[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SCHOOL OF TROPICAL MEDICINE OF THE UNIVERSITY OF PUERTO RICO, UNDER THE AUSPICES OF COLUMBIA UNIVERSITY, AND THE AGRICULTURAL EXPERIMENT STATION OF THE UNIVERSITY OF PUERTO RICO]

Puerto Rican Fatty Oils. VI. The Characteristics and Composition of "Molinillo" Seed Oil

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The "molinillo" (*Leonotis nepetaefolia* L.),[1] a member of the mint family indigenous to Africa, is an annual plant which many years ago became established in southeastern United States, northern South America and the West Indies. In Puerto Rico, where the plant is considered a weed, it flourishes in the fields and cultivated areas, being particularly abundant on the river banks at low elevations. The height of the plants varies from one to two meters. They produce dense globose clusters (about 6 cm. in diameter) of green flowers witha n orange or scarlet corolla. Normally, each flower produces seeds which at maturity are brownish or black; they are about 3 mm. in length and 1.5 mm. in diameter. The average weight of the individual air-dried seed is 0.7 mg. Their yield, on the basis of weight of the entire air-dried plants, ranges from 2 to 6%.

The "molinillo" is also known as lion's ears, "quina de pasto" and "botón de cadeta."

The present investigation was undertaken with a view to the future possibility of producing the seed oil commercially. No published data could be found on either the seed or its oil.

Experimental

Material.—The seeds for this investigation came from plants collected along the basin of the Plata River near the town of Toa Alta, Puerto Rico, and were gathered over a period of about six months from December, 1943, to July, 1944. The globous clusters were dried in a circulating air-oven at 60° for ten hours and then crushed in a mortar, thus liberating the seeds, which were finally separated from the rest of the material by sieving and winnowing.

The seeds thus obtained had the following approximate composition:

Moisture, %	8.82
Petroleum ether extract, %	28.00
Protein (N × 6.25), %	23.62
Crude fiber, %	14.31
Ash, %	5.92
N free extract, %	19.33

The extracted oil used for this investigation was green and it had a pleasant aromatic odor due to the essential oil in the seed. The color was partially removed by treatment of the oil with Darco charcoal. The oil was found to solidify between −5 and −8°.

Chemical and Physical Characteristics.—These were determined by the usual procedures.[2] The results are recorded in Table I.

The quantity of volatile oil determined by steam distillation was about 2%.

TABLE I

CHEMICAL AND PHYSICAL CHARACTERISTICS OF "MOLINILLO" SEED OIL

Specific gravity, $^{25}/_{25}$	0.8984
Refractive index, 20°	1.4673
Iodine no. (Hanus)	82.53
Saponification no.	191.2
Acid value	11.20
Reichert–Meissl no.	0.29
Polenske no.	0.15
Unsaponifiable residue, %	3.09
Acetyl value	4.87
Saturated acids, % (cor.)	14.48
Unsaturated acids, % (cor.)	76.55
Iodine no., unsatd. acids (Hanus)	105.00
Saponification no. of unsatd. acids	203.4

Free Fatty Acids.—Twelve grams of oil was mixed at room temperature with an excess of 10% sodium carbonate solution and placed in the ice-box for several hours. The sodium soaps formed were then removed and decomposed with hydrochloric acid, thus liberating the free fatty acids; these were, in turn, extracted with ether from the mixture.

The free fatty acids fraction was semisolid at room temperature (25–28°) and gave the following characteristics: saponification no. 233.0, iodine no. (Hanus) 83.1, Reichert–Meissl no. 6.02, Polenske no. 1.65. The relatively high Reichert-Meissl and Polenske values exhibited by this fraction, indicate that a large part of the volatile acids present in the oil are in the form of free acids.

Unsaturated Acids.—The unsaturated fraction of acids was separated from the saturated by the lead salt–ether method then brominated in the usual manner. No hexabromide separated from the ether solution and this indicated the absence of linolenic acid. After removal of the solvent, the residue was dissolved in petroleum ether and from this solution a considerable quantity of linoleic acid tetrabromide crystallized, which melted at 114°.

Using the formula of Lewkowitsch[3] and the iodine number of the unsaturated acids, which was 105, the percentage of linoleic and oleic acids was calculated with the results given in Table II.

Saturated Acids.—The saturated acids were converted into methyl esters by the method of Hilditch,[4] and freed of moisture and solvents by heating to 100–150° under diminished pressure. The distillation of the esters was carried out at 0.7–0.9 mm. pressure. Five fractions and a residue were collected between 130 and 165°, the composition of each fraction being determined by the method of Baughman and Jamieson[5] from which the percentage of each saturated acid was calculated with the results given in Table II. The acids present in each fraction were separated by fractional crystallization from 95% alcohol. The anilides of the acids thus obtained were prepared.

Myristic Acid (m. p. 53.8°).—From fractions 1 and 2 an acid with a melting point of 53° was obtained. Anilide derivatives prepared from this acid had a m. p. 84.5°. Myristic acid anilide melts at 83.4°.

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(1) N. L. Britton and P. Wilson, "Scientific Survey of Puerto Rico and the Virgin Islands—Botany," Vol. VI, New York Academy of Sciences, New York, N. Y., 1942, p. 153.

(2) Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C. 4th ed., 1935, pp. 404–429.

(3) J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th ed., Vol. I, Macmillan and Co., Ltd., London, 1921, p. 574.

(4) T. P. Hilditch, "The Chemical Composition of Natural Fats," John Wiley and Sons, New York, N. Y., 1941, pp. 371–372.

(5) Baughman and Jamieson, THIS JOURNAL, **42**, 157 (1920).

TABLE II

UNSATURATED AND SATURATED ACIDS IN EXTRACTED "MOLINILLO" SEED OIL

Acids	In unsatd. acids, %	In satd. acids, %	In original oil, %	Glycerides in oil, %
Linoleic	15.56		11.91	12.39
Oleic	84.44		64.64	67.55
Myristic		8.90	1.29	1.36
Palmitic		82.75	11.98	12.57
Stearic		8.35	1.21	1.26

Palmitic Acid (m. p. 62°).—From fractions 1, 2, 3, 4, 5 an acid melting between 56 and 62° was obtained. Anilide derivatives prepared from these acids had a m. p. 88.5°. Palmitic acid anilide melts at 89.5°.

Stearic Acid (m. p. 69.2°).—No pure stearic acid could be isolated from fractions 3, 4 and 5. After several recrystallizations these fractions yielded products melting at 64, 65 and 67°, respectively, which were mixtures of stearic and palmitic acids. The residue, however, yielded pure stearic acid m. p. 69.2°. An anilide prepared from this acid melted at 93°. Stearic acid anilide melts at 93°.

Summary

The characteristics and composition of "molinillo" (*Leonotis nepetaefolia* L.) seed oil have been determined.

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Vinyl Alcohols. XVI. Reduction of Hindered Diaryl Ketenes by the Grignard Reagent

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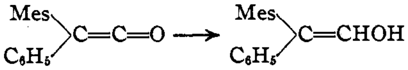
It has been found that excellent yields of 2,2-diarylvinyl alcohols can be obtained by reduction of the corresponding diaryl ketenes with the Grignard reagent. The reaction was discovered in connection with the preparation of various trisubstituted vinyl alcohols by condensation of ketenes with Grignard reagents.[1,2] The methyl, phenyl and mesityl reagents were observed to react normally and to afford satisfactory yields of the expected trisubstituted vinyl alcohols.

When mesitylphenylketene (I) was treated with cyclohexylmagnesium chloride, however, the reaction took a different course. The ketene was reduced to 2-mesityl-2-phenylvinyl alcohol (II) in a yield of 80% of the theoretical. The reaction seems to be general.



$$(\mathrm{Mes})(\mathrm{C_6H_5})\mathrm{C{=}C{=}O} \longrightarrow (\mathrm{Mes})(\mathrm{C_6H_5})\mathrm{C{=}CHOH}$$

I II

t-Butylmagnesium chloride also afforded excellent yields of the vinyl alcohols. For example, this reagent reduced dimesitylketene to 2,2-dimesitylvinyl alcohol; the yield was 86%. In addition, two new ketenes were reduced to the corresponding vinyl alcohols: durylphenyl- and 3-bromomesitylphenylketene yielded, respectively, 2-duryl-2-phenylvinyl alcohol and 2-(3-bromomesityl)-2-phenylvinyl alcohol. The 2-(3-bromomesityl)-2-phenylvinyl alcohol, although not obtained in pure form, yielded an acetate which gave a satisfactory analysis.

Before the reduction method was discovered an attempt had been made to prepare 2-duryl-2-phenylvinyl alcohol by the glycol method. 1-Duryl-2-phenylethylene glycol was made by hydrogenation of duryl phenyl diketone and subjected to the usual treatment with a mixture of glacial acetic acid and concentrated hydrochloric acid. In the single experiment which was carried out, no vinyl alcohol could be isolated from the resulting mixture.

The procedure used to make the alcohol, starting with acetodurene, is described in the experimental part and will serve to illustrate the relative ease with which such compounds can be produced. In particular, the procedure described for the reduction of durylphenylketene is illustrative of the method now being reported.

In view of the improved methods which have been developed for the production of hindered ketoketenes[2] the reduction method is by far the most direct procedure for the synthesis of 2,2-diarylvinyl alcohols. It not only gives high yields but produces the vinyl alcohols under conditions most favorable for their isolation.

The reduction of ketenes by Grignard reagents has not been reported previously. In fact, there seems to be no record of the reduction of a ketene by any method. From the results presently reported it is not clear what if any relationship exists between the reduction and the steric hindrance provided by the mesityl, 3-bromomesityl or duryl radical.

Experimental

Durylglycolic Acid.—Acetodurene was prepared in 88% yield by the method of Smith and Guss[3] and oxidized with selenium dioxide in dioxane. The solvent was removed by distillation *in vacuo*. The crude durylglyoxal obtained from 78 g. of acetodurene was added to 500 ml. of 10% potassium hydroxide solution and the mixture was heated on a steam-bath for ten hours. It was cooled and filtered to remove a dark brown, gummy solid (6 g.), and the filtrate was extracted with ether and then treated with Norite. The durylglycolic acid was precipitated from the solution by the addition of dilute hydrochloric acid and

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[1] Fuson, Byers, Rowland, Southwick and Sperati, THIS JOURNAL, **66**, 1873 (1944).

[2] Fuson, Armstrong, Chadwick, Kneisley, Rowland, Shenk and Soper, *ibid.*, **67**, 386 (1945).

[3] Smith and Guss, *ibid.*, **59**, 804 (1937).