[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF FRITZSCHE BROTHERS, INC.]

An Investigation of the Chemical Constituents of Distilled Lime Oil (*Citrus Medica*, L., Var. *Acida*, Brandis) (*Citrus Aurantifolia*, Swingle)*

BY ERNEST S. GUENTHER AND EDWARD E. LANGENAU

The oil distilled from the juice of the whole crushed fruit of *Citrus medica*, L., var. *acida*, Brandis (*Citrus aurantifolia*, Swingle) has long been produced in the West Indies and Mexico; this is the oil known in commerce as distilled lime oil. It must not be confused with the expressed oil which is obtained either by the *écuelle* method or by crushing the whole fruit and subsequently separating the oil from the juice by means of a high speed centrifuge.

Since a thorough study of distilled lime oil has not been reported previously in the literature, this investigation was undertaken to determine the chemical constituents of a normal oil.

Burgess and Page[1] investigated a distilled lime oil from which the terpenes had been removed by distillation. They established the presence of 1-α-terpineol as the main oxygenated constituent and the presence of bisabolene (their "limene") as the main constituent of the higher boiling fraction. The present investigation has confirmed the presence of these two constituents.

The α-terpineol isolated by Burgess and Page differs somewhat from that obtained in this investigation in respect to its optical rotation. These earlier investigators reported a rotation of −20° for the purified alcohol in a supercooled state; the α-terpineol isolated in this Laboratory showed a specific rotation of −11°.

From the mother liquor of the phenylurethan derivative of α-terpineol, Burgess and Page[2] isolated a second phenylurethan which crystallized in needles, m. p. 132°; they suggested this might be an unknown isomeric terpineol. Following the procedure outlined by them, we were unable to isolate a phenylurethan of m. p. 132°. Possibly the crystals obtained by them may have been an impure form of bornyl phenylurethan (m. p. 138–139°) which we obtained in the form of long thin needles upon recrystallization from alcohol.

According to Parry,[3] distilled lime oil contains pinene, limonene, dipentene and cymene; however, he gives no experimental data to substantiate this statement. The present investigation has established the presence of α-pinene, β-pinene, limonene, and dipentene; the presence of *p*-cymene was not established.

Experimental

The oil used in this investigation was distilled in Mexico from the juice of green crushed fruit: d_{15} 0.866; $n^{20}\text{D}$ 1.4761; $\alpha^{20}\text{D}$ +41°6′; solubility at 20°, 4.5 to 5 volumes and more of 90% alcohol; aldehyde (as citral), 1.15%.[4] Twenty-seven pounds of oil was fractionated under vacuum in a commercial still having a 6-foot column: the four main fractions and residue of Table I were obtained.

Fraction I

The first 10%, removed by distillation at 20 mm. with a 36-inch column of the Young type having 22 disks and bulbs, was repeatedly fractionated under vacuum. A final distillation at atmospheric pressure yielded fractions boiling at 150–160°, 160–170°, and 170–175°.

Identification of α-Pinene.—The fraction 150–160° (4 cc.) was rectified over metallic sodium at 20 mm.: d_{15} 0.860; $\alpha^{20}\text{D}$ +12°20′; $n^{20}\text{D}$ 1.4674. A nitrosochloride was prepared by the procedure of Wallach[5]: small shiny plates were obtained, m. p. 102–103°; a mixed m. p. with the nitrosochloride prepared from the corresponding fraction of American turpentine oil showed no depression.

Identification of Furfural.—The fraction 160–170° (4 cc.) possessed a strong musty odor suggestive of furfural. The aldehyde was separated by washing the oil with water and extracting the washings with ether; 0.3 g. of a yellow oil was obtained. A drop added to 2 cc. of 4% freshly distilled aniline in glacial acetic acid gave the intense red color characteristic of furfural. The oxime melted at 89–90° after three recrystallizations from dilute alcohol; a mixed m. p. with the oxime of furfural showed no depression.

Identification of β-Pinene.—The fraction 160–170° was now rectified over metallic sodium at 20 mm.: d_{15} 0.862; $\alpha^{20}\text{D}$ +30°25′; $n^{20}\text{D}$ 1.4748. These properties differ considerably from the accepted constants of pure β-pinene, and indicate that only a small amount of this terpene could be present. The oil was oxidized with alkaline potassium permanganate by Wallach's method[6]: the nopinic acid obtained melted at 124–126°. There was insufficient material for a recrystallization. According to Wallach,[6] pure nopinic acid melted at 126–127°.

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* Original manuscript received May 26, 1942.

(1) Burgess and Page, *J. Chem. Soc.*, **85**, 414 (1904).

(2) Burgess and Page, *ibid.*, **85**, 1329 (1904).

(3) Parry, "The Chemistry of Essential Oils and Artificial Perfumes," fourth edition, D. Van Nostrand Co., Inc., New York, N. Y., 1921, Vol, I, p. 440.

(4) Aldehydes were determined by the following procedure. To a 5.0-g. sample was added 25 cc. of a neutral 0.5 *N* hydroxylamine hydrochloride solution; after fifteen minutes the liberated hydrochloric acid was titrated with 0.1 *N* sodium hydroxide solution using brom phenol blue as indicator.

(5) Wallach, *Ann.*, **245**, 251 (1888).

(6) Wallach, *ibid.*, **356**, 228 (1907).

TABLE I

	Fraction I	Fraction II	Fraction III	Fraction IV	Residue V
Per cent. of original oil	75.0	2.4	14.9	3.8	3.4
Boiling range °C. mm.	Up to 68° at 14	68° at 14 to 76° at 12	76° at 12 to 105° at 12	105° at 12 to 129° at 12	Above 129° at 12
d_{15}	0.853	0.865	0.931	0.896	0.934
$\alpha^{20}\text{D}$	+54°15′	+26°40′	−7°0′	−17°55′	Too opaque
$n^{20}\text{D}$	1.4740	1.4805	1.4825	1.4923	1.5062
Aldehyde (as citral), %	0.3	0.5	2.3	2.4	2.7
Acid number	0.0	0.9	2.7	5.4	8.8
Ester number	0.9	0.9	2.7	13.2	13.0
Ester number after acetylation	0.9	34.4	219.5	70.6	80.6
Solubility at 20°	4.5 vols. a.m. 90% alc.	5 vols. a.m. 90% alc.	4.5 vols. a.m. 60% alc.	Clear up to 1 vol. 95% alc.; cloudy w.m. to 2.5 vols.; clear again in 2.5 vols. a.m.	Clear up to 1.5 vols. 95% alc.; cloudy w.m.

The aldehydes of the residual 90% were removed with sodium bisulfite. Five liters of oil was shaken with 2.5 liters of 40% sodium bisulfite solution for eight hours; after standing for seven days at 5°, the crystals which formed were filtered off and repeatedly washed with ether. Upon regeneration with 10% sodium carbonate solution and extraction with ether, 0.88 g. of a yellow oil having a pronounced odor of a fatty aldehyde was obtained: $n^{20}\text{D}$ 1.4210.

Identification of *n*-Octyl Aldehyde.—The semicarbazone of the regenerated aldehydes melted at about 88–92° after six recrystallizations from dilute alcohol. In an attempt to resolve this mixture, the semicarbazones were acidified with dilute sulfuric acid and the mixture steam distilled: a distillate of 100 cc. was collected, from which the liberated aldehydes were extracted with ether. The recovered aldehydes were fractionated by a micro-technique.[7] The semicarbazone of the first fraction (about 0.2 g.) melted at 96.5–97.5° after two recrystallizations from dilute alcohol. The semicarbazone of *n*-octyl aldehyde melted at 97–98°; mixed m. p. 96.5–97.5°.

One liter of the aldehyde-free oil was fractionated at 20 mm.; nine 100-cc. fractions were collected; these showed the following rotations: (1) +50°20′; (2) +54°50′; (3) +56°25′; (4) +57°10′; (5) +57°58′; (6) +58°21′; (7) +58°29′; (8) +57°38′; (9) +57°0′; (residue) +46°0′.

Identification of *d*-Limonene.—The sixth and seventh fractions, having the highest rotations, were combined and rectified over metallic sodium at atmospheric pressure: d_{15} 0.850; $\alpha^{20}\text{D}$ +58°30′; $n^{20}\text{D}$ 1.4730; b. p. 175–176°. The tetrabromide melted at 103–104° after recrystallization from dilute acetic acid and from ethyl acetate; a mixed m. p. with limonene tetrabromide, prepared from the terpene fraction of sweet orange oil, showed no depression.

Identification of Dipentene.—The crystals of limonene tetrabromide described above were recrystallized from boiling ethyl acetate. When crystals first appeared, they were removed immediately from the warm solution by filtration; the crystals obtained were again treated in this manner. Dipentene tetrabromide was separated from the more soluble limonene tetrabromide by this procedure. The silver-white crystals melted at 123.5–124.5° after two recrystallizations from dilute methyl alcohol and a further recrystallization from boiling ethyl acetate; a mixed m. p. with dipentene tetrabromide showed no depression.

A second 1-liter portion of the aldehyde-free oil was fractionated over metallic sodium at atmospheric pressure with a 20-inch Hempel column packed with glass beads: the presence of phellandrene, *p*-cymene, or terpinene could not be established in the fractions boiling at 177–178°, 178–179°, 179–180°.

Fraction II

The aldehydes were removed with sodium bisulfite solution; upon regeneration, 0.5 g. of a yellow oil having a pronounced odor of a fatty aldehyde was obtained: $n^{20}\text{D}$ 1.4340.

Identification of *n*-Nonylaldehyde.—The semicarbazone of the regenerated aldehydes melted at 98–99° after two recrystallizations from dilute alcohol; a mixed m. p. with the semicarbazone of *n*-nonylaldehyde showed no depression.

The primary and secondary alcohols were removed with phthalic anhydride. A mixture of 205 g. of the aldehyde-free oil, 205 g. of phthalic anhydride, and 205 g. of benzene was refluxed on a steam-bath for four hours. Upon cooling to room temperature, a considerable quantity of excess anhydride crystallized from the solution and was removed by filtration. The filtrate was shaken with two 500-cc. portions of 20% sodium carbonate solution and washed with 500 cc. of water. The combined aqueous layers were saponified with 800 g. of 50% sodium hydroxide solution, and the liberated alcohols were extracted with ether: 1 g. of a yellow oil having an odor suggestive of borneol and geraniol was obtained.

Identification of Borneol.—The phenylurethan of the recovered primary and secondary alcohols melted at 138–139° after two recrystallizations from petroleum ether; a mixed m. p. with the phenylurethan of borneol showed no depression. Since Fraction II had not been saponified, borneol is present as a free alcohol.

Fraction II, freed of aldehydes and primary and secondary alcohols, was fractionated at 20 mm.: the presence

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(7) Emich, "Microchemical Laboratory Manual" (English Translation), John Wiley & Sons, New York, N. Y., 1932, p. 34.

of phellandrene and *p*-cymene could not be established in the fraction 180–182° (762 mm.).

Fraction III

Citral, an important constituent of expressed lime oil, is destroyed under the influence of heat and acid; in the production of distilled lime oil, a small amount of this aldehyde might possibly escape decomposition. As Tiemann has shown,[8] sodium bisulfite solution is unsatisfactory for the isolation of citral because of the formation of a stable addition compound; he recommended the use of a solution of sodium sulfite buffered with sodium bicarbonate for the preparation of the soluble labile compound.

The aldehydes of Fraction III were removed by a modification of Tiemann's method. Eighteen hundred grams of oil was shaken with a solution of 126 g. of sodium sulfite and 168 g. of sodium bicarbonate in 2 liters of water for eight hours; after standing for seven days at 5°, the crystals which formed were filtered off and repeatedly washed with ether. Upon regeneration with 10% sodium carbonate solution and extraction with ether, 7.5 g. of a yellow oil was obtained, having a pronounced odor of a fatty aldehyde.

Identification of *n*-Decylaldehyde.—The regenerated aldehyde was rectified at 5 mm.: d_{15} 0.830; $\alpha^{20}\text{D}$ ±0°; $n^{20}\text{D}$ 1.4278; b. p. 80–81° at 5 mm.; oxime, m. p. 68–69° after recrystallization from dilute methyl alcohol. The semicarbazone melted at 100–101° after two recrystallizations from dilute alcohol; a mixed m. p. with the semicarbazone of *n*-decylaldehyde showed no depression.

The buffered sodium sulfite solution (which contained the soluble labile addition compound of any citral that might have been present in Fraction III) was thoroughly washed with ether. During the process of regeneration with 20% sodium hydroxide solution, the free aldehydes were protected from the continued action of the alkali by the addition of 1 liter of ether. Upon evaporation of the ether layer, 6 g. of a pale yellow oil having an odor suggestive of cuminic aldehyde was obtained: $n^{20}\text{D}$ 1.4925; $\alpha^{20}\text{D}$ +0°40′. To these aldehydes were added the corresponding aldehydes of Fraction IV.

The Presence of an Unidentified Aldehyde and the Identification of Citral.—The semicarbazone of these regenerated aldehydes melted at about 124–129°; repeated recrystallizations from ethyl, methyl, isopropyl alcohols, and from benzene and from ether raised the m. p. to 130–137°.

In an attempt to separate these aldehydes, they were fractionated at 16 mm. with a flask having a two-inch column packed with small beads. Arbitrary fractions were collected at 103–106°; 106–110°; 110–115°; all were pale yellow oils of similar odor: $n^{20}\text{D}$ 1.4882, 1.4900, 1.4912, respectively. Semicarbazones of these three fractions melted at 132–136° after two recrystallizations from dilute methyl alcohol. The third fraction was slightly darker in color than the first and second, and was considerably more viscid. The fact, which was uncovered later in this investigation, that these aldehydes polymerize very readily, may well account for the differences in properties of these three fractions.

Doebner's[9] naphthocinchoninic acid derivative of each of the above fractions melted at 187–195°. The derivatives were combined; repeated recrystallizations from alcohol yielded a small amount of yellow needles, m. p. 200–201°; a mixed m. p. with the naphthocinchoninic acid derivative of citral showed no depression. Attempts to secure crystals of sharp m. p. from the mother liquors proved unsuccessful.

The unidentified aldehyde proved very susceptible to polymerization: a small amount exposed to the air yielded a very viscid oil with an acid number of 4.0, indicating polymerization rather than oxidation had occurred. Nor was a solid acid obtained by oxidation with hydrogen peroxide. After seven days, the aldehyde had become so viscid that it poured with difficulty. A rectification at 3 mm. of the combined fractions was necessary to separate the unpolymerized aldehyde: more than 50% remained as a residue. However, the aldehyde polymerizes very slowly if dissolved in ether and protected from light.

The sodium bisulfite addition compound appears to be very soluble: 0.5 cc. of the aldehyde yielded no solid addition compound with 10 cc. of saturated sodium bisulfite solution. A pronounced loss of odor indicated that reaction had occurred. This offers a possible means of removing citral, if citral is the interfering substance. Unfortunately, there remained insufficient material to try this technique. We hope at a later date to isolate a larger amount and to identify the aldehyde with the odor suggestive of cuminic aldehyde.

The aldehyde-free oil was saponified with alcoholic sodium hydroxide solution. After removal of the alcohol by distillation, the saponified oil was washed with water: these aqueous washings were treated in the manner described under "Acidic Constituents."

After saponification, the primary and secondary alcohols were removed with phthalic anhydride: 6 g. of a viscid oil was obtained.

Identification of Geraniol.—The recovered primary and secondary alcohols were distilled at 20 mm.: three 2-cc. fractions were collected.

The first fraction was semi-solid and readily yielded colorless plates of borneol upon crystallization from petroleum ether: m. p. 204–206°; $[\alpha]^{22}\text{D}$ −31°0′ (10% alcoholic solution); phenylurethan, m. p. 138–139°.

The second and third fractions, having the odor of geraniol, were combined and purified through the calcium chloride addition compound of Jacobsen.[10] Rectification of the resulting oil yielded pure geraniol: $\alpha^{20}\text{D}$ ±0°; $n^{20}\text{D}$ 1.4781; d_{15} 0.884. One gram, oxidized with chromic and sulfuric acids, gave a distinct odor of citral. The diphenylurethan[11] melted at 81.5–82.5° after two recrystallizations from dilute alcohol; a mixed m. p. with the diphenylurethan of geraniol showed no depression.

Fraction III, freed of aldehydes, esters, and primary and secondary alcohols, was fractionated at 20 mm.: the properties of the fractions, after rectification at atmospheric pressure, are given in Table II.

Identification of Linalool.—Fraction IIIA was redistilled at atmospheric pressure. The desired phenylurethan of the portion boiling at 196–200° was separated from the less soluble derivative of terpineol with petroleum ether.

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(8) Tiemann, *Ber.*, **31**, 3297 (1898).

(9) Doebner, *ibid.*, **27**, 2020 (1894).

(10) Jacobsen, *Ann.*, **157**, 234 (1871).

(11) Erdmann and Hurth, *J. prakt. Chem.*, [2] **56**, 27 (1897).

TABLE II

	Boiling range, °C.	d_{15}	$\alpha^{20}D$	$n^{20}D$	Solubility at 20°
Fraction IIIA	Up to 212	..	...	..	...
Fraction IIIB	212–214	0.936	−6°23′	1.4808	3 to 3.5 volumes and more 60% alcohol.
Fraction IIIC	214–216	0.938	−8°28′	1.4818	
Fraction IIID	216–218	0.939	−9°55′	1.4832	
Fraction IIIE	218–220	0.940	−10°28′	1.4839	
Fraction IIIF	220–222	0.940	−11°17′	1.4848	
Fraction IIIG	222–224	0.940	−11°35′	1.4849	

It melted at 65–66° after four recrystallizations from dilute alcohol; a mixed m. p. with the phenylurethan of linalool showed no depression.

Identification of α-Terpineol.—Fractions IIIB to IIIG inclusive were viscid, colorless liquids having a pronounced odor of terpineol. All could be congealed at −5° to a semi-solid mass upon seeding with a crystal of solid terpineol. The phenylurethan of these fractions melted at 111–112° after two recrystallizations from dilute methyl alcohol. The nitrosochloride of Fractions IIIB, IIIE and IIIG, prepared by the method of Wallach,[12] melted at 121–122°.

From the combined Fractions IIID and IIIE, solid terpineol was separated by chilling, seeding and filtering. After two recrystallizations from ether, large colorless plates were obtained: m. p. 34–35°; $[\alpha]^{20}D$ −11°0′ (10% alcoholic solution); phenylurethan, m. p. 111–112°; nitrosochloride, m. p. 121–122°.

It is to be noted that the m. p. of the nitrosochloride and the phenylurethan correspond to the values given in the literature[13] for the inactive *dl*-modification. Probably these derivatives were formed because of the relatively small excess of *l*-terpineol over the *d*-modification: the specific rotation of an optically pure *l*-α-terpineol is −100.5°.[14]

Attempts to secure the phenylurethan, m. p. 132°, described by Burgess and Page,[2] were unsuccessful.

Fraction IV

The aldehydes were removed by the modified method of Tiemann. The aldehydes regenerated from the buffered sodium sulfite solution, 1 g., had an odor and index ($n^{20}D$ 1.4926) similar to the corresponding aldehydes of Fraction III; they were combined. From the crystalline bisulfite addition compound, 4 g. of a yellow oil having the odor of a fatty aldehyde was obtained.

Identification of Lauric Aldehyde.—The regenerated aldehyde was rectified at 10 mm.: d_{15} 0.838; $\alpha^{20}D$ ±0°; $n^{20}D$ 1.4370; b. p. 130–131° at 10 mm.; oxime, m. p. 74–75° after two recrystallizations from methyl alcohol. The semicarbazone melted at 100–101° after recrystallization from methyl alcohol and from isopropyl alcohol; a mixed m. p. with the semicarbazone of lauric aldehyde showed no depression.

After standing at 5° for twelve hours, a semisolid mass resulted. Upon drying between filter paper, the solid aldehyde melted at 10–11°; this is the low melting form of lauric aldehyde. A drop of dilute hydrochloric acid converted this aldehyde into a solid, m. p. 53–56°; this is probably the dimer reported by Zaar with a m. p. of 57°.[15]

After saponification of the aldehyde-free oil, the primary and secondary alcohols were removed with phthalic anhydride: 0.4 g. of a viscid brown oil was obtained. An attempt to prepare a phenylurethan proved unsuccessful.

Fraction IV, freed of aldehydes, esters, and primary and secondary alcohols, was fractionated at 4 mm.: a main fraction boiling at 110–112° was obtained.

Identification of Bisabolene.—This fraction had properties that approximate the values given in the literature[16] for bisabolene: d_{15} 0.891; $\alpha^{20}D$ −24°25′; $n^{20}D$ 1.4982; solubility at 20° = 5 volumes and more of 95% alcohol. A trihydrochloride,[16] prepared by passing dry hydrochloric acid into a cold ethereal solution of the oil, melted at 79–80° after recrystallization from alcohol. This is in agreement with the value reported in the literature. A 10% chloroformic solution of these crystals was optically inactive.

Anal. Calcd. for $C_{15}H_{24}\cdot3HCl$: Cl, 33.92. Found: Cl, 33.79.

Residue V

The aldehydes were removed with sodium bisulfite solution: upon regeneration, 0.14 g. of lauric aldehyde was obtained.

After saponification of the aldehyde-free oil, the primary and secondary alcohols were removed with phthalic anhydride: 2.5 g. of a viscid oil was obtained.

Identification of Lauric Alcohol.—After standing at 5° for twelve hours, a white waxy solid separated: m. p. about 19° after recrystallization from ether. The phenylurethan melted at 74–75° after recrystallization from petroleum ether; a mixed m. p. with the phenylurethan of lauric alcohol showed no depression. Since this alcohol was not identified in any other fraction, it is likely that it occurs as a high boiling ester.

Residue V, freed of aldehydes, esters, and primary and secondary alcohols, was fractionated at 4 mm., yielding a fraction boiling at 106–110° which was found to consist primarily of bisabolene, a fraction boiling at 115–119° which contained some bisabolene but no cadinene, a fraction boiling at 120–145° which had an intense blue color, and a residue which showed the absence of paraffinic hydrocarbons when treated with fuming sulfuric acid.

Separation of an Azulenic Compound.—The fraction having the intense blue color, 3 g., was shaken with 15 cc. of ice-cold phosphoric acid, following the procedure of Sherndal[17]: 0.2 g. of an intense blue-green oil was obtained. A minute amount of this oil dissolved in ether gave the yellow-green color characteristic of distilled lime oil.

Acidic Constituents

The combined aqueous washings from the saponifications of Fraction III, Fraction IV, and Residue V were evaporated to 1 liter. After washing with ether, the solution was acidified and steam distilled: distillation was continued as long as the runnings were acidic to litmus. Sodium carbonate was added until the distillate was alkaline; any phenols that might be present were extracted with ether.

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[12] Wallach, *Ann.*, **277**, 120 (1893).

[13] Simonsen, "The Terpenes," University Press, Cambridge, 1931, Vol. I, p. 227.

[14] Fuller and Kenyon, *J. Chem. Soc.*, **125**, 2304 (1924).

[15] Zaar, *J. prakt. Chem.*, [2] **132**, 169 (1931).

[16] Simonsen, *loc. cit.*, Vol. II, p. 493.

[17] Sherndal, THIS JOURNAL, **37**, 167 (1915).

Separation of a Phenol.—Evaporation of the ether yielded 0.2 g. of an oil with a phenolic odor suggestive of carvacrol. One drop, dissolved in 1 cc. of alcohol, gave an intense yellow color with ferric chloride solution; the color soon changed to a deep orange. Upon recrystallization from ether, the phenylurethan separated as a cluster of yellow needles, m. p. 134–137°. There was insufficient material for further purification.

The alkaline distillate was evaporated to 200 cc., acidified with sulfuric acid, and extracted with ether: 4.2 g. of an oily liquid were obtained. These free acids were distilled at atmospheric pressure: a fraction boiling at 95–110° was collected; the residue was rectified at 13 mm.

Identification of Acetic Acid.—The toluidide of the first fraction melted at 146–147°; a mixed m. p. with the toluidide of acetic acid showed no depression. The silver salt was ignited after recrystallization from boiling water. *Anal.* Calcd. for $C_2H_3O_2Ag$: Ag, 64.64. Found: Ag, 64.22.

Identification of *n*-Octylic Acid.—The toluidide of the rectified residue melted at 69–70° after repeated recrystallizations from dilute alcohol; a mixed m. p. with the toluidide of *n*-octylic acid showed no depression.

Identification of *n*-Decylic Acid.—The rectified residue deposited a solid acid upon standing at 5° for twelve hours: m. p. about 10°. A toluidide of this solid acid melted at 74–75° after repeated recrystallizations from dilute alcohol. The toluidide of *n*-decylic acid melted at 75–76°; mixed m. p. 74.5–75.5°.

Summary

An investigation of the chemical constituents of a Mexican distilled lime oil has established the presence of the following: α-pinene, β-pinene, *d*-limonene, dipentene, bisabolene, furfural, *n*-octylaldehyde, *n*-nonylaldehyde, *n*-decylaldehyde, lauric aldehyde, citral, *l*-borneol, geraniol, α-terpineol linalool, lauric alcohol, esters of acetic, *n*-octylic and *n*-decylic acids.

Borneol, geraniol and α-terpineol occur as free alcohols, and possibly also as esters; lauric alcohol probably occurs as an ester.

A high boiling oil of an intense blue-green color, probably an azulenic compound, was separated.

An unidentified aldehyde with an odor suggestive of cuminic aldehyde was not obtained in a state of sufficient purity for identification.

The presence of a trace of a phenol or phenolic ester was also established, although it was not identified.

The presence of phellandrene, *p*-cymene, terpinene, cadinene, or high boiling paraffinic hydrocarbons could not be established.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Conversion of Δ^2-Cyclohexenones and Cyclohexanones into Spirohydantoins[1]

BY HENRY R. HENZE, ROBERT CURTIS WILSON[2] AND ROBERT W. TOWNLEY[3]

During the past few years a considerable number of derivatives of hydantoin have been prepared in this Laboratory. These compounds have been tested elsewhere[4] and many have been shown to possess mild pharmacological activity, some as anticonvulsants and others as soporifics. As in the case of the barbiturates, some correlation may be noted between the type of activity and the structure of the substituents attached at the 5-position of the hydantoin nucleus. To date very few spirohydantoins[5] had been prepared for the purpose of being tested; this study supplied some examples of the desired type.

Substituted cyclohexanones react readily with aqueous–alcoholic solutions of potassium cyanide and ammonium carbonate to yield the anticipated substituted spirohydantoins. However, when Δ^2-cyclohexenones are condensed, addition of two equivalents of hydrogen cyanide leads to the formation of cyanospirohydantoins. When certain Δ^2-cyclohexenones are treated with alkali bisulfite and the products exposed to the action of potassium cyanide and ammonium carbonate solution, spirohydantoins containing a sulfonic acid substituent are obtained.

Five of these spirohydantoins have received preliminary pharmacological testing through the courtesy of Parke, Davis and Company. The spirohydantoin derived from 3-ethyl-5-methylcyclohexanone exhibited neither hypnotic nor anticonvulsant activity. However, the phenyl analog, namely, 2,4-dioxo-7-methyl-9-phenyl-1,3-diazaspiro(4,5)decane, did evidence a mild degree

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(1) From the Ph.D dissertation of R. C. Wilson, June, 1941.

(2) Present address: General Aniline and Film Corporation, Grasselli New Jersey.

(3) Present status: Past Assistant Public Hygiene Engineer U. S. Public Health Service.

(4) Our indebtedness to Parke, Davis and Company for this service is gratefully acknowledged.

(5) Henze and Speer [THIS JOURNAL, **64**, 522 (1942)] recorded the melting points of a few examples, but omit details of preparation and pharmacological activity.