caused the active acid to be converted into the racemic acid. This point will be studied further and reported on in a later paper.

Summary

dl-1,2-Dihydroxy-*iso*butyric acid was prepared by three different methods, two of them new. All three methods yielded a crystalline acid of melting point 104°. Mixed-melting-point determinations showed that the samples of acid from the three sources were identical substances. The phenylhydrazide, and the calcium, zinc, copper, cadmium and manganese salts were prepared and analyzed. Attempts at resolution were inconclusive although brucine gave some evidence of ability to resolve the acid.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE PHYTOCHEMICAL LABORATORY OF THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ODOROUS CONSTITUENTS OF THE COTTON PLANT. EMANATION OF AMMONIA AND TRIMETHYLAMINE FROM THE LIVING PLANT[1]

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RECEIVED APRIL 4, 1925 PUBLISHED JUNE 5, 1925

The investigation which is here described was undertaken at the request of Dr. L. O. Howard, Chief of the Bureau of Entomology, and the primary purpose was to ascertain the chemical character of the odorous constituents of the cotton plant. Inasmuch as this plant possesses a specific attraction for the boll weevil, it has been presumed that this was due to the emanation of some odorous substance which could be perceived by the insects at a considerable distance. It has furthermore been considered that if any odorous substance could be identified, which by chemotropic tests would be found attractive for the insects, it might be possible to produce it in sufficient quantities to permit of its use as a bait.

Some products from the cotton plant have previously been the subject of more or less extended investigations, particularly the fatty oil expressed from the seeds and also the residual press-cake. The flowers of the plant have been examined with respect to their coloring matters, chiefly by A. G. Perkin,[2] and cotton-root bark, which has been used to some extent medicinally, was examined most recently by Power and Browning,[3a] with consideration of its more important constituents.

An examination of the volatile products obtained from the cotton fiber

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[1] Communicated in abstract to the National Academy of Sciences at a meeting held in Washington, D. C. April 27, 1925.

[2] Perkin, (a) *J. Chem. Soc.*, **75**, 825 (1899); (b) **95**, 2181 (1909); (c) **109**, 145 (1916). See also (d) Viehoever, Chernoff and Johns, *J. Agr. Research*, **13**, 345 (1918) and (e) Stanford and Viehoever, *ibid.*, **13**, 419 (1918).

[3a] Power and Browning, *Pharm. J.* (London), [4] **39**, 420 (1914).

by the action of water and of sodium hydroxide under pressure has been made by Clifford and Fargher.[3b] They obtained, among other substances, methyl alcohol, acetone, ammonia, dimethylamine, trimethylamine, acetaldehyde and small amounts of other aldehydes or ketones. The production of methyl alcohol and acetone by the action of caustic alkalies suggested the presence of pectin in the cotton.

An attempt was made several years ago to obtain an essential oil from the cotton plant in order to test its chemotropic properties.[4] The material used for this purpose consisted chiefly of seedlings collected in the month of May in the vicinity of Tallulah, Louisiana and about 1820 kg. of the fresh plant was distilled. By extracting the entire distillate with ether a small quantity (28.9 g.) of a brown essential oil was obtained, which represented a yield of 0.0015%. A portion of this product (7.8 g.) was subjected to fractional distillation under ordinary pressure, when small quantities of distillate varying from a few drops to 1 or 2 cc. were collected at temperatures ranging from 200° to 300°. The oil was found to contain no furfural, and the higher-boiling fractions were observed to have a blue color, but otherwise none of its characters or constituents was determined.

In view of the economic importance of the cotton plant it was eminently desirable that a more complete chemical examination should be made of it than had been accomplished hitherto, and in the first instance with consideration of its volatile or odorous constituents. An opportunity for conducting such an investigation was afforded us by the Bureau of Entomology of the United States Department of Agriculture, and all the facilities of the Delta Laboratory of that Bureau at Tallulah were generously placed at our disposal.

Experimental Part

The material employed for this investigation was collected from a 10-acre field of choice, short staple, Upland cotton, near Tallulah, which had been specially reserved for our use. At the beginning of the operations in the early part of July, 1923, the plants were about 60 cm. high, but in the latter part of August, when the preliminary distillations were completed, they had attained a height of from 1.5 to 2.1 meters. The field was comparatively free from infestation with weevils. It was therefore not found necessary to spray the plants with any arsenical compound, and they were treated with no chemical except that employed as a fertilizer, which consisted of sodium nitrate.

The plants were cut off several centimeters above the ground or just below the lower branches and brought directly from the field to the large still which had been specially constructed for their distillation. The branches were first stripped from the coarse, woody stems and the material used therefore consisted chiefly of the foliage, together with the so-called squares and the flowers, with a few small bolls. All of this material was coarsely chopped before bringing it into the still; the latter was provided with three galvanized iron drums having perforated bottoms, the lower one of which was supported

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[3b] Clifford and Fargher, *J. Textile Institute*, **14**, 117 (1923).

[4] Ref. 2 d, p. 349.

about 2.5 cm. above the steam inlet. These drums were so arranged one above an other as to permit the free passage of steam through the entire mass, and when the distillation was finished they could readily be lifted out for removing the exhausted material. After each distillation the still and drums were thoroughly cleansed. The amount of fresh material used in each operation was about 90 kg., and the distillation was effected by the direct introduction of steam without any further addition of water. Not more than about two hours elapsed between the cutting of the plant in the field and the beginning of distillation.

The total amount of material subjected to distillation was 3290 kg. (7255 pounds) and the total original distillate amounted to about 5300 liters (1400 gallons). The dark colored aqueous liquid which was removed with the exhausted material from the still was observed to have a strongly acid reaction.

For convenience of transportation the original distillate was concentrated by successive cohobations with steam in a small copper still until practically all of the odorous constituents were contained in a volume of 295 liters (78 gallons). All of the odorless liquids remaining in the copper still after the numerous operations of concentrating the distillate were brought into a large copper kettle provided with a steam jacket, and after being made distinctly alkaline with sodium hydroxide they were evaporated to a small volume. The subsequent treatment of these liquids, which contained a large proportion of the volatile acids present in the original distillate, will be described later.

Characters of the Distillate.—The original distillate was a slightly turbid liquid and contained some globules of colorless oil floating on the surface. It had a characteristic, persistent and rather pleasant odor, although the first portions which passed over were somewhat pungent. The absence of sulfur compounds was ascertained by special tests. The distillate was neutral to litmus and gave a faint reaction with Schiff's reagent for aldehyde, the presence of which was much more strongly indicated after the concentration of the liquid by cohobation. It gave no coloration with ferric chloride.

The Essential Oil

As the essential oil was not sufficient in amount to permit its mechanical separation from the distillate, a quantity (about 19 liters) of a concentrated distillate, representing 179.6 kg. of the fresh cotton plant, was extracted with three successive portions of ether. After the ethereal liquids had been dried with anhydrous sodium sulfate, the greater part of the solvent was removed by distillation. The liquid was then brought into a small tared flask and the remaining ether allowed to evaporate spontaneously until a practically constant weight was attained. The amount of essential oil so obtained was 5.4202 g. or 0.00302%. In another extraction of a distillate, conducted at Tallulah, which represented 98 kg. of the cotton plant, the yield of essential oil was 3.0673 g. or 0.00313%.

The essential oil, as extracted by ether, was a pale, brownish-yellow, transparent, limpid liquid, which rapidly darkens in color on keeping, unless preserved in a sealed tube, when it remains unchanged. When cooled to 0° the oil became somewhat viscid, and at a temperature of —15° it congealed to a transparent, jelly-like mass, but without the separation of any solid substance. When a few drops of the oil were shaken with Schiff's reagent, a pink color was soon produced, thus indicating the presence of an aldehyde. With aniline and acetic acid it gave a strong reaction for furfural. The oil was tested for the presence of nitrogen by ignition with metallic sodium, according to the method described by Mulliken,[5] when a perfectly negative result was obtained.

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[5] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1905**, vol. I, p. 10.

The density of the oil, determined by means of a small Sprengel pycnometer, d_{25}^{25}, was 0.9261. The index of refraction, $n_D^{20°}$, was 1.4797. The optical rotation, α_D, was —1.81° in a 0.5dcm. tube, whence $[\alpha]_D^{20°} = -3.91°$.

Examination for Aldehydes

A quantity (7.6 liters) of a concentrated distillate, representing 89.5 kg. of the fresh cotton plant, was cohobated in a current of steam until the more volatile constituents were contained in a volume of 1.5 liters, the final distillate having been cooled with ice. This liquid possessed a strong, very persistent and agreeable odor and contained some large globules of yellowish oil floating on the surface. A very small portion of the liquid which first passed over was used for some preliminary tests. With Schiff's reagent it soon developed a pink color, and it rapidly reduced an ammoniacal solution of silver oxide. The presence of acetaldehyde was indicated by the production of a deep blue color with dimethylamine and sodium nitroprusside.[6]

The entire amount of the above-mentioned concentrated distillate was saturated with sodium hydrogen sulfite and the mixture allowed to stand for several days with occasional agitation. It was then extracted with three successive portions of aldehyde-free ether and a current of air subsequently passed through the liquid to expel the dissolved ether. After the addition of sufficient sodium carbonate to render the liquid distinctly alkaline it was distilled in a current of steam and 0.5 liter of distillate collected. This distilled liquid was slightly opalescent and possessed a pleasant odor, suggesting the presence of a minute quantity of a higher aliphatic aldehyde. A small portion of the distillate which first passed over was found to give all the previously-mentioned aldehyde reactions including the specific test for acetaldehyde. No reaction for formaldehyde was obtained by either the official tests with phenylhydrazine hydrochloride[7] or by Schryver's modification of the Rimini test.[8]

The distillate containing the aldehyde was treated with an alkaline solution of potassium permanganate until the red color remained for a time unchanged, after which the liquid was filtered, the excess of permanganate removed by the addition of a solution of ferrous sulfate in dil. sulfuric acid and the mixture distilled with steam. About 1 liter of distillate was collected, which was only very slightly acid. It was made alkaline with barium hydroxide, concentrated, the excess of the hydroxide removed by carbon dioxide and the liquid filtered and concentrated. On the addition of silver nitrate a small amount of a dark colored precipitate was first produced, which was removed by filtration. The liquid was then further concentrated and filtered while hot, when on cooling an appreciable amount of a perfectly white silver salt separated. This was collected, dried, and analyzed.

Anal. Subs., 0.0469, 0.0342: Ag, 0.0300, 0.0221. Calcd. for $AgC_2H_3O_2$: Ag, 64.6. Found: 64.0, 64.6.

The aldehyde contained in the plant was thus proved to be essentially acetaldehyde, with apparently a very small amount of a higher homolog.

Examination of the Original Concentrated Distillate for α,β-Hexylenic Aldehyde, $CH_3CH_2CH_2CH{=}CHCOH$

It has been observed that when plants containing chlorophyll are distilled with steam they yield volatile substances which possess reducing properties.[9] After the dis-

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[6] Power and Chesnut, This Journal, **42**, 1511 (1920).

[7] "Methods of Analysis of the Association of Official Agricultural Chemists," published by the Association at Washington, D. C., **1920**, pp. 124–125.

[8] Schryver, *Proc. Roy. Soc.*, **82B**, 226 (1910).

[9] Reinke, *Ber.*, **14**, 2145 (1881).

covery of the acid hydrazides, Curtius[10] and also Reinke[11] succeeded in obtaining these volatile substances from a great variety of leaves in the form of sparingly soluble, well characterized condensation products. With the use of *m*-nitrobenzhydrazide these products, after crystallization from alcohol, melted at 167–168° and agreed in composition with α,β-hexylenicaldehyde-*m*-nitrobenzhydrazide. Inasmuch as α,β-hexylenicaldehyde was found in all of the different leaves examined, it was concluded that it occurs in all plants that contain chlorophyll. The aldehyde was thoroughly characterized by its regeneration from the hydrazone, oxidation to α,β-hexylenic acid and the bromination of the latter, when it yielded α,β-dibromocaproic acid.[12]

In order to ascertain whether the above-mentioned aldehyde is contained in the leaves of the cotton plant, a portion (1.9 liters) of a concentrated distillate was used, which represented 23 kg. of fresh material consisting of leaves and stems. To this liquid, while being actively stirred by an electric motor, there was gradually added a solution of 7 g. of *m*-nitrobenzhydrazide (m. p., 153–154°) in 100 cc. of hot alcohol. The stirring was continued for one and a half hours when a slight turbidity ensued, and after the mixture had been set aside for a day a small amount of substance was deposited. This was collected by filtration and dried in a vacuous desiccator. It had a pale, brownish-yellow color and weighed 0.02 g. When purified by treating its solution in warm alcohol with a little animal charcoal it separated in the form of a colorless, felted mass of microscopic needles. It melted quite sharply at 248–249° to form a colorless liquid.

Another experiment was made with a portion of the concentrated distillate which represented 68.6 kg. of the fresh leaves and stems of the plant. In this case the aldehydic substances contained in the liquid were first separated by means of the acid sodium sulfite compound. The volume of liquid containing the regenerated aldehyde was 0.5 liter, and this was treated under the previously described conditions with a solution of 5 g. of *m*-nitrobenzhydrazide in 75 cc. of hot alcohol. After being allowed to stand for several days the mixture had gradually deposited a grayish product which, when collected and dried, weighed 0.45 g. This was first purified by crystallization from warm alcohol, when it melted at 240–241°. When crystallized from warm benzene, in which it was very sparingly soluble, it separated in fine, colorless needles; m. p., 244–245°.

Curtius and Franzen[13] had observed in the course of their investigation of green leaves that, in addition to the hydrazone of hexylenic aldehyde a small amount of a very sparingly soluble condensation product was formed which melted at 237–238°. This was not further examined, but it was possibly identical with the hydrazone of high melting point obtained by us from the cotton plant.

Although the amount of purified substance of high melting point obtained by us, as described above, was much too small for analysis, a little of it (about 0.002 g.) was used for the following test. The substance was mixed with a little water, the liquid strongly acidified with sulfuric acid and the mixture distilled in a current of steam. The distillate first obtained was again distilled and about 5 cc. of distillate collected. This liquid when tested with sensitized Schiff's reagent and with an ammoniacal solution of silver oxide gave slight but very positive reactions for the presence of an aldehyde. It probably represented the very small amount of a higher aliphatic aldehyde that we have indicated as accompanying the acetaldehyde in the cotton distillate.

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[10] Curtius, *Ber. botan. Ges.*, **15**, 201 (1897).

[11] Reinke, *ibid.*, **17**, 7 (1899).

[12] (a) Curtius and Franzen, *Sitzb. Heidelberger Akad. Wiss.*, **I**, p. 3 (1920). See also (b) Franzen, *Z. physiol. Chem.*, **112**, 301 (1921).

[13] Ref. 12 a, p. 5.

Notwithstanding the observations of Curtius and others regarding the occurrence of α,β-hexylenic aldehyde we have not been able to obtain any evidence of its presence in the leaves of the cotton plant. Inasmuch as the material used by Curtius consisted of fresh leaves which had been finely ground to a thick pasty mass which was mixed with a little water before distillation, it is thought possible that the above-mentioned aldehyde was a product of enzymic action. In support of this view it may be noted that no volatile oil can be obtained from the tea plant except upon distillation of the freshly fermented leaves, and from such an oil van Romburgh[14] isolated a hexylenic alcohol, $C_6H_{12}O$, which on oxidation yielded butyric acid. An alcohol of the composition $C_8H_{16}O$, which may be regarded as an octylenic alcohol, was isolated in very small amount by Power and Kleber[15] from gaultheria oil, and the latter, or at least the methyl salicylate of which it chiefly consists, is known not to pre-exist in gaultheria leaves but to be formed by the action of an enzyme on a glucoside.

Acetaldehyde-*m*-Nitrobenzhydrazide, $CH_3CH:NNHCOC_6H_4.NO_2$

Although the cotton distillate had been found by us to contain a relatively small amount of acetaldehyde, no substance was obtained in the course of the above-described experiments which could be considered to represent its condensation product with *m*-nitrobenzhydrazide. In order to ascertain whether such a compound could be formed and to determine its character the following experiment was made.

To 1.5 cc. of freshly prepared acetaldehyde (b. p., 21–22°), dissolved in 1 liter of water, was gradually added a solution of 3 g. of *m*-nitrobenzhydrazide in 50 cc. of hot alcohol, the whole being actively stirred by an electric motor. The liquid, which was at first only slightly cloudy, soon separated a quantity of fine, colorless, needle-shaped crystals. The stirring was continued for two hours, and the liquid then put aside for a day. As there was no further deposition of the crystalline substance, it was collected on a filter, well washed with water, and dried on a porous plate in a vacuous desiccator over sulfuric acid. The amount of substance obtained was 1.55 g., or somewhat less than one-half the yield of condensation product, as calculated from the amount of the reagent employed, the acetaldehyde having been considerably in excess. It was found, however, that the compound is soluble to an appreciable extent in water, and this property would also explain our inability to obtain it from the cotton distillate, which contained such a relatively small proportion of aldehyde. When dried over sulfuric acid, the substance melted quite sharply at 151–152° and was analyzed.[16]

Anal. Subs., 0.1551, 0.1581: CO_2, 0.2971, 0.3013; H_2O, 0.0612, 0.0633. Calcd. for $C_9H_9O_3N_3$: C, 52.17; H, 4.35. Found: C, 52.24, 51.97; H, 4.42, 4.48.

The substance is thus seen to agree in composition with acetaldehyde-*m*-nitrobenzhydrazide, and as no reference can be found to it in the literature it may be regarded as a new compound.

The substance is readily soluble in alcohol, especially on warming, but is very sparingly soluble in warm benzene from which, on cooling, it separates in minute, colorless needles.

In order to confirm further the composition of the compound, the acetaldehyde was regenerated from it. For this purpose a portion of the substance (0.7 g.) was brought

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[14] (a) Van Romburgh, *Verslag. Plantentuin te Buitenzorg*, **1895**, p. 119; **1896**, p. 166. Also (b) "The Volatile Oils," by Gildemeister and Hoffmann, Longmans, Green and Co., London, 1922, vol. 3, p. 162.

[15] Power and Kleber, *Pharm. Rundschau* (New York), **13**, 228 (1895). Ref. 14b, **1913**, vol. 1, p. 351; **1922**, vol. 3, p. 389.

[16] All the ultimate analyses recorded in this paper were made for us by Mr. R. M. Hann, of the Bureau of Chemistry, to whom our thanks may here be expressed.

into a small distilling flask with a little water, and to this liquid was added 50 cc. of dil. (1–5) sulfuric acid. The mixture was then distilled in a current of steam and the first 5 cc. of distillate separately collected, the receiver being cooled with ice. This liquid had a strong odor of acetaldehyde, gave a deep red color with Schiff's reagent, rapidly reduced an ammoniacal solution of silver oxide, and with dimethylamine and sodium nitroprusside it gave the deep blue color which is characteristic of acetaldehyde.

Constituents of the Concentrated Distillate from the Cotton Plant. Hydrolysis of the Esters

For the purpose of a preliminary examination of the constituents of the original concentrated distillate, a quantity (18.9 liters) of the liquid, representing 180.5 kg. of fresh cotton leaves and stems, was further concentrated by cohobation in a current of steam until the odorous and more volatile constituents were contained in a volume of 3 liters. In the course of these operations it was observed that the distillates possessed a basic odor, gave a distinctly blue color with bromothymol blue and also a pink color with phenolphthalein. These characters indicated the presence of a volatile alkali, which will subsequently be further considered. The practically odorless liquids remaining in the distillation flask after the above-described process of concentration were made alkaline with sodium hydroxide and, like the similar liquids obtained by the cohobation of the original distillate, reserved for the recovery of such volatile acids as they contained.

The above-mentioned concentrated distillate (3 liters), which contained some drops of essential oil, was brought into a flask provided with a reflux condenser, and a solution of 25 g. of sodium hydroxide added. In order to recover any volatile alkali that might otherwise escape during the process of heating, an apparatus consisting of a series of bulbs containing a 10% solution of hydrogen chloride was attached to the upper part of the condenser. On subsequently heating the alkaline liquid it soon acquired a bright yellow color and became slightly cloudy, owing to the separation of a little aldehyde resin. At the same time, the liberated volatile alkali was observed to possess a strong fishy odor, resembling that of trimethylamine. The alkaline liquid was kept in a state of active ebullition for two hours when, after cooling, the gas absorption apparatus was detached, and the acid liquid which it contained was reserved for subsequent examination.

After hydrolysis, the strongly alkaline liquid was distilled in a current of steam and about 2 liters of distillate was collected. This was a nearly clear liquid containing a thin layer of yellowish oil on the surface. The odor was fragrant, somewhat resembling that of cedar wood, and a slight odor of trimethylamine was likewise perceptible. With bromothymol blue it gave a deep blue color, thus confirming the presence of a volatile base in the original distillate. The alkaline liquid remaining in the distilling flask was reserved for obtaining the acid products of hydrolysis.

The entire distillate was first extracted five times successively with freshly prepared, aldehyde-free ether, the united ethereal liquids being subsequently washed with a little water. They were found to contain none of the volatile alkali, which had remained entirely in the aqueous portion of the distillate. The ethereal liquids were then dried with anhydrous sodium sulfate, and the greater part of the solvent was removed by distillation, the remaining bright-yellow liquid being transferred to a small tared flask in which it was allowed to evaporate spontaneously until the weight remained practically constant. The amount of oily product thus obtained was 4.6 g. or 0.0025% of the weight of cotton leaves and stems employed. It therefore represented 82.8% of the yield of essential oil, and was a clear, pale yellow, limpid liquid, having a fragrant odor.

The aqueous liquid from which the oily product of hydrolysis had been removed by extraction with ether, as above described, and which contained the volatile base, was acidified with hydrochloric acid and distilled, about 1 liter of distillate being collected. In order to test this distillate for methyl alcohol, it was first saturated with sodium chloride, then extracted with light petroleum ether and subsequently subjected to successive distillations until any alcohols present were contained in a volume of 50 cc. By the usual tests it was found to contain an appreciable amount of methyl alcohol, which, as will be shown later, was accompanied by a very small proportion of acetone.

The previously mentioned acid liquid which remained in the flask after distillation was evaporated at a gentle heat and the residue finally dried in a desiccator over solid potassium hydroxide. A somewhat impure crystalline product was thus obtained, which amounted to 0.4 g. When a little of the substance was brought into contact with sodium hydroxide it developed a strong odor of ammonia and also a very distinct odor of trimethylamine.

After the above-described preliminary examination of the products of hydrolysis, all of the remaining concentrated distillate from the plant was subjected in successive portions to a similar treatment in order to obtain sufficient material for the separation and identification of the individual constituents. The total amount of concentrated distillate thus employed represented 2669 kg. of cotton leaves and stems, and the amount of oily hydrolytic product obtained by extraction with ether was 57 g. This would correspond to a yield of 0.0021%, which is in very close agreement with the result of the preliminary experiment.

Separation and Identification of Methyl Alcohol

The accumulated distillates containing the alcoholic products of hydrolysis were first completely extracted with aldehyde-free ether, as previously described, the aqueous liquid was then acidified with hydrochloric acid to combine the volatile bases present, and subsequently distilled by direct heat until all the products of lower boiling point than water had passed over. The acid liquid remaining in the flask was reserved and will be further considered. The amount of neutral distillate obtained by the above operations was 4 liters. As it contained a layer of ether, this was separated, washed several times with water, and the washings were added to the aqueous liquid. The latter was distilled until about 1.5 liters had passed over. This concentrated liquid was saturated with sodium chloride and extracted with light petroleum ether (b. p., 35–55°). After separation of the latter solvent it was shaken many times successively with water to remove the acetone which was known to be present, and these washings were added to the aqueous liquid. The aqueous liquid was then distilled and, as the distillate was found to contain a little aldehyde, which had probably been formed from the ether, it was treated, together with the small amount of similar liquid from the preliminary experiment, with sodium hydroxide. The entire liquid, which had thus been made strongly alkaline, was heated for two hours in a flask provided with a reflux condenser, when it acquired a deep red color. It was then distilled and about 330 cc. of distillate collected, the receiver being cooled with ice. This liquid was again distilled with a 4-bulb column and the following fractions were collected: (1) a few drops below 60°, which gave a reaction for acetone;[17] (2) about 230 cc. between 60° and 71°, which had the odor of methyl alcohol; (3) about 85 cc. between 71° and 85° and a small residue above 85° which consisted of dil. ethyl alcohol.

Fractions 2 and 3 were allowed to stand over lime for several weeks, and then distilled thrice successively, when the following fractions were finally collected. They all possessed the characteristic odor of methyl alcohol.

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[17] Finnemore, "Year-Book of Pharmacy," J. and A. Churchill, London, **1914**, p. 383, Jones, *ibid.*, 1919, p. 409.

Fraction	B. p. °C. (Corr.)	Cc.
I	63.5–64.3	54
II	64.3–65	25
III	65–66	84
IV	66–68	13
	Total	176

Fraction I was found by the refractometer to contain 95.5% by weight of methyl alcohol, and it also gave a reaction for acetone by the method of Denigès.[18] The amount of acetone in this fraction was not more than about 1 part in 500, and in Fraction III the presence of acetone was also indicated, but in a proportion of not more than 1 part in 5000.

Fraction III, as was indicated by the boiling point and also by a refractometer reading, consisted of practically pure methyl alcohol. This was confirmed by a density determination, which gave $d_4^{25} = 0.78874$; $d_{25}^{25} = 0.79061$. Perkin[19] had found for pure methyl alcohol (b. p., 65.8–66°, corr.) $d_{25}^{25} = 0.78941$.

The alcohol when warmed with a little salicylic acid and a few drops of concd. sulfuric acid gave the characteristic odor of methyl salicylate.

The exceptionally large amount of methyl alcohol obtained from the cotton plant would appear to be particularly noteworthy. In order to confirm further its identity, a small portion was converted into the dimethyl oxalate, and for this purpose a part of Fraction I was employed. The respective ester was obtained in handsome, colorless plates melting at 51°. It may be noted that a property of this compound which does not seem to have been recorded is its volatility at ordinary temperatures when exposed to the air.

Identification of Ammonia and Trimethylamine

The liquid which had been acidified with hydrochloric acid, and from which the methyl alcohol had been distilled, contained the volatile bases that have previously been noted. To this liquid was added the contents of the small apparatus in which the vapors escaping from the condenser during the process of hydrolysis had been absorbed. The total acid liquid was then evaporated, when a quantity (4.5 g.) of a salt was obtained, which evidently consisted chiefly of ammonium chloride, but which also possessed the characteristic odor of an aliphatic amine. As the salt had a slightly brownish color, it was purified by dissolving it in water, liberating the bases with sodium hydroxide and distilling the liquid into a receiver containing a little dil. hydrochloric acid. During this operation a current of air was slowly aspirated through the entire apparatus. The acid liquid was then evaporated to a small volume when, on cooling, a quantity of a salt separated in handsome, colorless crystals. This salt was collected on a filter, thoroughly washed with alcohol, and the filtrate and washings were further evaporated, when an additional amount of a colorless salt was obtained. The total yield of this substance, which consisted of practically pure ammonium chloride, was 4.15 g. A small portion of it was converted into a platinum salt which, after drying at 110°, was analyzed.

Anal. Subs., 0.0393: Pt, 0.0173. Calcd. for $(NH_4)_2PtCl_6$: Pt, 43.96. Found: 44.02.

After the separation of the above-mentioned colorless salt the remaining clear liquid was evaporated and the residue treated repeatedly with absolute alcohol in order to

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[18] Denigès, *J. pharm. chim.*, [6] **9,** 7 (1899); *Analyst,* **24,** 92 (1899).

[19] Perkin, *J. prakt. Chem.*, [2] **31,** 505 (1885).

effect as completely as possible the removal of the ammonium chloride. The final alcoholic solution was allowed to evaporate over solid potassium hydroxide, when a small quantity (0.075 g.) of a liquid was obtained which possessed a strong, fishy odor. A little of this product, in aqueous solution, was tested with a specially prepared solution of potassium-mercuric iodide, when it gave a very distinct precipitate. The formation of this compound, which is stated to have the composition $(CH_3)_3N.HI.HgI_2$, may be regarded as evidence of the presence of a tertiary amine.[20]

The identification of the above-mentioned liquid product as a salt of trimethylamine was conclusively proved by the preparation from it of a gold salt, and for this purpose the remaining portion of the respective liquid was used. With a solution of auric chloride it yielded a precipitate which was redissolved by the aid of a gentle heat. On cooling, the gold double salt separated in distinct, golden-yellow crystals, which were collected, washed with a little water, and dried on a porous tile. The crystals were observed under the microscope to be doubly refractive and without any distinctive form. After drying at 110° they melted at 221°. The melting point of trimethylamine chloro-aurate has been recorded by Knorr[21] as 220°. The gold salt was analyzed with the following result.

Anal. Subs., 0.0273: Au, 0.0138. Calcd. for $N(CH_3)_3.HCl.AuCl_3$: Au, 49.4. Found: 50.5.

The slightly high percentage of gold found in this salt was probably due to the presence of a little ammonium chloro-aurate, which requires Au = 55.2%.

The occurrence of ammonia and trimethylamine as products from plants, and particularly as emanations from them, will be considered in a later part of this paper.

Constituents of the Oily Product of Hydrolysis

It has previously been noted that the distillates obtained after the operations of hydrolysis were first extracted with ether, and that an oily product was thus obtained which, after the removal of the solvent, amounted to 57 g.

The oily liquid was distilled twice under 10 mm. pressure and the following fractions were collected: (I) below 105°, about 5 cc.; (II) 105–150°, about 1 cc.; (III) 150–175°, about 2 cc.; (IV) 175–200°, about 26 cc.; (V) 200–220°, about 8 cc.

The last fraction was bright green, and only a small amount of a dark colored liquid was left in the flask.

Fraction I.—This was a colorless liquid of pleasant odor but suggesting the presence of amyl alcohol. It was distilled twice under ordinary pressure, and the following fractions were collected: (*a*) b. p. below 150°, about 0.7 cc.; and (*b*) b. p. 150–160°, about 3.5 cc.

The Fraction *a* was brought into a small pressure flask, 25 cc. of a chromic acid mixture[22] added and, after the flask had been closed, the whole was heated on a water-bath at about 90° for 15 minutes. After cooling, the liquid was diluted with water and extracted five times with aldehyde-free ether. The ethereal liquids were then washed with water, dried with anhydrous sodium sulfate, and the solvent was removed, when a few drops of an oily liquid were obtained. This product was mixed with a little water and distilled in steam. The first portion of the distillate was distinctly acid and contained some oily drops. It reduced an ammoniacal solution of silver oxide, but gave no coloration with Schiff's reagent, thus indicating the absence of aldehyde. The entire distillate was then made alkaline with a solution of barium hydroxide, evaporated,

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[20] Woodward and Alsberg, *J. Biol. Chem.*, **46**, 1 (1921).

[21] Knorr, *Ber.*, **22**, 184 (1889).

[22] *J. prakt. Chem.*, **45**, 599 (1892).

the excess of barium hydroxide removed by carbon dioxide, and the liquid filtered and concentrated. On the addition of silver nitrate some reduction of the silver ensued, and after the liquid had again been filtered and concentrated a very small amount of salt separated, which was collected and analyzed.

Anal. Subs., 0.0256: Ag, 0.0138. Calcd. for $AgC_5H_9O_2$: Ag, 51.7. Found: 53.9.

When a little of the salt was moistened with dil. sulfuric acid it developed a strong odor of valeric acid, and it evidently consisted chiefly of silver valerate which had become somewhat reduced. This indication of the occurrence of amyl alcohol in the oily product was subsequently confirmed by the examination of another fraction.

Fraction *b* was analyzed and its optical rotation determined.

Anal. Subs., 0.1072, 0.1508: CO_2, 0.2912, 0.4101; H_2O, 0.1144, 0.1581. Found: C, 74.08, 74.16; H, 11.94, 11.73. α_D in a 0.5dcm. tube at 20° = —0.149°.

The odor of this fraction indicated that it contained an appreciable amount of amyl alcohol, but it was evident that it also contained some substance richer in carbon. It will be further considered.

Fraction II (B. p., 105–150° (10 mm.)) **and Fraction** III (B. p. 150–175° (10 mm.)), which were very small in amount, were united and then fractionally distilled under ordinary pressure, when the larger portion was finally collected between 150° and 160° and another portion between 160° and 200°. These were further treated as noted below.

Fraction IV. (B. p., 175–200° (10 mm.)).—This fraction, which was the largest in amount, was analyzed.

Anal. Subs., 0.1111, 0.0694: CO_2, 0.3519, 0.2192; H_2O, 0.1123, 0.0711. Found: C, 86.38, 86.15; H, 11.31, 11.46.

The composition and boiling point of this fraction indicated that it consisted chiefly of a sesquiterpene, $C_{15}H_{24}$, which requires C = 88.2, H = 11.8%. It was distilled under ordinary pressure and the following fractions were collected: (*c*) b. p. 200–260° and (*d*) b. p. 260–265°. To the small residue in the flask Fraction V (b. p., 200–220° (10 mm.)) was added and the distillation continued, when the following fractions were collected: (*e*) b. p. 265–275° and (*f*) b. p. 275–290°. The last fraction had a bluish color.

A final distillation of all the fractions was then made under ordinary pressure.

To the Fraction I *b*, boiling at 150–160°, the liquids of the same boiling point from Fractions II and III were added and the whole was distilled, when a fraction was collected between 140° and 160°. To the residual liquid the small amount of liquid boiling at 160–200° from Fractions II and III was added and the distillation continued, when a further small amount of distillate was collected at 140–160°, which was added to the first portion. This product is designated in the following series as Fraction 1. A higher-boiling portion of the same liquids, collected at 160–180°, formed Fraction 2. To the residual liquid there was added the above-mentioned Fraction *c*, b. p. 200–260°, and the mixture distilled. Nothing then passed over below 220° and, on further heating, small amounts of liquid were collected between 220° and 240°, 240° and 255°, and 255° and 265°, which represent, respectively, Fractions 3, 4 and 5. To the residual liquid from the last fraction the previously mentioned Fraction *d* was added when, on further distillation, a little more was collected at 255–265°. On subsequently adding to the residual liquid Fraction *e*, b. p. 265–275°, and continuing the distillation, a relatively large portion of liquid was collected between 265° and 280°, which represents Fraction 6. To the residual liquid from this fraction the previously mentioned Fraction *f*, boiling at 275–290°, was added, and the distillation continued, when a small amount of liquid passed over at 280–290°, which is designated as Fraction 7. All of these fractions were subsequently examined with the results described below.

Fraction 1 (b. p., 140–160°).—This fraction amounted to 3.54 g. It was a pleasantly aromatic liquid, which also possessed the odor of amyl alcohol. It was oxidized with a chromic acid mixture in the manner previously described and the product extracted with ether. The ethereal extract, after the removal of the solvent, was then mixed with water and distilled with steam. The first portion of the distillate, which was separately collected, had an acid reaction and contained some drops of a colorless oil. It gave a deep red color with Schiff's reagent and reduced an ammoniacal solution of silver oxide, but as it did not give the specific reaction for acetaldehyde it probably contained one of the higher homologs. The entire distillate was made alkaline with sodium carbonate, and subsequently extracted five times with aldehyde-free ether in order to remove any non-acidic substances. The united ethereal liquids, after being washed and dried, yielded a small amount of a liquid which had a pleasant odor, and this was further treated as noted below.

The above-mentioned sodium carbonate solution, which had been extracted with ether, was acidified with sulfuric acid and distilled with steam. The distillate contained a small amount of an acid which was converted into a barium salt, and from this a silver salt was prepared and analyzed.

Anal. Subs., 0.0338: Ag, 0.0175. Calcd. for $AgC_5H_9O_2$: Ag, 51.7. Found: 51.8.

This salt thus appeared to consist of practically pure silver valerate, and when a trace of it was moistened with dil. sulfuric acid it developed a strong odor of valeric acid. The presence of amyl alcohol in the original liquid was thus established.

The above-mentioned ethereal extract of the sodium carbonate solution, after the removal of the solvent, was oxidized with a cold alkaline solution of potassium permanganate. After filtration and the removal of the slight excess of the reagent the acidified liquid was distilled with steam. The acid contained in the distillate was first converted into a barium salt, and from this a series of silver salts was prepared and analyzed.

Anal. I. Subs., 0.0884: Ag, 0.0438. Calcd. for $AgC_6H_{11}O_2$: Ag, 48.4. Calcd. for $AgC_5H_9O_2$: Ag, 51.7. Found: 49.5.

The behavior of this salt on ignition, together with its analysis, indicated that it was a mixture of silver caproate and valerate.

Anal. II. Subs., 0.1032: Ag, 48.4. Calcd. for $AgC_5H_9O_2$: Ag, 51.7. Found: 51.9.

This salt evidently consisted of nearly pure silver valerate, and afforded further confirmation of the presence of amyl alcohol in the original liquid.

The mother-liquor from the last-mentioned salt yielded on evaporation further small amounts of silver salt, which were successively collected and analyzed.

Anal. III. Subs., 0.0412: Ag, 0.0239. Found: 58.0.
IV. Subs., 0.0825: Ag, 0.0492. Found: 59.6.
V. Subs., 0.0610: Ag, 0.0370. Found: 60.6.

When small amounts of these salts were moistened with dilute sulfuric acid they developed a strong odor of valeric acid. They apparently consisted of mixtures of silver valerate and acetate.

Fraction 2 (b. p., 160–180°).—This fraction, which amounted to only 0.34 g., had a pleasant odor. When oxidized with a cold alkaline solution of potassium permanganate it yielded a small amount of an acid which was converted through the barium salt into a silver salt.

Anal. Subs., 0.0350: Ag, 0.0161. Calcd. for $AgC_7H_{13}O_2$: Ag, 45.6. Found: 46.0.

This result would indicate the presence of an heptylic alcohol in the respective fraction of oil.

Fraction 3 (b. p., 220–240°).—This fraction, which possessed a fragrant odor, amounted to 0.72 g. It was oxidized with a cold alkaline solution of potassium permanganate, and after the previously described treatment the acidified liquid was distilled with steam. The distillate was acid and contained a small amount of a colorless oil. The entire amount of acid in the distillate was converted into a barium salt, and the solution of the latter gave on the addition of silver nitrate a precipitate which was collected and analyzed.

Anal. Subs., 0.0285: Ag, 0.0137. Calcd. for $AgC_6H_{11}O_2$: Ag, 48.4. Found: 48.1.

A little of this salt, when moistened with dil. sulfuric acid, developed the characteristic odor of caproic acid.

The filtrate from the above-mentioned silver salt was concentrated when it deposited a further amount of a nearly colorless salt.

Anal. Subs., 0.0729: Ag, 0.0438. Calcd. for $AgC_2H_3O_2$: Ag, 64.6. Found: 60.1.

This portion of salt appeared to consist chiefly of silver acetate with a little caproate since it developed the odor of caproic acid when moistened with dil. sulfuric acid. As several compounds would yield caproic and acetic acids on oxidation the identity of the substance in the respective fraction of oil could not be determined.

Fraction 4 (b. p., 240–255°) **and Fraction 5** (b. p., 255–265°) were united and then distilled over metallic sodium at 60 mm. pressure. The distillate was collected between 155° and 170°, but mostly at about 165° and 60 mm. It was a pale yellow liquid that had a pleasant odor and amounted to 9 cc. An appreciable amount of a dark colored substance remained in the distilling flask.

Fraction 6 (b. p., 265–280°).—This fraction was likewise distilled over metallic sodium at 60 mm. pressure, when it passed over almost completely between 160° and 175°. The distillate was pale yellow, had pleasant odor and amounted to about 14 cc.

Inasmuch as the distillate from Fraction 6 appeared by special tests to be practically identical with the liquid obtained from the Fractions 4 and 5, it was united with the latter liquid and the whole again distilled over sodium at 60 mm. pressure. The distillate was then collected between 157° and 175°, but the greater portion passed over below 170° at 60 mm. When distilled a third time over sodium the entire liquid passed over between 155° and 170° at 60 mm. It was finally distilled under atmospheric pressure, when it was collected between 250° and 270°, but for the most part between 250° and 260°, and amounted to 14.2 g.

Isolation of an Optically Inactive, Dicyclic Sesquiterpene, $C_{15}H_{24}$

The above-mentioned liquid, which distilled chiefly between 250° and 260° under ordinary pressure, had a pale yellow color and a fragrant odor.

Anal. Subs., 0.2129: CO_2, 0.6884; H_2O, 0.2246. Calcd. for $C_{15}H_{24}$: C, 88.15; H, 11.85. Found: C, 88.18; H, 11.80.

Determinations of the density and refractive index gave the following values: $d_{15}^{15} = 0.9109$; $n_D^{20°} = 1.4987$. The liquid was optically inactive.

From the above factors the molecular refraction was calculated according to the formula, $[(n^2 - 1)/(n^2 + 2)] \times [(1/d)] \times 204$, which gives the value 65.78.

The boiling point, analysis and other characters of the above-described liquid have definitely shown that it consists of a sesquiterpene. The molecular refraction has furthermore indicated that it belongs to the group of dicyclic sesquiterpenes with two ethylenic linkings, the calculated value of which is 66.15.

A drop of the substance, when dissolved in about 5 cc. of glacial acetic acid, gives on the addition of a drop of concd. sulfuric acid a handsome pink color, which soon changes to a deep purple and eventually becomes brown.

When the sesquiterpene was saturated with dry hydrogen chloride it acquired a deep purple color, but no crystalline compound could be obtained. An attempt was made to prepare a nitrosochloride by the method of Schreiner and Kremers.[23] A deep green color was produced, but no crystalline substance separated, even on keeping and exposure to cold.

The sesquiterpene which is here described resembles very closely one which had been obtained for the first time by Power and Tutin[24] from an essential oil distilled from the fruits of *Pittosporum undulatum*, and would appear to be identical with it. The sesquiterpene from the latter source, which was obtained in very much larger quantity, and could therefore be more completely fractionated, had the following characters: b. p., 263–264°; $d_{15}^{15} = 0.9100$; $n_D^{20°} = 1.5030$; molecular refraction, 66.22. Furthermore, it was optically inactive, yielded only a liquid hydrochloride, and no nitrosochloride could be obtained from it. The color reactions of the sesquiterpene from the two sources are also very similar.

Fraction 7 (b. p., 280–290°).—This fraction represented the final liquid obtained by the fractionation of the oily product of hydrolysis and amounted to only 3 cc. It was a deep blue, and a small portion of it was found to reduce an alkaline solution of potassium permanganate rapidly. As in the case of similar blue oils, it probably contained the highly unsaturated hydrocarbon, azulene, $C_{15}H_{18}$, which has been described by A. E. Sherndal,[25] but the amount of liquid now available was too small to permit its further investigation.

Examination of an Oily Product Obtained by Rinsing the Receptacles of the Original Distillate with Ether

During the prolonged operations of distilling the cotton plant with steam an appreciable amount of oily material became attached to the large glass receptacles of the distillate. When these operations were finished all of the receptacles that had contained the distillate were rinsed with ether, the ethereal liquids dried with anhydrous sodium sulfate, and the greater part of the solvent was removed by distillation. On allowing the remaining ether to evaporate spontaneously an oily product was obtained which amounted to about 80 g. It had a yellowish color, a mild, pleasant odor and contained a small amount of a crystalline substance that was sparingly soluble in ether. The entire amount of oily material was mixed with water, 25 g. of sodium hydroxide was added, and the mixture heated for two hours in a flask provided with a reflux condenser. On subsequent distillation of the alkaline product with steam, it yielded a distillate which contained a quantity of nearly colorless oil floating on the surface of the aqueous liquid. The entire distillate was extracted five times successively with aldehyde-free ether, the ethereal liquids were dried with anhydrous sodium sulfate, and the solvent was removed, when about 15 g. of a pale yellow liquid was obtained. This liquid had a pleasant odor and will subsequently be more fully described.

The aqueous liquid from which the oily product of hydrolysis had been removed by extraction with ether amounted to about 2 liters. It was examined for the presence of methyl alcohol by first subjecting it to several successive distillations, whereby any substance of lower boiling point than water would be contained in a comparatively small volume of liquid. This liquid was then further treated in the manner previously described when reactions were obtained which definitely indicated the presence of a small amount of methyl alcohol. It was evident from the source and character of the original material that this alcohol could only have been present in the form of an ester.

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[23] Schreiner and Kremers, *Pharm. Arch.*, **2,** 293 (1899).

[24] Power and Tutin, *J. Chem. Soc.*, **89,** 1090 (1906).

[25] Sherndal, THIS JOURNAL, **37,** 167, 1537 (1915).

The strongly alkaline liquid which remained in the distilling flask after the operation of hydrolysis and subsequent distillation contained a considerable quantity of soft, resinous material. The liquid was filtered, and the filtrate added to the other portions of liquid obtained by the previous operations of hydrolysis, in order subsequently to recover the volatile acids. The resinous material, after being thoroughly washed with water, was extracted with hot alcohol. On cooling, a small amount of a crystalline substance separated, which was purified by recrystallization from hot alcohol. When collected and dried on a porous tile, it formed thin leaflets having a satiny luster, and was found to consist of a paraffin hydrocarbon. It melted quite sharply at 62°, and apparently was nearly pure triacontane, $C_{30}H_{62}$.

Isolation of a New, Optically Active, Tricyclic Sesquiterpene, $C_{15}H_{24}$

The previously mentioned oily liquid, which had been obtained by extracting the product of alkaline hydrolysis with ether, was first distilled twice under 10 mm. pressure. As an analysis of the distilled liquid indicated it to consist chiefly of a hydrocarbon, it was subsequently distilled twice over metallic sodium at 60 mm. pressure when it passed over entirely between 160° and 180°. It was finally distilled under ordinary pressure, when it passed over between 260° and 280° as a practically colorless, somewhat viscid oil, which amounted to 6.2 g. The liquid has a mild, pleasant odor somewhat resembling that of cedar wood.

Anal. Subs., 0.1835: CO_2, 0.5929; H_2O, 0.1926. Calcd. for $C_{15}H_{24}$: C, 88.15; H, 11.85. Found: C, 88.12; H, 11.75.

Determinations of the density, optical rotation and refractive index gave the following values: $d_{15}^{15} = 0.9276$; α_D in a 1dcm. tube —11.6°, whence $[\alpha]_D = -12.5°$; $n_D^{20} = 1.4981$; molecular refraction, 64.48.

The above results indicate that the substance is a tricyclic sesquiterpene with one ethylenic linking, the calculated molecular refraction of which is 64.45.

When a drop of the substance is dissolved in 5 cc. of glacial acetic acid, and a drop of concd. sulfuric acid added, a handsome purple color is produced. On saturating the sesquiterpene with dry hydrogen chloride it acquired a deep purple color, but no crystalline compound could be obtained.

As the above-described substance does not agree in its characters with any of the previously recorded tricyclic sesquiterpenes, of which but few are known, it may be regarded as a new compound.

Volatile Acidic Constituents of the Cotton Plant

It was noted in an early part of this paper that all of the practically odorless liquids that remained from the cohobation of both the original and the more concentrated distillates were made alkaline with sodium hydroxide and evaporated to a small volume. This product represented the liquids obtained in the manner described above from the distillation of approximately 3290 kg. of cotton leaves and stems.

The alkaline liquid, divided into several portions, was acidified with sulfuric acid and distilled in a current of steam until the distillate no longer had a decidedly acid reaction. The first portions of the distillate were strongly acid, possessed a somewhat phenolic odor, and contained some yellowish, oily drops floating on the surface. The total amount of acid distillate was about 14 liters.

The distillate was first made alkaline with sodium carbonate, which dissolved the oily drops, and then extracted thrice with ether, the ethereal liquids being subsequently washed with water, dried with anhydrous sodium sulfate, and the solvent removed. A quantity (2.54 g.) of a yellowish, sirupy liquid was thus obtained which had a pleasant, sweetish odor. This liquid gave no coloration with ferric chloride, and when treated with a 10% solution of sodium hydroxide the greater part remained undissolved, even when warmed. After this treatment the entire alkaline mixture was extracted with ether in order to remove the non-acidic substance. The ethereal liquid was washed, dried, and the solvent removed, when it yielded a sirupy product that had a pleasant, honey-like odor and amounted to 1.8 g. When it was dissolved in alcohol, the solution treated with a little animal charcoal, and the solvent evaporated, the substance was obtained in its original form. It was then mixed with a little water and distilled in a current of steam, when the greater portion passed over as a pale yellow, fragrant oil that was lighter than water, and only a small amount of resinous material remained in the flask. The distillate was extracted with ether, and about 1 g. of a fragrant, oily liquid was thus obtained. When a drop of this oil was dissolved in 5 cc. of glacial acetic acid, and a drop of concd. sulfuric acid added, a pink or purplish color was produced. The liquid was analyzed.

Anal. Subs., 0.1732: CO_2, 0.5577; H_2O, 0.1737. Calcd. for $C_{15}H_{24}$: C, 88.15; H, 11.85. Found: C, 87.82; H, 11.22.

The substance thus appeared to consist essentially of a sesquiterpene, which had remained dissolved in the original alkaline solution of the volatile acids. It was no doubt identical with one of the substances of this class which have previously been described or a mixture of them.

Isolation of a Phenol

After the alkaline mixture had been extracted with ether to remove the non-acidic substance, as described above, the clear liquid was acidified with dil. sulfuric acid and again extracted with ether. The etheral liquid was washed with water, dried with anhydrous sodium sulfate and the solvent removed. A very small amount (0.21 g.) of a yellowish-brown liquid was thus obtained which possessed a phenolic odor, somewhat resembling that of cresol, but it was evidently not a pure substance. In order to obtain some information respecting the character of the phenol it was examined for us spectrophotometrically by Dr. H. Wales[26] of the Bureau of Chemistry, to whom our thanks may here be expressed.

When the above-mentioned phenolic substance was coupled in a dilute alkaline solution with diazo-*p*-nitrobenzene, dyes were obtained which dissolved with development of a reddish-brown color in water, a deep red in alcohol, and a purple in acetone. These solutions were examined and gave the following absorption spectrum maxima: in water, 4925 Å.; in alcohol, 5200 Å.

The above values agree very closely with those observed for *m*-cresol under the same conditions, but in acetone readings of 5550 and 5650 Å. were obtained, depending on the amount of alkali used. A little of the dye was subsequently dissolved in an alcoholic solution of potassium hydroxide and the liquid evaporated to dryness. This product was then treated with acetone, when the small portion that dissolved gave an absorption maximum at 5900 Å., which is in very close agreement with that of the dye from *m*-cresol.

It may be concluded from these observations that the phenolic product described above contained either a derivative of *m*-cresol or a phenol that possesses similar characters.

Examination of the Volatile Acids

The original acid distillate which had been made alkaline with sodium carbonate and extracted with ether, as previously described, was first evaporated to a smaller

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[26] Compare "The Identification of Phenols by Means of the Spectroscope," by S. Palkin and H. Wales, THIS JOURNAL, **46,** 1488 (1924).

volume, whereby all of the dissolved ether was expelled. It was then acidified with sulfuric acid and distilled in a current of steam. The first portion of the distillate was very strongly acid, had a rather unpleasant odor reminding of the higher fatty acids, and contained some oily drops floating on the surface. This portion of the distillate was therefore set aside and the distillation continued until the liquid which passed over was only slightly acid. By means of a small separatory funnel the oily drops were collected and amounted to about 0.5 cc. This sparingly soluble acid was converted into a barium salt, and as a little formic acid was found to be present, this was removed by treatment with a dilute solution of potassium permanganate. On the subsequent addition of silver nitrate a sparingly soluble silver salt was precipitated, which was collected.

Anal. Subs., 0.0783, 0.0567: Ag, 0.0381, 0.0275. Calcd. for $AgC_6H_{11}O_2$: Ag, 48.4. Found: 48.6, 48.5.

It may thus be concluded that the oily drops consisted of nearly pure caproic acid.

The entire distillate from which the small amount of sparingly soluble acid had been mechanically separated, and which amounted to about 6 liters, was made alkaline with barium hydroxide, concentrated, and the excess of hydroxide removed by carbon dioxide. On evaporating the filtered liquid a quantity of a barium salt was obtained which was fractionally crystallized several times. Four crops of crystals were thus finally obtained, which are designated below as I, II, III and IV, and which amounted to 4.2, 10.5, 21.8 and 15.5 g., respectively. The total amount of purified barium salt was thus 52 g.

For the determination of the barium the salts were dried at 110°.

Crop I.

Anal. Subs., 0.2634: $BaSO_4$, 0.2405 = Ba, 0.1415. Calcd. for $Ba(C_2H_3O_2)_2$: Ba, 53.78. Found: 53.72.

From the barium salt a silver salt was prepared which was collected in successive fractions.

Anal. Subs., 0.0673, 0.0213: Ag, 0.0431, 0.0136. Calcd. for $AgC_2H_3O_2$: Ag, 64.6. Found: 64.0, 64.3.

These results show that the above-mentioned salts were those of nearly pure acetic acid.

Crop II.

Anal. Subs., 0.4042: $BaSO_4$, 0.3682 = Ba, 0.2166. Calcd. for $Ba(C_2H_3O_2)_2$: Ba, 53.78. Found: 53.60.

From this salt a silver salt was prepared and two fractions of it were analyzed.

Anal. Subs., 0.0900, 0.0697: Ag, 0.0581, 0.0449. Calcd. for $AgC_2H_3O_2$: Ag, 64.6. Found: 64.5, 64.4.

The second crop of crystals of barium salt was thus practically identical in composition with the preceding one.

Crop III.

This salt was found to contain formic acid, which was therefore first removed by treatment with a 4% solution of potassium permanganate. After this treatment some silver salts were prepared and analyzed.

Anal. Subs., 0.0576, 0.0761: Ag, 0.0372, 0.0491. Calcd. for $AgC_2H_3O_2$: Ag, 64.6. Found: 64.6, 64.5.

The third crop of crystals of barium salt was thus found to contain only formic and acetic acids.

Crop IV.

As this salt was found to contain an appreciable amount of formic acid, a portion of it was first treated with a solution of potassium permanganate. Some silver salts were subsequently prepared and analyzed.

Anal. Subs., 0.0897, 0.0796: Ag, 0.0576, 0.0513. Calcd. for $AgC_2H_3O_2$: Ag, 64.6. Found: 64.2, 64.4.

The mother liquor from this salt, when concentrated, yielded a further quantity of a crystalline silver salt, which was found to be nearly pure silver acetate.

The volatile acids contained in the aqueous liquids remaining after the concentration of the original distillate by cohobation are thus seen to have consisted chiefly of formic and acetic acids, with a very small proportion of caproic acid.

Examination of the Liquid Remaining in the Distillation Flask After the First Distillation of the Volatile Acids From the Original Solution of Their Sodium Salts

It has previously been noted that all of the nearly odorless liquids remaining from the cohobation of the original distillate from the cotton plant were made alkaline with sodium hydroxide and concentrated, and that this liquid was subsequently acidified and distilled with steam for the recovery of the volatile acids. The strongly acid liquid which then remained in the distillation flask had a dark color and contained some resinous material which was removed by filtration.

Isolation of Vanillin, $C_8H_8O_3$

The above-mentioned strongly acid liquid had a pleasant, aromatic odor that suggested the presence of vanillin. In order to isolate this substance, essentially the method of Tiemann and Haarmann[27] for the quantitative determination of vanillin was employed. The aqueous acid liquid was accordingly extracted several times with ether, the ethereal liquid washed with a little water and dried with anhydrous sodium sulfate. After the removal of a part of the solvent, the ethereal extract was bright yellow and amounted to 100 cc. It was shaken continuously in a glass-stoppered bottle for 20 minutes with 50 cc. of a solution of sodium hydrogen sulfite prepared by diluting 25 cc. of a saturated solution of the salt with an equal volume of water. After standing overnight, the aqueous solution was separated and the ethereal liquid shaken as before with 50 cc. of the diluted sodium hydrogen sulfite solution, the mixture being thereupon allowed to stand with occasional agitation for several days. The united salt solutions were first shaken twice with a little ether, which removed some indefinite material that was obtained after the evaporation of the solvent in the form of a dark colored, viscid sirup. After this treatment there was gradually added to the aqueous bisulfite solution 80 cc. of dil. sulfuric acid prepared by diluting 30 cc. of concd. sulfuric acid with 50 cc. of water. In order to remove the liberated sulfur dioxide, a current of carbon dioxide was passed through the liquid for some time. The liquid was then extracted five times successively with ether, the ethereal liquids were washed with a little water, dried with anhydrous sodium sulfate, and the solvent was removed, when a dark colored sirupy product was obtained which possessed a distinct odor of vanillin. This product was extracted several times with warm, light petroleum ether (b. p., 30–70°) and the liquids were filtered. On spontaneous evaporation these liquids yielded a small quantity (0.084 g.) of a colorless, crystalline substance in the form of star-shaped clusters of needles; which was collected and dried on a porous tile. It possessed the characteristic and persistent odor of vanillin, but as it fused a little below the proper melting point of 80–81°

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[27] Tiemann and Haarmann, *Ber.*, **8,** 1118 (1875).

it probably still contained a trace of impurity. Its aqueous solution gave a blue color with ferric chloride.

As the amount of substance obtained was not sufficient for analysis, its identity was further confirmed by the preparation of the very characteristic, sparingly soluble dehydrodivanillin $[C_6H_2(OH)\ (O.CH_3)CHO]_2$.[28] For this purpose the above-mentioned sirupy product, which had been extracted with light petroleum ether, was employed, as it evidently still contained a little vanillin that could not easily be obtained in a pure state. The sirupy material was accordingly extracted several times with hot water, when some resinous matter remained undissolved. The filtered aqueous liquid, after being deprived of color with a little animal charcoal, was treated according to the method of Herissey and Delauney[29] for the detection of small quantities of vanillin. A very small amount of dehydrodivanillin was thus obtained in the form of nearly colorless, crystalline needles.

The optical characters of the above-mentioned derivative of vanillin were determined for us by Mr. G. L. Keenan[30] of the Microchemical Laboratory, Bureau of of Chemistry, with the following results.

In ordinary light it appeared under the microscope as colorless rods and needles. The refractive indices $\left(\frac{20^\circ}{\mathrm{D}}\right)$ were $\alpha = 1.569, \pm 0.001$ (lengthwise on rods); β indeterminable; $\gamma = >1.733$ (crosswise on rods). In parallel polarized light the extinction was parallel and sign of elongation was $-$. In convergent polarized light no interference figures were obtainable.

All of the above-described optical characters were found to be in complete agreement with those of dehydrodivanillin that had been prepared from a specimen of pure vanillin. With the exception of the crystalline form these characters had not previously been recorded.

Acids Obtained by the Hydrolysis of the Esters

The strongly alkaline liquid remaining in the flask after hydrolysis of the esters contained in the concentrated distillate and subsequent distillation with steam was acidified with sulfuric acid and subjected to steam distillation. The first portion of the distillate was strongly acid, had an odor resembling that of the higher fatty acids, and separated some oily drops. The entire distillate, which amounted to about 4 liters, was made strongly alkaline with sodium carbonate and extracted thrice successively with ether. The united ethereal liquids were washed with water, dried with anhydrous sodium sulfate, and the solvent was removed. There was thus obtained 0.76 g. of a yellowish, sirupy liquid which had a pleasant and slightly phenolic odor. This sirupy liquid was examined in the same manner as a similar product obtained from the sodium carbonate solution of the acids remaining in the original aqueous liquids after cohobation. It was found to consist chiefly of a neutral substance, which evidently was a sesquiterpene, together with a small amount of a phenolic compound. The latter, when examined spectrophotometrically, was found to be identical in character with the phenol previously described.

The above-mentioned sodium carbonate solution of the acids, which had been extracted with ether, was concentrated, acidified with sulfuric acid and distilled in a current of steam. The distillate contained an appreciable amount of an acid which was converted into a barium salt. As the salt was found to contain some formic acid, this was removed by means of a dilute solution of potassium permanganate and the clear,

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[28] Tiemann, *Ber.*, **18,** 3493 (1885).

[29] Herissey and Delauney, *J. pharm. chim.*, [7] **28,** 257 (1923).

[30] The authors desire to express their thanks to Mr. Keenan for assistance during this work in all observations which required the use of a microscope.

filtered liquid allowed to evaporate in a vacuous desiccator over sulfuric acid. The barium salt was thus obtained in colorless crystals and amounted to 3.5 g. A portion of the salt was converted into the silver salt, which was obtained in several successive fractions, and these were analyzed.

Anal. Subs., 0.0457, 0.0910, 0.0454, 0.0858: Ag, 0.0287, 0.0582, 0.0391, 0.0555. Calcd. for $AgC_2H_3O_2$: Ag, 64.6. Found: 62.8, 63.9, 64.1, 64.6.

The acids obtained by the hydrolysis of the esters were thus found to consist chiefly of formic and acetic acids, together with a small amount of an acid of higher carbon content.

Emanation of Ammonia and Trimethylamine from the Cotton Plant

It has been observed by C. M. Smith[31] that the dew on the leaves of the cotton plant has an alkaline reaction to litmus, and that the alkalinity is also shown with phenolphthalein. This fact was noted by Smith[31] as "indicating the presence of soluble hydroxide or salts of very weak acids." The results of an analysis of the dew led him, however, to conclude that "the principal constituents are bicarbonates of calcium and magnesium." No attempt was made to determine the alkali metals, as the presence of but little of such material was indicated.

In connection with this investigation by the present authors of the odorous constituents of the cotton plant it was deemed desirable to ascertain whether the dew collected from the leaves might not contain some volatile organic compounds, as the occurrence of such substances in it had not previously been considered. Through the interest and assistance of Mr. Smith, we were able to obtain a quantity of dew, which was collected near Tallulah, in the summer of 1923.

The amount of dew available for our purpose was 2300 cc. The colorless, filtered liquid had a density of 1.0005 at 25°/25°, indicating the presence of a comparatively small amount of dissolved salt. With bromothymol blue it showed a decidedly alkaline reaction, but it gave no immediate reaction with litmus or phenolphthalein. The liquid did not respond to the biuret test for protein and it also gave no reaction with potassium-mercuric iodide. When a little of the liquid was heated in a test-tube, a distinctly ammoniacal odor was developed.

The entire amount of liquid was subsequently distilled in a current of steam and about 1 liter of distillate collected. This distillate, when tested with bromothymol blue, showed a distinct alkalinity. The liquid remaining in the distillation flask was then made strongly alkaline with sodium hydroxide and again distilled, but no further amount of volatile alkali was thus obtained. On acidifying the original distillate with hydrochloric acid, and evaporating the liquid, a small amount of a crystalline salt was obtained which had the appearance of ammonium chloride. The index of refraction was found to agree with that of the latter salt, and with platinic chloride the characteristic yellow, octahedral crystals of the double salt were obtained. With lime water it developed the odor of ammonia.

The crystalline substance was treated with absolute alcohol when the greater portion remained undissolved, but on evaporating the alcoholic liquid an appreciable residue was obtained. This residue still contained some ammonium chloride, but when a small portion of it was brought into contact with a caustic alkali it also developed the odor of trimethylamine. As the amount of the last-mentioned substance was too small to permit its separation, the entire amount of material was converted into a platinum salt. This was obtained in handsome yellow, octahedral crystals, and amounted to 0.3 g. After drying at 110°, it was analyzed.

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[31] Smith, *J. Agr. Research*, **26**, 192 (1923).

Anal. Subs., 0.1348: Pt, 0.0587. Calcd. for $(NH_4)_2PtCl_6$: Pt, 43.96. Found: 43.55.

It has thus been shown that the volatile alkali contained in the dew consisted chiefly of ammonia, together with a very small proportion of another base which was evidently trimethylamine. The presence of the latter would account for the somewhat low percentage of platinum found by analysis, since trimethylamine chloroplatinate requires Pt = 36.96%.

Another portion of the dew from the cotton plant was kindly obtained for us during the summer of 1924 by Mr. B. R. Coad of the Delta Laboratory at Tallulah. On account of the exceptional dryness of the season the quantity of dew that could be collected was only 435 cc. This was distilled without the use of steam and the distillate collected in dil. hydrochloric acid. On evaporating the liquid it yielded a very small amount (0.047 g.) of a crystalline salt, which showed under the microscope the characteristic forms of ammonium chloride together with some rod-shaped crystals that were doubly refractive. This optical property was found to be due to the presence of trimethylamine hydrochloride, since the latter salt in a pure state showed identical characters. A solution of the salt obtained from the distillate gave with platinic chloride the characteristic crystals of amomnium chloroplatinate, and with a caustic alkali it developed the odors of both ammonia and trimethylamine.

After the complete removal of the volatile alkali by distillation the liquid remaining in the distillation flask was examined. It showed an alkaline reaction with both litmus and phenolphthalein, and contained a small amount of sparingly soluble, brownish material which, when collected, thoroughly washed and dried, amounted to 0.134 g. This was found to consist chiefly of calcium and magnesium carbonates with a little iron and alumina. The filtered liquid (about 200 cc.) was evaporated to dryness in a platinum vessel when a brownish salt was obtained which amounted to 0.289 g. This was ignited at a gentle heat to destroy any organic matter, the residual salt treated with hot water, and the mixture filtered. The small amount of carbonaceous matter which remained on the filter was found to contain calcium carbonate. On evaporating the filtrate a perfectly white salt (0.213 g.) was obtained, which was not hygroscopic, and flame tests showed the presence of both sodium and potassium. When moistened with a little water it was found to be distinctly alkaline to litmus, but with phenolphthalein it gave only a slight and evanescent pink coloration. The entire amount of salt was then dissolved in water, when the solution was found to contain chloride and sulfate with a little calcium, but no magnesium. The presence of potassium was confirmed by the formation of the platinum double salt, and although not contained in the above-mentioned solution as a carbonate it may have been present as such in the dew.

Some experiments were subsequently made in the Laboratory with small cotton plants which had been grown in the greenhouse of the Department of Agriculture. Two of these plants, which were somewhat less than 30 cm. in height, and contained in pots, were covered by large bell jars resting on glass plates. The drops of liquid which collected on the leaves were strongly alkaline and imparted a deep and permanent coloration to both litmus and phenolphthalein test-papers. This indicated the presence of a fixed alkali carbonate in addition to the volatile alkali which will subsequently be mentioned. After some time a very small amount of a white powdery substance was observed on the surface of some of the leaves, and by microchemical tests this was found to consist of calcium carbonate.

The moisture that condensed on the inner surface of the bell jars was removed by rinsing with distilled water, and this operation was repeated at intervals of one or two days for a period of eight weeks, the soil in the pots being occasionally supplied with a little water. These rinsings from the bell jars, which were distinctly alkaline to bromothymol blue, were immediately acidified with hydrochloric acid and at the end of the various operations amounted to 4 liters. The entire acid liquid was evaporated to a small volume, filtered, and the concentrated filtrate allowed to evaporate in a vacuous desiccator over sulfuric acid to dryness. A very small amount (0.1 g.) of a nearly colorless salt was thus obtained. When examined under the microscope it was found to consist of a mixture of cubical crystals and some rod-shaped forms, the latter being doubly refractive. A little of the salt, when dissolved in water, yielded with platinic chloride the characteristic yellow, octahedral crystals of ammonium chloroplatinate. Another small portion of the salt, when treated with lime water and gently heated, developed a distinct odor of ammonia and trimethylamine.

Another test for the alkalinity of the emanation from the cotton plant was conducted with a few of the detached green leaves. These were placed on a glass tripod and covered with a large beaker, which rested in a shallow porcelain dish containing a little water. The leaves retained their freshness, without withering, for several days. On testing the water contained in the porcelain dish it was found to give a distinctly alkaline reaction with bromothymol blue and also a yellowish-brown precipitate with Nessler's reagent.

The results of the above-described experiments appear to have completely established the fact that both ammonia and trimethylamine are emanations from the cotton plant.

It is deemed of interest to note in this connection that the fresh leaves of the cotton plant, when triturated with water and the mixture filtered, yield a liquid which is distinctly acid to litmus and to bromothymol blue. It has furthermore been observed by us that an alcoholic extract of the plant has an acid reaction, but on removing the alcohol by distillation the presence of both ammonia and trimethylamine in the distillate was definitely established. In the last-mentioned experiment it was evident that the ammonia could only have been formed by the dissociation of an ammonium salt, while the trimethylamine was probably produced from a simple organic base such as choline, or a complex containing it, since it is well known that choline yields the respective amine when its aqueous solution is heated.

A consideration of all the preceding observations would appear to lead to the conclusion that the emanation of ammonia and trimethylamine from the cotton plant is due to their liberation on the surface of the leaves through the influence of a fixed alkali carbonate contained in the secretions. In this connection the interesting observations of A. Nestler[32] should be noted. It was found by this investigator that the drops of liquid secreted on the foliage leaves of the scarlet runner bean (*Phaseolus multiflorus*) and on the leaves of a number of plants belonging to the mallow family have a strongly alkaline reaction. It was furthermore definitely ascertained that this liquid contained potassium carbonate, with a relatively small proportion of calcium carbonate. The source of these secretions was believed to be the small glandular hairs contained on the epidermis of the leaf. It follows that if, under similar conditions, an ammonium salt and choline were secreted by the tissue fluids of the cotton-plant, the emanation of ammonia and trimethylamine would inevitably result.

The emanation of ammonia and trimethylamine is not restricted to the cotton plant. More than a century ago it was observed by Chevallier and Lassaigne,[33] and later by Chevallier,[34] that *Chenopodium vulvaria* spontaneously evolves a volatile alkali, which was recognized as ammonia, and that the plant has a fetid odor, resembling that of putrid fish. It was also noted that ammonia is evolved by a number of flowers, even by those which possess a pleasant odor. More recently it has been found by Wicke[35]

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[32] Nestler, *Ber. botan. Ges.*, **17**, 332 (1899).

[33] Chevallier and Lassaigne, *J. Pharm.*, **3**, 412 (1817).

[34] Chevallier, *ibid.*, **10**, 100 (1824).

[35] Wicke, *Bot. Z.*, **20**, 393 (1862).

that trimethylamine is constantly exhaled from the leaves of the above-mentioned species of *Chenopodium*, and he has regarded it as a secretion from the glands which cover the entire plant. Other references to the subject will be found in the literature of which citations are given below.[36] It may finally be noted that Kauffmann and Vorländer[37] have shown that so small an amount of trimethylamine as 0.0005 mg. can be distinctly detected by the odor.

The authors desire to express their thanks to Dr. L. O. Howard, Chief of the Bureau of Entomology, for promoting this investigation, and also their appreciation of the constant interest taken in its development by Dr. W. D. Hunter, in charge of Southern Field Crop Insect Investigations; Mr. B. R. Coad, in charge of the Delta Laboratory, both of the Bureau of Entomology; and Dr. C. A. Browne and Dr. W. W. Skinner, Chief and Assistant Chief, respectively, of the Bureau of Chemistry. We likewise wish to express our recognition of the valuable service rendered us in the field operations by Mr. J. O. Reed of the engineering staff of the Bureau of Chemistry.

Summary

The essential oil, as obtained by extracting a concentrated distillate of the cotton plant with ether, had the following characters. It was a pale brownish-yellow, limpid liquid, having a strong, rather agreeable and persistent odor, $d_{25}^{25} = 0.9261$; $n_D^{20°} = 1.4797$; $[\alpha]_D^{20°} = -3.91°$. It was found to contain an aldehyde and gave a strong reaction for furfural.

The concentrated distillate from the plant, which represented all its odorous and volatile constituents, was found to contain the following individual substances.

1. Methyl alcohol, in large amount, and traces of acetone.

2. Amyl alcohol, in relatively small amount, together with small amounts of higher homologs.

3. Acetaldehyde, and traces of an aldehyde of higher carbon content. A crystalline condensation product of acetaldehyde with *m*-nitrobenzhydrazide has been formed; m. p., 151–152°. This is apparently a new compound.

4. Vanillin, $C_8H_8O_3$, in very small amount.

5. A phenol, in exceedingly minute amount. This substance is either a derivative of *m*-cresol or a phenol that possesses very similar characters.

6. An optically inactive, dicyclic sesquiterpene, $C_{15}H_{24}$.

7. A new, optically active, tricyclic sesquiterpene, $C_{15}H_{24}$.

8. A small amount of a paraffin hydrocarbon, m. p. 62°, which apparently is triacontane, $C_{30}H_{62}$.

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[36] Dessaignes, *Compt. rend.*, **33**, 358 (1851). Challinor, *J. Proc. Royal Soc. N. S. Wales*, **47**, 236 (1913). Czapek, "Biochem. Pflanzen.," Gustav Fischer, Jena, **1913**, 2d ed., vol. I, p. 780.

[37] Kauffmann and Vorländer, *Ber.*, **43**, 2735 (1910).

9. A blue oil, which probably contains the highly unsaturated hydrocarbon, azulene, $C_{15}H_{18}$.

10. Formic, acetic and caproic acids, the last in small proportion, which evidently were present to some extent in combination with the previously mentioned alcohols as esters.

11. Ammonia.

12. Trimethylamine.

The two last-mentioned basic substances were present in appreciable amounts in the distillate, but the ammonia largely predominated. Both ammonia and trimethylamine were also found to be emanations from the living plant.

Although trimethylamine has been found by field tests to possess some attraction for the boll weevil, much more extended experiments have still to be undertaken by the entomologists in order to determine the practicability of its use as a bait.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

SYNTHESIS OF PHENYLETHYL ALCOHOL[1]

BY CLIFFORD SHATTUCK LEONARD

RECEIVED APRIL 7, 1925 PUBLISHED JUNE 5, 1925

Introductory

β-Phenylethyl alcohol (benzyl carbinol) is today a chemical substance of commercial importance. This colorless liquid possessing a faint but lasting rose odor is valuable to the perfume industry not only for its own odor but also because of the fact that when admixed with other essential oils it has the property of increasing, modifying and more permanently fixing their odors. Certain derivatives of the alcohol such as its formic, propionic benzoic and phenylacetic esters are also valuable perfume fixatives. Recently, phenylethyl alcohol has been found to have local anesthetic properties.[2]

Phenylethyl alcohol occurs in nature in the rose flower and constitutes about 60% of the oil extractable with ether from the flower. Rose oil of commerce, however, contains but a trace of the alcohol, for it is water-soluble and is thus separated in the process of steam distillation. It is

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[1] This paper is constructed from a thesis presented to Yale University in June, 1917, for the degree of Master of Science. The work was done on the J. B. Williams Company Industrial Fellowship. The results have recently been released for publication. The writer wishes to thank the J. B. Williams Company. Thanks are also due to Professors T. B. Johnson and Arthur J. Hill for their guidance and advice.

[2] Hjort and Eagen, *J. Pharmacol.*, **14**, 211 (1919). Thierfelder and Schempp, *Arch. ges. Physiol.*, **167**, 280 (1917). See *Physiol. Abstr.*, **2**, 465 (1917–18).