is not a serious handicap because bromide and iodide usually occur in relatively small amounts in plant materials and do not contribute a large error in chloride analyses.

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VEGETABLE OILS

Review of Chemistry and Research Potential of *Simmondsia Chinensis* (Jojoba) Oil

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The known chemistry and research potential of *Simmondsia chinensis* (Jojoba), a unique agricultural material that occurs only in the wild, is summarized. Its nuts contain 50% of an oil which is a liquid wax, similar in some respects to sperm whale oil. Current interest in this seed stems from the fact that the United States is dependent on foreign sources of plant wax. The cultivation of jojoba offers promise in reducing this dependence. Preliminary industrial evaluations of jojoba oil and hydrogenated wax are discussed.

Figure 1. *Simmondsia chinensis*

A. Flowering branch of male plant
B. Branch of female plant
1. A male flower, enlarged
2. Anther, more enlarged
3. Male flower, with stamens removed
4. Ovary, magnified and longitudinally divided
5. Ovule, more highly magnified
6. Longitudinal section of ovule
7. Seed, somewhat enlarged
8. Longitudinal section of seed
9. Transverse section of seed (*18*)

THE POTENTIAL VALUE of *Simmondsia chinensis* (jojoba), a wild desert shrub, native to southwestern United States and northern Mexico, is centered in the unusual oil that occurs in its seed. The seeds, or nuts, are reddish brown in color and measure approximately $^1/_2$ by $^3/_8$ inch (Figure 1). They contain up to 50% by weight of an oil which is a liquid wax (esters of long-chain acids and alcohols) rather than a glyceride fat (*5, 7–9, 11, 13, 20*). In this respect jojoba oil is most similar to sperm whale oil, which is an oddity in animal fats.

The current interest in jojoba stems from the fact that the United States is dependent on foreign sources for almost all of the plant waxes of commerce. Because of chemical similarity to sperm whale oil, the cultivation of jojoba offers promise of reducing the dependence of the United States on foreign sources of sperm waxes, large quantities of which are imported yearly (*5, 17*) (Table I).

Hydrogenation of jojoba oil produces a white, crystalline wax with a melting point of 70–4° C., of excellent hardness (*5, 6, 14, 16*). Melting point of carnauba wax is 85° C. and various grades and types of candelilla wax melt at 64° to 77° C. Jojoba appears to be a possible replacement for some applications of other imported vegetable waxes.

There have been several recorded domestic plantings of jojoba (*5, 17*). Wild jojoba plants produce approximately 2 pounds of seed per plant; this could, conceivably, be increased to 4 or more pounds under cultivation (*5, 16, 17*) because of more rapid growth under optimum conditions (*16, 17*). The cultivated plants are much larger than those found in the wild state, and some of them consistently produce more and larger seeds than others. The yield might be increased by selectively planting seeds of the best producers, vegetative propagation (*5, 17*), or grafting (*5, 17*). Because the plant is dioecious—bearing male and female flowers on separate plants (Figure 1)—yield could be further increased by reducing the one to one natural ratio of male to female plants to a one to five ratio in cultivated stands.

A major drawback to the cultivation of jojoba is the fact that it requires from 6 to 8 years to produce seed in sufficient quantity to justify harvesting on a commercial basis. If the plantings are irrigated, annual crops such as cotton or soybean could be grown between rows to bear part of the expense. The high yields of oil from the seeds, however, would appear to justify the planting even with the 6- to 8-year wait for the first harvest (*5*). Another difficulty would be harvesting. In the wild state the seeds fall to the ground when mature; hand collection is the only harvesting method used. Under cultivation, hedgerow or orchard-type plantings would simplify the problem, as underbrush could be kept to a minimum and the bushes pruned to a shape which would afford easy access to a suction-type mechanical harvester. Mechanical pickers might allow harvesting of the crop before the nuts fall to the ground (*5*).

The chemical and physical characteristics of the oil were first reported in detail by Greene and Foster (*8*) in 1933. On the basis of their findings it was determined that the oil was not a glyceridic fat. Other investigators later confirmed these findings (*7, 9, 11, 13*). Tables II and III show the characteristics of jojoba oil as reported in 1936 by McKinney and Jamieson (*13*).

The Plant Introduction Section, Agricultural Research Service, United States Department of Agriculture, is investigating problems involved in the introduction of the wild jojoba plant as a domestic crop.

The applications of the oil appear extremely diversified. The earliest article on the plant, which appeared in 1789 (*3*), ascribed remarkable medicinal properties to the seeds and their oil. Present-day research has indicated that the oil has some value in the case of the tubercle bacillus (*19*), and has recommended it as the best stabilizer for penicillin (*10, 12*). The Indians of the indigenous area are known to eat the roasted seeds, and to use the oil recovered by boiling the seed in water for culinary and medicinal purposes (*3, 5, 17*).

The oil should also be evaluated for suitability for sulfurization to produce special lubricating oils, greases, and a rubberlike factice for use in the manufacture of linoleum and printing inks (*5, 12, 16, 17, 20, 22*). The oil offers excellent possibilities as a lubricant for high speed machinery and equipment operating at high temperature and pressure and as a cutting and grinding oil for high speed precision works (*5*). As the oil resists oxidation even at elevated temperatures (*16*), it may solve many lubrication problems in food industries. Such use, however, would require approval by the Food and Drug Administration. The oil has a high dielectric constant, which may make it suitable for use as a transformer oil (*4, 12, 15*). It may also find use as an ingredient in the manufacture of carbon paper, stencils, pharmaceuticals (*5, 19*), and cosmetics (*5, 21*). The meal remaining after extraction of the oil contains 30 to 35% protein and may prove acceptable as a livestock feed (*5, 21*).

Yielding C_{20} and C_{22} straight-chain alcohols and acids (*5, 16*) on hydrolysis, jojoba oil is an excellent source of these chemicals. It is one of the very few agricultural sources of these materials, which are invaluable in the preparation of detergents, wetting agents, and modern lubricants (*16, 17*). Because naturally occurring compounds containing 20 or 22 carbon atoms are not readily available commercially, not much research has been conducted on them, but work that has been done points toward potential value in many directions. The oil has been shown to contain approximately 30% eicosenoic acid, 14% docosenoic acid, 14% eiconsenol (alcohol), and 33% docosenol (alcohol) (Table III). Eicosenoic (C_{20}) and docosenoic (C_{22}) acids could serve as intermediates in the preparation of long-chain alcohols, ketones, esters, amines, amides, nitriles, sulfated products, metallic soaps, and dibasic acids, which find application in disinfectants, surfactants, detergents, lubricants, driers, emulsifiers, resins, plasticizers, fibers, protective coatings, and corrosion inhibitors (*2, 22*). The C_{20} and C_{22} alcohols (eicosenol and docosenol) may be used by themselves or as intermediates in the preparation of dibasic acids, long-chain ethers, hydroxy ethers, esters, and sulfated products, as bases for creams and ointments, and in lubricants, surfactants, plasticizers, detergents, waxes, resins, emulsifiers, antifoamers, and other products (*2, 22*).

Ozonolysis, followed by oxidation or other suitable treatment, would yield many other potentially valuable compounds, such as long-chain aldehyde-alcohols, long-chain aldehyde acids, odd-number carbon dibasic acids (*14*), amines and amino acids, and dibasic acids containing even numbers of carbons, such as sebasic acid (*14*).

Preliminary experimental work at the Southern Utilization Research and Development Division and by other organizations, indicates that the oil can be produced by hydraulic pressing, screw pressing, and solvent extraction with various solvents, such as hexane, heptane, benzene, and perchloroethylene, using conventional equipment available in oil mills, currently processing cotton-

Table I. Plant Waxes Imported into United States (1951–1955)

Wax	Av. Imported, Million Lb.	Price Range, $/Lb.
Carnauba	16.5	0.60–1.45
Candelilla	4.6	0.58–0.78
Ouricuri	2.7	0.68–1.15
Miscellaneous other waxes	2.2	...
Sperm whale oil	28.2	0.10–0.175

Table II. Characteristics of Jojoba Oil

Chemical or Physical Characteristic	Value
Pour point, ° F.	50
Refractive index, 25°/25° C.	1.4648
Specific gravity, 25° C.	0.8642
Iodine No. (Hanus)	81.7
Saponification value	92.2
Acid value	0.32
Unsaponifiables, % (*1*)	48.3
Iodine No. of unsaponifiables (Rosenmund-Kuhnhenn)	77.2
Acetyl value of unsaponifiables	171.8
Saturated acids, %[a] (Bertram)	1.64
Iodine No. of total fatty acids (Hanus)	76.1
Neutralization value of total fatty acids	172.0
Flash point (COC), ° F.	555
Fire point (COC), ° F.	640
Viscosity, SU, at 100° F.	127

[a] No separation of saturated acids effected by lead salt method.

Table III. Chemical Composition of Jojoba Oil

Compound	%
Saturated acids (various C_{20} to C_{26})	1.64
Palmitoleic acid, $CH_3(CH_2)_7CH:CH(CH_2)_5COOH$	0.24
Oleic acid, $CH_3(CH_2)_7CH:CH(CH_2)_7COOH$	0.66
Eicosenoic acid, $CH_3(CH_2)_7CH:CH(CH_2)_9COOH$	30.30
Docosenoic acid, $CH_3(CH_2)_7CH:CH(CH_2)_{11}COOH$	14.20
Eicosenol, $CH_3(CH_2)_7CH:CH(CH_2)_9CH_2OH$	14.60
Docosenol, $CH_3(CH_2)_7CH:CH(CH_2)_{11}CH_2OH$	33.70
Hexacosenol[a], $C_{26}H_{51}OH$	2.00

[a] Hexacosenol is known to contain one double bond but its position has not been established.

seed or soybeans. Literature data indicate that the seed stores well with little or no deterioration. As this plant does well in areas of low rainfall, and under drought conditions, it could well supplement the oil-bearing materials currently being processed, particularly in dry years. These factors could be used to advantage in extending the processing season of oil mills.

Small quantities of the oil have been prepared on two occasions at the Southern Division by hydraulic pressing of jojoba seed meats. The seed were obtained from the Boyce Thompson Southwestern Arboretum, Superior, Arizona, through the cooperation of the Plant Introduction Section, Agricultural Research Service, U. S. Department of Agriculture. (It is understood that the seed cannot be supplied at present in large commercial quantities.) The first shipment was received in December 1952, and the second in December 1954, and in both instances were stored at 35° F. until used. While such low temperature storage is not necessary to maintain the quality of the seed, it was resorted to as an expedient to minimize insect infestation.

To prepare the seed for extraction, seed were spread thinly on trays and brought up to a temperature of 100° F. for 20 minutes in a forced draft oven. Upon removal from the oven, the seed were immediately cracked into 6 to 10 pieces by passing them through a dual stand of corrugated cracking rolls, spaced 0.050 inch apart. The cracked meats were then rolled through dual smooth rolls set at 0.018-inch clearance between rolls. The flakes produced had an average thickness of 0.025 inch. The flaked meats were formed into cakes of approximately 5 pounds each ($1^1/_2 \times 8 \times 18$ inches) and charged to the six-stack pilot plant model French hydraulic press and pressed at 4400-pound ram pressure for 50 minutes. From 130 pounds of jojoba seed the following fractions were recovered: 37.1 pounds of oil (after filtering), 87.4 pounds of press cake, 3.3 pounds of sweepings, 1.2 pounds of samples, and approximately 1.5 pounds of oil remaining in the press cloths.

Chemical characteristics of the oils and meals produced in these experiments are shown in Tables IV and V. As jojoba oil is known to be a wax, the unsaponifiable matter removed when the liquid phase from the reaction is separated from the solids would be expected to contain the long-chain alcohols of the wax and the solid phase, the fatty acids.

Fifteen pounds of the oil obtained by cold hydraulic pressing of the first lot of nuts (experiment 1) were hydrogenated to an iodine value of 0.8. This resulted in a hard, white, crystalline wax with a melting point of 67.6° C. This value is considerably lower than the 74° C. commonly found in the literature. No explanation for this difference can be given on the basis of these data.

In cooperation with the Plant Introduction Section, 19 samples of oil and 13 samples of the hydrogenated wax were distributed to 25 industrial companies for experimental evaluation, in an effort to establish possible immediate end uses (Table VI). Although the results of some of the tests appear to be contradictory, or to disagree, only cursory experimental work was carried out, and in most cases with specific applications in mind. In no case was sufficient material available for extensive experimentation on chemical behavior, modified products, or special treatments. Consideration of the data from this survey indicates that further organized study and evaluation of the products from jojoba nuts should be undertaken to determine the qualities desired by industry in waxes of this type, both liquid and solid, and means of processing or treating the oil or solid wax to obtain products having the desired properties.

Additional small samples of both liquid and hydrogenated wax will be available for evaluation in the near future. Requests for research samples should be addressed to the Southern

Table IV. Chemical Characteristics of Hydraulic Pressed Oil

Expt.	FFA, %	Acid Value	Index Refr. n_D^{25}	Iodine Value (Wijs)	Acetyl No.	Saponification No.	Unsaponifiables,[a] %	Sp. Gr. 80° F.
1	0.20	0.15	1.46417	84.2	1.15	94.0	50.33	0.8646
2	0.11	0.21	1.56440	83.2	1.40	94.1	...	0.8630

[a] (7).

Table V. Characteristics of Meals and Flakes

Sample	H_2O, %	Nitrogen, %	Nitrogen Solubility, %	Lipides, %
	Experiment 1			
Flaked nuts	7.2	2.41	...	46.2
Press cake	9.1	4.11	...	12.0
	Experiment 2			
Flaked nuts	3.7	2.47	87.5	44.0
Press cake	6.3	4.09	94.5	11.3

Table VI. Results of Evaluations and Suggested Uses

Company	Results of Evaluation	Possible Uses
A	Wax not satisfactory for bright drying water emulsion-type floor waxes. Appears to lend itself to use in blends of solvent type waxes, cleaners, and pastes. Good solvent properties	Paint removers, wood lubricants, cosmetics
B	Oil sulfonates and blends satisfactorily. Pour point and cloud point higher than desirable in sperm oil substitute	None suggested
C	Wax buffs satisfactorily and gives sufficiently hard coat to be used in both solvent and emulsion type floor waxes	Self-polishing wax formulations
D	Wax does not have good solvent holding properties for use in paste wax formulations	Cosmetics
E	Wax does not compare favorably with ouricuri, carnauba, or Chinese insect wax in application tested	Cosmetics
F	Wax not satisfactory in two applications tested	None suggested
G	Wax did not give as good results as carnauba when tested as mold release agent (emulsion type)	None suggested
H	Wax unsatisfactory for paste or liquid formulation or in carbon paper inks because it crystallizes to a dry powder from oil or solvent without swelling (due to poor solvent retention)	As blend with petroleum waxes which tend to form gels with solvents instead of lattice crystals
I	Oil has good stability at elevated temperature when used as a transformer oil. Serious objections: Oil increases in viscosity over a period of time probably because it tends to esterify or polymerize, and solidifies slightly below room temperature	This application after dewaxing or treating
J	Oil has good stability to heat. Good color. Would not take up more than 15% sulfur	Limited application as sulfurized lubricant
K	Promising raw material. Has advantages over sperm oil in area investigated	High pressure lubricant additive

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TOXIC GASES IN SILAGE

Production of Toxic Gas (Nitrogen Oxides) in Silage Making

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Because several deaths and serious illnesses have resulted from exposure to nitrogen dioxide produced in silage making, the attention of agricultural experimentation workers has been sharply focused on this problem. Five silos were tested in the summer and fall of 1956 for nitrogen dioxide production; all gave off the gas. In one instance the brown fumes were so extensive that good colored photographs of the gas were obtained. Many lots of experimental silage have been prepared to determine the factors involved in the production of nitrogen oxides in silage.

PRODUCTION OF THE TOXIC GAS, NITROGEN DIOXIDE, in the early stages of silage making has become recognized in recent years as a serious and insidious danger. Although previous reports of chickens found dead at the bottom of the silo chute had come to the College of Agriculture, no definite leads were obtained until September 1949, when a sample of silage in a closed bottle was received from a farmer who reported that he had been almost overcome trying to climb the ladder in the chute of his silo. When opened, the bottled silage gave off a strong bleach-like odor, had a peculiar orange color, and gave strong color tests for nitrites and nitrates.

A day or two later, one of the University Farm silos gave off a clearly visible brownish gas which accumulated in the unventilated chute of the silo and analyzed several hundred parts per million of nitrogen dioxide. Visible gas was not observed from any other silo that year, but evidence of its formation was indicated by the presence of orange to brown colored pieces of forage which gave positive nitrite tests. Following publication of results of these tests (*7, 15, 16*), letters from farmers and experiment station workers in Minnesota, South Dakota, Pennsylvania, and Wisconsin, were received telling of the occurrence of the gas in these regions and of its causing the death of some farm animals.

Medical Reports

Real impetus toward a recognition of the seriousness of nitrogen oxides in silage making came in 1955, when farmers in several parts of the country were brought to hospitals suffering from a mysterious pulmonary illness that could not be related to any known cause. In all cases the men had become violently ill, with coughing and shortness of breath, after going up into a silo soon after it was filled or partly filled with

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