

WEIGHT CHANGE OF LINOLEIC AND LINOLENIC ACIDS AND THEIR DERIVATIVES IN THE COURSE OF AUTOXIDATION

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Although there is a vast accumulation of studies on the autoxidation of linoleic and linolenic acids and their derivatives, little literature has appeared on the subject of the weight change of these compounds in a long course of the autoxidation. The present paper describes the results of our experiments which were performed with the purpose of investigating the weight change of these compounds in a long course of the autoxidation. The derivatives of linoleic and linolenic acids used in these experiments are their methyl and ethyl esters, the alcohols corresponding to the respective acids and their acetates, and the methyl alkyl ketones prepared from the respective acids.

Linoleic and Linolenic Acids and their Derivatives

Linoleic acid was obtained by saponification of methyl linoleate. For the preparation of the latter, tetrabromostearic acid obtained by bromination of corn oil fatty acids was debrominated with zinc, sulfuric acid and methanol. Ethyl linoleate was obtained by debromination of tetrabromostearic acid with zinc, sulfuric acid and ethanol. Linoleyl alcohol was prepared by reduction of methyl linoleate with ethanol and metallic sodium. Methyl heptadecadienyl ketone (10,13-nonadecadien-2-one) was prepared in the following way: Linoleic acid was first converted to

TABLE 1

	α_D^{25}	n_D^{25}	B.P. (°C/mm Hg)	Sap. value	Iodine value (Wijs)
Linoleic acid	0.8979	1.4681	190/1	199.8(200.1)	180.5(181.0)
Methyl linoleate	0.8805	1.4605	182-183/4	190.7(190.5)	171.6(172.4)
Ethyl linoleate	0.8764	1.4585	186/1-1.5	181.7(181.7)	164.2(164.6)
Linoleyl alcohol	0.8561	1.4690	199-201/12	—	189.5(190.5)
Linoleyl acetate	0.8785	1.4600	—	181.4(181.7)	161.7(164.6)
10, 13-Nonadecadien-2-one	0.8540	1.4625	175-176/3	—	179.9(182.3)
Linolenic acid	0.9119	1.4785	211-212/4	199.0(201.5)	271.5(273.5)
Methyl linolenate	0.8949	1.4690	182/2.5-3	192.0(191.8)	258.0(260.4)
Ethyl linolenate	0.8877	1.4672	179/3	183.2(183.1)	247.5(248.5)
Linolenyl alcohol	0.8679	1.4784	181/2.5	—	284.8(288.0)
Linolenyl acetate	0.8927	1.4678	—	183.9(183.1)	240.5(248.5)
10, 13, 16-Nonadecatrien-2-one	0.8659	1.4736	175-178/2	—	269.7(275.5)

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acid chloride which was then condensed with ethyl acetoacetate. The condensation product was decomposed with an aqueous alcoholic solution of sodium hydroxide, and methyl heptadecadienyl ketone was separated from the decomposition product and purified.

The corresponding compounds for linolenic acids were obtained in the same way starting from hexabromostearic acid which was prepared from linseed oil fatty acids.

Some properties of the compounds obtained above are shown in Table 1. The figures in the parentheses denote the values calculated for the respective compounds.

Experimental Results and Discussion

Each sample described above was taken in an amount of 100 ± 1 mg and spread on a 80 mm \times 50 mm glass plate with a fine glass rod. The glass plate together with the glass rod was placed on another glass plate which served to catch a small portion of the sample running down the edge of the upper glass plate as occurred in many cases in these experiments. Each set of glass plates was kept horizontally in a shallow box covered with a colorless transparent sheet of cellophane. In a series of experiments, the box was placed indoor without exposure to sun light during the entire course of the experiments. In another series of experiments, the box was placed outdoor in the day time, being exposed to sun light from 10 A.M. to 5 P.M., and placed indoor only in the night time. However, on the 6th, 7th, 12th, 13th, 20th-31st, 36th and 37th days in the experiments, the box was placed indoor throughout the whole day on account of rain fall or for some other reason. Each set of glass plates was weighed at the same hour every day, and the weight change of the sample was determined. The indoor and outdoor temperatures in the day time during these experiments were 32-22°C and 48-30°C, respectively. The results of the experiments are shown in Figs. 1-4. The curves for the respective compounds were denoted by the numbers: (1) acid; (2) methyl ester; (3) ethyl ester; (4) alcohol; (5) acetate; (6) methyl ketone.

The curves in Fig. 1, showing the weight increase of the compounds of linoleic series in the indoor experiments, do not always run parallel, but intersect with

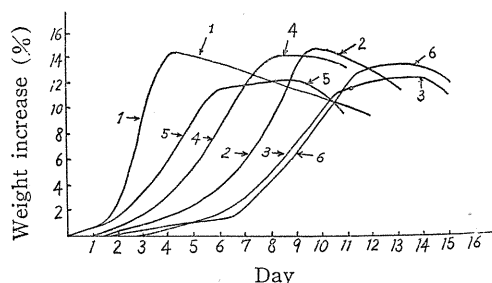


FIG. 1. Indoor experiments with the compounds of linoleic series.

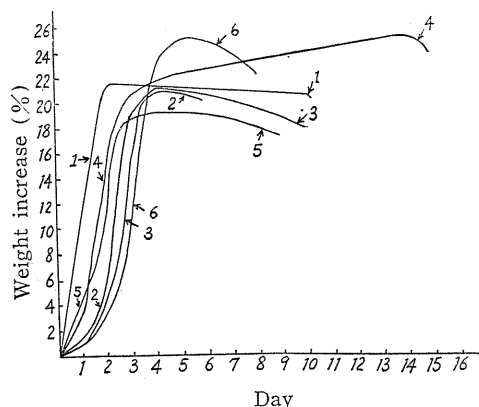


FIG. 2. Indoor experiments with the compounds of linolenic series.

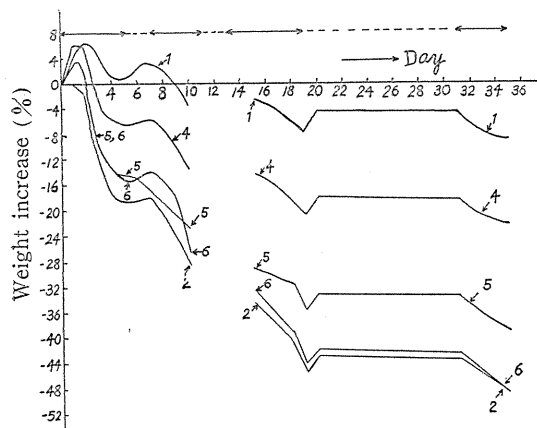


FIG. 3. Outdoor experiments with the compounds of linoleic series.

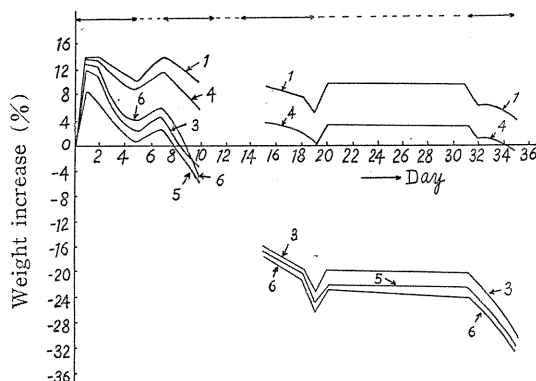
←→ Outdoor in the day time.

>.....< Indoor throughout the day.

FIG. 4. Outdoor experiments with the compounds of linolenic series.

←→ Outdoor in the day time.

>.....< Indoor throughout the day.



one another. For instance, the acetate shows a larger weight increase than the alcohol and methyl ester at first, but the rate of weight increase of the acetate after 6 days becomes so small that the weight increase of the acetate becomes smaller than that of the alcohol after 7 days, and smaller than that of the methyl ester after 9 days. However, comparing the rates of weight increase of the respective compounds of linoleic series at the stages when the weight increases are 2-10%, they are in the following order: acid > acetate > alcohol > methyl ester > ethyl ester > methyl ketone. The maximum weight increases for the compounds of linoleic series are largest for the methyl ester, 14.5% after 10 days, and smallest for the acetate, 12.1% after 8 days. As is seen from Fig. 2, the rates of weight increase for the compounds of linolenic series are in the similar order as those for the compounds of linoleic series; acid > acetate, alcohol > methyl ester > ethyl ester > methyl ketone. The maximum weight increases are largest for the alcohol, 25% after 14 days, and the methyl ketone, 25% after 5 days, and smallest for the acetate, 19.3% after 4 days. After passing the maximum weight increase, each compound shows a decrease in weight with the lapse of time. The weight increases of each compound after 20 and 40 days are shown in Table 2. Comparing the weight increases of the compounds of linoleic series and of linolenic series after 40 days, the former are considerably smaller than the latter.

Referring to the outdoor experiments, it is seen from Figs. 3 and 4 that the

TABLE 2

	Weight increase (%)	
	After 20 days	After 40 days
Linoleic acid	9.6	6.8
Methyl linoleate	5.9	—
Ethyl linoleate	8.2	3.2
Linoleyl alcohol	9.7	5.5
Linoleyl acetate	6.5	2.3
10, 13-Nonadecadien-2-one	9.3	3.3
Linolenic acid	20.4	17.4
Methyl linolenate	16.1	11.0
Ethyl linolenate	15.3	11.1
Linolenyl alcohol	23.2	20.8
Linolenyl acetate	15.0	12.0
10, 13, 16-Nonadecatrien-2-one	16.4	—

weight increases of the compounds of linoleic and linolenic series in the first day are larger than the corresponding values in the indoor experiments, and attain their maximum after one or two days. However, the maximum weight increase in the outdoor experiments is smaller than in the indoor experiments, the largest values being 6.7% for the acid among the compounds of linoleic series and 14.0% for the acid among the compounds of linolenic series. Since methyl linoleate showed scarcely any weight increase when it was weighed after one day, the weight of methyl linoleate must have passed through the maximum and begun to decrease within the first day. After 2-3 days all compounds became to decrease their weights so that they become sooner or later smaller than their original weights. The time required to attain at this stage of autoxidation is 10 days for the acid, 2 days for the methyl ester, and 3 days for the alcohol, acetate and methyl ketone among the compounds of linoleic series, and 9 days for the ethyl ester, 34 days for the alcohol, and 9 days for the acetate and methyl ketone among the compounds of linolenic series. The weight decrease after 35 days expressed on the basis of the original weight is nearly 50% for the methyl ester and methyl ketone, 9.1% for the acid and 22.3% for the alcohol among the compounds of linoleic series, and nearly 32% for the ethyl ester, acetate and methyl ketone and 1.3% for the alcohol among the compounds of linolenic series. Only linolenic acid still retains a weight increase of 3.7% after 35 days. It is of importance that when the samples under the outdoor experiments were placed indoor throughout the day on account of rain fall or for some other reason, they showed, in most cases, a slight increase or scarcely any change in weight. Thus the samples showed scarcely any change in weight during the 20th-31st days when they were placed indoor throughout the day, while they showed a decrease in weight on subsequent exposure to sun light. Comparing the results of the indoor and outdoor experiments, it is found that exposure to sun light has a great influence upon the weight change of each sample. It should be noted that the weight change of each sample in the course of autoxidation occurs in two directions; the absorption of oxygen results in an increase in weight, while the formation of volatile substances causes a decrease in weight. Although the exposure to sun light accelerates the absorption of oxygen, it appears also to accelerate the decomposition to a much greater degree. Consequently, the maximum weight increase obtained in the out-

door experiments will be smaller than that obtained in the indoor experiments, and the weight decrease in the outdoor experiments will proceed at a greater rate to a greater extent.

Another similar experiments was performed with a sample of ethyl linoleate of saponification value 182.1 and iodine value 164.0. In this experiment, 0.1072 g of sample was spread on a glass plate with an area of 51 mm×76 mm. The weight of the sample was determined immediately before placing it outdoor in the sun and immediately after placing it indoor. The temperatures in the day time were 28-10°C indoor and 36-17°C outdoor. The results are shown in Fig. 5. At the early stage of these experiments, the weight of the sample showed a greater increase when the sample was placed outdoor.

After passing the stage of maximum weight increase, however, the weight of the sample showed always a decrease in the outdoor period while it showed a certain increase or a very slight decrease, if any, in the indoor period.

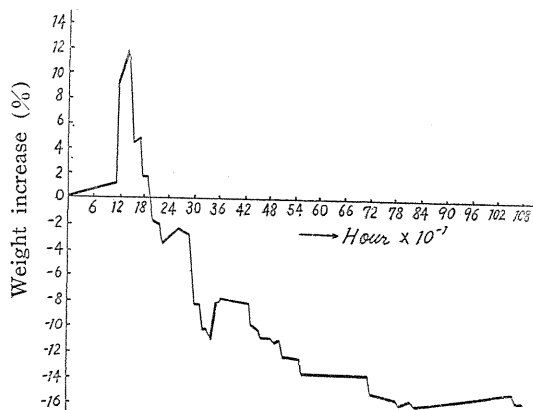


FIG. 5. Ethyl linoleate.
Thick line for indoor period; thin line for outdoor period.

Summary

Linoleic acid and its methyl and ethyl esters, linoleyl alcohol and its acetate, methyl heptadecadienyl ketone (10,13-nonadecadien-2-one) and the corresponding compounds of linolenic series were prepared. Each sample was spread on a glass plate so as to form a thin layer. In a series of experiments, the samples were placed indoor all the time without exposure to sun light. In another series of experiments, the samples were placed outdoor and exposed to sun light in the day time. Weight change of each sample in the course of these experiments was determined with the following results.

1. In the indoor experiments, the compounds of linoleic series showed smaller rates of weight increase and smaller maximum weight increases than the compounds of linolenic series, the maximum weight increases being 14.5-12.1% for the compounds of linoleic series and 25.0-19.3% for the compounds of linolenic series. Comparing the rates of weight increase at the stages when the weight increases are 2-10%, they were in the order: acid > acetate > alcohol > methyl ester > ethyl ester > methyl ketone in the case of the compounds of linoleic series. A similar order was found also for the compounds of linolenic series.

2. In the outdoor experiments, the weight increases in the first day were greater than in the indoor experiments. However, the maximum weight increases in the outdoor experiments were smaller than those obtained in the indoor experiments, the largest maximum weight increase in the outdoor experiments being 6.7% for

the acid among the compounds of linoleic series and 14.0% for the acid among the compounds of linolenic series. After 2-3 days, all samples became to decrease their maximum weight. The extents of weight decrease were different for each sample. After 35 days, methyl linoleate and methyl heptadecadienyl ketone showed a weight decrease of nearly 50% on the basis of the original weight.

3. The exposure to sun light has a great effect upon the weight change of the sample. Although it accelerates the absorption of oxygen, it seems to accelerate the decomposition in a much greater degree.