphuric esters. In this case there was no freezing mixture used, as the saturated acid is insoluble in ether at low temperatures. The process required about 15 minutes. The reaction product was freed from hydrochloric gas and ether in the usual manner, whereby a white-gray mass remained. This substance was reprecipitated and dried by standing over night in the desiccator. The compound separates in small lumps, which are easily soluble in alcohol, glacial acetic acid, and water only on the application of heat. It is insoluble in ligroin and melts at from 71°–73° to a slightly turbid liquid; (separation of sulphuric acid in small globules begins at 50°, at 65° small crystals separate out of the melt. They are in all probability hydroxystearic acid). The compound is of a very stable character; it is not decomposed on being heated in water. Upon addition of barium chloride solution to the solution of the compound in water, there follows precipitation of the barium salt, which is soluble in mineral acids, whereby the free organic acid is regenerated. The regenerated acid is still unchanged; it dissolves in water, but on long standing appears to decompose. Analysis, $C_{18}H_{36}SO_6$.

	Calculated. Per cent.	Found. Per cent.
C	56.72	56.64
H	9.64	10.11
Acid number	294.97	297.89

Supplement.

Action of Phosphorus Pentoxide on Ricinoleic Acid.

Formation of Poly-ricinoleic Acids.—Trial 1. The solution of 10 g. ricinoleic acid in 50 cc. absolute ether was treated with a like amount of phosphorus pentoxide, the addition taking place in small portions. The reaction mixture was allowed to stand 24 hours with frequent shaking. The ethereal portion was poured off, the ether evaporated and the residue treated with very dilute mineral acid (1 : 150) in order to decompose the phosphoric ester, until the residue upon being washed with water showed no more phosphoric acid reaction; it was then dried and analyzed, giving an acid number of 167.29. Theoretical for ricinoleic acid, 188.24.

The yield of neutral reaction product being so negligible, phosphorus pentoxide was allowed to react directly on ricinoleic acid in the next trial.

Trial 2. Thirty g. ricinoleic acid were treated with 25 g. phosphorus pentoxide in a mortar, and rubbed together until a clear, gelatinous solution was procured. (The temperature rose to 35° during the operation.) This solution was warmed for a short time at 100° and allowed to stand for 3 days in a desiccator. The very viscous syrup was put into water, whereby no rise in temperature was noticeable, and treated as in the first trial, with water containing a small percentage of mineral acid, in order to free it from phosphoric acid. As a result of this treatment about one-half of the reaction product melted into a clear oil, the rest remaining unchanged as a solid, crumblike mass. The two substances were separated by extraction with ether in a Soxhlet apparatus. The liquid portion dissolved in ether and remained as a thick oil after the ether was distilled off. The analysis of this substance gave an acid number of 83.00.

Trial 3. This was carried out in the same manner as Trial 2, except that the reaction mixture was not heated as above. The working up of the product yielded only a very small quantity of the substance insoluble in ether. After purifying in the above-described manner, the analysis of the oil gave an acid number of 84.24.

The liquid raw products obtained from both of these latter trials were doubtless identical and consisted of neutral reaction products and unchanged ricinoleic acid, no phosphoric acid being detectable.

Trial 4. The ricinoleic acid and phosphorus pentoxide were mixed in the same relation as in trial 3. In this case, the reaction product was boiled at 100° for a short time, then at from 60°–70° for several hours. After the product was freed from phosphoric acid, by repeated boilings with water, it was evident that only a small portion of the compound which is soluble in ether was formed. The principal part consisting of the insoluble solid body, only a small quantity of ricinoleic acid remained unchanged.

Isolation and Investigation of the Reaction products.

First Product.—(The substance obtained from trial 2 was investigated.) The neutral compound was separated from the mixed ricinoleic acid by means of its insolubility in alcohol. The ethereal solution was precipitated with alcohol 6 times. As the precipitated compound was still acid, it was necessary to neutralize an ether-alcohol emulsion of the same with alcoholic potassium hydroxide solution. The potassium ricinoleate thus obtained went into solution, while the neutral compound remained undissolved as an oil. The oil was dissolved in ether and then precipitated several times with alcohol, whereby it was obtained absolutely free from acid and potassium salt. It contained some alcohol and ether and was freed therefrom by standing in a desiccator over phosphorus pentoxide.

The product is, in a dry condition, a yellow, elastic mass, having the consistency of guttapercha, and being easily cut. The solution shows neutral reaction. It gives very stable emulsions with water. On the application of heat it expands extraordinarily and blackens. It is converted into potassium ricinoleate by being heated with alcoholic potassium hydroxide for three hours. Concentrated sulphuric acid dissolves the compound with decomposition and partial addition of sulphuric acid on the double bond. Analysis:

	Calculated for		
	$[C_{18}H_{32}O_2]_n$. Per cent.	$[C_{18}H_{34}O_3]_n$. Per cent.	Found. Per cent.
C	77.05	72.40	72.34
H	11.53	11.51	10.70

The analysis shows that the reaction product, regardless of its neutral reaction, is not the expected anhydride of ricinoleic acid, but is a polymerization product of the latter, $[C_{18}H_{34}O_3]_n$.

Second Reaction Product.—The solid product, which is insoluble in ether, proved to be a polymerization product of ricinoleic acid also, but on all accounts a much higher polymer. This compound is insoluble in all the commonly used organic solvents. It was purified, therefore, by treatment with these solvents, until the impurities were all extracted. A recrystallization or reprecipitation was entirely impossible. The compound was attacked, but very little, by boiling for several hours with a strong alcoholic potassium hydroxide solution, a negligible quantity of the compound being dissolved. Analysis, $[C_{18}H_{34}O_3]_x$.

	Calculated. Per cent.	Found. Per cent.
C	72.40	71.15 70.98
H	11.51	10.54 10.55

ZÜRICH, CHEMISCHES UNIVERSITÄTS-LABORATORIUM.