used and the manganese determined by the bismuthate method. Table IV shows the results. The percentage of manganese is figured on the oil.

TABLE IV—MANGANESE CONTENT OF RAW LINSEED OIL

Sample No.	Ash Per cent.	Manganese Per cent.	Sample No.	Ash Per cent.	Manganese Per cent.
1.....	0.16	0.0004	9.....	0.19	0.0008
2.....	0.02	0.0005	10.....	0.21	0.0006
3.....	0.03	Faint trace	11.....	0.05	Faint trace
4.....	0.16	0.0005	12.....	0.03	Faint trace
5.....	0.03	Faint trace	13.....	0.03	0.0005
6.....	0.18	0.0003	14.....	0.04	Faint trace
7.....	0.18	0.0002	15.....	0.16	0.0005
8.....	0.16	0.0003	16.....	0.16	0.0003

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PINE NUT OIL

By MAXWELL ADAMS AND AUGUST HOLMES

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The nut pine tree, *Pinus Monophylla*, also known as *Pinus Fremontiana*, Pinon Pine and Grey Pine, according to Heller¹ grows along the eastern slopes of the Sierra Nevada Mountains from Steamboat Springs on the North to Lower California on the South. It varies in height from a mere shrub, on the borders of the desert, to a magnificent tree almost a hundred feet in height, in the Tehachapi Mountains. On the middle scale of the cones of this tree is borne an oblong thin-shelled seed about 15 mm. in length and weighing about one gram. The color of the nut is yellowish on the upper surface and dark reddish brown on the lower. The endocarp is resinous and oily, possessing a rich and pleasant taste.

Capt. John C. Fremont,² who first discovered this species of pine, in January, 1844, near the present site of Carson City, Nevada, states that the nuts from this tree constituted the principal subsistence of several Indian tribes, whom he visited during his explorations in the Great Basin. At the present time the Indians still gather the nuts in large quantities; a part is sold in the local markets, the remainder is used by the Indians for food.

The nuts used in the following experiments were gathered from trees growing on the mountains west of Walker Lake, Nevada, in the Autumn of 1911. A routine analysis of the nut kernels gave the following results:

	Air-dry Per cent.	Green Per cent.	Water-free Per cent.
Water.....	7.88	61.57	...
Ash.....	2.60	1.08	2.82
Ether extract.....	22.77	9.49	24.70
Crude fiber.....	0.65	0.27	0.70
Crude protein.....	8.94	3.73	9.70
Nitrogen-free extract.....	57.21	23.86	62.08
Nitrogen.....	1.43	0.59	1.55

About eight kilograms of the nuts were partially air dried, hulled, the kernels ground and the oil extracted with ether in a Jacobson extractor.³ The nuts used in one extraction gave the following yield:

Weight of nuts used.....	522 grams
Weight of kernels obtained.....	400 grams
Weight of oil extracted.....	65 grams
Per cent. of oil in nuts.....	12.4
Per cent. of oil in kernels.....	16.2

¹ *Muhlenbergia*, 5, 335.

² Fremont's First and Second Expeditions, p. 221.

³ *Jour. Am. Chem. Soc.*, 23, 2052.

The oil obtained from the evaporation of the ether extract is of the consistency of ordinary olive oil and at first is light yellow in color, but upon standing in the laboratory the color gradually fades. A sample which remained near a window for a year became entirely colorless. The oil has a pleasing aromatic odor and agreeable taste. Blasdale¹ reports that a sample, bought in the open market, and supposed to be pine nut oil, examined by him, had a disagreeable odor and rancid taste. The oil in question must have been extracted from stale nuts, or obtained from the nuts of some pine other than *Pinus Monophylla*, for the physical constants, determined by him, differ markedly from those obtained by us, when examining the freshly extracted oil.

The oil melts at -15° , turns brown and decomposes without boiling at 320° , but when heated under a pressure of 60 mm. it begins to distill without decomposition at 305° . The saponification value, determined by the method of Kottstorfer, is 189.31, and the iodine absorption value, when determined by the method of Hübl, gives the following results:

	Expt. I	Expt. II
Weight of oil used.....	0.2466	0.2338
Weight of iodine absorbed.....	0.2663	0.2525
Iodine value.....	107.97	108.00

The refractive index, determined with an Abbé refractometer, is as follows:

Temperature Degrees	Refractive index
10	1.4747
15	1.4733
20	1.4716
25	1.4698
30	1.4680
35	1.4662
40	1.4543

The refractive index, saponification value and iodine number of the oil, which had been bleached in the sunlight, was determined but no change was noted, except that the iodine number showed a slight diminution, which is probably due to the absorption of oxygen by the semidrying oils present.

The oil was submitted to fractional distillation, at a pressure of 60 mm., and each fraction examined with the refractometer. in order, if possible, to separate it into distinct chemical compounds, with the following results: 150 cc. of the oil were used for fractionating.

Fraction	Temperature Degrees	Vol. of distillate Cc.	Ref. index at 40°
1	305	0.5	1.4522
2	305-15	20	1.4531
3	315-20	50	1.4550
4	320-50	30	1.4562
5	350-65	20	1.4570
6	365-70	5	1.4594

At 320° the oil in the distilling flask turns brown and begins to show signs of decomposition, which increases as the temperature rises. At the end of the experiment there is in the flask a black tar-like residue. The first three fractions are liquids, the last three solids, at room temperature. The change in the refractive index and the variation in the melt-

¹ *Jour. Am. Chem. Soc.*, 17, 935.

ing points indicate a difference in the composition of the several fractions, but when they were submitted to a second distillation they showed no tendency to produce substances with definite boiling points, and each decomposed somewhat when distilled and left a residue of tar.

The glycerine in the oil was determined by oxidizing with potassium permanganate in alkaline solution, according to the method of Benedikt and Zsigmondy,¹ and found to be 9.2 per cent.

When 200 grams of the oil, dissolved in alcohol, are saponified with potassium hydroxide, and evaporated to dryness, to free the residue from alcohol, it dissolves readily and completely in water, to a clear solution. This test indicates the absence of phytosterol.

The mixed fatty acids when precipitated from the soap solution with dilute sulfuric acid, washed and dried, are light yellow in color, have a sp. gr. of 0.904 at 15°, and the yield is about 90 per cent. of the total oil. The mixed acids, when separated by treating their slightly alcoholic solution with lead acetate, according to the method of Gusserow-Varrentrap,² yielded 82 per cent. of unsaturated acids and 8 per cent. of saturated acids. This method does not give exact quantitative results as Lewkowitsch³ has already pointed out, and the following iodine value determination shows that the saturated acids thus obtained are impure:

	Expt. I	Expt. II
Weight of saturated acid used.....	0.4054	0.3844
Iodine number.....	6.6	6.5
Weight of unsaturated acid used....	0.4016	0.3782
Iodine number.....	116.8	117.1

0.6031 gram of these mixed saturated acids was dissolved by warming with 100 cc. of alcohol, sp. gr. 0.91, which had previously been saturated with pure stearic acid at 0° C., and allowed to stand in a flask surrounded by ice water for twenty-four hours. The white, laminated crystals which separated were filtered from the solution and weighed when dry 0.0657 gram. Their melting point was 66°. This yield shows the presence of 10.8 per cent. stearic acid in the mixed saturated acids, or about 1 per cent. stearic acid in the original oil.

Using the iodine number of oleic acid as 90.07, and the iodine number of the impure saturated acids, determined above, as 6.6 in the following equation $\frac{100 \times 6.6}{90.07} = \text{per cent. oleic acid}$, we have 7.21 per cent. oleic acid present. Assuming that the impure saturated acids obtained by the lead salt method consisted wholly of stearic, palmitic and oleic acids, there would be, calculated by difference, 82 per cent. palmitic acid present in the saturated acids. There was, however, obtained by the crystallization from alcohol of the magnesium salt of the mixed saturated acids, a very small yield of an acid, which had a refractive index of 1.4236 at 72°. This is identical with that given by Partheil and Ferrie⁴ for lauric acid. The

quantity available was not sufficient for a more complete identification.

The unsaturated acids obtained are light yellow in color, have a sp. gr. at 15° of 0.938 and have a refractive index as follows:

Temperature Degrees	Refractive index
15	1.4657
20	1.4635
25	1.4623
30	1.4604
35	1.4588
40	1.4570
45	1.4550

The neutralization value of the mixed unsaturated fatty acids is 211.1, and the mean molecular weight calculated from this data is 265.7.

Oleic acid, according to the investigations of Hazura,⁵ is converted into hydroxystearic, and linolic acid into sativic acid, when the mixed acids are oxidized with potassium permanganate in dilute alkaline solution. After oxidizing ten grams of the mixed acids by this method, the acids were recovered by passing into the solution a stream of sulfur dioxide, until the solution had an acid reaction. The precipitated acids were then collected on a filter and separated by extracting the hydroxystearic acid in a Soxhlet apparatus with ether. The solution thus obtained was evaporated to a small volume and cooled, when the white laminated crystals of dihydroxystearic acid separated. The crystals thus obtained after a second recrystallization had a melting point of 132°. The dihydroxystearic acid obtained was 44 per cent. of the total unsaturated acids, which corresponds to 39.2 per cent. oleic acid. This method does not give quantitative results, since a considerable amount of the dihydroxystearic acid remains in the ether solution, used for extraction and purification, but it serves to fix the lower limit for the amount of oleic acid present.

The residue remaining in the Soxhlet apparatus, which was insoluble in the ether, was extracted repeatedly with hot water, and the sativic acid allowed to crystallize. The ten grams of mixed fatty acids used gave 0.8 gram of a white crystalline substance having a melting point of 171°, which is slightly lower than that given for tetrahydroxystearic acid. Were the acid pure this corresponds to 6.4 linolic acid. Besides the oleic and linolic acids the presence of small quantities of other unsaturated acids were indicated, but no confirmatory tests made were successful in proving their identity. Assuming that the mixed fatty acids consisted entirely of oleic and linolic acids, calculated from the following formula,

$$x + y = 100$$

$$\frac{90.07x}{100} \pm \frac{181.42y}{100} = 117.05$$

where x equals the per cent. of oleic, y equals the per cent. of linolic acid, and 117.05 the iodine number of the mixed acids, there would be present 70.5 per cent. of oleic and 29.5 per cent. of linolic acid. But by the method of Hazura we obtain only 6.4 per cent. of linolic acid. Experimental errors and inaccuracies of the two

⁵ *Mond. f. Chemie*, 1887, 147-260.

¹ *Jour. Soc. Chem. Ind.*, 1885, 610.

² *Liebig's Ann.*, 27, 153; 35, 197.

³ *Jour. Soc. Chem. Ind.*, 1890, 845.

⁴ *Archive. der Pharm.*, 1903, 545.

methods do not satisfactorily account for so great a variation in results. Careful tests by the method of Hazura failed to show the presence of linolenic acid, but from the high iodine absorption, some unidentified unsaturated acid appears to be present.

From these experiments we conclude that the oil from the nuts of *Pinus Monophylla* consists chiefly of the glyceride of oleic acid together with small amounts of the glycerides of stearic, palmitic, lauric and linolic acids.

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ANALYSES OF CERTAIN OF THE PACIFIC COAST KELPS¹

By E. G. PARKER AND J. R. LINDEMUTH

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While many kinds of kelp are to be found on both the Atlantic and Pacific coasts, the giant kelps, peculiar to the Pacific coast, are the most important to the United States from an economic standpoint because of their size and remarkable content of potassium salts. While the other varieties grow from two to twelve feet in length, the giant kelps are found from 30 to 200 feet in length, and in specific cases much longer.

The composition of the Pacific kelps was studied first by David M. Balch,² of Coronado Beach, California. He analyzed specimens of the giant kelps of the northern and southern Pacific coast of the United States, including *Nereocystis luetkeana*, *Macrocystis pyrifera*, and *Pelagophycus porra*. Later in the course of an investigation of the fertilizer resources of the United States, under the direction of Dr. Frank K. Cameron,³ the composition was studied by Dr. J. W. Turrentine,⁴ of this Bureau, who analyzed specimens of various algae collected from Alaska by Mr. E. C. Johnston, of the "Albatross," from Puget Sound (San Juan County), Washington, by Prof. Geo. B. Rigg, of the University of Washington; from the region of Monterey Bay, California, by Prof. F. M. McFarland, of Leland Stanford Jr. University; and from the vicinity of San Diego, California, by Capt. W. C. Crandall, of the La Jolla Marine Biological Station.⁵ From these analyses it has been concluded that the genuses to be considered as commercial sources of potash are, in the north—the *Nereocystis luetkeana* and *Macrocystis pyrifera*, and in the south—the *Macrocystis pyrifera* and the *Pelagophycus porra*; also, that the indications are that the northern kelps are richer in potassium chloride than the southern.

Samples.—Specimens of *Macrocystis pyrifera* and *Nereocystis luetkeana* were collected for analysis in Freshwater Bay, Washington, by Prof. George B. Rigg: from 34°–38° N, 120°–124° W, and also from 32°–33° N, 117°–118° W, by Capt. W. C. Crandall. The samples collected by Prof. Rigg were shipped dry, in glass jars, while those by Capt. Crandall were shipped dry, in canvas bags. In each case the entire

sample was dried at 103° C. until it would easily powder, and was then ground, care being taken not to lose any of the adhering salts, or salts shaken off into receptacle in transit. After grinding, the whole sample was mixed well to ensure homogeneity.

Method of Analysis.—The methods of analysis used were in the main those employed by Turrentine.¹ The results of the analyses are recorded in Table I, p. 288.

The determinations of nitrogen were made by Mr. T. C. Trescott, of the Bureau of Chemistry, to whom we are greatly indebted. The determinations were made on the oven-dried samples by the Kjeldahl method. The locations from which samples were collected by Crandall are given in latitude and longitude. A detailed description of this work by Crandall and Rigg, together with a complete set of working charts of the Pacific kelp groves from Puget Sound southward, will soon be published by the Bureau of Soils.

DISCUSSION OF ANALYTICAL DATA

In the second column are given the serial numbers of the kelp samples examined. There are three series consisting of three collections of samples secured during the year 1912. They are designated by the initial letter of the name of the collector: as R, Rigg; C, Crandall; C', Crandall (different collection).

An inspection of Table I (see p. 288) results in the following averages:

TABLE II

	KCl Percent.	I Percent.	N Per cent.
Series R (aver. of 11).....	27.63	..	2.14
Series C (aver. of 19).....	23.84	..	2.21
Series C' (aver. of 9).....	10.34	..	1.11
Macrocystis (aver. of 23).....	15.82	..	..
Nereocystis (aver. of 16).....	30.50	..	..
Series R (Mac) (aver. of 2).....	19.47	..	..
Series R (Ner) (aver. of 9).....	29.54	..	..
Series C (Mac) (aver. of 12).....	19.20	..	..
Series C (Ner) (aver. of 7).....	31.74	..	..
Series C' (Mac) (aver. of 9).....	10.54	..	..
Entire table (aver. of 39).....	21.85	0.20	1.93

From Tables I and II the following conclusions may be drawn:

1. That the average potassium chloride content is high.
2. That apparently no definite relation exists between the different constituents of kelp.
3. That the total average potassium chloride content of the *Nereocystis luetkeana* is greater than that of the *Macrocystis pyrifera* and that for the potassium chloride content of kelp from different localities the same is true; also that in every case the potassium chloride content of the *Nereocystis luetkeana* is greater than the average potassium chloride content of the *Macrocystis pyrifera*.
4. That apparently the northern kelps are richer in potassium chloride than the southern.
5. That the kelp from the southern coast of California (Series C', Table II) is comparatively low in potassium chloride. The fact that the average potassium chloride content of kelp from the same locality was found to be much higher both by Balch and Turrentine, and also that the nitrogen content is

¹ Published by permission of the Secretary of Agriculture.

² Balch, THIS JOURNAL, 1, 177 (1909).

³ Senate Doc. No. 190, 62nd Congress, 2nd Session, 1912.

⁴ Turrentine, THIS JOURNAL, 4, 431 (1912).

⁵ Now the Scripps Marine Biological Station, of the University of California.

¹ Turrentine, loc. cit.