

converted to a crystalline isomer when heated with alcoholic potassium hydroxide.

5. Consolidine is a crystalline base which can

be hydrolyzed to benzoic acid and amorphous con-soline.

OTTAWA, CANADA

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[JOINT CONTRIBUTION FROM THE KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY, WITH THE CALIFORNIA FOREST AND RANGE EXPERIMENT STATION<sup>1</sup>]

## Composition of Gum Turpentine of Torrey Pine

BY A. J. HAAGEN-SMIT, C. T. REDEMANN AND N. T. MIROV

The Torrey pine (*Pinus torreyana* Parry) is an endemic California pine found naturally only in two places: one, near La Jolla, California; the other, on Santa Rosa Island, California. It is occasionally planted in parks in California.

Botanically, the Torrey pine is related to the Coulter pine (*Pinus coulteri*) and the Digger pine (*Pinus sabiniana*); these pines form the morphologically distinct group *Macrocarpae*.

The composition of turpentine of Digger pine and of Coulter pine has been determined by previous investigators. It was found that Coulter pine turpentine is composed of *l*- $\alpha$ -pinene, and *l*- $\beta$ -phellandrene, together with the paraffin hydrocarbons *n*-undecane and *n*-heptane.<sup>2</sup> Similarly, the paraffin hydrocarbon *n*-heptane occurs in Digger pine turpentine to the extent of 95%<sup>3</sup>; the remaining 5% consists of normal saturated aldehydes.<sup>4</sup>

As most pines produce turpentine composed of terpenes, the paraffin hydrocarbons being found only in a few species, it appeared interesting to investigate the chemistry of the turpentines from this third pine of the *Macrocarpae*.

Conventional methods of chemical investigation revealed that Torrey pine turpentine consists of 75% *l*-limonene, together with 4% sesquiterpene, longifolene, 10% *n*-decyl aldehyde, 0.2% lauryl aldehyde, 0.2% of an unidentified C<sub>10</sub> carbonyl compound, and 5% *n*-undecane.

Mass distribution analysis of suitably purified fractions performed on a Consolidated Engineering<sup>5</sup> mass spectrometer confirmed the presence of *n*-undecane and revealed the presence of minute amounts of compounds having masses equal to those of nonane and *n*-heptane.

Although we could readily detect the presence of aldehydes containing an even number of carbon atoms in the molecule and of paraffins containing an odd number of carbon atoms, we were unable to detect aldehydes having an odd number of carbon atoms, or more than the minutest trace of a

paraffin with an even number of carbon atoms. We feel that this observation may bear considerable significance relative to the bio-synthesis of paraffin hydrocarbons by the pines.

### Experimental

**Collection of Oleoresin.**—About 4,000 g. of oleoresin was collected from three planted trees, about forty years old, growing in Golden Gate Park, San Francisco, California. Conventional turpentine methods were used; the trees were tapped once a week, and the oleoresin was collected also once a week. The tapping was started in May and discontinued in October. There was no difference in the yield of oleoresin throughout the summer; each tree yielded between 2.5 and 3 ounces per streak.

**Separation of Turpentine from Rosin.**—The volatile oil was expelled from oleoresin by heating it under vacuum, bringing the bath temperature to 200° and the pressure to 0.01 mm. There was no appreciable difference in the yield of volatile oil in the oleoresin samples obtained during different months of the operation; neither was there any difference in the yield of the oil by the three trees. The average figures, based on distillation of 17 batches of oleoresin were as follows

Volatile oil (turpentine)	17.1%
Rosin	81.9
Water	1.0

**Physical Constants of Turpentine.**—The turpentine samples obtained from the three trees at the different months of the season were analyzed with respect to their physical properties: density, index of refraction and optical rotation. These values showed no distinct trend with respect to time of collection of the oleoresin, nor did they vary greatly from tree to tree.

The maximum observed values of density,  $d^{23.5}$ , index of refraction,  $n^{25D}$ , and specific rotation,  $[\alpha]^{25D}$ , were 0.8366, 1.4660 and  $-121.95^\circ$ , respectively. The minima were 0.8355, 1.4650 and  $-115.47^\circ$ .

The composite turpentine sample with which this paper deals had for  $d^{23.5}$ ,  $n^{25D}$  and  $[\alpha]^{25D}$  the values 0.8360, 1.4656 and  $-118.12^\circ$ , respectively.

**Fractional Distillation of Turpentine.**—A batch of 300 g. of Torrey pine turpentine was fractionated into 20 parts by distillation through a 12-inch column packed with glass helices, surrounded by a heating jacket, and provided with a constant reflux ratio still-head. The 20 g. of residue was then separated into an additional 5 fractions by distillation through a 4-inch Vigreux column equipped with a variable take-off still-head.

The results of this fractionation are tabulated in Table I.

**Preparation of Low-boiling Fractions for Mass Spectroscopy.**—The low densities and refractive indices of the lower-boiling fractions indicated the presence of compounds other than terpene hydrocarbons. A micro analysis<sup>6</sup> of Fraction 1, however, showed a composition of 12.47%

(6) The authors are indebted to Dr. G. Oppenheimer and Mr. G. Swinehart of the California Institute of Technology for carrying out all microanalysis reported in this paper.

(1) Maintained by the Forest Service, U. S. Department of Agriculture, in cooperation with the University of California.

(2) Mirov, *Ind. Eng. Chem.*, **38**, 405-408 (1946).

(3) Schorger, "An Examination of the Oleoresins of Some Western Pines," *U. S. Dept. Agr. Forest Serv. Bull.*, 119 (1913).

(4) Uhl, *J. Am. Pharm. Assoc.*, **24**, 380 (1935).

(5) The authors wish to express their sincere appreciation to Mr. Harold W. Washburn and Miss Sibyl M. Rock of Consolidated Engineering Corporation for furnishing the mass distribution data presented in this paper.

TABLE I  
FRACTIONAL DISTILLATION OF 300 G. OF TORREY PINE  
TURPENTINE

Frac-tions	Distillation range $t_c$ , Pres., °C.	Dis-till-ate, mm., grams	Dens-ity $d_{25}^{25}$ , 23.5°	Index of refrac-tion $n_D^{25}$	Specific rotation $[\alpha]_D^{25}$
1	57-63	23	1.0	0.8266	1.4597
2	63-65	23	2.7	.8263	1.4620
3	65-67	23	4.0	.8308	1.4649
4	67-68	23	3.5	.8321	1.4655
5	68-69	23	18.7	.8337	1.4674
6	69-70	23	28.5	.8353	1.4677
7	69-70	23	40.8	.8359	1.4680
8	69-70	23	43.6	.8376	1.4687
9	69-70	21	17.3	.8366	1.4683
10	69-70	21	6.7	.8366	1.4689
11	69-70	21	17.7	.8366	1.4682
12	70-71	21	9.5	.8347	1.4676
13	71-72	21	24.3	.8353	1.4676
14	71-72	21	8.7	.8356	1.4676
15	72-75	21	20.1	.8295	1.4644
16	75-80	21	5.5	.8045	1.4696
17	80-83	21	8.8	.7649	1.4265
18	80-83	21	7.1	.7494	1.4170
19	83-93	21	1.9	.8071	1.4283
20	93-97	21	1.4	.8396	1.4357
			24.5°		
21	53-55	0.1	5.5	.9109	1.4841
22	60-62	.3	2.9	.9225	1.4932
23	62-64	.2	5.8	.9271	1.4939
24	64-65	.2	3.3	.9206	1.4927
25	65-85	.2	1.1	.9021	1.4838

Residue, semisolid, amber-colored.

hydrogen and 87.54% carbon, leaving little room for the presence of compounds other than hydrocarbons.

Accordingly, fractions 1 and 2 were combined and bromine was added dropwise at 0.5° until a persistent yellow tint developed in the reaction mixture. The brominated product was then distilled at atmospheric pressure, that material boiling between 90 and 155° being collected. This distillate was then redistilled over metallic sodium in order to remove halogen compounds present. The greater part of this material boiled between 145 and 155°.

Following distillation, the oil was shaken out twice with cold fuming sulfuric acid. The clear, centrifuged insoluble residue consisted of about 0.1 g. of a colorless oil of  $n_D^{25}$  1.4174 and  $d_{25}^{25}$  0.761. This sample was submitted to a mass distribution analysis in a Consolidated Engineering mass spectrometer.

**Detection of an Unidentified Nonane.**—From the mass spectrogram obtained from this low-boiling hydrocarbon concentrate, Miss Sibyl M. Rock of Consolidated Engineering Corporation was able to make a rough estimate of the quantities of compounds present in the sample. Her figures are presented in Table II.

Unfortunately, the small quantity of material at our disposal prevented our obtaining evidence relative to the structural details of the C<sub>9</sub> paraffin or of the compound of mass 138.

TABLE II  
APPROXIMATE MASS DISTRIBUTION FOR LOW BOILING  
HYDROCARBON CONCENTRATE

C <sub>7</sub> Paraffin hydrocarbons	3%
C <sub>8</sub> Paraffin hydrocarbons	1
C <sub>9</sub> Paraffin hydrocarbons	70
Compounds of mass 138	23
Compounds of mass 140	3
Compounds of mass 142	1/2

**Identification of *l*-Limonene.**—The experimental evidence for the presence of *l*-limonene in fraction 7 is summarized in Table III.

*l*-Limonene tetrabromide was prepared from fraction 7 by adding liquid bromine dropwise to a solution of the oil in six times its volume of a mixture of equal volumes of ethyl alcohol and ethyl ether. During the addition, the temperature of the solution was maintained below 5° with the help of an ice-bath. Addition of bromine was discontinued as soon as the solution had assumed a persistent yellow tint. The residue which remained after spontaneous evaporation of the solvent at room temperature was recrystallized four times from ethyl ether before microanalysis.

TABLE III  
IDENTIFICATION OF *l*-LIMONENE IN TORREY PINE TURPENTINE

Property	<i>l</i> -Limonene	Fraction 7
Boiling point, °C.	176 at 760 mm. <sup>a</sup>	69-70 at 23 mm.
Density	$d_{25}^{25}$ 0.8422 <sup>a</sup>	$d_{25}^{25}$ 0.836
Index of refraction	$n_D^{25}$ 1.47468 <sup>b</sup>	$n_D^{25}$ 1.4680
Specific rotation	$[\alpha]_D$ -122.6 <sup>b</sup>	$[\alpha]_D$ -14.5
% Carbon	88.16 (calcd.)	88.29
% Hydrogen	11.84 (calcd.)	12.18
Tetrabromide	{ Melting point 104-105 <sup>a</sup>	104-105
	{ % Carbon 26.36 (calcd.)	26.62
	{ % Hydrogen 3.54 (calcd.)	3.89

<sup>a</sup> Von Braun and Lemke, *Ber.*, **56**, 1652 (1923).  
<sup>b</sup> Bruhl, *J. Chem. Soc.* **91**, 121 (1907).

**Identification of *n*-Undecane.**—Although the density and the index of refraction of fraction 18 indicated that it probably consisted chiefly of a paraffin hydrocarbon, the optical rotation of -1.90° showed the presence of some extraneous material, probably *l*-limonene. Accordingly, this fraction was further purified before analysis was attempted.

This purification was carried out by shaking a sample of fraction 18 with an equal volume of cold, fuming sulfuric acid, allowing the material to stand overnight, separating the hydrocarbon from the acid, and repeating the process.

The twice treated hydrocarbon was then distilled at atmospheric pressure prior to measurement of its physical constants. This treatment caused very little loss in volume of fraction 18.

The evidence for the identity of the purified hydrocarbon of fraction 18 with *n*-undecane is presented in Table IV.

TABLE IV  
IDENTIFICATION OF *n*-UNDECANE IN TORREY PINE TURPENTINE

Property	<i>n</i> -Undecane	Purified fraction 18
Boiling point, °C.	195.8 at 760 mm. <sup>a</sup>	194-195 at 740 mm.
Density	$d_{25}^{25}$ 0.73667	$d_{25}^{25}$ 0.736
Index of refraction	$n_D^{25}$ 1.41495 <sup>a</sup>	$n_D^{25}$ 1.4155
Melting point, °C.	-25.6 <sup>a</sup>	-26.2 to -25.6
% Carbon	84.52 (calcd.)	84.49
% Hydrogen	15.48 (calcd.)	15.25

<sup>a</sup> Shepard, Henne and Midgley, *THIS JOURNAL*, **53**, 1951, 1953, 1958 (1931).

**Confirmation of Presence of *n*-Undecane.**—According to a mass distribution analysis made on a Consolidated Engineering mass spectrometer by Miss Sibyl M. Rock, the purified sample of fraction 18 contained a trace of heptanes, a small amount of nonanes, and probably more than 95% undecane. Hexanes, octanes and decanes were absent.

**Identification of *n*-Decyl Aldehyde.**—The fact that fractions 19 and 20 consist largely of *n*-decyl aldehyde was established by preparation of the 2,4-dinitrophenylhydrazones of these fractions, as well as by measurement of the physical properties of the fractions. The experimental

TABLE V  
 IDENTIFICATION OF *n*-DECYLALDEHYDE IN TORREY PINE TURPENTINE

Property	<i>n</i> -Decylaldehyde	Fraction 19	Fraction 20
Boiling point, °C.	207–209 at 760 mm. <sup>a</sup>	83–93 at 21 mm.	93–97 at 21 mm.
Density	$d^{20}_D$ 0.850 <sup>b</sup>	$d^{23.5}_D$ 0.807	$d^{23.5}_D$ 0.840
Index of refraction	$n^{20}_D$ 1.4287 <sup>b</sup>	$n^{27}_D$ 1.4283	$n^{27}_D$ 1.4357
2,4-Dinitrophenylhydrazone			
Melting point, °C.	104 <sup>c</sup>	104	104
Melting point, °C. when mixed with <i>n</i> -decylaldehyde 2,4-dinitrophenylhydrazone	104	104	104
Crystal habit	Yellow needles <sup>c</sup>	Yellow needles	Yellow needles
% Carbon	57.14 (calcd.)		57.17
% Hydrogen	7.19 (calcd.)		7.24
% Nitrogen	16.66 (calcd.)		16.53

<sup>a</sup> Stephan, *J. prakt. Chem.*, (A) **62**, 525 (1900). <sup>b</sup> Reference 4. <sup>c</sup> Allen, *THIS JOURNAL*, **52**, 2958 (1930).

evidence for the identity of these fractions is summarized in Table V.

Each derivative was prepared by adding 100 mg. of 2,4-dinitrophenylhydrazine to 100 mg. of the oil, and adding just a sufficient quantity of boiling glacial acetic acid to effect complete solution of the reagent. The solution was permitted slowly to cool to room temperature, whereupon the 2,4-dinitrophenylhydrazone separated. The product was twice recrystallized from 95% ethyl alcohol prior to analysis.

Inasmuch as a mixture of the 2,4-dinitrophenylhydrazones of fractions 19 and 20 showed no depression in melting point, the two were assumed identical.

**Detection of an Unidentified C<sub>10</sub> Carbonyl Compound.**—The presence of perhaps 10% of an unidentified C<sub>10</sub> carbonyl compound in fraction 21 was ascertained by preparing the corresponding 2,4-dinitrophenylhydrazone from fraction 21.

Two hundred mg. of fraction 21 was heated to boiling with a solution of 100 mg. of 2,4-dinitrophenylhydrazone in 2 ml. of glacial acetic acid. The crystals which separated on cooling were filtered off and dissolved in 100 ml. of 60–80° petroleum ether. The yellow solution was passed through a 21 × 130 mm. column of "Alorco" F-20 grade, minus 80-mesh activated alumina.

Following development with 100 ml. of benzene, two distinct bands appeared on the column. One was a 3 mm. wide orange band located 3 mm. beneath the top of the column. The second, 28 mm. wide brown band appeared 3 mm. beneath this narrow band.

The column packing was extruded and cut into sections, each section being eluted with 20 ml. of a mixture of equal volumes of ethyl ether and ethyl alcohol. Following filtration, the eluates were evaporated to dryness. Since only a very small quantity of material was obtained from the top band, it was not further investigated. The main material resulting from elution of the lower band consisted of approximately 20 mg. of yellow platelets, which melted at 93–94° following two recrystallizations from ethyl alcohol.

*Anal.* Calcd. for C<sub>16</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>: C, 57.14; H, 7.19. Found: C, 57.40; H, 7.52.

**Identification of Laurylaldehyde.**—Laurylaldehyde was identified as a minor constituent of fraction 23 by preparing its 2,4-dinitrophenylhydrazone.

One gram of fraction 23 and 100 mg. of 2,4-dinitrophenylhydrazine were dissolved in 10 ml. of glacial acetic acid heated to boiling. As the solution cooled, a mass of yellow needles formed in it. These crystals were filtered off, the filtrate was brought to a boil, and an additional 100 mg. of 2,4-dinitrophenylhydrazine was dissolved in the hot filtrate. On cooling, only crystals of the reagent separated. This observation indicates that the initial precipitate represented most of the aldehyde present in fraction 23.

The yellow precipitate of this 2,4-dinitrophenylhydrazone was dissolved in 40 ml. of benzene and absorbed on

a 20 × 130 mm. column of "Alorco" F-20 grade, minus 80 mesh activated alumina. After development with 110 ml. of benzene, there appeared a minor band 2 mm. wide 11 mm. beneath the top of the column. Directly beneath this was the main, 50 mm. wide brown band.

The column packing was extruded and the lower, main band cut apart from the remainder of the material. The desired compound was eluted from the alumina with 20 ml. of a mixture of equal volumes of ethyl ether and ethyl alcohol. The eluate was evaporated to dryness, and the residue recrystallized twice from 96% ethyl alcohol. The resultant yellow needles melted at 106–107°.

Lauraldehyde 2,4-dinitrophenylhydrazone is reported<sup>7</sup> to melt at 106°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>: C, 59.32; H, 7.74. Found: C, 59.66; H, 7.71.

The identity of this compound with lauraldehyde 2,4-dinitrophenylhydrazone was confirmed by the observation that a mixture of the two compounds showed no depression in melting point.

**Identification of Longifolene.**—The experimental evidence that fraction 23 consists chiefly of the sesquiterpene, longifolene, is presented in Table VI.

In order to prepare longifolene hydrochloride, we dissolved 1 g. of fraction 23 in 5 ml. of anhydrous ethyl ether. The solution was surrounded by an ice-bath, and saturated with dry hydrogen chloride gas. The test-tube containing the solution was then tightly stoppered and placed in the refrigerator (4°) for one week.

At the end of this time, the solution was poured out on a watch glass, and the solvent was permitted to evaporate. After standing exposed to the laboratory air for four days, the oily residue solidified. It was then pressed out on a porous clay plate to dry. The dried crystals were recrystallized twice from glacial acetic acid prior to microanalysis.

TABLE VI

IDENTIFICATION OF LONGIFOLENE IN TORREY PINE TURPENTINE			
Property	Longifolene	Fraction 23	
Boiling point, °C.	150–151 at 36 mm. <sup>a</sup>	62–64 at 0.2 mm.	
Density	$d^{30}_{30}$ 0.9284 <sup>a</sup>	$d^{24}_4$ 0.927	
Index of refraction	$n^{30}_D$ 1.495 <sup>a</sup>	$n^{27}_D$ 1.494	
% Carbon	88.16 (calcd.)	87.46	
% Hydrogen	11.84 (calcd.)	12.34	
Hydro {	Melting point, °C. 59–60 <sup>a</sup>	59–60	
chlo- {	% Carbon 74.81 (calcd.)	74.62	
ride {	% Hydrogen 10.46 (calcd.)	10.47	

<sup>a</sup> Simonsen, "The Terpenes," Vol. II, Cambridge University Press, England, 1932, p. 541.

### Summary

Physical constants of typical samples of Torrey pine gum turpentine are presented, together with

(7) Reference c, Table V.

data showing the yields of turpentine from an average tree.

Experiments are described, which show that the gum turpentine from Torrey pine contains approximately 75% *l*-limonene, 10% *n*-decylaldehyde, 5% *n*-undecane, 4% longifolene, 0.2% laurylaldehyde and 0.2% of an unidentified C<sub>10</sub>

carbonyl compound, together with less than 0.1% each of nonane and heptane. The occurrence of the paraffin hydrocarbon in Torrey pine turpentine is indicative that the Torrey pine is closely related biochemically, as well as morphologically, to the Digger pine and the Coulter pine.

PASADENA, CALIF.

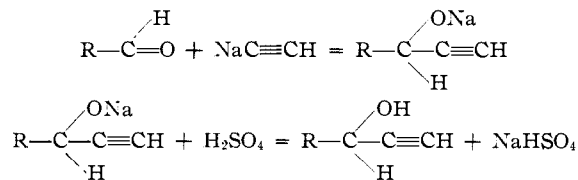
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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF INDIANA UNIVERSITY]

## Concerning Aromatic Acetylenic Carbinols

BY PHYLLIS RUTAN<sup>1</sup> AND CLARENCE E. MAY

Numerous aldehydes and ketones have been combined successfully with sodium acetylide under varying conditions to form acetylenic carbinols. Of the aromatic aldehydes reported<sup>2,3</sup> benzaldehyde was the only aromatic aldehyde that gave a good yield of its corresponding acetylenic carbinol.



Two methods of synthesis of acetylenic carbinols are those of Jones and McCombie<sup>4</sup> and Zeitner and Genas.<sup>5</sup>

The present authors have attempted the synthesis of acetylenic carbinols from the following aromatic aldehydes: phenylacetaldehyde, *p*-dimethylaminobenzaldehyde, cinnamic aldehyde, *t*-ethoxyvanillin, *p*-methoxybenzaldehyde, *o*-methoxybenzaldehyde, *p*-chlorobenzaldehyde and salicylaldehyde.

Since phenylethynylcarbinol was produced in a 61% yield by the use of the Jones-McCombie method and in a 35% yield by the Zeitner-Genas method, most of our work centered around the use of the various aldehydes with the former method. To ascertain whether an acetylenic carbinol had been formed we found useful the production of an explosive yellowish silver acetylide.<sup>6</sup>

### Experimental

***p*-Methoxyphenylethynylcarbinol.**—In a three-necked flask equipped with a mechanical stirrer, cooled with a bath of Dry Ice in methanol, 23 g. of sodium in a liter of liquid ammonia was treated with acetylene until the blue color of the solution had disappeared. A steady stream of acetylene generated by water under pressure dripping on a charge of 100 g. of calcium carbide was passed through

the ammonia solution. The acetylene was purified by passage respectively through a solution containing 10% chromic acid in 20% sulfuric acid, a 10% copper nitrate solution in 20% nitric acid, a 10% sodium hydroxide solution and a calcium chloride drying tube.

To the sodium acetylide solution was added gradually a solution of 135 g. anisaldehyde dissolved in 100 ml. of dry ether. An hour was usually required for the addition of the aldehyde solution. Meanwhile, acetylene was passed through the ammonia solution in a continuous fast bubbling stream. This was continued for three hours after the aldehyde was added.

After the evaporation of the ammonia the residue was treated with ice and 50% sulfuric acid until the mixture became acidic toward congo red paper. The mixture was then ether extracted and the extract was dried with calcium chloride. A few crystals of hydroquinone were added to protect the product during the final distillation in an atmosphere of nitrogen. A 61.9% theoretical yield of *p*-methoxyphenylethynylcarbinol, b. p. 123.5°, 0.5 mm., was obtained.<sup>7</sup> It was pale yellowish oil that crystallized on standing and melted at 172–173°. The product gave no color with ferric chloride and formed no 2,4-dinitrophenylhydrazone. The dry silver acetylide burned with explosive violence.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>: C, 74.05; H, 6.22. Found: C, 73.59; H, 5.96.

*p*-Methoxyphenylethynylcarbinol yielded a mercury derivative when 1.62 g. of the carbinol dissolved in 35 ml. of ethanol was allowed to react with 160 ml. of the alkaline mercuric iodide solution of Johnson and McEwan.<sup>8</sup> The mercury derivative was obtained as a white precipitate. This was crystallized from alcohol and 2.4 g. of white needles, m. p. 185°, was recovered.

***o*-Methoxyphenylethynylcarbinol.**—*o*-Methoxybenzaldehyde was made in 88% yield by the Blatt method.<sup>9</sup> In the same manner as previously described for making *p*-methoxyphenylethynylcarbinol, an 88% yield of *o*-methoxyphenylethynylcarbinol was obtained as a pale yellow oil, b. p. 115.7°, 1.0 mm., from *o*-methoxybenzaldehyde.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>: C, 74.05; H, 6.22. Found: C, 73.65; H, 6.68.

From this preparation of *o*-methoxyphenylethynylcarbinol was made a mercury derivative that melted at 138°.

***p*-Chlorophenylethynylcarbinol.**—*p*-Chlorobenzaldehyde gave a 6.0% yield of *p*-chlorophenylethynyl carbinol, b. p. 105°, 3.0 mm., when distilled in an atmosphere of nitrogen. A cryoscopic molecular weight determination showed a value of 164.8. The theoretical value for C<sub>10</sub>H<sub>10</sub>OCl is 166. The corresponding mercury derivative was made and found to melt at 195°.

(1) Abstracted from a thesis submitted May 1, 1946 to the faculty of the Graduate School in partial fulfillment of the requirements for the degree Master of Arts, Indiana University.

(2) Hess and Munderloh, *Ber.*, **51**, 377 (1918).

(3) Campbell, Campbell and Eby, *THIS JOURNAL*, **60**, 2833 (1938).

(4) Jones and McCombie, *ibid.*, **64**, 933 (1942).

(5) Zeitner and Genas, U. S. Patent 2,345,170, March 28, 1944.

(6) Rupe and Vonaesch, *Ann.*, **442**, 79 (1925).

(7) All boiling points and melting points mentioned are uncorrected.

(8) Johnson and McEwan, *THIS JOURNAL*, **48**, 469 (1926).

(9) Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 619.