Mexican Prickly Poppy Seed Oil*

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The Mexican prickly poppy (Argemone mexicana) is an annual plant indigenous to Mexico, where it is known as "chicacote," but it has been introduced into many tropical and subtropical countries. In Brazil the plant is known as "Cardo santo" and "Cardo amarello"; in India it is known as "katakar." The seeds are small dark-brown striated spheres about 1.5 to 2 mm. in diameter and somewhat resemble mustard seed in appearance. One thousand seeds weigh 2.519 grams and occupy a volume of 4.5 ml.

Several investigators haxe expressed or extracted the oil from Argemone seeds grown in various places, and some have reported the characteristics of the oil they obtained. An anonymous report (1) gave the following characteristics of Argemone oil obtained from seed collected in South Africa: Sp. gr. 15°, 0.9220; $n_D^{40°}$, 1.466 (equivalent to $n_D^{25°}$ 1.472); iodine value, 123.7; saponification value, 192.7; and unsaponifiable, 1.14%. Argemone oil from seed grown in India was studied by Watson and Sudborough (2) and by Iyer, Sudborough and Ayyar (3). The characteristics of this oil are: $n_D^{60°}$, 1.4601 (equivalent to $n_D^{25°}$ 1.4734); iodine value, 121; saponification value, 190; acid value, 12.0; acetyl value, 39; unsaponifiable, 1.3%. The similarity of refractive index, iodine and saponification values of this oil and of the oil studied in this laboratory indicate that the two specimens had the same composition. Iyer, Sudborough, and Ayyar (3) reported the following composition for the Argemone mixed fatty acids: Palmitic, 7.95%; stearic, 5.95%; palmitoleic, 5.87%; oleic, 21.79%; linoleic, 48.02%; linolenic, 0.58%; and ricinoleic, 9.84%. Our results differ from these in several respects, as is brought out fully in the experimental part of this paper.

In India and the West Indies, Argemone oil is used as an illuminant and in medicine as a purge. Sarkar (4) stated that Argemone oil is a violent poison and reported a case in which Argemone oil was unintentionally mixed with mustard oil used in frying cakes. Persons who ate the cakes suffered with pain throughout the body, inflammation from toes to hips, diarrhea or constipation and fever (38.3°C.). The oil could probably be used by the soapmaker. Although it has been stated that the oil is used in paints (5), we found that a film of the oil on a glass slide showed no tendency to form a film when exposed to bright sunlight for several days.

Experimental

The oil used in this investigation was expressed from seed grown in Mexico, which was obtained through the courtesy of the Sherwin Williams Co. The seed contained 35.9 per cent of oil and 8.4 per cent of moisture. The oil was expressed from the seed in this laboratory in an expeller press; it was yellow in color and had the characteristics reported in Table 1.

TABLE 1

Characteristics of Argemone Oil

Acid value	2.28
Refractive index at 25°	1.4731
Iodine value, Wijs, 1 hr. 20°	127.8
Thiocyanogen, value, 0.1 *N*, 24 hrs. 20°	77.7
Saponification value	190.8
Acetyl value	6.3
Unsaponifiable, per cent	1.4
Saturated acids, Bertram method, per cent	13.2
Saturated acids, lead salt-ether method, per cent	13.3
Unsaturated acids, per cent	80.3

Fatty Acids of Argemone Oil

The characteristics of the mixed Argemone fatty acids, from which the unsaponifiable matter had been removed, are given in Table 2.

TABLE 2

Characteristics of Argemone Fatty Acids

Iodine value, 1 hr. 20°	133.4
Thiocyanogen value, 0.1 *N*, 24 hrs. 20°	78.7
Saponification value	200.5
Acetyl value	0.12
Saturated acids, Bertram	14.0

Unsaturated Acids

It has been stated that Argemone oil contains ricinoleic (9.8%), hexadecenoic (5.8%) and linolenic (0.6%) acids (2), in addition to the more common oleic and linoleic acids.

When bromine was added to a sample of the oil, dissolved in ether and cooled to 0° C., a small quantity of a brownish-red precipitate was obtained. This was doubtless due to a reaction between certain unsaponifiable constituents and the bromine, since no precipitate of hexabromstearic acid was obtained on adding bromine to a cold (0°) solution of the total fatty acids in ether. In order to be certain that linolenic acid was absent, the following experiment was conducted. The unsaturated acids obtained from the lead salt-ether separation were esterified with methanol. The distilled methyl esters (78.5 g.) were dissolved in 800 ml. acetone and cooled to —40° C. by addition of solid carbon dioxide to the solution. The precipitated esters were filtered and recrystallized from 100 ml. of acetone at this same temperature, the mother-liquors from this recrystallization being added to the mother-liquors from the first precipitation. These combined mother-liquors were then further cooled to —60° C. by further addition of dry ice and the precipitated esters again filtered. This crop was crystallized from 400 ml. of acetone at —60° and the filtrates again combined. These combined filtrates were then cooled to —67°C. by further addition of solid carbon dioxide. Each of the precipitates and the residue were freed of solvent by heating to 90-95° C. in vacuo and were then distilled at less than 1 mm. pressure. Wijs iodine values (1 hour, 20° C.) and thiocyanogen values (0.1 *N*, 24 hours, 20°C.) were determined on these methyl ester fractions. These data are reported in Table 3.

One and four-tenths grams of the residue, in which any linolenic ester would be concentrated, if it were

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TABLE 3

Methyl Ester Fractions, Obtained by Freezing

Fraction	Crude Wt.	Distilled Wt.	Iodine Value	Thiocyanogen Value
	g.	g.		
I	1.1	0.9	....	....
II	16.5	16.3	82.1	78.4
III	34.2	33.8	163.6	87.7
Residue	26.7	26.4	161.2	86.5

present in the oil, was dissolved in 30 ml. of dry ether, the solution cooled to —10° C. and bromine added until a yellow color persisted. No precipitate of insoluble hexabromide was obtained, thus demonstrating the absence of even small quantities of linolenic acid.

The Argemone oil examined in this investigation contained less than one per cent of hexadecenoic acid. In order to concentrate the hexadecenoic acid and to estimate the amount present, 125 grams of the free fatty acids were dissolved in 800 ml. of acetone and the solution cooled to —18° C. The saturated acids that separated from the solution at this temperature were filtered and recrystallized from 200 ml. of acetone. The combined filtrates were then concentrated to 300 ml., and again cooled to —18° C. The saturated acid fractions obtained by distilling these precipitates amounted to 14.11 and 2.20 g., respectively, and had iodine values of 2.5 and 1.7, respectively. The equivalent weight of these fractions was 263.0 and 260.0, respectively. The acetone was removed from the filtrate, and the unsaturated acids were fractionally distilled in vacuo through a jacketed, electrically heated column previously described (6). Five fractions were collected, but only the first fraction, weighing 10.71 g. differed from the others in boiling range or in equivalent weight. Fraction I was refractionated at 1 mm. pressure, through a shorter column, collecting three subfractions. Data on these fractions are reported in Table 4.

TABLE 4

Concentration of Methyl Hexadecenoate

Fractions	Boiling Range	Wt.	I	SCN	Equiv. Wt.	Satd. Acids (Bertram)
		g.				percent
I_1	160-167°C.	1.43	120.2	69.4	269.2	18.02
I_2	167-169°C.	4.57	144.3	83.0	276.0	9.03
I_3	169-170°C.	4.02	153.8	88.0	277.5	4.03

The amount of oil available was not sufficient to enable us to isolate and characterize the low-boiling, unsaturated acid which we have assumed to be hexadecenoic acid, since this has been shown to be a common constituent of vegetable oils. We were unable to make a precise determination of the hexadecenoic acid present in these three subfractions. Attempts to calculate the percentages of hexadecenoic, oleic and linoleic acids present in each of these fractions from simultaneous equations gave impossible results, due to the small difference between the thiocyanogen absorption values of the oleic, linoleic and hexadecenoic acids, which are 89.9, 93.0, and 99.8, respectively. It was possible to make an estimate of the hexadecenoic acid content of these subfractions, however, based on the neutralization equivalents of these fractions, and the assumption that the ratio of oleic and linoleic acids in these fractions was the same as in the unfractionated fatty acids. Errors introduced by making this assumption are slight, since this ratio could vary as much as 100% and cause only a slight error in the final result because the neutralization equivalent of linoleic acid is only two units lower than that of oleic acid, whereas that of hexadecenoic acid is 28 units lower than that of oleic acid. The neutralization equivalent of each subfraction was first corrected for that of the saturated acids, determined by the Bertram oxidation method. In this way it was estimated that fraction I_1 contained 34.8% of hexadecenoic acid and fractions I_2 and I_3 contained 12.9% and 3.3%, respectively. These values are equivalent to 0.98% of hexadecenoic acid in the unsaturated acids fraction.

The acetyl value of 6.3 of Argemone oil would indicate that the oil contained 4.0% of ricinoleic acid; this value is less than half of that reported by Iyer, Sudborough and Ayyar (3). However, the data obtained in the fractionation experiments described above, involving both fractional crystallization and fractional distillation gave no evidence for the presence of even traces of ricinoleic acid. An acetyl determination on the fatty acids gave a value of 13.5. In making the determination, however, it was observed that the acids tended to emulsify with water, making it difficult to completely remove the uncombined acetic acid dissolved in the acetylated fatty acids. When the acetylated acids were dissolved in ether to facilitate the washing procedure, and washing was continued until the wash water required no more than one drop of 0.1 *N* alkali to produce a pink color with phenolphthalein indicator, the acetyl value of the fatty acids was 0.12, equivalent to 0.073% ricinoleic acid. The acetyl value of the oil must be due to unsaponifiable constituents, or to mono- or diglycerides, since the above value was verified, even when the thorough washing technique described above was applied to the acetylated oil.

The percentage of oleic and linoleic acids present in the mixed fatty acids of Argemone oil was calculated from the equations,

$$\text{linoleic acid} = 1.1365\ (\text{I-SCN})$$
$$\text{oleic acid} = (1.1123\ \text{I}) - (2.2882\ [\text{I-SCN}].)$$

These equations are obtained by solving simultaneous equations in which the iodine values of oleic and linoleic acids are taken to be 89.9 and 181.0, respectively, and the thiocyanogen values 89.9 and 93.0, respectively, are employed, since it has recently been pointed out (7) that thiocyanogen does not react with linoleic acid or its esters in accordance with the amount required by theory to saturate one of the two double bonds, as proposed by Kaufmann (8). It is of interest to compare the results obtained when the calculations are based on the empirical value proposed by Kass, Lundberg and Burr (7b) with that obtained by the use of equations that employ the theoretical value for the thiocyanogen absorption of linoleic acid. This is done in Table 5.

TABLE 5

Calculated Composition of Argemone Fatty Acids

Using Empirical SCN Values			Using Theoretical (Kaufmann) SCN Values		
Saturated	Oleic	Linoleic	Saturated	Oleic	Linoleic
14.4	23.4	62.4	12.9	26.7	60.4

It will be noted that the value calculated for the saturated acids using the empirical thiocyanogen values is in much better agreement with the value ob-

tained in the Bertram oxidation (14.0%), or the lead salt-ether determinations (14.1%), than is the value calculated with the theoretical thiocyanogen value. The value for oleic acid includes the hexadecenoic acid, and is corrected for the quantity of hexadecenoic acid estimated to be present. The amounts of the unsaturated acids are reported in Table 6.

TABLE 6

Unsaturated Acids

	Total Unsaturated Acids	Unsaturated Acids on Basis of Oil
	percent	*percent*
Oleic	26.4	21.3
Hexadecenoic	1.0	0.8
Linoleic	72.6	58.6
	100.0	80.7

Saturated Acids

The fatty acids were separated into saturated and unsaturated acid fractions by the lead salt-ether method. The saturated acids so obtained were esterified with anhydrous ethyl alcohol in the presence of dry hydrogen chloride. The esters, amounting to 66.6 grams were fractionally distilled at a pressure of less than 1 mm., through the packed electrically heated column previously mentioned. Five fractions were collected and analyzed by methods previously described (9). These results are given in Table 7.

TABLE 7

Saturated Acids

	Total Saturated Acids	Saturated Acids on Basis of Oil
	percent	*percent*
Myristic	2.0	0.26
Palmitic	83.4	11.09
Stearic	13.7	1.83
Lignoceric	0.9	0.12
	100.0	13.30

The acids were recovered from each of the ester fractions, and the small (2.05 g.) undistilled residue by saponifying with alcoholic potash, liberating the acids from the soaps with hydrochloric acid and remelting the acids with hot distilled water to eliminate hydrochloric acid and potassium chloride. The acids were then fractionally crystallized from ethyl alcohol and were identified by melting points and saponification values. The results in each case confirmed the deductions made from the molecular weights of the saturated ester fractions. Lignoceric and stearic acids constituted the undistilled residue.

Summary

Oil from the Mexican prickly poppy (Argemone mexicana) seed was found to contain the following percentages of acids: Myristic, 0.3; palmitic, 11.1; stearic, 1.8; lignoceric, 0.1; hexadecenoic, 0.8; oleic, 21.3; and linoleic, 58.6. Ricinoleic and linoleic acids, which had been reported by other investigators (2, 3) as constituents of this oil, were not found in the oil from Mexican seed.

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Report of the Uniform Methods and Planning Committee

Fall Convention — October 8 and 9, 1942

The report of the Uniform Methods and Planning Committee will be rather short, owing to the fact that only two committees have submitted reports for action at this meeting.

The Soap Analysis Committee make only one recommendation, which is as follows:

> "The volumetric method for determination of tetra sodium pyrophosphate in soap was recommended for tentative adoption by the Committee at the 1941 Fall Meeting. It is now recommended that this method be considered for official adoption at this time."

The Uniform Methods and Planning Committee approve this recommendation.

The Fat Analysis Committee recommended the adoption of new constants to be used in the calculation of the thiocyanogen value determination. However, the constants recommended apply only to the analysis of fatty acids and not to the analysis of glycerides. In discussing this report with the Chairman of the Fat Analysis Committee it was his opinion that action should be deferred until the committee has an opportunity of studying the constants for the calculation of glycerides, so that they may all be adopted at one time. This has the approval of the Uniform Methods and Planning Committee, so that no action on this report is necessary.

Upon motion by the Chairman of the Uniform Methods and Planning Committee the recommendation of the Soap Analysis Committee was unanimously adopted.

J. T. R. Andrews — T. C. Law
E. B. Freyer — C. P. Long
James J. Ganucheau — H. P. Trevithick
J. J. Vollertsen, *Chairman.*