

## SPECTROPHOTOMETRIC STUDIES OF THE COMPOSITION OF THE SEED OILS OF PLANTS OF THE MAYDEAE TRIBE<sup>1</sup>

RICHARD H. WILEY AND PHIL H. WILKEN

Received May 7, 1951

Current systematic practice divides the Maydeae tribe of the Gramineae (grass) family into six or seven genera. These include three genera—*Zea* (maize), *Euchlaena* (teosinte), and *Tripsacum*—native to America; one genus—*Coix lacryma* (Job's Tears)—a native of Asia; and three or four less well known genera. The economic importance of corn and the question of the origin of corn have resulted in several studies of the genetic and morphologic relations among these genera. The purpose of this study is to obtain comparative information about the chemical composition of the seed oils from plants of this tribe.

At this time we wish to report data on the physical properties and on the chemical composition as determined by ultraviolet spectroscopy of the seed oils of representatives of four of these genera—*Coix*, *Euchlaena*, *Tripsacum*, and *Zea* (maize). The data for the seed oils from five varieties of maize, previously unrecorded, have been obtained during this study and are reported also.

### RESULTS

The per cent oil obtained from these seeds is given in Table I. The five varieties of corn studied here contained 3.78–4.33% oil. These values are in the same ranges as those reported elsewhere. The seeds of *Coix*, *Tripsacum*, and *Euchlaena* contained 8.75–10.30% oil which indicates a distinctly greater oil content than corn.

The physical constants for the oils are given in Tables I and II. The specific gravity values of the eight oil samples are nearly identical; the refractive index values (Table I) for the oils from the corn samples, teosinte, and *Tripsacum* are in the range 1.472–1.474. That for *Coix* oil, 1.467, is distinctly lower than the others. The saponification values (Table I) of the oils from the corn samples, teosinte, and *Tripsacum* vary from 169–192 with the corn oil values in the high part of this range. Again the value for *Coix* oil, 151, is distinctly low. The iodine values (Table II) of the oils range from 109 to 133 again except for *Coix* oil which has an iodine value of 94.8. The iodine values for corn oil fall in the range 109–127; that for teosinte oil is at the low end of this range; and that for *Tripsacum* oil, 133, is highest of the group. These variations in iodine value are greater than those usually given for the iodine values of corn oil or linseed oil (1). The data indicate rather clearly that *Coix* oil is distinct from the oils of other members of the group.

The ultraviolet absorption spectra before and after alkali-isomerization have been obtained by standard procedures using recognized precautions. Only general absorption is observed before isomerization. After isomerization varying

<sup>1</sup> Presented at the Cleveland meeting of the American Chemical Society, April, 1951.

absorption at 234  $m\mu$  is observed with maxima as reported in Table II. Low intensity absorption at 270  $m\mu$  has been observed after isomerization. The only major difference in the absorption curves is the intensity of the absorption maxima at 234  $m\mu$ . In general all curves have the same shape. These data indicate the absence of any significant amount of triene structures and varying amounts of diene structure in the oils.

TABLE I  
PHYSICAL PROPERTIES OF OILS

OIL	$n_D^{20}$	Sp. Gr. 20/20	SAPONIFICATION VALUE	PER CENT OIL
Corn <sup>a</sup>	1.473-1.474	0.921-0.927 <sup>b</sup>	188-193	3-6.5
Corn <sup>c</sup>	1.473	.920	173	3.18
<i>Coix lacryma</i>	1.467	.917	151	10.18
Teosinte	1.472	.918	169	8.75
<i>Tripsacum</i>	1.472	.919	175	10.30
Corn <sup>d</sup>	1.474	.920	187	3.30
Corn <sup>e</sup>	1.472	.921	192	4.33
Corn <sup>f</sup>	1.473	.919	185	3.60
Corn <sup>g</sup>	1.474	.922	184	4.20

<sup>a</sup> From Jamieson (1), p. 177. <sup>b</sup> At 15°. <sup>c</sup> Truckers Favorite. <sup>d</sup> Hickory King (Flint). <sup>e</sup> T.N.T. pop corn. <sup>f</sup> Hybrid (U.S. 13). <sup>g</sup> Yellow Dent.

TABLE II  
COMPOSITION OF OILS FROM SPECTROMETRIC DATA

OIL	IODINE VALUE	SPECIFIC ABSORPTION <sup>a</sup>	DIENE, %	MONOENE, %	SATURATED, %
<i>Coix lacryma</i>	94.8	19.8	22.8	59.6	17.6
Teosinte	109	31.7	36.4	47.8	15.8
<i>Tripsacum</i>	133	43.8	50.4	46.4	3.2
Corn <sup>b</sup>	—	—	56	30	10.6
Corn <sup>c</sup>	—	—	34.0	50.4	15.6
Corn <sup>d</sup>	127	45.7	52.4	35.6	12.0
Corn <sup>e</sup>	109	31.6	36.3	48.2	15.5
Corn <sup>f</sup>	122	38.6	44.3	46.5	9.2
Corn <sup>g</sup>	123	31.0	39.9	56.3	3.8
Corn <sup>h</sup>	114	34.8	35.7	55.1	9.2

<sup>a</sup> At 234  $m\mu$  after alkali isomerization. <sup>b</sup> Reference 3. <sup>c</sup> Reference 4. <sup>d</sup> Truckers Favorite. <sup>e</sup> Hickory King (Flint). <sup>f</sup> T.N.T. pop corn. <sup>g</sup> Hybrid (U.S. 13). <sup>h</sup> Yellow Dent.

Following procedures given in the literature (2) the absorption data were used to calculate the percentages of saturated and unsaturated structures present. The data for all of the oils are given in Table II. Apparently this is the first time this method has been reported for determining the composition of a corn oil. The compositions thus determined fall within the rather wide range that has been established using other methods (3-5). With respect to per cent diene structure teosinte oil (36.4% diene) is at the low and *Tripsacum* oil (50.4%

diene) is at the high end of the corn oil range (35.7–52.4% diene). Coix oil (22.8% diene) is significantly below the corn oil range. With respect to monoene structure teosinte oil (47.8%) and Tripsacum oil (46.4%) are in the middle of the corn oil range (35.6–56.3%) and Coix oil (59.6%) is slightly over the range. The per cent saturated structure is highest for Coix oil (17.6%) and lowest for Tripsacum oil (3.2%) with corn oil ranging from 3.2 to 15.5% and teosinte oil at 15.8%. This variation in the per cent saturated structure in the corn oil samples is greater than is usually observed in oils of a given species and perhaps should be studied in more detail before final acceptance.

## DISCUSSION

It is generally recognized (6) that seed fats from morphologically related plants show similarities in their composition. Thus, in some cases a plant family will produce a highly characteristic structural type as the chaulmoogric and hydnocarpic acids produced by the Flacourtiaceae. Some species of a genus

TABLE III  
COMPARISON OF COMPOSITION OF SEED OILS OF THE GRAMINEAE FAMILY<sup>a</sup>

OIL	DIENE, %	MONOENE, %	SATU- RATED, <sup>b</sup> %	OTHERS
Sorghum	Ca. 24	Ca. 48	28	
Oat (germ)	31	59	10	Linolenic (0.5–1)
Barley (seed)	54	33	12	Linolenic (0.5)
Rice (bran)	40	42.5	17.5	
Rye (seed)	61	18	21	Linolenic (3)
				Arachidic (0.2)
Wheat (germ)	57	12	22	Linolenic (6)
Millet	58	24.5	12	Linolenic (5.5)
Corn (germ)	56	30	10	Various (3.0)

<sup>a</sup> Selected from Hilditch (6), p. 207. <sup>b</sup> Mostly palmitic acid.

produce distinctive fatty acids as the ricinoleic acid produced by *Ricinus communis* of the Euphorbiaceae. Moreover, Hilditch (6) has made extensive comparisons which show that oils from plants which are morphologically related are similar in the relative proportions of the common acids. A significant qualifying factor is that climatic factors are known to influence the relative saturation of oils of plants of a given species. More unsaturation is present in oils from seeds grown in cooler climates.

The oils of the Gramineae family are characterized as having 10 to 15% of palmitic, 30 to 60% of oleic, and 60 to 30% of linoleic acid glycerides. Comparative data are given in Table III. The available data are not complete enough to make a precise evaluation of variations within this extremely large and diverse family in accordance with tribal subclassifications used by taxonomists. Some relations have been pointed out by Hilditch. The data made available in this study permit a preliminary comparison of the seed oils of several genera of the Maydeae tribe of the Gramineae family among themselves and with seed oils

from members of other tribes of the family. This is of interest in connection with genetic and morphological studies of relations among these important plants.

The data in Tables II and III show that the oils of the *Tripsacum*, *Euchlaena*, and *Coix* genera are similar to oils produced by other plants of this family. The component acids are predominately oleic and linoleic with the remainder being principally saturated. The oil of *Coix lacryma* has the lowest iodine number and is thus most saturated. This arises from a higher saturated acid content and lower linoleic acid content although the oil has the highest oleic acid content (59%) of the eight oils. In fact, the oleic acid content is at the upper limit observed for oils of the entire family.

Comparisons within the tribe show that our samples of teosinte oil and corn oil are similar and that *Tripsacum* oil resembles these two more closely than does *Coix* oil. Genetic and morphologic relations show teosinte and corn to be most alike: *Tripsacum* to be somewhat different; and *Coix* to be most unique.

#### EXPERIMENTAL

The seeds used in this study were obtained from various sources. *Coix* seeds, purchased from the Bunton Seed Company, Louisville, Kentucky, were described as California raised. *Tripsacum* seeds were collected during the late fall of 1950 from plants growing in Spencer County, Indiana.<sup>2</sup> Two gallons of seeds in the hulls were gathered in four hours by two workers. Teosinte seeds (*Euchlaena mexicana*) were obtained from the Oficina Estudios Especiales Sag., San Jacinto, Mexico.<sup>3</sup> The Flint corn was grown in Baren County, Kentucky;<sup>4</sup> the Yellow Dent in Knox County, Kentucky;<sup>4</sup> the pop corn was grown in southern Indiana; the Hybrid in Jefferson County, Kentucky;<sup>5</sup> and the Truckers Favorite corn was grown in Jefferson County, Kentucky.<sup>6</sup>

*Isolation of the oils.* The kernels of the *Coix*, *Euchlaena*, and *Tripsacum* seeds were separated from the hulls by breaking the hulls with a small hammer; when necessary the kernels were removed from the broken hulls with a glass rod which had been drawn to a sharp point on one end. In the case of corn the whole grain was used. The Truckers Favorite corn was partly ground by passing it through a food chopper while the other four corn samples were partly ground by hitting a few kernels at a time in a mortar with a pestle. It was found desirable to extract the kernels for a few hours before grinding. Kernels which were ground without an initial extraction period showed a tendency to form a pasty-like mass which caused the contents of the mill jar to adhere to the walls of the jar thereby effectively stopping the grinding. The powdered meal from the grinding process was transferred to a 500-ml. Soxhlet extractor. The extraction, using petroleum ether, b.p. 60–80°, was continued for a period of 3 to 5 days after which time continued extraction with a fresh charge of solvent gave no further yield of oil in any case. After extraction, most of the solvent was removed by distillation in a water-bath at about 80°. Last traces of solvent were removed under a vacuum. A light yellow oil was recovered in each instance and stored in an inert atmosphere.

*Isomerization of the oils.* The procedure of Mitchell, Kraybill, and Zscheille (2) was employed except that 95% ethanol was substituted for 98% ethanol as a solvent for absorption

<sup>2</sup> The authors are indebted to Dr. Paul Weatherwax of Indiana University for assistance in helping us locate this growth.

<sup>3</sup> The authors are indebted to Dr. Efraim Hernandez for the gift of these seeds.

<sup>4</sup> The authors are indebted to Ross Seed Company for the gift of these samples.

<sup>5</sup> The authors are indebted to Mr. K. H. Maddox for the gift of this sample.

<sup>6</sup> The authors are indebted to Mr. E. K. Dienes for the gift of this sample.

measurements. Reasonable care was used in carrying out the isomerization under standardized conditions. The standardization was, however, less rigorous than that suggested elsewhere (7).

*Ultraviolet absorption.* Measurements were made with a Beckman Model DU quartz spectrophotometer using 1.00-cm. cells.

*Iodine values, saponification values, specific gravity, index of refraction:* These values were found using procedures previously described (7). Because only limited supplies of oils were available, saponification values were determined on 1-gram samples.

#### SUMMARY

Previously undescribed seed oils of three genera of the Maydeae tribe of the Gramineae family—*Coix lacryma* (Job's Tears), *Tripsacum*, and *Euchlaena mexicana* (teosinte)—have been isolated and characterized by saponification value, iodine value, refractive index, and specific gravity. The saponification values range from 151–175; the iodine values from 95–133; the refractive index values from 1.467–1.472; and the specific gravity values from 0.917–0.919. The oil was obtained in yields of 8 to 10% from the kernels.

Ultraviolet absorption spectra of these oils compared with those of oils obtained from five varieties of corn before and after alkali isomerization show these oils to fall within the general pattern for the composition of oils of the Gramineae. The Coix oil is most saturated with an iodine number of 94.8 and differs most clearly from the others. The oils consist of 22.8 to 50.4% of diene structure, 46.4 to 59.6% of monoene structure, and 3.2 to 17.6% of saturated structure.

LOUISVILLE 8, KENTUCKY

#### REFERENCES

- (1) JAMIESON, *Vegetable Fats and Oils*, Reinhold Publishing Company, New York, 1943, pp. 15, 178, 270.
- (2) MITCHELL, KRAYBILL, AND ZSCHEILLE, *Anal. Chem.*, **15**, 1 (1943).
- (3) BAUR AND BROWN, *J. Am. Chem. Soc.*, **67**, 1899 (1945).
- (4) LONGNECKER, *J. Biol. Chem.*, **129**, 13 (1939).
- (5) BAUGHMAN AND JAMIESON, *J. Am. Chem. Soc.*, **43**, 2696 (1921).
- (6) HILDITCH, *Chemical Constitution of Natural Fats*, John Wiley and Sons, New York, 1949, pp. 8–15.
- (7) Official Methods of the American Oil Chemists' Society.