The Composition of Seven American Linseed Oils*

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COMPOSITION studies of linseed oil have been made from time to time, chiefly by European investigators. In this connection it is interesting to note that Sleightholme (J. Oil and Col. Chem. Assoc., *15*, p. 287 (1932)) indicated the need for a thorough knowledge of the constitution of this oil, there being no satisfactory data on the proportions of its fatty acids present as glycerides. It will be shown why this situation has remained unchanged up to the present time.

For the present investigation seven sizeable samples of flaxseed were selected with a view to getting oils having iodine numbers which covered a considerable range, in order to ascertain in what respects they differed from one another. Five of these samples were obtained through the cooperation of A. C. Dillman, Division of Cereal Crops and Diseases, U .S. Bureau of Plant Industry, and included three which were supplied by R. S. Carpenter of the Archer-Daniels Midland Company. The Bison No. 1 oil listed in the table was from seed grown in the southern part of North Dakota, whereas Bison No. 2 and No. 3 were from seed produced in the northern part of the State. Mr. A. K. Schwartz of the South Texas Cotton Oil Company sent us a sample of Bison Flaxseed which was grown in Nueces County and another of Punjab flaxseed from Hidalgo County, Texas. The samples of Abyssinian and Punjab varieties of flaxseed from the Imperial Valley were supplied by L. G. Goar of the local California Experiment Station. The assistance of all those who made it possible for us to get these samples is much appreciated.

The oils in each case were expressed by means of our oil expeller and promptly filtered through paper to remove the press foots. The more important characteristics of the oils were determined; the results are given in Table I.

Saturated Acids. The total quantity of saturated acids in each oil was determined by the Bertram procedure. By means of the lead salt-ether method, from 60 to 80 grams of the saturated-acid fraction were obtained from each of the seven oils. These fractions were esterified with ethyl alcohol by the aid of dry hydrogen chloride, and finally each preparation was fractionally distilled in the usual manner under diminished pressure. The composition of the fractions was determined by methods previously described in J. Amer. Chem. Soc., *46*, 775 (1924). The acids from each ester fraction were subjected to fractional crystallization from ethyl alcohol, and the identity of each isolated constituent was determined in the customary manner. No myristic acid could be detected, although very small quantities of this acid in linseed oils from other countries had been reported by previous investigators (cf. T. P. Hilditch and E. C. Jones, J. Soc. Chem. Ind., *53*, 13T (1934). Further search was made for it in the lowest-boiling fraction obtained by the distillation of the esters prepared from 50 grams of the unsaturated-acid fraction separated from the Abyssinian oil, but none was found. As would be expected in such cases, several milligrams of palmitic acid were isolated. From the data obtained in this part of the investigation, the proportions of the individual saturated acids present in each of the oils were calculated; the results are given in Table 2.

Unsaturated Acids. The percentages of oleic, linoleic, and linolenic acids in the oils were calculated, using their respective iodine and thiocyanogen values. Mention should be made that the iodine numbers were determined in the usual manner by allowing the Wijs reagent to react with the oils for one hour within the temperature range 20° to 23° C. The thiocyanogen values were determined with a tenth-normal solution of thiocyanogen, using from 150 to 200 percent of the amounts expected to be required by the samples taken for analysis. After allowing the reaction to continue for 24 hours in a constant-temperature room maintained at 20°C., the solutions were titrated in our customary manner.

When the values are to be used for calculating the quantities of individual unsaturated acids present, it has been found necessary to conduct thiocyanogen determinations under very carefully controlled conditions. In calculating the individual unsaturated acids in these oils, the theoretical iodine number for each acid was used. Likewise, the theoretical thiocyanogen value for oleic acid was used because this acid was found to react in a normal manner with thiocyanogen under the prescribed conditions, in contrast to the abnormal reaction of this reagent with linoleic and linolenic acids. In the case of linoleic acid, the empirical value 93 was used (cf. R. W. Riemenschneider and D. H. Wheeler, this journal, *16*, 219 (1939), and Kass, et. al., ibid., *17*, 118 (1940)). For linolenic acid, the empirical value 163.8 was used. It should be noted that these values are not identical with those determined experimentally by means of a 0.2-N solution of thiocyanogen, which gives somewhat higher results than does the 0.1-N solution used in this investigation.

The final results of the calculations are given in Table 3.

In order to see how much these results differ from those calculated from the theoretical thiocyanogen values for linoleic and linolenic acids, in accordance with the previous assumptions of H. P. Kaufmann (Z. Unters. Lebensm., *51*, 15 (1926) and Berichte *70*, 2545 1937)). Table 4 was prepared.

Discussion. Prior to the introduction of a method for the determination of the thiocyanogen value (loc. cit.), the quantity of linolenic acid in an oil could be estimated only through the use of the (ether-insoluble) linolenic hexabromide value. Also, after the separation of the hexabromide, it was formerly customary to separate as completely as possible the crystallizable linoleic tetrabromide from a petroleum ether solution of the remaining halogenated acids; from the bromine content of the soluble bromides the quantities of soluble linoleic and oleic bromides were calculated on the assumption that no soluble hexabromide was present. This was shown later to be in error. From the total amount of tetrabromide as found directly and indirectly, it had been customary to calculate the percentage of linoleic acid in the sample. However, since about

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1926 it has been known that the use of the thiocyanogen value in calculating the weight of each unsaturated constituent in mixtures which contain oleic, linoleic and linolenic acids is the only method now available which affords any possibility of accurate determination.

H. P. Kaufmann (Arh. Pharm., *263*, *675* (1925)), who devised the thiocyanogen method, described the use of the values obtained for calculating the amounts of oleic, linoleic and linolenic acids present, on the assumption that each acid reacted in exactly theoretical proportions with this reagent. He believed that the reagent saturated the one double bond in oleic acid, one in linoleic acid, and two in linolenic acid. On the basis of this assumption, Kaufmann and other investigators had used thiocyanogen values in their calculations over a period of some years before it became generally known that, in contrast to oleic acid, the other two did not react in the expected manner. Apparently, W. Kimura (J. Soc. Chem. Ind., Japan, *32*, 141 Supl. Bdg. (1929)) was the first to call attention to the failure of thiocyanogen to completely saturate two of the three double bonds of linolenic acid. Further criticism of the Kaufmann method and the use of the thiocyanogen value in calculating the amount of each of the unsaturated acids present in linseed oil was made by J. van Loon (Chem. Umschau., *38*, *279* (1931)), and P. J. Gay (J. Soc. Chem. Ind., *51*, 126T (1932)), as well as by H. van der Veen and J. van Loon (Chem. Umschau., *39*, 56 (1932)). More recently, G. Y. Shinowara and J. B. Brown (J. Amer. Chem. Soc., *60*, 2734 (1938)), and Kass and associates, as well as Riemenschneider and Wheeler, (loc. cit.) and Hilditch and Murti (Analyst *65*, *437* (1940)), have reported on the results of investigations on the reaction of thiocyanogen with these unsaturated acids. It has been found that linoleic acid, in contrast to linolenic acid, reacts with somewhat more thiocyanogen than the amount required to saturate one of its double bonds.

The use of empirical values in the calculations under discussion is only applicable when the thiocyanogen values have been determined with extreme care under carefully controlled, known conditions which include the concentration of the reagent, the temperature, and the time allowed for the reaction. The changing of any of these factors would necessitate using other predetermined empirical values. Consequently, in the majority of cases where thiocyanogen values are given in the literature for linseed and other oils of the same type containing notable quantities of linolenic acid, there is apparently no way of knowing the empirical values which should be used for recalculating the percentages of the individual unsaturated acids in these oils.

We concur with the suggestion of Hilditch and Murti (loc. cit.), that further investigation should be made of the quantitative aspects of the reaction of thiocyanogen, particularly the more commonly used 0.2 N solution, with linolenic acid and its esters, with the hope that an agreement may be reached by the interested investigators in regard to what is the closest estimation possible of the true thiocyanogen value of this acid.

Summary. The more important characteristics of, and the percentages of the individual acids in, seven samples of linseed oil expressed from seed grown in California, North Dakota and Texas have been determined. The iodine numbers of the oils ranged from 144 to 197.3; the saturated acids, from 7 to about 12 percent; oleic acid, from 15 to 34 percent; linoleic acid, from 9 to 23 percent; and linolenic acid, from 28 to 61 percent. In calculating the amounts of each of the three unsaturated acids present, use has been made of the recently determined empirical thiocyanogen values for linoleic and linolenic acids instead of the theoretical ones which have been shown to be incorrect.

TABLE I.

The Characteristics of Expressed Linseed Oils.

Source and Variety of Seed	Refractive Index at 25°C.	Iodine Number (Wijs, 1 hr.)	Thiocyanogen Value (0.1-N Sol. at 20°C.)	Unsaponifiable Matter	Saturated Acids
North Dakota:				%	%
Bison No. 1	1.4742	144.1	95.7	1.11	11.97
Bison No. 2	1.4772	160.7	103.1	1.12	10.45
Bison No. 3	1.4784	179.8	110.7	1.11	9.00
Texas:					
Bison	1.4771	174.0	109.2	1.35	7.03
Punjab	1.4773	168.1	107.4	1.24	8.72
California:					
Punjab	1.4787	184.9	116.9	0.90	10.13
Abyssinian	1.4799	197.3	122.2	0.89	9.32

TABLE 2

Saturated Acids of Linseed Oils

Source and Variety of Seed	Palmitic Acid	Stearic Acid	Arachidic Acid	Lignoceric Acid
North Dakota:	%	%	%	%
Bison No. 1	6.29	4.46	0.86	0.36
Bison No. 2	5.94	4.00	0.30	0.21
Bison No. 3	5.93	2.37	0.50	0.20
Texas:				
Bison	4.38	2.32	0.28	0.05
Punjab	3.84	4.61	0.22	0.05
California:				
Punjab	4.98	4.84	0.29	0.00
Abyssinian	6.87	2.17	0.28	0.00

TABLE 3

Unsaturated Acids in Linseed Oils
Calculations Based on Empirical Thiocyanogen Values for Linoleic and Linolenic Acids (See Text).

Source and Variety of Seed	Oleic Acid	Linoleic Acid	Linolenic Acid
North Dakota:	%	%	%
Bison No. 1	34.45	20.04	28.13
Bison No. 2	27.49	20.37	36.28
Bison No. 3	17.95	22.81	44.82
Texas:			
Bison	23.52	23.31	40.50
Punjab	26.53	19.01	40.21
California:			
Punjab	20.68	9.20	54.77
Abyssinian	14.92	9.63	60.92

TABLE 4

Unsaturated Acids in Linseed Oils
Calculations Based on Theoretical Thiocyanogen Values (See Text).

Source and Variety of Seed	Oleic Acid	Linoleic Acid	Linolenic Acid
North Dakota:	%	%	%
Bison No. 1	29.44	29.20	23.03
Bison No. 2	20.68	33.85	29.58
Bison No. 3	9.40	39.78	36.40
Texas:			
Bison	15.95	38.47	32.93
Punjab	18.88	34.17	32.63
California:			
Punjab	9.78	30.80	44.14
Abyssinian	2.75	33.70	49.02