

THE SOLVENT EXTRACTION OF CASTOR OIL SEEDS.

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Castor oil seeds consist of about 23–35% seed coats that are rich in mineral matter and low in oil (10%), and 65–75% of kernel. The kernel is made up of about 46% fixed oil, 2.3% gum, 20% starch, albuminoids, lignin, etc. Ricinolein makes up the greater part of the fixed oil. Also found in the kernel are small amounts of (a) ricin, a very poisonous toxalbumin insoluble in alcohol and precipitable with steam, (b) ricinine, a non-toxic, basic substance soluble in the organic solvents and volatile with steam and (c) a powerful, fat-splitting enzyme that hastens the hydrolysis of the oil after the seed coats are broken. The fixed oil is the main commercial product. However, only a small fraction of the supply is used in medicine, the major portion being used as a lubricant in motors, and in the manufacture of artificial leather.

The present method for the commercial preparation of castor oil consists of pressing the seeds and extracting the cake. By this means seeds that contain 45% oil will yield about 30–34% of a No. 1 oil by expression, and 9.5–15% of a No. 3 oil by extraction; thus leaving 0.6–2% of the oil in the pomace. The solvent extracted oil is not used for medicinal purposes.

There has been a strong prejudice against solvent-extracted oils. They are said to be inferior in quality, darker in color, higher in acidity and to retain small amounts of the solvent. The French are said to have used solvent extraction for the preparation of their oil, but found that the product became rancid more rapidly than the expressed oils. Many different solvents have been used previously for castor oil extraction. Farbenind (1) claims that chloroform, carbon tetrachloride and methylene chloride alone and when mixed with benzene are very good solvents. Slashchev (2) found that benzene darkened the oil. Shrader (3) reports that he extracted a No. 1 oil from the seeds using benzene. Although the oil was a greenish color, he thought that it could be decolorized. Perin (4) found acetone to be very valuable because its greater affinity for water than for the oil made it possible to remove the solvent by treating the mixture with water. Shrader (3) states that gasoline yields a yellow oil, while methyl acetate, methyl ethyl ketone, acetone and ethyl alcohol yield red oils.

EXPERIMENTAL.

TABLE I.

Solvent.	Yield.	Efficiency.*	Color of Oil.
Petroleum ether	6.5%	14%	Yellow
Benzene	13.3%	28%	Yellow
Ethyl ether	15.4%	34%	Light yellow
Acetone	22.8%	50%	Light yellow
Toluene	23.0%	51%	Red
Alcohol	42.0%	93%	Yellow

* The total content of the beans was 45.21%.

In order to ascertain the relative merits of several organic solvents for castor oil extraction, 150-Gm. samples of the seeds were percolated with 500 cc. of the solvent. Care was taken that the rate of percolation be kept as nearly uniform

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as possible. The solvent was removed at reduced pressure. The relative efficiency of the various solvents is shown in Table I.

To be satisfactory a solvent must (*a*) remove the maximum percentage of oil, (*b*) remove the minimum amounts of impurities (such as gums, coloring matter, albumins—especially ricin), (*c*) be sufficiently volatile to be removed easily and completely at low temperatures and (*d*) cheap enough so that the loss from volatilization will make its use practical on a commercial scale. We found that a mixture of methanol and ethanol met each of these requirements.

The seeds freed from any foreign particles, were placed in an ice box over night or until they had reached a temperature of 5° C. This makes the seeds more brittle, minimizes expression of the oil when they are run through the grinder, and lessens the action of the lipase on the oil. The whole seed was run through the grinder and the product mixed either with a No. 10 previously washed and dried sand, or, with white excelsior previously percolated with the solvent to be used. The material was packed in a two-quart glass percolator and continuous downward percolation used. The time required to remove the oil completely from 1000–1200 Gm. of the seed was twenty to twenty-four hours, and it was necessary to use about four liters of solvent.

The solvent was removed at reduced pressure. When only a few cc. of the solvent remained, a wax-like, amber-colored material settled out on the sides of the container. This waxy material was strained off before purification of the oil. By work now in progress the authors hope to be able to determine the nature and value of this waxy material. The crude castor oil obtained was reddish yellow in color, had a bitter acrid taste and a disagreeable odor.

The oil was deodorized by using steam distillation. After the oil had been treated with twelve times its volume of water (as steam) the disagreeable odor was gone but an acrid taste, irritating to the throat, remained. After the oil had been treated with sixteen to eighteen times its volume of water (as steam) the acrid taste was gone and a faint pleasant nutty odor and taste remained. The steam distillate had a characteristic bitter, nauseating odor. During the steam distillation the small amounts of ricin and ricinine extracted by the solvent were removed or precipitated. The color of the oil was reduced in proportion to the amount of steam passed through the oil. This is shown in Table II.

TABLE II.

Sample.	Water per cc. of Oil.	Color Expressed in mg. I ₂ per 100 cc.
The crude oil reddish	4.26	151.8
yellow in color	7.00	115.5
	8.18	97.5
	12.13	56.25
	16.67	24.21

After complete removal of the water from the deodorized oil, it was further decolorized by a mixture of a commercial activated carbon and a commercial clay. It has been found that clays are very effective for removing yellow coloring materials but are much less efficient if red coloring matter is also present. On the other hand the carbons are particularly useful in removing red coloring matter. We found that 5–10% clay and 0.2–2% carbon was much more effective for decolorizing

the oil than greater amounts of either used separately. After the mixture had been heated to 65–75° and stirred with a mechanical stirrer for 30–60 minutes, the product was filtered by suction. A practically colorless oil (pale yellow in two-inch layers), with a faint nut-like odor and taste was obtained. There was no taste and no odor of castor oil, and no irritating action on the throat. The effect of the decolorizing mixture on the acid number is given in Table III.

TABLE III.

Decolorizing Agent.	% Used.	Temp. ° C.	Original.	Acid Value, Final.	Change.
Carbon	2.5	65–75	1.746	1.280	0.466
Carbon	5	65–75	1.746	1.164	0.582
Carbon	1				
Clay	9	65–75	1.746	1.164	0.582
Clay	5	26	1.138	0.980	0.358
Carbon	1				
Clay	4	26	1.138	1.101	0.227

The constants of the deodorized, decolorized, extracted castor oil are compared with the constants of standard oils in Table IV.

TABLE IV.

	U. S. P.	Extracted Oil.
Odor	Faint, mild	Faint, nut-like
Taste	Bland, afterwards slightly acrid and usually nauseating	Pleasant, nut-like free from acrid or nauseating taste
Sp. Gr.	0.945–0.965	0.959–0.961
Acidity (cc. 0.1 N NaOH)	Not more than 1.5	0.25 – 0.53
Acid value	Not more than 4.2 (calc.)	0.93 – 1.55
Saponification value	178–185	179 – 180
Iodine value	83–88	91 – 96
Refractive index	(1.4783–1.4789, standard)	1.4769–1.4771

Samples of the extracted oil were stored (*a*) at room temperature, (*b*) at 40° C. and (*c*) at 30–35° in the sunlight for periods of eight to fifteen weeks. Those kept in filled bottles at room temperature for thirty weeks, and those kept at 40° for eight weeks (equivalent to room temperature for from one to two years) did not develop a castor oil taste or odor, showed a slight increase in acid number, but practically no change in the other constants. Comparisons made with similarly treated expressed commercial oils indicated that the extracted oil was more stable. Those samples kept in the sunlight at 30–35° developed a disagreeable odor and taste unlike that of castor oil, and showed a decided increase in acidity and in refractive index.

The effect of nitrogen and of carbon dioxide on the preservation of the oil before storage was determined. It was found that carbon dioxide hastened the formation of acid, but nitrogen had some preservative action.

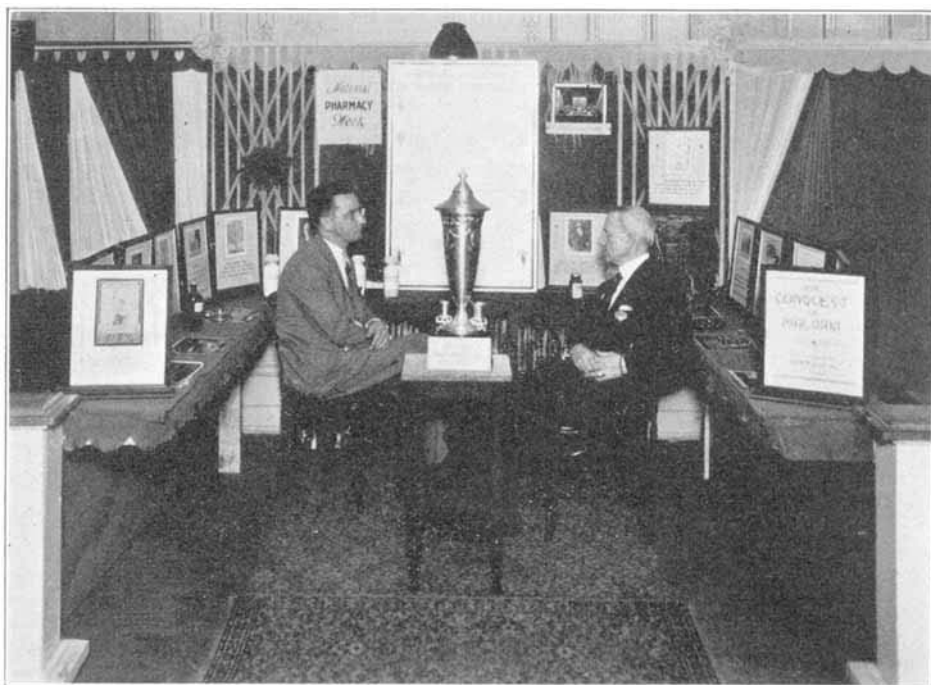
SUMMARY.

1. A practical solvent extraction process which removes 99% of the total oil as a No. 1 oil from castor seeds is described.

2. All of the solvent can be readily removed.
3. The purification process gives an oil that is almost colorless, has a pleasant nut-like odor and taste, has neither an acrid nor a castor oil taste, and meets all of the U. S. P. requirements excepting the iodine value.
4. The decolorizing action of steam on the oil is noted.
5. The removal of some of the acid by the clay and carbon decolorizing mixture is noted.
6. This extracted oil has keeping qualities superior to the commercial expressed oils.
7. The addition of carbon dioxide to bottles of the oil before storing was found to hasten the formation of acid. The addition of nitrogen to the containers before storing had some preservative action.

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President Walter D. Adams and Chairman Anton Hogstad talking over Pharmacy Week matters at Texas Pharmaceutical Association exhibit.