TABLE 5

Evaluation of Soybean Oil Content of Various Mixtures of Soybean Oils with Cottonseed Oils and Peanut Oils

Oils in Mixtures*			Soybean Oil in Mixture	Linolenic Acid in Mixture (Calculated)	Linolenic Acid Found	Soybean Oil Found	Deviation of Soybean Oil Found from Amount Present
Soybean	Cottonseed	Peanut					
			Percent	*Percent*	*Percent*	*Percent*	*Percent*
S-3	C-4		4.9	0.71	0.68	4.8	—0.1
S-3	C-4		10.0	1.10	1.02	9.4	—0.6
S-2	C-2		7.1	.93	.98	8.8	+1.7
S-3	C-6		15.0	1.40	1.47	15.5	+0.5
S-6	C-4		3.1	.54	.84	6.9	+3.8
S-6	C-6		9.9	.90	1.14	11.0	+1.1
S-1		P-1	7.3	.78	.85	7.1	—0.2
S-3		P-2	10.2	1.18	1.12	10.8	+0.6
S-6		P-2	15.0	1.39	1.50	15.9	+0.9
S-4	C-3		7.0	.75	.82	6.7	—0.3
S-5	C-3		5.0	.69	.80	6.4	+1.4
S-4		P-3	3.0	.56	.70	5.0	+2.0
S-5		P-3	5.0	.78	.83	6.8	+1.8

* See Table 4 for description of oils.

triene conjugation, due to the linolenic acid content of the soybean oil and the apparent linolenic acid content of the cottonseed oil. Thus, for unknown mixtures only average value corrections can be made for apparent linolenic acid content and the accuracy of a particular analysis will depend upon how well the composition of the oils in the particular mixture follows those of the average mixture.

The method described can be extended to mixtures other than those of soybean and cottonseed oils. Thus, soybean oil may be determined in admixture with a peanut oil. In general, any oil which has an unsaturated fatty acid capable of producing triene conjugation upon alkali isomerization can be determined in the presence of any other oil containing no appreciable quantity of unsaturated fatty acids which can produce triene conjugation by such treatment.

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Buttonweed Seed Oil A Source of Linoleic Acid

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BUTTONWEED is listed as one of the secondary noxious weeds of the state of Iowa. The botanical name is *Abutilon theophrasti,* and it is a member of the *Malvaceae* family. It is also known as velvet weed and butterprint. The weed is an annual, but its seeds retain their vitality in the soil so long that many think it is perennial. Mature plants are frequently six feet high with few branches. The seeds are borne in a capsule, shaped like a butter print.

In fields where its growth is abundant the plant is of uniform height of about four to five feet. The seeds are among the most abundant which are screened out of soybeans and are frequently sold to feed companies along with other screenings to be ground into feed.

One of the best ways of controlling this weed, which is becoming a serious menace to crops, would be to collect the seed along with the soybeans and subsequently separate them for extraction of the oil. At the present time an average size seed cleaning plant will produce about five tons of buttonweed seeds during a season.

A search in the literature revealed that Jolson (1) had made a brief study of some of the properties of a cultivated variety of Abutilon seed. No attempt was made to obtain a component analysis of the oil, however. The statement is made that the oil is similar in all its properties to cottonseed and soybean oils.

Experimental

Extraction. Buttonweed seeds for the present study were collected in the vicinity of Newton, Iowa, and were ground in an attrition mill to prepare them for extraction. The oil was extracted with hexane in a large modified Butt extractor. The main portion of the solvent was removed from the oil by straight distillation. Last traces of solvent were removed by bubbling in nitrogen under vacuum. The extracted oil, amounting to 16 to 18%, was dark, yellow green with an iodine value of 130 to 133.

It was observed that seeds obtained at different locations gave oil with a wide variation in iodine value. In one particular field the seeds yielded an oil with an iodine value of 115. The yield of oil from these seeds was somewhat lower, being about 15%.

TABLE I

Physical and Chemical Characteristics of Buttonweed Seed Oil and Meal

	Wild Buttonweed	Cultivated Abutilon (1)
Weight per 1,000 seeds, g.	9.6	17.5
Moisture content of air-dry seeds, %....	11.1	9.7
Oil content, %.....	16.9	16.5
Protein content of air-dry, oil free meal, %.....	9.3	19.8
Iodine value of oil (Wijs).....	130.7	131.7
Acid value of oil, %.....	3.41	4.42
Specific gravity.....	$0.9227\,^{25}_{25}$	$0.9282\,^{20}_{20}$
Refractive index @ 25° C.	1.4730	.....
Saponification value.....	193.17	190.6
Unsaponifiable matter, %.....	1.36	0.8
Acetyl number.....	6.8	.....
Hydroxyl number.....	6.8	.....
Gardner break, %.....	0.09	.....
Total saturated acids (Bertram Oxidation), %.....	14.0	.....

Apparently, however, the higher iodine value oil predominates because seeds obtained from a seed cleaning establishment gave the higher iodine value oil.

In order to obtain oil which had not been subjected to any heat some ground seed was extracted with isopentane for six hours. The oil recovered was never subjected to a temperature higher than 30° C., and for the most part the solvent was removed at 0° to 20° C. under high vacuum. The iodine value of this oil was 132.1. The oil was a very light yellow color and amounted to 14.4% of the ground seed.

When the pentane-extracted meal was further extracted with hexane, 2.5% more oil was removed, which was a very dark yellow green. It had an iodine value of 127.6. This oil from the meal when completely extracted with hexane had an iodine value of 130.7.

The physical and chemical properties of the seeds and freshly extracted crude oil are shown in Table I and are compared with the properties reported by Jolson. Obviously, from a comparison of the weight per 1000 g. of seeds the cultivated seeds are about twice the size of the wild variety.

Composition of the Buttonweed Oil. In order to obtain the composition of the buttonweed seed oil, 500 g. of crude hexane-extracted oil was converted to the methyl esters by refluxing with 160 g. of absolute methanol and 2.5 g. of sodium hydroxide. 420 g. of crude esters and 91 g. of a mixture of phosphatides and glycerine were produced. The crude esters were subjected to vacuum distillation from an ordinary distilling flask at about 1 mm. pressure. Next 97.4% distilled over, having an iodine number of 136.02.

Then 308 g. of these distilled esters were subjected to fractional distillation in a 19 mm. diameter column with a 4-foot packed section of 1/8" single turn stainless steel helices. The column was the Whitmore and Lux type with a total reflux and partial takeoff distilling head. The column had an efficiency of 26 theoretical plates. The distillation was carried out at 3.2 to 3.4 mm. until 90.2 weight per cent had distilled over; the temperature in the head of the column began to fall even though the pot temperature had risen to 315° C. The pot was then removed from the column and the contents distilled over by straight distillation at 3 mm. pressure until the vapor temperature rose to 338°C.

The distillation was followed by plotting the weight of each fraction against refractive index. This is shown in Fig. I. Fractions amounting to about 3% of the charge were taken. By combining fractions

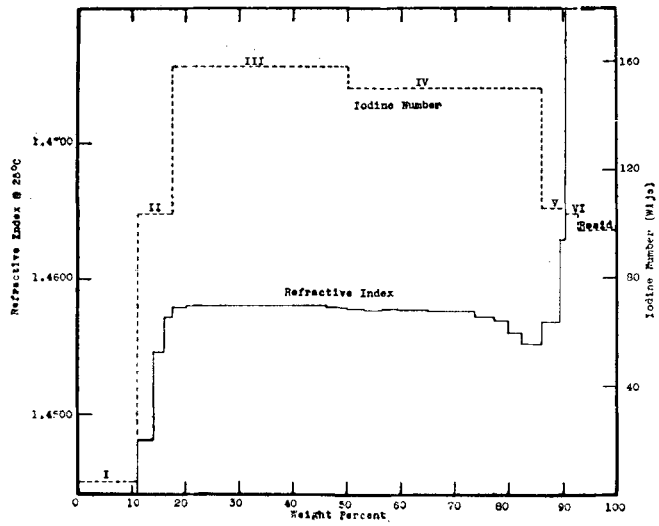

FIG. I. Fractionation of buttonweed oil methyl esters.

according to refractive index and with the aid of the temperature of distillation a cut (I) containing only C_{16} fatty acids, an intermediate cut (II), C_{18} front ends (III), a C_{18} heavy ends (IV), fractions distilling higher than C_{18} (V and VI) and a distillation residue was obtained. Iodine, thiocyanogen, saponification values, and refractive indexes were determined on each fraction and the composition determined. The iodine values of the combined fractions are also shown in Fig. I.

In the case of the C_{18} methyl esters Bertram oxidations were run on each of the combined Fractions III and IV. Fraction III contained only a trace while Fraction IV contained 2.6% saturated acid. This latter solid fatty acid was recrystallized and a melting point taken. The material was shown to be stearic acid. It is of considerable interest that merely by fractionation the composition of Fraction III contained 83.8% methyl linoleate, 16.2% methyl oleate, and a trace of methyl stearate and methyl linolenate. This made up 32.3% of the total methyl esters. Fraction IV which was 35.7% of the total product contained 74.6% methyl linoleate, 22.8% methyl oleate, and 2.6% stearic acid.

Fraction V distilling over following the C_{18} plateau and amounting to 3.3% of the total product had a saponification value of 198.39, an iodine value of 106.8, a thiocyanogen value of 60.3, and refractive index @ 25° of 1.4600. From the saponification value the mean molecular weight of the fraction was 282.4, which is considerably lower than the molecular weight of a methyl ester of a C_{18} fatty acid. Lack of sufficient sample prevented further investigation, but a possible component of this fraction is an unsaturated hydroxy-fatty acid of a lower fatty acid.

Fraction VI which was obtained from a crude distillation of the pot residue following completion of Fraction V had a saponification number of 184.00, an average molecular weight of 304.4, iodine value of 103.89, thiocyanogen value of 28.95, and a refractive index of 1.4800 @ 25° C. It distilled over the range 271° to 338° C. @ 3 mm. The fraction was obviously a mixture and consisted of 5.1% of the total. No further attempt was made to characterize this product.

The residue, amounting to 4.7%, was mostly polymer formed during the prolonged heating of the

methyl esters. It was a dark brown viscous semi-solid with an iodine value of 98.29.

The total composition of the oil is reported in Table II as calculated from the above fractionation.

Spectrophotometric analysis of the pentane-extracted oil previously mentioned in this paper showed 0.14% of conjugated diene acids and 0.01% conjugated triene acids. After alkali conjugation it was estimated that 1.0% linolenic acid was present. Analysis of the individual fractions by thiocyanogen and iodine value did not indicate more than a trace of linolenic acid. It is possible that the conjugated triene acid was from a fatty acid of different molecular weight than linolenic acid. We, therefore, have indicated linolenic acid as present but not in significant quantities.

TABLE II

Composition of the Mixed Fatty Acids of Buttonweed Seed Oil

Fatty Acid	Weight Percent
Myristic	trace
Palmitoleic	0.6
Palmitic	12.2
Linolenic	trace
Linoleic	58.0
Oleic	14.1
Stearic	0.9
Boiling above C_{18} fatty acids	9.4
Residue	4.7
	100.0

The outstanding fact from this analysis is the very high percentage of linoleic acid in the C_{18} fatty acid group. The ease of separation of this fraction from the rest of the product makes this oil an unusually good source of linoleic acid.

Discussion

The composition of the variety of buttonweed (Abutilon) studied by the authors is considerably different from either cottonseed or soybean oil and disagrees with the work of Jolson in this respect.

The importance of buttonweed seed oil appears to be primarily in its high linoleic acid content. This is particularly valuable because of the ease with which a high concentrate of linoleic acid may be obtained by simple fractionation.

In view of the present shortage of oils the recovery of this oil from seeds which at the present time are either thrown away or sold as screenings to feed mills appears to have considerable promise. The most serious drawback is the relatively low oil content. However, this is largely offset by the low cost of the seed.

Summary

Buttonweed seeds (Abutilon theophrasti) contain 15 to 17% oil. The oil contains about 58% linoleic acid which may be concentrated by simple fractionation into fractions containing as high as 83% of the acid. This suggests the possible use of the oil as a source of linoleic acid. The seed also has an appreciable sterol content.

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Dilatometric Investigations of Fats

III. The Density, Expansibility, and Melting Dilation of Some Simple Triglycerides and Other Fats

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PREVIOUS papers (2, 8) in this series have called attention to the usefulness and the convenience of dilatometry as a tool in phase investigations of fats. However, in general, dilatometric data can be interpreted quantitatively only if one knowns accurately the volume changes associated with phase transformations in the material examined, as well as the thermal expansibility of the material, in both solid and liquid states.

There are data in the literature on the thermal expansibility of liquid commercial fats (9, 15) and also on certain pure liquid triglycerides (7). However, accurate information on the expansibility of fats in the solid state or on the volume changes accompanying melting and polymorphic transformations is wholly lacking. The purpose of this investigation has been to supply such information.

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Samples

Samples of trilaurin, trimyristin, tripalmitin, tristearin, triolein, and trielaidin were prepared from purified fatty acid chlorides, as described previously (1). Neutralization values of the saturated fatty acids and iodine and thiocyanogen values of the unsaturated acids agreed with theoretical values for pure materials within experimental errors of the methods. Previous experience had shown that the method of esterification employed, using acid chlorides in 10% excess over the glycerol, produces a material containing less mono- or diglycerides than can be detected by chemical methods.

The samples of partially hydrogenated and highly hydrogenated cottonseed oil, which had iodine values of 59.5 and 0.85, respectively, were the same as those employed in previous calorimetric investigations (10, 12). The lard used was a commercial sample of prime steam lard which had an iodine value of 66.6.