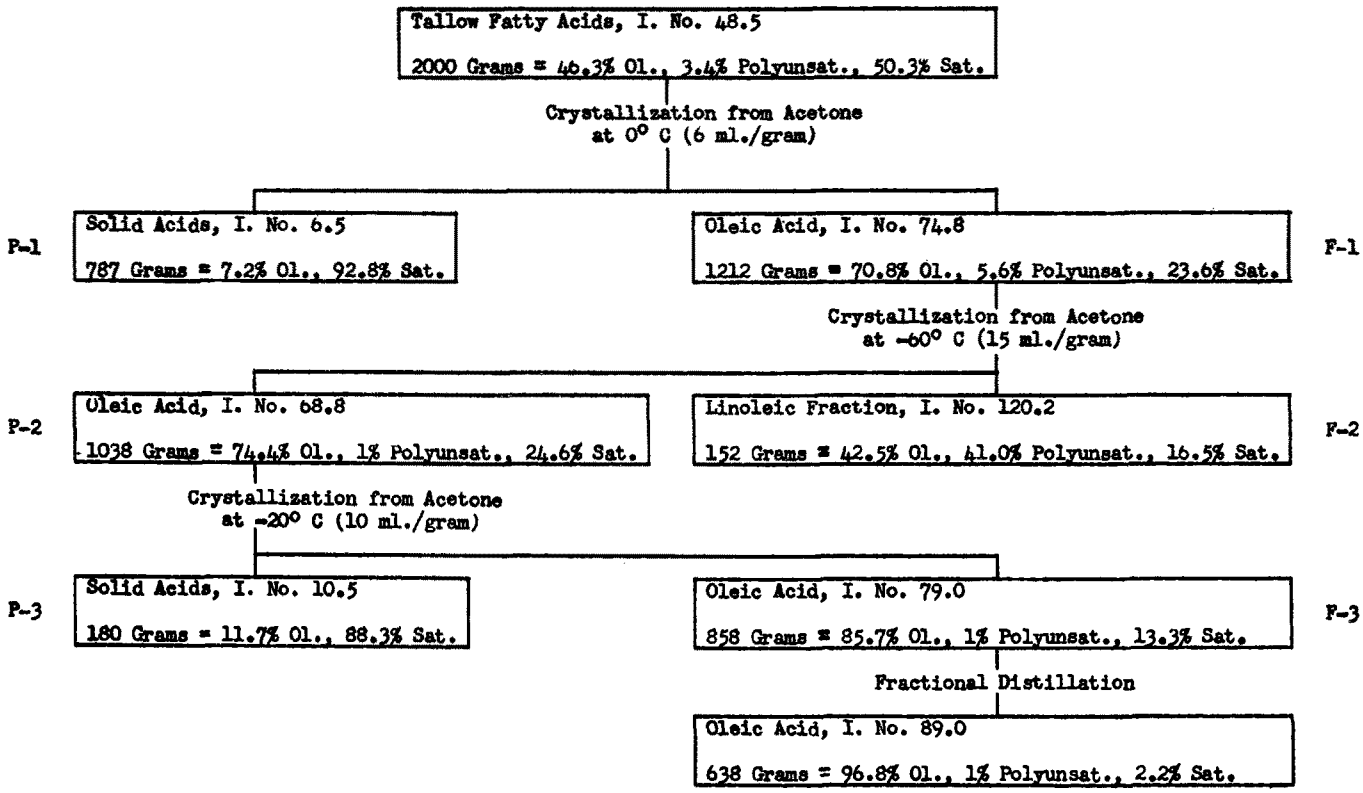

FIG. 2. Alternative method for preparation of purified oleic acid which also yields a saturated acid fraction of good quality.

pared by crystallization of tallow fatty acids at —20° C. (see comparable Fraction F-1, Figure 1), after straight-run distillation to remove color, was reacted with slightly less than the calculated quantity of anhydrous glycerol at 190° C. in an inert atmosphere and under vacuum until the acid number of the mixture became constant. The unreacted oleic acid was separated by vacuum distillation. The synthetic triglyceride, obtained in almost quantitative yield, was a pale-yellow oil with the following characteristics: iodine number, 84.2; acid number, 3; melting point, <0° C.

Summary

Tallow fatty acids have been fractionally crystallized from acetone at temperatures ranging from 0° to —60° C.

By crystallizing at 0° to —20° C., a saturated acid fraction which amounts to 40 to 50% by weight of the starting material has been obtained. This fraction corresponds to "double- or triple-pressed stearic acid."

The filtrate acids from the crystallization at —20° C. contain over 90% of the oleic acid present in the starting material, and in fatty acid composition this mixture is similar to olive oil. From this fraction, which amounts to about 50% by weight of the starting material, a synthetic triglyceride with properties approximating those of olive oil has been prepared.

By low-temperature crystallization of this oleic-acid-rich fraction at —50° to —60° C., followed by fractional distillation, a good yield of purified oleic acid (oleic acid content, over 95%) has been obtained.

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Sunflower and Safflower Seeds and Oils*

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SUNFLOWER and safflower seeds have recently received increased attention as possible sources of domestic oils and protein feeds when grown in the North Central States area. During the past year sunflowers were grown on a small acreage near Monticello, Illinois, and safflowers were grown near Alliance, Nebraska. The plants and their products are well known in many foreign countries, but in North America most of the recent experience and published information have come from Canada, and experience in the United States is limited to relatively few companies. References to sunflowers are frequent in the Annual Reports of the Grain Research Laboratory, Winnipeg, Manitoba (1), and current research on this crop is carried out at the Oil Seeds Laboratory, University of Saskatchewan. Cultural practices in

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TABLE I.

Physical Analyses (Air-Dry Basis) of Four Varieties of Sunflower Seeds (Grown at Seven Locations) and of Eight Varieties of Safflower Seeds (Grown at One Location)

Variety	Weight per bushel	Weight per 1,000 kernels	Proportion of	
			Hulls	Hulled seed
Sunflowers:	*Pounds*	*Grams*	%	%
Mennonite	25.3	70.7	43.1	56.9
Sunrise	31.7	38.3	39.0	61.0
Greystripe	27.8	93.6	44.3	55.7
Manchurian	26.6	108.0	46.0	54.0
Average	27.8	77.7	43.1	56.9
Safflowers:				
Pusa No. 2	37.9	33.5	47.8	52.2
Pusa No. 7	44.4	50.7	49.7	50.3
Pusa No. 25	40.1	40.7	50.4	49.6
Sholapur No. 1	44.7	53.1	49.6	50.4
Simla 66/1508	46.2	50.5	49.3	50.7
Kardai (1068)	44.1	47.6	48.6	51.4
Abmednagar No. 1	46.2	44.9	48.9	51.1
Karar (1885)	40.8	56.9	47.6	52.4
Average	43.0	49.2	49.0	51.0

Canada have been summarized recently (2), and a brief discussion of the two crops, together with analytical data, was published in 1943 (3). A recent analysis of one sample of safflower oil was given by Bickford, Mann, and Markley (4).

Analyses have been completed at the Northern Regional Research Laboratory on 28 samples of sunflower seed and eight samples of safflower seed. The sunflower seed samples comprise four varieties, each grown in 1943 at the seven locations of Beltsville, Maryland; Ames, Iowa; Columbus, Ohio; Manhattan, Kansas; Columbia, Missouri; Davis, California; and Urbana, Illinois. The eight safflower varieties were all grown at Huntley, Montana, in 1943. All of these samples were obtained through the Bureau of Plant Industry, Soils, and Agricultural Engineering, with M. T. Jenkins of the Division of Cereal Crops and Diseases furnishing the sunflower seed and Frank Rabak of the Division of Drug and Related Plants furnishing the safflower seed samples. The latter samples were grown in cooperation with the Division of Western Irrigation Agriculture.

Methods

One-pound lots of sunflower seed were obtained by a mechanical sampler. Each pound was then carefully hulled by hand in order to obtain the maximum amount of information from the chemical analyses made on the resulting fractions. The safflower seed samples were cracked in an attrition mill and the hulls successfully removed by aspiration, followed by hand-picking. Other portions of the safflower samples, treated in the same way except without the final hand-picking, were used to obtain oil samples for analysis. Both procedures resulted in much cleaner separations than are ordinarily obtained so that the analyses on the separated hulls and hulled seeds were made on exceptionally "pure" materials. The hulls and hulled seeds were analyzed separately, and from these data and the weights of the two fractions the composition of the whole seed was calculated.

The high oil content of the hulled seeds prevented an initial fine grind on the samples. The hulled safflower seeds were cracked in an attrition mill with the plates set just close enough to crack the kernels. Since the whole kernels were rather small, the cracked kernels were considered fine enough for adequate sampling. On this material there were determined: 1. Moisture, by heating for one hour at 130° C.; 2. ash, by heating at 550° C. for four hours; 3. oil, by extraction in a Butt extractor for 16 hours with Skellysolve F, regrinding in a mortar, and extracting for an additional two hours; and 4. nitrogen, by the Kjeldahl method. Analysis of the safflower hulls, ground in a Wiley mill with a 1-mm. screen, was quite similar except that ashing was for only two hours and the oil extraction was run overnight without the regrind.

The hulled sunflower seeds were also cracked in the attrition mill, but the resulting particles were considered too coarse for satisfactory sampling. The entire sample was extracted with Skellysolve F in a large extractor for several hours, then finely ground, and re-extracted. The total extraction time was about 20 hours. The residue was analyzed by much the same procedure as the hulled safflower seeds except 1. mois-

TABLE II.

Chemical Analyses (Moisture-Free Basis) of Sunflower Seeds Grown at Seven Stations in 1943 (Averages by Variety)

Variety	Ash	Nitrogen	Protein (Nx6.25)	Sugar[1]	Oil
Whole seed:	%	%	%	%	%
Mennonite	3.45	3.24	20.27	3.76	27.47
Sunrise	3.45	3.42	21.40	3.79	30.78
Greystripe	3.36	2.89	18.04	2.83	30.69
Manchurian	3.46	2.93	18.31	2.79	28.23
Average	3.43	3.12	19.50	3.29	29.29
Hulls:					
Mennonite	2.17	.59	3.70	.....[2]	1.07
Sunrise	2.47	.72	4.49	.....	1.16
Greystripe	2.28	.49	3.08	.....	1.20
Manchurian	2.39	.57	3.55	.....	.79
Average	2.33	.59	3.70	.....	1.05
Hulled seed:					
Mennonite	4.36	5.17	32.3	6.38	46.6
Sunrise	4.07	5.12	32.0	6.14	48.8
Greystripe	4.18	4.70	29.4	4.87	53.2
Manchurian	4.31	4.86	30.4	5.21	50.5
Average	4.23	4.96	31.0	5.65	49.8

[1]Total soluble sugars as glucose.

[2]A sugar determination on a composite hull sample showed the presence of 0.2% sugar.

TABLE III.

Chemical Analyses (Moisture-Free Basis) of Safflower Seeds of Eight Varieties Grown at Huntley, Montana, in 1943

Variety	Ash	Protein (Nx6.25)	Sugar[1]	Oil
Whole seed:	%	%	%	%
Pusa No. 2	3.63	15.63	1.90	31.5
Pusa No. 7	3.18	13.69	1.60	32.1
Pusa No. 25	3.25	14.19	1.65	31.6
Sholapur No. 1	3.03	12.44	1.52	33.1
Simla 66/1508	3.03	13.00	1.44	33.3
Kardai (1068)	3.14	12.62	1.55	33.8
Abmednager No. 1	3.08	13.00	1.49	33.1
Karar (1885)	3.18	13.69	1.72	33.8
Average	3.19	13.53	1.61	32.8
Hulls:				
Pusa No. 2	2.37	4.19	.....[2]	1.88
Pusa No. 7	2.14	2.56	.....	1.32
Pusa No. 25	1.92	4.44	.....	1.95
Sholapur No. 1	1.89	2.44	.....	1.53
Simla 66/1508	2.08	2.44	.....	1.97
Kardai (1068)	2.07	2.38	.....	1.90
Abmednager No. 1	2.04	2.44	.....	1.48
Karar (1885)	2.13	2.38	.....	1.51
Average	2.08	2.91	.....	1.69
Hulled seed:				
Pusa No. 2	4.78	26.12	3.37	58.6
Pusa No. 7	4.21	24.62	2.88	62.5
Pusa No. 25	4.60	24.06	3.02	61.8
Sholapur No. 1	4.15	22.25	2.72	64.1
Simla 66/1508	3.94	23.25	2.55	63.7
Kardai (1068)	4.14	22.31	2.73	64.0
Abmednager No. 1	4.08	23.12	2.63	63.4
Karar (1885)	4.13	23.94	3.01	63.1
Average	4.25	23.71	2.86	62.6

[1]Total soluble sugars as glucose.

[2]A sugar determination on a composite hull sample showed the presence of 0.3% sugar.

ture was determined by heating for two hours at 130° C., 2. ashing time was six hours, and 3. residual oil was determined by extraction in the Butt extractor for six hours without regrind. In all of these analyses moisture determinations were made where needed to correct results to a moisture-free basis.

The analytical methods used and described above are derived from the official methods of the American Oil Chemists' Society or the Association of Official Agricultural Chemists with some modifications. These modifications were developed through laboratory experiments. For example, ashing was carried out at 550° C. because this was the lowest temperature at which an ash of constant weight and satisfactory appearance could be obtained in a convenient length of time.

Each of the 28 sunflower and eight safflower oils was examined separately. The free fatty acids and iodine numbers were determined by the A.O.C.S. method. The thiocyanogen determinations and the calculations of glyceride composition were carried out in accordance with the last report of the Committee on Analysis of Commercial Fats and Oils (5). Linolenic acid was measured by alkali conjugation and ultraviolet absorption (6).

Results and Discussion

The results of the physical and chemical determinations are presented in tables I through V. In the case of the sunflower seed and oil data only averages of the seven locations are given. Differences between locations are, for the most part, minor; but, in the case of the iodine number of sunflower oil, except for the Greystripe variety, extremely wide variations occurred. The range in iodine number between locations was 108.6 to 133.4 for Mennonite, 109.5 to 131.6 for Sunrise, 133.4 to 139.7 for Greystripe, and 114.6 to 133.8 for Manchurian. The oil of lowest iodine number for each variety came from samples grown either at Manhattan, Kansas, or at Ames, Iowa. The presence of very small but definite amounts (0.1% or less) of linolenic acid in some sunflower oils was established by spectrophotometric analysis. It is possible that traces of this acid were present in all sunflower samples, but this could not be definitely established. All samples of safflower oil contained linolenic acid in amounts from 0.04 to 0.13%. It should be borne in mind that no great significance can be attached to variations which are based on results obtained on samples from only one season. In Table V are given the F values for a statistical analysis of the data on sunflowers. The effects of variety and station are marked on almost all quantities determined.

The oily material extracted from the sunflower hulls, although called "oil", is obviously not closely related to sunflower seed oil. All hull extracts were combined, and the light, semi-solid, waxy material had a saponification equivalent of 270.8 and an iodine number of 62.3. Spectrophotometric examination indicated 1.8% linolenic and 10.1% linoleic acid. The quantity of such material available was not sufficient for further investigation, but it is probable that it contained a large amount of unsaponifiable matter.

The analyses for both sunflower and safflower seeds and oils are in general agreement with the values listed by Jamieson (7). Oils from both crops have been imported and are being utilized commercially. Future domestic production of these oilseeds depends chiefly on agronomic and cultural factors not pertinent to this study. Mennonite and Sunrise are sunflower varieties low in height when mature whereas Greystripe and Manchurian averaged 11½ and 6½ feet in height, respectively, for the seven test plots analyzed. Mennonite and Sunrise are the two varieties most studied and recommended in the Canadian reports. One disadvantage of these sunflowers, particularly Sunrise, is that their smaller seeds are very attractive to birds so that small acreages of these crops if grown near wooded areas may be very severely damaged. Although much experience in growing these crops, in processing the seeds, and in using the oils, is available, it is probable that an extensive, long-term program of work involving the cooperation of agronomists, farmers, processors, and users must be carried out before the advisability of large-scale cultivation is established. Information such as is presented in this paper is necessary for the preliminary consideration of such a project.

Summary

Chemical analyses of sunflower and safflower seeds, the hulled seed, and the hulls and oils have been made. The 28 samples of sunflower seed, representing

TABLE IV.

Characteristics of Oils From Hulled Seeds (Averages by Variety)

Variety	Free fatty acid	Unsaponifiable	Refractive index n_D^{25}	Iodine No.	Thiocyanogen No.	Glycerides[1]		
						Saturated	Oleic	Linoleic
Sunflowers (Grown at seven stations in 1943):	%	%				%	%	%
Mennonite	0.97	0.8	1.47230	122.4	80.8	9.7	39.1	51.2
Sunrise	.38	.8	1.47234	122.8	78.4	12.8	32.3	54.8
Greystripe	.34	.7	1.47376	136.6	81.3	10.5	21.2	68.3
Manchurian	.40	.8	1.47316	130.5	80.4	11.1	27.0	62.0
Average	0.52	0.8	1.47289	128.1	80.2	11.0	29.9	59.1
Safflowers (Grown at Huntley, Montana, in 1943):								
Pusa No. 2	0.37	.....[2]	1.47489	147.2	85.2	6.7	16.7	76.6
Pusa No. 7	1.05	.....	1.47520	149.6	85.7	6.3	14.7	79.0
Pusa No. 25	.95	.....	1.47476	149.8	86.7	5.0	17.0	78.0
Sholapur No. 1	1.40	.....	1.47499	148.8	86.2	5.6	17.0	77.4
Simla 66/1508	1.70	.....	1.47497	149.8	85.9	6.0	15.0	79.0
Kardai (1068)	1.82	.....	1.47494	148.8	86.3	5.4	17.3	77.3
Ahmednager No. 1	1.55	.....	1.47489	149.2	86.1	5.7	16.3	78.0
Karar (1885)	.88	.....	1.47510	149.4	86.6	5.0	17.3	77.7
Average	1.22	.....	1.47497	149.1	86.1	5.7	16.4	77.9

[1]The average linolenic acid content was less than 0.1% and was neglected in calculating the glyceride compositions.
[2]A determination on a composite sample of safflower oil showed the presence of 0.5% unsaponifiable matter.

TABLE V.

F-Values for Physical and Chemical Analyses. Data From Four Varieties of Sunflower Seeds Grown at Seven Stations in 1943

	Bu. test weight	Weight per 1000 kernels	Proportion hulled seed	
Whole seed (air-dry basis):				
Varieties	9.84[1]	108.82[1]		9.60[1]
Stations	2.89[2]	6.24[1]		8.99[1]
Hulls (moisture-free basis):	Ash	Nitrogen	Oil	
Varieties	1.02	7.25[1]	1.85	
Stations	6.06[1]	10.26[1]	1.85	
Hulled seed (moisture-free basis):	Ash	Nitrogen	Sugar	Oil
Varieties	.80	2.13	3.70[2]	5.81[1]
Stations	6.35[1]	7.01[1]	3.02[2]	5.78[1]
Oil from hulled seed:	Iodine No.	Oleic acid	Linoleic acid	
Varieties	13.00[1]	11.93[1]	12.62[1]	
Stations	5.27[1]	7.16[1]	6.42[1]	

[1] Significant, 1% point.
[2] Significant, 5% point.

four varieties grown at seven locations, contained an average of 29% oil which was composed chiefly (51 to 68%) of linoleic acid glycerides. The eight varieties of safflower seeds grown at Huntley, Montana, contained an average of 33% oil, with an average content of 78% linoleic glycerides. Data on the amounts of ash, nitrogen, sugar, as well as oil, are presented for the whole seeds and their fractions.

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Some Factors Which Affect the Determination of Oil in Soybeans[1]

F. I. COLLINS and ORLAND A. KROBER[2]

ACCURATE determination of the percentage of oil in soybean seed is of great importance to the plant breeder in the development of high oil producing strains. It is equally important that cooperating laboratories be able to secure comparable analyses. Commercial processors of soybeans are also vitally interested in improving the accuracy and reproducibility of their analyses. The present official A.O.C.S. method (1, 2) is still subject to considerable variation as shown by the fact that in the analysis of seven samples by 79 collaborating laboratories the standard deviation was about 0.34% oil. Some of the variations in results may be caused by differences in fineness of initial grinding, moisture content of the meal, relative humidity, and different techniques at regrind time. It was the purpose of this investigation to study the effect of these factors on the determination of oil in soybean seed.

Materials and Methods

The soybeans studied comprise lots of four varieties (Chief, Dunfield, Lincoln, and Illini) each of which was carefully cleaned and divided with a Boerner sampler into portions of several hundred grams each. Some of these samples were predried, using the official A.O.C.S. method (1), and immediately placed in one quart metal containers with tightly fitting lids. Other portions were predried under vacuum over Drierite for more than a month. These soybeans were ground with the following mills: Wiley mill, with 2 mm, 1 mm, and 35 mesh screens, Mikro-Pulverizer, Bauer, and Arcade Mills. The samples were ground in laboratories using these mills in their regular work and by operators familiar with their best operation. All the samples were kept as dry as possible during the initial grinding and subsequent analysis. Two ranges of relative humidity (determined with Friez Hygro-Thermograph) were used, the lower range being 30-34% and the higher range 60-65%. Condensers were capped with lead foil during the oil extraction to prevent possible condensation of atmospheric moisture inside of the condensers. Moistures were determined by the official method (1) except that 2 grams of the sample were used instead of 5 grams.

Moistures were determined in partially extracted samples by means of a modified Karl Fischer reagent as prepared by Krober and Collins (3). Samples for this moisture determination were placed in 200 ml centrifuge bottles, and 50 or 100 ml of methanol added. The bottles were tightly stoppered and allowed to stand overnight. These samples were centrifuged 30 minutes, and a suitable aliquot of the clear solution was taken for analysis. The aliquot was treated with excess modified Karl Fischer reagent and then back titrated with standard water methanol solution using an electrometric titrimeter.

Iodine numbers were determined by the official A.O.C.S. Wijs method and were also calculated from the refractive index of the oil according to the equation developed by Majors and Milner (4) from 1938 Butt extracted soybean oil.

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