observations are made for what they may be worth:

(1) Neutralization of fatty acids and especially presence of potassium acetate are very important factors.
(2) The temperature is critical.
(3) Time of crystallization, volume of alcohol and concentration of lead acetate are less important factors.

CONCLUSIONS

1. The linoleic, oleic and saturated acid content of most common oils, except for limitations stipulated, may be estimated satisfactorily by the thiocyanogen method of analysis. None of the four methods generally employed for separation of liquid and solid fatty acids, which depend upon the insolubility of lead salts of saturated fatty acids, are entirely trustworthy.

2. The determination of isoöleic acid, by the Twitchell method of separation, is subject to the error of partial solubility of lead isoöleate. In some cases, a low linoleic/oleic ratio may cause a partial precipitation of lead oleate with the lead salts of isoöleic and saturated acids.

3. The Cocks-Christian-Harding method, for estimation of isoöleic acid, is no improvement on the Twitchell method.

4. While the Baughman-Jamieson modification is apparently free from the second error mentioned above, more work on hydrogenated oils is needed to establish the reliability of its isoöleic acid figures.

5. Further work should be done toward development of a dependable method for isoöleic acid estimation. It should be borne in mind that a method to be satisfactory need not necessarily concern itself with the determination of linoleic or saturated acids.

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CHEMICAL CONSTITUTION OF THE OILS FROM SUPERIOR AND INFERIOR FLAXSEEDS. (a) (b)

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THE oil of flaxseed consists of a mixture of glycerides of saturated and unsaturated fatty acids, and about 1% unsaponifiable matter. Substances composing the unsaturated fatty acid portion of linseed oil include the various isomers of oleic acid, α- and β-linoleic acid, and α- and β-linolenic acid. The change in the degree of unsaturation of an oil ordinarily is presumed to be caused by a change in the relative amounts of the three general types of unsaturated fatty acids present.

This paper describes a detailed study made on the unsaturation of two varieties of flaxseed oil grown in different localities; it shows the extent of variation of the iodine number with the change in the index of refraction, and the percentages of the unsaturated fatty acids composing the oils.

The two kinds of linseed oils studied were those obtained by extracting ground Abyssinian Yellow and Bison flaxseed in the customary Soxhlet fat extractor with petroleum ether. Abyssinian Yellow linseed oil is a superior oil having a relatively high iodine number, while Bison linseed oil is an inferior oil and usually has a somewhat lower iodine absorption value.

Experimental

Five samples each of the two varieties, grown in as many localities, were ground in a roller mill having 40 corrugations to the inch. The oil content of the seed was determined by extraction with petroleum ether (30°-60° C. B. P.). On occasion, samples of 50-60 grams in weight were extracted with the same solvent in order to obtain larger quantities of oil for examination.

Index of refraction was determined by an Abbé refractometer at 20° C., or corrected to this temperature.

The iodine numbers were determined according to the Rosenmund and Kuhnhenn[1] method, using a solution of bromine and pyridine sulfate in glacial acetic acid as the active halogen reagent. Such determinations were made on the oils as well as on the saturated and unsaturated fatty acid fractions obtained by the use of the Twitchell lead salt alcohol procedure. In each case, the lead salts were decomposed by treatment with dilute nitric acid and the free fatty acids were extracted with diethyl ether. An aliquot of the ether solution containing from 0.2 to 0.4 gram of fatty acids was evaporated to dryness under vacuum, and accurately weighed. The residue was dissolved in 10 cc. of chloroform and treated in a similar manner as the linseed oil, or unsaturated fatty acids.

Thiocyanogen numbers were determined according to the procedure of Kaufmann and Keller[2] with the added precaution that all the glass apparatus used in these determinations was dried in an electric oven at about 110° C. overnight, or longer before being used. By having all the glassware perfectly dry, very good check values were obtained among individual determinations of the thiocyanogen numbers for any one variety of linseed oil.

For the preparation of the free fatty acids, approximately 30 gram samples of linseed oil were saponified with a 0.75N solution of potassium hydroxide in alcohol. The ethyl alcohol used in the saponification process was made aldehyde-free by the method described by Dunlap.[3] Nitrogen saturated with alcoholic vapors by bubbling it through ethyl alcohol was passed through the saponification flask to prevent any

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(b) Condensed from a thesis presented to the Graduate School of the University of Minnesota by R. A. Gross, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, March, 1937.

possible oxidation of the unsaturated fatty acids, and the oil slowly refluxed for 3 hours.

At the end of the saponification period, the saponified oil was cooled somewhat; the vertical compound condenser was replaced by a horizontal compound condenser, and approximately one-half of the ethyl alcohol was distilled off. When the saponification mixture had cooled to room temperature, 400 cc. of distilled water was added. From the time that the oil was saponified and up to the point where the alkaline saponification mixture was diluted with water, the freed fatty acids were always kept under an atmosphere of nitrogen.

Unsaponifiable matter was separated from the aqueous solution containing the fatty acids as the potassium salts by extracting the mixture five times with 100 cc. portions of diethyl ether. These were combined in a liter separatory funnel and washed four times with 50 cc. portions of 0.5 N sodium hydroxide to remove any traces of alkaline soap which may have been carried over with the unsaponifiable matter. These washings were added to the main bulk of the liquid containing the soap. Then the ethyl extract was washed many times with 50 cc. portions of distilled water until the washings were neutral to phenolphthalein.

The ethereal solution of the unsaponifiable matter was concentrated to 100-200 cc., dried with anhydrous sodium sulfate, filtered into a 250 cc. volumetric flask, and made up to volume with small portions (25 cc.) of anhydrous ethyl ether with which the sodium sulfate was washed, in order to remove any unsaponifiable matter that may have been absorbed on the drying agent. From a pipette two 10 cc. aliquots were then run into as many weighed evaporating dishes; the ether driven off on a steam bath, then dried in an electric oven at 70° C, placed in a desiccator to cool, and weighed.

Aqueous solutions of the fatty acids as the sodium and potassium salts were then made acid with 1 : 1 HCl to liberate the fatty acids, and then extracted three times with 100 cc. portions of ethyl ether. The combined diethyl ether extracts were washed with 50 cc. portions of cold distilled water several times until the washings were neutral to methyl orange, dried with anhydrous sodium sulfate, filtered into a 500 cc. volumetric flask, and made up to volume with water-free ethyl ether. Two 10 cc. aliquots were evaporated in flasks under a water pump vacuum with the containers immersed in a water bath maintained at a temperature of about 90° C., and finally cooled to room temperature under vacuum and then weighed.

Estimation of Fatty Acids

Fatty acids recovered after the removal of the unsaponifiable matter were separated into saturated and unsaturated fatty acid fractions according to the experimental procedure of Twitchell.[4] The saturated fatty acid fraction from a known, weighed amount of fatty acids was made up to volume in a 100 cc. volumetric flask with anhydrous ethyl ether. An aliquot of the ethereal extract was pipetted into a tared 125 cc. erlenmeyer flask, the ether evaporated off under vacuum with the flask in a water bath, and the residual solid fatty acids weighed.

This is not a complete quantitative separation, but a fractional precipitation in which some lead oleate and a small amount of linoleic acid as the lead salt co-precipitate with the saturated acids in the cold alcoholic solution; therefore the percentage of saturated fatty acids as obtained must be corrected for the quantity of unsaturated acids present. From the iodine numbers of the saturated and unsaturated fatty acid fractions, the percentage of saturated fatty acids can be calculated as suggested by Jamieson.[7]

$$\frac{\text{Iodine number of saturated acid fraction}}{\text{Iodine number of unsaturated acid fraction}} \times 100 = \text{A.}$$

A = per cent of unsaturated acids in saturated acid fraction.

The correction was then calculated by means of the formula $\frac{A \times B}{100}$, in which B is the percentage of impure saturated acids as determined by analysis. This correction was then subtracted from the percentage of impure saturated acids, and the percentage of saturated fatty acids (corrected) was thus computed.

Kaufmann and Keller[2] have shown that linseed oil dissolved in chloroform, or carbon tetrachloride, is partially saturated to a definite end point by the use of a thiocyanogen solution. Oleic acid is completely saturated and therefore has a theoretical thiocyanogen value of 90.1; linoleic acid absorbs thiocyanogen in only one of its two centers of unsaturation and therefore its theoretical thiocyanogen value is 90.7; linolenic acid is acted upon by thiocyanogen in only two of its three double bonds and for this reason has a theoretical thiocyanogen value of 182.7. The thiocyanogen number is the number of grams of thiocyanogen absorbed by 100 grams of the oil calculated in iodine equivalents.

Since iodine adds to all the double bonds in the fatty acid series, Kaufmann[6] has shown it is possible to calculate from the iodine and thiocyanogen values and the percentage of saturated fatty acids the percentages of the various unsaturated fatty acids in a mixture of fatty acids.

Bromination of Unsaturated Fatty Acids

The unsaturated fatty acids were brominated according to the procedure as recommended by Jamieson.[5] One gram of unsaturated fatty acids separated by the Twitchell method and accurately weighed was brominated in anhydrous ethyl ether. The hexabromide precipitate which was obtained was pure white, and was completely soluble in boiling benzene showing that no octabromides were present as octabromides are insoluble in boiling benzene. From the weight of linolenic acid hexabromide obtained, the percentage of α-linolenic acid was calculated by the formula:

$$\alpha\text{-linolenic acid in per cent} = \frac{\text{M.W.Ln}}{\text{M.W.Ln H.}} \times \text{per cent linolenic acid hexabromide.}$$

M. W. Ln = Molecular weight of linolenic acid.

M. W. LnH. = Molecular weight of linolenic acid hexabromide.

The percentage of β-linolenic acid is then the algebraic difference between the percentage of linolenic acid as calculated by means of the iodine and thiocyanogen numbers, and the percentage of α-linolenic acid.

The ethereal mother liquor and ethyl ether washings of the hexabromide precipitate were evaporated to dryness, and the residue was dissolved in ligroin (b. pt. 30-60° C.) under a reflux condenser. Upon cooling a precipitate of linoleic acid tetrabromide crystallized out. Using the following formula, the percentage of α-linoleic acid was calculated in which

M.W.L. = molecular weight linoleic acid,

M.W.L.A.T. = molecular weight linoleic acid tetrabromide,

Per cent α-linoleic acid = $\frac{\text{M.W.L.}}{\text{M.W.L.A.T.}} \times$ % linoleic acid tetrabromide.

The percentage of β-linoleic acid was then obtained by the difference between the percentage of linoleic acid and α-linoleic acid.

Per cent β-linoleic acid = % linoleic acid — % α-linoleic acid.

The difference between the α and β forms of the double and triple bond fatty acids is one of chemical definition only. The α forms of the acids are those which form insoluble bromo addition compounds, while the β isomers are those acids which form soluble bromo addition compounds with the solvents employed.

DISCUSSION OF RESULTS

The oil content of the Abyssinian Yellow variety of flaxseed grown in different geographical localities is not constant, but varies from one locality to another. Bison flaxseeds raised in the five experimental stations contained approximately the same percentages of oil. Small variations in the oil content may be due to experimental inaccuracies in the determinations of the amounts of oil in the flaxseeds. Apparently, the experimental results seem to indicate that the geographical factors do not influence the oil content of the Bison variety of flaxseed to a great extent, but that the peculiarities of soil and climate in certain sections of the state of Minnesota have more influence on the percentage of oil which is formed in the seeds of the Abyssinian Yellow flax.

The geographical conditions of climate and sectional characteristics of soil influence to some extent the degree of unsaturation of oil which a plant deposits in its seeds. The changes of the iodine numbers for each individual variety of flaxseed oil is relatively small, but nevertheless is perfectly definite and occurs in a regular manner.

The index of refraction does not vary a great deal for the same varieties of linseed oil, but when there is a relatively large difference in unsaturation between two oils there is some change in the refractive index of the oil. An increase in unsaturation was accompanied by an increase in the refractive index, and the change in the index of refraction for the change in constitution was relatively small and perfectly definite; although, there were slight discrepancies to this general statement when the numerical values of the iodine numbers were nearly identical. Taylor[8] found that the index of refraction and the iodine numbers of several varieties of linseed oil which he studied differed notably, showing that the composition of the oil was affected by conditions of climate and soil. The index of refraction was quite variable in many instances and was not easily correlated with variety, or locality.

TABLE I

Characteristics of oil extracted from flaxseed grown at Waseca, Minnesota.

	Abyssinian Yellow		Bison	
Oil in flaxseed, %	37.00	37.11	35.43	35.08
Refractive index (20.0° C.)		1.4802		1.4785
Iodine number of oil	176.8	176.1	154.4	154.0
Thiocyanogen number of oil	99.6	99.2	98.5	98.6
		99.1		100.4
Unsaponifiable matter, %	1.15	1.13	1.29	1.31
Fatty acids in oil, %	93.20	93.04	91.83	91.72
Iodine number of solid acid fraction	10.4	10.4	39.3	39.3
Iodine number of unsaturated fatty acids	187.1	187.0	166.1	165.5
Saturated fatty acids, % (uncorrected)	10.32	10.29	11.79	11.66
Saturated fatty acids, % (corrected)		9.74		8.95
Unsaturated fatty acids, %		90.26		91.05
Hexabrom stearic acid, %	42.41	42.63	31.05	30.84
α—linolenic acid, %	15.57	15.65	11.40	11.32
β—linolenic acid, %		3.76		7.11
Tetrabrom stearic acid, %	22.82	24.67	11.80	12.13
α—linoleic acid, %	10.66	11.53	5.51	5.66
β—linoleic acid, %		54.76		36.67
Oleic acid, %		5.03		30.33

TABLE II

Oil contents of two varieties of flaxseeds. Refractive indices at 20° C., and iodine numbers of oils obtained from flaxseeds grown in different localities in Minnesota.*

	Oil extracted, %		Refractive indices	Iodine numbers	
Abyssinian Yellow					
Coon Creek, Minn.	34.25	34.26	1.4810	174.9	174.9
Crookston, Minn.	37.57	37.48	1.4812	181.6	181.2
Morris, Minn.	36.10	35.83	1.4810	170.7	171.2
University Farm, St. Paul, Minn.	33.36	33.71	1.4810	174.5	173.9
Waseca, Minn.	37.00	37.11	1.4802	176.8	176.1
Bison					
Coon Creek, Minn.	35.96	36.04	1.4780	151.2	151.5
Crookston, Minn.	36.13	36.22	1.4792	157.0	156.5
Morris, Minn.	36.62	36.47	1.4785	150.2	149.6
University Farm, St. Paul, Minn.	35.38	35.56	1.4785	151.2	150.6
Waseca, Minn.	35.43	35.08	1.4785	154.4	154.0

*All samples of flaxseed were grown in the year 1935.

TABLE III

Thiocyanogen numbers of oils extracted from flaxseeds grown in different localities in Minnesota

	Thiocyanogen numbers		
Abyssinian Yellow			
Coon Creek, Minn.	103.1	103.1	103.1
Crookston, Minn.	114.0	110.9	113.8
Morris, Minn.	113.4	110.6	111.5
University Farm, St. Paul, Minn.	98.5	98.9	99.3
Waseca, Minn.	99.6	99.2	99.1
Bison			
Coon Creek, Minn.	91.8	91.3	92.3
Crookston, Minn.	104.0	104.7	104.1
Morris, Minn.	91.0	89.8	91.3
University Farm, St. Paul, Minn.	92.9	93.6	92.9
Waseca, Minn.	98.5	98.6	100.4

TABLE IV

Per cent saturated fatty acids (uncorrected),* and iodine numbers of the saturated and unsaturated fatty acid fractions obtained from the various saponified flaxseed oils.

	Per cent solid acids		Iodine numbers of fatty acid fractions: Saturated		Unsaturated	
Abyssinian Yellow						
Coon Creek, Minn.	11.51	11.49	7 1	6.8	196.3	196.1
Crookston, Minn.	11.71	11.73	41.5	41.2	194.9	195.1
Morris, Minn.	12.98	13.00	36.4	36.2	186.3	186.5
University Farm, St. Paul, Minn.	11.82	11.83	44.3	44.1	195.6	195.7
Waseca, Minn.	10.32	10.29	10.4	10.4	187.1	187.0
Bison						
Coon Creek, Minn.	16.43	16.49	63.0	62.5	175.1	175.8
Crookston, Minn.	12.20	12.04	53.2	53.1	176.7	177.3
Morris, Minn.	14.58	14.45	66.4	65.9	165.9	166.4
University Farm, St. Paul, Minn.	15.03	15.06	71.7	71.3	167.1	166.3
Waseca, Minn.	11.79	11.66	39.3	39.3	166.1	165.5

*The saturated acid fractions contained a small percentage of unsaturated fatty acids as impurities.

TABLE V

Composition of the liberated fatty acids.

	Per cent acids			
	Oleic	Linoleic	Linolenic	Saturated
Abyssinian Yellow				
Coon Creek, Minn.	9.64	54.36	24.91	11.09
Crookston, Minn.	15.15	41.75	33.87	9.23
Morris, Minn.	24.24	31.53	33.83	10.40
University Farm, St. Paul, Minn.	7.83	64.57	18.45	9.15
Waseca, Minn.	5.03	65.68	19.37	9.74
Bison				
Coon Creek, Minn.	23.63	53.88	11.92	10.57
Crookston, Minn.	33.56	34.33	23.63	8.48
Morris, Minn.	25.84	56.43	8.93	8.80
University Farm, St. Paul, Minn.	27.59	52.43	11.38	8.60
Waseca, Minn.	30.33	42.25	18.47	8.95

Iwanoff[9] showed that the amount of moisture in the atmosphere under which a flax plant is raised influences the unsaturation of the oil deposited during growth. Linseed oil obtained from flaxseed grown under humid conditions had iodine numbers of 167.8 to 170.6, while under arid conditions of growth, the same variety gave an oil having an iodine number of 181.8 to 187.0. Considering the above factors, unsaturation in linseed oil is influenced by environment for the percentage of each of the three unsaturated fatty acids differed for the same variety of flaxseed grown in different geographical localities.

It is naturally expected that of two oils, one of lower and the other of higher iodine number, the oil having the higher iodine number would contain a lower percentage of saturated fatty acids. However the oil extracted from the Bison variety of low iodine number, grown in the same vicinity with the Abyssinian Yellow variety contained a smaller percentage of saturated fatty acids than the oil from the latter. The percentage of saturated fatty acids in the Bison oil was more nearly uniform and did not vary as much as in the oil obtained from the Abyssinian Yellow seed.

SUMMARY

All seed oils of the Bison flax variety contained a higher percentage of oleic acids and a lower percentage of linolenic acids than the Abyssinian Yellow flax variety. Abyssinian Yellow seeds yielded oils which contained a relatively low percentage of oleic acid and a higher per cent of linolenic acid than the Bison variety grown in the same locality.

The amount of unsaturation in an oil, or its iodine number, appears to be a varietal characteristic, and the components of the oil are blended by nature to give a certain degree of unsaturation which can be varied by growing the flax plants under different environmental conditions.

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EDIBLE OIL DEODORIZING EQUIPMENT AND METHODS:

A Short Historical Sketch

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Abstract

Edible oil deodorizing equipment and processes have been developed as a result of advances in hot-pressing and extraction of oil-bearing materials. Early methods included masking of odors by means of aromatics, washing out of odors and neutralization or destruction of odors by means of various chemical treatments.

Commercial deodorization methods involve steam distillation in vacuo. Processes have been developed independently in several European countries and in the United States. Most efficient equipment uses low absolute pressures and high temperatures in equipment constructed of corrosion-resistant metals and supplied with suitable recording instruments.

Current trend is toward continuous processes with automatic control.

THE deodorizing of oils for edible purposes was an unknown, even an unnecessary art, until comparatively recent years. The ancients were acquainted with olive oil and undoubtedly with coconut oil, but in early practice both of these oils were expressed by means of cold-pressing processes, from fresh raw materials and both therefore were entirely suitable for edible uses without further processing of any sort.

As the world progressed, new methods of pressing developed and it was discovered that cooking or heating oil-bearing raw materials before pressing, results in marked increase in the yield of oil. Further developments in agronomic economics brought about storage of oil-containing seed or fruit from one harvest period until the arrival of the next, as well as shipment of the materials over great distances before expression of the oil. All these factors contributed to reduction in the average quality of the expressed oil from the standpoint of edibility. Both storage and cooking before pressing cause increase of free fatty acid in the oil. The latter operation, particularly, may account for the presence of small amounts of aldehydes, ketones and other bodies which impair the flavor of the freshly-expressed oil, but which are not soluble in the oil at the low temperatures employed in cold-pressing. The same impurities result from slight decomposition of the seed and of its contained oil during storage and shipment.

In a cold-pressed oil are to be found minute quantities of phosphatides, vitamines and other unsaponifiable organic materials which appear to act as inhibitors of or buffers against fermentative decomposition of the oil with attendant increase of free fatty acids and subsequent onset of rancidity. In hot-pressed oils, on the other hand, the beneficent effect of such substances apparently is decreased, either by the presence of other substances which accelerate fermentative action or by the presence of increased volume of the same phosphatides, which, although acting protectively when present in small amounts, may themselves become subject to fermentation when their relative volume is greater, as in hot-pressed oils. It is possible, also, that certain protective vitamines present in cold-pressed oils, may be destroyed or may lose their protective capacity when subjected to the temperatures incidental to the hot-pressing operation.

Hot-pressing of oils results also in the presence in the oil of larger amounts of the natural coloring matters of the oil-bearing fruit, the solubility of such coloring matters in the oil during the pressing operation generally being directly proportional to temperature. The pres-

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