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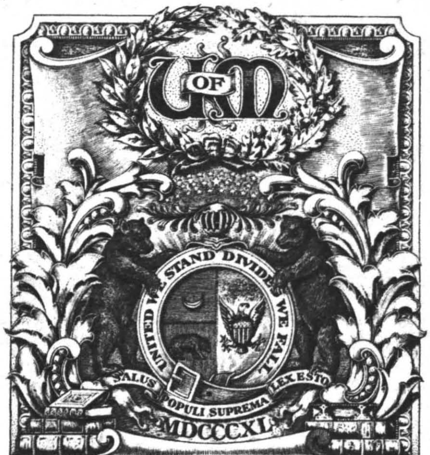

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AN INVESTIGATION OF THE UNSATURATED ACIDS OF COTTONSEED OIL

by

Philip Anson Wright, A. B.

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INTRODUCTION.

Cottonseed oil, as generally accepted, consists of approximately seventy percent liquid or unsaturated fatty acids. Actual analysis has shown that the unsaturated acids are free from acids of as high unsaturation as linolenic acid and accordingly consist of oleic and linolic acids only. Direct experiment has shown that the iodine absorption value of the mixed liquid fatty acids of cottonseed oil is approximately <u>150</u>, from which is deduced a theoretical composition of approximately sixty-five percent linolic and thirty-five percent oleic acids.

Farnsteiner(1) however on separation of the liquid fatty acids by means of their bromides, oleic dibromide being a liquid and ordinary linolic tetrabromide being a solid compound, was able to obtain linolic tetrabromide corresponding to approximately only twenty-four percent of the mixed liquid fatty acids. Lewkowitsch,(2) studying the same problem, obtained a percentage of acid as its linolic tetrabromide, from cottonseed oil, which was also much below the theoretical value, he obtaining only twenty-one percent of the acid. A great discrepancy is thus apparent, as Lewkowitsch himself admits.

As intimated, linolic acid is an unsaturated fatty

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(1) Zeit. f. Unters. Nahr. u. Genussm, Vol. 2, p. 1, (1899).
(2) Oils, Fats & Waxes. Vol. 2, p. 157, (1909 edition).

acid with four unsaturated bonds and accordingly will add four atoms of bromine, thus forming a tetrabromide. This compound as obtained by many investigators is a white solid flaky substance with a characteristic and definite melting point of 113°-114°C, or 114°-115°C.

In the course of a study of the methods of analysis of cottonseed oil for linolic acid, by means of the isolation of the acid as its bromine compound, the end product of the analysis which should have been linolic tetrabromide with a melting point of 113°-115°C was instead a white crystalline compound with properties widely different from the linolic tetrabromide which is described by Lewkowitsch(1) Hazura(2) Farnsteiner(3) etc. The crystals obtained were large needle shaped prism forms arranged in radiating clusters, with a specific gravity much less than that of linolic tetrabromide. After several purifications from ninty-five percent alcohol, the crystals possessed a definite melting point of 58°-58½°C. The crystals were also much more soluble in ninty-five percent alcohol, glacial acetic acid, petroleum ether and other organic solvents than linolic tetrabromide and could be crystallized from all these solvents in the same form as obtained from alcohol.

It at once became apparent that the body thus obtained was worthy of careful study as a possible means of

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(1) Oils, Fats & Waxes, Vol. I, p. 154. (1909 edition).
(2) Monatshefte für chemie, 9,p. 180,(1888). J. Soc. Chem. Ind. (1888), p. 506.
(3) loc. cit.

explaining the wide discrepancy between the theoretical percentage of linolic acid in cottonseed oil and the percentage which has been obtained by actual analysis. The importance of the body was considerably enhanced, also on account of the fact that an isomer of the ordinary linolic tetrabromide of cottonseed oil has been obtained by Thoms(1) from Telfairia oil, which according to that author gave a tetrabromide with a melting point of 57°-58°C.

The investigation, which is here reported was carried out with the purpose of explaining the formation of the unknown compound, its chemical composition, its relation to the isomeric linolic acid obtained by Thoms, and its relation to the composition of cottonseed oil.

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(1) Arch. d. Pharm., 48, p. 238, (1900).

HISTORICAL.

Hazura and Grüssner(1) were among the earliest investigators to work with linolic acid. By subjecting the unsaturated acids of hemp oil in glacial acetic acid solution, to the action of bromine they obtained a solid and a liquid product. They found the solid product to consist of two substances, one of which had a melting point of 114°-115°C and was soluble in alcohol, ether and glacial acetic acid, and crystallized from alcohol in nacreous plates having the composition $C_{18}H_{32}Br_4O_2$. They found by heating this compound in alcoholic solution with zinc and hydrochloric acid that bromine was liberated with the formation of an unsaturated acid $C_{18}H_{32}O_2$ which however absorbed but two atoms of iodine from Hübl's solution. For this acid the authors suggested the name of linoleic acid.

In another paper Hazura(2) gives the approximate composition of the cottonseed oil liquid acids, as sixty percent linolic acid and forty percent oleic acid, the values being obtained from the yields of the hydroxy derivatives. The iodine value of the total acids he found to be <u>113</u> and of the liquid acids <u>145</u>.

Reformatsky(3) In 1890 claims to have made ethyl

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(1) loc.cit.
(2) Monatshefte f. chemie.Vol.9, (1888).
(3) j.f.prakt.chemie., (2)41, (1890),534. Beilstein, Handbuch der Organischen Chemie, Vol.I,(IIIAuflage)536.

linolate by dissolving linolic acid in absolute alcohol and passing in hydrochloric acid gas. He obtained a boiling point for ethyl linolate of 270°-275°C at 180mm. pressure. He also claims(1) to have produced a pure linolic acid by hydrolizing ethyl linolate but Lewkowitsch(2) is of the opinion that his product was a mixture of the unsaturated acids of linseed oil. Reformatsky also claims that an excess of bromine converts part of the linolic tetrabromide into another bromide soluble in petroleum ether at ordinary temperatures. He says that at higher temperatures twenty-two percent are so converted.

The next investigators of note to attack the analysis of the unsaturated fatty acids were Otto Hehner and C. A. Mitchell(3). In an examination of the unsaturated acids of linseed oil they found the residue after the separation of the hexabromide to be a semi-solid mass, consisting of dibromide and tetrabromide. However they did not attempt a separation. They obtained the tetrabromide of the maize oil acids however, and found it to have a melting point of 113.4 (corr) and a bromine percentage of 51.97 against the theoretical value of 53.33.

They found on boiling the hexa- and tetrabromides with alcoholic potash that the bromine was entirely eliminated but that the free acids obtained from their alkali salts yielded no crystallizable substance, only a yellow

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(1) loc. cit.
(2) j.f.prakt.chemie (2) 41 (1890) 529. Lewk. Oils, Fats & Waxes, Vol.I, p. 154. (1909 edition).
(3) Analyst, (1898) 303.

viscid oil showing the absence of any hydroxy-acid. These yellow viscid oils on rebromination, evolved hydrobromic acid, and the resulting product in the case of the hexabromide, was not the original hexabromide. The resulting product in the case of the tetrabromide is not mentioned by the authors. They state however that it had a low iodine absorption.

Farnsteiner(1) in 1899 has added more to our knowlege of linolic acid and cottonseed oil than almost any other investigator.

In an attempt to separate the bromides of oleic and linolic acids, despairing of any other way, he tried to secure their separation by the lead salts of their bromides. He found the lead salt of oleic debromide to be a viscous substance, difficultly soluble in cold ninty-five percent alcohol and easily soluble in ether, petroleum ether, ether-alcohol, benzol and benzol-alcohol. The lead salt of the tetrabromide, he found to be difficultly soluble or insoluble in ether and benzol at ordinary temperatures, but dissolving easily on warming in a mixture of two parts benzol to one part alcohol. The method of separation did not prove successful.

Farnsteiner found that 100 c. c. of petroleum ether will dissolve .021 grams of linolic tetrabromide on standing two hours at 12°C, and will dissolve .0065 grams if

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(1) loc. cit.

allowed to stand twelve hours at room temperature and three hours at 0°C. He found also that less than 4-5 percent of the tetrabromide could be recovered, by the petroleum ether method, from a mixture of oleic dibromide and linolic tetrabromide.

Practically pure linolic tetrabromide was obtained by Farnsteiner by brominating a mixture of oleic and linolic acids in petroleum ether solution with a freshly prepared twenty percent solution of bromine in petroleum ether.

Studying the influence of an excess of bromine on the separation of linolic tetrabromide, Farnsteiner found that while no hexabromide was obtained, yet the amount of bromide soluble in petroleum ether was appreciably increased.

Farnsteiner found after repeated crystallisation that the melting point of the tetrabromide was 113°-114°C instead of 114°-115°C as stated by Hazura.

The molecular weight of the tetrabromide he determined as follows: .4-.8 gram of bromide was dissolved with the least possible heating in 50-100c.c. neutral alcohol and after the addition of phenophthalein the solution was titrated with N/10-N/20 alcoholic potash. The end-point is described as being very sharp and the color, as remaining a long time.By this method a value of <u>600</u> was obtained as the molecular weight of linolic tetrabromide.

In obtaining the bromides of the liquid acids of cottonseed oil, Farnsteiner dissolved one gram of these acids in about ten c.c. of chloroform and brominated with one gram of bromine dissolved in ten c.c. of chloroform. He separated the dibromide and the tetrabromide by means of petroleum ether and recrystallized his tetrabromide from petroleum ether. He obtained a melting point of 113°-114°C (uncorr.), and a molecular weight of 600.1. In a quantitative estimation of linolic acid, brominating both in chloroform and petroleum ether, he obtained in five trials, respectively 18.9 percent, 18.45 percent, 18.2 percent, 17.3 percent and 18.2 percent linolic acid in the mixed fatty acids of cottonseed oil.

Thoms(1) in 1900 reports the investigation of an oil from the seeds of a plant called Telfairia pedata, which he secured from East Africa. By separation of the solid and liquid acids by the difference in solubility of their lead salts in ether and subsequent distillation under diminished pressure, he obtained an acid which boiled at 220°-225°C at 13 mm. pressure, and gave a bromide both in ether and glacial acetic acid solution, melting at 57°-58°C, which acid had a carbon and hydrogen content as follows:

	Found		Required for $C_{18}H_{32}O_2$
C.	77.2 percent	....	77.15 percent
H.	11.49 " "	....	11.42 " "

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(1) loc. cit.

and his bromide, a bromine content of 52.76 and 52 percent (required for $C_{18}H_{32}Br_4O_2$-53.33 percent). Thoms obtained a molecular weight of 284 for the acid using the cryoscopic method with glacial acetic acid as a solvent. The molecular weight of $C_{18}H_{32}O_2$ is 280. He concluded that he was dealing with an isomer of linolic acid. He named his acid telfairic acid. By oxidation with potassium permanganate, he obtained from telfairic acid a tetrahydroxy-stearic acid melting at 177°C.

S. Fokin(1) in 1902 found that the chief constituent of linseed oil acids was a linolic acid isomeric with that from cottonseed oil and sunflower oil. It gave an amorphous mass of bromide melting at 98°-101°C.

Bedford(2) as also Fokin(3) are of the opinion that an isomeric linolic acid exists which they call beta-linolic acid which gives a liquid tetrabromide, while ordinary linolic acid (alpha-linolic acid) gives the solid tetrabromide.

Peters and Reformatsky(4) claim to have obtained stearic acid by heating linolic acid with phosphorus and hydriodic acid to 200°C, but this is doubted by Bedford. According to Lewkowitsch, it appears very likely however, that linolic acid could be reduced to stearic acid by means of hydrogen in the presence of a catalyst.

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(1) J.Russ.Phys.Chem.Soc.,1902, 34, 501-503. J.Chem.Soc. Abstracts, Vol. 83, pt.I, (1902) p. 740.
(2) Inaugural Dissert. Halle a. S. 1906.
(3) Zeit. für Electro chemie. (1906) 759.
(4) Lewk., Fats, Oils and Waxes, Vol.I, p. 154, (1909 edition).

Lewkowitsch(1) states the following concerning the metallic salts of linolic acid: they are amorphous with the exception of the zinc salt, the barium and calcium linolates are soluble in boiling alcohol; the calcium, barium, zinc, copper and lead salts dissolve in ether; barium linolate is easily soluble in benzene and petroleum ether; the lead salt of the tetrabromide is sparingly soluble in cold ether and in benzene; and linolates absorb oxygen more readily than the free linolic acid.

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(1) loc. cit.

EXPERIMENTAL PART.

Methods of Analysis.

Tortelli and Ruggeri(1) have worked out a method for obtaining the liquid acids of fats and oils, which is based on the difference in solubility of the lead soaps of the solid and liquid acids in ethyl ether and except for a few minor changes, their method was adopted in the investigation which is here reported.

The slightly modified method is as follows: twenty grams of a fat or oil are saponified with 15 c.c. of a 50 percent aqueous caustic potash solution and 45 c.c. of 95 percent alcohol (if less quantity of oil is used a proportionately less amount of reagents and solvents are used). The soap solution is carefully neutralized with ten percent acetic acid using phenophthalein as an indicator. Three hundred c.c. of a 7 percent lead acetate solution are heated to boiling in a 750 c.c. Erlenmeyer flask and the hot neutral soap solution poured into it in a thin stream while the flask is in constant agitation. The flask is held under running water with agitation until cooled to room temperature. Then when cool, it is allowed to stand until the supernatant liquid has become clear, when this is poured off and the soaps

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(1) L. Orosi, (1900) April, Lewk., Oils, Fats, & Waxes, Vol.I, p. 447 (1909 Edition).

adhering to the sides and bottom of the flask are washed quickly with 200 c.c. portions of water at 40°-50°C. The flask is allowed to cool (inverted) and the larger drops of adhering water touched off with a roll of filter paper. Two hundred and twenty c.c. of ether are immediatly added to the flask and the flask is shaken with careful heating until the ether begins to simmer and the lead soaps loosen from the glass and become granular. The flask is then allowed to cool two hours at 8°-10° C and filtered thru a plaited filter into a 200 c.c. narrow-neck flask being washed carefully with ether until the flask is full. This flask is let stand immersed in running water at 18°C or below for 12-15 hours. Usually a precipitate will settle out. The solution is poured thru a plaited filter into a separatory funnel and the lead soaps decomposed with 150 c.c. of twenty percent hydrochloric acid. The precipitated lead chloride which has settled into the acid layer is run off and the solution washed first with 100 c.c. of twenty percent hydrochloric acid, then three times with cold water until the last washing shows no acid reaction to congo-red. The acid-free solution is washed into a 750 c.c. Erlenmeyer flask and diluted with ether up to a volume of 360 c.c.

The method of Tortelli and Ruggeri for the separation of the liquid and solid acids, is abandoned at this point, and the bromination proceeded with directly in the ether solution in which the free liquid acids are found after the

removal of the lead from their lead soaps.

No one entirely satisfactory method was found in the literature for the bromination of unsaturated fatty acids.

Farnsteiner(1) makes use of both chloroform and petroleum ether as solvents. The evident objection to the former is its specific gravity, which being greater than water makes difficult any washing with water in the separatory funnel. Petroleum ether is also objectionable as bromine forms addition products with this solvent giving off hydrobromic acid and enhancing the danger of an impure product.

Thoms(2) makes use of glacial acetic acid as a solvent for the liquid acids at bromination, but here again the solvent is open to objection, since it is necessary to salt out the bromides from the solution due to the high boiling point (118°C) of glacial acetic acid.

However as the liquid acids are already in ether solution and as ether is easy to remove by distillation, from the mixed bromides, it was decided to use ether.

Lewkowitsch(3) in his "Bromide Test" gives the following method for the bromination of oils: 1-2 grams are dissolved in 40 c.c. of ether, to which a few c.c. of glacial acetic acid has been added, the solution is cooled in a corked flask to 5°C and bromine is added drop by drop, until the brown color remains permanent.

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(1) loc. cit.
(2) loc. cit.
(3) Fats, Oils & Waxes, Vol. I, p. 382, (1909 edition).

This method was thought applicable to the bromination of the free, unsaturated acids. However it was found that the presence of the glacial acetic acid was objectionable in a great many cases, being difficult to remove after the bromination, due to its high boiling point (118°C), without causing the mixed bromides to char badly. It was also found difficult to remove the acetic acid by repeated washing with water, due to the fact that glacial acetic acid is nearly as soluble in ether as in water. Therefore it was decided to leave out the acetic acid entirely.

Many investigators in using the bromination method for identifying the liquid acids, brominate the solutions, using the same solvent for the bromine as for the liquid acids. For instance, Farnsteiner(1) brominated the chloroform and petroleum ether solutions of the liquid acids with chloroform and petroleum ether solutions of bromine and Thoms(2) brominated the ether and glacial acetic acid solutions of the liquid telfairic acid with ether and glacial acetic acid solutions of bromine.

However it was found more convenient in these investigations to use liquid bromine for bromination, with the exception of the cases which will be reported later.

Farnsteiner's(3) method for the separation of the mixed bromides was adopted in the investigations reported in this paper. Farnsteiner used petroleum ether of a

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(1) loc. cit.
(2) loc. cit.
(3) loc. cit.

boiling point 35°-$67.5^{\circ}C$ as a means of separating the oleic dibromide and the linolic tetrabromide. He found oleic dibromide to be completely soluble in petroleum ether, which however dissolved but a very small amount of tetrabromide at low temperatures. He found 100 c.c. of petroleum ether at $12^{\circ}C$ would hold in solution .014-.021 grams of linolic tetrabromide.

After the liquid fatty acids had been secured in ether solution by the method of Tortelli and Ruggeri(1) as given above, a method of bromination and separation of the mixed bromides for their individual identification, was adopted, which combined, not only several features of the bromination and separation methods just described, but also included a method of purifying the brominated solution from excess bromine by washing with a solution of sodium thiosulphate.

The combined method which was used is as follows: The ether solution of the liquid acids is made up to 360 c.c. volume is cooled in a corked flask to $5^{\circ}C$ and brominated slowly to a permanent brown coloration with liquid bromine. The brominated solution is allowed to stand 12-15 hours and is then poured into a separatory funnel and washed with 50-100 c.c. of a ten percent solution of sodium thiosulphate. This removes the excess bromine. The ether solution is then washed three or four times with cold distilled water, and poured into the original flask and

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(1) loc. cit.

allowed to stand over fused calcium chloride 2-5 hours. The dry ether solution is then carefully decanted through a funnel into a convenient sized distilling flask and the ether driven off, keeping the temperature of the water-bath below 60°C. While the mixed bromides are still liquid, 100 c.c. of petroleum ether (boiling point 30°-50°C)is poured into the flask and the whole cooled to 5°C for 1-2 hours. The solid tetrabromide separates out in a finely granular state and may be filtered off immediately and recrystallized from ninty-five percent alcohol.

As stated in the introduction to this paper, the purpose of this investigation was to determine the chemical composition and factors causing the formation of the unknown body, crystallizing in needle-shaped prisms, melting at 58°-58½°C, which occured by applying the process of analysis described above, to cottonseed oil; to determine its relation to the isomeric linolic acid obtained by Thoms(1); and also its relation to the composition of cottonseed oil.

It was therefore necessary before proceeding further, to lay out a definite plan of investigation.

Plan of Investigation.

1. During what variation in the method of analysis is the white crystalline body formed which melts at 58°-58½°, and which is probably a bromide?

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(1) loc. cit.

2. What is the molecular weight, chemical composition and formula of the body under investigation?

3. If a tetrabromide or bromine addition product of a distinct acid other than oleic or linolic acids, is this body present in the original oil as a glyceride?

4. If the formation of the body is due to some change in constitution from oleic or linolic acids, before or during bromination, what is the general mechanism of the change and how may it be brought about?

5. If this body is a bromide, and not a pure addition product, but wholly or partly a substitution product, from what acid does it originate and when does the substitution take place?

6. If the body is formed from a distinct acid present as a glyceride in the original oil, in what proportion is it so present?

7. Whether an addition or substitution product has the body under investigation any relation to the tetrabromide from an unsaturated acid in telfairia oil, described by Thoms, and if so, what relation?

A Study of the Variation of the Methods of Analysis.

As already intimated a number of times, the unknown low melting-point body of which this investigation is a study, was obtained during the study of the application to cottonseed oil of the slightly modified method of Tortelli and Ruggeri for the separation of the liquid and

solid fatty acids, and in addition the separation of the liquid acids by means of their bromides.

The first experiment recorded which resulted in the low melting-point product in place of ordinary linolic tetrabromide is as follows: twenty grams of cottonseed oil were saponified with 15 c.c. of fifty percent aqueous caustic potash solution and 45 c.c. of ninty-five percent alcohol. After neutralizing the excess of caustic potash with acetic acid, the hot soap solution was poured in a thin stream into 300 c.c. of seven percent lead acetate solution. After cooling, the flask and contents were allowed to stand forty-eight hours, the supernatant liquid was poured off through a filter, and the soaps washed three times with two-hundred c.c. portions of water at 40°-50°C. After the soaps were cool, 220 c.c. of ether was poured into the flask and the whole allowed to stand, with occasional shakings, until pulverized. This took about two days and was accompanied by a change in the color of the ether solution from colorless to a carmine red. When the lead soaps were thoroughly pulverized, the ether solution was heated nearly to boiling in a warm water bath, for nearly twenty minutes, and brought at last to a gentle simmer. The ether solution was then cooled two hours at 8°-10°C, after which the insoluble lead soaps, together with the ether solution of soluble lead soaps were poured on a Büchmer funnel and filtered quickly by suction, the insoluble portion spreading in a thin layer on the filter-paper. These insoluble soaps were washed

slightly with ether which had been cooled to 10°C or below. The filtrate was transferred to a five-hundred c.c., round-bottom flask, the ether distilled off to 150 c.c. volume, and transferred to a 200 c.c., narrow neck flask. The flask was well filled up to the cork and immersed in running water for twelve hours. The ether solution was then filtered into a separatory funnel and the lead soaps decomposed with 150 c.c. of twenty percent hydrochloric acid, then washed with 100 c.c. of the same strength of acid and with water till free from acid.

The solution was made up with ether to a volume of 400-500 c.c. and brominated. No glacial acetic acid was added at bromination, and an excess of liquid bromine was added. However the bromination seemed to occur as readily as it had when glacial acetic acid was in the ether solution. After standing some time in the cold, the brominated solution was poured into a separatory funnel, and the attempt was made to wash out the excess bromine with water. After some eight or ten washings, it was decided to try a solution of sodium thiosulfate. This worked excellently and removed the bromine completely. The solution was then washed twice with water to remove the excess sodium thiosulfate. The ether solution was dried over fused calcium chloride and the dry ether distilled on the water-bath. The mixed bromides, having been allowed to cool and solidify, were melted on the steam bath and petroleum ether was added. They were next cooled to 0°C. The bromide crystals sep-

arated in flocculent masses, and after filtration from the petroleum ether were crystallized from ninty-five percent alcohol. The crystals separated from the alcohol in star shaped bunches like bundles of needles radiating from a center. They were recrystallized from alcohol and possessed a melting point of 56°-57°C. The crystals were light and fluffy and they seemed to have a peculiar saffron glisten or sheen. A second fraction melted at 56°-57°C (mostly near 57°C). A third fraction melted at 56°-57° showing a very definite melting point. The crystals were very soluble in glacial acetic acid.

The most striking characteristic of the product which was thus unexpectedly obtained was in its definite melting-point. The product was thus naturally assumed to be a bromide and in the light of this assumption, was especiallyinteresting in view of the isomeric linolic tetrabromide, with almost identical melting point, which Thoms obtained from Telfairia oil.

The possibility at once arose of the existence of this isomeric linolic acid in cottonseed oil, which had accidentally been revealed by some unintentional modification or variation of the generally accepted method, for isolating the bromide of linolic acid, as applied to cottonseed oil. A study of the procedure, which resulted in the first yield of the low-melting-point bromide, shows that there were at least two variations in the methods, which might have been contributing factors. In the first place the ether solution of liquid acids was brominated in

the absence of glacial acetic acid and with liquid bromine, and in view of the fact that the resulting body could not be assumed to be other than a bromide, a study of the variations in the methods of bromination seemed to be the first and most important undertaking. In the second place, the lead soaps of the liquid acids were dissolved away from the lead soaps of the solid acids by allowing the entire mass to become pulverulent by standing under ether for several days, rather than dissolving them away quickly at the temperature of boiling ether. The chief object, of this modification, was to cause a more complete pulverizing of the lead soaps, in order to completely dissolve away the lead soaps of the liquid acids in warm ether. At first this modification was not considered very important in the formation of the new "bromide" but a study of this factor eventually became important, as the results which are about to be reported will disclose. In addition to these two factors, was studied, namely: the effect of the large amount of hydrochloric acid used for the decomposition of the lead soaps of the liquid acids.

The following variations were studied with the bromination of the liquid fatty acids: (1) bromination in the presence or absence of glacial acetic acid; (a) with liquid bromine; (b) with an ether solution of bromine; (2) brominating in both concentrated and dilute solution; (3) brominating slowly or rapidly; (4) brominating with a large or small excess of bromine.

Influence of the Methods of Bromination on the Formation of the Unknown Body under Investigation.

A report of the bromination experiments performed is as follows:

Experiment I. An ether solution of the liquid acids from forty grams of cottonseed oil, obtained by the adopted method, was divided into eight equal parts and brominated according to the following scheme:

No.	Solvent	Bromine		Glacial acetic acid	M. pt. of crude product	Remarks
		Kind	Addition			
1	Ether	Liquid Bromine	In excess	None	65°-70°C	
2	"	"	"	a few c. c.	90°-92°C	
3	"	"	Not in excess	None	98°-101°	
4	"	"	"	A few c.c.	100°-102°C	
5	"	normal solution in ether	In excess	a few c.c.	105°C	
6	"	"	"	None	90°-96°C 65°-75°C 80°-83°C	 flaky nodules
7	"	"	Not in excess	"	Would not crystallize.	
8	"	"	"	A few c. c.	Would not crystallize.	

The results of this experiment indicate that the method of bromination, in so far as it involves the use of liquid bromine or an ether solution of bromine does not seem particularly, to be a factor in the production of the low melting body. Neither does the presence or absence of glacial acetic acid seem to be a factor. This last point is brought out even more clearly in experiment 2.

Experiment 2. The ether solution of liquid acids, from 20 grams of cottonseed oil, was divided into four equal parts and brominated as follows:

No.	Solvent	Bromine		Glacial acetic acid	M. pt. of crude product.	Remarks
		Kind	Addition			
1	Ether	5 grams liquid bromine	To excess in rapid stream	None	113°C	Shows very pure linolic tetrabromide
2	"	"	"	5 c.c.	110°C	
3	"	"	To sat. slowly, excess in rapid stream	None	112½°-113°C	Shows very pure linolic tetrabromide
4	"	"	"	5 c.c.	108°-110°C	

The results of this experiment show conclusively that the presence or absence of glacial acetic acid in the ether solution at bromination is not a factor in the formation of the low melting body. They also show that neither the addition of an excess of bromine in bromination, nor the

rapidly with which the bromine is added a factor in the formation of the low-melting body, for in all cases the resulting product was ordinary linolic tetrabromide.

Experiment 3. The ether solution of the liquid acids, from five grams of cottonseed oil, was divided into two equal parts and brominated as follows:

No.	c.c. Ether	Grams Bromine	Addition	Glacial acetic acid	Melting point	Remarks
1	50 c.c.	2.5c.c	rapidly	None	112°-113°C	Very pure linolic tetrabromide
2	10 c.c.	2.5c.c.	"	"	111°-112°C	"

The results of this experiment show that the concentration of the ether solution of the liquid acids at bromination is not a factor in the production of the low-melting body.

It is apparent from the study of the wide variation in the method of bromination that the unknown compound is not formed during the bromination of the liquid fatty acids.

Since only negative results were gained from a study of the methods of bromination, attention was next directed to the study of the second varying factor which was recorded in the original experiment, where the unknown crystalline body was first produced, namely: allowing the lead soaps of the fatty acids to stand in contact with ether until the insoluble soaps become pulverized, before filtering

the ether soluble lead soaps. In this connection, as was described in a report of the original experiment where the low melting body first occured, it was noticed that if the lead soaps of the mixed acids are allowed to stand in contact with ether for a more or less variable period of time, but always exceeding twenty-four hours, this pulverizing of the insoluble lead soaps is accompanied by a coloration of the ether solution. This color varied from yellow to deep crimson and always occured to some degree if the ether solutions were allowed to stand more than twelve hours, the depth of color apparently depending in most cases upon the length of time the solution stood before decomposing the lead soaps with hydrochloric acid.

Experiments to determine the effect of the second factor in the production of the low-melting-point body, are as follows:

Effect of Allowing the Ether Solution of Soluble Lead Soaps to Stand Twenty-four Hours or More before Liberating the Acids from the Lead Soaps with Hydrochloric Acid.

Experiment 1. The lead soaps of the fatty acids from five grams of cottonseed oil, in ether solution were allowed to stand forty-two hours at room-temperature. The ether solution assumed a crimson-red color. The liquid acids were obtained as usual, divided into two equal parts and brominated as follows:

No.	Vol. of Ether sol.	Glacial acetic acid	Bromine	Melting pt. of crude prod.
1	90 c.c.	Glacial acetic acid	Liquid bromine in excess	Fract. (1)56°-57°C " (2)55°-56°C " (3)56°-59°C
2	90 c.c.	None	"	" (1)58°-60°C " (2)58°-62°C " (3)58°-60°C " (4)67°-70°C

It should be noted that results of this experiment show once more that the presence or absence of glacial acetic acid at bromination is not a factor in the production of the low-melting-body.

Experiment 2. The lead soaps of the fatty acids from twenty grams of cottonseed oil were allowed to stand in ether solution, until they showed a pulverulent form, when shaken in ether solution, or about twenty-seven to thirty hours.

They were filtered without heating above or cooling below room temperature. The ether solution of the free liquid acids was brominated in the absence of glacial acetic acid with an excess of liquid bromine. The first and largest crop of crystals melted at 110°C. The second, third and fourth crops were very much smaller and melted at 57°-60°C.

Experiment 3. The ether solution of the lead soaps of the fatty acids from four 5 gram samples of cottonseed oil were treated as follows: (1) The ether solution of lead soaps of the fatty acids was allowed to stand, with occasional shaking until the lead

soaps were pulverized (two days) then was heated to simmering, cooled to room-temperature for one-half hour and filtered. (2) The ether solution of the lead soaps of the fatty acids was allowed to stand four days, with occasional shaking, and filtered without heating above or cooling below room temperature. (3) After standing four days, the ether solution of the lead soaps was heated to simmering several minutes, cooled to room temperature and filtered. (4) This was treated as <u>two</u> and <u>three</u> except that the ether solution was heated to simmering several minutes and cooled two hours at 8°-10°C, before filtering. The ether solution of the lead soaps of the liquid acids was in each case treated according to the adopted method, the liquid acids brominated, without the presence of glacial acetic acid, in the solution. The following melting points were obtained on the crude crystals isolated:

Sample	Fraction I	II	III	IV
(1)	110°-112°C	165°-107°C	78°-82°C	57°-59°C
(2)	59°-62°C	54°-55°C		
(3)	60°-64°C	52°-54°C		
(4)	163°-105°C	55°-63°C		

Experiment 4. The ether solutions from the lead soaps of the fatty acids from four 5 gram samples of cottonseed oil were treated as follows: (1) The ether solution was allowed to stand three days (72 hours) and filtered without heating above or cooling below room temperature. (2) The ether solution of the lead soaps

was allowed to stand three days heated to 30°C for 4½ minutes on the water-bath and 1 minute to boiling under a reflux condenser, then cooled two hours at 8°-10°C and filtered. (3) The ether solution of the lead soaps after standing three days was heated to 30°C for 15 minutes on the water-bath and to boiling for 5 minutes under a reflux condenser and cooled two hours at 8°-10°C. (4) The ether solution was allowed to stand twenty-four hours only, heated and cooled as in (3) and filtered. In all four the liquid acids were brominated with a moderate excess of liquid bromine in the absence of glacial acetic acid and the petroleum ether insoluble substance crystallized from ninty-five percent alcohol. The following is a table of the melting points obtained on the crude products.

No.	Melting point of crude product.	Remarks
1	Fract.I 57°-60°C " III 51°-52°C	fluffy, impure-looking crystals.
2	" I 59°-67°C	Nearly all melted between 64°-67°C
	II 47°-51°C	Very impure looking crystals.
3	" I 102°- 105°C	Precipitated from petroleum ether.
	" II 57°-61°C	Crystallized from ninty-five percent alcohol.
	" III 56°-57°C	Fract.II reprecipitated from petroleum ether.
4	" I 108°-110°C	Large crop, melts nicely.
	" II 50o_60°C	Very small crop-meltsobscurely-impure.

The results of all four of the preceding experiments agree closely and all give positive evidence that allowing the lead soaps of the fatty acids to stand in ether solution twenty-four hours or longer, during which time the ether solution generally assumes a carmine red color, is an important factor in the formation of the unknown compound under investigation.

The results of experiment one show quite conclusively that whether glacial acetic acid is or is not present in the ether solution of the liquid acids during bromination, the low melting body is produced if the lead soaps have been allowed to stand a sufficient length of time in ether solution.

Experiment two shows that while some of the low melting body is formed during the first twenty-four to thirty hours, yet it is necessary for the solution to stand longer than thirty hours in most cases.

Experiments three and four also show that the raising of the temperature of the ether solution, immediately preceding filtration from the insoluble lead soaps, has no tendency either to retard or to hasten the formation of the low melting body. For instance in Experiment three, number (4) was filtered without heating above room-temperature and a very pure specimen of the low melting body produced. A like result was obtained in Experiment four, number (1) where the conditions were also the same.

On the other hand in Experiment three, number (3) and (4) and in Experiment four, numbers (2) and (3), where the only variation in the method, was heating the ether solution above room temperature for varying times before filtering, no marked improvement in the yield or quality of the product could be observed. Indeed in two of these just mentioned, a certain amount of crystals were obtained, which showed the presence of linolic tetrabromide.

The results of Experiment three, number (1) and Experiment four, number (4) indicate that in these cases the ether solutions did not stand long enough to allow the change, which is the cause of formation of the low melting body, to take place to any marked degree.

However in comparison with the experiments with the methods of bromination, the results of this set of experiments, are distinctly positive and indicate the causative factor in the formation of the body under investigation, is located in the ether solution of the lead soaps and that the completeness of its action is influenced to a marked degree by the length of time the ether solution of the lead soaps is allowed to stand, before liberating the liquid acids from their lead soaps.

Effect on the Formation of the Unknown Body of Using a Large Excess of Hydrochloric Acid in Decomposing the Lead Soaps of the Liquid Acids.

On calculation, it was found that the amount of acid

recommended by Tortelli and Ruggeri for decomposing the lead soaps of the liquid fatty acids from twenty grams of oil is much in excess of the actual required amount. The method calls for 250 c.c. of twenty percent hydrochloric acid while about 10 c.c. of that strength is all that is actually necessary. Therefore it seemed likely that the great excess of hydrochloric acid present while decomposing the lead soaps, might be a contributing factor in the production of the low melting body. In other words, if the proper conditions were obtained in the ether solution of soluble lead soaps, as shown by the preceding set of experiments, the presence of an excess of hydrochloric acid might complete the formation of some compound, which, when subjected to the action of bromine would be the low melting body. To test out this hypothesis, the following experiment was carried out: the ether solution of the lead soaps of the fatty acids from twenty grams of cottonseed oil was allowed to stand three days and filtered, without heating above or cooling below room temperature. The filtrate after standing sixteen hours in a narrow neck flask, in running water, during which time no precipitate settled out, was divided into two equal parts. These two portions were poured into separatory funnels and treated as follows: (1) The lead soaps were decomposed with 75 c.c. of a twenty percent hydrochloric acid solution, the lead chloride run off and the solution first washed with 50 c.c. of a twenty per-

cent hydrochloric acid solution, then four times with water, until the wash water showed no acid to congo-red. (2) The lead soaps were decomposed with 75 c.c. of a hydrochloric acid solution, made by diluting 10 c.c. of twenty percent hydrochloric acid to one hundred and twenty-five c.c. volume, the precipitated lead chloride run off, and the solution washed first with fifty c.c. of the diluted hydrochloric acid solution, and then three times with water, until the last washing showed no acid to congo-red.

Both solutions were cooled to 5°C and brominated to a brown color, with liquid bromine in the absence of glacial acetic acid. The mixed bromides were washed with petroleum ether and the petroleum ether insoluble bromides crystallized from ninty-five percent alcohol. The melting points on the different fractions of portions (1) and (2) were as follows:

No.	Fraction I	Fraction II	Remarks
(1)	108°-111°C	65°-70°C	Fraction II gave an obscure melting point.
(2)	168°-111°C	55°-60°C	

In both portions,Fraction I, melting at 108°-111°C, was much the larger, being at least two thirds the entire yield. The results of this experiment show that a great excess of hydrochloric acid in the ether solution, while decomposing the lead soaps is not a factor in the formation

of the low melting compound. It is interesting to note, also that in these experiments the changes which cause the formation of the low melting product, evidently had not been carried to completion, before decomposing the lead soaps with hydrochloric acid. One is therefore forced more and more to the conclusion, that the changes which are responsible for the low melting body, take place in the ether solution of the lead soaps of the unsaturated fatty acids.

Determination of the Molecular Weight Chemical Composition and Formula.

Having determined, with a reasonable certainty, the conditions necessary for the formation of the low melting body, or rather the step in the proceeding during which the body is formed, which when subjected to the action of bromine, gives the low melting body, it becomes necessary to determine its molecular weight, chemical composition and formula.

Molecular Weight.

(a) Molecular weight by titration method.

The attempt was first made to determine the molecular weight of the low-melting body by the titration method of Hazura(1), described and used by Farnsteiner(2). In this

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(1) Monatshefte für chemie (1888).
(2) loc. cit.

method, as described in connection with a report of that author's work, Farnsteiner made use of the neutralization value of the various acids and bromo-acids. He dissolved 0.5 grams of substance in cold neutral alcohol and using phenophthalein as an indicator, titrated to a pink color with N/10-N/20 alcoholic potassium hydroxide. In attempting to follow exactly the method of Farnsteiner, it was found that the body had practically no titration value at all. Therefore it was decided to use 0.2 gram of substance and titrate with N/100 alcoholic potassium hydroxide. In this experiment, the neutralization values, as well as the molecular weight of linolic tetrabromide are tabulated for purposes of comparison. The results are as follows:

	Linolic tetrabromide		Low melting body	
	1	2	1	2
Substance in grams	.2148	.2600	.2012	.2044
c.c. N/100 alcoholic potash used.	32.70	38.20	2.46	2.50
Grams K.O.H. used.	.01935	.02261	.001413	.001435
Neutralization no.*	90.10	86.96	7.023	7.021
Molecular weight	622.7	658.5		

*Neutralization number equals milligrams potassium hydroxide per gram of substance.

The results of this experiment shows that the low melting compound has practically no neutralization value and therefore, that the carboxyl hydrogen must be displaced by a group not broken off by dilute alcoholic

potassium hydroxide in the cold.

Being unable to determine the molecular weight of the low-melting body by the titration method, the cryoscopic method, using benzene as a solvent was tried. It was found however, that bromides of the fatty acids associated in benzene solution. The same difficulty was found with ninty-five percent alcohol using the ebullioscopic method. So glacial acetic acid of ninty-nine percent purity was finally used, and the molecular weight determined by the lowering of the freezing point of the solvent. Use was made of a magnetically propelled stirrer, and it was necessary to apply corrections both for water present in the acid and for the excessive supercooling of 2°C or over which occured with the glacial acetic acid, which was used in the determination.

(b) Molecular weight in glacial acetic acid solution, by the cryoscopic method.

The crystals of the low melting body were recrystallized many times from ninty-five percent alcohol and were freed from moisture by being dried for several weeks over sulfuric acid in a vacuum dessicator. They possessed a constant melting-point of 58°-59°C. About 0.5 gram of crystals was introduced at each time, three additions being made. 18.791 grams of ninty-nine percent acid were used as solvent, the acid freezing at approximately 15°-15½°C. The first addition of the substance was .4908 gram.

	Calculated Δ	Calculated Molecular Weight.
Readings	.177	585.2
	.174	603.6
	.178	590.9
	.171	615.8
	.180	583.0
	Average	595.7

The second addition of the substance was .5259 gram.

Total solute present 1.0167 grams.

	Calculated Δ	Calculated Molecular Weight.
Readings	.325	668.6
	.328	657.9
	.331	654.8
	.325	669.4
	.325	668.3
	.325	665.3
	Average	664.05

The third addition of the substance was .4989 gram.

Total solute present 1.5156 grams.

	Calculated Δ	Calculated Molecular Weight.
Readings	456	706.9
	462	659.3
	468	690.4
	477	673.0
	471	685.2
	478	671.1
	Average	680.98

Average of seventeen readings 646.91.

The widely varying results may be explained as partly due to the tendency of glacial acetic acid to supercool excessively, and also to the hygroscopic properties of the acid, making it difficult to control accurately. It is likely that there was also association taking place in the glacial acetic acid solution. In fact this was probably the most important factor in causing the wide divergence in results. About all that the results can be taken to mean is that the molecular weight of the low melting body under investigation lies between 600 and 700 near to that of linolic tetrabromide.

Chemical Composition.

It was assumed that the low-melting body was a bromide, so the body was first analyzed for its bromine content.

(a) Bromine Content.

The silver bromide method was used,which is as follows: The bromide (0.1-0.2 gram) is dissolved in hot ninty-five percent alcohol, a small stick of potassium hydroxide is added and the solution boiled about one hour on the steam bath under a reflux condenser. An Erlenmeyer flask is used and the hot alkaline solution quantitatively washed out of the flask into a beaker with hot water and the solution diluted with an equal quantity of water. The solution in the beaker is heated on the steam-bath until most of the alcohol has

been dispelled, A slight excess of nitric acid is now added, using phenophthalein as an indicator and the heating continued until the fatty acids rise to the top in a clear layer. The solution, which must not become too concentrated, is allowed to cool and is washed with water and ether into a separatory funnel. The aqueous solution is carefully shaken with one-half volume of ether, to dissolve out the fatty acids. The aqueous layer is then drawn off and the ether solution carefully washed two or three times with water ,adding the washings to the first portion drawn off. The combined washings are heated on the steam-bath until the ether has been dispelled. At this point especial care is necessary to avoid losing some of the solution by spattering. It is necessary to keep the beaker covered with a watch-glass until the ether is entirely expelled. The watch-glass is rinsed into the beaker and the solution evaporated to about 250-300 c.c. volume. The solution is precipitated hot with a calculated amount of silver nitrate solution, boiled with constant stirring, until clear, and allowed to stand several hours or over night, protected from the light. The precipitated silver bromide is filtered on a Gooch crucible and washed free from silver nitrate with hot water. The filtrate is tested for the presence of an excess of silver nitrate with hydrochloric acid. The precipitate is dried to constant weight at 150°C and the bromine content of the sample calculated. The

determinatinn is done in duplicate.

The following results were obtained on four samples of the low melting body.

	1	2	3	4
Wt. of sample	.1208	.1166	.1148	.1110
" of silver bromide	.1448	.1371	.1364	.1329
Percentage bromine in sample	51.01	50.01	50.56	50.94

Average of Numbers 1, 3 and 4 = 50.84 percent.
Percentage bromine in linolic tetrabromide 53.33..
Percentage bromine in telfairic tetrabromide,,52. and 52.76 percent.

(b) Carbon and Hydrogen Content.

The combustion tube was filled two-thirds full with a mixture of equal parts copper oxide and fused lead chromate, the latter to absorb the bromine given off, and the combustion conducted in a stream of pure oxygen. The results on four combustions are as follows:

	1	2	3	4
Weight of sample	.1810	.1896	.1923	.1945
" of water	.0981	.1004	.0996	.1045
" of carbon dioxide	.2401	.2710	.2719	.2776
Percentage of hydrogen	6.064	5.924	5.795	6.012
" of carbon	36.18	38.97	38.56	38.92

Formula

By averaging the most closely checking results for bromine, carbon and hydrogen, the following data is obtained for comparing the low melting bromide with linolic tetrabromide.

Element	Low melting bromide	Calculated for linolic tetrabromide. $C_{18}H_{32}Br_4O_2$
Carbon	38.82 percent	35.99 percent
Hydrogen	5.95 "	5.36 "
Bromine	50.84 "	53.30 "
Oxygen (by diff.)	4.39 "	5.35 "
Total	100.00 "	100.00 "

It is readily seen that the low-melting bromide has a composition very close to that of linolic tetrabromide, but containing a slightly smaller proportion of bromine and oxygen and a slightly larger propertion of carbon and hydrogen than linolic tetrabromide. As any variation in the number of bromine and oxygen atoms of linolic tetrabromide would make a much greater variation in their respective percentages than can be observed here, whatever difference exists between the composition of linolic tetrabromide and the low melting bromide must lie in the carbon and hydrogen atoms.

Basing the calculation on the assumption that the unknown compound is a tetrabromide, the following formula

is calculated from the percentage composition:

Carbon $\frac{38.82}{12} \times \frac{4}{.6359}$ = = = 20.34

Hydrogen$_1\frac{5.95}{1.008} \times \frac{4}{.6359}$ = = = 37.15

Bromine $\frac{50.84}{79.96} \times \frac{4}{.6359}$ = = = 4.00

Oxygen $\frac{4.39}{16} \times \frac{4}{.6359}$ = = = 1.726

From this data the following simple formula is calculated: i.e. $\underline{C_{20}H_{37}Br_4O_2}$

If the formula were $C_{20}H_{36}Br_4O_2$ the compound could be $C_{17}H_{31}Br_4COOC_2H_5$, having an ethyl group where the hydrogen of the carboxyl is found in linolic tetrabromide. In fact, basing the calculation on the values of 50.84 as the percentage of bromine and 5.795 and 38.56 as the hydrogen and carbon percentages, as obtained by combustion number 3, the empirical formula $C_{20}H_{36}Br_4O_2$ is very closely approximated.

Carbon $\frac{38.56}{12} \times \frac{4}{.6359}$ = = = 20.21

Hydrogen $\frac{5.795}{1.008} \times \frac{4}{.6359}$ = = = 36.18

Bromine $\frac{50.84}{79.96} \times \frac{4}{.6359}$ = = = 4.00

Oxygen $\frac{4.805}{16} \times \frac{4}{.6359}$ = = = 1.889

If the structure of the unknown compound is $C_{17}H_{31}Br_4COOC_2H_5$, it should possess no neutralization value, and as a matter of fact, experiments reported in connection with the molecular weight determination,

showed that the unknown body had no neutralization value.

Furthermore, if the unknown body is merely the ethyl ester of linolic tetrabromide, it should be possible to prepare the body synthetically from linolic tetrabromide.

Reformatsky(1) states that ethyl linolate $C_{17}H_{31}COOC_2H_5$ can be formed by dissolving linolic acid in absolute ethyl alcohol and passing hydrochloric acid gas through the solution. If ethyl linolate can be made in this way from linolic aced, there is no reason why ethyl-brom-linolate cannot be made in the same way from brom-linolic acid (linolic tetrabromide). The following experiment was accordingly carried out to satisfy the above supposition.

About one-half gram of linolic tetrabromide melting at 111°-112°C was dissolved in about 50 c.c. of absolute ethyl alcohol and hydrochloric acid gas passed in for nearly an hour. From this solution were obtained crystals melting as follows:

Fraction	I	60°-61.5°C
"	II	58°-61.5°C
"	III	58°-60°C
"	IV	58°-59°C

This body, which the method of synthesis proves to be ethyl-brom-linolate, being made from linolic tetrabromide and absolute ethyl alcohol by the action of hydrochloric acid gas, is identical in melting-point and physical

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(1) loc. cit.

appearance with the body under investigation.

Therefore the white crystalline body, obtained from the mixed bromides of the liquid acids of cottonseed oil, after the lead soaps of its fatty acids have been allowed to stand in ether solution several days before decomposing with hydrochloric acid, is the ethyl ester of brom-linolic acid which has the empirical formula $C_{17}H_{31}Br_4COOC_2H_5$.

GENERAL DISCUSSION.

The results of this investigation have a two-fold interest, on the one hand, in relation to the progress of organic chemical synthesis and on the other, in connection with the practical analysis of fats and oils.

In the first place, the body, ethyl-brom-linolate is of interest as an entirely new compound of linolic acid. Hitherto only metallic salts of the bromides of the fatty acids have been reported. Indeed, in the case of linolic tetrabromide, lead-brom-linolate is the only salt of a tetrabromide, described in the literature. This body as described by Farnsteiner(1) is a powder and completely soluble only in a mixture of two parts benzol to one part ninty-five percent alcohol. It is in all cases, difficult to work with. Ethyl-brom-linolate has proven, on the contrary to be quite soluble in most organic solvents, in this respect, somewhat closely resembling the mother substance, linolic tetrabromide.

Ethyl-brom-linolate is easier to purify by crystallization from alcoholic solution than is linolic tetrabromide and also comes down in much nicer crystals.

Then too, ethyl-brom-linolate proves to be a very stable compound. It is not decomposed by hydrochloric

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(1) loc. cit.

acid, and is broken down completely ,only by boiling for some time with fairly concentrated potassium hydroxide. In these features, the body, while having a large and somewhat complex molecule, shows a stability comparable with ethyl acetate.

Thus it will be seen that there is opened up, in a promising way, the whole new field of the investigation of the estersof the bromo-fatty acids, which field is at present practically unexplored.

Further than this, the results of the investigation, proving that the ethylation of linolic acid occurs in ether solution and merely on prolonged standing at ordinary room temperature, suggests that the investigation may have a bearing on the chemistry of ether. No statement in the literature was found which even suggested the possibility of a change, such as quite evidently takes place to a greater or less degree when lead linolate is allowed to stand in ether solution for twenty-four hours or more.

The reaction which evidently takes place here is a shifting of the metallic ion of lead linolate and one ethyl group of the ether, with the formation of ethyl linolate and lead alcoholate, as follows:

$(C_{17}H_{31}COO)_2Pb\ (C_2H_5OC_2H_5)_2 = (C_{17}H_{31}COOC_2H_5)_2\ (C_2H_5O)_2Pb.$

Whether the reaction is a definite one or is brought about by the agency of, or due to the presence of lead oleate and the lead soaps of the solid acids or possibly to the presence of unavoidable traces of water and lead acetate can

only be explained by future investigations. It is interesting to note here, that the only visable evidence of the reaction that evidently takes place in the ether solution is the development of a carmine red color. Of course it is very possible that this has nothing whatever to do with the process of the reaction.

In the second place however, laying aside all claims to purely scientific interest, which the synthesis of this body may possess, we are confronted by the quite definite practical bearing, the results of the investigation have, on the analysis of cottonseed oil, and the relation the analytical methods may have to the study of oils and fats, closely related to cottonseed oil, or to the search for a linolic acid content in oils and fats, in which it is suspected to occur in small percentages.

In the first place, if a quantitative estimation of linolic acid, by means of its tetrabromide is desired, care must be taken not to allow ethylation of the linolic acid to occur while the lead soaps of the solid and liquid acids are being separated. In other words, after the lead soaps are immersed in ether, the process of separation must be carried as quickly as possible to the point, where the lead soaps of the liquid acids may be decomposed. The necessity for this speed is even more evident in a case where the possible percentage of linolic acid is small.

The formation of the ethyl ester of linolic acid in the ether solution of its lead soap points out the great

possibility of other changes occuring during the process of analysis, which would account for the discrepancy between the theoretical percentage of linolic acid in cottonseed oil as calculated from the iodine number of the liquid acids and the percentage of linolic acid found by actual isolation of its tetrabromide. In answer to the other questions raised, in the "Plan of Investigation" it may be said in the first place that since it has already been determined, during what step in the process of separation and identification of linolic acid as its bromide, the body ethyl linolate is formed which on bromination gives ethyl-brom-linolate, it becomes quite clear that ethyl-brom-linolate has as its mother substance in the cottonseed oil, the glyceride of linolic acid and not the glyceride of an acid other than oleic or linolic acids, as was at first thought possible.

Again, the body, ethyl-brom-linolate is not formed by any change in constitution from oleic or linolic acids, such as oxidation or the addition of hydroxyl groups, or by any isomeric shifting within the molecule.

Ethyl-brom-linolate, however, as has been shown, is partly a substitution product, since the hydrogen of the carboxyl of linolic acid has been displaced by an ethyl group, and partly an addition product, due to the free carbon bonds of the acid having been saturated by bromine.

In answer to another question raised in the "Plan of Investigation" it is interesting, to refer again briefly to a point already discussed, namely: that, though

a great deal is known about linolic acid in a qualitative way, yet the quantitative estimation of the acid in oils and fats is still very unsatisfactory, most especially so in cottonseed oil where it is the acid occuring in largest percentage. So it is almost unnecessary to state that the proportion of the mother substance of ethyl-brom-linolate present in the original oil cannot at present be stated.

In answer to the remaining point it may be said that, as far as can be discovered without an actual repetition of Thoms work on telfaria oil, ethyl-brom-linolate has no relation to the tetrabromide of telfairic acid.

However, in view of the fact that the two bodies are tetrabromides, and both so closely related to linolic tetrabromide, and especially the fact that their melting points are so close to each other, being 57°-58°C for telfairic tetrabromide and 58°-$58\frac{1}{2}^{\circ}$C for ethyl-brom-linolate, and again the fact that Thoms work has never been confirmed, a reinvestigation of Thoms work on telfairia oil would be desirable before accepting his results as final.

SUMMARY AND CONCLUSIONS.

1. If the lead soaps of the liquid acids of cottonseed oil are allowed to stand in ether solution several days, the lead soaps will become finely pulverized and in most cases a carmine red color will develop in the ether solution.

2. If the free fatty acids obtained from the lead soaps of the liquid acids, dissolved in the above ether solution, are brominated, a bromide is obtained, which has definite and characteristic properties, which properties are distinct from those of the ordinary linolic tetrabromide obtained if the lead soaps are pulverized and the soluble lead soaps decomposed as quickly as possible.

3. This body is ethyl-brom-linolate whose empirical formula is $C_{17}H_{31}Br_4COOC_2H_5$ and which is formed by the substitution of an ethyl group for the carboxyl hydrogen of linolic tetrabromide.

4. Ethyl-brom-linolate crystallizes in rosette-shaped bunches of needle shaped prisms, having a lower specific gravity than linolic tetrabromide and a definite melting point of 58°-$58\frac{1}{2}^{\circ}C$.

5. Ethyl-brom-linolate can be synthesized directly from linolic tetrabromide by dissolving the tetrabromide in absolute ethyl alcohol and passing hydrochloric acid gas into the solution.

6. As far as can be discovered without a repetition of the work on Telfairia oil, ethyl-brom-linolate has no relation to the bromide of telfairic acid described by Thoms.

7. The study of ethyl-brom-linolate opens up an entirely new field of investigation, namely: the esters of the bromo-fatty-acids.

8. The data presented relating to the cause of the formation of ethyl-brom-linolate, proves that especial care must be taken in adhering to an exact method, if a pure linolic tetrabromide is to be obtained.

9. While the problem of adjusting the actual percentage of linolic acid in cottonseed oil, as found by analysis to the calculated percentage, as found by the iodine number of the mixed liquid acids, remains yet to be solved, the data obtained in this investigation is a distinct advance in that direction.

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