slopes of the tangents to the curves (of pressure-drop against time) when 80 and 67% of the gases have reacted, increases with the decrease of oxygen in the mixture. The increase in the rate is especially noticeable when the partial pressure of oxygen is well below 2 mm.

The sensitivity of the rate of the reaction to small amounts of oxygen, together with the evidence that the reaction occurs largely at the surface, suggests a chain mechanism with short chains initiated at the surface.

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[CONTRIBUTION FROM THE UNIVERSITY OF TEXAS]

Organic Nitrogen Bases from Pyrolysis of Cottonseed Meal[1]

BY IVY PARKER, C. L. GUTZEIT, A. C. BRATTON AND J. R. BAILEY

Introduction

Research on the bases in petroleum distillates[2] has shown a preponderance of non-aromatic types, not previously obtained from any other natural source. On the assumption that petroleum is of vegetable or animal origin, it may be assumed that carbohydrates and fats, as well as proteins, contributed to the formation of nitrogen compounds; in any event an explanation of the genesis of non-aromatic petroleum bases, among which are probably compounds of cyclopentane structure, might have an important bearing on the origin of petroleum itself.

In an attempt to determine whether similar non-aromatic bases would result from pyrolysis of a material containing proteins, carbohydrates and fats, the present investigation was undertaken. The Union Oil Company of California contributed 337 pounds of crude bases obtained from the distillation of 23 tons of cottonseed meal with nitrogen-free lubricating oil as a liquid medium, through which low temperature pyrolysis could be controlled.[2a]

Previous work by other investigators on bases formed in protein pyrolysis are of little interest as concerns the present investigation, because in these studies pure proteins were employed.[3]

The complexity of the cottonseed meal bases is comparable with that of petroleum bases. An unexpected difference is that, unlike bases from other important natural products, those from protein material are at least 50% *petroleum ether insoluble* and, besides, the higher boiling fractions have a much greater nitrogen content than can be accounted for on the assumption of a single nitrogen in the molecule. Furthermore, there is no evidence of naphthenic structure, such as is highly probable for certain petroleum bases. From the lower boiling fractions there have been isolated pyridine, and a number of its homologs, identical with products from coal, shale or bones.

The coal tar bases, quinoline, isoquinoline, quinaldine and lepidine, along with the kero base, 2,3,8-trimethylquinoline[2b] (p. 1245), have been found. A beautifully crystallizing diazine, $C_{11}H_{14}N_2$, of undetermined structure is probably a dihydroquinazoline, as indicated by its amphoteric character.

Upon vacuum distillation of the high boiling protein bases in an atmosphere of nitrogen, colorless distillates are obtained which, unlike corresponding petroleum base cuts, soon darken and precipitate tar. This instability renders difficult the isolation of individual products. So far the petroleum ether insoluble bases have been only superficially studied.

In the boiling range of 135 to 172° a total of 876 cc. (14 fractions) of petroleum ether soluble material was available with d^{25}_{4} values between 0.9418 and 0.9652 and n^{25}_{D} values between 1.4947 and 1.4992. These physical constants clearly indicate a preponderance of pyridines. From the high nitrogen content of these fractions pyrazines and pyrimidines were suspected but a search for diazines was fruitless. The comparatively small volume of material in this range can be attributed

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(1) In part from dissertations submitted by Ivy May Parker and C. L. Gutzeit to the Faculty of the Graduate School of the University of Texas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1935.

(2) (a) E. J. Poth, W. D. Armstrong, C. C. Cogburn and J. R. Bailey, *Ind. Eng. Chem.*, **20**, 83 (1928); (b) E. J. Poth, W. A. Schulze, W. A. King, W. C. Thompson, W. W. Floyd and J. R. Bailey, THIS JOURNAL, **52**, 1239 (1930); (c) W. C. Thompson and J. R. Bailey, *ibid.*, **53**, 1002 (1931); (d) B. F. Armendt and J. R. Bailey, *ibid.*, **55**, 4145 (1933); (e) G. R. Lake and J. R. Bailey, *ibid.*, **55**, 4143 (1933); (f) T. S. Perrin and J. R. Bailey, *ibid.*, **55**, 4136 (1933); (g) B. S. Biggs and J. R. Bailey, *ibid.*, **55**, 4141 (1933); (h) R. W. Lackey and J. R. Bailey, *ibid.*, **56**, 2741 (1934).

(2a) The preliminary work in this connection was carried out in the Texas Laboratory by Ivy Parker.

(3) Pictet and Cramer, *Helv. Chim. Acta*, **2**, 188 (1919); T. B. Johnson and Daschavsky, *J. Biol. Chem.*, **62**, 197 (1924).

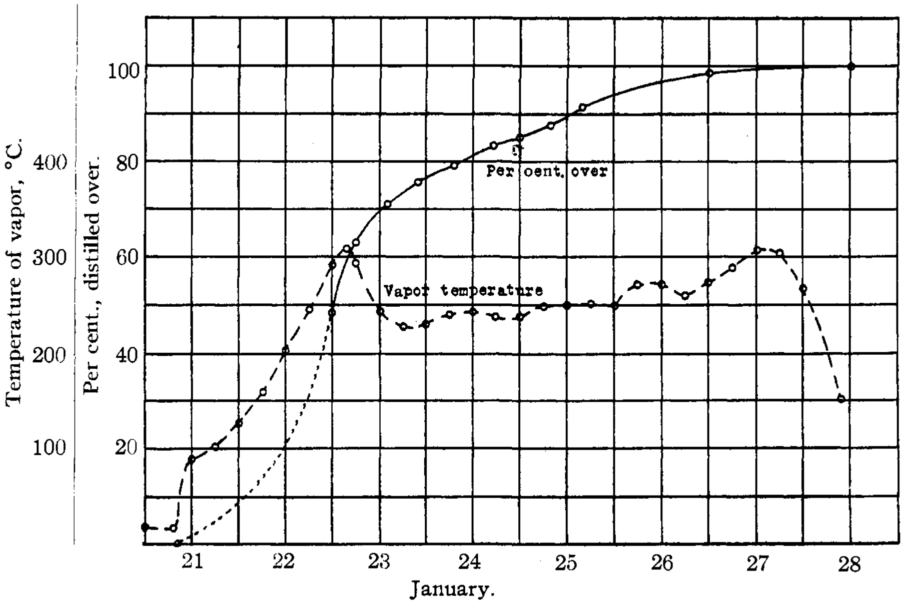

Fig. 1.—Distillation of cottonseed meal.

to the fact that no attempt was made at the Union Oil Company plant to isolate water soluble bases.

In the 172 to 215° range 2468 cc. of material (17 fractions) was available. Here there exists a progressive exaltation of the d^{25}_4 values from 0.9514 to 1.0189 and of the n^{25}_D values from 1.5010 to 1.5375. These constants, taken with an abnormally high nitrogen content, exclude the presence in quantity of pyridines, as well as quinolines.

The results of this investigation should not be accepted as proof that so-called petroleum bases are not of vegetable or animal origin. From the assumption that the complex nitrogen compounds in crude oil came from protein material, it does not follow that a high temperature was involved in their formation; it is more probable that they resulted from bacteriological decay at ordinary temperature;[4] at least, so far as California petroleum is concerned, the nitrogen does not exist in preformed *basic* compounds beyond a negligible amount and, therefore, the bases first encountered in distillates, are products of pyrolysis.[5,2a,b]

A recently developed practical method of indirect micro distillation, termed Amplified Distillation,[6] has proved of indispensable service in processing the cottonseed meal bases. In this process, which is even more effective than straight distillation, a fraction of bases is added to petroleum hydrocarbon oil boiling evenly over a somewhat broader range than the bases. After fractional distillation, the bases are withdrawn from the hydrocarbon fractions with sulfurous acid and then precipitated in the form of picrates or other suitable salts. In this way the components of a complex mixture, even where the total volume is only a fraction of a cubic centimeter, can be segregated in the order of their boiling points.

Another general method employed in resolving mixtures of protein bases, termed Cumulative Extraction,[2e] depends on the relative distribution ratio of base hydrochlorides between chloroform and water. This process enables a very satisfactory separation into aromatic and non-aromatic types.

The improved laboratory technique now available in this line of research, coupled with the advances made in our knowledge of the types and properties of the bases to be expected, should attract the attention of other investigators to the study of protein pyrolysis, especially the biochemist, whose interest in this practically unexplored domain of organic chemistry need not be emphasized.

To chemists who may become interested in protein pyrolysis as an attractive field for re-

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[4] *Cf.* McKenzie Taylor, *J. Inst. Petr. Tech.*, **14**, 825 (1928); B. T. Brooks, *ibid.*, **20**, 177 (1934).

[5] D. T. Day, "Handbook of the Petroleum Industry," Vol. 1. 1922, p. 530.

[6] A. C. Bratton, W. A. Felsing and J. R. Bailey, *Ind. Eng. Chem.*, **28**, 424 (1936).

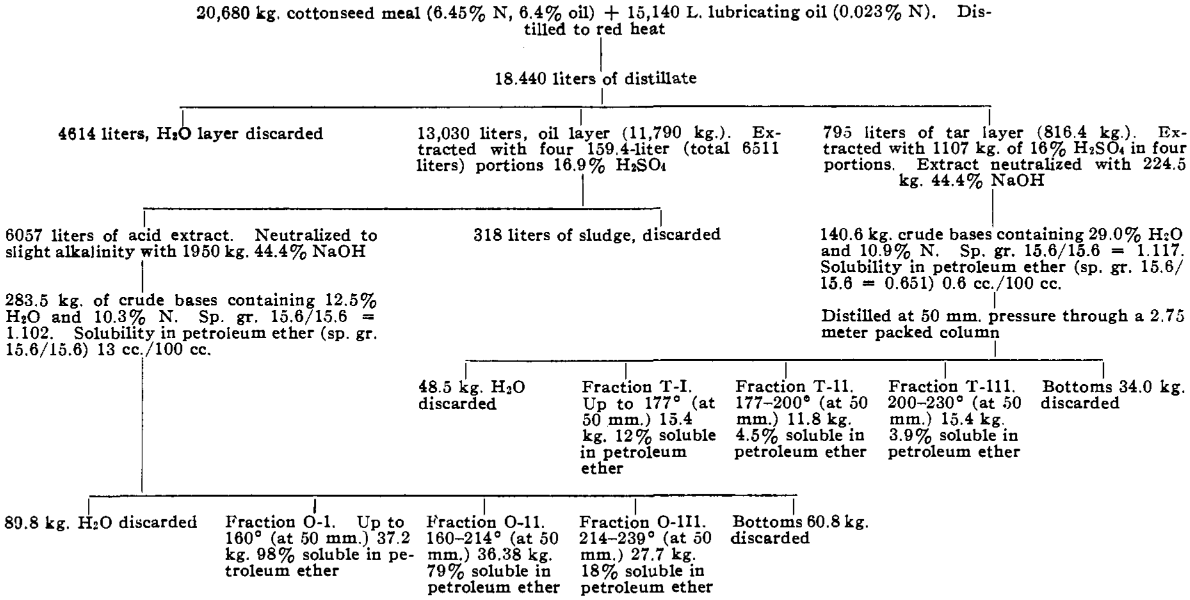

Fig. 2.

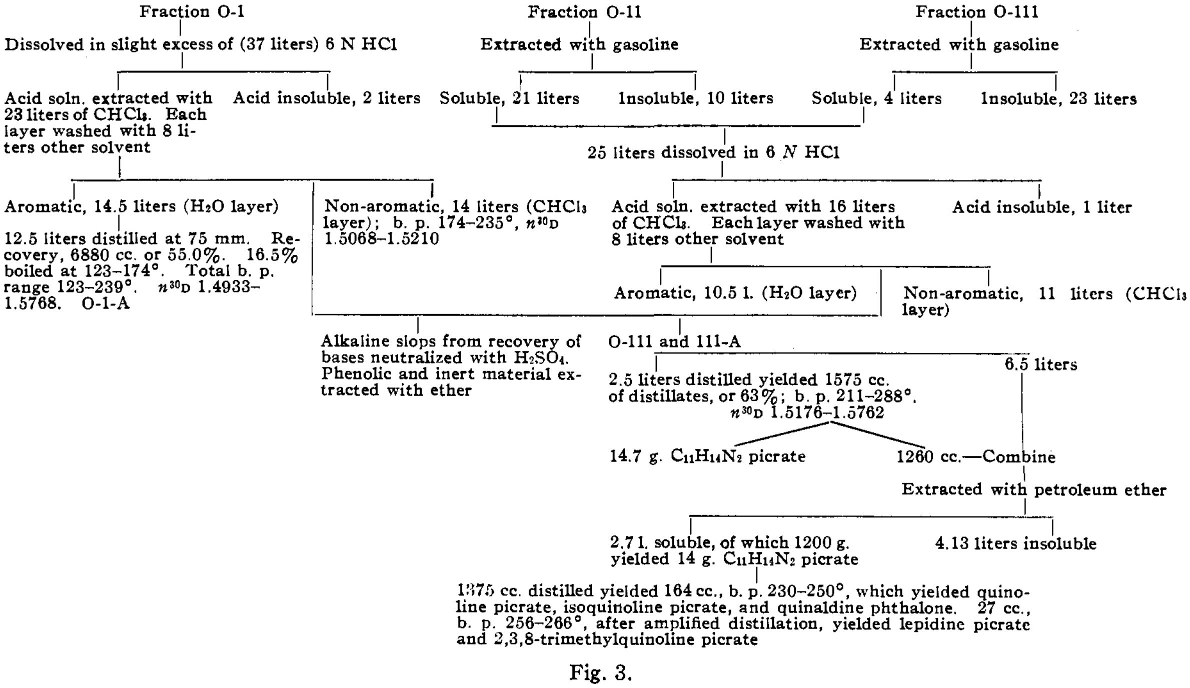

Fig. 3.

search, it may be emphasized that the cost of neither material nor equipment is prohibitive. In our preliminary investigation, an insulated iron still 3 feet (94 cm.) in height, 2 feet (61 cm.) in diameter and provided with a stirrer was used. For each of the six runs made, the charge consisted of 100 pounds (45 kg.) of cottonseed meal ($25–35 per ton (910 kg.)) and 8 gallons (30 liters) of lubricating oil. The distillates from 600 pounds (272 kg.) of meal processed in the usual way yielded a total of 5.5 liters of crude bases.

One of the most important considerations, especially where the distillation is carried out in the laboratory, is the obnoxious mercaptan odor developed. This nuisance can be suppressed conveniently by the use of two filter flasks connected separately with water pumps and serving interchangeably as receivers.

TABLE I

DISTILLATION OF O-I-A BASES

No.	Temp. range, °C.	Press., mm.	Vol., cc.	d^{25}_4	n^{25}_D	N, %	Bases isolated
1	100–135	750	1				Pyridine 2-Methylpyridine
2	135–140	750	8	0.9522	1.4968	17.41	4-Methylpyridine
3	140–142.5	751	10	.9503	1.4978	17.36	3-Methylpyridine 2,6-Dimethylpyridine
4	142.5–145	751	16	.9511	1.4989	15.65	
5	145–147.5	752	25	.9652	1.4968	16.03	
6	147.5–150	752	20	.9652	1.4968	16.34	
7	150–152.5	753	37	.9507	1.4990	15.84	
8	152.5–155	753	45	.9522	1.4947	17.66	
9	155–157.5	754	38	.9418	1.4990	17.71	2,4-Dimethylpyridine
10	157.5–160	754	44	.9442	1.4990	16.92	
11	160–162.5	755	59	.9556	1.4968	15.22	
12	162.5–165	755	119	.9480	1.4962	15.24	
13	165–167.5	756	130	.9531	1.4988	15.96	3-Ethylpyridine
14	167.5–170	756	189	.9491	1.4990	15.98	3,5-Dimethylpyridine 2,4,6-Trimethylpyridine
15	170–172.5	756	136	.9504	1.4992	14.77	
16	172.5–175	758	157	.9514	1.5010	13.93	
17	175–177.5	758	170	.9559	1.5025	13.65	
18	177.5–180	758	120	.9594	1.5055	13.36	
19	180–182.5	758	133	.9598	1.5090	13.85	
20	182.5–185	757	160	.9612	1.5119	13.86	
21	185–187.5	757	200	.9631	1.5140	14.71	
22	187.5–190	757	99	.9677	1.5160	14.66	
23	190–192.5	756	191	.9716	1.5170	13.31	
24	192.5–195	756	140	.9781	1.5199	13.34	
25	195–197.5	756	183	.9820	1.5212	13.25	
26	197.5–200	756	162	.9882	1.5260	12.84	
27	200–202.5	757	221	.9917	1.5270	12.89	
28	202.5–205	757	130	.9971	1.5303	12.53	
29	205–207.5	757	92	1.0026	1.5328	12.14	
30	207.5–210	758	144	1.0093	1.5342	13.23	
31	210–212.5	758	106	1.0165	1.5363		
32	212.5–215	758	60	1.0189	1.5375		
33	Residue	758	20				

Experimental

In the production of nitrogen bases from cottonseed meal at the Oleum Plant of the Union Oil Company,[7] a shell still, 8 by 29 feet (2.5 × 8.8 meters) was used in distillation of the cottonseed meal–lubricating oil mixture, air from the spider of the still being used for agitation. The still run occupied seven days; however, most of the distillate was collected in four days. After completion of the distillation, the still was allowed to cool for four days and even then difficulty was experienced in handling the coke,[8] due to a tendency to spontaneous combustion. Distillation temperature and rate are summarized in Fig. 1. Acid extraction and distillation data, along with yields of base fractions are compiled in Fig. 2.

Fractions O-I, O-II and O-III, Fig. 2, were processed through petroleum ether extraction, cumulative extraction and fractional distillation, as shown in Fig. 3.[9] The material O-I-A, Fig. 3, boiling below 215° was carried through exhaustive fractionation by three separate distillations in a carbon dioxide atmosphere under reflux through a spirally indented column, 1 × 105 cm.

Volumes, boiling points, nitrogen content, d^{25}_4 values and n^{25}_D values of the 33 fractions obtained are collected in Table I.[10]

Investigation of O-I-A Forerun

BY A. C. BRATTON

The small volume of forerun (1 cc. of bases in 9 cc. of water) precluded direct fractional distillation under reflux. Amplified distillation was conceived to obviate the difficulty, and this first experiment in its use as an indirect method of microdistillation was carried out successfully as follows: to the 1 cc. of bases, 25 cc. of acid-and-caustic-washed hydrocarbon oil, b. p. 80–140°, was added and the mixture was distilled through a 0.5 × 100 cm. column packed with a copper spiral. The rate of distillation was

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[7] The data in this connection were furnished by Mr. T. F. Ott, Assistant Manager of Research at Oleum, California.

[8] This proved a very effective decolorant.

[9] This work was carried out by Ivy Parker.

[10] This work was carried out by A. C. Bratton and C. L. Gutzeit.

0.6 cc. per hour, and nine 2.5-cc. cuts and a 3-cc. residue were collected in the ranges shown in Table II.

TABLE II

AMPLIFIED DISTILLATION OF THE BASES IN O-I-A FORERUN

Cut no.	B. p. base-hydrocarbon fractions, °C.	Products isolated, mg.	
1	55–85	30	Pyridine picrate
2	85–95		
3	95–100		
4	100–107	300	2-Methylpyridine picrate
5	107–109		
6	109–115	450	Mixed picrates
7	115–122		
8	122–124		
9	124–138	10	2,6-Dimethylpyridine picrate
Residue			

Each fraction was extracted twice with an equal volume of 6 *N* sulfuric acid, the bases were liberated from the extracts with sodium hydroxide and steam distilled, and finally precipitated with aqueous picric acid.

Pyridine.—The combined picrates from cuts 1 and 2 were recrystallized from water, ethyl acetate and isopropyl alcohol. The product, m. p. 167.7–168°, proved to be pyridine picrate through a mixed melting point with an authentic sample.

Anal. Calcd. for $C_{11}H_8O_7N_4$: N, 18.19. Found: N, 18.30.

2-Methylpyridine.—After similar treatment of the picrates from cuts 4 and 5, a salt melting at 166° was identified as 2-methylpyridine through a mixed melting point.

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: N, 17.40. Found: N, 17.62.

2,6-Dimethylpyridine.—Fraction 9 yielded a picrate melting at 163° after recrystallization from water and isopropyl alcohol. It was identified as 2,6-dimethylpyridine by a mixed melting point.

Investigation of O-I-A Fractions 135–170°

BY C. L. GUTZEIT

3-Methyl-, 4-Methyl- and 2,6-Dimethylpyridine.—These bases boiling at 144, 145.3 and 144.6°, respectively, were suspected in the 140–145° fractions, and, after their separation through picrates proved tedious and unsatisfactory, the following procedure was employed: a solution of 10 cc. of crude bases in 500 cc. of saturated mercuric chloride and 10 cc. of concentrated hydrochloric acid was evaporated to 150 cc. The precipitate was recrystallized from alcohol and then dissolved in 1000 cc. of a hot saturated solution of mercuric chloride containing 100 cc. of concentrated hydrochloric acid. On cooling, the 2,6-dimethylpyridine double salt of the composition $C_7H_9N \cdot HCl \cdot 2HgCl_2$ separated in granular crystals melting at 167°.[11] The picrate prepared from this salt melted at 162° as reported by Eguchi. In final identification of these salts, they were prepared from 2,6-dimethylpyridine, synthesized from 2-methylpyridine methiodide according to the general method of Ladenburg.[12] Mixed melting points carried out in the usual way showed no depression.

Anal. of picrate. Calcd. for $C_{13}H_{12}O_7N_4$: C, 46.42; H, 3.57; N, 16.67. Found: C, 46.35; H, 3.58; N, 16.52.

Anal. of base. Calcd. for C_7H_9N: C, 78.50; H, 8.41; N, 13.08. Found: C, 78.42; H, 8.43; N, 13.29.

For the separation of 4-methylpyridine, the filtrate from the mercuric chloride salt of 2,6-dimethylpyridine was neutralized with sodium hydroxide and then made just acid to methyl orange. After twelve hours, a salt separated which was recrystallized from water in long slender needles melting at 128–129°, as found by Ladenburg for the mercuric chloride salt, $C_6H_7N \cdot HCl \cdot 2HgCl_2$, of 4-methylpyridine[12] (p. 13). Final identification was effected through a mixed melting point with a sample of picrate made from 4-methylpyridine synthesized from pyridine methiodide.[13]

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: C, 44.72; H, 3.11; N, 17.39. Found: C, 44.66; H, 3.15; N, 17.49.

Anal. of base. Calcd. for C_6H_7N: C, 77.42; H, 7.53; N, 15.09. Found: C, 77.36; H, 7.51; N, 15.12.

In isolation of 3-methylpyridine, the low melting picrates from purification of 4-methyl- and 2,6-dimethylpyridine were used. After it was found impractical to segregate this picoline through the picrate, mercuric chloride salt[12] (p. 8) or the zinc chloride salt,[14] advantage was taken of the non-reactivity of 3-methylpyridine with benzaldehyde in contrast to the ease with which condensation takes place with the associated pyridine homologs.[15]

The bases recovered from the low melting picrates were mixed with twice their volume of benzaldehyde, a small piece of zinc chloride was added and the mixture was heated at 225° for six hours. The unchanged 3-methylpyridine was extracted with benzene from the reaction mixture made alkaline with sodium hydroxide. The dried extract was distilled and the 140–145° fraction was treated with a benzene solution of picric acid. The third recrystallization from alcohol gave a pure product in the form of long glistening needles melting at 149°, as reported for 3-methylpyridine picrate[11] (pp. 229, 241).

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: C, 44.72; H, 3.11; N, 17.39. Found: C, 44.64; H, 2.93; N, 17.50.

Identification was further confirmed by a mixed melting point with the picrate prepared from the synthetic base.[16]

The 135–140° fraction of bases was investigated in a fruitless search for methylpyrazine. Since only 8 cc. of material was available, amplified distillation was resorted to in fractionation. A small amount of 3-methyl- and 2,6-dimethylpyridine was isolated, but none of the 4-methylpyridine.

3,5-Dimethylpyridine.—This base is easy to isolate and identify because of the difficult solubility and high melting point of its picrate. Three fractions of bases in the 165–170° range were picrated in two volumes of alcohol to one

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[11] *Cf.* Takashi Eguchi, *Bull. Chem. Soc. Japan*, **3**, 181, 241 (1928); *Chem. Zentr.*, **100**, 331 (1929).

[12] A. Ladenburg, *Ann.*, **247**, 2 (1888).

[13] Otto Lange, *Ber.*, **18**, 3439 (1885); ref. 12, p. 12.

[14] J. G. Heap, W. J. Jones and J. B. Speakman, THIS JOURNAL, **43**, 1936 (1921).

[15] Paul Schwarz, *Ber.*, **24**, 1676 (1891); Fr. Schuster, *ibid.*, **25**, 2398 (1892); A. Marcuse and R. Wolffenstein, *ibid.*, **32**, 2526 (1899).

[16] Ludwig Storch, *ibid.*, **19**, 2456 (1866).

volume of bases, picric acid solution being added to where no further separation of picrates resulted. The crude material melted at 234–236°. After two recrystallizations from acetone, the most satisfactory solvent for this salt, the melting point was raised to 242.5–243.5°.[17]

Anal. of picrate. Calcd. for $C_{13}H_{12}O_7N_4$: C, 46.43; H, 3.57; N, 16.67. Found: C, 46.61; H, 3.59; N, 16.54.

Anal. of base. Calcd. for C_7H_9N: C, 78.50; H, 8.41; N, 13.08. Found: C, 78.44; H, 8.36; N, 13.35.

The identity of the picrate was confirmed further by a mixed melting point with a sample made from synthetic 3,5-dimethylpyridine.[18]

3-Ethylpyridine.—From the 165–167.5° fraction of bases oily picrates admixed with crystalline 3,5-dimethylpyridine picrate were obtained. After removal of the latter, long yellow needles followed in about two weeks and, after several recrystallizations from alcohol, the melting point 129° agreed with that of 3-ethylpyridine picrate.[19]

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: C, 46.43; H, 3.57; N, 16.67. Found: C, 46.32; H, 3.54; N, 16.56.

In further structural proof, 0.3 g. of the base in 100 cc. of water containing 2 g. of potassium permanganate was allowed to stand three days when the colorless solution was filtered hot and neutralized with acetic acid. On addition of copper acetate, followed by concentration of the solution to a small volume, a deep blue copper salt precipitated. After removal of the copper with hydrogen sulfide and evaporation of the filtered solution, the residue, recrystallized several times from alcohol, melted at 229° in agreement with nicotinic acid.[20]

2,4,6-Trimethylpyridine.—This pyridine was isolated from the 167.5–170° fraction of bases through the following procedure. The mixed bases (20 cc.) in 100 cc. of a saturated alcoholic solution of mercuric chloride containing 10 cc. of concentrated hydrochloric acid were allowed to stand for twelve hours, oily impurities were removed and the residue was dissolved in a small volume of hot alcohol. After twenty-four hours a dense crystalline precipitate separated. On one recrystallization from a saturated solution of mercuric chloride containing 5% hydrochloric acid,[21] and three recrystallizations from very dilute acid, the characteristic needles of the double salt of 2,4,6-trimethylpyridine, $C_8H_{11}N \cdot HCl \cdot 2HgCl_2$ melting at 156° were obtained.

The picrate melting at 155° was prepared and compared in the usual way with a sample made from the synthetic base.[22]

Anal. Calcd. for $C_{14}H_{14}O_7N_4$: N, 16.00. Found: N, 15.89.

2,4-Dimethylpyridine.—The 155–157.5° fraction of bases was treated with mercuric chloride in the way described under 2,4,6-trimethylpyridine. The more soluble mercuric chloride salts thus obtained were recrystallized three times from a mercuric chloride solution containing 5% hydrochloric acid. Since a pure product was not obtained, the bases were liberated in the usual way and converted to picrates. After four recrystallizations, a pure product melting at 182° in agreement with 2,4-dimethylpyridine picrate[11] (pp. 232, 241) was obtained. A mixed melting point with the picrate of the synthetic base[23,12] showed no depression.

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.56.

Investigation of Base Fractions in the 236–280° Boiling Range of O-II and III-A

BY IVY PARKER

Quinoline and Isoquinoline.—The combined 236, 238 and 240° fractions (50 cc.) were dissolved in 75 cc. of 6 *N* hydrochloric acid and extracted with eight successive portions of chloroform. From the aqueous layer 27 cc. of bases was recovered. This material, extracted with 10 cc. of 3.5 *N* sulfuric acid, left undissolved 19 cc., which was treated with an excess of picric acid in alcoholic solution. The precipitate, after extraction with boiling benzene and next with boiling alcohol, was recrystallized from glacial acetic acid, yielding 2.5 g. of a picrate in the form of needles melting at 203°. Identification of this product was effected by a mixed melting point with an authentic sample of quinoline picrate.

Anal. Calcd. for $C_{15}H_{10}O_7N_4$: C, 50.28; H, 2.79; N, 15.64. Found: C, 50.21; H, 2.68; N, 15.74.

For the isolation of isoquinoline, 3 cc. of bases, recovered from the quinoline picrate washings above, was dissolved in 3 cc. of alcohol and fractionally precipitated in 11 stages with successive 3-cc. portions of a saturated solution of picric acid in alcohol. To induce crystallization, it was necessary to seed with a small crystal of isoquinoline picrate. The first eight isoquinoline picrate precipitates, leached out with boiling alcohol, yielded on recrystallization from glacial acetic acid 0.25 g. of light yellow needles melting at 221–222°. The identity of the product was established by a mixed melting point with an authentic sample of isoquinoline picrate.

Anal. Calcd. for $C_{15}H_{10}O_7N_4$: N, 15.64. Found: N, 15.92.

Quinaldine.—After it was found that the 246° fraction, unlike the lower boiling bases, showed phthalone formation, 5 cc. was heated for four hours at 200° with 2 g. of phthalic anhydride and the reaction mixture, after being dissolved in 17 cc. of concentrated sulfuric acid, was poured into 400 cc. of water. From the crude phthalone, admixed phthalic anhydride was sublimed at reduced pressure and the residue, after a leaching out with boiling alcohol, was dissolved in glacial acetic acid and poured into a large volume of water. From the impure product (0.22 g.) which precipitated, a pure phthalone was sublimed[24] in the form of

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(17) This determination is in agreement with 244° reported by Eguchi, ref. 11, pp. 231, 241. Beilstein, 4th ed., Vol. XX, p. 246, gives 228–230°.

(18) E. Durkoff and H. Göttsch, *Ber.*, **23**, 685, 1113 (1890).

(19) C. Stoehr, *J. prakt. Chem.*, [2] **45**, 38 (1892).

(20) A. Ladenburg, *Ann.*, **301**, 152 (1898).

(21) With water the solvent at this stage, an amorphous insoluble salt with an indeterminate decomposition point around 200° also separates and interferes with further purification. This type of salt, encountered in connection with all fractions of bases investigated, is very soluble in dilute acid, even with a high concentration of mercuric chloride, and cannot be converted to a crystalline picrate.

(22) Gattermann, "Die Praxis des organischen Chemikers," 1927, p. 332.

(23) The 2,4-dimethylpyridine used here was obtained as a by-product in the synthesis of 2,6-dimethylpyridine.

(24) E. Jacobson and C. L. Reimer, *Ber.*, **16**, 1082 (1883).

glistening yellow needles melting at 235°. A mixed melting point with an authentic sample of quinphthalone (m. p. 234–235°) showed no depression.

For hydrolysis of the phthalone a 0.5-g. sample was heated in a sealed tube for twenty-four hours with 2 cc. of concentrated hydrochloric acid and from the solution, made alkaline with caustic, an oil was distilled in steam. From the base a picrate was prepared which crystallized from alcohol in rosets of short slender needles melting at 189°. A mixed melting point of 190–191° was obtained with an authentic sample of quinaldine picrate (m. p. 190–192°).

Anal. Calcd. for $C_{16}H_{12}O_7N_4$: N, 15.05. Found: N, 15.18.

Lepidine.—Four fractions of bases (190 cc.) of b. p. 260–270° and with $n^{30}D$ 1.5770–1.5817, were separately fractionated through a Podbielniak column, 4-cc. cuts being collected. The fractions (50 cc.) of b. p. 257–262° and with $n^{25}D$ 1.5785–1.5806 were combined in 68 cc. of 6 *N* hydrochloric acid and carried through cumulative extraction by four successive extractions with 50-cc. portions of chloroform. The bases (32 cc.) from the acid layer were fractionated under reflux at 25 mm. pressure into nine 3-cc. cuts, with a 5-cc. residue. Cuts 1 and 2 were combined, as were also cuts 7, 8 and 9.

Amplified distillation of these fractions with 10 volumes of hydrocarbon oil was carried out under reflux at 20 mm. pressure, a total of 61 4-cc. fractions being collected. The bases were extracted from the hydrocarbon oil with sulfurous acid and directly converted to picrates. Where smears appeared, they were leached out with cold acetic ether. Then the crystalline material was recrystallized successively from alcohol, glacial acetic acid and 50% acetic acid. Nine of the 32 cuts from original fractions 1–2, 3 and 4 yielded a total of only 0.2 g. of a pure picrate melting at 212–213°. This product was identified as lepidine picrate in the usual way by a mixed melting point determination. Lepidine (b. p. 263°) appeared only in the 225–242° (atmospheric pressure) fractions of hydrocarbon fractions from amplified distillation.

Anal. Calcd. for $C_{16}H_{12}O_7N_4$: N, 15.05. Found: N, 15.25.

2,3,8-Trimethylquinoline.[25]—Here a procedure, involving cumulative extraction and amplified distillation, and similar to that employed in search of lepidine was employed on six fractions of bases (45 cc., b. p. 274–279°, $n^{30}D$ 1.5815). In the hydrocarbon fractions of b. p. 259–283°, 2,3,8-trimethylquinoline (b. p. 280°) was suspected. The mixture of picrates obtained was leached out with boiling alcohol and recrystallized from glacial acetic acid. In this way there resulted an apparently pure product crystallizing in characteristic short rods and melting with decomposition at 242–243°. A mixed melting point with an authentic sample of 2,3,8-trimethylquinoline picrate showed no depression.

Anal. Calcd. for $C_{18}H_{16}O_7N_4$: N, 14.00. Found: N, 13.81, 13.98.

Isolation of $C_{11}H_{14}N_2$ Base.—In processing Fractions O-II and O-III, there was encountered in very small amount among the aromatic, petroleum ether soluble bases a product easy to isolate through its difficultly soluble picrate. This picrate of the composition $C_{11}H_{14}N_2 \cdot C_9H_3O_7N_3$ (*cf.* Fig. 3) remained in the residue, after leaching out with benzene, alcohol and glacial acetic acid the complex mixture of picrates obtained in this boiling range. In final purification, it was recrystallized from diacetone alcohol in characteristic glistening plates which darkened at 259° and melted with decomposition at 261–263°.

Anal. Calcd. for $C_{17}H_{17}O_7N_5$: C, 50.62; H, 4.22; N, 17.37. Found: C, 50.38; H, 4.05; N, 17.60.

The base was liberated from the picrate with ammonium hydroxide and extracted with ether. For purification, it was distilled between 187–192° at 34 mm. pressure. It boils at 283° (750 mm.) and has an $n^{30}D$ value of 1.5790. The free base has an unpleasant odor, and on standing in contact with air is converted in part to a white solid which dissolves in potassium hydroxide but is insoluble in ether. Nitrous acid and both alkaline and acid permanganate react with the base in the cold. The analysis along with the decided amphoteric character of this substance is in agreement with an alkylated dihydroquinazoline. The small amount of material available precluded its further study.

Anal. Calcd. for $C_{11}H_{14}N_2$: C, 75.86; H, 8.05; N, 16.09; mol. wt., 174. Found: C, 75.5; H, 7.66; N, 16.33; mol. wt. 167.

Mercuric Chloride Salt.—The base in a slight excess of dilute hydrochloric acid gave with a saturated solution of mercuric chloride a precipitate which was recrystallized from water in rosets of needles. This salt sintered at 153° and melted at 173–174°.

Anal. Calcd. for $C_{11}H_{14}N_2 \cdot HCl \cdot HgCl_2$: N, 5.81. Found: N, 5.84.

Summary

The present investigation was undertaken in order to determine whether in low temperature pyrolysis of a natural product, containing proteins, carbohydrates and fats, products of the same structural types as the *non-aromatic* bases from petroleum distillates would be encountered. Although only negative results, so far as the main objective of this research is concerned, were obtained, it was found that cottonseed meal, in contrast to pure proteins, like egg albumin, casein and serine, yields on destructive distillation basic nitrogen compounds in preponderant amount which are different in three main respects from bases previously obtained from a natural source: *these properties are petroleum ether insolubility, an exceptional tendency to tar formation and an abnormally high nitrogen content.*

From the low boiling fractions pyridine, and seven pyridine homologs, identical with coal tar for shale oil bases, were isolated and in the higher fractions quinoline, isoquinoline, quinaldine, lepidine, the kero base, 2,3,8-trimethylquinoline and

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[25] Originally obtained from California asphalt base petroleum, W. A. King and J. R. Bailey, THIS JOURNAL, **52**, 1245 (1930).

a diazine, $C_{11}H_{14}N_2$, of undetermined structure were isolated.

This research will be concluded with an investigation now in progress on 18 fractions in the boiling range of 172.5–215°, in an effort to explain the abnormally high nitrogen content of these bases, coupled with a progressive exaltation of densities and refractivities from d^{25}_4 0.9514 and $n^{25}\text{D}$ 1.5025 to d^{25}_4 1.0189 and $n^{25}\text{D}$ 1.5375, respectively.

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[CONTRIBUTION FROM DIVISION OF CHEMISTRY, NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

A Phase Rule Study of the Calcium Arsenates[1]

BY G. W. PEARCE AND L. B. NORTON

Calcium arsenate is a product of uncertain composition and variable properties, both in the form of the commercial insecticide and of the so-called pure salt. Although commercial preparations are generally assumed to consist essentially of tricalcium arsenate and an excess of hydrated lime, recent work[2,3,4] has shown that this assumption is inadequate to account for the variations in properties among products of similar gross composition. These variations suggest that other arsenates of calcium are probably present in the products prepared by the usual methods. Since data concerning the identity and the ranges of stability of the calcium arsenates are at present incomplete, a study of the equilibrium conditions in the system $CaO–As_2O_5–H_2O$ has been carried out.

A number of calcium arsenates have been reported in the literature. Smith,[5] in a study of the equilibrium conditions in the more soluble portion of the system, established the existence of two acid salts: monocalcium arsenate, $CaH_4(AsO_4)_2$, and dicalcium arsenate, $CaHAsO_4$. The dicalcium salt has also been prepared and studied by a number of other workers, and is known in the form of the minerals Haidingerite and Pharmacolite. Robinson[6] has reported the preparation of pure tricalcium arsenate, $Ca_3(AsO_4)_2$, from calcium chloride and sodium arsenate. Tartar *et al.*[7] obtained a basic product having the composition $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$, by the repeated hydrolysis of calcium ammonium arsenate and of tricalcium arsenate prepared by Robinson's method.[6] Smith and Murray[8] concluded from complete analyses of a number of commercial preparations, that these products consist mostly of a compound more basic than tricalcium arsenate. Clifford and Cameron,[9] however, considered that some of the calcium arsenates reported were merely solid solutions of calcium oxide and arsenic oxide incidentally having the composition of possible compounds.

Experimental

The experiments were confined to the ranges of compounds more basic than dicalcium arsenate, since the work of Smith[5] on the acid compounds appears quite conclusive. Smith was unable to reach complete equilibrium in a reasonable time in the more basic region of the system at 35°, so a higher temperature was chosen for the present work. Preliminary experiments showed that changes in the system tend to occur more rapidly at higher temperatures, in spite of the decreased solubility of most of the compounds involved. Accordingly, a bath of petroleum oil maintained at 90 ± 0.1° was used for all of the work.

The calcium oxide was prepared by precipitating calcium carbonate from calcium chloride with ammonium carbonate, and igniting the product in an electric muffle furnace. It was found to be free from appreciable amounts of magnesium. Baker C. P. arsenic acid was used without further purification.

All analyses for calcium were made by the precipitation of calcium oxalate and titration with permanganate. Arsenic was determined by distillation as the trichloride and titration with bromate solution.[10] Application of these procedures to samples of pure calcite and of Bureau

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[1] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 136, April 8, 1936.

[2] Pearce, Norton and Chapman, N. Y. Agr. Expt. Sta. Tech. Bull. 234 (1935).

[3] Chapman, Pearce, Dean and Hammer, *J. Econ. Entomol.*, **27**, No. 2, 421 (1934).

[4] Howard and Fletcher, U. S. Bur. Entomol. Paper E-304, mimeographed (1933).

[5] Smith, THIS JOURNAL, **42**, 259 (1920).

[6] Robinson, *J. Agr. Research*, **13**, 281 (1918).

[7] Tartar, Wood and Hiner, THIS JOURNAL, **46**, 809 (1924).

[8] Smith and Murray, *Ind. Eng. Chem.*, **23**, 207 (1931).

[9] Clifford and Cameron, *ibid.*, **21**, 69 (1929).

[10] The bromate method for arsenic in foods [*J. Assoc. Official Agr. Chem.*, **16**, 75 (1933)] was modified by using hydrazine sulfate instead of the ferrous sulfate–sodium bromide mixture as reducing agent.