equivalents of sodium, disodium tetramethylstanno-ethane, $NaMe_2Sn.SnMe_2Na$, is formed. On treating two molecular equivalents of disodium dimethylstannide with one of dimethyltin dibromide, disodium hexamethylstannopropane, $NaSn(CH_3)_2.Sn(CH_3)_2.Sn(CH_3)_2Na$, is formed.

2. Diethyl hexamethylstannopropane has been prepared by treating disodium hexamethylstannopropane with ethyl bromide. Dodecamethylstannopentane has been prepared by treating the same disodiumstannopropane with trimethyltin bromide. Both compounds are difficultly volatile liquids which oxidize in the atmosphere.

3. The free dimethyltin group, $[Sn(CH_3)_2]_x$, in the polymerized form has been prepared by two different methods. Both products are yellow solids, insoluble in organic and inorganic solvents and oxidizing readily, one being spontaneously inflammable.

4. The stanno-ethylene, $(CH_3)_2Sn:CH_2$, has been prepared by the action of methylene chloride on disodium dimethylstannide. This compound is a liquid at ordinary temperatures which oxidizes slowly in air and is reactive toward the halogens. Its properties undergo change with time, apparently due to polymerization. The molecular weight in benzene solution indicates a high degree of polymerization.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE CALIFORNIA FRUIT GROWERS EXCHANGE]

THE VOLATILE CONSTITUENTS OF VALENCIA ORANGE JUICE

BY J. ALFRED HALL AND C. P. WILSON

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General

The purpose of this investigation was to discover the nature of the substances responsible for the characteristic aroma of freshly prepared orange juice. This juice aroma appears to be due to certain substances existing in the juice itself, which are distinctly different from the "Oil of Orange," which occurs only in the peel.

This was demonstrated in the following manner: 135 liters of juice was prepared by means of Sunkist Extractors from halved oranges without crushing the oil cells. This juice was distilled under conditions to be described, and from the distillate about 0.75 cc. of a fragrant oil was obtained whose odor was distinctive and quite different from that of peel oil.

Since the flavor of orange juice changes very rapidly after removal from the fruit, it was practically impossible by the use of Sunkist Extractors to get a sufficient quantity of burred juice for this investigation without appreciable changes taking place in the first runnings by the time enough for a complete run had been obtained. Therefore, in this work, juice was prepared by crushing the entire fruit by means of rolls. In this process, some peel oil was mixed with the juice. Most of this oil was separated by centrifuging. Under these conditions, some interchange of soluble compounds probably took place between the juice and the oil from the peel.

While these general remarks are applicable to the juice of all varieties of sweet oranges, there are varietal differences in flavor. The work here reported was confined to California Valencia oranges.

The Method of Isolating Volatile Constituents of the Juice

The juice of fresh, ripe Valencia oranges, prepared as described above, was taken directly from the oil separators to the still. The time from the crushing of the fruit until the juice was in the still was never over 30 minutes.

The still was an Elyria, glass-enameled, cast-iron vacuum pan of 135 liters operating capacity, equipped with an agitator, thermometer and the usual gages. The receivers were designed to facilitate the convenient removal of the distillate without lowering the vacuum. The condenser was adequately supplied with water at or near 0°. The condenser tubes were of block tin and other parts of the condenser, as well as the receivers, were heavily lined with block tin.

It was desired to distil the juice at as low a temperature as possible and yet retain all volatile substances in the distillate. The following conditions were found to be most suitable: pressure, 120 mm.; distilling rate, 12 liters per hour. With a higher vacuum or a more rapid distilling rate, aromatic constituents were lost through the pump. Under the conditions described above, 6 liters of distillate was removed from each 135 liters of juice, and this distillate contained practically all of the odorous constituents of the juice.

The Separation of the Peel Oil

This first distillate carried a variable quantity of oil from the peel, which was separated by siphoning off the lower aqueous liquid after a few hours' standing. The aqueous liquid was then cohobated in the same equipment and under the same conditions of temperature and pressure as in the first distillation. Usually the first distillates of an entire day, 90 liters from 2025 liters of juice, were redistilled together, 20 liters of the second distillate being collected.

On standing, a little oil separated from the second distillate also. Again, the aqueous liquid was siphoned off and cohobated, this operation being carried out in a special, tin-lined copper still of 6 liters' operating capacity under the same conditions of temperature and pressure as with the larger one. In this case, however, live steam was used as a source of heat, being introduced through a perforated pipe in the bottom of the still. Nearly constant volume was maintained in the still by means of a small flame. The steam-generating flask was fed with still residues from third distillations of similar preceding series of cohobations.

CHART I

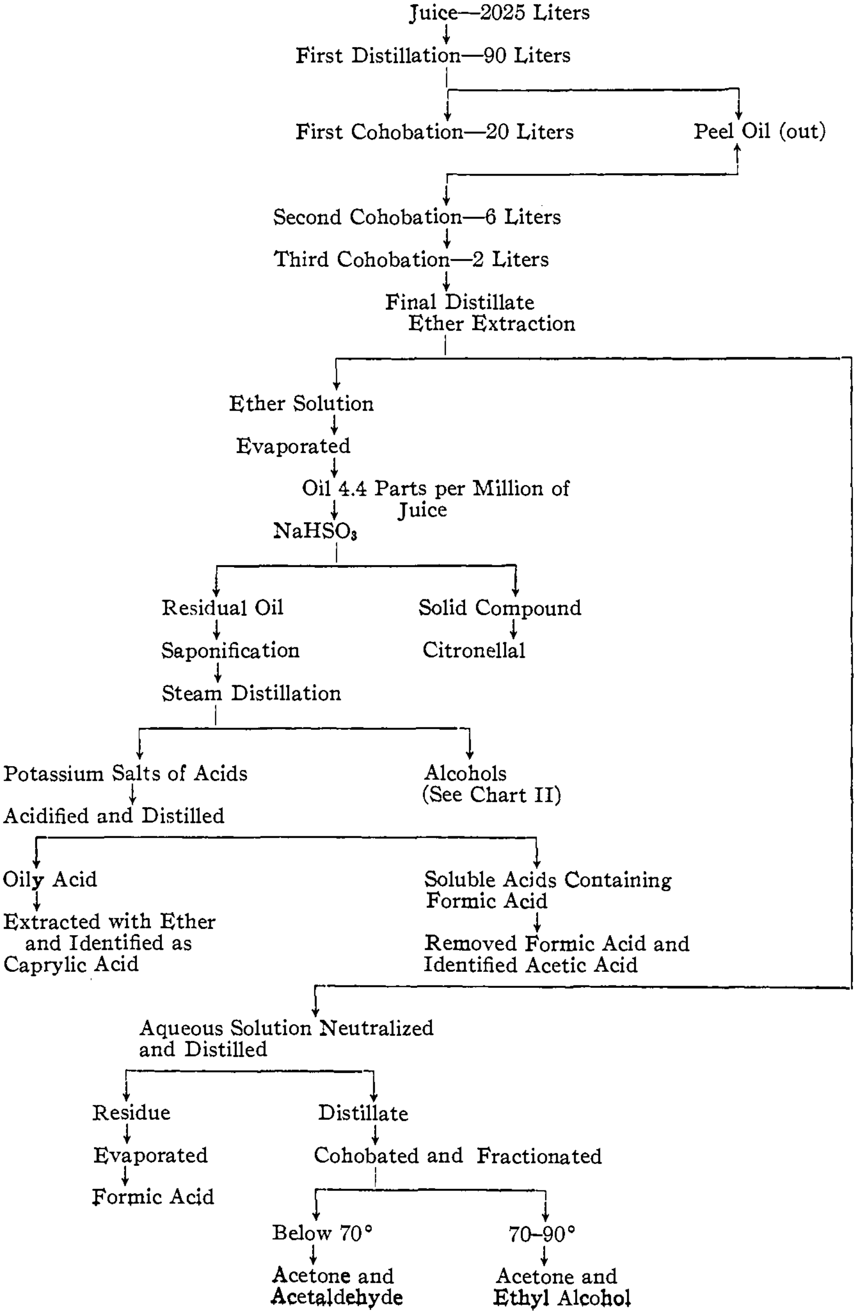
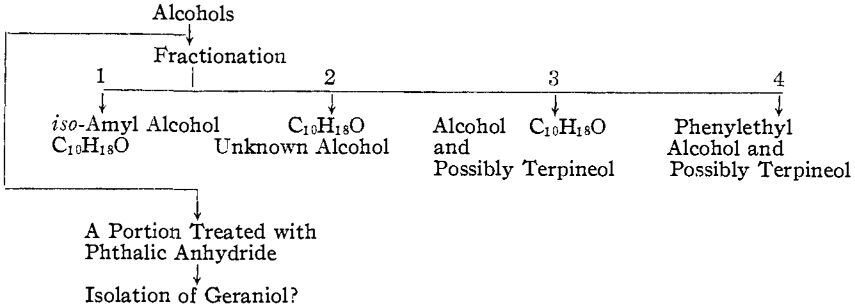

Juice—2025 Liters
First Distillation—90 Liters
First Cohobation—20 Liters
Peel Oil (out)
Second Cohobation—6 Liters
Third Cohobation—2 Liters
Final Distillate
Ether Extraction
Ether Solution
Evaporated
Oil 4.4 Parts per Million of Juice
$NaHSO_3$
Residual Oil
Solid Compound
Saponification
Citronellal
Steam Distillation
Potassium Salts of Acids
Alcohols (See Chart II)
Acidified and Distilled
Oily Acid
Soluble Acids Containing Formic Acid
Extracted with Ether and Identified as Caprylic Acid
Removed Formic Acid and Identified Acetic Acid
Aqueous Solution Neutralized and Distilled
Residue
Distillate
Evaporated
Cohobated and Fractionated
Formic Acid
Below 70°
70–90°
Acetone and Acetaldehyde
Acetone and Ethyl Alcohol

Chart II



Insoluble Oils from the Distillates

The mixed oils separated from the first and second distillates had the following constants: d_{20}^{20}, 0.8450; n_D^{20} 1.4723; α_D^{20}, +98.2°.

When distilled at 738 mm. pressure, about 97% of this mixture boiled at 175°, the boiling point of limonene.

This evidently is practically identical with the distilled orange oil obtained from the peel. The wide difference between the character of this oil and that obtained by subsequent cohobations shows how slight is the interchange of constituents referred to above.

The several steps in the treatment of the distillates may be conveniently followed by reference to Charts I and II.

Separation of the Odorous Constituents of the Juice

The 20 liters of the second distillate was cohobated to 6 liters which was further reduced by cohobation to 2 liters. In all cases the residues were odorless. The two liters from each day's run represented, therefore, 2025 liters of fresh orange juice, or about 0.1%. The final cohobates were extracted thrice with ether that was free from acids, aldehydes and ketones. The aqueous residues were examined later for soluble constituents.

The ether was removed from the extracts by evaporation on a water-bath. The residues were solutions of the odorous constituents in various amounts of ethyl alcohol. When much alcohol was present as indicated by the volume of the solution, the latter was distilled to smaller volume under a bead column. The flavoring oils were precipitated from this solution by the addition of water. The oil was removed by a separatory funnel and the aqueous portion returned to the distillation system. In this way losses of oil were minimized.

A total of 39,085 liters of juice was processed and 182 g. of oil obtained. Taking the average density of orange juice as 1.05, the amount of flavoring oil obtained is equivalent to 4.4 parts per million of juice by weight.

Examination of the Aqueous Residues from the Ether Extraction

The aqueous residues from the ether extractions were very slightly acid to litmus. The entire quantity, about 25 liters, was exactly neutralized with sodium hydroxide and distilled to half its volume. The distillate was cohobated several times under a 30cm. bead column and two final fractions were collected, one below 70° and one between 70° and 90°.

The lower-boiling fraction, which consisted largely of ether, gave a red color with potassium nitroprusside which was discharged by mineral acids. It gave the iodoform reaction in the cold, indicating the presence of acetone. It colored fuchsin bisulfite solution red. This fraction was shaken with 35% sodium bisulfite solution and the solid precipitate separated and decomposed with sodium carbonate. The solution, amounting to 10 cc., was distilled, ice water being used in the condenser; 2 cc. of distillate was collected; this had the odor of acetaldehyde. Tested according to Power,[1] it developed a very deep blue color, proving the presence of acetaldehyde. No formaldehyde or methyl alcohol could be detected in the fraction below 70°. Schryver's test for formaldehyde gave a negative result. Likewise, the resorcinol test for methyl alcohol as described by Mulliken[2] gave a negative result.

Identification of Ethyl Alcohol

The portion boiling above 70° also contained some acetone, but consisted chiefly of dil. ethyl alcohol. By fractionation, a portion was isolated whose odor and iodoform reaction, showed it to be ethyl alcohol; b. p., 78°.

A separate determination of the alcohol content of 90 kg. of absolutely fresh juice preserved against fermentation by the addition of 0.5% of sodium benzoate showed it to be about 0.018%. From the large quantities of fresh juice distilled during the main operation, several liters of 95% alcohol was recovered.

Identification of Formic Acid

The neutralized still-bottoms remaining from the distillations in which were obtained the substances described above were evaporated to a volume of 5 cc. The solution so obtained reduced cold potassium permanganate solution. When acidified, it gave an orange color with ferric chloride. When boiled with mercuric chloride solution, the latter was reduced to mercurous chloride, proving the presence of a trace of free formic acid in orange juice. When the solution was further concentrated, after removal of formate with potassium permanganate, no silver salt could be formed from it, indicating the absence of other volatile acids.

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[1] Power, This Journal, **42**, 1511 (1920).

[2] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, London, **1904**, vol. 1, p. 171.

Examination of the Oil

The oil as recovered from the ether extract was freed from traces of ethyl alcohol and water by distillation at 20 mm. pressure on a water-bath. The condenser was cooled with ice water and the distillate added to the following batch to be similarly treated. The dry oil was stored in a cool place for later examination; α_D^{20} (100mm. tube), +25.76°; n_D^{20}, 1.4691; d_{20}^{20}, 0.8866; ester value (aldehyde-free oil), 8.4; ester content (as $C_{11}H_{18}O_2$), 2.71%.

Aldehyde

The oil contained less than 0.5% of an aldehyde which was extracted with saturated sodium bisulfite solution. The aldehyde was recovered from the solid addition compound by decomposing the latter with sodium carbonate; n_D^{20}, 1.4520; the value for citronellal is 1.448–1.449.

The semicarbazone was prepared; recrystallized from petroleum ether, it melted at 82–82.5°. Mixed with the semicarbazone of citronellal, m. p. 82.5°, prepared from a specimen of citronellal obtained from Fritszche Brothers, the mixture melted at 81–82°, proving the identity of this aldehyde with citronellal. The odor of this aldehyde suggested also the probable presence of a trace of some high aliphatic aldehyde.

Acids as Esters

Saponification of the aldehyde-free oil with alcoholic potassium hydroxide solution on the water-bath caused the formation of resinous substances. Therefore the oil was saponified for 15 hours at room temperature with an excess of 0.5 *N* alcoholic potassium hydroxide solution. The saponification mixture was diluted with water and the alcohols were extracted with ether. The aqueous, alkaline residue was distilled with steam to remove volatile material. It was then acidified with sulfuric acid and the acids distilled with steam.

A trace of oily acid floated on the distillate. This was extracted with ether, neutralized with sodium hydroxide, and the silver salt prepared.

Anal. Subs., 0.0525. Calcd. for $C_8H_{16}O_2$: Ag, 43.03. Found: 41.4, 42.5, 42.5, 42.7.

When the salt was ignited, the odor of a high aliphatic acid was developed. This acid was evidently caprylic acid.

The aqueous distillate, after extraction with ether, was neutralized with sodium hydroxide and concentrated to a small volume. This solution when cold reduced potassium permanganate solution and when boiling hot, mercuric chloride solution, and therefore contained formic acid. This was removed with potassium permanganate. The filtrate from the manganese dioxide was evaporated to dryness, and the residue, 0.2355 g., treated according to the method of E. E. Reid[3] to form the *p*-nitro-

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[3] Reid, THIS JOURNAL, **39**, 124 (1917).

benzyl ester which, thrice recrystallized from dil. alcohol, melted at 77–78°. The ester prepared from sodium acetate gave the same melting point and, further, the melting point of a mixture of the two showed no depression. Therefore, acetic acid was present.

The acids present as esters were formic, acetic and caprylic, with formic acid predominating.

Examination of the Alcohols

The ethereal solution of the alcohols obtained by extracting the saponification mixture was dried with sodium sulfate. The solution was filtered, and the ether and ethyl alcohol were evaporated on the water-bath, finally under a moderate vacuum.

To 16.4 g. of the mixed alcohols, 2 g. of phthalic anhydride was added. The mixture was heated in a boiling water-bath for two hours, extracted with sodium hydroxide solution, the alkaline extract saponified by warming, and steam distilled. It yielded a few drops of an oil, n_D^{20} 1.4763, which corresponds to geraniol (n, 1.476–1.478). When oxidized with chromic acid mixture, it developed the odor of citral. Geraniol was probably present in very small amount, but the procedure necessary for its positive identification caused such deep changes in the bulk of the oil, as evidenced by odor, color and increase in the refractive index, that the treatment of more oil in this manner was prevented by the small supply available.

When the alcohols were distilled at 20 mm. pressure, with a small stream of air bubbling into the distilling flask to prevent bumping, extensive decomposition took place. Nitrogen was substituted for air, and the distillation was then carried out without discoloration or impairment of odor. The manometer was connected directly to the distilling flask. Table I summarizes this distillation and the physical constants of each fraction.

TABLE I

DISTILLATION OF ALCOHOLS

62 cc. distilled

Fraction	Quantity Cc.	B. p., °C. (20 mm.)	n_D^{20}	d_{20}^{20}	$[\alpha]_D^{20}$
1	8	89–92	1.4600	0.8668	+23.03
2	40	92–93	1.4660	.8863	+26.81
3	9	93–95	1.4713	.8939	+35.86
Residue	5	95	1.4922	viscous and dark	

It is understood that Table I is a typical summary of the distillation of the alcohols. The remainder of the alcohols was similarly fractionated, and corresponding fractions were combined when necessary to provide sufficient material for further work.

Fraction 1 had an odor reminding of an amyl alcohol. A similar preparation from navel oranges had given a small fraction with a boiling point 130–132° by Siwoloboff's method. Upon oxidation with chromic-acid mixture and analysis of the silver salt of the resulting acid, a valeric acid was shown to be present. In view of the boiling point of the alcohol, it was probably derived from *iso*-amyl alcohol. In distilling Fraction 1 at 738 mm., about 1 cc. came over below 170°. This was oxidized with chromic acid mixture, and the silver salt of the acid so obtained was prepared through the sodium salt.

Anal. Subs., 0.0757. Calcd. for $C_5H_9O_2Ag$: Ag, 51.67. Found: 51.9.

The oil, therefore, contained an amyl alcohol, probably *iso*-amyl alcohol.

The residue was viscous and rather dark, due to the accumulation of all the color of the oil in this small volume. A portion was oxidized with chromic acid mixture. The oxidation mixture was steam distilled and the acid distillate neutralized with 3 cc. of *N* sodium hydroxide solution, evaporated to dryness and treated according to the method of Reid[3] with *p*-nitrobenzyl bromide. A crystalline product was obtained; m. p., 64–65°. This is the melting point of *p*-nitrobenzyl-phenyl acetate, and indicated the presence of phenylethyl alcohol in the oil.

The high rotation of Fraction 3 indicated the possible presence of terpineol in it and the residue. This fraction was, therefore, treated according to Wallach's directions for the preparation of terpineol nitrosochloride, except that *iso*-amyl nitrite was substituted for ethyl nitrite. The same technique applied to technical terpineol gave a crystalline nitrosochloride, but with Fraction 3 and the residue no crystalline product resulted. That a nitrosochloride was formed was indicated by the persistent blue color of the oil separated from the reaction mixture of Fraction 3. In the residue, the dark oil obscured any blue color that may have existed. Terpineol may have been present in Fraction 3 and the residue but no positive evidence was obtained. Fraction 3 evidently consisted chiefly of the principal constituent of the oil, most of which was contained in Fraction 2.

Fraction 2 made up the bulk of the oil; 47 cc. of oil corresponding to this fraction was redistilled with results shown in Table II.

TABLE II

REDISTILLATION OF FRACTION 2

Fraction	Vol. Cc.	B. p., °C. (20 mm.)	n_D^{20}	d_{20}^{20}	$[\alpha]_D^{20}$
5	4	Below 92			
6	40	92–93	1.4650	0.8706	+23.67°
7	3	Above 93			

The density, boiling point and refractive index of this fraction indicated the presence of linaloöl. The rotation, however, was higher than any ever reported for linaloöl, whose maximum rotation is probably +20°. It is entirely possible that the oil still contained a little of the more highly rotatory substance present in the higher-boiling fraction. However, Fraction 6 was undoubtedly sufficiently pure to give definite indications of identity. The characteristics of this oil are as follows.

It reacts with sodium, liberating hydrogen.

When carefully oxidized with chromic acid mixture, no citral or aldehydic body is formed. The same technique applied to linaloöl gives citral.

It does not yield terpin hydrate when allowed to stand for periods of time up to six months with 5% sulfuric acid.

When it was allowed to stand in contact with phenylisocyanate, after three weeks some carbanilide and a very small quantity of a heavy oil had been formed. The oil did not yield crystals from the usual solvents. It did not solidify at —10°. Several attempts to prepare a crystalline phenylurethan gave negative results. Crystalline linalyl-phenylurethan was easily prepared from linaloöl obtained from the Eastman Kodak Company.

Likewise, only a little heavy, reddish oil could be obtained as the reaction product with α-naphthylisocyanate.

No crystalline product could be isolated from the mixture resulting from the reaction with diphenylcarbamine chloride.

Warm formic acid dehydrated this alcohol with the formation of a complex terpene mixture; b. p., 170–185°. No crystalline bromide or nitrosochloride could be prepared from any of the fractions of this mixture.

When it was distilled at atmospheric pressure, there was a marked change in odor and slight decrease in rotation.

The following analyses are the results of four combustions.

FRACTION 6

Calcd. for $C_{10}H_{18}O$, %	Found, %				
	(1)	(2)	(3)	(4)	Av.
77.86	C 77.63	77.67	77.50	77.57	77.59
11.77	H 11.69	11.52	11.72	11.43	11.59
10.37	O 10.68	10.82	10.78	11.00	10.82

Ten cc. of this alcohol was oxidized with potassium permanganate solution according to the directions of Tiemann and Semmler[4] for linalool. The volume of the mixture was about 1000 cc.; 400 cc. was distilled. This distillate, treated with alkali and iodine, gave a good precipitate of iodoform in the cold. The colorations with potassium nitroprusside were similar to those given by dil. acetone. An attempt to prepare benzylidine acetone failed. The purified oxidation mixture was concentrated to 150 cc., acidified with sulfuric acid and extracted with ether. There was obtained a very small quantity of an apparently liquid acid with the odor of acetic acid. This acid did not give iodoform, even when warmed. Its *p*-nitrobenzyl ester melted at 89–90°. That of levulinic acid[5] melts at 60.5–61°, and that of acetic acid at 78°. It is certain that this is not levulinic or acetic acid, but the very small yield prevented further attempts at identification.

At present, we must be content with these primary attempts at determination of the nature of this substance, as it was not desired to use up all the available material in oxidations. The structure is unknown. It seems quite probable that the substance is closely related to linaloöl, but it is clear that it is not identical with it.

Summary

The volatile constituents of Valencia orange juice are as follows: those very soluble in water are ethyl alcohol, acetone, acetaldehyde and formic

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[4] Tiemann and Semmler, *Ber.*, **28**, 2130 (1895).

[5] Lyons and Reid, THIS JOURNAL, **39**, 1727 (1917).

acid; those less soluble in water are an olefin alcohol ($C_{10}H_{18}O$, constituting 90% of the non-water-soluble constituents), an amyl (probably *iso*-amyl) alcohol, phenylethyl alcohol, esters of formic, acetic and caprylic acids. Geraniol and terpineol were indicated but not positively identified.

San Dimas, California

[Contribution from the Pathological Division, Bureau of Animal Industry, United States Department of Agriculture]

LUPINE STUDIES. IV. ISOLATION OF *d*-LUPANINE FROM LUPINUS KINGII (S. WATSON)

By James Fitton Couch

Received June 12, 1925 Published October 6, 1925

This paper reports an investigation of the alkaloidal constituents of an American species of lupine, *Lupinus kingii*, not hitherto examined chemically, and the isolation from it of an alkaloid that has been identified as *d*-lupanine. This alkaloid has been isolated from several European species[1] of the genus *Lupinus*, and from a single American species, the perennial *L. polyphyllus*.[2]

The plant material used in this investigation was collected on July 28 and August 1, 1922, on the summit of Flat Top Mountain, in the Wasatch Range, Utah.[3] At that time the plants were well grown; some were still in flower while others were in fruit. The collected material was carefully dried in the shade, bagged and shipped into Washington where the chemical study was made.

The plant yielded a total of 0.83% of crude alkaloid. All of this material consisted of *d*-lupanine; a careful search was made for *dl*-lupanine and for hydroxylupanine, both of which alkaloids sometimes accompany *d*-lupanine in species of this genus, but no evidence of their presence was obtained. The hydrochloride prepared from this alkaloid melted at 127°. When this salt was mixed with an authentic sample of *d*-lupanine hydro-

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[1] Hagen, *Dissertation, Halle*, **1885**. Siebert, *Arch. Pharm.*, **229**, 531 (1891). Soldaini, *ibid.*, **231**, 321 (1893). Davis, *ibid.*, **235**, 199, 218 (1897). Gerhard, *ibid.*, **235**, 355 (1897). Callsen, *ibid.*, **237**, 566 (1899). Bergh, *ibid.*, **242**, 416 (1904).

[2] Schmidt [*ibid.*, **235**, 192 (1897)] has reported the isolation of *d*-lupanine from *L. perennis* by his pupils, Gerhard and Bergh. Both of these latter, however, term the plant with which they worked *L. polyphyllus*, a perennial species that is a commercial article in Germany. I am informed by Mr. W. W. Eggleston that it is very unlikely that Schmidt and his pupils could have obtained the American species *L. perennis* in the quantities reported in their memoirs and that, undoubtedly, the plant they studied was the American perennial, *L. polyphyllus*. Investigation of authentic specimens of *L. perennis* is now in progress in this Laboratory.

[3] The plant material was identified by Mr. W. W. Eggleston, Botanist at the Bureau of Plant Industry, United States Department of Agriculture, to whom the writer expresses his gratitude.