the removal of nickel by roasting the tails from the copper flotation separation free from sulfur, reducing with charcoal, roasting with niter cake, and extracting with water, the nickel to be recovered electrolytically or by precipitation with lime after the removal of iron by means of calcium carbonate. The complexity of this treatment would be an important factor in determining whether the process could be used.

The Alaska ore might be treated with nitric acid, heated to remove most of the oxides of nitrogen, and the nickel extracted with water, the nitric acid being recovered by water absorption. The quantity of nitric acid recovered on large runs would largely determine the availability of this treatment.

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BUREAU OF MINES
GOLDEN, COLORADO

THE MODIFICATION OF THE COMPOSITION OF VEGETABLE OILS, WITH SPECIAL REFERENCE TO INCREASING UNSATURATION¹

By HORACE L. WHITE

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INTRODUCTION

The possibility of the modification of the constants of fats and oils of animal and vegetable origin, but more particularly because of the abundance of those of vegetable origin, is a matter of great economic importance. If a vegetable oil could be dehydrogenated, that is, if its fatty acids could be modified so as to contain more unsaturated linkages, there is the possibility of greatly increasing its value in the paint industry. A brief consideration of the respective iodine values of linseed and soy bean oils will indicate this more clearly. Linseed oil with an iodine number around 180 is one of the best examples of a drying oil, while soy bean oil with an iodine number around 126 is classified as a semidrying oil. Nemzek² has pointed out the limited uses of soy bean oil in paints and he is authority for the statement that in 1916 there were imported into the United States 98,171,275 lbs. of soy bean oil. If some of the constants of this oil could be modified, its value, particularly in the paint industry, would be greatly increased.

Many observers have pointed out the modifications of oils that seem to take place spontaneously, but which in reality are caused by the influence of light, temperature, bacterial and enzyme action, and inorganic

catalysts. This investigation is devoted to a study of the biochemical reactions induced by the processes of germination, and of enzyme and bacterial action on the degree of unsaturation and the extent of hydrolysis of linseed and soy bean oils. In addition, attention has been directed to the action of light, heat, and the presence of inorganic catalysts on the same constants.

EXPERIMENTAL

From reference in the literature it is evident that but few attempts have been made to dehydrogenate oils. The use of nickel³ in the absence of hydrogen has been suggested. In the field of biochemistry the observations of Hartley and others^{4,7} on the desaturating power of the pig's liver, as shown in the fatty acids obtained from the liver, is of great interest. The results^{8,9} obtained in a study of the effects of germination of various oil-bearing seeds seems to indicate a saturation of unsaturated fatty acids during the process, yet the behavior of the castor bean¹⁰ in this particular shows some variation.

The question was raised as to whether there might not be conditions of metabolism during germination and growth of soy beans (*Glycine hispida*) of such a nature as to increase the degree of unsaturation of the fatty acids. The prevailing idea in the arrangement of the conditions of growth was to make them abnormal in order to develop any latent powers of the plant. This was accomplished by growing the plants in a greenhouse in diffuse light and at lower temperatures than ordinarily employed.

Other samples were sprouted in darkness and some were grown in the sunlight at ordinary temperatures. The germination was carried through three stages: Stage I, in which the sprout was $\frac{1}{2}$ cm. long; Stage II, in which the plants were from 4 to 6 cm. in height with cotyledons standing at right angles to the hypocotyls; and Stage III, in which the plants were from 6 to 12 cm. long and the first set of leaves had formed.

TABLE I—CONSTANTS OF THE OIL OF SOY BEANS GERMINATED AND GROWN IN DIFFUSE LIGHT

	Resting Seed Control	Stage I Germinated Sprout $\frac{1}{2}$ Cm. Long	Stage II Growth Height 4 to 6 Cm.	Stage III Growth Height 6 to 12 Cm.
Wt. 100 beans, grams.....	15.6800	37.0520	71.1560	
Moisture, per cent.....	4.80	61.90	86.60	
Ether extract (moisture-free), per cent.....	18.44	18.51	13.31	10.11
Color of oil.....	Amber	Green	Red Green ¹	Greenish
Specific gravity.....	0.9234	0.9215	0.9272	
Acid number.....	1.0	30.2	2.6	
Iodine number.....	131.1	122.6	133.1	121.10
	129.9	...	133.0	120.95
Iodine number.....	133.9	125.5	136.2	117.7
Fatty acids.....	135.6	125.2	133.6	116.1
Reichert-Meissl number.....	0.30	...	1.05	
Unsaponifiable matter, per cent.....	1.21	1.01	1.14	2.75
Sterols, per cent.....	0.27	0.43	0.46	0.86

¹ Red by reflected light, green by transmitted light.

The whole plant was used for analysis. Each plant was washed free from sand, dried at 37° C. in an incubator, and the oil extracted by ethyl ether in the cold. After distilling off most of the ether, the oil was heated to 110° C. for 2 hrs., while a current of dry carbon dioxide was bubbled through it to remove traces of ether and water. The method of analysis and of purification of reagents used were those described by Holland.¹² Iodine numbers were deter-

¹ Abstract of a thesis submitted to the University of Wisconsin for the degree of doctor of philosophy in agricultural chemistry, 1917.

* Numbers refer to corresponding numbers in "Bibliography," p. 651.

mined by the Hanus method. Table I shows some of the constants of the oils.

The results given in Table I show that the iodine number of the ether extract of soy beans grown in diffuse light does not fall much below that obtained from the seed, and seem to indicate that while the oil is being used for the nourishment of the growing plant in diffuse light the processes of metabolism continue to supply fatty acids of practically the same degree of unsaturation, at least up to the formation of the first set of leaves. The drop in iodine number of fatty acids in Stage III indicates a rapid utilization of unsaturated acids, possibly for the formation of sugars.

For comparison, beans were planted in sand and grown in the light to Stages II and III. The results are shown in Table II.

TABLE II—CONSTANTS OF SOY BEAN OIL FROM BEANS GROWN UNDER VARYING CONDITIONS

DESCRIPTION	Ether Extract (Dry Basis) Per cent	Acid Number	Iodine Number	Iodine Number Fatty Acids
Resting seed.....	18.44	1.0	131.1	133.9
			129.9	135.6
Stage I—Germinated seed.....	18.51	29.8	122.6	125.2
				125.5
Stage II—Diffuse light.....	13.31	2.6	133.1	133.6
			133.0	136.2
Stage II—Sunlight.....	5.00	16.6	134.1	...
			133.7	...
Stage III—Diffuse light.....	10.11	12.5	121.10	116.1
			120.95	117.7
Stage III—Darkness.....	8.34	...	128.7	...
			130.1	...
Stage III—Sunlight.....	3.61	1.85	128.1	...
			130.5 ¹	...
			130.4	...

¹ Petroleum ether extract.

From the analytical results given in Table II, the conclusion is reached that the processes of germination and growth of soy beans up to the stage of the formation of the first set of true leaves do not greatly modify the degree of unsaturation of the oils in the ether extract. There is, moreover, no evidence of increasing unsaturation of the oil.

Working along the same general line, that of creating abnormal conditions, the effect of carbon dioxide on germination and iodine number of oil was studied. Carbon dioxide was bubbled through a mass of beans in distilled water, with chloral hydrate (0.1 g.) for a preservative, for varying lengths of time. The effect of carbon dioxide is shown in Table III.

TABLE III—EFFECT OF CARBON DIOXIDE ON GERMINATION AND IODINE NUMBER

TREATMENT	EXTENT OF GERMINATION	Iodine No. Ether Extract
Resting seed, control.		{ 129.9 131.1
Carbon dioxide for 1 hr. a day, 2 days.	Slight, seed coat intact	{ 128.0 129.0
Carbon dioxide for 1/2 hr. a day, 6 days.	Slight, seed coat intact	{ 118.1 121.8

It is evident that the exclusion of oxygen by carbon dioxide for a period of 6 days decreases the degree of unsaturation of the oil.

The possible stimulating effect of dilute solutions of manganous chloride which was noted by Brenchley¹⁵ as favoring germination and growth of starchy seeds was studied with soy beans, but with inconclusive results.

BACTERIAL AND ENZYME ACTION

From many samples of raw linseed oil there separates out on standing a heavy flocculent deposit which

is known to the trade as "foots." From the oil filter presses the same material is obtained as a dark colored semisolid material known as "filter press foots."

A sample of raw linseed oil, containing 40 per cent "foots" by volume, was used in a preliminary examination as to the nature of the bacterial contents of the foots, and the effects of their metabolism on some of the constants of linseed oil.

On shaking some of this oil in a mixture of sterile sand and water and plating out the resultant liquid on nutrient agar, a heavy growth of organisms, chiefly bacteria with some molds, was obtained. The bacterial colonies seemed to be of the same general form. A pure culture was obtained from one of the colonies and was used in a further study of the characteristics of the organisms which were similar to those of *B. subtilis*.

In order to determine whether the organisms in linseed oil "foots" had any relation to the acid number and iodine number of the oil, samples of raw linseed were inoculated with "foots" known to contain the organism described above. Four-ounce sterilized sample bottles were filled with oil, plugged with cotton, and a short cork inserted in the neck of the bottle above the cotton. Controls were prepared by heating at 10 lbs. pressure on each of three successive days. In some cases 10 per cent of water was added. The samples were analyzed after decantation and filtration through anhydrous sodium sulfate.

TABLE IV—OILS INOCULATED WITH BACTERIA AND KEPT AT 38° C.

TREATMENT OF SAMPLE	ACID No.			IODINE No.		
	At once	5 Mo.	18 Mo.	At once	5 Mo.	18 Mo.
Oil, not filtered.....	2.75	4.3	5.7	184.06	173.3	154.2
				184.43	173.5	...
Oil, filtered through paper....	2.9	5.6		...	170.6	153.9
					172.6	155.4
Oil, sterilized.....	3.0	6.0		...	172.2	149.5
					173.4	151.6
Oil + "foots".....	3.8	5.5		...	170.7	157.7
					172.5	158.6
Oil sterilized + "foots".....	3.7	5.4		...	171.4	157.6
					174.0	...
Oil + 10 per cent water....	7.2	6.5		...	169.3	157.0
					171.2	...
Oil sterilized + 10 per cent water, sterilized.....	3.3	4.1	6.4	184.49	171.8	153.7
				184.83	173.0	155.0
Oil sterilized + "foots" + 10 per cent water.....	8.6	7.6		...	174.6	164.4
					175.2	164.4

In all samples the acid number has doubled in 18 mo. The inoculation with organisms affects the acid number when water is present, but not otherwise. As already pointed out,^{16,19} the necessity for heating and clarifying oils to prevent rapid hydrolysis is further shown by the difference in the rate of change of acid number in 5 mo. between the unfiltered oil and the samples of filtered and of sterilized oil.

TABLE V—HYDROLYSIS OF OILS KEPT AT 37° C. 50 g. Oil Emulsified with 50 g. Water Containing 1 Per cent Gum Arabic. Kept at 37° C.

SAMPLE	ACID No.		DESCRIPTION OF OIL
	At Beginning	5 Wks.	
D 18	18.6	20.2	Acid-refined linseed oil
D 19	1.2	1.8	Alkali-refined linseed oil
D 20	3.0	6.7	Raw linseed oil
D 21	5.1	12.6	Acid-refined oil
D 22	5.9	6.8	Boiled linseed oil
D 23	9.1	11.9	Corn oil (old sample)
D 24	17.5	19.7	Cottonseed oil (old sample)
D 25	5.5	5.8	Castor oil (old sample)
D 26	1.8	5.9	Soy bean oil, imported
D 27	2.7	12.3	Soy bean oil, American No. 2

In order to observe the effect of naturally occurring impurities, such as bacteria and enzymes in the oils,

when mixed with water, emulsions of equal weights of oil and water with gum arabic were kept in full, stoppered bottles at 37° C. for 5 wks. The changes are shown in Table V.

The acid numbers of the untreated oils, as raw linseed oil and the soy bean oils, show an increase of from 100 to 600 per cent in 5 wks. These results emphasize the necessity of heating and filtering such oils before storage and use.

Extensive experiments were carried on, the details of which cannot be given here, to determine if there were any enzymes in flaxseed that could desaturate soy bean oil, as it is recognized that there is inherent in the flax plant the ability to synthesize an oil with a larger per cent of unsaturated acids than is found in soy bean oil. The results were negative in all experiments. Similar attempts were made with fresh pig's liver which has been shown⁶ to have the power of desaturating fatty acids to a marked degree. After incubation of oil and tissue for 42 days at 37° C. there was no increase in iodine number.

ACTION OF LIGHT, HEAT, AND CATALYSIS

The extent of the hydrolysis of oils by various agencies is a matter of great economic importance in certain industries, and methods for its control are being given consideration in industrial laboratories. The agencies causing hydrolysis are discussed in detail by workers in industrial and biological chemistry.^{16,19,2,17,18} Neuberg²² has shown, also, that triolein when emulsified with a little sodium oleate is easily hydrolyzed by the action of sunlight if a uranyl salt is present. It was decided to repeat some of his work, using salts of other metals in addition to uranyl acetate, and replacing sodium oleate by a vegetable emulsifier. Two sets of samples of emulsified oil were prepared, using Indian gum as an emulsifier, and adding 0.1 g. of the catalyst in each case. One set of samples were kept at 37° C. in absence of light for 100 days, while the second set of samples was kept in a greenhouse for the same period. The catalysts employed were lead acetate, uranyl acetate, ferrous sulfate, manganous chloride, cobalt acetate, and zinc lactate. At the close of the 100-day period the oils were separated from the emulsification by filtration through anhydrous sodium sulfate, or by extraction with ether, and acid and iodine numbers determined.

Summarizing the results obtained by the use of catalysts: At 37° C. for 100 days the acid number of the control increased from 2.5 to 4.3. Only one sample of oil, that containing manganous chloride, showed a higher acid number, being 23.7. No satisfactory explanation can be given for this high number and it is not given much weight in the final conclusion arrived at relative to the use of catalysts. Exposed to the light for 100 days, the acid number of the control did not change. The oil containing zinc lactate had an acid number of 6.3, while that containing cobalt acetate had an acid number of 4.8. All other samples were below 3.0. A peculiar action of zinc lactate was noted—the oil was bleached to a marked degree, while the iodine number of the sample was the lowest (176.6)

of any in the series, the control being 184.9. In no instance was the iodine number increased by the use of catalysts.

EFFECT OF HEAT AND THE ULTRAVIOLET LIGHT

Continuing the general line of experiments on the effect of heat and light on oils, it was decided to study the effect of ultraviolet light on these constants. Accordingly, samples of raw soy bean oil were subjected to the action of ultraviolet light while exposed in Petri dishes at a distance of 10 cm. from the bulb of a Cooper-Hewitt lamp. Other samples, consisting of 40 g. oil, 80 cc. water, or 80 cc. of a *N*/100 solution of a catalyst, were thoroughly emulsified and exposed to the light for 6 hrs. In another series, lampblack and finely divided nickel on kaolin was used. It was soon noticed that the heat from the lamp was intense, and its effect might be sufficient to explain any action taking place. However, the acid number of the sample of raw oil, emulsified oil, oil and lampblack, and oil emulsified with lampblack are about the same as that of the untreated raw oil; therefore, the higher acid number obtained by the use of *N*/100 ferrous sulfate and manganous chloride and of nickel may be considered as due to catalytic action. In every experiment, however, the iodine number has been lower, indicating an increase in the degree of oxidation of the acids set free. In this connection a sample of soy bean oil was mixed with lampblack and heated to 250° C. in an atmosphere of carbon dioxide. While hydrolysis proceeded rapidly under these conditions, the iodine number remained fairly constant, due to the protective influence of the atmosphere of carbon dioxide.

The effect of ultraviolet light and of heating in presence of carbon dioxide on acid number and iodine number are shown in Table VI.

TABLE VI—ACTION OF ULTRAVIOLET LIGHT ON ACID AND IODINE NUMBERS OF OILS IN THE PRESENCE OF CATALYSTS

Time of Exposure Hrs.	Treatment of Sample	Acid Number	Iodine Number
0	Raw soy bean oil.....	2.4	132.0 123.4
6	Oil, only.....	2.7	115.5 116.5
6	Oil, emulsified.....	2.8	117.4 118.1
6	Oil emulsified + <i>N</i> /100 FeSO ₄	4.4	108.6 108.7
6	Oil emulsified + <i>N</i> /100 MnCl ₂	3.8	110.3 110.3
6	Oil + 1 g. lampblack.....	2.9	112.9 113.9
6	Oil emulsified + 1 g. lampblack.....	2.7	114.3 114.4
7	Oil + 1 g. Ni.....	3.4	108.7 108.9
7	Oil emulsified + 1 g. Ni.....	3.7	110.5 111.5
To note effects of heat alone, oil + lampblack heated to 110° for 6 hrs., then to 250° for 1 hr. in atmosphere of carbon dioxide. Results obtained were.....		13.9	119.4 119.9

The effect of heat was studied by the use of an acid-refined oil, which was presumably free from enzymes and bacteria. The results shown in Table VII indicate the changes brought about by heat alone and by heat and storage at 37° C. for 35 days.

TABLE VII—EFFECT OF HEAT ON ACID NUMBER OF HIGH ACID OIL

Days Time	Treatment of Sample	Acid Number
0	Oil used in series.....	7.0
0	Heated at 15 lbs. pressure for 1/2 hr.....	11.7
35	Heated 1/2 hr. and kept at 37° C.....	25.0
35	Oil, control at 35° C.....	7.7

Oils which have not been acid-refined do not react to heat in such a degree. The hydrolytic action of heat over 100° is marked, and this must be taken into consideration in bacteriological examinations involving the sterilization of oils.

CONCLUSION

1—The processes of germination and growth of soy beans up to a height of 8 to 12 cm., even under favorable conditions of growth, do not result in an increase of unsaturated acids in the ether extract from such plants. On the other hand, while there is a decrease in iodine number of the extracted material, this decrease is not as pronounced as is the case with some other oily seeds. The soy bean seems to maintain acids of a high degree of unsaturation for the metabolism of the young plant up to the stage of the formation of the first set of leaves.

2—Bacteria and enzymes exert a marked hydrolytic action on oils in the presence of sufficient water, but in dry oils their action is slight. They have no action tending to increase the unsaturation of oils. From a practical standpoint, because of their presence in oils and sediments of oil containers, the possibilities of their hydrolytic action should be carefully considered.

3—The hydrolytic action of heat should be kept in mind in the sterilization of all fatty materials for bacterial culture purposes.

4—Salts of some metals, in certain concentrations, at 37° C. or in sunlight, act as catalyzers and increase hydrolysis, but they do not act to increase unsaturation.

5—Ultraviolet light acting on oils and emulsions containing salts exerts a slight hydrolyzing action.

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UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

REACTION PRODUCTS OF ALKALI-SAWDUST FUSION ACETIC, FORMIC, AND OXALIC ACIDS AND METHYL ALCOHOL¹

By S. A. MAHOOD AND D. E. CABLE

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In 1829 Gay-Lussac² discovered that oxalic acid is formed by fusing cellulose, sawdust, sugar, etc., with caustic potash. This process was used in the manufacture of oxalic acid by Dale³ in 1856. Later Thorn⁴ made a systematic study of the formation of oxalic acid by fusion of sawdust with sodium and potassium hydroxides separately and with mixtures of the two.

These earlier investigators, however, say very little about other products formed by the action of alkalis on sawdust. In connection with researches on the formation of acetic acid by the decomposition of lignocellulose, W. H. Higgin patented a process for the production of sodium acetate from alkaline waste liquor from straw and esparto boiling in paper manufacture.⁵ Following this, Cross, Bevan, and Isaac⁶ conducted a series of experiments on the action of alkalis on typical carbohydrates at elevated temperatures, with the object of determining, among other things, the maximum yield of acetic acid. Although their work was confined largely to the simpler carbohydrates, they obtained from 18 to 28 per cent of acetic acid from pine wood. Gases given off were found to be one-third to one-half hydrogen and to amount to 2 to 3 per cent of the substance decomposed. Oxalic acid was formed to some extent. They also found the yield of acetic acid was increased as the proportion of alkali to carbohydrates is increased from one to three. Potassium hydroxide proved better than sodium hydroxide and acted at a lower temperature.

In 1911 patents were taken out covering the production of oxalates⁷ and acetates⁸ by the action of alkali and air on woody fiber at elevated temperatures. Patents have also been obtained for the production of organic acids from waste pulp liquor⁹ and attempts to improve the method of producing oxalic acid from sawdust have been made.¹⁰

Whatever success these various processes have met with in practice, the facts are that prior to the war the chief sources of oxalic and acetic acids were producer gas and hardwood distillates, respectively.

The demand for acetic acid for war purposes has exceeded the supply and has led to the seeking of new sources of this important chemical. The present investigation was therefore undertaken to determine the amount of acetic acid obtainable from various species of wood, in the form of sawdust, by fusion with

¹ Read at the 56th Meeting of the American Chemical Society, Cleveland, September 10 to 13, 1918.

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