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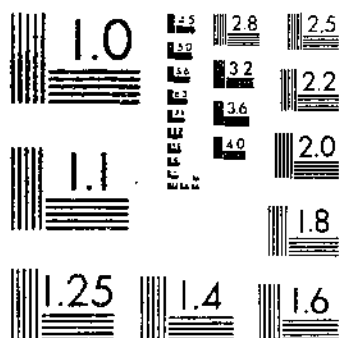
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ANALYSES AND COMPOSITION OF CALIFORNIA LEMON AND ORANGE OILS
POORE, H. D.

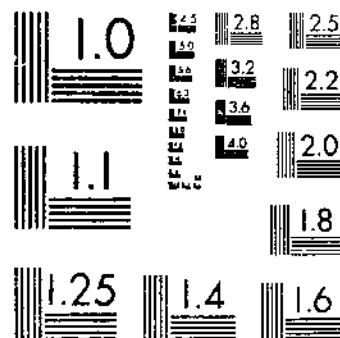
USDA TECHNICAL BULLETINS
ANALYSES AND COMPOSITION OF CALIFORNIA LEMON AND ORANGE OILS

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UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

ANALYSES AND COMPOSITION OF CALIFORNIA
LEMON AND ORANGE OILS

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INTRODUCTION

The citrus industry of California, with a total bearing area of 238,000 acres (9)² in 1927, is confined principally to the southern part of the State (fig. 1), only 2 per cent being in the northern part and 20 per cent in the central part of the State. Practically all the grapefruit acreage, comprising 8,000 acres, and the lemon acreage, 43,000 acres, is in the south. The 1926-27 crop of citrus fruits yielded a total of about 650,000 boxes of grapefruit, 7,700,000 boxes of lemons, and 28,000,000 boxes of oranges.

The harvesting and marketing of the lemon and orange crops vary considerably. There are three varieties of lemons, Lisbon, Eureka, and Villa Franca, the first two predominating. Harvesting is carried on throughout the year, but the largest pickings are made in the spring. The lemons are picked according to size, and although most of them are green, many are yellow or tree ripe. Before being sorted and culled for shipment, the fruit is placed in cold storage for periods ranging from two weeks to several months. No distinction between varieties is made at the packing houses.

There are two principal orange crops: The Valencia, which extends from April to November, and the Washington Navel, from November to May. The oranges, picked only after reaching a maturity standard, are graded and culled upon arrival at the packing house and generally shipped within a few days.

It has been estimated that from 5 to 10 per cent of the citrus crop fails to reach the market standards. This cull fruit is valuable for by-products, and an important industry based on the utilization of

¹ Appreciation is hereby expressed for the assistance of E. M. Chace, chemist in charge, laboratory of fruit and vegetable chemistry, under whose supervision the work was conducted.

² Italic numbers in parentheses refer to Literature Cited, p. 29.

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cull citrus fruit has developed in southern California in the past 10 years. During the years in which freezes occur or market demands are below the average, still more fruit is utilized for by-products. One of the principal by-products is the citrus oil, but although several hundred thousand pounds of both the expressed and distilled

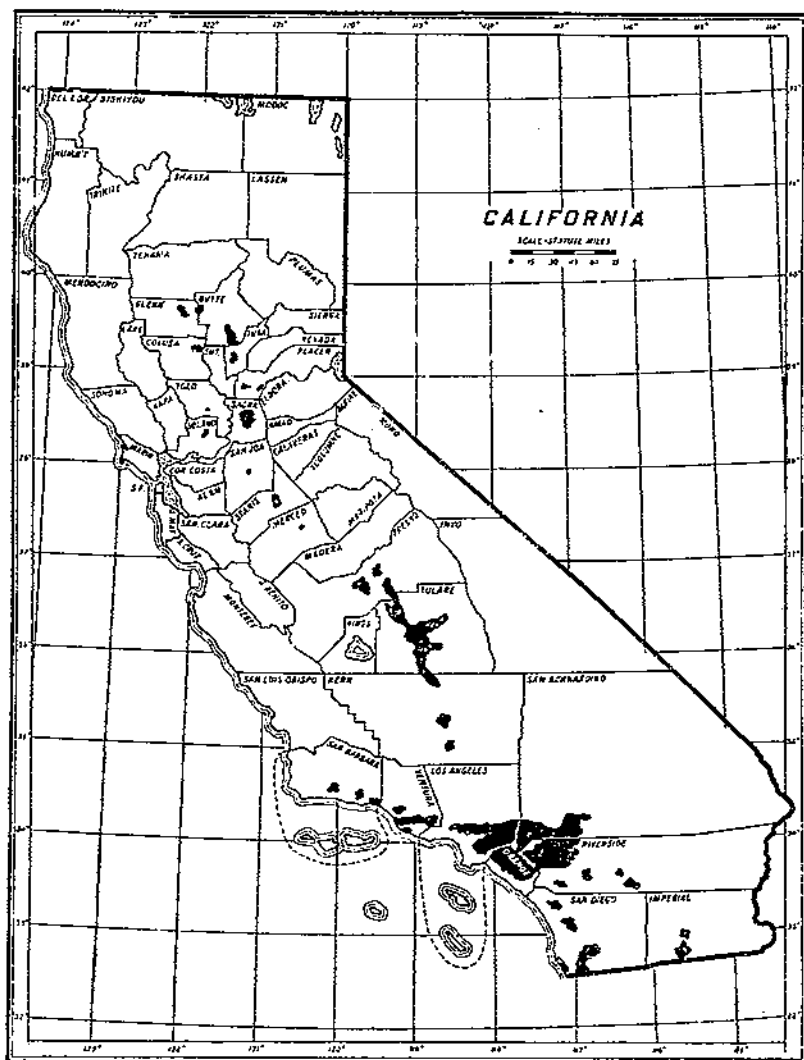


FIGURE 1.—Map showing by black patches and dots the distribution of the citrus-producing area in California on January 1, 1924

oils have been produced, very little has appeared in the literature pertaining to their analyses and composition. Data on the physical constants are very much needed in order to judge the purity of commercial oils and to compare them with imported oils. The chemical composition is also of considerable interest. The work reported in this bulletin was done to obtain these data.

During the years 1923-1926, inclusive, samples of lemon oil were supplied to this laboratory by a lemon by-products company, and during the same period an orange by-products company furnished samples of Washington Navel and Valencia orange oils.³ These samples, each weighing about a pound, were from lots of oil commercially produced at the by-products plants by crushing the whole fruit between large rollers, and then separating the oil from the juice by centrifuging. The condition and quantity of fruit in each lot were noted, as well as the district from which it came. The samples, collected in dark bottles, were dried by adding a small quantity of anhydrous sodium sulphate and allowing them to stand in the ice box for several days. They were then filtered and analyzed to determine the physical constants and the citral and the ester content. After this analysis the samples were stored in the ice box, and at the end of each season they were combined in large containers for the determination of their chemical composition.

As these machine-made oils were in contact with the citrus juice during the process of manufacture, it was expected that they would show some variations from the hand-pressed Italian oils. The climatic and soil conditions of California, together with the fact that the fruit had been handled differently from that in Italy, might also affect the composition to a considerable extent. All the oils were from fruit from the southern counties, as there are no by-products plants in the north.

ANALYSES OF CALIFORNIA LEMON AND ORANGE OILS METHODS OF ANALYSES

The methods given in the Journal of the Association of Official Agricultural Chemists were used in the analyses of the oils (2, p. 355).

The specific gravity, however, was determined at $\frac{25^{\circ}\text{C}}{25^{\circ}\text{C}}$ as recommended in the United States Pharmacopœia. These results may be calculated to $\frac{15.6^{\circ}}{15.6^{\circ}}$ by adding 0.0054, and to $\frac{20^{\circ}}{20^{\circ}}$ by adding 0.0025. If desired, the results at $\frac{20^{\circ}}{20^{\circ}}$ may be calculated to $\frac{20^{\circ}}{4^{\circ}}$ by multiplying by 0.99823, the density of water at 20°.

The total solids⁴ were determined by evaporating 10 cubic centimeters of the sample measured at 20° nearly to dryness on a water bath, then transferring to a water-jacketed oven and drying at the temperature of boiling water for two and one-half hours.

Citral was determined by the Kleber method and also by the Parker and Hiltner method (13). The latter, a modification of the old official Hiltner method, is now official (3, 13).

As the California orange oils are more deeply colored than the imported oils, it was necessary in using the Hiltner method to decolorize them with charcoal, in order to compare them with the standard citral solution. This was accomplished by diluting 4 grams of oil to 50 cubic centimeters with alcohol, and placing 5 cubic centimeters of the diluted oil in a 50 cubic centimeter Erlenmeyer flask with about 15 cubic centimeters of alcohol and enough charcoal to decolorize.

³ The oils used in this investigation were supplied by the Exchange Lemon Products Co., Corona, Calif., and the Exchange Orange Products Co., Ontario, Calif.

⁴ Total solids is here used for the substance designated as evaporation residue by Glidemeister and Hoffmann (6, v. 3, p. 30, 62).

It was then filtered and washed into a 50 cubic centimeter flask, 10 cubic centimeters of the metaphenylenediamine hydrochloride solution was added, and the whole was made up to mark with alcohol.

The aldehyde in orange oil is decylic, although as a rule it is reported as citral. As metaphenylenediamine hydrochloride apparently does not react quantitatively with decylic aldehyde, the results by the Hiltner method are always much lower than by the phenylhydrazine method (Kleber method). The latter method as used in this work requires that the phenylhydrazine shall stand with the oil for half an hour. This is long enough for lemon oil, but as reported by Gilde-meister and Hoffmann (6, *v. 3*, p. 56), two hours are necessary for orange oil, as decylic aldehyde reacts more slowly than citral. In tests made with several samples of orange oil the oils showed about 1 per cent of aldehyde as citral in half an hour, but yielded 0.2 per cent more when they were allowed to stand for two hours with the phenylhydrazine.

Although both α and β pinene were identified in the lemon oil, the official pinene test gave negative results because it is not delicate enough to reveal mere traces. No pinene was found in the orange oil.

The saponifiable substances (esters) were determined by the following unpublished method of A. F. Seeker and W. E. Kirby: Place 4 grams of oil, 25 cubic centimeters of 95 per cent alcohol, and 1 cubic centimeter of 50 per cent hydroxylamine hydrochloride in a separatory funnel. Titrate to a faint pink with a 4 per cent alcoholic solution of potassium hydroxide, using phenolphthalein as indicator. Discharge the color at once by adding 1 drop of a 20 per cent solution of hydroxylamine hydrochloride, add 25 cubic centimeters of benzene, purified as directed below, and shake. Then add 50 cubic centimeters of a saturated salt solution and shake again vigorously. Allow the mixture to separate, draw off and discard the salt solution, and wash three times more in the same manner, using each time 25 cubic centimeters of salt solution. Finally wash with 4 cubic centimeters of water, and after drawing off the water, run the benzene solution into a 200 cubic centimeter Erlenmeyer flask. Rinse the separatory funnel once with 25 cubic centimeters of alcohol and add this alcohol to the solution in the Erlenmeyer flask.

Add sufficient approximately tenth normal alcoholic potassium hydroxide to make the mixture neutral to phenolphthalein, and then add exactly 30 cubic centimeters more. Boil under a reflux condenser for one hour, cool, and titrate with a tenth normal aqueous solution of hydrochloric acid. Deduct the volume of acid required for this titration from the quantity required to titrate a blank conducted by refluxing for one hour a mixture containing 25 cubic centimeters each of benzene and alcohol and 30 cubic centimeters of the approximately tenth normal alcoholic potassium hydroxide. One cubic centimeter of tenth normal hydrochloric acid is equivalent to 0.0196 gram of the esters linalyl and geranyl acetates.

Most grades of benzene on the market require purification for this purpose. It may be purified as follows: Reflux 2 liters of the benzene for two hours with sodium ethylate (3 grams of metallic sodium dissolved in 100 cubic centimeters of 95 per cent alcohol). Then distill, rejecting the first and last portions, and wash the distillate in a separatory funnel twice with distilled water to remove alcohol and other soluble substances.

The Seeker-Kirby method has been found to determine about 90 to 95 per cent of known amounts of linalyl acetate which had been

added to mixtures of citral and terpenes. It is quite satisfactory to use for comparison of the California and imported oils. According to Gildemeister and Hoffmann (6, v. 1, p. 571) esters in oils which contain aldehydes can not be determined by the ordinary quantitative saponification method, as, owing to the decomposition of the aldehyde, alkali is consumed. This consumption increases with the length of time of the reaction. In the Seeker-Kirby method the aldehyde is removed with the hydroxylamine hydrochloride.

The results of the analyses of the oils are given in Tables 1, 2, and 3. The pinene tests, made on the first 64 samples of lemon oil, on the first 21 samples of Valencia orange oil, and on the first 3 samples of Washington Navel orange oil, were negative. The determination of esters made on the first 21 samples of Valencia oil, combined according to counties, showed the following averages: Los Angeles, 1.03 per cent; Orange, 1.08 per cent; San Bernardino, 1.08 per cent. Average analyses of distilled oils obtained from the first 11 lots of Valencia oranges are included in Table 2. These oils were produced at the plant by steam distilling the residue, after removal of the juice and expressed oil. These combined oils contained 0.49 per cent of esters.

TABLE 1.—Analyses of California lemon oils

Source of fruit (county) and number of samples	Quantity of fruit	Specific gravity	Total solids	Refractive index ¹			Optical rotation ¹			Citral		
				Original	10 per cent distillate	Difference	Original	10 per cent distillate	Difference	Kleber	Hiltner	Esters
Ventura (14 samples):	Tons		P. ct.				°	°	°	P. ct.	P. ct.	P. ct.
Minimum	16.7	0.8485	2.27	1.4739	1.4727	0.0010	52.71	47.58	2.92	2.7	2.0	1.85
Maximum	27.5	.8525	4.28	1.4749	1.4733	.0016	66.17	63.25	5.82	3.7	3.7	3.04
Average	21.5	.8504	3.02	1.4744	1.4731	.0013	59.53	55.02	4.52	3.2	2.8	2.40
San Bernardino (2 samples):												
Minimum	18.0	.8482	2.24	1.4738	1.4729	.0012	62.28	58.67	3.61	2.1	1.6	1.76
Maximum	30.0	.8511	3.19	1.4747	1.4732	.0015	66.20	60.90	4.30	2.8	2.5	3.04
Average	19.0	.8490	2.72	1.4742	1.4730	.0014	63.74	59.78	2.94	2.4	2.0	2.40
Los Angeles (16 samples):												
Minimum	10.0	.8481	2.01	1.4738	1.4726	.0011	60.48	55.91	1.80	2.3	1.8	1.90
Maximum	28.1	.8511	4.52	1.4748	1.4732	.0016	69.07	61.91	5.07	3.2	2.9	2.84
Average	20.9	.8493	3.02	1.4742	1.4720	.0013	64.29	60.14	4.15	2.6	2.2	2.24
Riverside (10 samples):												
Minimum	14.7	.8475	2.21	1.4738	1.4727	.0010	63.11	57.00	3.74	2.6	1.4	1.80
Maximum	30.6	.8506	3.86	1.4745	1.4733	.0014	70.18	65.74	6.11	2.6	2.6	2.50
Average	22.1	.8487	2.96	1.4742	1.4730	.0012	65.80	60.98	4.82	2.3	2.0	2.12
San Diego (12 samples):												
Minimum	15.2	.8488	2.22	1.4742	1.4729	.0011	53.12	46.47	2.92	2.5	1.6	1.76
Maximum	21.6	.8517	3.48	1.4746	1.4732	.0015	67.55	61.63	6.65	3.2	2.9	3.12
Average	17.8	.8501	2.66	1.4744	1.4730	.0013	61.76	57.13	4.64	2.8	2.2	2.62
Santa Barbara (2 samples):												
Minimum	17.5	.8506	3.76	1.4742	1.4730	.0012	51.21	47.44	6.79	3.0	2.4	1.91
Maximum	24.1	.8515	4.43	1.4742	1.4730	.0012	54.93	43.74	6.80	3.1	2.7	2.34
Average	20.8	.8510	4.10	1.4742	1.4730	.0012	54.53	47.79	6.80	3.0	2.6	2.12
Orange (14 samples):												
Minimum	16.6	.8480	2.08	1.4738	1.4728	.0005	59.25	53.82	2.89	2.2	1.9	2.21
Maximum	30.1	.8516	4.07	1.4746	1.4737	.0015	66.73	61.96	6.79	3.3	3.1	2.84
Average	20.9	.8498	2.94	1.4743	1.4731	.0011	62.13	57.41	4.73	2.9	2.4	2.50
Seven counties (73 samples):												
Minimum	10.0	.8475	2.01	1.4738	1.4726	.0005	52.71	46.47	1.80	2.0	1.4	1.70
Maximum	30.6	.8525	4.52	1.4749	1.4737	.0017	70.18	65.74	6.80	3.7	3.7	3.12
Average	20.3	.8497	2.90	1.4743	1.4730	.0013	62.48	57.99	4.57	2.8	2.3	2.38

¹ Wherever used in this bulletin, refractive index and optical rotation refer to sodium light and 20°C; that is, n_D^{20} and α_D^{20} . Determinations of specific gravity were always made at 25°C .

TABLE 2.—Analyses of California Valencia orange oils

County or season and number of samples	Quantity of fruit	Specific gravity	Total solids	Refractive index			Optical rotation			Citral		Esters?
				Original	10 per cent distillate	Difference	Original	10 per cent distillate	Difference	Kleber	Hiltner	
Orange County (23 samples):	Tons		P. ct.				°	°	°	P. ct.	P. ct.	P. ct.
Minimum	5.0	.8425	2.74	1.4728	1.4719	0.0009	96.12	97.94	0.56	1.1	0.16	0.46
Maximum	12.4	.8482	5.87	1.4745	1.4726	.0021	98.50	99.88	-3.47	1.8	.36	1.76
Average	9.2	.8448	4.22	1.4736	1.4722	.0014	97.29	99.17	-1.87	1.4	.24	1.03
Los Angeles County (30 samples):												
Minimum	4.1	.8413	1.93	1.4728	1.4718	.0007	95.71	98.21	0.90	1.0	.13	.35
Maximum	13.6	.8460	4.82	1.4741	1.4727	.0020	99.58	100.44	-3.05	2.2	.32	1.37
Average	9.0	.8434	3.15	1.4734	1.4723	.0011	98.04	99.10	-1.14	1.4	.22	.81
San Bernardino County (4 samples):												
Minimum	3.0	.8425	2.55	1.4735	1.4723	.0010	97.81	99.10	-1.10	0.8	.14	.64
Maximum	8.3	.8464	6.26	1.4740	1.4725	.0023	98.62	100.02	-1.94	1.2	.23	1.09
Average	5.8	.8447	4.29	1.4742	1.4724	.0017	98.22	99.04	-1.42	1.0	.17	1.00
All counties (63 samples):												
Minimum	4.1	.8413	1.93	1.4728	1.4718	.0007	95.71	97.94	.96	.8	.13	.44
Maximum	13.6	.8482	6.26	1.4746	1.4727	.0023	99.58	100.44	-3.47	2.2	.30	1.70
Average	8.8	.8440	3.61	1.4735	1.4723	.0013	97.78	99.21	-1.43	1.4	.22	.83
Distilled (11 samples)												
Average		.8406	1.46	1.4722	1.4720	.0002	96.28	98.87	.41	1.2	.21	.49
Season 1923 (21 samples):												
Minimum	3.0	.8418	1.93	1.4732	1.4720	.0007	95.71	98.21	-5.4	0.8	.15	-----
Maximum	11.0	.8467	6.26	1.4746	1.4727	.0023	98.64	100.44	-3.47	1.8	.35	-----
Average	7.0	.8439	3.93	1.4737	1.4723	.0014	97.46	99.34	-1.88	1.3	.23	1.05
Season 1924 (11 samples):												
Minimum		.8425	2.74	1.4728	1.4718	.0009	96.12	98.62	-8.3	1.3	.22	.49
Maximum		.8449	4.81	1.4731	1.4721	.0012	98.21	99.60	-3.20	2.2	.36	1.37
Average		.8438	3.76	1.4730	1.4720	.0010	97.16	99.10	-1.94	1.7	.28	.96
Season 1925 (31 samples):												
Minimum	5.0	.8413	2.07	1.4730	1.4720	.0007	95.99	97.94	.96	1.0	.13	.35
Maximum	13.6	.8482	5.65	1.4742	1.4726	.0019	99.58	100.02	-3.33	1.8	.26	1.70
Average	9.9	.8442	3.85	1.4736	1.4724	.0012	98.21	99.16	-.94	1.4	.19	.78

TABLE 3.—Analyses of California Washington Navel orange oils

County or season and number of samples	Quantity of fruit	Specific gravity	Total solids	Refractive index			Optical rotation			Citral		
				Original	10 per cent distillate	Difference	Original	10 per cent distillate	Difference	Kiebel	Hiltner	Esters
Los Angeles County (18 samples):												
Minimum.....	1.3	0.8419	1.49	1.4731	1.4723	0.0008	94.18	97.79	0.41	0.6	0.12	0.59
Maximum.....	12.4	.8503	3.17	1.4748	1.4727	.0024	99.32	99.59	-4.71	1.0	.27	2.53
Average.....	5.0	.8456	4.75	1.4733	1.4724	.0014	96.93	98.77	-1.84	.8	.19	1.50
San Bernardino County (7 samples):												
Minimum.....	1.0	.8425	2.20	1.4732	1.4723	.0009	95.29	98.05	.00	.7	.14	.49
Maximum.....	11.6	.8489	6.84	1.4746	1.4727	.0020	98.77	99.31	-3.74	.9	.21	2.11
Average.....	5.4	.8466	4.91	1.4738	1.4724	.0014	96.76	98.64	-1.88	.8	.17	1.27
Riverside County (9 samples):												
Minimum.....	1.1	.8426	2.31	1.4732	1.4722	.0009	95.84	97.93	.69	.7	.16	.54
Maximum.....	11.6	.8478	6.20	1.4742	1.4727	.0017	98.62	98.91	-2.92	.9	.23	2.22
Average.....	7.2	.8449	4.02	1.4730	1.4724	.0012	97.12	98.60	-1.48	.8	.19	1.18
All counties (31 samples):												
Minimum.....	1.0	.8410	1.49	1.4731	1.4721	.0008	94.18	97.51	.69	.6	.12	.49
Maximum.....	12.4	.8503	6.17	1.4746	1.4727	.0024	99.32	99.59	-4.71	1.0	.27	2.53
Average.....	6.5	.8455	4.53	1.4738	1.4724	.0013	96.93	98.71	-1.78	.8	.19	1.38
Season 1924 (3 samples):												
Minimum.....		.8423	2.07	1.4731	1.4721	.0008	98.21	98.49	-.14	.7	.22	.69
Maximum.....		.8444	3.91	1.4734	1.4723	.0013	98.91	99.05	-.56	.9	.27	.93
Average.....		.8433	2.77	1.4732	1.4722	.0010	98.45	98.77	-.32	.8	.24	.82
Season 1925 (10 samples):												
Minimum.....	5.5	.8419	1.49	1.4731	1.4722	.0008	95.99	97.93	.69	.6	.12	.49
Maximum.....	12.4	.8458	5.05	1.4736	1.4727	.0011	99.32	99.32	-2.92	.9	.21	1.22
Average.....	9.3	.8436	2.68	1.4733	1.4723	.0010	98.13	98.86	-.67	.7	.16	.72
Season 1926 (18 samples):												
Minimum.....	1.0	.8449	4.40	1.4737	1.4723	.0013	94.18	97.51	-1.65	.8	.15	1.37
Maximum.....	8.7	.8583	8.17	1.4748	1.4727	.0024	96.96	99.59	-4.71	1.0	.25	2.58
Average.....	3.4	.8472	5.91	1.4741	1.4725	.0016	96.01	98.65	-2.64	.9	.19	1.85

Table 4 contains summaries of published analyses of pure Italian hand-pressed lemon oils made by Chace (5), for comparison with the California machine-made oils, and also unpublished data on Italian orange oils as supplied by Mr. Chace.

Table 5 contains the analyses of hand-pressed oils made by the Italian 2-piece method and laboratory machine-made oils produced from the same lots of peels. The oil machine (15) developed by W. E. Sutton of the laboratory of fruit and vegetable chemistry handles about 300 pounds of peel an hour, and has given satisfactory yields with lemon peel.

TABLE 4.—Analyses of Italian lemon and orange oils

LEMON OILS¹

Source and number of samples	Specific gravity	Refractive index			Optical rotation			Total aldehydes (sulphite method)	Cltral	
		Original	10 per cent distillate	Difference	Original	10 per cent distillate	Difference		Kleber	Hiltner
Authentic samples collected in factories in Sicily, 1907-08 (15 samples):										
Minimum.....	0.8503	1.4745	1.4726	0.0019	57.96	53.70	3.16	Per cent	Per cent	Per cent
Maximum.....	.8542	1.4758	1.4739	.0028	63.03	58.75	5.78	7.03		
Average.....	.8526	1.4751	1.4727	.0024	59.97	55.74	4.23	5.57		
Collected from bowls of workmen in factories in Sicily, 1907-08 (139 sam- ples):										
Minimum.....	.8503	1.4743	1.4720	.0017	54.16	49.08	1.01	4.07		
Maximum.....	.8552	1.4758	1.4735	.0028	60.28	53.98	6.17	6.43		
Average.....	.8522	1.4748	1.4726	.0024	60.40	56.69	3.83	5.30		
Collected from bowls of workmen in fac- tories in Sicily, 1909-10 (50 samples):										
Minimum.....	.8508	1.4740	1.4720	.0017	54.68	50.71	0.18	3.8	3.4	2.6
Maximum.....	.8539	1.4753	1.4732	.0028	63.62	62.57	4.58	5.4	5.2	5.3
Average.....	.8522	1.4747	1.4725	.0023	59.18	56.77	2.74	4.8	4.5	4.2

ORANGE OILS

Collected from bowls of workmen in fac- tories in Sicily, 1907-08 (6 samples):										
Minimum.....	0.8410	1.4725	1.4710	0.0010	96.9	96.3	0.6	2.0		
Maximum.....	.8447	1.4730	1.4716	.0018	99.6	99.1	-1.0	3.3		
Average.....	.8432	1.4727	1.4713	.0014	98.4	98.4	0.0	2.8		
Collected from bowls of workmen in fac- tories in Sicily, 1909 (22 samples):										
Minimum.....	.8435	1.4723	1.4712	.0008	92.03	95.00	-0.42	1.58	1.47	0.43
Maximum.....	.8476	1.4737	1.4723	.0021	98.44	99.40	-0.53	2.64	2.50	0.71
Average.....	.8447	1.4729	1.4717	.0012	97.19	98.56	-1.35	2.03	2.12	0.53

¹ Data derived from Table XI, U. S. Dept. Agr., Bur. Chem. Circ. 46, The Occurrence of Pinene in Lemon Oil.

TABLE 5.—Analyses of laboratory machine-made and hand-pressed lemon and orange oils

LEMON OILS

No.	Date	Description of sample	Weight of peel	Amount of oil	Yield of oil per ton of peel	Specific gravity	Total solids	Refractive index			Optical rotation			Citral		Esters
								Original	10 per cent distillate	Difference	Original	10 per cent distillate	Difference	Kleb-er	Hilt-ner	
72	May 12, 1926	Factory sample No. 72 of Table 1				0.8502	P. cl. 3.00	1.4744	1.4734	0.0010	61.31	57.42	3.89	P. cl. 3.3	P. cl. 2.1	P. cl. 2.35
72M	May 13, 1926	Peel from same lot as No. 72, made in small laboratory machine	300			.8514	3.95	1.4746	1.4733	.0013	61.31	57.18	4.13	3.6	2.5	2.45
73	May 25, 1926	Factory sample No. 73 of Table 1				.8489	3.76	1.4742	1.4737	.0005	60.61	53.82	6.79	3.0	2.7	2.21
73M	May 26, 1926	Peel from same lot as No. 73, made in small laboratory machine	300			.8511	4.20	1.4744	1.4731	.0013	60.19	55.34	4.85	3.5	2.8	2.70
1M	July 22, 1926	Made in small laboratory machine	92	6.1	8.4	.8537	3.93	1.4749	1.4732	.0017	56.73	49.93	6.80	4.2	2.5	2.50
2M	Aug. 19, 1926	do	100	4.0	5.0	.8513	3.00	1.4747	1.4731	.0016	57.98	52.57	5.41	3.7	2.9	2.74
3M	Nov. 4, 1926	Made in large laboratory machine	450	13.8	3.8	.8511	3.92	1.4743	1.4730	.0013	60.06	57.42	2.64	2.7	2.0	2.99
4M	Dec. 2, 1926	do	128	6.0	5.7	.8508	4.95	1.4746	1.4733	.0013	59.51	58.12	1.39	3.3	2.5	3.18
5M	Jan. 27, 1927	do	1,038	61.0	7.34	.8495	3.52	1.4746	1.4731	.0015	67.52	67.13	.39	2.5	2.1	2.70
5H	do	Peel from same lot as 5M, hand pressed	85	7.0	10.34	.8505	3.76	1.4746	1.4731	.0015	67.69	66.05	1.64	3.0	2.5	2.55
6M	Mar. 12, 1927	Made in large laboratory machine	815	54.6	8.34	.8499	5.27	1.4746	1.4731	.0015	64.36	60.89	3.47	3.5	2.7	2.30
6H	do	Peel from same lot as 6M, hand pressed	74	6.6	11.1	.8517	6.27	1.4751	1.4732	.0019	63.52	62.28	1.24	3.8	3.0	3.04
7M	Mar. 21, 1927	Made in large laboratory machine	1,555	83.8	6.76	.8494	4.29	1.4743	1.4729	.0014	67.69	65.05	2.64	2.3	2.0	2.50
7H	do	Peel from same lot as 7M, hand pressed	70	4.0	7.34	.8517	7.01	1.4747	1.4729	.0018	66.02	66.30	-.28	2.6	2.3	3.48
		Average of laboratory machine-made oils (9 samples)				.8508	4.11	1.4746	1.4731	.0015	61.71	58.19	3.53	3.3	2.4	2.68
		Average of hand-pressed oils (3 samples)				.8516	5.68	1.4748	1.4731	.0017	65.74	64.88	.86	3.1	2.6	3.02

ORANGE OILS

1H	Apr. 2, 1926	Hand pressed Washington Navel oil	180	2.1	1.44	0.8455	8.30	1.4737	1.4724	0.0013	93.90	99.59	-5.69	1.3	0.15	1.57
2H	Apr. 8, 1926	do	190	2.5	1.69	.8462	6.76	1.4742	1.4724	.0018	95.44	99.73	-4.29	1.0	.12	1.32
3H	Apr. 16, 1926	do	200	3.5	2.2	.8455	7.82	1.4741	1.4723	.0018	94.04	100.00	-5.96	1.3	.16	1.47
4M	June 4, 1926	Valencia oil made in small laboratory machine	300			.8428	2.38	1.4731	1.4721	.0010	98.75	99.03	-.28	1.6	.27	.54
5M	Mar. 9, 1927	Washington Navel oil made in large laboratory machine	385	3.2	1.04	.8439	4.10	1.4734	1.4725	.0009	97.51	98.50	-1.38	1.3	.29	1.06
5H	do	Peel from same lot as 5M, hand pressed	51	4	.9	.8438	4.60	1.4735	1.4725	.0016	96.40	97.50	-1.10	.7	.25	1.32
6M	Apr. 6, 1927	Seedling oil made in large laboratory machine	1,405	11.5	1.03	.8453	7.02	1.4741	1.4725	.0016	95.70	100.28	-4.58	.7	.12	1.23
6H	do	Peel from same lot as 6M, hand pressed	45	3	.9	.8470		1.4742			92.03				.12	
7M	Apr. 12, 1927	Seedling oil made in large laboratory machine	1,670	20.5	1.53	.8453	4.59	1.4738	1.4725	.0013	97.78	100.00	-2.22	.9	.18	1.19
7H	do	Peel from same lot as 7M, hand pressed	96	1.4	1.8	.8481	8.05	1.4744	1.4723	.0021	95.01	100.29	-5.28		.25	1.86
8M	May 11, 1927	Valencia oil made in large laboratory machine	2,025	38.7	2.39	.8444	5.10	1.4735	1.4723	.0012	96.13	99.31	-3.18	1.0	.20	.98
8H	do	Peel from same lot as 8M, hand pressed	85	3.2	4.71	.8453	5.24	1.4734	1.4722	.0012	95.29	99.31	-4.02	1.7	.26	1.62

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DISCUSSION OF RESULTS

LEMON OIL

In Table 1 the averages of results, by counties, show a noticeable variance only in the lower optical rotation and higher percentage of citral from Ventura and Santa Barbara Counties, which adjoin. The highest average optical rotation is found in Riverside County and the next highest in Los Angeles County. Otherwise the averages are fairly uniform. In optical rotation and citral the difference between the maximum and minimum of all the samples is large, the difference in optical rotation being 17.47° and the difference in percentage of citral determined according to the Kleber method being 1.7. Comparison of the California machine-made lemon oils given in Table 1 with the Italian hand-made lemon oils in Table 4 shows the Italian oils to be about 0.0025 higher in specific gravity and 0.0005 higher in refractive index, whereas in optical rotation they are about 2.4° lower. The Italian oils contain more citral, the difference in percentage being 1.7 according to the Kleber method and 1.9 according to the Hiltner method. Fifty-nine samples of Italian lemon oil imported at New York averaged 2.5 per cent total solids; the California oils averaged 2.96 per cent—that is, a difference of 0.5. Fifty other imported samples averaged 3.01 per cent esters by the Seeker and Kirby method, being higher by about 0.6 than the California oils, which averaged 2.38 per cent. Comparison of the laboratory machine-made lemon oils 72M and 73M (Table 5) with the factory machine-made oils 72 and 73 shows that they are about the same except that the citral is higher in the laboratory machine-made oils. The average of citral and of esters in the 9 laboratory machine-made oils (Table 5) is higher than the average of these in the factory samples (Table 1), the difference in percentage being 0.5 (Kleber method) and 0.3, respectively. The hand-pressed oils are from 0.3 to 0.5 per cent higher in citral than the corresponding laboratory machine-made oil. Only one of the oils, No. 1M, contained more than 4 per cent citral. By the Kleber method the average percentage of citral in the 3 hand-made oils was less than that in the Italian oils by 1.4.

ORANGE OIL

The averages by counties of the Valencia oils, shown in Table 2, are uniform, except that the refractive index is higher and the citral content lower in the oils from San Bernardino than in those from the other two counties. The tabulation by seasons shows even more uniformity than by counties, although the refractive index is lower and the citral content higher for 1924. The 11 samples of distilled oil resemble the 10 per cent distillate from the cold-pressed oils, containing, however, nearly as much aldehyde as the cold-pressed oils and two-thirds the quantity of esters.

The averages by counties of the Washington Navel orange oils, in Table 3, are exceptionally uniform so that no striking differences are noted. The tabulation by seasons, however, shows that the excessive quantity of total solids during 1926 produced an average specific gravity 0.0041 higher and a refractive index 0.0009 higher than those in 1924 and 1925. The optical rotation in 1926 is lower by about 2° , and the ester content is more than 1 per cent higher. The ester content appears to vary with the total solids, although not proportionately.

Comparison of the averages of the Valencia and Washington Navel oils (Tables 2 and 3) shows that the content of aldehydes in the Valencia

oil is 0.6 per cent higher than that in the Washington Navel oil by the Kleber method and 0.02 per cent higher by the Hiltner method, and the content of esters is about 0.5 per cent lower. The physical constants, however, are fairly uniform. The Italian orange oils shown in Table 4 have a refractive index about 0.0008 lower than that of the California oils, and the percentage content of citral determined by the Kleber method is higher than that in the Valencia oil by about 0.7. The Hiltner method shows about twice as much citral in the Italian oils. Twenty-seven samples of Italian oil imported at New York averaged 2.8 per cent of total solids, about 0.8 per cent less than the Valencia oils and 1.7 per cent less than the Washington Navel. Imported oils yielded about 0.5 per cent of esters, considerably less than the California oils. No striking differences are noted upon comparing the laboratory machine-made and hand-pressed oils shown in Table 5 with the factory machine-made samples in Tables 2 and 3.

EFFECT OF TEMPERATURE, WATER, AIR, AND LIGHT ON LIMONENE AND THE CITRUS OILS

Ogston and Moore (12) reported that a sample of Italian lemon oil held in a sealed container for 10 years showed very little difference in analysis and no material change in quality. Konnerth (10) found that lemon and orange oils kept well when stored in bottles under nitrogen.

In order to determine the effect of temperature and air on the California oils, 20 cubic centimeters each of lemon and orange oil previously dried over anhydrous sodium sulphate were placed in Erlenmeyer flasks closed with corks containing a small opening to permit air to enter. One set was allowed to remain in the laboratory, while the other was placed in the refrigerator, the temperature of which ranged from 2° to 10° C., and which of course was dark. During the storage period of 20 months, eight determinations of the refractive index and optical rotation were made at irregular intervals. The former gradually increased, and the latter decreased, except in the orange-oil sample in the ice box, which showed practically no change. The viscosity also increased until the oils had a sirupy consistence. During the same period, both clear and amber bottles filled full with 60 cubic centimeters of the oils were sealed and held at the two temperatures. At the end of the 20 months all samples were analyzed. The results are shown in Table 6. The specific gravity had increased to more than 1 in the open samples at room temperature, and the acid values of the lemon oil had multiplied 32 times and that of the orange 35 times. On the other hand, all sealed samples remained unchanged, the slight differences in the results at the end of the 20-month period coming within the error of analysis. The color and odor also remained unchanged. These results show that if the oils are kept at room temperature in colorless bottles the exclusion of air alone is all that is necessary to prevent change. In the open orange-oil sample held in the ice box, the temperature was evidently low enough to prevent oxidation.

TABLE 6.—Effect of temperature, air, and light on lemon oil and orange oil and limonene from lemon oil; and the effect of water on limonene

Oil treatment	Specific gravity			Refractive index			Optical rotation			Acid value		
	Original	After 20 months		Original	After 20 months		Original	After 20 months		Original	After 20 months	
		At room temperature	In ice box		At room temperature	In ice box		At room temperature	In ice box		At room temperature	In ice box
Lemon oil.....	0.8511			1.4744			60.20	°	°	0.0		
20 c. c. exposed to air in open Erlenmeyer flask.....	1.0250	0.9279		1.4980	1.4851		22.21	45.35		29.2	8.8	
60 c. c. sealed in clear bottle.....	.8511	.8512		1.4733	1.4744		59.92	59.92		.8	.8	
60 c. c. sealed in amber bottle.....	.8516			1.4744			59.64			.9		
Orange oil.....	.8435			1.4733			69.03			.7		
20 c. c. exposed to air in open Erlenmeyer flask.....	1.0323	.8445		1.4980	1.4735		35.00	68.37		24.4	.7	
60 c. c. sealed in clear bottle.....	.8436	.8435		1.4734	1.4733		98.75	98.61		.6	.0	
60 c. c. sealed in amber bottle.....	.8439			1.4734			98.61			.6		
Limonene.....	.8450			1.4733			69.63			.1		
20 c. c. exposed to air in open Erlenmeyer flask.....	1.0721	.9809		1.5025	1.4607		15.81	36.33		37.8	17.4	
60 c. c. sealed in clear bottle.....	.8444	.8445		1.4733	1.4734		69.35	69.35		.1	.1	
60 c. c. sealed in amber bottle.....	.8451			1.4732			69.49			.1		
105 c. c. sealed in amber bottle with 25 c. c. water.....	.8444	.8448		1.4733	1.4733		70.32	70.32		.1	.1	
85 c. c. exposed to dry air in clear bottle.....	.9884	.9489		1.4943	1.4889		33.57	43.41		14.3	8.0	
85 c. c. exposed to dry air in amber bottle.....	.9907			1.4945			32.56			14.4		
85 c. c. with 20 c. c. water, exposed to air in clear bottle.....	.9640	.0461		1.4887	1.4878		37.03	43.00		39.2	25.7	

At the same time that the lemon and orange oil samples were stored, samples of limonene from lemon oil were set aside under the same conditions, and with additional samples in clear and amber bottles open to the air, which was dried, however, by entering through calcium chloride tubes. Also, bottles filled with 105 cubic centimeters of limonene and 25 cubic centimeters of water were sealed and stored. One containing limonene and water was left open to the air. The results of the analysis at the end of 20 months as given in Table 6 showed that the limonene was unaffected in the presence of water if air was excluded. Marked changes occurred in the presence of dry air. Water and air together appeared to cause the greatest increase in acid value as shown by those samples having the large acid values in Table 6. As in the lemon and orange oils, all sealed samples remained unchanged.

COMPOSITION OF CALIFORNIA LEMON AND ORANGE OILS

LEMON OIL

DISTILLATION OF LOT 1

The first 26 samples of lemon oil were combined, making a total of 6,860 grams, and called lot 1. The physical constants were: $d_{25}^{25^{\circ}\text{C.}} = 0.8499$, $n_{D}^{20^{\circ}} = 61.72^{\circ}$, $n_{D}^{20^{\circ}} = 1.4742$. The composition was:

Total solids, 3.87 per cent; citral (Kleber), 2.8 per cent; (Hiltner), 2.3 per cent.

A general outline of the method used for the identification of the constituents of the oil is shown diagrammatically in Figure 2.

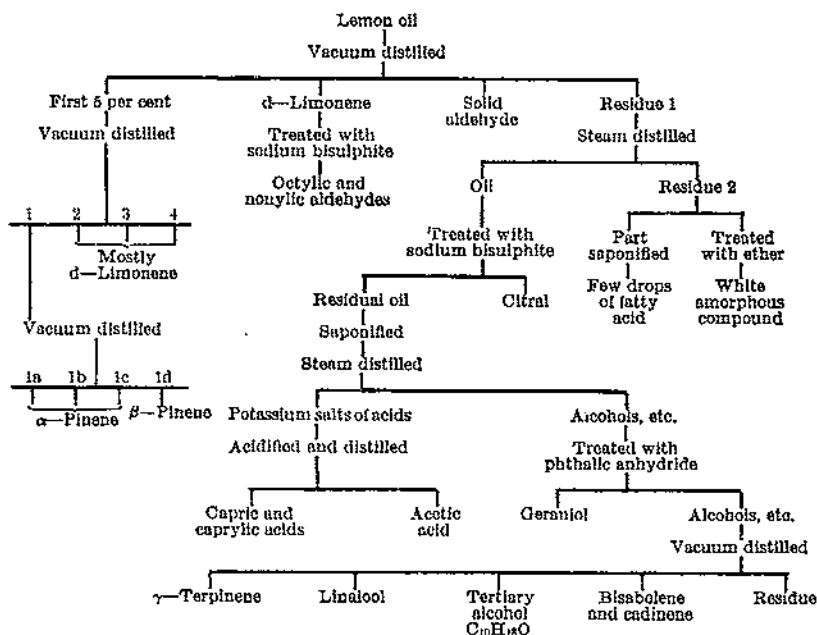


FIGURE 2.—General outline of method used for identification of constituents of lemon oil

The oil was distilled in 1,600-gram batches under a pressure of 3 millimeters with a 15-disk Young fractionating column and a Bogert receiver. The first fractions, consisting of 5 per cent by volume of each lot, were combined and refractionated several times, the four fractions in Table 7 being finally separated.

TABLE 7.—Fractions obtained from the first 5 per cent fraction of lot 1 of lemon oil

Fraction	Weight	Optical rotation	Refractive index
	Grams	°	
1	37	6.24	1.4723
2	51	16.51	1.4730
3	132	52.44	1.4739
4	60	76.16	1.4749

IDENTIFICATION OF α-PINENE

About four-fifths of the nitrosochloride crystals (6, *v. 1*, p. 296) obtained from 10 cubic centimeters of fraction 1 (Table 7) were the characteristic pinene crystals, the remainder being limonene. These mixed crystals and the compounds formed from them had the following melting points: Nitrosochloride, 98° to 99°; nitrol-benzylamine, 121° to 122°; and the nitrol piperidine, 119° to 120°. The

melting points of the corresponding α -pinene compounds are: Nitrosochloride, 103°, nitrol-benzylamine, 122° to 123°, and nitrol piperidine, 118° to 119°. The melting points, therefore, together with the fact that β -pinene does not form nitrosochloride crystals, show that the fraction is largely α -pinene.

Fraction 2 yielded only limonene nitrosochloride crystals. Fractions 3 and 4 were assumed to be limonene and discarded.

IDENTIFICATION OF A SOLID ALDEHYDE

After the first fraction, consisting of 5 per cent of the lemon oil, was removed, the greater part of the remainder distilled at about 45° C. and 3 millimeters. The fraction coming over at this temperature and pressure had the following constants: $\alpha \frac{20^\circ}{D} = 68.39^\circ$, $n \frac{20^\circ}{D} = 1.4733$. By raising the temperature of the bath gradually from 70° to 120°, five fractions of decreasing optical rotation were obtained, the final fraction having $\alpha \frac{20^\circ}{D} = -8.74^\circ$, $n \frac{20^\circ}{D} = 1.4809$. Each successive fraction had an increasing refractive index except the fourth, which was considerably lower, having $n \frac{20^\circ}{D} = 1.4647$, $\alpha \frac{20^\circ}{D} = 11.79^\circ$. After this fourth fraction of 21 grams had remained a number of days in the ice box a white crystalline precipitate weighing 0.4 gram settled out. Recrystallized several times from dilute alcohol, this crystalline precipitate melted at 58-59°. It had a bitter taste, but it had no odor, and it had too high a melting point to be camphene. Burgess and Child (1) have reported finding *l*-camphene in Italian lemon oil. After remaining in a sulphuric acid desiccator for five days, it melted at 64° to 65°. It was set aside again in the desiccator, and after five days the crystals had largely liquefied. These results indicate that this is the same as the substance first reported by Romeo in 1925 (17). It is apparently an aldehyde, as it gave a positive test with fuchsine aldehyde reagent, and reduced ammoniacal silver nitrate solution. It was more soluble in hot water than in cold water, being only slightly soluble in the latter. It gave no color with ferric chloride, but it produced a red color with concentrated sulphuric acid, and an aqueous solution decolorized potassium permanganate and aqueous bromine. Romeo reported that the anhydrous form had the composition $C_{10}H_{18}O_2$.

The liquid part of the fraction containing this solid aldehyde was tested for camphene by the isoborneol test, but no crystals appeared. Not enough of the first fractions was available from this or a later lot of lemon oil to carry out the camphene test as described by Burgess and Child.

As no deposit appeared in the other four fractions they were set aside and combined with corresponding fractions from lot 2 of lemon oil.

STEAM DISTILLATION OF THE RESIDUE

After the distillation at 120° C. and 3 millimeters the 402 grams of residue, called residue 1, was distilled with steam at ordinary pressure. Four fractions were separated. (Table 8.) As these showed no marked variation in optical rotation or refractive index, they were

combined and later mixed with a corresponding fraction from another lot of lemon oil.

TABLE 8.—Fractions obtained from lot 1 of lemon oil by steam distillation of the residue after distillation at 120° C. and 3 millimeters

Fraction	Quantity obtained	Time distilled	Optical rotation	Refractive index
	Grams	Hours	°	
1	110	6	-12.48	1.4799
2	45	3	-14.50	1.4804
3	46	6	-17.20	1.4809
4	19	6	-20.53	1.4834

DISTILLATION OF LOT 2

The remainder of the lemon-oil samples, Nos. 27 to 73, inclusive, were combined and called lot 2. This lot weighed 13,816 grams, and had the following physical constants and composition: $d_{25^{\circ}\text{C.}}^{20^{\circ}} = 0.8503$; $\alpha_{D}^{20^{\circ}} = 62.28^{\circ}$, for the 10 per cent distillate, 57.70° ; $n_{D}^{20^{\circ}} = 1.4743$, for the 10 per cent distillate, 1.4728; citral (Kleber), 2.8 per cent, (Hiltner) 2.3 per cent; residue, 2.87 per cent. This lot was distilled in 1,600-gram batches at 10 millimeters.

IDENTIFICATION OF β -PINENE IN THE FIRST FRACTION

The first fraction, $n_{D}^{20^{\circ}} = 1.4735$, consisting of 5 per cent of lot 2, weighing 650 grams, was redistilled several times at 10 millimeters. The Young column and finally a Claisen flask were used. Four fractions with a total weight of 274 grams were separated (Table 9), and the residue, consisting of limonene, was discarded.

TABLE 9.—Fractions obtained from the first 5 per cent fraction of lot 2 of lemon oil

Fraction	Boiling point at 10 mm.	Weight	Optical rotation	Refractive index	Specific gravity
	°C.	Grams	°		
1	47-52	24	9.57	1.4719	0.8625
2	52-54	43	15.23	1.4725	.8675
3	51-56	102	29.24	1.4730	-----
4	56-58	105	59.33	1.4735	-----

These fractions were kept in the ice box for several days and treated separately with 40 per cent sodium bisulphite. The small quantities of bisulphite compound formed were combined. Only a few drops of aldehyde were regenerated with sodium carbonate. It gave a positive test with fuchsine aldehyde reagent and had an odor resembling octylic and nonylic aldehyde, but it had no resemblance to citral or methyl heptenone. The refractive index was $n_{D}^{20^{\circ}} = 1.4359$.

Fraction 1, aldehyde free, was then redistilled at 10 millimeters. (Table 10.)

TABLE 10.—Fractions obtained from fraction 1, aldehyde-free lemon oil, shown in Table 9

Fraction	Temperature	Weight	Optical rotation	Refractive index
	°C.	Grams	°	
1a	47-48	3	-5.83	1.4710
1b	48	3	-2.77	1.4712
1c	48-49	6	+2.08	1.4718
1d ¹	-----	-----	+13.87	1.4736

¹ Residue in flask.

The nitrosochloride crystals obtained from 1a melted at 103° to 104° C., and were all α -pinene except for a trace of limonene and a few cube-shaped crystals. Pure pinene nitrosochloride melts at 103°. The nitrosochloride crystals from 1b melted at 102° to 103° and were about four-fifths pinene and one-fifth cubes with a trace of limonene. The nitrosochloride crystals from 1c were all α -pinene except for a trace of limonene, whereas 1d yielded about half pinene and half limonene. No cubes were obtained from either 1c or 1d.

As β -phellandrene has been reported in lemon oil (6, v. 3, p. 25), it was thought that possibly the cubes were β -phellandrene nitrosochloride crystals. α -Phellandrene does not yield a crystalline nitrosochloride. Attempts to obtain a known sample of β -phellandrene for comparison were unsuccessful, and as none of 1a or 1b remained, it was impossible to carry out the crystalline nitrosite compound test (8, p. 109).

When 10 grams of 1d was oxidized according to Wallach's (6, v. 1, p. 299) directions, crystals of nopinic acid which melted at 125° to 126° were obtained, proving that lemon oil contains β -pinene.

FORMATION OF THE TETRABROMIDE FROM THE *d*-LIMONENE

After the first 5 per cent fraction, the limonene fraction, $n_{D}^{20} = 1.4734$, was collected at 57° to 58°. Crystals of limonene tetrabromide melting at 103° to 104° were produced by treating part of this fraction of the oil in glacial acetic acid solution with bromine.

OCTYLIC AND NONYLIC ALDEHYDES

As methyl heptenone, which has been reported in lemon oil (19, p. 39) and which boils at 173° to 174°C., would have passed over with the limonene fraction during the vacuum distillation, 6 liters of this fraction was treated in the ice box for four days with 40 per cent sodium bisulphite. When the crystals obtained were treated with sodium carbonate solution and distilled, 2.9 grams of oil was obtained. It gave a positive test with the fuchsine aldehyde reagent, and had the constants $d_{25}^{25} = 0.8333$, $\alpha_{D}^{20} = +1.39^{\circ}$, $n_{D}^{20} = 1.4252$.

The odor resembled that of octylic and nonylic aldehyde, but it did not resemble the odor of methyl heptenone, citral, or citronellal. This is probably the same as the few drops of aldehyde obtained from the first 5 per cent distillate. The refractive index of octylic aldehyde is 1.4196; that of nonylic is 1.4245. The semicarbazone melted at

91° C. and the naphthocinchonic acid at 238° to 239° (corrected). Burgess (4) first reported a similar aldehyde, which Von Soden and Rojahn (21) showed consists of two aldehydes, octylic and nonylic, the latter predominating. The results obtained here show that both octylic and nonylic aldehydes are in lemon oil.

ISOLATION OF CITRAL

After the limonene was distilled off, the residue (residue 1), 1,221 grams, was steam distilled. Two main fractions separated (Table 11). Fraction 2 was combined with the corresponding fraction obtained from lot 1.

TABLE 11.—Fractions obtained from lot 2 of lemon oil by steam distillation of the residue

Fraction	Weight	Optical rotation	Refractive index
1	Grams 432	+5.88	1.4775
2	684	-13.87	1.4804

After the fractions were shaken with equal volumes of ether and 40 per cent sodium bisulphite and the bisulphite compound was decomposed with sodium carbonate, 30 grams of aldehyde was obtained from fraction 1 and 35 grams from fraction 2. It had an odor of citral. The constants were: $\alpha_{D}^{20} = 0.0^{\circ}$, $n_{D}^{20} = 1.4855$. The aldehyde from the two fractions, a total of 65 grams, was combined and distilled at 10 millimeters. The results are given in Table 12. A few grams of dark substance remained in the flask.

TABLE 12.—Fractions obtained by distillation of aldehydes removed from residue of lot 2 of lemon oil by steam distillation

Fraction	Boiling point at 10 mm.	Weight	Optical rotation	Refractive index	Specific gravity
1	°C. 100-105	Grams 18	° 0.0	1.4848	0.8903
2	105-106	43	.0	1.4878	

Schimmel & Co. (6, v. 1, p. 409) report the following constants on carefully purified citral from Italian lemon oil: $\alpha_{D}^{20} = 0.0^{\circ}$, $n_{D}^{20} = 1.4885$, $d_{15} = 0.8926$.

A 2-gram portion of fraction 2 (Table 12) in absolute alcohol was heated three hours on the steam bath with 2 grams pyruvic acid and 2 grams β -naphthylamine, then cooled and filtered. Crystals of α -citryl β -naphthocinchonic acid were recrystallized three times. The melting point was 199° to 200° C. (corrected). When they were recrystallized again the melting point was 199° to 200° (corrected).

The semicarbazone was prepared from 1 cubic centimeter of fraction 2 and 1 gram semicarbazid hydrochloride with 1 gram

sodium acetate. After recrystallizing three times from alcohol, the crystals melted at 134° to 135°. The fact that the melting point of the recrystallized crystals was 134° to 135° showed the crystals to be a mixture of α - and β -citral semicarbazones. When the mixture was treated with ether, according to Parry (14, p. 186), crystals of α -citral semicarbazone were obtained which melted at 163° to 164°.

No indication of citronellal was given by odor or tests.

IDENTIFICATION OF ACETIC AND OILY ACIDS

After the citral was removed from the fractions obtained by steam-distilling residue 1 of lots 1 and 2, the combined aldehyde-free oil amounted to 677 grams. The constants were $\alpha \frac{20^\circ}{D} = -10.40^\circ$, $n \frac{20^\circ}{D} = 1.4769$. Ten grams was acetylated and 2 grams of the acetyl compound was saponified. The ester value obtained was 127.4, equivalent to 38.7 per cent of the alcohol $C_{10}H_{18}O$. Then 222 grams was saponified with alcoholic potassium hydroxide. After the oily portion was removed with ether, the aqueous layer was steam distilled to remove any oil, then acidified with sulphuric acid and distilled. After removal of the thin layer of oily acid with ether, 33.3 cubic centimeters half normal sodium hydroxide was required to neutralize the aqueous distillate. Then tests for formic acid were made on the neutralized distillate. It did not reduce permanganate solution or yield a precipitate with mercuric chloride, and no mirror or precipitate appeared when the distillate was warmed with silver nitrate solution, showing that it did not contain formic acid.

Upon evaporation to dryness, 1.09 grams of a white salt was obtained. On the assumption that this was sodium acetate, the test of Reid (16) was carried out to form the p-nitro benzyl acetate with p-nitro benzyl bromide. The crystals melted at 77° to 78° C. An ester prepared from sodium acetate melted at 77° to 78°, and a mixture of the two showed no depression of the melting point. Therefore acetic acid was present.

The remainder of the aldehyde-free oil was saponified, and a total of 2.3 grams of oily acid obtained. The constants were: $n \frac{20^\circ}{D} = 1.4523$, $d \frac{25^\circ}{25^\circ} = 0.9222$. The boiling point was approximately 240° to 245° C. After the acid was neutralized with sodium hydroxide, three determinations of the silver salt were made. (Table 13.)

TABLE 13.—Silver salts of oily acids in aldehyde-free lemon oil

Lot	Crop of crystals	Weight of silver salts	Weight of silver	Percentage of silver
		Grams	Grams	
1	First.....	0.0527	0.0203	38.7
	Second.....	.0476	.0192	40.3
2	Total.....	.1195	.0467	39.1
3	do.....	.1243	.0492	39.6

¹ Silver salt of capric acid ($AgC_{10}H_{19}O_2$) contains 38.7 per cent silver; silver salt of caprylic acid ($AgC_8H_{15}O_2$) contains 43 per cent silver.

These results and the fact that an odor of a high aliphatic acid developed upon ignition indicate that the oily acid is a mixture of caprylic and capric acids, the latter predominating.

ISOLATION OF GERANIOL

The oil remaining after saponification of the aldehyde-free fractions 1 and 2 was treated with 35 grams of powdered phthalic anhydride and refluxed on the steam bath for one hour. After it had cooled, 26 grams of sodium carbonate in solution was added, and the oil not esterified by the phthalic anhydride was removed with ether. The primary alcohol ester was then saponified with 20 grams of sodium hydroxide by refluxing for half an hour. After this had been steam distilled, 6.2 grams of primary alcohol having an odor of geraniol was obtained. The constants were: $d_{25}^{25} = 0.8769$, $n_D^{20} = 1.4736$, $\alpha_D^{20} = 0.0^\circ$. This was distilled at 10 millimeters pressure. (Table 14.)

TABLE 14.—Fractions obtained from lemon oil by distillation of primary alcohol

Fraction	Weight	Boiling point at 10 mm.	Refractive index	Specific gravity	Optical rotation
1	2	105-109	1.4733	-----	0.0
2	4	109-110	1.4746	0.8801	.0

One gram of fraction 2 (Table 14) gave a strong odor of citral when oxidized with chromic acid. The oil removed by steam distillation yielded a precipitate in sodium bisulphite solution, indicating that an aldehyde had been formed from an alcohol in fraction 2.

The diphenylurethane of the compound was formed according to the method of Erdmann and Huth (*6, v. 1, p. 361*) by heating 1 gram of fraction 2 with 1.5 grams of diphenyl carbamine chloride and 1.35 grams pyridine for two hours in a water bath. After it had been steam distilled the first crystals obtained melted at 77° C. After they had been recrystallized from alcohol several times the melting point reached 81° to 82° . A diphenylurethane prepared from geraniol obtained from Fritzsche Bros. melted at 81° to 82° , and a mixture of the two melted at the same temperature. Therefore the primary alcohol in the lemon oil is geraniol.

EXAMINATION FOR TERTIARY ALCOHOLS AND IDENTIFICATION OF γ -TERPINENE

The oil (420 grams) not esterified by the phthalic anhydride was dried over anhydrous sodium sulphate and distilled with a Hempel fractionating column at 10 millimeters into four fractions. These fractions were redistilled twice in Claisen flasks at 10 millimeters, and the fractions given in Table 15 were obtained.

TABLE 15.—Fractions obtained from lemon oil not esterified by phthalic anhydride

Fraction	Boiling point at 10 mm.	Weight	Optical rotation	Refractive index	Specific gravity
	°C.	Grams	°		
1	56-61	14	+56.17	1.4762	-----
2	61-64	13	+54.79	1.4760	-----
3	64-66	20	+48.68	1.4767	0.8487
4	68-87	5	24.41	1.4747	.8598
5	87-100	5	0.0	1.4750	.8609
6	100-105	19	-8.32	1.4784	.8848
7	105-110	91	-11.93	1.4803	.8823
8	110-116	75	-14.98	1.4824	.8809
9	116-126	56	-20.63	1.4875	.8818
10	126-134	58	-38.42	1.4912	.8792
11	134-142	6	-42.30	1.4920	.8896
(1)					

¹ 30 grams of dark oil remained in the flask.

Fractions 4, 5, 6, 7, and 8 were again distilled in order to separate fractions at approximately the boiling points of linalool and terpineol, which have been reported as present in Italian lemon oils (6, v. 3, p. 27). Table 16 shows the results obtained on these fractions.

TABLE 16.—Redistillation of fractions 4, 5, 6, 7, and 8 of lemon oil shown in Table 15

Fraction	Boiling point at 10 mm.	Subfraction	Weight	Optical rotation	Refractive index	Specific gravity
	°C.		Grams	°		
4	104-70	4a	2.5	+20.63	1.4744	0.8491
	70-85 (3)					
5	120-88	5a	4	-4.16	1.4746	.8855
	88-104 (3)					
6	90-88	6a	4	0.0	1.4762	.8806
	98-109 (1)	6b	11	-11.60	1.4782	.8844
7	101-105	7a	10	-6.24	1.4788	.8818
	105-107	7b	44	-10.62	1.4793	.8834
	107-108	7c	17	-11.51	1.4800	.8822
	108-110 (6)	7d	8	-12.48	1.4804	-----
		7d ₁				.8814
8	109-110	8a	51	-12.48	1.4810	-----
	110-115	8b	12	-17.06	1.4831	.8817
	115-120 (7)	8c	5	-23.58	1.4860	-----
		8d	6	-36.06	1.4923	-----

¹ Discarded.

² About 1 gram left. Was added to fraction 5.

³ About 0.5 gram left. Was added to fraction 6.

⁴ 4 grams left. Was added to fraction 7.

⁵ After the refractive index determination 7d and 8a were combined and designated as 7d₁.

⁶ 12 grams left. Was added to fraction 8.

⁷ Left in flask.

All the fractions in Table 16 except 4a liberated hydrogen in the metallic sodium test, showing that they contained an alcohol. Fraction 8d gave only a slight test.

Attempts to form phenylurethanes with phenylisocyanate on fractions 4a, 5a, 6b, 7b, and 7d₁ were unsuccessful, although no difficulty was encountered in forming them on known samples of linalool and terpineol. Even when 7d₁ was allowed to remain for two weeks with the phenylisocyanate, it did not yield crystals of phenylurethane. Likewise crystals of terpin hydrate did not form when 4a, 5a, 7c, and 7d₁ were allowed to stand with 5 per cent sulphuric acid for 10 days, being shaken several times a day.

Crystals of the dihydrochloride of terpineol could not be produced on 7d₁ according to the method of Wallach (24), although a sample of terpineol yielded crystals melting at 49°. Crystals were not obtained upon passing dry hydrochloric acid gas into a cold ether solution of 7d₁ or upon carrying out the nitrosochloride test as given by terpineol.

Elementary analysis of 6b and 7a combined gave the following results:

For C ₁₀ H ₁₈ O:	
Calculated.....	C, 77.86 per cent; H, 11.77 per cent.
Found I.....	C, 77.58 per cent; H, 11.80 per cent.
Found II.....	C, 77.43 per cent; H, 11.85 per cent.

These results show the presence of an alcohol, C₁₀H₁₈O, which, however, has not yielded to the tests for linalool and terpineol. The phthalic anhydride had removed the geraniol, as was shown by the fact that tests for geraniol on these fractions were negative. That the oil contains a trace of linalool was indicated by the following test. Two grams of 6a was oxidized in the cold with chromic acid mixture. After this had been made alkaline with sodium carbonate, and distilled, and the distilled oil had been treated with 40 per cent sodium bisulphite in the ice box, crystals were obtained. When these were decomposed with sodium carbonate a few drops of oil having a strong odor of citral distilled over.

The presence of γ -terpinene was established by oxidizing 45 grams of a mixture of fractions 1, 2, and 3 (Table 15) with permanganate according to Wallach (6, v. 1, p. 321) and forming the erythritol C₁₀H₁₈(OH)₄, which melted at 238–239° (corrected). The quantity of γ -terpinene in the lemon oil was no doubt small, as only 0.1 gram of erythritol crystals was obtained after a period of five weeks. At ordinary pressure, these fractions boiled at about 175°–185°, the range in which γ -terpinene boils.

In order to see whether more distinctive fractions could be obtained, fractions 6b to 7d₁, inclusive, were combined and distilled at atmospheric pressure. Although 10 fractions were separated, their physical constants were similar to those given in Table 16.

IDENTIFICATION OF THE SESQUITERPENES BISABOLENE AND CADINENE

The higher boiling fractions 10 and 11 (Table 15) were examined for sesquiterpenes. The physical constants resembled those given for bisabolene, formerly called limene. Upon passing dry gaseous hydrogen chloride into an ice-cold ether solution of these fractions, crystals of bisabolene trichlorhydrate were obtained, which, after recrystallizing from hot alcohol, melted at 79° to 80° C. Upon addition of hydrochloric acid gas to the ether solution of fraction 10, it turned red, then purple. Fraction 11 turned a red which increased in intensity. The crystals were optically inactive in chloroform solution.

As the sesquiterpene cadinene boils at a higher temperature than bisabolene, part of the 30 grams of substance remaining in the flask after fraction 11 was distilled off was treated with dry hydrochloric acid gas in ether solution. The crystals obtained were bisabolene trichlorhydrate, melting at 79° to 80° C. Cadinene dichlorhydrate

melts at 117°. A positive test for cadinene was obtained by dissolving a portion of fraction 10 in chloroform and shaking it with a few drops of concentrated sulphuric acid according to the directions of Heusler (8, p. 415). It became green, then blue, and when it was warmed the color deepened, and a slight red appeared. Fraction 11 gave deeper shades of these colors. As bisabolene does not yield a solid nitrosochloride or nitrosate, attempts were made to form these cadinene compounds on fractions 10 and 11, and also on the residue, according to Heusler's method. Only the residue yielded a precipitate, very slight, of nitrosochloride, which melted at 63°. Not enough was available to recrystallize and purify. Cadinene nitrosochloride melts at 93° to 94°.

In the nitrosate test, yellow precipitates were obtained on all fractions, but efforts to form crystals by dissolving the precipitates in several solvents were unsuccessful. The precipitate, which melted at 72° C. to an opaque liquid, was finally raised to 76° to 77° by dissolving it several times in ether. Cadinene nitrosate melts and decomposes at 105° to 110°.

Evidently the higher boiling portion of the lemon oil is largely bisabolene, with probably a trace of cadinene.

SEPARATION OF AN AMORPHOUS COMPOUND FROM THE RESIDUE

The pastelike substance (residue 2) remaining after steam distillation of residue 1 was soluble in hot 95 per cent alcohol, hot benzene, and carbon tetrachloride. A small quantity remained undissolved when treated with ether, ethyl acetate, and petroleum ether. After 40 grams was exhausted with ether, there remained 1.38 grams of white powder, which was not very soluble in methyl or ethyl alcohol, ethyl acetate, or chloroform. It dissolved in hot benzene, carbon tetrachloride, and acetone. Numerous efforts to produce crystals were unsuccessful, the substance always appearing in the amorphous state. Even when the solutions were warmed with charcoal and filtered they did not yield crystals upon standing. It had a definite melting point of 71° to 72°. All the tests of Mulliken (11) made to establish the identity of the compound gave negative results. The bromine test for unsaturation was also negative. The fact that concentrated sulphuric acid had no effect on it indicated the presence of a paraffin hydrocarbon.

This substance is different from citroptene, which was found in Italian lemon oil by Schmidt (20) and has a melting point of 146°. Theulier (23) mentions an amorphous compound melting at 76° which he separated from the nonvolatile residue and which may have been the same as this substance.

Only a few drops of fatty acid were obtained upon saponifying 50 grams of residue 2.

ORANGE OIL

DISTILLATION OF THE OIL

In determining the composition of the orange oil, the samples of Washington Navel and Valencia oils were combined, and each kind was distilled separately. As the results, however, were similar, they will be taken up as a whole, and the few differences noted. Table 17 contains the results of analyses of the combined lots of oils.

TABLE 17.—Analyses of composite lots of orange oils

Lot No.	Type	Weight	Specific gravity	Optical rotation		Refractive index		Residue	Citrus		Esters
				Original	10 per cent distillate	Original	10 per cent distillate		Kleber	Hiltner	
1	Washington Navel	10,890	0.8426	98.20	98.48	1.4733	1.4723	Per cent	Per cent	Per cent	Per cent
2	do.	5,490	.8450	97.23	98.34	1.4736	1.4724	2.18	1.1	0.20	0.78
3	Valencia	5,024	.8445	97.52	—	1.4735	—	6.35	0	.13	—
4	do.	3,390	.8432	97.52	—	1.4731	—	4.55	1.3	.24	—
5	do.	0,530	.8443	98.48	98.89	1.4736	1.4723	4.76	1.7	.29	1.06
								3.54	1.4	.10	.70

A general outline of the method used for the identification of the constituents of the orange oils is shown diagrammatically in Figure 3.

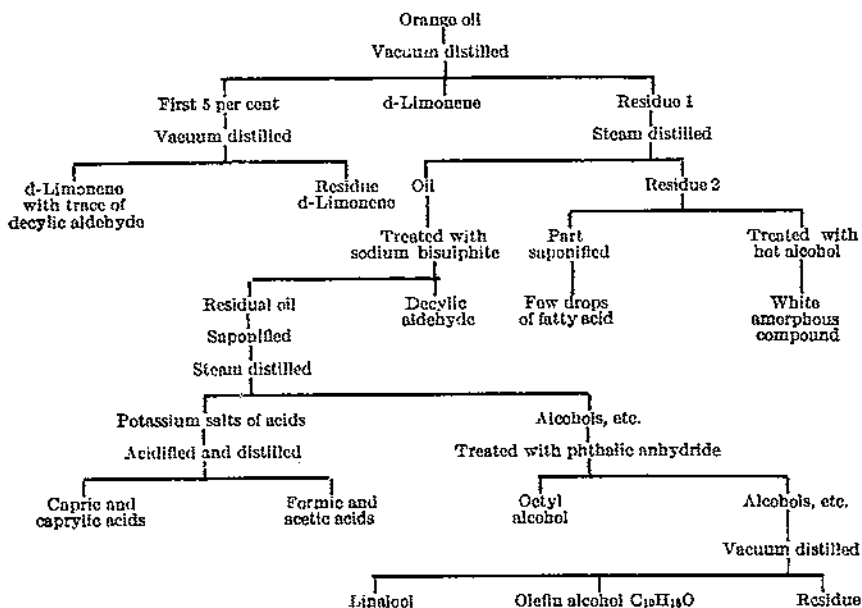


FIGURE 3.—General outline of method used for identification of constituents of orange oils

The following summary of the distillation of lot 1 at 12 millimeters pressure will illustrate the various fractions obtained when the oils were distilled.

The first 5 per cent distilled at 59° to 62° C. The temperature of the water bath in which the flask rested was 75° to 80°. Upon redistilling, two fractions were separated. (Table 18.)

TABLE 18.—Fractions obtained from the first 5 per cent fraction of orange oil

Fraction	Weight	Optical rotation	Refractive index
	Grams	°	
1	169	89.94	1.4716
2	76	92.47	1.4719
(¹)	305	98.89	1.4732

¹ Left in flask. The boiling point was 175° (760 mm.).

From fraction 1 a small quantity of aldehyde (0.26 gram) was isolated with sodium bisulphite. The odor resembled that of decylic. The

constants were: $d_{25}^{25} = 0.8597$, $n_D^{20} = 1.4276$. From 0.15 gram of the

aldehyde a small quantity of semicarbazone crystals was obtained, which melted at 49° to 50° C. From this fraction of the Valencia

oil, a few drops of aldehyde, $n_D^{20} = 1.4350$, yielded a semicarbazone

melting at 68° to 69° C. The small quantities of aldehyde available were not satisfactory for the semicarbazide-hydrochloride test. It is no doubt a part of the decylic aldehyde, some of which distilled over with the first fraction and some of which was later isolated from the residue by steam distillation.

Fraction 1, aldehyde-free, was distilled at 10 millimeters. (Table 19.)

TABLE 19.—Fractions obtained from fraction 1 (Table 18), aldehyde-free orange oil

Fraction	Weight	Boiling point at 10 mm.	Optical rotation	Refractive index	Specific gravity
	<i>Grams</i>	<i>° C.</i>	<i>°</i>		
1a	20	50-54	78.5	1.4704	0.8471
1b	10	54-56	85.9	1.4713	
(¹)			92.5	1.4725	

¹ Residue.

The nitrosochloride crystals from 1a and 1b were all limonene, no pinene crystals being present. Tests made according to Mulliken (11) were all negative on these fractions, so the first fraction of the orange oil is apparently made up of limonene and possibly other hydrocarbons, with a trace of aldehyde, probably decylic.

After the first 5 per cent, most of the oil distilled at about 62° C. and was mainly limonene with the constants $\alpha_D^{20} = 100.97^\circ$; $n_D^{20} =$

1.4728, boiling point 175° to 176° (760 mm.). The flask was then placed in a calcium chloride bath, which was gradually raised to 110°. A total of 211 grams, called fraction 3, distilled. The constants of

this fraction were $\alpha_D^{20} = 100.27^\circ$; $n_D^{20} = 1.4731$, boiling point 176° to 177° (760 mm.). It was largely limonene. When the limonene fractions were treated in glacial acetic acid with bromine, the tetrabromide was formed. The melting point was 103° to 104°.

While the temperature of the bath remained at 110°, the pressure was reduced to 7 millimeters. Fraction 4, consisting of 15 grams, was then obtained. The constants were $\alpha_D^{20} = 69.77^\circ$, $n_D^{20} = 1.4716$.

As with the lemon oil, it was necessary to steam-distill the residue (residue 1) in order to recover the oxygenated constituents of the

orange oil. Fraction 5, 56 grams, resulted. The constants were $\alpha \frac{20^\circ}{D} = 35.23^\circ$, $n \frac{20^\circ}{D} = 1.4736$.

ISOLATION OF DECYLIC ALDEHYDE

Fractions 4 and 5 were combined. The aldehyde was removed with sodium bisulphite. It had the following constants: Boiling point, 205° to 207° C. (corrected) at 756 mm., $d \frac{25^\circ}{25^\circ} = 0.8352$, $n \frac{20^\circ}{D} = 1.4296$, $\alpha \frac{20^\circ}{D} = 0.0^\circ$. The aldehyde from the Valencia oils had the constants: $d \frac{25^\circ}{25^\circ} = 0.8256$, $n \frac{20^\circ}{D} = 1.4283$, $\alpha \frac{20^\circ}{D} = 0.0^\circ$. The naphtho-cinchonic acid, made with β -naphthylamine and pyruvic acid, from the Washington Navel oil melted at 242° to 243° (corrected) and from the Valencia oil at 238° to 239° (corrected). The semicarbazone melted at 101° to 102°. Elementary analysis gave the following results:

For $C_{10}H_{20}O$:

Calculated.....	C, 76.9 per cent; H, 12.8 per cent.
Found I.....	C, 76.58 per cent; H, 13.09 per cent.
Found II.....	C, 76.38 per cent; H, 13.09 per cent.
Found II.....	C, 76.67 per cent; H, 12.98 per cent.

These results, together with the fact that the odor compared with that of a known decylic sample, indicate that the only aldehyde present in California orange oil is decylic. Stephan (22) reported only decylic aldehyde in Italian orange oil.

EXAMINATION OF OILY ACID

Ten grams of the combined aldehyde-free fractions 4 and 5 was acetylated, and 0.78 gram of the acetyl compound was saponified. The ester value obtained was 50.3, equivalent to 14.4 per cent of the alcohol $C_{10}H_{18}O$. The remainder of aldehyde-free fractions 4 and 5 was then saponified, and the oil was removed with ether. The aqueous portion was acidified and steam distilled, and the small quantity of oily acid removed from the distillate with ether was converted to its silver salts. The results are shown in Table 20.

TABLE 20.—Silver salts of oily acids in aldehyde-free orange oil

Lot	Crop of crystals	Weight of silver salts	Weight of silver	Percentage of silver ¹
		Gram	Gram	Per cent
1.....	Total.....	0.6302	0.0368	40.8
2a.....	First.....	.0563	.0195	38.8
	Second.....	.0466	.0191	41.0
2b.....	First.....	.0579	.0227	39.2
	Second.....	.0494	.0200	40.5
2c.....	Total.....	.0819	.0333	40.6
3, 4 and 5, combined, a.....	do.....	.0553	.0217	39.2
3, 4, and 5, combined, b.....	do.....	.0472	.0184	39.0

¹ Silver salt of caprylic acid ($AgC_8H_{15}O_2$) contains 43 per cent silver; silver salt of capric acid ($AgC_{10}H_{19}O_2$) contains 38.7 per cent silver.

Apparently the oily acid consists of caprylic and capric acids, the latter predominating.

IDENTIFICATION OF FORMIC AND ACETIC ACIDS

After removal of the oily acid, the aqueous distillate was neutralized with sodium hydroxide, and the following positive tests for formic acid were obtained: It reduced permanganate solution and formed a precipitate of mercurous chloride when heated with mercuric chloride. It formed a precipitate and mirror when warmed with silver nitrate.

The formic acid was removed with potassium permanganate, and the filtrate evaporated to dryness. The residue was then identified as sodium acetate by converting it to p-nitro benzyl acetate with p-nitro benzyl bromide according to the method of Reid (16). It melted at 77° to 78° C., and when it was mixed with the ester prepared from pure sodium acetate, the melting point did not change.

IDENTIFICATION OF A PRIMARY ALCOHOL

The oil remaining after saponification of the aldehyde-free fractions 4 and 5 was treated with powdered phthalic anhydride to remove the small quantity of primary alcohol. The Washington Navel oil yielded 0.5 cubic centimeter of a compound having the constants $d_{25}^{25} = 0.8801$ and $n_D^{20} = 1.4663$. The Valencia oil yielded the same quantity. The constants were $d_{25}^{25} = 0.8506$ and $n_D^{20} = 1.4493$. Because of the small quantities these compounds are no doubt impure.

When the acids obtained by oxidation with Beckman's chromic acid mixture were transformed into their silver salts, the silver content was 43, 43.5, and 44 per cent. The average was 43.5. The silver salt of caprylic acid from octyl alcohol contains 43 per cent silver; the silver salt of pelargonic acid from nonyl alcohol contains 40.8 per cent silver. These results indicate that a small quantity of octyl alcohol is in orange oil.

EXAMINATION OF TERTIARY ALCOHOLS

The oil remaining after the treatment with phthalic anhydride was fractionated several times at 10 millimeters. Table 21 shows the fractions obtained from 69 cubic centimeters of the total 83 cubic centimeters of the combined Washington Navel oils. After fraction 5 was obtained the temperature of the oil bath was slowly raised to about 150° C. During this time the distillation gradually decreased until the thermometer failed to register the upper limit of the boiling point of fraction 6.

TABLE 21.—Fractions obtained from the Washington Navel orange oil after treatment with phthalic anhydride

Fraction	Boiling point at 10 mm.	Volume	Refractive index	Optical rotation	Specific gravity
	° C.	c. c.		°	
1	63-82	20	1.4740	92.51	-----
2	82-84	1.3	1.4764	47.16	-----
3	84-88	1.6	1.4738	26.83	-----
4	88-102	5.5	1.4830	24.41	-----
5	102-107	7.5	1.4888	22.75	0.9194
6	107-up	21	1.5024	57.42	-----

The metallic sodium test for alcohol was positive on all fractions except No. 6. Fraction 3 was examined especially for linalool and fraction 5 for terpineol, but attempts to form the phenylurethane, nitroschloride, and terpin hydrate gave negative results.

Table 22 shows the fractions obtained from the Valencia oil. The metallic sodium test for alcohols was positive on all fractions except No. 6. Fraction 3 was examined for linalool and fraction 5 for terpineol, but as with the Washington Navel oil, attempts to form the phenylurethane, nitroschloride and terpin hydrate were unsuccessful. Upon oxidizing 1.5 cubic centimeters of fraction 3 in the cold, however, and treating the distillate with sodium bisulphite, a small quantity of precipitate was obtained which yielded a drop of oil with an odor of citral, indicating that it contained a trace of linalool.

TABLE 22.—Fractions obtained from the Valencia orange oil after treatment with phthalic anhydride

Fraction	Boiling point at 10 mm.	Refractive index	Optical rotation	Specific gravity
	° C.		°	
1	63-80	1.4993	62.83	-----
2	80-84	-----	33.42	-----
3	84-88	1.4945	23.85	0.8712
4	88-102	-----	27.05	-----
5	102-107	1.4804	28.43	.9005
6	107-up	1.4996	54.37	-----

Elementary analysis of fraction 3 gave the following results:

For $C_{10}H_{15}O$:

Calculated.....C, 77.86 per cent; H, 11.77 per cent.
 Found I.....C, 76.93 per cent; H, 11.88 per cent.
 Found II.....C, 77.16 per cent; H, 11.99 per cent.

The results obtained on fraction 3, together with its physical constants, show that it is practically the same as the olefin alcohol $C_{10}H_{15}O$ that Hall and Wilson (7) found in the volatile constituents of Valencia orange juice. They state that it seems quite probable that the substance is closely related to linalool, but not identical with

it. At the suggestion of Mr. Hall the fraction was allowed to remain four months in a sealed tube in the ice box. A phenylurethane melting at 60° to 61° C. was then obtained. Crystals resulted only after the pasty mass was dissolved in a 50 per cent alcoholic solution of ethylene glycol.

Fractions 6 (Tables 21 and 22) were refractionated, but crystals were not obtained on attempting to form a nitrosate, nitrosochloride, or chlorhydrate, as tests for sesquiterpenes.

SEPARATION OF AN AMORPHOUS COMPOUND FROM THE RESIDUE

The pastelike substance (residue 2) remaining after steam distillation of residue 1 was nearly all soluble in cold alcohol, cold petroleum ether, benzene, and ethyl acetate. After 40 grams of it was treated with ether, 0.65 gram of brown solid remained, which would not dissolve in carbon tetrachloride, chloroform, and several other solvents, and would not melt when heated to 260° C. A similar substance remained after residue 2 was treated with hot alcohol. Upon cooling, the hot alcohol deposited 0.2 gram of a white amorphous compound, which melted at 62° to 63°, but did not yield to crystallization. Tests to establish its identity gave negative results. The compound appears to be similar to that found in the lemon residue.

Only a few drops of fatty acid was obtained upon saponifying 50 grams of residue 2.

SUMMARY

The bulletin contains the results of analyses of commercial California machine-made lemon and orange oils, and the chemical composition of the oils.

Seventy-three samples of lemon oil, 63 of Valencia orange oil, and 31 of Washington Navel orange oil, all obtained from commercial by-products plants, were analyzed over a period of four years. Summaries of the results have been compared with those of Italian hand-made oils, and also with those of California oils made by the sponge method, and in a laboratory machine.

The effect of temperature, air, and light on lemon and orange oils over a storage period of 20 months was determined.

Besides the d-limonene, which comprises about 90 per cent or more of the oil, the following constituents were found in commercial California lemon oil: α - and β -pinene, citral, octylic and nonylic aldehydes, acetic, capric, and caprylic acids, geraniol, γ -terpinene, and the sesquiterpene bisabolene. The following substances were not completely identified: A solid aldehyde melting at 58° to 59° C., a tertiary alcohol $C_{19}H_{38}O$, and a white amorphous compound melting at 71° to 72° C. Traces of linalool and cadinene were found.

The substances identified in commercial California Washington Navel and Valencia orange oils were practically the same. Besides the d-limonene, which comprises 90 per cent or more of the oil, the following constituents were found: Decylic aldehyde; formic, acetic, capric, and caprylic acids; octyl alcohol; an olefin alcohol, $C_{10}H_{18}O$, closely related to linalool; and an unidentified white amorphous compound melting at 62° to 63°. It was indicated that the oils contain a trace of linalool.

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