

SALTS OF LINOLENIC HEXABROMIDE FROM LUMBANG OIL

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The glycerides of linolenic, linolic, and oleic acids occur naturally in vegetable drying oils. These unsaturated glycerides, particularly linolenic and linolic, are the substances that absorb oxygen from the air and cause the oil to dry.

The commercial value of an oil suitable for the manufacture of paint and varnish depends on its drying power, which is really the oxygen-absorbing capacity of the particular unsaturated compounds contained in the oil. Previous experiments¹ carried out on the oxidation of Philippine lumbang oil showed that linolenic glyceride was oxidized more readily than was linolic glyceride; also, the latter absorbed oxygen more rapidly than did oleic glyceride.

Linolenic glyceride has a greater capacity for the absorption of oxygen than has any of the other compounds contained in drying oils. This glyceride and the corresponding free linolenic acid are, therefore, substances of considerable importance, since the amount of this glyceride present in a drying oil determines to a considerable extent the commercial value of the oil.

Although linolenic glyceride and the free linolenic acid are substances which oxidize readily, they may be separated from an oil in the form of a stable hexabromide.² Since this linolenic hexabromide (hexabrom stearic acid) is a stable form of linolenic compounds, it is an important substance in the chemis-

¹ West, A. P., and A. I. De Leon, *Philip. Journ. Sci.* 24 (1924) 123; Lewkowitsch, J., *Chemical Technology and Analysis of Oils, Fats, and Waxes* 2 (1922) 42.

² Lewkowitsch, J., *Chemical Technology and Analysis of Oils, Fats, and Waxes* 1 (1921) 212.

try of vegetable drying oils. Only a very few derivatives of this substance (hexabromide) have ever been prepared. Erdmann and Bedford³ state that they prepared the potassium and barium salts of the hexabromide and also the methyl and ethyl esters, but they do not give the experimental details. Nor do they give the melting point or analysis of the salts.

In view of the fact that very little is known about linolenic hexabromide we thought it might be of interest to make a few salts of this substance and determine their solubility in various organic solvents. The data thus obtained may be useful in devising new methods of analysis and in working out more-accurate separations of mixtures of halogen stearic acids, such as linolenic hexabromide, linolic tetrabromide, and oleic dibromide.

In order to study the chemical behavior of the unsaturated acids (which occur as glycerides in drying oils), or to make pure derivatives of these acids, it is necessary to separate each individual acid from the mixture of substances contained in the oil. The method commonly used is to decompose the glycerides and convert them into a mixture of free unsaturated acids. Since the unsaturated acids absorb oxygen readily when exposed to the air, they are treated with bromine and converted into the mixed bromo addition products⁴ (linolenic hexabromide, linolic tetrabromide, and oleic dibromide). The mixed bromides are very stable substances. Both the hexabromide and the tetrabromide may be separated from the dibromide and from each other by treatment with solvents, and they may be converted back again into the free acids by reduction⁵ with zinc in alcoholic solution. Thus it is possible experimentally to separate from an oil, such as lumbang, individual unsaturated acids and to study the chemistry of these acids and their derivatives.

EXPERIMENTAL PROCEDURE

In preparing a supply of linolenic acid hexabromide for our experiments, we used Philippine lumbang oil, which is a drying oil used in making paints, varnishes, and similar products.⁶ The lumbang oil we used was pressed from nuts of good quality and filtered first through glass wool and then through filter

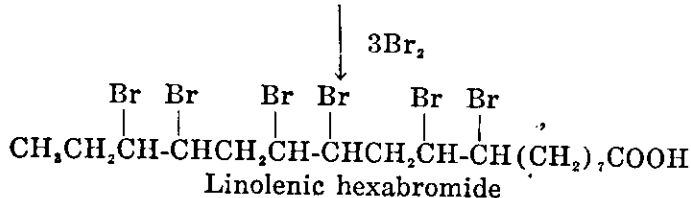
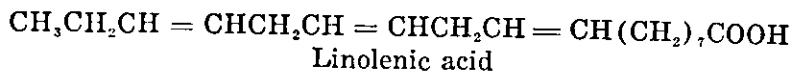
³Ber. Deut. Chem. Gesell. 42 (1909) 1324.

⁴Lewkowitsch, J., *Chemical Technology and Analysis of Oils, Fats, and Waxes* 1 (1921) 585.

⁵Ibid 1 (1921) 201, 202, and 210.

⁶West, A. P., and F. L. Smith, *Bull. P. I. Bur. Forestry* 24 (1923).

paper. Lumbang oil consists almost entirely of glycerides⁷ of the unsaturated acids, linolenic, linolic, and oleic. It serves as excellent material for preparing linolenic and linolic acids and their derivatives. When lumbang oil is decomposed and the glycerides are converted into mixed unsaturated acids and these mixed acids brominated in ether solution, linolenic hexabromide is precipitated according to the following equation:



Linolenic acid hexabromide.—Freshly prepared lumbang oil was saponified with aldehyde-free alcoholic potassium hydroxide in batches of 530 grams each. The resulting soaps were converted into mixed unsaturated acids which were extracted with ether and the ether solution was dehydrated with sodium sulphate. The ethereal solution of mixed acids, containing about 500 grams of acids, was poured into a 5-liter flask and diluted with redistilled ether to a volume of 4 liters. The flask containing the acids was immersed in a freezing bath of ice, salt, and water. The solution of mixed acids was stirred mechanically by means of a hot-air motor, and brominated according to the method of Eibner and Muggenthaler.⁸ When the thermometer immersed in the acid solution registered -10°C . or below, a slight excess of the calculated quantity of bromine (135.3 cubic centimeters of specific gravity 3.12) was allowed to drop rather rapidly into the acid solution from a dropping funnel, the end of which was drawn out to a rather fine opening. The temperature of the acid solution was not allowed to rise above -5°C . In about three hours the required amount of bromine was added to the acid solution. To complete the reaction the mixture was allowed to remain in the ice bath and the stirring continued for about two hours longer. The reaction product was then filtered to separate the insoluble hexabromide. The hexabromide was washed thoroughly with ether until white and then dried on layers of filter paper.

⁷ West, A. P., and Z. Montes, *Philip. Journ. Sci.* 18 (1921) 619.
⁸ Lewkowitsch, J., *Chemical Technology and Analysis of Oils, Fats, and Waxes* 1 (1921) 585.

When the unsaturated acids of lumbang oil are brominated at a low temperature, and especially in dilute solution, sticky products are not formed so readily as when the bromination is carried out in a more concentrated solution. It is also advisable to use a very slight excess of bromine, so that when the reaction is complete the mixture has a slightly yellow color. Incomplete bromination usually gives a reaction product that is somewhat oily and does not filter well.

To purify the linolenic hexabromide, samples of about 40 grams were washed thoroughly with ether, after which the hexabromide was crystallized, in small portions, first from ethyl acetate and then from benzene. After each crystallization the acid was filtered through a Buchner funnel with the aid of a partial vacuum and then washed well with ether, dried, and powdered. After standing in a vacuum desiccator for some hours the melting point was determined and found to be 179.5° C. to 180.5° C.

The acid was analyzed by determining the bromine content. This was done by boiling about 0.1 gram of the substance with a concentrated aqueous solution of silver nitrate (containing about 0.5 gram of silver nitrate) and 30 cubic centimeters of pure concentrated nitric acid. The precipitated silver bromide was collected on a Gooch crucible.

** Analysis of linolenic hexabromide.*

[0.1388 gram of sample gave 0.2078 gram silver bromide.]

Calculated for $C_{18}H_{30}Br_6O_2$	Bromine. Per cent.
Found	63.27
	63.71

In endeavoring to make derivatives of linolenic hexabromide, considerable difficulty was experienced, because the acid is rather insoluble in the ordinary organic solvents and it is necessary to work with very dilute solutions. Linolenic hexabromide does, however, dissolve to a certain extent in various solvents such as benzene, benzyl alcohol, ethyl acetate, xylene, pyridine, and the propyl and butyl alcohols.

Salts of linolenic hexabromide were prepared by first converting the acid into the potassium salt. A methyl alcohol solution of the potassium salt was then treated with a methyl alcohol solution of an inorganic salt such as barium bromide. The precipitated salt thus obtained was purified and the melting point and solubility in various solvents were determined. The

lead salt was, however, prepared directly from the free linolenic hexabromide.

Potassium salt of linolenic hexabromide.—Ten grams of linolenic hexabromide were dissolved in about 250 cubic centimeters of hot benzyl alcohol. To the clear solution 12 cubic centimeters of hot alcoholic potassium hydroxide solution (1 cubic centimeter = 0.061994 gram potassium hydroxide) containing a very slight excess of the calculated amount of potassium hydroxide, were added with vigorous shaking. The potassium salt of the hexabromide was thrown down as a white, gelatinous precipitate. About 200 cubic centimeters of absolute alcohol were then added and the mixture heated (reflux) on a water bath for about five hours. The mixture was cooled, the supernatant liquid poured off, and the salt washed well with ether by decantation in order to remove all the benzyl alcohol. If the benzyl alcohol is not entirely removed, the salt is somewhat oily and difficult to dry.

In order to purify the potassium salt, it was washed with hot benzene to dissolve any unchanged hexabromide which might be present. The salt was then washed with ether and dried in a desiccator. Experiments showed that it is not desirable to dry salts of the hexabromide in an oven at 80° C., because continued heating tends to turn them somewhat brown, due to slight decomposition.

A determination of the melting point showed that at 180° C. the salt begins to turn slightly brown and that it melts, with decomposition, to an opaque brown liquid at 185° C. to 190° C.

In preparing the potassium salt, propyl alcohol, isopropyl alcohol, and isobutyl alcohol can be used in place of benzyl alcohol to dissolve the hexabromide. However, the acid is not so soluble in these solvents as in benzyl alcohol, so that about 500 cubic centimeters are required for each 5 grams of the acid and the solution is turbid.

Analysis of potassium salt of linolenic hexabromide.

[0.1569 gram salt gave 0.2200 gram silver bromide.]

Calculated for $C_{18}H_{32}Br_6O_2K$
Found

Bromine.
Per cent.
60.25
59.67

Barium salt of linolenic hexabromide.—Five grams of the potassium salt of linolenic hexabromide were dissolved in about 2 liters of hot methyl alcohol and filtered. The solution was then heated again on a water bath. A solution of barium bromide was prepared by dissolving the salt in about 5 cubic centimeters

of water and adding 100 cubic centimeters of methyl alcohol. This solution of barium bromide, containing about 2.3 grams of the salt, was heated and then added with constant shaking to the hot alcoholic solution of the potassium salt. A white precipitate was formed immediately. The mixture was divided into two portions which were heated (reflux) for about nine hours. The liquid above the precipitate was then perfectly clear, an indication that the reaction was complete. The whole mixture was distilled to a volume of about 500 cubic centimeters, after which it was allowed to cool, and then thrown into about 1.5 liters of water, stirred, and filtered immediately. This treatment with water removed the potassium bromide and also the excess barium bromide, as shown by the bromide test with silver nitrate. The residue was washed with methyl alcohol and ether. It was then dried on layers of filter paper, powdered, and placed in a desiccator.

A melting point determination showed that, without crystallization, the barium salt of linolenic hexabromide turned slightly brown at 197° C., and became a brownish black mass at 200° C. without melting completely.

The formula of the salt was checked by determining the percentage of barium. A weighed quantity of the salt, placed in a porcelain crucible, was treated with a few drops of concentrated sulphuric acid and heated gently by heat reflected from a hot asbestos board placed above the crucible. In this way spattering of material was avoided. After ignition with a Bunsen flame the barium was weighed as barium sulphate.

Analysis of barium salt of linolenic hexabromide.

[0.5160 gram of the salt gave 0.0726 gram barium sulphate.]

	Barium. Per cent.
Calculated for $C_{20}H_{30}Br_{12}O_2Ba$	8.32
Found	8.28

Zinc salt of linolenic hexabromide.—The zinc salt of linolenic hexabromide was prepared in the same way as the barium salt by mixing a hot solution of the potassium salt of linolenic hexabromide in methyl alcohol with a hot solution of zinc chloride in methyl alcohol (95 per cent). A white flocculent precipitate was formed. The mixture was then heated (reflux) until the methyl alcohol above the precipitate was completely clear, after which it was distilled to about one-sixth its volume and then allowed to cool. The precipitate was thrown into water, stirred, and filtered immediately. It was washed with methyl alcohol and ether, and then dried.

A melting point determination showed that, without crystallization, the salt decomposed sharply at 174° C.

The formula of the salt was checked by analysis in the same manner as was the formula of the barium salt. A weighed quantity of the salt was converted into zinc sulphate by treating it with sulphuric acid. The zinc sulphate was then heated and weighed as zinc oxide.

Analysis of zinc salt of linolenic hexabromide.

[0.6139 gram of the salt gave 0.0292 gram zinc oxide.]

	Zinc. Per cent.
Calculated for $C_{18}H_{32}Br_{12}O_4Zn$	4.14
Found	3.82

Lead salt of linolenic hexabromide.—Five grams of linolenic hexabromide were dissolved in about 500 cubic centimeters of boiling ethyl acetate. To the clear acid solution there was added with constant shaking a boiling, turbid, alcoholic solution of normal lead acetate, containing a slight excess of the calculated amount of the salt. A white flocculent precipitate was formed. The mixture was heated (reflux) until the solution above the precipitate was completely clear. It was then distilled to about one-third the volume, thrown into water, and the mixture stirred and filtered. The residue was washed thoroughly with alcohol and ether, and then dried.

When the melting point was determined the salt turned slightly brown at 160° C., and melted, with decomposition, at 190° C. to 195° C.

Analysis of lead salt of linolenic hexabromide.

[0.2536 gram of salt gave 0.0452 gram lead sulphate]

	Lead. Per cent.
Calculated for $C_{18}H_{32}Br_{12}O_4Pb$	12.04
Found	12.18

Solubility.—Qualitative solubility experiments on the free linolenic hexabromide and the salts that we prepared were made at room temperature (about 30° C. and designated as cold), and also in hot solvents. For low-boiling solvents like acetone, the solubility in hot solution was determined at the boiling temperature of the solvent. With high-boiling solvents, such as xylene, the temperature for solubility determination was about 90° C. In reporting the qualitative solubility data, the term "soluble" is used for solvents which dissolve the acid or the salts to the extent of about 1 to 4 per cent. For solubility below 1 per cent the terms "insoluble" or "slightly soluble"

are used. The term "very soluble" is used when about 5 per cent or more of the acid or the salts is dissolved.

TABLE 1.—Solubility of linolenic hexabromide and some of its salts in different solvents.

[I=insoluble; ss=slightly soluble; S=soluble; VS=very soluble.]

Solvent.	Hexabromide.		Potassium salt.		Barium salt.		Zinc salt.		Lead salt.	
	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.
Acetic acid, glacial.....	ss	S	ss	S	ss	S	ss	S	ss	VS
Acetone.....	I	ss	I	ss	ss	ss	ss	ss	I	I
Amyl alcohol.....	ss	VS	I	ss	I	I	I	I	I	I
Amyl nitrate.....	ss	S	I	I	I	ss	I	I	I	I
Benzaldehyde.....	ss	VS	ss	VS	ss	VS	ss	VS	ss	VS
Benzene.....	ss	S	I	I	I	I	ss	ss	I	I
Benzyl alcohol.....	ss	VS	I	ss	I	S	I	S	I	S
Chloroform.....	I	ss	I	I	I	I	I	ss	I	I
Carbon tetrachloride.....	I	ss	I	I	ss	ss	I	ss	I	I
Ether.....	ss	ss	I	I	I	I	I	ss	I	I
Ethyl alcohol.....	ss	ss	ss	ss	I	ss	I	ss	ss	ss
Ethyl acetate.....	ss	S	I	ss	I	ss	I	ss	ss	ss
Ethyl benzoate.....	ss	VS	I	ss	I	I	I	ss	I	ss
Ethyl bromide.....	ss	ss	I	I	ss	ss	ss	ss	ss	ss
Ethylene bromide.....	ss	VS	ss	ss	ss	ss	ss	ss	ss	ss
Isopropyl alcohol.....	ss	ss	ss	ss	I	I	I	I	I	I
Isobutyl alcohol.....	ss	S	ss	ss	ss	ss	ss	ss	ss	ss
Ligroin.....	I	I	I	I	I	I	I	I	I	I
Methyl alcohol.....	ss	ss	ss	ss	ss	ss	ss	ss	ss	ss
Methyl salicylate.....	ss	VS	I	ss	I	I	I	ss	ss	ss
Nitro benzene.....	I	VS	I	I	I	I	I	S	I	S
Propyl alcohol (n).....	ss	S	ss	S	ss	ss	ss	ss	I	ss
Petroleum ether.....	I	I	I	I	I	I	I	I	I	I
Pyridine.....	VS	VS	I	I	I	ss	ss	VS	ss	ss
Toluene.....	ss	S	I	I	I	I	I	I	I	I
Terpinol.....	ss	VS	I	I	I	ss	I	ss	I	ss
Xylene.....	ss	VS	I	I	I	I	I	I	I	I
Water.....	I	I	I	I	I	I	I	I	I	I

As shown by the solubility data given in Table 1, linolenic hexabromide and the salts prepared from it are not very soluble in the ordinary organic solvents. Experiments showed that about 10 grams of the acid will dissolve in 200 cubic centimeters of benzyl alcohol at 100° C. Five grams of the acid will dissolve in 500 cubic centimeters of warm isobutyl alcohol, and 21 grams of acid will dissolve in 400 cubic centimeters of warm xylene.

Although linolenic hexabromide is somewhat soluble in various solvents, salts of the acid are mostly insoluble or only slightly soluble. All of them, however, are soluble in hot benzaldehyde and glacial acetic acid. The barium salt is soluble in hot benzyl alcohol; the zinc salt dissolves in hot benzyl alcohol, nitro ben-

zene, and pyridine; and the lead salt is soluble in hot benzyl alcohol and nitro benzene. Hot normal propyl alcohol dissolves the potassium salt.

Melting point.—A determination of the melting point of the salts showed that they all decompose when heated to a sufficiently high temperature. This is not surprising since, according to the literature,⁹ various salts of long-chain aliphatic acids do not give a sharp melting point.

Several salts of acids such as myristic, palmitic, daturic, and stearic have been prepared by other investigators, but the melting-point data¹⁰ of these salts are not recorded in the usual reference books.

Of the various salts that we prepared the zinc salt seemed to give the best melting point, although it melted sharply with decomposition.

In this connection it may be noted that, of the various salts prepared from linolenic and linolic acids, the zinc salt¹¹ appears to be the most stable.

SUMMARY

A considerable quantity of linolenic hexabromide (melting point, 179.5° C. to 180.5° C.) was prepared.

The lead salt of linolenic hexabromide was prepared by treating a solution of the free acid with an alcoholic solution of lead acetate.

The potassium salt of linolenic hexabromide was prepared by neutralizing the free acid, dissolved in an organic solvent, with an alcoholic solution of potassium hydroxide.

From the potassium salt of linolenic hexabromide, the barium and zinc salts were prepared.

The solubility of linolenic hexabromide and of the potassium, barium, zinc, and lead salts of this acid was determined for various solvents. The melting point of these compounds was also determined.

⁹ Lewkowitsch, J., *Chemical Technology and Analysis of Oils, Fats, and Waxes* 1 (1921) 156, 157, 160, 163, 172, 175, 191, 192, 200, 204; *Beilstein's Handbuch der organischen Chemie, Vierte Auflage*, 2 (1920) 361, 369, 372, 395, 396, 473; Caspari, C. E., *Am. Chem. Journ.* 27 (1902) 307, 310.

¹⁰ Lewkowitsch, J., *Chemical Technology and Analysis of Oils, Fats, and Waxes* 1 (1921) 160, 163, 165, 168, 169, 191; *Beilstein's Handbuch der organischen Chemie, Vierte Auflage*, 2 (1920) 365, 372, 379, 387, 465, 496.

¹¹ Lewkowitsch, J., *Chemical Technology and Analysis of Oils, Fats, and Waxes* 1 (1921) 213; Reformatzky, A., *Journ. für Prak. Chem.* 41 (1890) 537.