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

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It is very clear, from the previous paper,(2) that the light fraction from Fushun shale tar, consists, for the greater part, of the basic compounds of the pyridine series, being rich in the α and γ alkyl derivatives. A complete chemical examination should be made of the bases in order to get more precise knowledge of the constituents, and to find more satisfactory data on the constants of the pyridine bases by isolating them in a state of purity, since the data which have been reported for these compounds are often regarded as contradictory in their discordancies, and many even of the simple derivatives are still left awaiting identification, notwithstanding, that a great deal of work in that field has been set forth in the literature.(3)

4-Methylpyridine. The presence of 4-methylpyridine in coal tar has already been recognized by K. E. Schulze,(4) A. Ladenburg,(5) O. Flaschner,(6) and many others but the fact seems to have been left alone by workers on the shale tar bases. The procedure followed in the preparation of this base has been, as in the case of other lower members of pyridine series, generally carried out by first refining the characteristic double salts of mercury or zinc-chloride, and then by regenerating and drying the free base. The mercuric chloride-method, however, includes much difficulty in the separation of the 3- and 4-methylpyridines in their fractions, for no marked features which might be utilised in such a practice, are recognized between them. Attempts were made to isolate 4-methylpyridine from the mixture of 2 : 6-dimethyl, 3-, and 4-methylpyridines by the aid of mercuric chloride but proved unsuccessful so far as the writer's experiments were concerned.

The base was accordingly treated successively with an insufficient amount of picric acid in alcohol, the crystallization being performed in a

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(1) Contribution from the Scientific Research & Experimental Branch, Imperial Naval Fuel Depot, No. 2.

(2) This journal, **2** (1927), 176.

(3) V. Meyer & P. Jacobson, "Lehrbuch d. organ. Chem.", II, 3, p. 782–1047 ; N. V. Sidgwick, "The Organic Chemistry of Nitrogen", (1910); P. E. Spielmann, "The Constituents of Coal Tar", (1924) ; R. H. McKee, "Shale Oil", (1925); C. Hollins, "The Synthesis of Nitrogen Ring Compounds", (1924); A. R. Warnes, "Coal Tar Distillation and Working up of Tar Products", (1923).

(4) *Ber.*, **20** (1887), 411.

(5) Ibid., **21** (1888), 287.

(6) *J. Chem. Soc.*, **95** (1909), 668.

thermostat with very great caution. Three kinds of picrate were formed; (1) a dark yellow rhombic thick plate, m.p. 160°–162°, (2) a light yellow thin plate, m.p. about 155°, (3) a dark yellow prism, m.p. about 125°, which appeared in the last stage. On recrystallizing the picrate (2) from boiling alcohol, flat needles, gathering in tufts, grew to several mm. in length showing a m.p. of 165°; 44 gr. of the picrate again recrystallized from 600 c.c. of boiling ethyl alcohol, 41 gr. of a very slender prism with a m.p. of 167° resulted, which remained constant after further recrystallization. The base regenerated from 40 gr. of the purified picrate was dried over fused potash. **yield 10.9 gr.**

The base resembles 2:4-dimethylpyridine in odour, and is completely miscible with water at room temperature. It distils completely at 145.45°–145.47° under 763.9 mm. The physical constants are; $d^{25}_{4}=0.9502$ (in vac.); $n^{25}_{D}=1.5029$; $n^{25}_{C}=1.4986$; $n^{25}_{F}=1.5143$; $n^{25}_{G'}=1.5240$.

0.1115 Gr. subst. gave 0.0756 gr. H_2O & 0.3165 gr. CO_2. 0.1753 Gr. subst. gave 22.5 c.c. N_2 at 18° & 761 mm. (Found: C=77.42; H=7.59; N=15.08. C_6H_7N requires C=77.36; H=7.58; H=15.05 %)

The base was identified as 4-methylpyridine from its oxidation product being proved to be isonicotinic acid; 1.7 gr. of the base was oxidised with 6 gr. of potassium permanganate; the filtrate from manganese oxide was treated with copper acetate after being neutralised with dilute sulphuric acid and 1.7 gr. of a blue microscopic crystalline powder deposited. Analysis shows: Found: C=38.09; H=4.53; Cu=16.69. $(C_5H_4N\,CO_2)_2Cu.4H_2O$ requires C=37.92; H=4.25; Cu=16.74 %.

The free acid from the salt, recrystallized from water, has a m.p. of 315° when rapidly heated, but all sublimes without melting when slowly heated in a capillary. It has no colour reaction with ferrous sulphate.

0.1055 Gr. free acid gave 0.0395 gr. H_2O & 0.2256 gr. CO_2. (Found: C = 58.32; H = 4.19. $C_5H_4N.COOH$ requires C = 58.51; H = 4.10 %).

Some salts of the base were examined: $C_6H_7N{\cdot}HCl{\cdot}AuCl_3$—slightly sol. in cold, but moderately in hot water, m.p., 218°; $C_6H_7N{\cdot}HCl{\cdot}2HgCl_2$—needles; m.p., 130°.

3–Methylpyridine. 3–Methylpyridine is a possible constituent of various kinds of tar bases and has many records of being isolated⁽¹⁾ from them and synthesised.⁽²⁾

In view of the observations made during the investigation, mercuric

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(1) H. Weidel, *Ber.*, 12 (1879), 2008; J. Mohler, ibid., 21 (1888), 1009; O. Flaschner, *J. Chem. Soc.*, 95 (1909), 668; J. G. Heap, W. I. Jones & J. G. Speakman, *J. Am. Chem. Soc.*, 43 (1921), 1936.

(2) E. Zanoni, *Ber.*, 15 (1882), 528; L. Storch, ibid., 19 (1886), 2456; P. Schwarz, ibid., 24 (1891), 1676.

chloride is not recommendable for isolation of the base in a pure state, as is the case with γ–picoline, because the work does not always prove successful. The purification, therefore, was carried out as in the preceding experiment with picrate.

The melting-point of picrate (3) written in the former section was raised to 149° by repeated crystallizations in alcohol, which in total, amounted to 41.5 gr.

The base regenerated and dried over fused potash was 11.3 gr. It has somewhat a sweetish odour and completely distils at 144.17°–144.18° under 763.0 mm. pressure, and shows $d_4^{25}=0.9518$ (in vac.); $n_D^{25}=1.5038$; $n_C^{25}=1.4994$; $n_F^{25}=1.5155$; $n_{G'}^{25}=1.5256$.

It yields the following double salts with metallic chlorides :

$(C_6H_7N\cdot HCl)_2PtCl_4$,	m.p., 208°.
$C_6H_7N\cdot HCl\cdot AuCl_3$,	a pale yellow fibre, melts at 187°.
$C_6H_7N\cdot HCl\cdot HgCl_2$,	long needles melting at 145°–146°.
$C_6H_7N\cdot HCl\cdot 2HgCl_2$,	m.p., 146°.
$C_6H_7N\cdot HCl\cdot 3HgCl_2$,	produced when treated with excess of $HgCl_2$, white granular crystalls with a m.p., 170°.

The base was proved to be 3-methylpyridine by the analysis of the base and its oxidation products, as follows :

0.1025 Gr. base gave 0.0700 gr. H_2O & 0.2901 gr. CO_2. 0.1851 Gr. base gave 23.6 c.c. N_2 at 17° & 761 mm. (Found : C=77.19 ; H=7.65 ; N=15.04. C_6H_7N requires C=77.36 ; H=7.58 ; N=15.05%).

The base (1.4 gr.) was oxidised with the calculated amount of potassium permanganate (5 gr.) ; the free nicotinic acid crystallizes from hot water in a white mass, has no colour reaction with ferrous sulphate, partly, sublimes without decomposition and has a m.p. of 236°.

0.1050 Gr. subst. gave 0.2250 gr. CO_2, & 0.0397 gr. H_2O. (Found : C=58.44 ; H=4.23. Theory : C=58.51 ; H=4.10%).

The copper salt was a bright blue crystalline powder, and gave on analysis,

C=45.83 ; H=2.78 ; Cu=20.77. $(C_5H_4N\cdot CO_2)_2\cdot Cu$ requires C=46.81 ; H=2.62 ; Cu=20.66%.

2:3–Dimethylpyridine. F. C. Garrett and J. A. Smythe⁽¹⁾ have already proved the existence of this base in Scottish shale oil by isolating it with the aid of mercuric chloride in a certain grade of purity.

The method of procedure described in their report, however, is not appropriate in this case for getting it free from other isomers such as 2:5–dimethylpyridine, etc., owing to difficulty in obtaining it in a definite form

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

with mercuric chloride. The picric acid method, in this respect, is superior to the mercuric chloride method in handling such bases.

The procedure for the isolation of this base from the fraction, b.p. 158°–160°, in which 2:4–lutidine and 2:6–collidine had been found, is briefly described below.

The fraction was dissolved into ten parts of hot alcohol. It yielded immediately a light yellow crystalline powder on adding picric acid dissolved in hot alcohol; and next, with some picric acid, gave partly the same crystals and partly flat needles. The former picrate has a m.p. of 188° after recrystallization from an excess of boiling alcohol. The free base regenerated from the picrate is a colourless liquid with a faint characteristic odour, soluble in 10 parts of water at 23°. It completely distils at 160.7° under 760 mm. The constants are: $d_4^{25}=0.9419$; $n_D^{25}=1.5057$; $n_C^{25}=1.5014$; $n_F^{25}=1.5172$; $n_{G'}^{25}=1.5272$.

It was identified as 2:3–dimethylpyridine by analysis and by converting into quinolinic acid by oxidation.

0.1794 Gr. of the base gave 20.4 c.c. N_2 at 25°.0 & 762 mm. (Found: N=13.05. C_7H_9N requires N=13.08%).

It yields a double salt with mercuric chloride, $C_7H_9N \cdot HCl \cdot 6HgCl_2$ m.p. 194°.

The acid obtained in a free state from its copper salt shows an orange-red colour with ferrous sulphate, and a m.p. of 247° when slowly heated in a capillary, but by rapid heating sinters at about 190° and then melts at 233°.

0.1385 Gr. subst. gave 0.0386 gr. H_2O & 0.2575 gr. CO_2. (Found: C=50.71; H=3.12. Theory: C=50.28; H=3.02%).

2:5–Dimethylpyridine.(1) During the course of the fractional crystallization, shown in the foregoing section, the writer obtained flat needles, to a fair amount, after a powdery picrate of 2:3–dimethylpyridine had been removed, and this, on decomposing with an alkali, gave quite a different odour from those of the dimethylpyridines described above, but rather resembling that of β–picoline, which in connection with the odours of the β–methylpyridines affords some idea, that it might be 2:5–dimethylpyridine.

Twenty three grams of the pure salt with a m.p. of 167° obtained by repeating the recrystallization from hot alcohol, yielded 5 gr. of the free base.

It is a colourless liquid with a sweetish odour, less pungent than β–picoline. It boils constantly at 156.82°–156.88° under 759.1 mm. and is soluble in 12 parts of water at 23°. The physical constants are: $d_4^{25}=0.9261$ (in vac.); $n_D^{25}=1.4982$; $n_C^{25}=1.4939$; $n_F^{25}=1.5095$; $n_{G'}^{25}=1.5194$.

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(1) G. Lunge & J. Rosenberg, *Ber.*, **20** (1887), 134; F. C. Garrett, & J. A. Smythe, *J. Chem. Soc.*, **81** (1902), 453.

It yields the salts: $(C_7H_9N{\cdot}HCl)_2PtCl_4$ (214°); $C_7H_9N{\cdot}HCl{\cdot}6HgCl_2{\cdot}H_2O$ (203°).

The base was noticed to be the same compound as the 2:5–dimethylpyridine, which were synthesised by G. Errera,(1) and for comfirmation it was analysed and then oxidized by the usual method to isonicotinic acid.

0.1071 Gr. subst. gave 0.0826 gr. H_2O & 0.3070 gr. CO_2. 0.1838 Gr. subst. gave 20.6 c.c. N_2 at 21° & 763 mm. (Found: C=78.18; H=8.64; N=13.07. C_7H_9N requires C=78.45; H=8.47; N=13.08%).

The free acid recovered from the copper salt of pale blue colour, is almost insoluble in cold water, slightly in hot, but more soluble in hot hydrochloric acid. When recrystallized from dilute hydrochloric acid it melts at 254°, while from boiling alcohol, it melts at 238° (with decomposition).

The free acid on analysis, responded as a pyridine-dicarboxylic acid with one mol of the water of crystallization.

0.1129 Gr. of the free acid lost 0.0105 gr. on drying. 0.1024 Gr. of the dried acid gave 0.0295 gr. H_2O & 0.1869 gr. CO_2. (Found: C=49.78; H=3.23; combined water=9.30. $C_7H_5O_4N{\cdot}(H_2O)$ requires C=50.27; H=3.02; combined water=9.74%).

3:5–Dimethylpyridine.(2) The presence of 3:5–dimethylpyridine in a coal tar base, has already been proved by F. B. Ahrens(3) and his co-workers.

The writer has also succeeded in isolating it, with the aid of picric acid, from the fraction b. p. 170°–172° of shale tar base in a pure state. The base which was isolated from the picrate has a faint odour somewhat resembling horse urine and β–picoline. The physical constants of the dried base are: b. p. 171.6° (760 mm.); $d^{25}_{4}=0.9385$; $n^{25}_{D}=1.5032$; $n^{25}_{C}=1.4988$; $n^{25}_{F}=1.5146$; $n^{25}_{G'}=1.5244$.

0.1033 Gr. subst. gave 0.0771 gr. H_2O & 0.2964 gr. CO_2. (Found: C=78.37; H=8.36. C_7H_9N requires C=78.45; H=8.47%).

The base yields by oxidation, nicotinic acid which melts at 327°.

0.1097 Gr. subst. gave 0.2016 gr. CO_2 & 0.0313 gr. H_2O. (Found: C=50.12; H=3.19. $C_7H_5O_4N$ requires C=50.28; H=3.02%).

3:4–Dimethylpyridine. In view of certain relations between the chemical structure of compounds and their physical constants being symphonious, the data exhibited by the series of pyridine homologues which the writer has isolated in a highly pure state, are likely to be of value in affording excellent examples, especially in offering a distinct regularity displayed by the boiling points; that is, if the hydrogen atom combined with the α–position of pyridine is replaced by a methyl group, the rise of the boiling-point is approxi-

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(1) G. Errera, *Ber.*, **34** (1901), 3691.

(2) E. Dürkopf & H. Gottsch, *Ber.*, **23** (1890), 1113.

(3) Ibid., **37** (1904), 2064.

mately one-half as compared with that of the β or γ–methyl derivative. 3:4–Dimethylpyridine, which is the only one left awaiting identification among the theoretical dimethylpyridines, as the others have been already isolated in a pure state by the writer, was discovered by pursuing it in the fraction of b.p. 178°–180°, with the expectation that the boiling point would not be lower than that of 3:5–dimethylpyridine, though we find it lower than that in the literature.⁽¹⁾

The fractions boiling at 177°–178° (25 gr.) and at 178°–179° (30 gr.) were treated with the calculated amount of picric acid in boiling methyl alcohol and slowly cooled, producing three kinds of crystals, which separated mechanically into

(1) upper crop of needles or prisms, m.p. 114°,
(2) middle crop of aggregates of small needles, m.p. 120°–140°, and
(3) bottom crop of prisms, m.p. about 163°.

The picrate which has a m.p. of about 163° was the main product in each case, and 19.4 gr. of the pure salt of m.p. 163° by recrystallizing twice from methyl alcohol were obtained.

The free base is a colourless liquid with a faint aromatic odour, soluble in 20 parts of water at 22°, and distilling completely at 178.82° under 759 mm., and yields the following salts:

$(C_7H_9N{\cdot}HCl)_2PtCl_4$,	orange-red prism, m.p. 276° (decomp.)
$C_7H_9N{\cdot}HCl{\cdot}3HgCl_2{\cdot}2H_2O$,	slender needles, easily soluble in hot, but only slightly in cold water, (Hg. found 60.66 ; theory 60.72 ; m.p. 130.5°–131°)
$C_7H_9N{\cdot}HCl{\cdot}AuCl_3$,	fern-like crystals, m.p. 187°.

It gave the constants: $d^{25}_{4}=0.9537$ (in vac.); $n^{25}_{D}=1.5099$; $n^{25}_{C}=1.5055$; $n^{25}_{F}=1.5209$; $n^{25}_{G'}=1.5305$.

The base was identified as 3:4–dimethylpyridine, by analysis of the base and also by the oxidation to cinchomeronic acid with a m.p. of 265°–266°.

0.1016 Gr. of the base gave 0.0766 gr. H_2O & 0.2920 gr. CO_2. 0.1512 Gr. of the base gave 17.6 c.c. N_2 at 24° & 758 mm. (Found: C=78.38; H=8.44; N=13.09; mol. wt.=108.6. C_8H_9N requires C=78.45; H=8.47; N=13.08%; mol. wt.=107.1).

0.1081 Gr. of the free acid gave 0.0306 gr. H_2O & 0.1997 gr. CO_2. (Found: C=50.38; H=3.17. $C_5H_3N{\cdot}(CO_2H)_2$ requires C=50.28; H=3.02%).

2:4–Methyl-ethylpyridine.⁽²⁾ In the fraction of 178°–180°, the writer has found 2:4–methylethylpyridine presumably together with 2:6–parvoline from an amorphous picrate.

The fraction, which removed 3:4–dimethylpyridine etc. by means of

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(1) *Ber.*, **29** (1896), 2996.

(2) H. Weidel & B. Pick, *Ber.*, **18** (1885), Ref. 117; M. Schultz, ibid., **20** (1887), 2720.

picric acid in alcohol, consisted mostly of a base forming an oily picrate. The oily picrate contaminated with crystalline picrates was separated mechanically from the latter after standing in an open vessel for six months in a dark and cool place.

The base recovered from the oily picrate was about a half of the original sample in the fraction of 178°–180°, and is a colourless liquid with a highly disagreeable odour incomparable to those of the methylpyridines, and soluble in water to a slight degree. The constants are: b.p.=179°–180°; $d^{25}_{D}=0.9130$; $n^{25}_{D}=1.4953$.

The main portion of the base was considered to be 2:4–methylethylpyridine on the whole, as it was oxidised to a lutidinic acid with a m.p. of 246°, though the results of combustion and mean molecular weight determination slightly exceeded the values for collidine.

Found: C=79.42; H=9.37; mol. wt.=126. C_7H_9N requires C=79.27; H=9.16%; mol. wt.=121.

Found: C=45.03; H=3.96. $C_7H_5O_4N \cdot H_2O$ requires C=45.39; H=3.81%.

2:3:6–Trimethylpyridine. If an idea which is based on the fact that the methyl group attached to the carbon atoms of the pyridine nucleus has some definite effects upon the boiling points of the methyl derivatives of pyridine, be extended to the higher members of the series, the boiling point of 2:3:6–trimethylpyridine would be considered to stand near with that of 2:4:6–trimethylpyridine which is the main constituent in the fraction b.p. 170°–172°. The attempt, therefore, was advanced to find it out in that fraction which, after the most of the 2:4:6–trimethylpyridine had been removed with mercuric chloride, was found to consist of a mixture of the bases when they were regenerated from the double salts. The bases which were recovered from the salts were colourless liquids with highly disagreeable odour which produced three kinds of crystalline picrates on treating them successively with an insufficient amount of picric acid in alcohol, viz.,

(1) light yellow needles of 2:4:6–trimethylpyridine picrate, m.p. 156°,
(2) a powdery picrate of 3:5–dimethylpyridine with a m.p. of 241°,
(3) a large hexahedron, orange in colour, easily crystallizable from alcohol, m.p., about 147°, with a yield of 48 gr.

The third picrate was purified twice from boiling methyl alcohol, yielding 41 gr. of the salt with a m.p. of 147°–148°.

The base regenerated from the salt by usual method and dried over fused potash, boils at 172.88°–172.90° under 761.2 mm., and is soluble in 32 parts of water at 26°.

The constants are: $d^{25}_{4}=0.9220$ (in vac.); $n^{25}_{D}=1.5018$; $n^{25}_{C}=1.4976$; $n^{25}_{F}=1.5133$; $n^{25}_{G'}=1.5232$.

It gave the following salts:

$C_8H_{11}N\cdot HCl\cdot AuCl_3$,	scales or needles, m.p. 139°,
$(C_8H_{11}N\cdot HCl)_2PtCl_4$,	blackens from about 220°,
$C_8H_{11}N\cdot HCl\ 2HgCl_2\cdot H_2O$,	a slender prism, m.p. 104° (Hg. found, 56.3; theory, 55.8%),
$C_8H_{11}N\cdot HCl\cdot 6HgCl_2$,	white granular crystals, m.p. 165° (Hg. found, 66.7; theory, 66.7%).

For identification it was analysed with the following results:

0.1118 Gr. of the base gave 0.0918 gr. H_2O & 0.3247 gr. CO_2. 0.1947 Gr. of the base gave 19.7 c.c. N_2 at 25° & 759 mm. (Found: $C=79.21$; $H=9.19$; $N=11.58$. $C_8H_{11}N$ requires $C=79.27$; $H=9.16$; $N=11.50\%$).

The acid obtained from the base by oxidation with a potassium permanganate solution is extremely soluble in water, and shows a deep orange-red colouration with ferrous sulphate, which on neutralizing with a dilute sodium carbonate solution changes to a beautiful carmine-red. It melts at 245° with decomposition and agrees with 2:3:6-pyridinetricarboxylic acid written in the literature.(1)

(To be continued on next page)

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(1) L. Weiss, *Ber.*, **19** (1886), 1305.