pressure, when a nitrogen concentration of 6 per cent is present in the bomb gases. With coal, to which sufficient pyrites had been added to furnish a sulfur content of 7 per cent, only about three-fourths of the sulfur was obtained as SO_3 when a gram of the fuel was burned at 20 atmospheres pressure, with 0.53 per cent nitrogen by volume in the bomb gases. Under these conditions, estimation of the sulfur content of the fuel from the bomb washings would be much in error. However, with a greater percentage of nitrogen in the bomb gases and at a higher pressure, satisfactory results may be obtained.

VI—We have calculated the heating value of sulfur as pyrites burning to SO_3 , applying the proper corrections, and have found that the average of our results gave us 4975 calories per gram sulfur.

VII—The corrections prescribed in the proposed Standard Method¹ for the oxidation of sulfur in coal in a bomb calorimeter are shown to be correct only within certain limits.

In the usual procedure, when coal with less than 2 per cent of sulfur is burned in a bomb calorimeter from which the initial charge of air is not removed by rinsing out with oxygen, there will be sufficient formation of oxides of nitrogen to ensure the oxidation of almost all the sulfur to SO_3 . Under these conditions the corrections prescribed by the committee are proper. If coals are high in sulfur there may be a material amount of the sulfur left as sulfide in the ash and as SO_2 in the gas. If oxygen of high purity is used and the air in the bomb blown out, as recommended by the Committee on Coal Analysis, so that the concentration of nitrogen in the bomb may be only a fraction of 1 per cent, and if a fuel free from nitrogen is being burned, then only a small amount of oxides of nitrogen will be formed, and even if the fuel contain only 2 per cent sulfur, only a part (sometimes only one-half) of the sulfur will appear as SO_3 .

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ETHYL ESTER OF LINOLIC TETRABROMIDE AS A PRODUCT IN THE ANALYSIS OF COTTONSEED OIL²

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In the course of some studies of the composition of cottonseed oil, in which we were isolating the unsaturated acids according to the method of Tortelli and Ruggeri,³ *i. e.*, making use of the solubility of their lead soaps in ether, and eventually recovering the linolic acid as the tetrabromide, we obtained instead large clustering needles melting sharply at 58–58.5° C.⁴ The crystals, in addition, showed a much greater solubility in ninety-five per cent alcohol, glacial acetic acid, petroleum ether, etc., than linolic tetrabromide, from all of which solvents the crys-

¹ "Report of Committee on Coal Analysis," THIS JOURNAL, 5 (1913), 526–527; Technical Paper No. 8, Bureau of Mines, p. 15.

² The greatest part of the investigation here reported is taken from the Thesis presented by Philip Anson Wright to the Faculty of the Graduate School of the University of Missouri in 1913, in partial fulfilment of the requirements for the degree of Master of Arts.

³ L'Orosi, April, 1900; Lewkowitsch, "Oils, Fats and Waxes," Vol. I, p. 447 (1909 edition).

⁴ Linolic tetrabromide melts at 113–115° C.

tals could be recovered in the same form and with the same melting point.

The new compound was very readily shown to be a bromide; and its melting point was so strikingly similar to the melting point of the tetrabromide of the isomeric telfairic acid of Thoms,¹ *i. e.*, 57–58° C., that it suggested the presence of a similar, heretofore undiscovered acid in cottonseed oil.

Attempts to determine the molecular weight of the low-melting bromide by the titration method of Farnsteiner² showed, however, that it had no neutralization value. Molecular weight determinations by the cryoscopic method in glacial acetic acid were also of little value, the results varying between 600 and 700, although great care was taken to exclude moisture.³

Ultimate analysis of the low-melting bromide gave the following results:

Determination No.	Bromine Per cent	Hydrogen Per cent	Carbon Per cent	Oxygen (by diff.) Per cent
1.....	51.10	6.064	36.18	..
2.....	50.01	5.924	38.97	..
3.....	50.56	5.795	38.56	..
4.....	50.94	6.012	38.92	..
Average.....	50.63	5.95	38.16	5.24
Calculated for linolic tetrabromide.....	53.30	5.36	35.99	5.35

The bromine content was determined on separate samples. Since methods of determining the bromine in compounds of this character are not commonly described in the literature, the method used by us may be of interest at this point.

The substance⁴ was dissolved in 95 per cent alcohol, a small stick of KOH added, and the solution boiled under a reflux for one hour. The hot alkaline solution was washed out into a beaker with hot water and the solution diluted to 300 or 400 cc. with water. The beaker was then allowed to stand on the steam bath until most of the alcohol was dispelled. A slight excess of HNO_3 was added, and heating continued until the fatty acids rose to the top in a clear layer. The solution, which was not allowed to be too concentrated at this point, was then cooled and washed with water and ether into a separatory funnel. It was then shaken carefully with ether, and the aqueous layer drawn off. The ether extract was washed carefully several times with fresh water, the washings being added to the first portion drawn off. The combined aqueous solutions were then heated on the steam bath until the ether was dispelled, care being taken to use a very gentle heat to avoid spattering. The solution was then evaporated to 250–300 cc. and the bromine determined in this solution by precipitating with AgNO_3 . The determination was carried out from this point in the usual way for determining AgBr.

A comparison of the analyses obtained with the calculated composition of linolic tetrabromide shows that the low-melting bromide has a lower content of bromine and oxygen and a higher content of car-

¹ Arch. d. Pharm., 238 (1900), 48.

² Zeit. f. Untersuch. Nahr. u. Genussm., 3 (1899), 1.

³ Stirring was accomplished by means of a magnetically propelled stirrer.

⁴ Approximately 0.1 g. of the bromide was used, and an excess of the amount of KOH required to combine with the bromine.

bon and hydrogen. As any variation in the number of bromine and oxygen atoms of linolic tetrabromide would make much greater variations in their respective percentages than are found for the low-melting bromide it was apparent that whatever difference existed between the composition of the two compounds must lie in the number of carbon and hydrogen atoms.

Calculation of formulae from the ultimate analyses indicated a very close agreement of the low-melting bromide with the formula for ethyl-bromo-linolate, $C_{17}H_{31}Br_4COOC_2H_5$, as is shown below:

	Calculated for $C_{17}H_{31}Br_4COOC_2H_5$	Found for low- melting bromide
Carbon.....	38.22	38.16
Hydrogen.....	5.78	5.95
Oxygen.....	5.09	5.35
Bromine.....	50.97	50.63

By taking particular analyses even closer agreement is obtained. The conclusion, therefore, seemed justified that the low-melting bromide is merely the ethyl ester of linolic tetrabromide.

In order to verify this conclusion, ethyl-bromo-linolate was prepared from linolic tetrabromide according to the method of Reformatsky¹ for preparing ethyl linolate from linolic acid. The tetrabromide was dissolved in absolute ethyl alcohol and dry HCl gas passed in for an hour. The product which resulted was crystallized out. After purification it showed all the properties, including the melting point of 58–58.5° C., of the compound obtained from cottonseed oil.

It is probably a mere coincidence that the ethyl ester of linolic tetrabromide has a melting point so nearly identical with the melting point of the tetrabromide of the isomeric telfairic acid. It is possible, however, that Thoms' work on the unsaturated acids of kœme oil requires repetition. It was our intention to do this, but we were unable to secure any of the oil in this country.

The cause of the production of the ethyl ester instead of the ordinary linolic tetrabromide in our studies of cottonseed oil has been the object of much speculation. We have given the matter some study without, however, being able to arrive at any definite conclusions.

As previously stated, the unsaturated acids were isolated from the oil according to the method of Tortelli and Ruggeri, by making use of the ready solubility of their lead soaps in ether. The lead soaps thus obtained were decomposed with dilute HCl, the ether solution of the acids washed free from HCl with water, and the fatty acids brominated directly in this solution at a low temperature, using liquid bromine. Excess bromine was washed out with dilute sodium thiosulfate solution. The ether was then washed with water, dried over fused $CaCl_2$, decanted, evaporated at a low temperature, and the liquid mixed bromides treated with petroleum ether (b. p. 30–50° C.). The oleic and linolic bromides were thus roughly separated, the latter being but little soluble in this solvent at a low temperature. The insoluble tetrabromide was recrystallized from alcohol. The

ethyl ester was obtained while using the above procedure.

Without describing our investigations in detail, which included many variations in the method of bromination, amount of HCl used in decomposing the lead soaps, etc., it may be stated that apparently the step in the isolation that determines the character of the linolic acid end product is the solution of the lead soaps in ether. When the mixed lead soaps of the cottonseed oil acids are allowed to stand under the ether for 48 hours or more before filtering off and decomposing with HCl, the ether takes on a carmine-red color. This color is completely destroyed when the lead soaps are decomposed with HCl. It seems almost assured, however, that the changes that result in the ultimate production of the ester instead of the ordinary tetrabromide are associated in some way with the production of this red color. Whether a definite chemical reaction takes place at this point was not determined, although such a condition seems very probable. That the reaction was sometimes only partially complete was shown in a number of test cases where the lead soaps were allowed to stand for varying lengths of time under ether, with the result that the ultimate product was a mixture of linolic tetrabromide and the ester, crystals of each being obtained. The ester usually crystallized out first from a mixed alcoholic solution.

The foregoing results present several points of interest. In the first place it appears that some care is required not to allow the lead soaps to stand under ether, in isolating the unsaturated acids of cottonseed oil by the lead soap ether method, if the product desired is ordinary linolic acid or its bromide. In the second place there is opened up a field of new products of the unsaturated acids, namely the esters of the bromides. Heretofore esterification has been confined to the acids themselves.¹

We have prepared a few of these bodies, namely, methyl bromo-linolate and the methyl and ethyl esters of oleic dibromide. We found the methyl ester of linolic tetrabromide to crystallize from alcohol in white glistening plates resembling the ethyl ester. The slightly impure crystals melted between 50° and 56° C. The two esters of oleic dibromide were found to be yellow oils, very soluble in most solvents, but very little soluble in their corresponding alcohols saturated with HCl gas.²

At present actual analysis of cottonseed oil for linolic acid falls far short of the theoretical value indicated by the iodine value of the oil or the mixed unsaturated acids.³ It is hoped that the ease with which esters of the bromides of the unsaturated acids are formed, especially linolic acid, may eventually be of value in clearing up the composition of cottonseed oil.

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¹ With the exception of the ethyl ester of hexabromolinolenic acid which has been prepared by brominating the ethyl ester of α -linolenic acid.

² The esters of the bromo-linolates are very soluble in alcohol saturated with HCl. Attempts to make use of this difference for the quantitative separation of oleic and linolic acids have, however, not proved successful.

³ Compare Lewkowitsch, Vol. II, p. 157 (1909 Edition).

¹ Beilstein, "Handbuch. der Organ. Chem.," Vol. I, p. 536