Para Rubber Seed Oil

Contribution from the Oil, Fat and Wax Laboratory, Bureau of Chemistry and Soils, United States Department of Agriculture

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THE tree *Hevea brasiliensis*, which is the source of Para rubber, is a native of the Amazon valley; but in the latter part of the nineteenth century it was planted in several tropical colonies of the British Empire. Cultivation in those lands and various other tropical countries has been increasing ever since. Today the greater part of the world's supply of crude rubber comes from the rubber plantations of Malaya, Dutch East Indies and Ceylon. These plantations now cover millions of acres. Small amounts of rubber are also produced in India, Saranak, Borneo, French Indo-China, Siam and various parts of Africa. The Para rubber tree produces a fruit which contains, as a rule, three seeds. On ripening, the fruit bursts, and the seeds fall to the ground. Plantations on which full bearing trees are growing produce approximately 300 pounds of seed per acre. The seeds, which average 3 grams in weight, consist, on the average, of about 50 per cent, by weight, of shell containing no oil and 50 per cent of kernel containing 40 to 50 per cent oil[2-a]. The number of the plantations that have come into bearing has been increasing rapidly of late, and the problem of finding use for the large quantity of seed produced has been gaining importance. It has been given especial attention by the Department of Agriculture of the Federated Malay States and by the Imperial Institute of England. Several reports have been issued by these two institutions[1-2].

Concerning the commercial possibilities of rubber seed, Spring and Day[1-a] reported that the oil possesses less drying power than linseed oil and that the press cake is a useful cattle food, although care is required in its use for immature animals. Eaton[1-b] extracted the oil from a consignment of 25¾ tons of whole seed. The yield of oil was 19.3 per cent. He found that the drying properties of the oil were poor but thought that it could be used as a partial substitute for linseed oil. His opinion was that it would be preferable to extract the oil from decorticated seed by hydraulic pressure. The Imperial Institute[2-b] submitted samples of oil for technical trials to a number of manufacturers using drying oils and reported that the results showed the oil to be somewhat inferior to linseed oil for paint and varnish making but that it could be used as a partial substitute. It was found suitable for the manufacture of soft soap and possibly for the manufacture of rubber substitutes. In the same report it is stated that "trials with the cake left after expression of oil from the seeds were arranged for . . . and the results clearly establish its value as a food for cattle." Gardner[3] made a number of drying tests on the oil and found it to be much inferior to linseed oil. Some of the physical and chemical characteristics were determined by the investigators already mentioned, as well as by Pickles and Hayworth[4], Trevithick and Lauro[5] and by six independent observers of American Society for Testing Materials[6]. All the analyses recorded show high acidity. The acid value ranges from 6 to 50; it usually is between 30 and 40.

Pickles and Hayworth (*loc. cit.*) reported that the mixed fatty acids consist of 86.0 per cent unsaturated and 14.0 per cent saturated acids; that the saturated acid fraction is composed of stearic and palmitic acids, and that the unsaturated acid fraction consists of 32.6 per cent oleic acid, 50.9 per cent linolic acid, and 2.5 per cent linolenic acid. Gardner (*loc. cit.*) found the hexabromide number to be 16.3, which is equivalent to 6 per cent linolenic acid in the total fatty acids. Oil solvent-extracted in the United States from kernels imported from Sumatra has been sold in the markets for several years. The statement in the Malayan Agricultural Journal[1-c] is interesting, "that an American corporation has offered to purchase seed in Malaya; that the seed is decorticated, the kernels dried and chemically treated to destroy enzymes and afterwards bagged and shipped to America." Many experiments have been made in recent years at Sumatra with a view to treating the seeds so that a low acid oil might be obtained, but up to the present, in so far as we are informed, no satisfactory treatment has been discovered. In fact, the air-dried kernels shipped to this country without further treatment have so far given the best results.

A quantity of rubber-seed kernels was furnished by the Prosco Oils Corporation, Norfolk, Va. An analysis of the kernels by R. S. McKinney of this laboratory gave the following results: Moisture, 5.04 per cent; oil, 42.53 per cent. The oil was expressed in an expeller and filtered.

Chemical and Physical Characteristics

THE oil had a clear dark-red color but was lighter than the commercial solvent-extracted oil. The important characteristics are reported in Table I. The acid value (40.9) is equivalent to 20.6 per cent oleic acid. This acid value was determined soon after the oil was expressed, and nine months later it had increased only to 42.4. This indicates that the oil as it existed in the kernels was highly acid. The thiocyanogen-iodine number was determined by the Kaufmann method[7]. The hexabromide number[8] on this sample is practically the same as the value observed by Gardner (*loc. cit.*). The hexabromide precipitate melted at 179°-180° with darkening. After one recrystallization from amyl alcohol it melted sharply at 181° with no discoloration. The percentages of saturated and unsaturated acids were determined by the lead salt-ether method, and corrections were made for the small quantity of unsaturated acids that remains with the saturated acid fraction. The percentage of unsaturated acids also has been corrected for the unsaponifiable matter which separates with the unsaturated acid fraction. The percentage of saturated acids in the oil is 2.7 higher than the value calculated from the Pickles-Hayworth results, and the unsaturated acid percentage is 2.3 lower.

Unsaturated Acids

THE percentages of oleic, linolic and linolenic acids in the oil were calculated from the iodine number of the oil and the thiocyanogeniodine number according to the Kaufmann scheme (*loc. cit.*), which is based on the conclusion that free thiocyanogen quantitatively saturates two double bonds of linolenic acid and one double bond of linolic and oleic acids. The results from this calculation are given in Table II. The hexabromide number (percentage of hexabromide in total free fatty acids) is equivalent to 5.5 per cent linolenic acid in the oil. Evidently there are present at least two isomers of linolenic acid. Five and a half per cent of one forms a crystalline hexabromide, melting at 181°, and insoluble in ether, and 14.1 per cent of one or more produces hexabromide soluble in ether.

Saturated Acids

THE total saturated acids were separated from a portion of the oil by the lead salt-ether method and esterified by heating for eight hours, under a reflux condenser, with absolute methyl-alcohol which previously had been saturated with hydrogen chloride. The mixture of methyl esters which weighed 104.5 grams was subjected to fractional distillation under diminished pressure as follows: A preliminary distillation from a 1-liter Claissen flask divided the mixture into five fractions and a residue, and these fractions were redistilled from a 150 cc. Ladenburg flask. The data for the distillation is given in Table III.

The iodine numbers and the saponification values of the final fractions are recorded in Columns 2 and 3, Table IV. The iodine numbers measure the amounts of unsaturated acid esters which contaminated the fractions. From these values the mean molecular weight of the saturated acid esters in each fraction was calculated[10]. The results are given in Column 6. The mean molecular weights indicate the saturated acid esters that may be present in each fraction. Thus the value for the small Fraction I is slightly higher than the theoretical value for methyl palmitate (270.3) and indicates the absence of methyl myristate. The values for the first five fractions lie between the molecular weights of methyl palmitate and methyl stearate (298.4), from which fact it is concluded that the fractions contain these two esters in varying proportions. The figure for Fraction 6 which is between the theoretical values for methyl stearate and methyl arachidate (326.4) suggests the presence of the latter compound in the final fraction and in the residue. These deductions were confirmed by recovering the free fatty acids from several fractions and isolating them by fractional crystallization from ethyl alcohol. Palmitic acid, melting at 63°, was obtained from Fraction I; stearic acid, melting at 69°, was separated from Fraction 5 and arachidic acid, melting at 77° was crystallized from the residue. These melting points remained constant on further crystallization and were not altered when the isolated acids were mixed with equal portions of other samples of the respective acids, the purities of which had been established by elementary analysis. No myristic acid could be detected in Fraction I, and no acid with a molecular weight higher than arachidic acid was found in the residue.

The quantities of the saturated acids in the fractions were calculated from the mean molecular weights of the saturated acid esters (Column 6, Table IV) and the theoretical molecular weights of the esters present. The results are given in Columns 7-12, Table IV. The percentage composition of the saturated acid fraction is recorded in Column 2, Table V. These values calculated to the basis of the original oil are given in Column 3, and the equivalent percentages of glycerides are shown in Column 4.

The results of the determination of the composition of rubber-seed oil are summarized in Table VI. This represents the composition of the oil before it became highly acid.

Discussion of Results

THE composition as recorded in Table VI suggests that the oil should have good drying power and in this respect should be superior to soya bean oil, which has a limited application in the paint and varnish industry when mixed with linseed oil. However, the commercial samples of the oil which have been submitted to drying tests by some of the investigators referred to above have been found to possess poor drying properties. It is probable that the high content of free fatty acids in the oils tested has been partly responsible for these reports. Gardner[3-a] expressed a similar opinion and to confirm it conducted the following experiment. Fifty grams of crude rubber-seed oil, with an acid value of 57, and 2 grams of glycerine were heated with 3 grams of lime resinate (as a catalyst) to 260° for 90 minutes. Water was given off, and the mixture darkened considerably. The product was found to have an acid value of 5.1, showing that esterification had take place. A small amount of cobalt drier was added to a portion of the resulting oil, and the sample flowed on a glass plate. It dried over night to a film more firm than one produced with soya bean oil which had been treated with cobalt drier.

Apparently rubber seeds are so sensitive that they die shortly after maturity, and then a considerable portion of the fatty acids are liberated from the glycerides by the hydrolytic enzymes in the seeds. If the oil is filtered soon after manufacture its acidity upon standing increases very slowly. Attempts are being made in rubber producing countries to find some way to prevent the formation of so much free fatty acids in the seeds. If future attempts prove successful the oil may find considerable use in the paint and varnish industry.

References

[1] Malayan Agric. Jour.[a] *6*, 231 (1918);[b] *7*, 73 (1919);[c] *17*, 39 (1929).

[2] Bull. Imp. Inst. *1*, 156 (1903); *2*, 22 (1904); *7*, 95 (1909); *9*, 35 (1911); *11*, 551 (1913)[a] *17*, 543 (1919); *21*, 150 (1923); *27*, 340 (1929).

[3] Gardner, Paint Manufacturers Assoc. of U. S., Scientific Section, Circulars[a] 118, 154, 323.

[4] Pickles and Hayworth, Analyst *36*, 491 (1911).

[5] Trevithick and Lauro, Cotton Oil Press *5*, No. 9, 33 (1922).

[6] Proc. Amer. Soc. Test. Materials *1*, 367 (1922).

[7] Kaufmann and Keller, Z. angew. Chem. *42*, 20 and 73 (1929).

[8] Steele and Washburn, Ind. Eng. Chem. *12*, 52 (1920).

[9] J. Amer. Chem. Soc. *42*, 2398 (1920); Cotton Oil Press *6*, No. 1, 41 (1922).

[10] J. Amer. Chem. Soc. *42*, 152 and 1197 (1920).

TABLE I

RUBBER SEED OIL
CHEMICAL AND PHYSICAL CHARACTERISTICS

Specific gravity, 25°/25°	0.9185
Refractive index, 20°	1.4737
Acid value	40.9
Saponification value	191.8
Unsaponifiable matter (%)	0.8
Reichert-Meissl number	0.3
Polenske number	0.2
Iodine number (Hanus)	135.2
Thiocyanogen-iodine number	88.8
Hexabromide number	15.7
Saturated acids (corrected) %	16.0
Unsaturated acids (corrected) %	78.4
Iodine number of unsaturated acids	163.8

TABLE II

RUBBER SEED OIL

Unsaturated Acids	Acids in Original Oil %	Glycerides in Original Oil %
Linolenic	19.6	20.5
Linolic	31.5	32.9
Oleic	27.3	28.5
	78.4	81.9

TABLE III

RUBBER SEED OIL
FRACTIONAL DISTILLATION OF METHYL ESTERS OF SATURATED ACIDS

Preliminary Distillation Under 5 mm. Pressure

Fraction	Temperature °C.	Weight G.
A	172-7	18.90
B	178	21.63
C	178-81	23.00
D	182-5	20.40
E	188-98	18.40
Residue		2.10

Final Distillation Under 4 mm. Pressure

Fractions A and B mixed	1	162-7	9.30
	2	168-76	23.20
Fractions C and D added	3	180-2	21.60
Fractions E added	4	183-5	22.04
Residue added	5	186-91	17.65
	6	192-215	10.00
	Residue		0.64

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RUBBER SEED OIL

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TABLE IV

Results of Analyses of Fractions Obtained by Distilling Methyl Esters of Saturated Acids

Fraction	Iodine Number	Saponification Value	Mean Molecular Weight	Esters of Unsaturated Acids %	Mean Molecular Weight of Esters of Saturated Acids	Palmitic Acid %	Palmitic Acid g.	Stearic Acid %	Stearic Acid g.	Arachidic Acid %	Arachidic Acid g.
1	1.5	206.4	271.8	0.96	271.6	89.55	8.33	4.38	0.41		
2	1.5	202.1	277.6	0.96	277.5	69.77	16.19	24.27	5.63		
3	1.9	198.6	282.5	1.22	282.3	53.52	11.56	40.35	8.72		
4	2.7	193.3	290.3	1.73	290.3	26.63	5.87	66.90	14.74		
5	3.1	188.9	296.9	1.99	296.9	4.65	0.82	88.74	15.66		
6	3.4	186.0	301.6	2.18	301.8			81.57	8.16	11.71	1.17
Residue									0.12		0.45
							42.77		53.44		1.62

TABLE V

RUBBER SEED OIL
Saturated Acids

	Acids in Saturated Acid Fraction g.	Acids in Saturated Acid Fraction %	Acids in Original Oil %	Glycerides in Original Oil %
Palmitic	42.77	43.72	7.00	7.3
Stearic	57.10	54.62	8.74	9.1
Arachidic	1.62	1.66	0.26	.3
	101.49	100.00	16.00	16.7

TABLE VI

COMPOSITION OF RUBBER SEED OIL

		Per Cent
Glycerides of	Linolenic acid	20.5
	Linolic acid	32.9
	Oleic acid	28.5
	Palmitic acid	7.3
	Stearic acid	9.1
	Arachidic acid	0.3
	Unsaponifiable matter	0.8

Statement of the ownership, management, circulation, etc., required by the Act of Congress of August 24, 1912, of Oil & Fat Industries, published monthly at New York, N. Y., for Oct. 1, 1930.
State of New York, County of New York.

Before me, a Notary Public in and for the State and county aforesaid, personally appeared Alan Porter Lee, who, having been duly sworn acording to law, deposes and says that he is the Editor of the Oil & Fat Industries and that the following is, to the best of his knowledge and belief, a true statement of the ownership, management (and if a daily paper, the circulation), etc., of the aforesaid publication for the date shown in the above caption, required by the Act of August 24, 1912, embodied in section 411, Postal Laws and Regulations, printed on the reverse side of this form, to wit:

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Sworn to and subscribed before me this 24th day of September, 1930.

Al. J. Ruggiero, Notary Public, Kings Co., No. 509, Reg. No. 1162; Cert. filed in N. Y. Co., No. 309, Reg. No. 1R242; Commission expires March 30th, 1931.

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Apparatus designed to permit the measurement of the foam volume of soap solutions consists essentially of an aspirator bottle connected with a foaming tube immersed in the soap solution. Five hundred cc. of water are allowed to flow from the bottle in thirty seconds, thus drawing air through the solution. The foaming power varies with the concentration of the soap, there being two maxima, one at a concentration of 0.2-0.5% and the other at 0.8-0.9%. Temperature has little effect upon the position of these maxima. Solutions of the sodium soaps of castor oil fatty acids foam very little, even when heated. Addition of soda ash raises the foaming power of castor oil or rosin soaps. *Maslob Zhirov. Delo,* No. 2 (55), 40-4 (1930).