1% or less, as is the aim in present industrial solvent extraction of cottonseed. The capacity of the extractor would thus probably be doubled since the last 3 or 4% of oil in flakes is removed during the diffusion stage, the most lengthy, difficult, and expensive part of the extraction. The weak miscella from the differential settling process containing the 3 or 4% oil could then be used in place of solvent in the solvent extraction plant. The resulting savings could be applied to the cost of the differential settling process when combined with an existing solvent extraction installation. The enhanced value of the meal obtained by the use of the combined process should result in additional economic gain.

The second possible commercial process is one in which undefatted flakes would be fed directly to the disintegrator. After the usual disintegration, settling, and product recovery steps, the emerging meal containing 6 to 10% oil could be extracted by solvent-washing, the meal recovered by centrifugation, and the oil and solvent recovered in the conventional manner. Fresh solvent would be used on this meal permitting efficient extraction, and the resulting miscella could in turn be used in preparing the slurry for the original disintegration.

Summary and Conclusions

A fractionation process termed "differential settling" has been developed to produce a cottonseed meal substantially free of oil, pigment glands, and hulls from either defatted or undefatted flakes. The development of the process was initiated during the work on a mixed solvent flotation method of fractionation which showed several inherent disadvantages. The investigation of the flotation method had shown that cottonseed meal essentially pigment-gland-free (gossypol content as low as 0.006%) had a high nutritional value and was a source of protein for industrial uses. The meal produced by the differential settling process has as low a gossypol content as the meal produced by the flotation principle and overcomes the disadvantages.

The advantages of the differential settling process are as follows: 1. It requires only one solvent and is more readily adaptable to present solvent-extraction plants than a process using mixed solvents—the preferred solvent, commercial hexane, is commonly used in practically all vegetable oil solvent-extraction plants, and is much cheaper and less toxic than the high specific gravity solvents, such as tetrachlorethylene, used in the mixed-solvent method; 2. fractionation of solvents and control of specific gravity is eliminated; 3. power consumption for the disintegration and centrifugation steps is less since a lighter weight slurry is used; 4. less total heat and lower temperatures are required in desolventizing both the oil and meal, thereby decreasing the possibility of darkening the oil and denaturing the protein of the meal; and 5. the time required for the separation of the slurry into the fine meal suspension and sediment is considerably less than required for the separation of glands from the meal fraction in the mixed-solvent flotation process.

Two methods, centrifugal and tube settling, of the differential settling process have been developed which show promise for commercial separation of the components of cottonseed, namely meal, pigment glands, hulls and oil. Removal of the pigment glands from the coarse fraction or sediment will depend on pharmaceutical or other uses developed.

Commercial possibilities of using the differential settling process in combination with present cottonseed solvent-extraction processes have been outlined.

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Studies on Candelilla Wax. I. Its n-Acids and n-Alcohols

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DESPITE its wide technological use candelilla wax has not been very intensively investigated. A need exists for a re-examination of published work—some of it could profitably be reviewed, particularly the statement that it contains a lactone (6)—and the application of some of the newer analytical techniques to the problem of filling some of the obvious gaps in our knowledge of the composition of this substance. That which follows is the first of several communications in which are reported results of such a study.

This plant wax covers the entire surface of several species of Euphorbiaceae, *Pedilanthus pavonis* and *Euphorbia cerifera*—the latter is probably *E. antisyphilitica* (4) of an earlier day—that grow in the semiarid regions of northern Mexico and southern Texas. In form they are leafless, reed-like stems, one to three feet high and from one-eighth to five-sixteenths inch in diameter. Sometimes as many as 100 of these spring from a single root. The plants grow without benefit of cultivation, interspersed with other desert flora, and must be harvested by hand.

They yield approximately 3.5% of their weight in wax which can be recovered by simply immersing the plant in boiling water and removing the melted wax, which floats to the surface, either before or after it has congealed.

Our present knowledge of the constitution of candelilla wax comes almost entirely from the investigations of Chibnall and associates (3). In the light of X-ray and melting-point evidence resulting from a study of the *whole* acid and alcohol fractions respectively they suggested that the C_{30}, C_{32}, and C_{34} homologues apparently compose the former and that the latter consists of either a binary mixture of the C_{30} and C_{32} individuals or a ternary mixture of these plus the C_{34} alcohol. Sanders (8), probably unaware of the possibility of having at hand a mixture, has reported, without supporting evidence, the presence herein of an alcohol which he described as the myricyl form.

Experimental

Characteristics. The regular article of commerce* was used for this study. Its principal physical and chemical constants were determined by conventional procedures except that the resistance of this wax to saponification made necessary certain modifications which did not however affect the general principle of the method. For example, ethylene glycol proved to be the only reliable medium in which to carry out hydrolysis of this wax; and acid numbers were determined by titrating a benzene solution of the sample with an alcoholic solution of potassium hydroxide.

Analysis revealed that the characteristics were within the general limits of those reported by others (5). They are: melting point 69-71°; saponification number 49; acid number 19; iodine number (Wijs) 32.8; hydroxyl number 17.5; fatty acids 20.7%; unsaponifiable matter 74.6%.

Isolation of Acids and Alcohols. The wax, mixed with solid potassium hydroxide, was dissolved in a boiling solution of benzene and ethyl alcohol. Little or no saponification was apparent. Solid barium chloride was then added. The resulting curd of barium salts of the free fatty acids, admixed with unsaponified wax esters and other substances, was removed, dried, and exhausted with petroleum ether (60-68°) in a Soxhlet extractor. The ether extract, after removal of the solvent, yielded a green residue of paraffins. The paraffin-free barium salt mixture was decomposed with hydrochloric acid solution and the resulting mixture of wax esters and fatty acids was saponified with an ethylene glycol sodium hydroxide solution. The resulting sodium soaps were then converted to barium soaps as before which, after desiccation, were extracted with benzene in order to remove alcohols. Finally the acids were regenerated in the usual manner.

By the above described method there were obtained three distinct fractions: paraffins, alcohols, and acids. The fact that no free alcohols were found in the first petroleum-ether extract suggests the possibility of their existence here in the esterified rather than in the free form and that the presence of hydroxylated compounds is indicated by the appreciable hydroxyl number of this wax. Contributive to the success of the method was in all probability the high content of free fatty acids which, as barium soaps, gave to the whole mass a loose, porous structure thus permitting extraction of the paraffins and making for retention of the wax esters.

Candelilla wax is probably unique in yielding to this procedure. Whether or not it is one that can be recommended as a general method of attack on other waxes containing paraffins poses a question the answer to which requires further study.

Analysis of Acid Fraction. The acids were given a preliminary treatment with methanol and sulfuric acid and a final one with diazomethane (1) to ensure a quantitative conversion to methyl esters. They were white, crystalline, and without iodine number. Fractional distillation was made with a Fenske type electrically heated, helix-packed, 12 by 530-mm. column. The still head and condenser also were electrically heated.

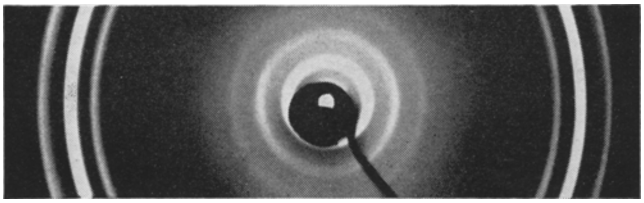
Examination of the distillation fractions showed that none were binary mixtures (Table I) as determined by the solidification-point method (9). Each fraction, after saponification, was converted to barium soaps from which, after extraction with benzene, the acids were recovered. Their molecular weights were determined by titration of their benzene solutions with alcoholic potassium hydroxide solution.

TABLE I

Analysis of Candelilla Wax Acids

Methyl esters			Acids		
Fraction	Weight g.	Boiling point range (0.1 mm. Hg.) °C.	Molecular weight	B spacing Å	Composition C_n
1	1.2	195-200	443	76.3	28+30+32
2	4.2	200-207	454	76.28	28+30+32
3	2.4	209-215	465	76.3	30+32+34
4	2.8	215-218	467	74.6	30+32+34
5	12.0	220-228	484	79.5	30+32+34
6	2.0	228-246	495	77.56	30+32+34
Residue	3.2	....	499	80.6	30+32+34
Total	27.8				

X-ray analysis for B spacings were made of the acid mixtures which had been crystallized from very dilute benzene solution. Proper crystal structure could only be obtained when the solvent was allowed to evaporate spontaneously at room temperature. Powder photographs (Figure 1) were taken with a General Electric XRD unit, using iron irradiation with a manganese dioxide filter. Two-hour exposures were made.



Acids derived from ester mixture I
76.3 Å

FIG. 1. Powder photograph of fatty acid mixture.

Analysis of Alcohol Fraction. A phthalic acid treatment (2) of the whole fraction indicated the absence of secondary alcohols. After fractional distillation (Table II) the alcohol mixtures were oxi-

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* Furnished by S. C. Johnson and Son inc., Racine, Wisconsin.

dized to the corresponding acids with chromic oxide in glacial acetic acid medium. The resulting crude acid mixtures were purified via the barium salt route, after which molecular weights and B spacings were determined as described above.

TABLE II
Analysis of Candelilla Wax Alcohols

Alcohols			Acids		
Fraction	Weight g.	Boiling point range (0.1 mm. Hg.) °C.	Molecular weight	B Spacing Å	Composition C_n
1	1.1	198-207	439	70.9	28+30+32
2	1.7	210-215	458	76.3	28+30+32
3	1.8	215-224	469	76.3	30+32+34
4	4.8	224-230	472	76.3	30+32+34
5	3.1	230-237	470	76.3	30+32+34
6	2.6	240-243	477	80.5	30+32+34
7	2.1	245-260	488	80.5	30+32+34
Residue	3.0	....	486	80.5	30+32+34
Total	20.2				

Search for a Lactone. The wax was repeatedly extracted with 95% ethyl alcohol until a residue (m.p. 89-90°) was obtained. Under similar conditions Meyer and Soyka (6) obtained a product which melted at 88°C. The residue obtained in this study when saponified with an ethylene glycol solution of potassium hydroxide yielded two fractions, one of which was acidic, the other alcoholic. Both proved to be identical with the alcohol and acid fractions isolated from this wax by other methods and identified by X-ray analysis. The "lactone" therefore was in reality a mixture of wax esters and free fatty acids.

Discussion of Results

The generalizations made by the Piper-Chibnall group (7) were used to interpret the X-ray data. Pertinent to the problem in hand are the following: The B spacing of the highest melting acid in a ternary mixture will appear alone if this acid constitutes 20% or more of the whole. If however the longest chain constitutes 10% or less of the whole the spacing will be near that of the intermediate chain. The molecular weight alone shows that Fractions 1 and 2 (Table II) contain the C_{28} acid. That the C_{32} acid comprises more than 20% of these fractions is evidenced by the appearance of its spacing, which is 76.3 for the pure compound. The remaining fractions contain the C_{30}, C_{32}, and C_{34} acids, the spacing depending upon the quantity of the latter.

Summary

A method has been described for separating the constituents of candelilla wax into three fractions, viz., paraffins, acids, and alcohols. To the list of acids and alcohols reported by others as constituents of this wax may now be added the C_{28} individuals. The presence of the C_{30}, C_{32}, and C_{34} homologues of both compounds has been confirmed. All are of the *n*-type. Not confirmed however was the alleged presence of a lactone.

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Solvent Extraction of Rice Bran. Production of B-Vitamin Concentrate and Oil by Isopropanol Extraction[1,2]

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ABSTRACT

Freshly milled rice bran was extracted with hot 91 and 95% isopropanol to obtain the oil, sugars, and a considerable portion of the B-complex vitamins. After concentration of the micella a sugar-syrup phase separated from the oil. This syrup phase contained most of the extracted vitamins. Yields of oil and syrup were observed and vitamin assays made on the syrup and on the bran before and after extraction. The vitamins measured were biotin, folic acid, riboflavin, pantothenic acid, pyridoxine, thiamin, niacin, and inositol.

Introduction

RICE bran is a valuable by-product of the rice milling industry which is now poorly utilized. It contains generous quantities of most of the B-vitamins and from 12 to 20% oil. The quantity of oil available annually in the United States from this source is approximately 30 million pounds (1). This oil is quite bland and should be valuable for edible purposes.

The bran is subject to a rapid deterioration after milling, due to its finely divided state and to the great activity of the hydrolytic enzymes in splitting the fats. The oil also becomes rancid and makes the product unpalatable as a feed. Another objection to the bran is the tendency of the oil to produce soft pork when fed to swine (2, 3). These undesirable properties could be eliminated by extracting the oil from the bran immediately after milling.

Feuge *et al.* (1) have demonstrated that rice bran oil extracted by hexane can be refined to a high grade edible product. A disadvantage however is the difficulty of preventing fatty acid increase and a resulting high oil-refining loss. Colman (4) has prepared a vitamin B concentrate from rice bran by extracting the oil with 99% isopropanol and re-extracting the bran several times with 40% isopropanol. The con-

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[2] Presented at the 40th annual meeting of the American Oil Chemists' Society, New Orleans, La., May 10-12, 1949.