Summary

1. The infra-red absorption spectra of molten α-naphthylamine at 65°, methyl- and ethyl-α-naphthylamine, and dimethyl- and diethyl-α-naphthylamine have been examined between 1.0 and 12.0μ.

2. The data obtained indicate a general parallelism with the behavior of aniline and the alkyl anilines previously studied.

3. The marked qualitative differentiation between aniline and mono-alkyl anilines and dialkyl anilines previously found in the region from 2.7μ to 3.4μ is apparently valid in the case of α-naphthylamine and its mono- and dialkyl derivatives.

4. The striking similarity in the absorption spectra of α- and β-naphthylamine renders it very probable that the alkyl β-naphthylamines follow this same differentiation.

5. The possibility of another region of absorption displaying a similar differentiation has been suggested for the region of 6.2μ.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE COMPOSITION OF YELLOW OIL OBTAINED IN THE MANUFACTURE OF *N*-BUTYL ALCOHOL BY FERMENTATION

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RECEIVED AUGUST 17, 1925 PUBLISHED DECEMBER 12, 1925

"Yellow oil"[1] is the high-boiling material that is produced as a by-product in the fermentation process now used for the preparation of butyl alcohol. In this process a suitable mash, which is made from corn, is inoculated with a pure culture of the Weizmann bacillus and fermented under carefully controlled conditions, optimum for the formation of the solvents. Large quantities of hydrogen and carbon dioxide are produced during the fermentation. The fermented mash is run through a continuous beer-still heated with live steam and the solvents are concentrated in the distillate. This distillate is fractionated in pot stills and the three main products of the fermentation, ethyl alcohol, acetone and butyl alcohol, are separated. The high-boiling residue in the stills amounts to 0.5 to 1.0% of the total yield of solvents and is technically known as yellow oil. It is a dark, amber-colored liquid with the odor of crude butyl alcohol. It usually contains considerable suspended material that may be removed by filtration.

Ethyl alcohol, acetone, butyl alcohol, acetic acid and *n*-butyric acid are well-known products of this fermentation, but there is no report in the

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[1] The yellow oil was kindly furnished by Mr. B. K. Brown of the Commercial Solvents Corporation, Terre Haute, Indiana. The authors are greatly indebted to this Company for the aid which has been received in carrying out this investigation.

literature concerning the nature of this high-boiling residue from the solvent fraction. It seemed quite possible that the higher-boiling products were esters of butyl alcohol with these acids. With this in mind an attempt was made to separate the various constituents of the oil by a direct fractional distillation. However, no sharp fractions could be obtained and qualitative tests showed that the material was a mixture of alcohols and esters.

A large sample of the oil was saponified and the alcohols and nonsaponifiable material were separated from the acids produced by hydrolysis. These two portions were examined separately. The alcoholic and nonsaponifiable portion, after being thoroughly dried, was fractionally distilled. In this way a definite separation of *n*-butyl alcohol, a mixture of active amyl and *iso*-amyl alcohols, and *n*-hexyl alcohol was obtained.

In addition there was a higher-boiling fraction which was distilled under reduced pressure. The only substance that could be identified in this fraction was naphthalene. It is not believed that naphthalene is a product of the fermentation but that it was introduced into the fermentation mixture by an accidental sucking back of the disinfecting solutions through which the fermentation gases escape. These solutions are made of the crude cresol fraction from coal tar and undoubtedly contain some naphthalene.

After the naphthalene fraction, two higher-boiling fractions were obtained. These were liquid and retained a yellow color even after repeated distillation under reduced pressure. Only a small amount of these products has been isolated and as yet no substances have been identified.

The alcohols were identified by conversion to the alpha acid esters of 3-nitrophthalic acid.[2] Two new esters of this acid, the *n*-amyl and the *n*-hexyl, have been prepared for comparison with esters from the unknown alcohols.

The acids produced in the saponification have been identified as *n*-butyric, caprylic and capric. Butyric acid was identified by means of the Duclaux constants[3] and the melting point of its *p*-toluidide. Caprylic acid was identified by the melting point of its *p*-bromophenacyl ester.[4] Capric acid was identified by means of mixed-melting-point determinations with known capric acid.

The suspended material in the yellow oil was found to be a mixture of copper and iron salts of the acids which were found in the esters. These salts were undoubtedly produced in the stills and storage tanks.

The amounts of the various pure substances isolated from 12 liters of

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[2] (a) Wegscheider and Lipschitz, *Monatsh.*, **21,** 787 (1900). (b) Nicolet and Sacks, THIS JOURNAL, **47,** 2348 (1925).

[3] Duclaux, *Ann. chim. phys.*, [5] **2,** 289 (1874). Richmond, *Analyst,* **20,** 193 (1895). Upson, Plum and Schott, THIS JOURNAL, **39,** 731 (1917). Lamb, *ibid.*, **39,** 746 (1917).

[4] Judefind and Reid, THIS JOURNAL, **42,** 1055 (1920).

crude yellow oil are as follows: *n*-butyl alcohol, 5100 cc.; mixed amyl alcohols, 220 cc.; *n*-hexyl alcohol, 100 cc.; naphthalene, 5 g.; butyric acid (in water solution), about 700 g.; caprylic acid, 12 g.; capric acid, 28 g. Considerable material occurs in intermediate fractions and there is much mechanical loss in repeated distillation. In the saponification a large amount of tarry material was formed and this also accounts for some of the loss. It is thought that this may be a polymerized product formed from the original unsaturated acids of the corn oil.

Experimental Part

Preliminary Tests.—The yellow oil was filtered with suction. The liquid portion had a specific gravity of 0.86–0.88 at 25°. It was neutral to litmus. A 3200cc. sample was fractionally distilled using a modified Claisen flask[5] until the volume of the fractions did not change appreciably. The material boiling above 170° was not distilled. There was a solid residue of 184 g. Each fraction was examined qualitatively and found to be a mixture of esters and alcohols. A sample of each fraction was saponified with standard alkali solution and the approximate ester content was thus determined. Table I gives a summary of these results.

Table I

Approximate Composition of Yellow Oil

B. p. of fraction °C.	Volume Cc.	Cc. of 0.1 *N* alkali to saponify 1 g. of material	Duclaux constants for acid
90–100	43	3.11	15.2, 14.5, 13.0
100–110	26	2.65	16.7, 15.3, 14.0
110–114	120	3.11	17.5, 15.3, 14.0
114–120	791	1.91	17.5, 15.7, 14.7
120–125	146	6.57	16.8, 16.0, 14.3
125–130	15	10.08	17.2, 15.2, 14.1
130–135	51	17.42	17.2, 15.7, 13.9
135–140	26	26.01	17.9, 15.7, 13.4
140–145	36	37.47	....
145–150	29	47.80	17.5, 16.7, 14.5
150–155	30	53.31	18.1, 16.1, 14.1
155–160	105	60.21	17.6, 15.9, 14.2
160–165	663	62.06	17.8, 16.1, 14.7
165–170	434	62.38	18.7, 16.9, 14.9
Liquid above 170	395	...	....

The Duclaux constants for *n*-butyric acid are 17.9, 15.9, 14.6.

The saponification products were separated from each fraction. The alcohol portion was found to be mainly *n*-butyl alcohol since it gave a 3,5-dinitrobenzoate that melted at 64° and the melting point was not affected by mixing this product with known *n*-butyl-3,5-dinitrobenzoate. The water-soluble acid obtained from each fraction was identified as *n*-butyric

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[5] Noyes and Skinner, This Journal, **39**, 2718 (1917).

acid by determining the Duclaux constants for each portion. This was confirmed by converting a small amount of the acid into the *p*-toluidide which was found to melt at 72° while the pure amide melts[6] at 73–74°.

Composition of the Solid Material Suspended in Yellow Oil.—Some of the solid material filtered from the oil was incinerated; 0.7594 g. gave 0.3372 g. of non-volatile ash. A sample of the solid was treated with dil. sulfuric acid and the mixture was steam distilled. The distillate contained a water-soluble acid which was identified as *n*-butyric acid by the Duclaux constants, 17.7, 15.9, 14.3. The sulfuric acid solution was examined qualitatively for metals, and iron and copper were identified.

Saponification of Yellow Oil.—In a large copper kettle fitted with a mechanical stirrer and a reflux condenser were placed 12 liters of crude yellow oil and a considerable excess of 25% sodium hydroxide solution. The mixture was stirred and refluxed for about 20 hours. The condenser was then arranged for distillation and the solution was steam distilled as long as any water-insoluble material came over. The first 12.5 liters of distillate contained most of the alcohol portion. However, a small amount of a yellow oil continued to come over and was saved separately; it amounted to 240 cc.

After the alcohols and non-saponifiable material had been completely removed from the saponification mixture, a quantity of 50% sulfuric acid which was slightly more than equivalent to the alkali used, was added. Stirring was maintained during the addition of the acid. The volatile fatty acids were then distilled with steam. About 30 liters of distillate was collected.

When the copper kettle was opened a large amount of black, tarry material was found floating on the water. This material was brittle at 20° but softened at about 30°. No attempt was made to purify it. It was probably polymerized products of some sort.

Separation and Identification of the Acids Obtained by Saponification.—The acid distillate from the saponification contained traces of sulfur dioxide and was redistilled from a small amount of sodium dichromate.

Ten 2.5-liter portions of distillate were collected. In each portion there was a small amount of water-insoluble material that was separated. This was fractionally distilled as described later. The Duclaux constants were determined on the first and last portions of the water solution. These were 18.6, 17.2, 15.2 and 17.4, 16.0, 14.1, respectively, which check fairly well with those for *n*-butyric acid, and since this acid had been definitely determined as the water-soluble acid in the preliminary tests, no further work was done on the water-soluble portion.

The water-insoluble acids were distilled at 10 mm. pressure, and after six fractionations the main fractions were: (1) 27 g., b. p. 64–65° (10–11 mm.); (2) 12 g., b. p. 116–118° (10–11 mm.) and (3) 28.5 g., b. p. 142–143° (10 mm.). Fraction 1 was water soluble and the Duclaux constants were found to be 18.4, 16.8, 15.0, which agree well with those for *n*-butyric acid.

Fraction 2 was converted into the sodium salt and the *p*-bromophenacyl ester was prepared by the method of Judefind and Reid.[4] After purification the ester melted at 65° and the melting point was not changed by mixing this ester with known *p*-bromophenacyl caprylate.

Fraction 3 solidified on cooling. The solid material was dried on a clay plate to remove a little oil; m. p., 30–31°, unchanged by mixing with pure capric acid.

Separation and Identification of the Alcohols and Non-saponifiable Material.—The alcohols were salted out of the water with potassium

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[6] Fichter and Rosenberger, *J. prakt. Chem.*, [2] **74**, 323 (1906).

carbonate and carefully dried with the same reagent. The dry alcohol mixture was then carefully distilled seven times through a good column. There was practically no change in the volume of the various fractions in the last distillation. The fractions thus obtained are given in Table II.

TABLE II

ALCOHOLIC AND NON-SAPONIFIABLE FRACTIONS FROM YELLOW OIL

Fraction	B. p., ° C.	Volume, cc.	Fraction	B. p., ° C.	Volume, cc.
1	-110	125	10	135–140	22
2	110 -116.5	160	11	140–145	16
3	116.5–118	5100	12	145–150	28
4	118 -119	105	13	150–155	46
5	119 -120	90	14	155–160	54
6	120 -122.5	175	15	160–165	10
7	122.5–125	60	16	165–170	6
8	125 -130	220	17	170–190	14
9	130 -135	90	18	above–190	110
					Total 6,431

Fraction 18, b. p. above 190°, was combined with the 240 cc. of yellow insoluble oil obtained in the saponification and the mixture further fractionated under reduced pressure. After ten distillations, the main fractions seemed to remain constant and are given in Table III.

TABLE III

HIGH-BOILING FRACTIONS OF ALCOHOLS AND NON-SAPONIFIABLE MATERIAL FROM YELLOW OIL

Fraction	B. p., ° C. (10 mm.)	Volume, cc.	Fraction	B. p., ° C. (6 mm.)	Volume, cc.
19	36–38	26	22	74– 78	10
20	46–48	50	23	78–100	42
21	76–78	38	24	100–135	27
					Total 193

Considerable thick, tarry material remained in the flask after each distillation and this accounts for the high loss.

The fractions that seem to be fairly definite substances and not transition fractions are numbered 3, 8, 13, 14 in Table II and 21 in Table III. These were examined first.

Fraction 3 (Table II) was recognized as *n*-butyl alcohol and the identification was confirmed by preparing the 3,5-dinitrobenzoate, m. p. 64°, and the alpha acid ester of 3-nitrophthalic acid; m. p., 146–147°. This melting point agrees with that given by Nicolet and Sacks.[2b]

Fractions 8 and 9 (Table II) were examined in the polariscope and gave a rotation of —3.5°, showing the presence of active amyl alcohol. A small portion was converted into the acid 3-nitrophthalate, and after purification the ester melted at 158° and gave a neutral equivalent of 279.1. The active amyl ester melts at 155° and the *iso*-amyl ester[2b] at 157–158°. The neutral equivalent for either is 281. It is apparent that both of the fusel oil amyl alcohols are present in these fractions of yellow oil.

Fraction 13 (Table II), b. p. 150–155°, was converted into the acid 3-nitrophthalate and on purification the product melted at 121–122°. Some of the *n*-hexyl ester was prepared as described later and the mixture of the two products melted at 121–122°, thus completing the identification of the fraction. In the same way Fraction 14 was found to be very largely *n*-hexyl alcohol. Fractions 19 and 20 (Table III) were identified as *n*-butyl and *n*-hexyl alcohol, respectively.

Fraction 21 (Table III) solidified partially on cooling. The fraction was cooled in ice and the solid filtered off. The liquid portion was found to be mainly *n*-hexyl alcohol. About 5 g. of the solid substance was obtained. After two crystallizations from petroleum ether it melted rather sharply at 76°. Several analyses were made and the average of these indicated about 92.76% of carbon and 6.39% of hydrogen. Since this leaves less than 1% unaccounted for, it was thought that the combustions were not complete. A molecular-weight determination was then made.

Mol. wt. Solute, 0.5647 g.: solvent (benzene), 22.8787 g. Δt, 3.046°. Found: mol. wt., 124.7.

The analysis and molecular weight indicated naphthalene although the rather characteristic odor was not present. A mixture of the unknown with pure naphthalene melted at 78–80°. The picrate melted at 149° and the melting point did not change when the product was mixed with known naphthalene picrate. A small sample of the unknown was recrystallized from benzene and then melted at 80° and had the characteristic odor of naphthalene.

The higher fractions are of unknown composition. Fraction 22, b. p. 74–78° (6 mm.), was analyzed.

Anal. Subs., 0.2726: H_2O, 0.2223; CO_2, 0.8027. Found: H, 9.06; C, 80.31.

Fraction 23 (Table III) was also analyzed.

Anal. Subs., 0.1778: H_2O, 0.1646; CO_2, 0.8027. Found: H, 10.22; C, 78.82.

These last two fractions were yellow. The color did not disappear during distillation. They did not decolorize a carbon tetrachloride solution of bromine and did not react with sodium nor the aldehyde and ketone reagents, phenylhydrazine, hydroxylamine and semicarbazide. They had no optical activity.

These fractions were easily oxidized by cold potassium permanganate solution. When the manganese dioxide was removed by filtration and the filtrate acidified an acidic substance could be extracted with ether; b. p., 210–215°. By cooling the distilled product a small amount of a solid acid was obtained; m. p. 96–97°; neutral equivalent 118.3.

α-Mono-*n*-amyl Ester of 3-Nitrophthalic Acid.—*n*-Amyl alcohol was heated on a steam-bath in a test-tube with the calculated amount of 3-nitrophthalic anhydride. The product was then recrystallized several times from 40–50% ethyl alcohol. The pure acid ester melted at 132–133° and had a neutralization-value of 279.8; calcd., 281.

Anal. Subs., 0.2521: H_2O, 0.1198; CO_2, 0.4111. Calcd. for $C_{13}H_{15}O_6N$: C, 55.52; H, 5.34. Found: C, 55.31; H, 5.28.

α-Mono-*n*-hexyl Ester of 3-Nitrophthalic Acid.—This ester was prepared in a manner exactly analogous to that used for the *n*-amyl ester; m. p., 121–122°; neutralization value, 292.6; calcd. 295.

Anal. Subs., 0.2061: H_2O, 0.1059; CO_2, 0.4346. Calcd. for $C_{14}H_{17}O_6N$: C, 56.95; H, 5.76. Found: C, 56.68; H, 5.71.

Summary

1. The high-boiling material obtained as a by-product from the manufacture of *n*-butyl alcohol by fermentation has been found to be a complex mixture of *n*-butyl alcohol, active amyl alcohol, *iso*-amyl alcohol, *n*-hexyl alcohol and the *n*-butyric, caprylic and capric esters of these alcohols.

2. The acid *n*-amyl and *n*-hexyl esters of 3-nitrophthalic acid have been described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE PREPARATION OF SOME PRIMARY AMINES BY THE CATALYTIC REDUCTION OF NITRILES

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RECEIVED AUGUST 15, 1925 PUBLISHED DECEMBER 12, 1925

The preparation of primary amines by the reduction of nitriles with the usual chemical reagents is frequently unsatisfactory. The catalytic method has been studied by several investigators[1] with diverse results. Apparently the course of the reaction is greatly influenced by the nature of the nitrile, the catalyst, the solvent, the conditions of temperature and pressure, etc. Secondary amines are usually formed as well as primary, and the former may frequently constitute the chief reaction products.

The platinum oxide catalyst described and extensively applied by Adams[2] and his students has been found extremely effective in a variety of reductions. There is here presented a brief study of the behavior of this catalyst in the reduction of certain nitriles. Especial attention was directed toward elimination of the formation of secondary amines, and the reactions were carried out on such a scale that the results might be of some practical use in synthetic work.

Preliminary small-scale experiments showed that the reduction of benzyl cyanide proceeded at a practicable rate in glacial acetic acid, acetic anhydride, and absolute alcohol, but only very slowly in absolute ethyl ether. It was then established that reduction of benzonitrile and

TABLE I

RELATIVE AMOUNTS OF PRIMARY AND SECONDARY AMINES FORMED IN ALCOHOL AND ACETIC ACID SOLUTIONS

Nitrile	Solvent	% Primary amine	% Secondary amine
Benzonitrile	Alcohol	21	79
Benzonitrile	Acetic acid	62	38
p-Tolunitrile	Alcohol	33	67
p-Tolunitrile	Acetic acid	4	84

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[1] (a) Rupe and Gisiger, *Helvetica Chim. Acta*, **8,** 338 (1925). (b) v. Braun, Blessing and Zobel, *Ber.*, **56,** 1988 (1923). (c) Rosenmund and Pfankuch, *Ber.*, **56,** 2258 (1923). (d) Grignard and Escourrou, *Compt. rend.*, **180,** 1883 (1925); and other references in these papers.

[2] THIS JOURNAL, (a) **44,** 1397 (1922); (b) **45,** 1071, (c) 2171, (d) 3029 (1923); (e) **46,** 1675, (f) 1684 (1924); (g) **47,** 1047, (h) 1098, (i) 1147 (1925).