# California Raisin (Grape) Seed Oil

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MORE than 34 years ago a plant was established in Fresno, California, by the California Products Company for the manufacture of oil and meal from the seeds separated at the seeded raisin plants. Those interested in the history and development of this raisin by-product industry, which includes the manufacture of alcohol from the pulp of the raisins adhering to the separated seed, are referred to in A. M. Paul's excellent article in Food Industries *6*, p. 444, 1934.

In addition to making soap, much raisin seed oil has been used by the paint industry, particularly in the production of protective coatings for canvas (awnings, airplane wings, etc.). The refined oil is used in making salad dressings and certain cosmetic preparations, as well as for coating raisins, which requires about one gallon of oil per ton of fruit. This treatment improves the appearance of the raisins, renders them free flowing and less liable to insect infestation, and keeps them soft and pliable for a long time in comparison with the untreated fruit.

Since 1913, when F. Rabak published the results of his extensive investigation on the seed and oil in U. S. Department of Agriculture Bulletin No. *276* no other chemical study of California raisin seed oil has been reported. In view of the growing interest in the oil, particularly in the newer uses being made of it, our attention was called to the desirability of making an investigation of it by modern methods. For this purpose a sample of the seed and a half gallon of the refined expressed oil were sent to us. The seed, which was chiefly from muscat grapes, contained 17.1 per cent of oil and 8.2 per cent of moisture. The average oil content of the seed crushed for oil and meal is about 15 per cent. R. F. Eaton, chemist for the Calavo Growers of California, has recently reported to us in private correspondence that both the freshly expressed crude oil and the refined oil gives positive Kreis tests. Consequently, this test is of no value so far as testing the condition of the oil is concerned.

The chemical and physical characteristics which were determined on the refined oil are given in Table I.

TABLE 1

Chemical and Physical Characteristics of Raisin Seed Oil

| | |
|---|---|
| Refractive index at 25 deg. | 1.4740 |
| Iodine number (Hanus) | 129.1 |
| Thiocyanogen value (Kaufmann) | 80.03 |
| Saponification value | 192.1 |
| Acid value | 0.03 |
| Acetyl value (Andre-Cook) | 18.8 |
| Unsaponifiable matter, percent | 0.53 |
| Hexabromides (Steele and Washburn), percent | 0.29 |
| Saturated acids (corrected) percent | 8.72 |
| Unsaturated acids (corrected) percent | 86.30 |

F. Rabak (loc. cit.) reported the following characteristics for the oil extracted by ether: Refractive index at 25°, 1.4702; iodine number (Hübl), 131; saponification value, 188; unsaponifiable matter, 0.76 per cent; acetyl value, 16; acidity as oleic acid, 0.62 per cent; solid acids, 8.4 per cent; and liquid acids, 84.7 per cent.

## UNSATURATED ACIDS

The percentage of oleic, linoleic and linolenic acids in the oil were calculated in the customary manner, from the iodine and thiocyanogen values. The results are given in Table 2. The presence of these three unsaturated fatty acids in raisin seed oil was previously shown by F. Rabak (loc. cit.) through the identification of their respective hydroxyl acids obtained in the usual manner by alkaline permanganate oxidation. No evidence of the presence of any erucic acid, which has been reported by different investigators as a constituent of the oil, was found, and this confirms the conclusions of E. André and the more recent conclusions of K. Taufel and H. Thaler (Fettchem. Umschau *41*, 196-8 (1934).

TABLE 2

Unsaturated Acids

| | Percent | Percent in Oil |
|---|---|---|
| Oleic | 37.19 | 32.1 |
| Linoleic | 60.14 | 51 9 |
| Linolenic | 2.67 | 2.3 |
| | 100.0 | 86.3 |

## SATURATED ACIDS

The saturated acids, which were separated from the saponified oil by the lead-salt ether method, were esterified with anhydrous ethyl alcohol in the presence of dry hydrogen chloride gas (J. Amer. Chem. Soc. *42*, p. 1200, 1920). The esters, amounting to 80.9 grams, after being freed from solvent and moisture, were fractionally distilled under a pressure of 5 mm. from a Ladenburg fractionation flask. Four fractions were collected, and from the results of their analyses the composition of each was determined by the methods previously described (J. Amer. Chem. Soc. *46*, p. 775, 1924). The final results calculated from the analytical data are given in Table 3.

TABLE 3

Saturated Acids

| | Percent | Percent in Oil |
|---|---|---|
| Palmitic | 68.62 | 5.98 |
| Stearic | 30.62 | 2.67 |
| Arachidic | .76 | .07 |
| | 100.00 | 8.72 |

The acids were recovered from the ester fractions and the small undistilled residue by saponifying them with alcoholic potash and decomposing the soaps with hydrochloric acid. The acids were collected and completely separated from potassium chloride and any hydrochloric acid by remelting them with hot distilled water in the usual manner. The acids obtained from the four ester fractions and the undistilled residue were subjected to fractional crystallization from ethyl alcohol. Myristic acid could not be detected. The larger part of the arachidic acid (.470 g.) was found in the undistilled ester residue, from which also a very small quantity of melissic acid melting at 86° was obtained. E. André (Compt. rend. *175*, p. 107, 1922) also isolated a small quantity of this acid in his investigation of grape seed oil. The source of this acid is probably a wax on the seed coats, which is extracted along with the oil.

The acids from the several distilled ester fractions, which were isolated and identified in each case, confirmed the deductions previously made from the mean molecular weights of the saturated acid esters.

The composition of the oil in terms of glycerides is given in Table 4.

TABLE 4

Percentages of Fatty Acids as Glycerides

| Glycerides of | Percent |
|---|---|
| Oleic | 33.5 |
| Linoleic | 52 7 |
| Linolenic | 2.4 |
| Palmitic | 6 3 |
| Stearic | 2 9 |
| Arachidic | 0.07 |