

ON THE BASIC NITROGEN COMPOUNDS FROM FUSHUN SHALE TAR, I.⁽¹⁾

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The presence of nitrogen compounds in shale tar has long been recognized, but little is known of their chemical nature, owing to the fact that they may be present in tar in an amount rarely exceeding 1% and that the character of the bases would vary according to the conditions of the distillation of the shale, such as the type of retort used, the temperature and the time of heating.

Moreover, in the beginning of the tar industry, the nitrogen constituents of shale or of coal were utilized by transforming them into ammonia, and the use of high temperature in distillation, tends to increase the yield of ammonia at the expense of the basic compounds normally found in the tars, which are for the most part relatively unstable toward heat.⁽²⁾

Since the Great War, the rapid increase in the consumption of gasoline, making heavy demands on pyridine bases as denaturants for the grain alcohol which is used as one of the constituents of some gasoline substitutes, opens the way for scientific researches into the nature of the nitrogenous substances in tars.⁽³⁾

Pyridine and its homologues have already been reported as present in Scottish and American Shale Oils; T. C. Garrett and J. A. Smythe⁽⁴⁾ who worked on the basic constituents extracted from Scottish shale tar, have reported that pyridine, 2-methyl pyridine, 2:6-dimethyl pyridine, 2:4-dimethyl pyridine, 2:5-dimethyl pyridine, 2:3-dimethyl pyridine and 2:4:6-trimethyl pyridine were composed of the "green naphtha," with about a 0.3 per cent. yield by volume.

G. C. Robinson and his co-workers⁽⁵⁾ have confirmed that the bases of the isoquinoline series occurred in basic fractions boiling at 270° and 390°. The basic nitrogen compounds of American shale oil,⁽⁶⁾ especially of the oil of the Colorado field, according to the investigations which are being carried

(1) Contribution from the Scientific Research & Experimental Branch, Imperial Naval Fuel Depot, No. 1.

(2) P. E. Spielmann, "The Constituents of Coal Tar," (1924), 157; R. H. McKee, "Shale Oil" (1925), 116.

(3) E. H. Leslie, "Motor Fuels," (1923), 13 & 482.

(4) *J. Chem. Soc.*, 81 (1902), 449; 83 (1903), 763.

(5) R. H. McKee, "Shale Oil," (1925), 175.

(6) *Ibid.*, p. 120.

out in the Chemical Engineering Laboratories of Columbia University, seem to be composed mostly of pyridine and its homologues, but not of the quino-line or the isoquinoline bases. It is remarkable, though the significance of the basic compounds in the natural product is not immediately apparent, that the majority of the nitrogen compounds in the shale oil are nitrogen-ring compounds, but not substitution products of the aromatic series as we noticed of the nitrogen bases occur in petroleum.⁽¹⁾

The low temperature tar of Fushun coal, according to Y. Oshima and K. Ishibashi,⁽²⁾ contains 0.67% of basic substances and among these substances 2-methyl pyridine, 3:4-dimethyl pyridine and 2:4:6-trimethyl pyridine were confirmed to occur, and the presence of aniline and its homologues were also confirmed. To our interest, the crude tar of Fushun shale has the highest nitrogen base content of any known, viz., 2-4%. It stands in nitrogen content near to Californian petroleum, which is 2.39%.⁽³⁾

The isolation in a pure state of the nitrogenous substances from the Fushun shale oil, and the study of the chemical and physical properties of the purified substances, aroused the writer's interest, in relation to some evidences for the significance of the presence of nitrogenous compounds in tar, which might give some suggestion for the consideration of the mechanism of the chemical processes in the distillation of the shale, and the present investigation was undertaken.

The crude tar used for the experiment was obtained by the distillation of Fushun shales of the composition (A & B) in the vertical retort, the Oakbank Retort, in Scotland, which shows the following properties:⁽⁴⁾

| | A. | B. |
|------------------|--------|--------|
| Water | 3.04% | 2.67% |
| Volatile matter. | 21.05% | 15.89% |
| Fixed carbon. | 4.47% | 1.34% |
| Ash. | 71.41% | 80.10% |

Tar. C=83.80; H=11.53; N=0.45; O=3.63; S=0.59; $d_4^{15}=0.864$.

| | Fractions. | Yield (Vol.) |
|----|-------------|--------------|
| 1. | — 200° | 3% |
| 2. | 200° - 250° | 25% |
| 3. | 250° - 300° | 27% |
| 4. | 300° - 350° | 23% |
| 5. | above 350° | 22% |

600 litres of the crude tar were fractionated under atmospheric pressure

(1) Engler-Höfer, "Das Erdöl," I. (1913), 479.

(2) *J. Soc. Chem. Ind. Japan*, 29 (1923), 445.

(3) C. F. Mabery & L. G. Wesson, *J. Am. Chem. Soc.*, 42 (1920), 1014.

(4) Refer: T. Kimura, *Reports of Invest. (Japanese) Central Lab., South Manchuria Railway Co. Ltd.*, 10 (1925), 507.

TABLE 1.

| Fraction. | Distillate in gr. | $\frac{dw}{dT}$ | d_4^{25} | n_D^{25} | Mol. wt. |
|-----------|----------------------|-----------------|------------|------------|----------|
| 128°-130° | 32.5 | 16.3 | 0.9420 | 1.4970 | 95.4 |
| 130-132 | 8.8 | 4.4 | 0.9441 | 1.4970 | |
| 132-134 | 4.0 | 2.0 | 0.9476 | 1.4963 | |
| 134-136 | 1.5 | 0.8 | | | |
| 136-138 | 2.0 | 1.0 | 0.9376 | 1.4965 | |
| 138-140 | 2.0 | 1.0 | | | |
| 140-142 | 5.0 | 2.5 | 0.9328 | 1.4977 | 103.3 |
| 142-143 | 17.7 | 17.7 | 0.9322 | 1.4979 | |
| 143-144 | 70.0 | 70.0 | 0.9320 | 1.4980 | |
| 144-145 | 44.5 | 44.5 | 0.9330 | 1.4979 | |
| 145-146 | 15.0 | 15.0 | 0.9363 | 1.4973 | |
| 146-148 | 20.0 | 10.0 | 0.9312 | 1.4979 | |
| 148-150 | 11.5 | 5.8 | 0.9367 | 1.4958 | |
| 150-153 | 12.5 | 4.1 | 0.9312 | 1.4962 | |
| 153-156 | 15.3 | 5.1 | 0.9305 | 1.4964 | |
| 156-157 | 9.5 | 9.5 | 0.9265 | 1.4972 | |
| 157-158 | 39.3 | 39.3 | 0.9271 | 1.4969 | 110.0 |
| 158-159 | 104.4 | 104.4 | 0.9260 | 1.4977 | |
| 159-160 | 74.0 | 74.0 | 0.9265 | 1.4977 | |
| 160-161 | 14. | 14 | 0.9312 | 1.4979 | |
| 161-163 | 26 | 13 | 0.9269 | 1.4979 | |
| 163-165 | 26 | 13 | 0.9272 | 1.4975 | 120.0 |
| 165-167 | 18 | 9 | 0.9235 | 1.4975 | |
| 167-169 | 36 | 18 | 0.9214 | 1.4974 | |
| 169-170 | 29 | 29 | 0.9201 | 1.4973 | |
| 170-171 | 70 | 70 | 0.9180 | 1.4976 | |
| 171-172 | 73 | 73 | 0.9185 | 1.4981 | 120.1 |
| 172-173 | 37 | 37 | 0.7202 | 1.4985 | 121.7 |
| 173-174 | 32 | 32 | 0.9213 | 1.4990 | 121.4 |
| 174-175 | 24 | 24 | 0.9240 | 1.4990 | 121.6 |
| 175-176 | 29 | 29 | 0.9242 | 1.4989 | 121.4 |
| 176-177 | 24 | 24 | 0.9271 | 1.4988 | 121.7 |
| 177-178 | 28 | 28 | 0.9268 | 1.4986 | 121.5 |
| 178-179 | 34 | 34 | 0.9241 | 1.4986 | 123.0 |
| 179-180 | 23 | 23 | 0.9237 | 1.4977 | 125.3 |
| 180-182 | 23 | 12 | 0.9186 | 1.4976 | 127.4 |
| 182-184 | 22 | 11 | 0.9194 | 1.4975 | 131.1 |
| 184-186 | 45 | 23 | 0.9145 | 1.4977 | 132.1 |
| 186-187 | 30 | 30 | 0.9133 | 1.4182 | 131.9 |
| 187-188 | 52 | 52 | 0.9173 | 1.4985 | 133.3 |
| 188-189 | 29 | 29 | 0.9178 | 1.4991 | 131.7 |
| 189-190 | 41 | 41 | 0.9191 | 1.4994 | 132.1 |
| 190-191 | 29 | 29 | 0.9183 | 1.4996 | 131.9 |
| 191-192 | 26 | 26 | 0.9212 | 1.5000 | 131.8 |
| 192-193 | 15 | 15 | 0.9249 | 1.5001 | 133.4 |
| 193-194 | 16 | 16 | 0.9258 | 1.5001 | 133.9 |
| 194-196 | 24 | 12 | 0.9251 | 1.5001 | 133.9 |
| 196-198 | 20 | 10 | 0.9285 | 1.5022 | 137.2 |
| 198-200 | 14 | 7 | 0.9313 | 1.5032 | 137.2 |
| 200-202 | 61 | 31 | 0.9261 | 1.5042 | 141.5 |
| 202-204 | 49 | 25 | 0.9268 | 1.5041 | 141.6 |
| 204-206 | 32 | 16 | 0.9257 | 1.5043 | 140.9 |
| 206-208 | 25 | 13 | | 1.5050 | 142.1 |
| 208-210 | 16 | 8 | | 1.5060 | |
| 210-214 | 24 | 6 | | 1.5065 | |
| 214-218 | 29 | 7 | | 1.5086 | |

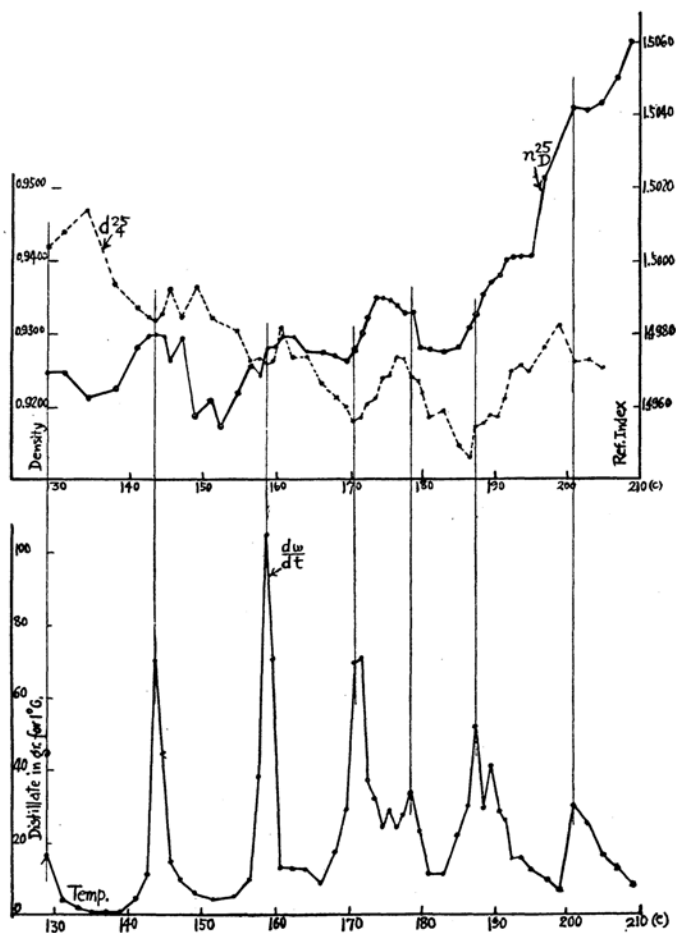


Fig. 1.

and thereby 106 litres of the fraction b. p. 220°–250° were obtained which were used in this experiment, and treated with 30% sulphuric acid to extract the basic substance; the crude base recovered amounted to 3550 c.c., (corresponding to about 0.6% by volume of the crude tar used), and they were distilled out between 100°–280°, and the specific gravity was about 0.979 at 15°. The nitrogen bases occurring in the fraction faintly show pyrrol reactions, but negatively the carbylamine reaction for primary amines and the Liebermann nitroso reaction for secondary amines. The presence of the tertiary bases of the pyridine series is shown in the behavior toward picric acid, ferrocyanic acid and mercuric chloride.

For the isolation of individual bases in an approximately pure state, 1965 gr. of the basic fraction boiling to 220°, was subjected to fractional dis-

tillation; it was fractionated carefully three times in a flask with a Norton & Otten's Six-column dephlegmator of 45 cm. length, and then seven successive fractional distillations through Hempel's glass dephlegmator of 120 cm. length, 2 cm. diameter, which contains 600 glass beads of 4 mm. diameter, the operation was continued at the rate of one or two drops of distillate every two seconds, and the results of the 10th distillation, the weight of each distillate, the ratio of weight and temperature range dw/dt , specific gravity, and index of refraction are shown in Table 1. The temperature-weight curve of the results shown in Fig. 1 shows the seven maxima which indicate the presence of some definite compounds in the regions.

1. 2-Methyl Pyridine.⁽¹⁾ 2-Methyl pyridine which was assumed to be composed of the fraction, b. p. 128° – 130° ; $d_4^{25}=0.9420$; $n_D^{25}=1.4970$, 30 gr. of the fraction dissolved in dilute hydrochloric acid were added to 181 gr. of mercuric chloride dissolved in 2000 c.c. of water, and on standing the solution for a while at 20°C ., 215 gr. of prismatic crystals of the double salt of mercury chloride were deposited. On purifying by recrystallisation twice from a dilute acidic solution, the pure double salt of melting-point 153° – 154° , was isolated, the yield was 180 gr. On analysis, Hg was found to be 69.06%, while theory requires 69.67% for $\text{C}_6\text{H}_7\text{N}\cdot\text{HCl}\cdot 2\text{HgCl}_2$.

To liberate the free base, 60 gr. of sodium hydroxide were added to 180 gr. of the purified salt dissolved in 2000 c.c. of water, the free base extracted with benzene, distilled off the solvent, after fixed with hydrochloric acid, decomposed with caustic soda, dried with fused caustic potash and then distilled. It distilled completely at $129^{\circ}.20$ – $129^{\circ}.25$ under 758.5 mm. and show the following physical constants:

$d_4^{25}(\text{in vacuo})=0.9400$; $n_D^{25}=1.4983$; $n_D^{20}=1.4939$; $n_F^{25}=1.5097$; $n_D^{20}=1.5197$.

0.1320 Gr. of the subst. gave 0.3745 gr. CO_2 and 0.0895 gr. H_2O . 0.2500 Gr. subst. gave 33.0 c.c. N_2 at 25° and 671 mm. (Found: C=77.42; H=7.59; N=15.15; Mol. wt., 93.8. $\text{C}_6\text{H}_7\text{N}$ requires C=77.36; H=7.58; N=15.05%; Mol. wt., 93.1).

It was identified as 2-methyl pyridine by the oxidation of 3 gr. of the purified base with a 2% aqueous solution of 10.4 gr. potassium permanganate, the pyridine-2-carboxylic acid, thus obtained, was purified by converting it into the copper salt with a copper acetate solution. The copper salt, showing the characteristic appearance of the bluish-violet platy crystals of the salt of pyridine-2-carboxylic acid, was analysed for confirmation with the following results:

0.113 Gr. of the salt gave 0.0115 gr. loss on heating, 0.1694 gr. CO_2 , 0.0252 gr. H_2O and 0.0258 gr. CuO . (Found: C=41.53; H=2.53; Cu=18.52;

(1) P. E. Spielmann, "The Const. Coal Tar," (1924), 183.

$\text{H}_2\text{O}=10.33$. $(\text{C}_6\text{H}_4\text{N}\cdot\text{CO}_2)_2\text{Cu}\cdot 2\text{H}_2\text{O}$ requires $\text{C}=41.90$; $\text{H}=2.35$; $\text{Cu}=18.50$; $\text{H}_2\text{O}=10.48\%$).

The free acid isolated from the copper salt shows a reddish yellow colour reaction with ferrous sulphate.

2. 2:6-Dimethyl Pyridine.⁽¹⁾ The fractions (1) b. p. $143^\circ\text{--}144^\circ$; $d_4^{25}=0.9320$; $n_D^{25}=1.4980$; (2) b. p. $144^\circ\text{--}145^\circ$; $d_4^{25}=0.9330$; $n_D^{25}=1.4979$ were regarded as a mixture of mono- and dimethyl pyridine from their physical constants and the molecular weight determination (mean Mol. wt. 103), and 40 gr. of the former fraction and 50 gr. of the latter were combined together, dissolved in a dilute hydrochloric acid solution, to which 250 gr. of mercuric chloride in total were added in several doses and 185 gr. of platy crystals of the double salt were obtained. Purifying twice from the dilute acidic solution, 171 gr. of pure salt of a melting point $191^\circ\text{--}191.5^\circ$ were obtained, which on analysis, agrees in composition with the formula $\text{C}_7\text{H}_9\text{N}\cdot\text{HCl}\cdot\text{HgCl}_2\cdot\text{H}_2\text{O}$. ($\text{Hg}=46.85$; $\text{Cl}=24.61\%$). 170 gr. of the pure salt were decomposed with a concentrated sodium hydroxide solution, and the free base was dried over fused caustic potash and distilled. 39.5 gr. of the pure base, thus obtained, were distilled out completely at $143.85^\circ\text{--}143.87^\circ$ under 757.4 mm.

It was a non-disagreeable odours oil, completely miscible with water at 25° , and showed the following constants:

d_4^{25} (in vacuo) = 0.9183; $n_D^{25}=1.4953$; $n_C^{25}=1.4910$; $n_F^{25}=1.5065$; $n_G^{25}=1.5164$.

0.0967 Gr. subst. gave 0.0738 gr. H_2O and 0.2780 gr. CO_2 . 0.2951 Gr. subst. gave 38.8 c.c. N_2 at 29° and 759 mm. (Found: $\text{C}=78.41$; $\text{H}=8.54$; $\text{N}=13.32$; Mol. wt., 106.5. $\text{C}_7\text{H}_9\text{N}$ requires $\text{C}=78.45$; $\text{H}=4.47$; $\text{N}=13.08\%$; Mol. wt., 107.1)

5 Gr. of the base were oxidized with 35 gr. of potassium permanganate in dilute solution, and dipicolinic acid formed by the oxidation, was obtained, and this was recrystallized from the aqueous solution. The yield was 5.3 gr. It melts at 238.5° , whereas Conrad & Epastein⁽²⁾, and Collie⁽³⁾ have recorded its melting point as 237° and 236° , respectively. The acid recrystallized from boiling alcohol, was found to melt at $226.5^\circ\text{--}227^\circ$, as stated by A. Ladenburg & C. F. Roth⁽⁴⁾ (226°) and also by C. Paal and C. Demeler⁽⁵⁾, ($226^\circ\text{--}227^\circ$) for the melting point of the same acid.

On analysis of the acid with m. p. 226° , the results obtained were:

0.1008 Gr. subst. gave 0.1858 gr. CO_2 and 0.0278 gr. H_2O . (Found: $\text{C}=50.27$; $\text{H}=3.09$. $\text{C}_6\text{H}_3\text{N}(\text{CO}_2\text{H})_2$ requires $\text{C}=50.28$; $\text{H}=3.02\%$)

(1) P. E. Spielmann, loc. cit., P. 187.

(2) *Ber.*, 20 (1887), 162.

(3) *J. Chem. Soc.*, 59 (1891), 177.

(4) *Ber.* 18 (1885), 52.

(5) *Ibid.*, 30 (1897), 1502.

3. **2:4-Dimethyl Pyridine.**⁽¹⁾ Both of the two fractions (1) b. p. 158°–159°; $d_4^{25}=0.9260$; $n_D^{25}=1.4977$, (2) b. p. 159°–160°, $d_4^{25}=0.9265$; $n_D^{25}=1.4977$, seem to be a mixture of lutidines and collidines as indicated by the mean molecular weight 110. To isolate the lutidine-2:4-dimethyl pyridine, in a pure state, the mixed oil derived from 55 gr. of the first fraction, and 55 gr. of the second, dissolved in a dilute hydrochloric acid solution, was added to the solution of 544 gr. of mercuric chloride dissolved in 8 litres of hot water. Long needle crystals (m. p. 124°) of glasswool-like lustre were deposited, recrystallized twice from hot water, and 240 gr. of the pure double salt of mercuric chloride with a melting-point of 131°–132° were obtained. It gave $Hg=57.17$, on analysis, which corresponds to $Hg=56.94$ for $C_7H_9N \cdot HCl \cdot 2HgCl_2 \cdot H_2O$. 210 gr. of the salt were decomposed with 600 c.c. of a 10% caustic soda solution, and 30.5 gr. of a colourless base were separated, and this was dried with fused caustic potash and distilled.

It distilles completely at 157°.83–157°.85 under 758 mm., and dissolves in an equal quantity of water at 35° and shows these constants:

d_4^{25} (in vacuo) = 0.9271; $n_D^{25}=1.4984$; $n_C^{25}=1.4942$; $n_F^{25}=1.5095$; $n_G^{25}=1.5190$.

0.1184 Gr. subst. gave 0.3392 gr. CO_2 and 0.0915 gr. H_2O . 0.3319 Gr. subst. gave 40.2 c.c. N_2 at 33° and 760 mm. (Found: C=78.13; H=8.65; N=13.27; Mol. wt., 106.5. C_7H_9N requires C=78.45; H=8.47; N=13.08%; Mol. wt., 107.1)

The base was identified as 2:4-dimethyl pyridine by oxidation, 4 gr. of the base with an aqueous solution of 28 gr. potassium permanganate, and the dicarboxylic acid obtained by the oxidation was converted into the copper salt with copper acetate, which was separated into two crops by their solubility in water, the one being cobalt-coloured crystals which are insoluble in water, and the other bluish green crystals, more soluble in water than the former, and the yield is 2.3 gr. and 3.1 gr., respectively.

On analysis 0.1024 gr. of the former salt gave 0.1496 gr. CO_2 , 0.0264 gr. H_2O and 0.0192 gr. CuO . (Found: C=39.84; H=2.89; Cu=15.21. $(C_5H_3N \cdot CO_2H \cdot CO_2)_2Cu \cdot H_2O$ requires C=40.61; H=2.44; Cu=15.37%)

The free acid recovered from the copper salt by means of hydrogen sulphide gas, shows the melting point (244°) of 2:4 lutidinic acid.

The second copper salt also gave 2:4 lutidinic acid with a m. p. of 247° and the analytical results of the free acid and its copper salt, agree well with those of the acid mentioned in the literature.

0.1665 Gr. subst. gave 0.0131 gr. loss on heating at 96° for 4 hours, and 0.0533 gr. CuO . (Found: Cu=27.76. $C_5H_3N \cdot (CO_2)_2Cu \cdot H_2O$ requires Cu=27.81 %).

(1) P. E. Spielmann, loc. cit., p. 186.

0.1002 Gr. free acid gave 0.0103 gr. loss on heating at 110° for 3 hours. 0.0873 Gr. dried acid gave 0.1623 gr. CO_2 and 0.0250 gr. H_2O . (Found: $\text{C}=50.70$; $\text{H}=3.28$. $\text{C}_6\text{H}_3\text{N}(\text{CO}_2\text{H})_2 \cdot \text{H}_2\text{O}$ requires 10.28 % of the water of crystallization).

4. 2:6-Methyl Ethyl Pyridine. The mother liquor separated from the crystals of the double salt of mercuric chloride of 2:4 dimethyl pyridine hydrochloride, remains on concentration a colourless oily salt which liberates a base of disagreeable odour, even when the salt is diluted with water. The free base which is composed mostly of methyl ethyl pyridine with some dimethyl pyridine, was treated in a benzene solution with picric acid to remove the latter base completely from the former by converting it into picrate which is slightly soluble in solvents and methyl ethyl pyridine was isolated in a free state from the amorphous picrate which remained in the mother liquor separated from dimethyl pyridine picrate in an benzene solution. The yield is 10 gr. and in consequence of the small quantity of the substance no accurate reading of the boiling point was possible; it distiles at 160° – 161° und 760 mm., dissolves in 55 times of water at 30° , and shows the following constants: $d_4^{25}=0.9207$; $n_D^{25}=1.4950$; $n_C^{25}=1.4908$; $n_F^{25}=1.5057$; $n_D^{20}=1.5151$.

0.1073 Gr. subst. gave 0.3114 gr. CO_2 and 0.0881 gr. H_2O . 0.3537 Gr. subst. gave 36.2 c.c. N_2 at 29° and 759 mm. (Found: $\text{C}=78.93$; $\text{H}=9.19$; $\text{N}=11.56$; Mol. wt., 118. $\text{C}_8\text{H}_{11}\text{N}$ requires $\text{C}=79.27$; $\text{H}=9.16$; $\text{N}=11.57\%$; Mol. wt., 121.1)

The base was confirmed as 2:6-methyl ethyl pyridine, by oxidation of 2.5 gr. of the base with 27 gr. potassium permanganate, the free dicarboxylic acid purified from the copper salt isolated from the oxidation product was found to melt at 227° .

5. 2:4:6: Trimethyl Pyridine. For isolation of this base in a pure state, two fractions, 50 gr. of one fraction with a b.p. of 170° – 171° ; $d_4^{25}=0.9180$; $n_D^{25}=1.4976$; Mol. wt. 120, and 50 gr. of the other with a b.p. of 171° – 172° ; $d_4^{25}=0.9185$; $n_D^{25}=1.4981$: Mol. wt. 120, combined together and treated with a mercuric chloride solution, and collected a crop of platy crystals with a m.p. of 156° deposited on each addition of the mercuric chloride. The yield was 240 gr. On purifying, 205 gr. of the crystals melting at 157° – 157.5° were obtained, and these gave $\text{Hg}=56.71$ ($\text{C}_8\text{H}_{11}\text{N} \cdot \text{HCl} \cdot 2\text{HgCl}_2 \cdot 1/2\text{H}_2\text{O}$ requires $\text{Hg}=56.54\%$).

The free base isolated in pure state from 200 gr. of the purified salt as usual amounted to 32.5 gr. It distils completely at 170.47° – 170.51° under 762.3 mm. and has a nondisagreeable characteristic odour. It dissolves in 30 times of water at 20° and shows the following constants:

d_4^{25} (in vacuo)=0.9101; n_D^{25} =1.4959; n_C^{25} =1.4919; n_F^{25} =1.5069; $n_{D'}^{25}$ =1.5164.

0.1055 Gr. subst. gave 0.3061 gr. CO_2 and 0.0862 gr. H_2O . 0.3150 Gr. subst. gave 32.0 c.c. N_2 at 25° and 767 mm. (Found: C=79.13; H=9.15; N=11.75, Mol. wt., 121.8. $\text{C}_8\text{H}_{11}\text{N}$ requires C=79.27; H=9.16; N=11.57%; Mol. wt., 121.1).

For identification of the base to be 2:4:6-trimethyl pyridine, 5 gr. of the purified base were oxidized with an aqueous solution of 53 gr. of potassium permanganate, and pyridine-2:4:6 tricarboxylic acid resulted by oxidation of the base purified from its silver salt, was found to melt at $227^\circ.5$. The yield was 5.3 gr.

0.1000 Gr. subst. gave 0.1441 gr. CO_2 and 0.0341 gr. H_2O . (Found: C=39.30; H=3.82. $\text{C}_6\text{H}_2\text{N}(\text{CO}_2\text{H})_3 \cdot 2\text{H}_2\text{O}$ requires C=38.85; H=3.61%).

The nitrogeous substances were isolated by extraction from the fraction b.p. 220° – 250° , of Fushun shale oil by dilute sulphuric acid, liberation with alkali, drying and fractionation. Each fraction is treated in its dilute hydrochloric acid solution with mercuric chloride, from which the bases were separated as a double salt of mercuric chloride, purified from the dilute acid solution, and finally they were again liberated in a free state by alkali, and distilled. 2-Methyl pyridine, 2:6-dimethyl pyridine, 2:4-dimethyl pyridine, 2:6-methyl ethyl pyridine and 2:4:6-trimethyl pyridine were proved to occur in the tar and identified by oxidation with a potassium permanganate solution, transforming them to the corresponding carboxylic acids.

The writer's samples which were isolated from the shale tar were in a highly purified state and no work of preparation of such highly purified bases of the pyridine series has been described except that of J. G. Heap, W.I. Jones and J.B. Speakman.⁽¹⁾ They prepared the bases of the pyridine series from tar by fractionation and purification through the zinc chloride compounds.

In the following table, the physical constants of the writer's samples are shown with those of the bases of the pyridine series obtained by other chemists.⁽²⁾

(1) *J. Am. Chem. Soc.*, **43** (1921), 1926.

(2) K. V. Auwers & R. Kraul, *Z. physik. Chem.*, **116** (1925), 448; Landolt-Börnstein-Roth, "Tabellen."; "International Critical Tables." I.; T. C. Garrett and J. A. Smythe Loc. cit.

TABLE 2.

| | Pyridine | 2-Methyl Pyridine | 2-6-Dimethyl Pyridine | 2-4-Dimethyl Pyridine | 2-6-Methyl- ethyl Pyridine | 2-4-6-Trim- ethyl Pyridine |
|------------------------------|------------------------|----------------------|--------------------------|--------------------------|-------------------------------|-------------------------------|
| b. p. | (1) 115°-6° | 129°5 (763 mm.) | 142°5 | 159°-5° | — | 170°5 (763 mm.) |
| | (2) 115°3 (760 mm.) | 128°-9° (760 mm.) | 137°5 (about) | 157°1 (760 mm.) | — | — |
| | (3) 115°3 (760 mm.) | 129°3 (759 mm.) | 143°9 (758 mm.) | 157°9 (758 mm.) | 160°-1° | 170°5 (762 mm.) |
| d ₄ ²⁵ | (2) 0.9776 | 0.9404 | 0.9200 | 0.9273 | — | — |
| | (3) — | 0.9400 | 0.9183 | 0.9271 | 0.9207 | 0.9101 |
| n _C ²⁵ | — | 1.4939 | 1.4910 | 1.4942 | 1.4908 | 1.4919 |
| n _D ²⁵ | — | 1.4983 | 1.4953 | 1.4984 | 1.4950 | 1.4959 |
| n _F ²⁵ | — | 1.5097 | 1.5065 | 1.5095 | 1.5057 | 1.5069 |
| n _G ²⁵ | — | 1.5197 | 1.5164 | 1.5190 | 1.5151 | 1.5164 |
| Ma | 23.89 | 23.82 | 33.77 | 33.64 | 38.08 | 38.60 |
| MD | 24.04 | 29.04 | 34.02 | 33.88 | 38.36 | 38.86 |
| Mβ | 24.55 | 29.60 | 34.67 | 34.52 | 39.06 | 39.59 |
| Mγ | 24.96 | 30.09 | 35.24 | 35.06 | 39.67 | 40.22 |
| Mγ-Ma | 1.07 | 1.27 | 1.47 | 1.42 | 1.59 | 1.62 |
| Mβ-Ma | 0.66 | 0.78 | 0.90 | 0.88 | 0.98 | 0.99 |
| (C) | -1.44 | -0.82 | -0.51 | -0.58 | -0.42 | -0.25 |
| „ | — | -0.90 | -0.43 | -0.56 | -0.60 | -0.18 |

(1) F. C. Garrett and J. A. Smythe, loc. cit.

(2) J. G. Heap, W. I. Jones and J. B. Spielman, loc. cit.

(3) Writer.

(A) & (B) Landolt, Börnstein-Roth: Tabellen.

(C) K. V. Auwers & R. Kraul; *Z. Physik. Chem.*, **116** (1925), 448.

As will be seen in the forgoing table, the molecular refractive power and the dispersive power of the bases for the α , β and γ hydrogen lines and also the sodium D line have been determined, since Brühl⁽¹⁾ has already shown that these physical constants offer an excellent means of determining the structure of organic compounds, especially as dispersive power is more readily influenced by constitution than refractivity.

The average value for the refractive effect of the hydrogen lines α , β , γ and the sodium D line of the CH₂ group which combined with the α or γ position of the pyridine nucleus, has been calculated,⁽²⁾ and the increment for the α position compared with the γ position varies about 0.13 to 0.18.

(1) *Z. physik. Chem.*, **7** (1891), 140; **16** (1895), 201; **79** (1912), 481.(2) Refer: K. V. Auwers and R. Kraul, *Ibid.*, **116** (1925), 448; *Ber.*, **57** (1924), 457.

There is no doubt that the effect of CH_2 depends to a certain extent on the position by which it combines with the carbonatom of the pyridine nucleus of the compounds, and it was able more exactly to elucidate the constitutive nature of the properties in the molecular dispersive power than in the molecular refractive power.

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