Preparation of Methyl Linoleate Hydroperoxide[1]

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A SIMPLE batch procedure for the preparation of methyl linoleate hydroperoxide was suggested by previous countercurrent distribution studies of oxidized methyl linoleate (1) and methyl oleate (2). Calculation from the measured partition coefficients of methyl lineoleate (K=5.5) and of methyl linoleate hydroperoxide (K=0.57) for the system pentane-hexane and 80% ethanol indicated that effective separations could be obtained with a limited number of contacting stages. Since extracts were eventually to be combined, a further reduction in number of operations was visualized over that required for the equivalent Craig operation.

The present paper describes a procedure which yields methyl linoleate hydroperoxide of reasonably high purity and has the advantage of requiring only simple and universally available equipment.[3] Variations and adaptations which will increase the purity and yield of product or will facilitate the mechanics of the process will undoubtedly suggest themselves to the reader.

Experimental Procedure

Two kilograms of the safflower oil methyl esters was placed in an open battery jar and irradiated from the top with ultraviolet light from a Quartz Hanovia Mercury Arc lamp at a temperature of 37° C. for approximately 16 hours. Meanwhile the oil was vigorously stirred, and oxygen was bubbled into the oil through an immersed filter disc. When the oil reached the desired peroxide value of 1,000 to 1,600, it was diluted to 10 liters with purified hexane-pentane. It was then extracted in a countercurrent fashion with four successive equal volumes of 80% ethanol in three contacting stages consisting of three 5-gal. glass bottles. They were placed at three different levels such that the alcoholic hypophases could be siphoned from one stage to the next, and finally from the last stage into collection vessels. The first bottle contained diluted oxidized ester; the second and third bottles each contained 10 liters of pentane-hexane which had been previously equilibrated by shaking with 80% ethanol. The countercurrent procedure then consisted of introducing 10 liters of 80% ethanol, previously equilibrated with pentane-hexane, into the first bottle (No. 0), of mixing the layers with an air-driven stirrer, and of allowing the layers to separate. After siphoning the alcoholic hypophase, consisting primarily of oxidized esters, into the next bottle (No. 1), the operations of mixing, settling, and siphoning were repeated until the hypophase had been passed into and through the third bottle (No. 2). The first alcoholic phase collected was designated as A. Subsequent collections of alcoholic hypophases, passed through the three contacting stages, were designated as B, C, and D. Hydroperoxides were recovered by diluting the 80% alcohol hypophases with water to 50% concentration whereupon a thin layer of hyperphase separated, which was composed of hydroperoxides dissolved in pentane-hexane. After this layer was washed with water to remove the dissolved alcohol, it was taken to dryness at room temperature with the aid of vacuum and a stream of prepurified nitrogen.

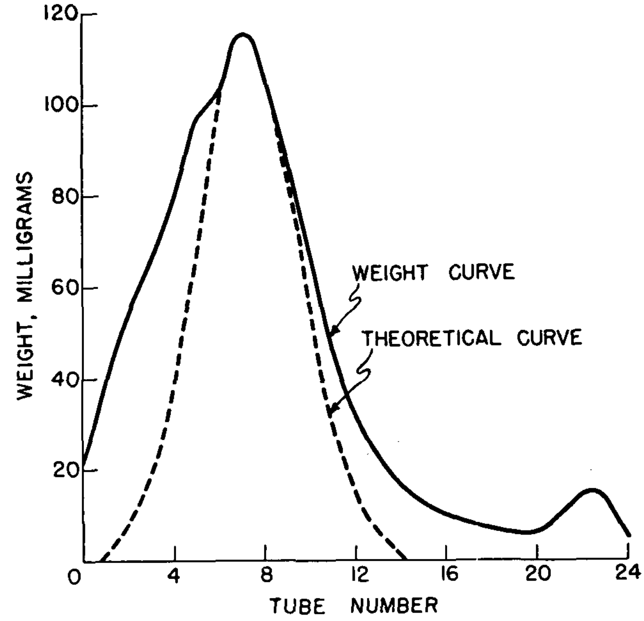

FIG. 1. An analytical countercurrent distribution of the methyl linoleate hydroperoxide preparation.

Example of Preparation. With the use of the procedure described, three batches, or a total of 700 grams of linoleate hydroperoxide, were prepared over a period of 6 days. In order to eliminate secondary oxidation products, collection A of each batch was discarded. A typical run is recorded in Table I.

It is apparent that removal of hydroperoxides from the hexane layers was effective since the peroxide values of the esters dropped from 1,594 to 181. In this experiment a 63% yield of hydroperoxides was recovered. However when the original oxidation was car-

TABLE I

Typical Autoxidation and Preparation of Methyl Linoleate Hydroperoxide

Stage or collection no.	Peroxide value	Refractive index	Weight of hydroperoxide
	me/kg.	$n^{31°}_{D}$	*grams*
0	181	....	....
1	160	....	....
2	132	....	....
A	....	....	....
B	4,245	1.4797	162.0
C	4,458	1.4805	130.2
D	4,380	1.4783	60.0

Peroxide value of autoxidation mixture: 1,594.
Theoretical yield: 560 g.
Actual yield: 352 g.

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[1] Presented at the fall meeting of American Oil Chemists' Society in Chicago, Ill., Oct. 8-10, 1951.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Report of a study made under the Research and Marketing Act of 1946.

[3] Subsequent to the preparation of this manuscript the annual report of 1949-50 of the Hormel Institute, University of Minnesota Press, Minneapolis, Minn., has come to our attention. After oxidation of 100 g. of pure methyl linoleate the linoleate hydroperoxide has been isolated in high purity and high yield by countercurrent extraction procedures.

ried only to a peroxide value of 1,185, a yield as high as 96% has been obtained.

In order to test the purity of hydroperoxides prepared by this procedure a sample of the 700-gram preparation was subjected to countercurrent distribution. The results given in Figure 1 show that this preparation contained 4% of unoxidized ester (Tubes 20-24). The non-Gaussian shape of the left side of the hydroperoxide peak reveals the presence of a small amount of more highly oxidized esters.

Notes and Discussion

Safflower oil constitutes a good starting material for the preparation of linoleate hydroperoxide. The oil used in this work was over 80% linoleic acid; the remainder was made up of oleic acid and saturates. Since the rate of oxidation of oleic acid is $\frac{1}{16}$ to $\frac{1}{12}$ that of linoleic acid (3, 5) and since it is present in an amount only $\frac{1}{5}$ that of linoleic acid, the contamination of linoleate hydroperoxide with oleate hydroperoxide is indeed small.

Previous work has shown that, if autoxidations reach a peroxide level higher than 1,000, appreciable amounts of secondary oxidation products are formed which would contaminate the hydroperoxide fraction if the first extract were not discarded. A high level of oxidation is desirable to obtain the maximum yield from a given weight of ester. However low levels of oxidation are required for purity and nearly quantitative recovery of hydroperoxides.

Dilution of the autoxidation mixture with pentane-hexane is a necessary step prior to extraction with 80% ethanol. Whereas the partition coefficient for linoleate hydroperoxide is 0.57 in dilute solution for pentane-hexane and 80% ethanol, its partition coefficient was greater than 2 in an equal volume mixture of pentane-hexane and ester. It is apparent therefore that a high concentration of methyl ester greatly alters the solubility properties of the hyperphase and hence the partition coefficient of methyl linoleate hydroperoxide. In fact, dilution greater than 1 part ester to 3 parts of pentane-hexane was found necessary to drop the partition coefficient below 1.

TABLE II

Calculation of Separation for Methyl Linoleate and Methyl Linoleate Hydroperoxide

Tube no.	Terms of binomial expansion	Fraction of linoleate hydroperoxide (k=1/.58)	Fraction of linoleate (k=1/5.2)
0	$\frac{1}{(k+1)^6}$	0.00	0.35
1	$\frac{6k}{(k+1)^6}$	0.03	0.40
2	$\frac{15k^2}{(k+1)^6}$	0.11	0.19
3	$\frac{20k^3}{(k+1)^6}$	0.25	0.05
4	$\frac{15k^4}{(k+1)^6}$	0.33	0.007
5	$\frac{6k^5}{(k+1)^6}$	0.22	0.0005
6	$\frac{k^6}{(k+1)^6}$	0.06	....

$$\text{Percent purity} = 100 - \left(\frac{.0575}{.92} \times 100\right) = 94.$$

Improved separations of unoxidized ester and hydroperoxides will be obtained if more contacting stages are used. From inspection of the nomograph describing the countercurrent separation of binary systems, it is apparent that the equivalent of a 5 to 10-plate countercurrent distribution is required to yield hydroperoxides of 90% purity (4). A more accurate prediction of purity can be made, of course, by application of the binomial equation

$$\left[\frac{1}{k+1} + \frac{k}{k+1}\right]^n$$

where n is the number of transfers or plates applied and k is the reciprocal of the partition coefficient (6).

Table II gives the fraction of material calculated to be present in each tube of a six-transfer countercurrent distribution using a partition coefficient of 0.58 for the hydroperoxide ester and 5.2 for the unoxidized ester. This calculation is applicable to the procedure described if the distribution is divided between tubes 2 and 3 and tubes 3 to 6 are combined. According to this calculation, the purity of the hydroperoxide fraction would be 94% for the separation of an equal mixture of hydroperoxide and unoxidized ester and correspondingly less for lower proportions of hydroperoxide. Calculations of this type provided the theoretical basis for the separation procedure and the decision to use three contacting stages and four volumes of hypophase.

Advantage was taken of the variation of partition coefficient for the hydroperoxide with solvent composition for recovery of the hydroperoxides. It was found that the partition coefficient of linoleate hydroperoxide between pentane-hexane and methanol varied between 0.57 for 80% ethanol to large values for 50% ethanol, or from greater solubility in the alcohol layer to a greater solubility in the hexane layer. Thus liquid-liquid extraction of the hydroperoxides was not required; merely increasing the water content of the alcohol caused the separation of peroxides and hydrocarbon solvent.

A 400-gram batch of the hydroperoxide prepared as described herein has been tested in redox formulae for the cold polymerization of rubber. The evaluation of this and methyl oleate hydroperoxide will be the subject of a future communication.

Summary

A simple procedure for the preparation of methyl linoleate hydroperoxide was suggested by previous countercurrent distribution studies of oxidized methyl linoleate. Calculations from the measured partition coefficients of methyl linoleate and methyl linoleate hydroperoxide indicated that effective separations could be achieved in an operation which required only three contacting stages.

A 2-liter batch of safflower oil methyl esters was oxidized with ultraviolet catalysis to approximately 0.2 mole oxygen per mole ester. At these low levels little of the secondary oxidation products are formed. Countercurrent extraction of methyl linoleate hydroperoxide from the unoxidized methyl linoleate was achieved in three 5-gallon glass bottles. The first bottle contained the oxidized ester diluted with pentane-hexane in a ratio of 1 to 4. The following two bottles contained 10 liters each of pentane-hexane. Four 10-liter volumes of 80% ethanol were successively stirred with each of the pentane-hexane hy-

perphases in countercurrent procedure. The first extract containing secondary oxidation products was discarded; the second, third, and fourth extracts, when collected, constituted the hydroperoxide fraction. When the alcohol extract was diluted to 50% with water, the dissolved hydroperoxides and hexane separated.

After evaporation of the pentane-hexane the resulting hydroperoxide was checked for purity by distribution in the Craig apparatus. Unoxidized methyl esters were found to be present to the extent of 4% along with a small percentage of secondary oxidation products.

Acknowledgment

The authors are indebted to C. R. Scholfield, J. A. Cannon, Catherine R. Lancaster, and E. P. Jones for assistance in various phases of the preparation.

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ABSTRACTS . . . . Don Whyte, Editor

NOTE: We have been fortunate in being able to add an abstractor, Sinitiro Kawamura, for the Japanese journals. His abstracts will cover all our fields of interest. In order to give Mr. Kawamura credit for his work we will insert his name in front of each series of abstracts for which he is responsible.

• Oils and Fats

R. A. Reiners, Abstractor

Variations in the composition of some linolenic-rich seed oils. T. P. Hilditch and Collaborators (Univ. Liverpool). *J. Sci. Food Agr.* 2, 543(1951). Candlenut oils seem prone to exhibit variations, usually of a minor but occasionally a major order, in their content of linolenic; definite but minor variations occur in oils from different fruits of the same tree. Rubber seed oils have, thus far, shown very little difference in composition. Linseed oils from seed grown in England or South Africa have proved satisfactory as regards a high content of linolenic acid. The few specimens of hemp seed oil studied in detail show considerable similarity in composition.

The alpha-naphtholphthalein (ANP) method for measuring fat hydrolysis. I. Application to butter. T. V. Armstrong and W. J. Harper (Ohio State Univ., Columbus). *J. Dairy Sci.* **35**, 59(1952). The water insoluble fatty acid content of butter may be measured to an accuracy of 100 mg. per 100 g. of fat using a modified *α-naphtholphthalein* test. The ANP method is not affected by the presence of butyric and lactic acids but does measure caproic and higher fatty acids. Results indicate close agreement with the WIA method of Hillig.

The structure of sterculic acid. J. R. Nunn (Nat. Chem. Res. Lab., Pretoria, S. Africa). *J. Chem. Soc.* **1952**, 313. Sterculic acid, the main constituent of the kernel oil of *Sterculia foetida* has been isolated in a pure state by means of its urea complex, and evidence is presented for its being ω-(2-n-octylcyclo-prop-1-enyl) octanoic acid. Sterculyl alcohol has been prepared.

Sulphur analysis of Canadian erucic acid oils. H. J. Lips (Nat. Res. Labs., Ottawa). *Can. J. Tech.* 30, 61(1952). Using an improved method of sulphur analysis it was shown that crude erucic oils contained less than 0.001% sulphur. Alkali refined and bleached oils had no detectable sulphur content.

Constitution of the lipid from stored Florida valencia orange juice. C. W. Huskins, L. J. Swift and M. K. Veldhuis (U. S. Citrus Products Station, U.S.D.A.). *Food Res.* **17**, 109(1952). Canned Valencia orange juice was stored for 2 years at about 75°F. During storage considerable breakdown occurred in the lipid fraction. The amount of conjugated acids increased while the non-conjugated acids decreased.

The oxidation of monoethenoid fatty acids and esters. Union of gaseous oxygen with ethyl, n-propyl and n-butyl oleate. A. J. Fevell and J. H. Skellon (Acton Tech. College, Acton, W. 3). *J. Chem. Soc.* **1952**, 59. Catalytic oxidation of ethyl, n-propyl and n-butyl oleate in the presence of uranium oleate at 120°, 85° and 55° showed that peroxide formation and subsequent decomposition are characteristic of autoxidations at the higher temperatures. Prolonged oxidation at 120° produces some dimerization together with the formation of reducing substances. The nature of the terminal alkyl group influences the course of the reaction, maximum peroxide formation decreasing progressively from ethyl to n-butyl. The oleic esters react more readily than the corresponding elaidic esters.

Azeo-extraction process overcomes fire hazards, fines in rendering. Anon. *Food Proc.* 15(3), 9(1952). A batch extractor is described in which wet meat scraps are extracted with trichloroethylene. Excellent extraction is obtained and no fines are produced.

A preliminary study of some factors affecting the hydraulic pressing of cottonseed. C. L. Carter (Univ. Tenn.). *Oil Mill Gaz.* **56**(8), 86(1952). Cottonseed meats were cooked at 220°F. at atmospheric pressure for one hour and cakes of about 0.75 in. thickness were formed at different pressing moisture contents using a Carver laboratory press. Under one set of pressing conditions, an increase in pressing temperatures from 130° to 230°F. resulted in a decrease in minimum residual oil from 5% to less than 4% (dry, oil-free basis). It was found that the shape and position of the curve of residual oil vs. moisture are appreciably altered by changes in pressing temperature, rate of application of pressure and hull content of the meats. It was also found that the effects on the residual oil vs. moisture relationship of pressing temperature, total pressure, rate of application of pressure and hull content of meats are not mutually independent.

Problems arising from the use of chemicals in food. Antioxidants. C. H. Lea (Univ. Cambridge). *Chem. Ind.* **1952**, 178. The effectiveness and toxicity of antioxidants used in fats are discussed.

A continuous method of extraction for high proportions of unsaponifiable matter. P. Sherman and J. E. Dillistone (Gestelner Ltd., London N. 17). *Chem. Ind.* **1952**, 130. A continuous method for extracting the unsaponifiable matter with ether from saponified oils is described.

Fatty acids of the lipids from freshly canned Florida valencia orange juice. L. J. Swift (U. S. Citrus Prod. Station, Winter Haven, Florida). *Food Res.* **17**, 8(1952). The methyl esters of the fatty acids from freshly canned orange juice contain 1.3% conjugated diene, 8.8% linolenate, 32.5% linoleate, 18.1% oleate, 10.4% palmitoleate, 18.8% palmitate and 1.7% stearate. Possibly oxidative rancidity is the origin of flavor deterioration.

The antioxidant properties of natural spices. J. R. Chipault, G. R. Mizuno, J. M. Hawkins and W. O. Lundberg (Hormel Inst., Austin, Minn.). *Food Res.* **17**, 46(1952). The antioxidant properties of 32 spices have been determined and all except one sample of ginger exhibited an antioxidant effect on prime steam lard when tested by the A.O.M. at 98.6°. Rosemary and sage exhibited pronounced antioxidant effects. Citric acid exerts a synergistic effect with some spice fractions. The predominant antioxidants in sage and rosemary are soluble in aqueous alkali. These fractions did not contain the characteristic odor components of these spices.

Glyceride oils and the Southwest. K. S. Markley (So. Reg. Res. Lab., New Orleans, La.). *Chemurgic Digest* **11**(3), 4 (1952). A review.

Mixed monolayers. Molecular interaction in the mixed monolayers of fatty acids. T. Isemura and K. Hamaguchi. *Mem. Inst. Sci. and Ind. Research, Osaka Univ.* **8**, 131-9(1951). Bi-