ON THE BASIC NITROGEN COMPOUNDS FROM FUSHUN SHALE TAR. II.

By **Takashi EGUCHI.**

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(Continued from the last page).

2 : 3 : 5–Trimethylpyridine. The writer has succeeded in isolating 2 : 3 : 5–trimethylpyridine, a new base, as one of the chief constituents in the fraction of 186°–190°, which has never been before submitted to a satisfactory investigation and forms the sixth upheaval in the fractionation curve, (cf. previous report p. 179).

The fraction (71 gr.) was treated with the calculated amount of picric acid, in an alcohol solution, and the crystalline picrate was collected, and yielded 30 gr. of the free base. The base was again treated with an insufficient quantity of picric acid in an excess of alcohol out of which the picrate was produced in the form of cilia first which melts at 184° after purification.

Twenty one gr. of the purified picrate gave 6.8 gr. of the base with a faint agreeable odour resembling 3 : 5–dimethylpyridine in a way. The boiling point of the dried base over fused potash remained constant during the distillation at 186.75° (761.1 mm.).

The constants are ; $d^{25}_{4}=0.9310$ (in vac.) ; $n^{25}_{D}=1.5057$; $n^{25}_{C}=1.5014$; $n^{25}_{F}=1.5171$; $n^{25}_{G'}=1.5270$.

$(C_8H_{11}N\cdot HCl)_2PtCl_4$ . . . . . an orange-red prism, m.p. 212°. (0.1032 Gr. subst. gave 0.0297 gr. Pt. Found Pt=28.8, theoretical Pt=28.7%).

$C_8H_{11}N\cdot HCl\cdot 3HgCl_2$ . . . . . needles ; soluble in hot, slightly in cold water ; m.p. 110°.

Picrate . . . . a needle from hot alcohol ; slightly soluble even in hot alcohol.

0.1016 Gr. base gave 0.0830 gr. H_2O and 0.2954 gr. CO_2. 0.1872 Gr. base gave 19.3 c.c. N_2 at 26° and 757 mm. (Found : C=79.29 ; H=9.15 ; N=11.73. $C_8H_{11}N$ requires C=79.27 ; H=9.16 ; N=11.56 %).

1.3 Gr. of the base was oxidised with potassium permanganate and the oxidation product was purified as a silver salt, and decomposed with hydrogen sulphide, yielding 1.5 gr. of the free acid.

The free acid is easily soluble in hot water, but not in cold, crystallizes out from water as white granules ; melts at 320°–322° with decomposition, and becomes deep orange-red with ferrous sulphate. The analysis and properties of the free acid agree well with those of 2 : 3 : 5–pyridinetricarboxilic acid.(1)

0.1452 Gr. free acid lost 0.0200 gr. on drying at 110° for 2 hours. To neutralise 0.1013 gr. of free acid required 12.5 c.c. of N/10 NaOH using phenolphthalein as indicator. 0.1127 Gr. dried acid gave 0.0290 gr. H_2O and 0.1862 gr. CO_2. (Found : water of crystallization$=13.77$; $C=45.06$; $H=2.88$; mol. wt.$=243$. $C_5H_2N\cdot(CO_2H)_3\,2H_2O$ requires water of crystallization$=14.58$; $C=45.49$; $H=2.39\%$; mol. wt.$=247$).

2 : 4 : 5–Trimethylpyridine.(2) In view of a certain relationship among the boiling-points of the methyl-pyridines which was stated above, we can assume that among the trimethylpyridines, 2 : 3 : 4–, 2 : 3 : 5–, and 2 : 4 : 5–methyl pyridines would exist in the fraction of b. p. 186°–190°, and the last two substances have been isolated.

By treating the fraction with picric acid 2 : 3 : 5–collidine was separated out in ciliform-like crystals (cf. former section) and then, the scaly crystals of 2 : 4 : 5–trimethyl pyridine appeared polluted by the former, which transformed gradually into thick plates in alcohol and could be readily separated from the latter mechanically by decantation. The melting-point of the picrate, on purifying from the alcohol solution, showed constant at 161° and the yield was 29 gr.

The base has a characteristic odour like the kidney-bean, and is soluble in 50 parts of water at 25°. The dried base completely distils at 190.04°–190.05° under 766. 1 mm. and has the constants : $d_4^{25}=0.9330$ (in vac.) ; $n_D^{25}=1.5054$; $n_C^{25}=1.5013$; $n_F^{25}=1.5165$; $n_{G'}^{25}=1.5260$.

$(C_8H_{11}N\cdot HCl)_2PtCl_4$ . . . . . needles, m.p. 192°

$C_8H_{11}N\cdot HCl\cdot 3HgCl_2\cdot 2H_2O$ . . glass-wool-like needles, m.p. 112° (Hg found$=59.5$; theory$=59.7\%$)

0.1067 Gr. of the base gave 0.0875 gr. H_2O and 0.3107 gr. CO_2. 0.1900 Gr. base gave 19.3 c.c. N_2 at 25° and 759 mm. (Found : $C=79.42$; $H=9.18$; $N=11.63$; mol. wt.$=121$. $C_8H_{11}N$ requires $C=79.27$; $H=9.16$; $N=11.56\%$; mol. wt.$=121.1$).

The base (1.2 gr.), on oxidation with potassium permanganate solution yielded 1.6 gr. of free acid (m.p. 244°) which was ascertained to be " berberonic acid(3) from its form, solubility in water and colour reaction toward ferrous sulphate.

To neutralise 0.1017 gr. of free acid required 12.2 c.c. N/10 NaOH. 0.1629 Gr. free acid lost 0.0221 gr. on drying at 96° for 3 hours. 0.1065 Gr. dried acid gave 0.0235 gr. H_2O and 0.1775 gr. CO_2. (Found : water of

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(1) E. Dürkopf and M. Schlaugk, *Ber.*, 21 (1888), 835.

(2) F.B. Ahrens, *Ber.*, 29 (1896), 2999.

(3) O. Mumm and H. Hüneke, *Ber.*, 51 (1918), 150.

crystallization = 13.56 ; C = 45.46 ; H = 2.47 ; mol. wt. = 250. $C_5H_2N{\cdot}(CO_2H)_3{\cdot}2H_2O$ requires H_2O = 14.58 ; C = 45.49 ; H = 2.39% ; mol. wt. = 247).

2 : 3 : 4 : 6-Tetramethylpyridine. It was assumed that the two isomers of tetramethylpyridine, (2 : 3 : 4 : 6– and 2 : 3 : 5 : 6–) would occur in the last fraction b.p. 200°–202°.

On treating the base of this portion with picric acid in an alcohol solution, crystalline and amorphous picrates were obtained. The amorphous picrate was extremely soluble even in cold alcohol, but only slightly in hot water, and this picrate on decomposition with alkali liberated a colourless base of a strong offensive odour. It was neutralised with a very dilute hydrochloric acid and when treated with picric acid, a brownish-red oily picrate was deposited, which on standing for a week or so, was gradually transformed into pale yellow fur-like crystals, and on being purified from a dilute methyl alcohol solution, the yield of pure picrate (m.p. 107°) was 18 gr.

The free base is a hygroscopic colourless liquid with a faint odour resembling 2 : 4 : 6–trimethylpyridine, and is soluble in 150 parts of water. Dried base completely distils at 203.9° under 771 mm. The constants are: $d_4^{25} = 0.9229$; $n_D^{25} = 1.5084$; $n_C^{25} = 1.5043$; $n_F^{25} = 1.5195$; $n_{G'}^{25} = 1.5290$.

The base was proved to be 2 : 3 : 4 : 6–tetramethylpyridine in the following manner :

0.1027 Gr. base gave 0.0896 gr. H_2O and 0.2993 gr. CO_2. 0.2066 Gr. base gave 18.9 c.c. N_2 at 24° and 762 mm. (Found : C = 79.48 ; H = 9.77 ; N = 10.49 ; mol. wt. = 137. $C_9H_{13}N$ requires C = 79.93 ; H = 9.70 ; N = 10.37% ; mol. wt. = 135.1).

The base (1.04 gr.) was oxidised with 1.2 gr. of $KMnO_4$; the filtrate from the manganese oxide was concentrated into a small bulk, neutralised with dilute sulphuric acid and treated with a saturated solution of copper acetate. The resulting copper-salt was bluish-green in colour and was ascertained on analysis to be the neutral copper-salt of pyridine-tetracarboxylic acid.

0.1607 Gr. copper salt (dried at 100°) gave 0.0299 gr. H_2O, 0.1383 gr. CO_2 and 0.0549 gr. CuO. (Found : C = 23.46 ; H = 2.08 ; Cu = 27.29. $C_5HN{\cdot}(CO_2)_4{\cdot}Cu_2{\cdot}4H_2O$ or $C_5HN{\cdot}(CO_2H)_4{\cdot}2Cu(OH)_2$ requires C = 23.99 ; H = 2.01 ; Cu = 28.24%).

The free acid is readily soluble in cold water. A drop of a ferrous sulphate solution on the free acid develops a deep violet colouration, while a dark reddish-purple colour appears when a drop of an acid solution was added inversely to the ferrous sulphate ; sinters at about 190° and melts at 236° with decomposition : these results agree well with those of pyridine –2 : 3 : 4 : 6– tetracarboxylic acid.(1)

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(1) O. Mumm and H. Hüneke, loc. cit.

0.1155 Gr. free acid lost 0.0181 gr. on drying at 110° for 2 hours. 0.0971 Gr. dried acid gave 0.0204 gr. H_2O and 0.1471 gr. CO_2. To neutralise 0.1002 gr. of dried acid required 14.8 c.c. of N/10 NaOH. (Found : C=41.32 ; H=2.35 ; water of crystallization=15.7. $C_5HN{\cdot}(CO_2H)_4{\cdot}3H_2O$ requires C=42.34 ; H=1.98 ; water of crystallization=17.6%).

2 : 6 : 4–Dimethyl-ethylpyridine.⁽¹⁾ The fractions b.p. 187°–188° and b.p. 189°–190° were treated with the calculated amount of picric acid in hot alcohol, the mother liquor which separated from the crystals, was left to stand for a long time in an open flask. The brownish-red syrupy picrate filtered from any solid matter which might have been contained in it, gave 20 gr. of free base. The base is a colourless liquid but taking a slight colouring on long exposure to the light, soluble in 160 parts of water at 23°, possesses a characteristic odour of α and γ–methyl-ethylpyridines. B.p.=187°.5–188°.0 (758 mm.) ; $d_4^{25}=0.9089$; $n_D^{25}=1.4964$.

The base corresponds to a parvoline, on analysis, and the oxidation with $KMnO_4$ gives rise to a "trimestic acid" as will be seen from what follows, which compels one of the three side-chains to take an ethyl group. Naturally, we can consider two isomers of such a parvoline according to the position to which the ethyl group is attached, and a close identity in the properties is recognized with 2 : 6–dimethyl–4–ethylpyridine which may therefore be assumed to be the chief constituent of the fraction metioned.

$(C_9H_{13}N{\cdot}HCl)_2PtCl_4$ . . . . m.p. 203° (0.1006 gr. subst. gave 0.0290 gr. Pt. Pt found=28.8, theory=28.7)

Analysis: 0.0974 gr. base gave 0.0840 gr. H_2O and 0.2850 gr. CO_2. (Found : C=79.79 ; H=9.65. $C_9H_{13}N$ requires C=79.93 ; H=9.70%).

The base (3.7 gr.) gave 1.0 gr. of free acid on oxidation with potassium permanganate, which becomes a violet-red with ferrous sulphate, and melts at 228°.

Analysis : 0.1296 gr. acid lost 0.0184 gr. on drying at 115° for 2 hours. 0.1000 Gr. dried acid gave 0.0217 gr. H_2O and 0.1660 gr. CO_2. (Found : water of crystallization=14.20 ; C=45.28 ; H=2.43. $C_5H_2N{\cdot}(CO_2H)_3{\cdot}2H_2O$ requires water of crystallization=14.58 ; C=45.50 ; H=2.39%).

Dimethyl-ethyl-pyridine (2 : 3 : 6 ?) From the fraction b.p. 189°–190°, a base was isolated by means of picric acid, which slightly differs from 2 : 4 : 6–parvoline in odour and physical constants. B.p.=190°–190.5° (764 mm.) ; $d_4^{25}=0.9107$; $n_D^{25}=1.4970$.

The base was subjected to partial oxidation to form methyl-ethyl pyridine carboxylic acid which yields by heating with soda-lime, a modicum of 2 : 6–methyl-ethyl-pyridine.

Analysis : 0.1068 gr. base gave 0.0928 gr. H_2O and 0.3120 gr. CO_2.

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(1) F. Engelmann, *Ann.*, **231** (1885), 44 ; *Ber.*, **19** (1886), Ref. 16.

0.1728 Gr. base gave 15.7 c.c. N_2 at 30° and 756 mm.. (Found ; C=79.67 ; H=9.74 ; N=10.3 ; mol. wt.=136. $C_9H_{13}N$ requires C=79.93 ; H=9.70 ; N=10.37% ; mol. wt.=135.1).

When, however, the base was oxidized completely with potassium permanganate, an acid with a m.p. of 245° resulted, which agrees in all respects with 2 : 3 : 6–pyridine tricarboxylic acid.

0.1046 Gr. of the dried acid gave 0.0262 gr. H_2O and 0.1725 gr. CO_2. (Found : C=44.98 ; H=2.80. $C_8H_5O_6N$ requires C=45.49 ; H=2.39%).

Pyrindane. Seeking to find any other compound of the pyridine series such as 3 : 4 : 5–trimethyl pyridine in the last fraction (200°–202°), the writer came upon a peculiar base, which on pursuit with careful examination, of the picrate, was unveiled unexpectedly to be a new and interesting base that has never been found in shale or coal tars, and it would be worthy of note in the sence that it might be a mother substance of the pyrindane series.

The picrate crystallizes from an excess of hot alcohol in flat needles with a m.p. 181°, which was converted into a free base of a hygroscopic, colourless liquid, possessing a faint odour like that of 2 : 3–dimethylpyridine, and one part of the base is soluble in 40 parts of water at 25°. The yield of the base from 9.5 gr. of the salt was 3 gr. The dried base distils completely at 199.8° (761 mm.) and the constants are : $d^{25}_4=1.029$; $n^{25}_D=1.541$; $n^{25}_C=1.536$.

0.1210 Gr. and 0.1169 gr. base gave 0.0813 and 0.0800 gr. H_2O, and, 0.3561 and 0.3442 gr. CO_2 respectively. (Found ; C=80.27 & 80.30 ; H=7.52 & 7.66 ; mol. wt.=121. C_8H_9N requires C=80.62 ; H=7.62% ; mol. wt.= 119).

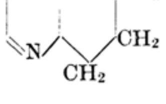
0.1124 Gr. and 0.1747 gr. $(B\cdot HCl)_2PtCl_4$ gave 0.0337 and 0.0522 gr. Pt respectively.

Oxidation of base ; 1.0 gr. of the base was oxidised with 9 gr. of potassium permanganate ; the acid formed by the oxidation was converted into a copper salt which showed the characteristic feature of copper quinolinite. The yield of quinolinic acid was 0.8 gr.

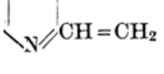
0.1048 Gr. free acid gave 0.0284 gr. H_2O and 0.1944 gr. CO_2. (Found ; C=50.17 ; H=3.03. $C_7H_5O_4N$ requires C=50.27 ; H=3.02%).

The structural formula for the base would eventually be settled in determining the manners in which the three carbon atoms combine together and are also attached to the pyridine ring :

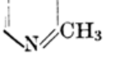
(I)



(II)



(III)



From such a point of view the molecular refractivity was first examined. The value calculated from the experimental data shows $M_D=36.34$, while formula I will give $M_D=37.18$, II and III, $M_D=38.89$, in which the specific exaltation ΣE_D is calculated as -0.70 and -2.15 respectively, the latter being considered abnormal. The behavior of the base toward bromine being practically inert at room temperature, is favorable in supporting the structure (I) for the base, and moreover, considering the abnormality in density compared with that of the alkyl-pyridines and the behavior toward the oxidizing agent, such facts seem to compel formula II or III to be rejected.

Some considerations on the boiling-points of the methylpyridines. Although the effect of the methyl group on the boiling-points of certain homologous series, such as the hydrocarbons, alcohols, and acids has been studied by many investigators, there can be little doubt that it is impossible, as conjectured from the stereochemical view point, to contemplate such an attempt in the series of the methylpyridines with all the data hitherto given in the literature. But with the data which the writer has observed throughout the members many regular relations are recognized in them as already stated, if we ascend the series or among the isomers themselves. Convinced that the effect of the methyl group in α–position on the "boiling-point-rise" of the methylpyridines is about half of that of the β– or γ–position throughout the members, yet some anomalies are always found in connection with such members which have methyl groups successively attached unsymmetrically to the pyridine ring. If this is corrected by C the boiling points of the methylpyridnes can be expressed by a fairly simple empirical formula, that is,

$$T=115.3^\circ + 14m + 28m' + C$$

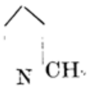
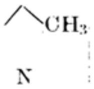
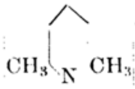
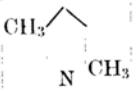
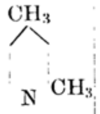
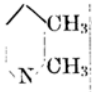
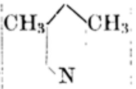
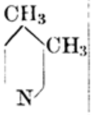
where T is a b.p. of methylpyridine, m the number of the α–methyl group m' the number of the β– or the γ–methyl group, and C the correction term.

The correction term C is variable with the position in the pyridine nucleus, by which the methyl groups connected, that is, 4° for the 2.3 ($\gamma : \beta$)-methyls, 8° for the 3 : 4 ($\beta : \gamma$), and these values are diminished to one half if two side-chains are situated in the 1 : 4 positions or para-position.

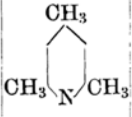
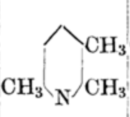
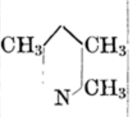
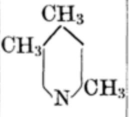
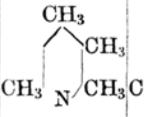
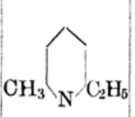
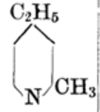
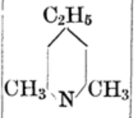
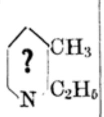
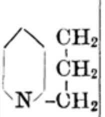
For the methyl derivatives of ethyl-pyridine, 115.3 (b.p. of pyridine) in the above formula should be replaced by the b.p. of ethylpyridine.

In the following table the results of such calculations are given with the author's experimental data in which slight corrections are made in order to compare them under 760 mm.

Physical Constants of Pyridine Series.

										
B.p. (760 mm.) obs.	115.3	129.3	144.0	145.3	144.0	157.0	158.0	160.8	171.6	178.9
calc.	115.3	129.3	143.3	143.3	143.3	157.3	157.3	161.3	171.3	179.3
d_4^{25}	0.9781	0.9400	0.9518	0.9502	0.9183	0.9261	0.9271	0.9419	0.9385	0.9537
n_D^{25}	1.5068	1.4983	1.5038	1.5029	1.4953	1.4982	1.4984	1.5057	1.5032	1.5099
n_C^{25}	1.5022	1.4939	1.4994	1.4986	1.4910	1.4939	1.4942	1.5014	1.4988	1.5055
n_F^{25}	1.5187	1.5097	1.5155	1.5143	1.5065	1.5095	1.5095	1.5172	1.5146	1.5209
$n_{G'}^{25}$	1.5290	1.5197	1.5256	1.5240	1.5164	1.5194	1.5190	1.5272	1.5244	1.5305
M_D	24.04	29.04	28.94	28.95	34.02	33.90	33.88	33.76	33.74	33.58
M_C	23.86	28.82	28.73	28.74	33.77	33.66	33.64	33.52	33.49	33.34
M_F	24.52	29.60	29.51	29.50	34.67	34.55	34.52	34.41	34.38	34.19
$M_{G'}$	24.93	30.09	30.00	29.97	35.24	35.12	35.06	34.96	34.93	34.72
D (G'-C)	1.07	1.27	1.27	1.23	1.47	1.46	1.42	1.44	1.44	1.38
D (F-C)	0.66	0.78	0.78	0.76	0.90	0.89	0.88	0.89	0.89	0.85
ΣE_D	-1.44	-0.90	-1.01	-1.00	-0.43	-0.54	-0.56	-0.67	-0.69	-0.84
Picrate (m.p.)	167	165	149	167	162	167	182	188	244	163
$(B\cdot HCl)_2PtCl_4$ (m.p.)	268	205	208	253	211	214	217		263	276
$B\cdot HCl\cdot AuCl_3$ (m.p.)		181–2	186–7	218						187
$B\cdot HCl\cdot (X)HgCl_2$ (m.p.)	(X) = (2) : 176	(2):153–4	(1):145–6 (2):146 (3):170	(2):130	(1):191.5 (2):167	(6):203	(2):131–2	(6):194		(3):131
Sol. in X pts. of water	any rate (20°)	any rate (20°)	any rate (20°)	any rate (20°)	any rate (20°)	12(23°)	11.5(35°)	10(23°)	32(23°)	20(22°)

Physical Constants of Pyridine Series. (Continued.)

										
B.p. (760 mm.) obs.	170.3	172.8	186.8	189.8	203.3	160–1	179–80	187.5–8.0	190–.5	199.8
calc.	171.3	173.3	187.3	189.3	203.3	162	179	193	190	——
d_4^{25}	0.9101	0.9220	0.9310	0.9330	0.9229	0.9207	0.9130	0.9089	0.9107	1.029
n_D^{5}	1.4959	1.5018	1.5057	1.5054	1.5084	1.4950	1.4953	1.4964	1.4970	1.541
n_C^{25}	1.4919	1.4976	1.5014	1.5013	1.5043	1.4908		1.4925		1.536
n_F^{25}	1.5069	1.5133	1.5171	1.5165	1.5195	1.5057		1.5071		
$n_{G'}$	1.5164	1.5232	1.5270	1.5260	1.5290	1.5151		1.5163		
M_D	38.86	38.75	38.62	38.52	43.34	38.36		43.46		
M_C	38.60	38.47	38.35	38.26	43.05	38.08		43.17		
M_F	39.59	39.50	39.35	39.24	44.14	39.06		44.25		
$M_{G'}$	40.22	40.14	39.98	39.84	44.81	39.67		44.92		
D (G'–C)	1.62	1.66	1.63	1.58	1.77	1.59		1.75		
D (F–C)	0.99	1.02	1.00	0.98	1.09	0.98		1.08		
ΣE_D	–0.18	–0.28	–0.38	–0.47	–0.26	–0.60		–0.17		
Picrate (m.p.)	157	148	184	161	107					
$(B\cdot HCl)_2PtCl_4$ (m.p.)	220	220	212	192						
$B\cdot HCl\cdot AuCl_3$ (m.p.)		139								
$B\cdot HCl\cdot(X)HgCl_2$ (m.p.)	(2):157	(2):104 (6):165	(3):110	(3):112						
Sol. in X pts. of water	34(20°)	38(26)°	66(20°)	50(25°)	150(28°)	55(30°)				

With the expectation that the constituents of the shale tar base boiling at 100°–200° must probably be the mixture of simple pyridine homologues such as the methyl or ethyl-pyridines, the writer has succeeded in isolating seventeen compounds of the pyridine series, three monomethyl pyridines, six dimethyl pyridines, four trimethyl pyridines, one tetramethyl pyridine, two methyl-ethyl-pyridines, one dimethyl-ethyl-pyridine in a highly pure state and in confirming that the theoretically possible isomers of the monomethyl, dimethyl and trimethyl derivatives occur in the shale tar as will be indicated in the table.

1st fraction (128°–130°) . . . . . picoline (main).
2nd ,, (143°–145°) . . . . . 2 : 6–lutidine (main), γ and β-picolines.
3rd ,, (157°–160°) . . . . . 2 : 4–lutidine (main), 2 : 6–collidine, 2 : 3–and 2 : 5– lutidines.
4th ,, (170°–172°) . . . . . 2 : 4 : 6–collidine (main), 2 : 3 : 6–collidine, 3 : 5–lutidine (little).
5th ,, (178°–179°) . . . . . 3 ; 4–lutidine, 2 : 4–collidine.
6th ,, (186°–190°) . . . . . 2 : 4 ; 6–parvoline (main), 2 : 3 : 5–and 2 : 4 : 5–collidine, 2 : 3 ; 6–parvoline.
7th ,, (200°–202°) . . . . . 2 : 3 : 4 ; 6–parvoline, pyrindane.

Thus not only most of the constituents of the shale tar base boiling at 170°–200°, which had been left in the haziness of uncertainty in spite of all endeavours of many investigators, have been cleard up, but also consistent data throughout the members have been determined by rectifying some discrepancies which had crept into the literature.

Besides these pyridine bases, the writer has isolated a new base which has never before been synthesised nor yet isolated from any tars. The base, on analysis and examination of its physical and chemical properties is very likely to have the structure of a "Cyclopenteno-pyridine" and was called pyrindane from its close resemblance in its structure to indane as pyridine to benzene.

The writer desires to make grateful acknowledgment to Vice-Admiral G. Yamashita, Director of the Imperial Naval Fuel Depot, and Engineer Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch for promoting this investigation, and also to Professor S. Komatsu of the Kyoto Imperial University for his invaluable advice and encouragement in carrying out of this research.

The Scientific Research and Experimental Branch,
Imperial Naval Fuel Depot, Tokuyama.