# *Separations of Lutidines, Collidines and 2, 3-Cyclopentenopyridines from Coal Tar Bases*

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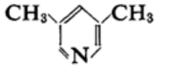
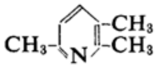
In order to examine the tertiary amines in coal tar bases, especially in a forerunning of quinoline, methods of picrate and urea adduct formation, countercurrent extraction and chromatography were applied in order to effect the isolation of the bases. Selective separations could be carried out easily for some of the high boiling bases. From a fraction boiling at 170°C, 3, 5-lutidine[1] (I) was separated relatively easily as a zinc chloride adduct, and 2, 3-disubstituted pyridines such as 2, 3, 6-collidine[1] (II), 2, 3, 4, 6-tetramethylpyridine[2,3] (III), 2, 3-cyclopentenopyridine[2] (IV) and 2, 3-cyclopenteno-6-methylpyridine[3-5] (V) were isolated as urea adducts from the fractions with corresponding boiling points. Furthermore, using a chromatographic column of cupric chloride-aluminum oxide which was effective for separations of pyridine, picolines and lutidines[6,7] 2, 3-cyclopenteno-6-methylpyridine and 3, 4, 5-collidine[4,8-10] (VI) were separated. The latter was isolated for the first time from coal tar bases by the author[8]. With the same chromatographic column, 2, 3, 5-collidine[10] (VII) could also be separated and purified.


(I)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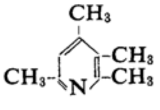
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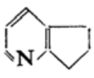
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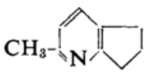
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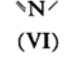
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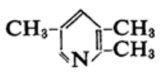
(VII)

The properties and physical constants of the bases which were separated are shown in the following tables.

## Experimental

**Materials.**—The materials used in the present investigation were all supplied by Yawata Chemical Industry Co.; their properties are shown below.

TABLE I. 3, 5-LUTIDINE

| | B. p. °C | $d_4^{25}$ | M. p. of $B(HgCl_2)_2HCl$ °C | M. p. of picrate °C |
|---|---|---|---|---|
| Isolated | 171～172 | 0.9390 | 169～170 | 244～244.5 |
| Reported[1] | 171 | 0.9385 | 170 | 240 |

TABLE II. 2, 3, 6-COLLIDINE

| | B. p. °C | M. p. of picrate °C | $n_D^{25}$ |
|---|---|---|---|
| Isolated | 171～171.5 (uncorr.) | 147.4～148.4 | 1.5020 |
| Reported[1] | 172.8 | 148 | |

TABLE III. 2, 3, 4, 6-TETRAMETHYLPYRIDINE

| | B. p. °C | $n_D^{25}$ | N % | M. p. of picrate °C | M. p. of picrolonate °C | Ultraviolet spectrum in cyclohexane | |
|---|---|---|---|---|---|---|---|
| | | | | | | $\lambda_{max}$ mμ | $\varepsilon_{max}$ |
| Isolated | 202.5 | 1.5088 | 10.35 | 122～122.5 | 226.4～226.9 | 266 | 3294 |
| Reported[2] | 203.3 | 1.5087 | (10.37)* | 122.5～123 | 225.5 | 266.5 | 3210 |

* Calcd.

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1) T. Eguchi, This Bulletin, **3**, 227 (1928).

2) P. Arnall, *J. Chem. Soc.*, **1954**, 4040.

3) S. Jifuku, S. Nakayama, H. Suzumura and M. Uemura, *J. Japan Tar Ind. Association*, **10**, 126 (1958).

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5) S. Tanaka et al., *Japan Analyst* (*Bunseki Kagaku*), **6**, 281 (1957).

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7) E. Funakubo, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **59**, 220 (1956).

8) Annual Meeting of Japan Tar Industry Association, October, 1956.

9) A. S. Bailey et al., *J. Chem. Soc.*, **1959**, 2554.

10) K. Tsuda et al., *Pharm. Bull.*, **1**, 283 (1953).

TABLE IV. 2,3-CYCLOPENTENOPYRIDINE

| | B. p. °C | $n_D^{25}$ | M. p. of picrate °C | M. p. of picrolonate °C | Ultraviolet spectrum $\lambda_{max}$ m$\mu$ | Ultraviolet spectrum $\varepsilon_{max}$ |
|---|---|---|---|---|---|---|
| Isolated | 199.5 | 1.538 | 183.5~184 | 238.8 | 272 | 4090 |
| Reported[2] | 199.3~199.4 | 1.541 | 182~183 | 239 | | |

TABLE V. 2,3-CYCLOPENTENO-6-METHYLPYRIDINE

| | B. p. °C | F. p. °C | $n_D$ | M. p. of picrate °C | M. p. of picrolonate °C |
|---|---|---|---|---|---|
| Isolated | 210.5~211 | 35.0~35.7 | 1.527 (40°C) | 152.1~152.6 | 205.5~206.5 |
| Reported[4] | 211.9(761mmHg) | 31.8 | 1.5297(32.5°C) | 155 | 170 |
| Reported[5] | | 35·0 | | 152.8~153.1 | |

TABLE VI. 3,4,5-COLLIDINE

| | B. p. °C | M. p. °C | $d_4^t$ | $n_D$ | M. p. of picrate °C | M. p. of picrolonate °C | N % |
|---|---|---|---|---|---|---|---|
| Isolated | 210.3~210.8 | 32.6~35.6 | 0.955 (35°C) | 1.5115 (35°C) | 173.6~174.3 | 224 | 11.25 |
| Reported[4] | 211.4~211.5 (759 mmHg) | 36.8 | 0.947 (40°/20°C) | 1.5132 (37°C) | 178 | 232 | |
| Reported[9] | — | — | — | — | 174~175 | 228 | |
| Reported[10] | 205~207 | 10~13 | 0.9616 (15°C) | 1.5103 (15°C) | 174 | 188 | Calcd. 11.52 |

TABLE VII. 2,3,5-COLLIDINE

| | B. p. °C | $n_D^{25}$ | M. p. of chloroplatinate °C | M. p. of picrate °C |
|---|---|---|---|---|
| Isolated | 185~185.8 | 1.5045 | 211 | 184.5~185.2 |
| Reported[10] | 186.8 | 1.5057 | 212 | 184 |

TABLE VIII

Forerunning of quinoline ($S_1$)

↓

Toluidine fraction
b. p. 199.8~202.2°C (28%)
↓
Tertiary amines (21%) ($T_3$)
↓ distilled
b. p. 183~189°C 32%
b. p. 200~201°C 17%

↓

Xylidine fraction
b. p. 210.5~225°C (12%)
↓
Tertiary amines (50%) ($X_3$)
↓ distilled (30 mmHg)

| No. of fraction | Temp. of distillation °C | Yield* % |
|---|---|---|
| 2 | 95~ 96 | 8.8 |
| 3 | 96~100.5 | 13.2 |
| 4 | ~102 | 11.0 |
| 5 | ~104 | 8.0 |
| 6 | ~105 | 14.6 |
| 7 | ~108 | 17.2 |
| 8 | 108 | 13.0 |

* The yield in each step is based on an immediately preceding material.

TABLE IX. 2,3-CYCLOPENTENO-6-METHYLPYRIDINE

| No. of fraction | Urea adduct Amount g. | Urea adduct M. p. °C | Base recovered from urea adduct g. | Picrate Amount g. | Picrate M. p. °C |
|---|---|---|---|---|---|
| 7 | — | 86~129 | 1.4 | 0.35 | 149~150.5 |
| 8 | 2.4 | 88~129 | 1.3 | 0.80 | 150~150.5 |
| 9 | 2.6 | 88~129 | 1.3 | 0.90 | 150~150.5 |

TABLE X. 3,4,5-COLLIDINE AND 2,3-CYCLOPENTENO-6-METHYLPYRIDINE

| No. of band | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Base recovered from each band, g. | 0.25 | 0.25 | 0.39 | 2.6 | 2.4 | 1.9 | 0.8 |
| M. p. of picrate, °C | 170.5~172.5 | 171~172 | | 150~151 | 150~151 | 192~195 | |
| Amount of picrate, g. | 0.7375 | 0.6425 | | 3.0 | 1.4 | 0.4 | |
| Compound | 3,4,5-Collidine | | | 2,3-Cyclopenteno-6-methylpyridine | | Unidentified | |

TABLE XI.

| No. of fraction | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Amount, g. | 8.4 | 5.0 | 3.4 | 5.4 |
| $n_D^{25}$ | 1.5093 | 1.5094 | 1.5115 | 1.5201 |
| M. p.* of picrate, °C | 124~138 | 113~125 | 124~150 | 178~179 |

* After recrystallized twice from ethanol.

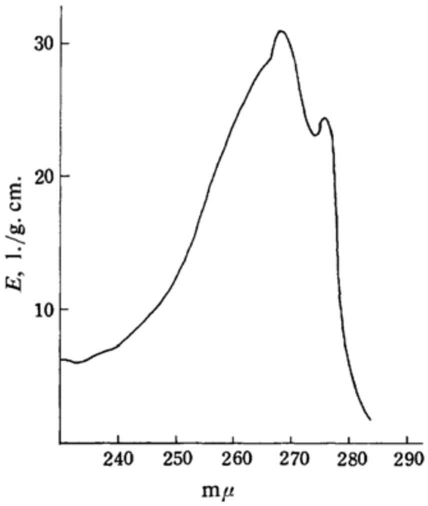

Fig. 1. 3,5-Lutidine in ethanol.

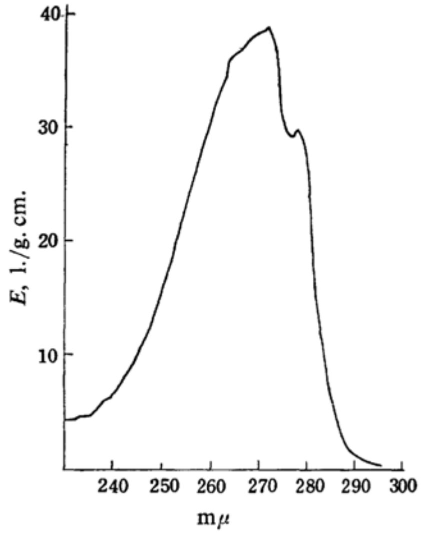

Fig. 3. 2,3-Cyclopentenopyridine.

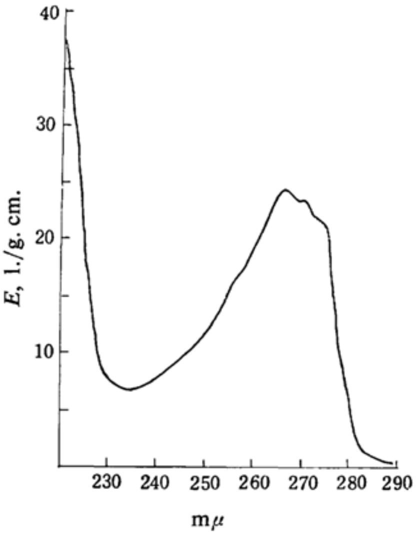

Fig. 2. 2,3,4,6-Tetramethylpyridine.

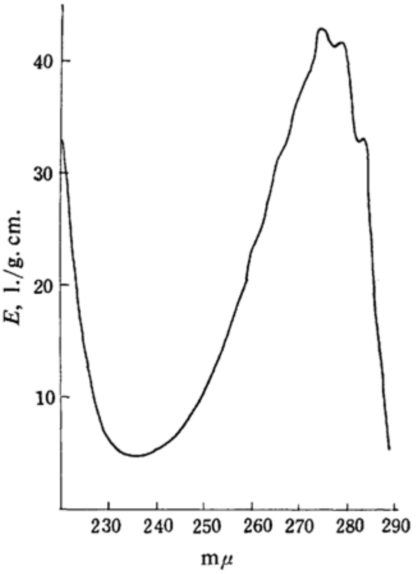

Fig. 4. 2,3-Cyclopenteno-6-methylpyridine.

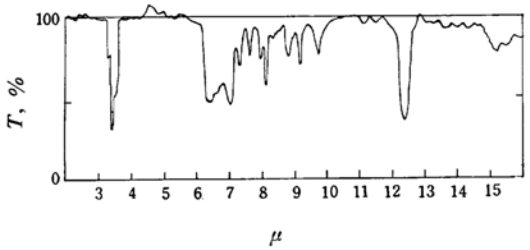

Fig. 5. 2,3-Cyclopenteno-6-methylpyridine.

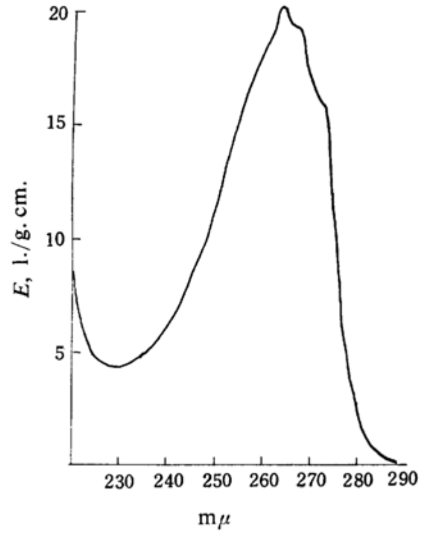

Fig. 6. 3,4,5-Collidine.

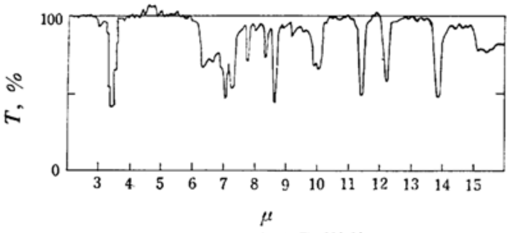

Fig. 7. 3,4,5-Collidine.

(1) Industrial grade collidine grade 1

| Sample | First drop | 10% | 50% | 90% | Dry point |
|---|---|---|---|---|---|
| A | 165.7 | 171.7 | 173 | 178 | 180 |
| B | 161.0 | 166.0 | 172 | 181 | 185 |

(2) Tertiary amines boiling at 200 and 210°C. A forerunning of quinoline (Fig. 8) was obtained when the crude quinoline was first extracted with sulfuric acid from the middle oil of coal tars and then fractionally distilled. Fractionating through a packed column 3 m. in height, this forerunning was separated into toluidine and xylidine fractions. Primary amines in these fractions were removed by acetylation, and the mixture of tertiary amines thus obtained was fractionally distilled as shown in Table VIII.

**Separation of 3,5-Lutidine by Zinc Chloride.**— Industrial grade collidine grade 1 (Sample A) (1250

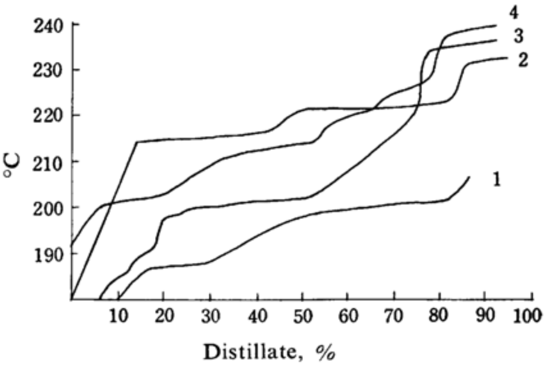

Fig. 8

1 $T_3$ ($S_1$)
2 $X_3$ ($S_1$)
3 Forerunning of quinoline ($S_1$)
4 $X_3$ ($S_4$)

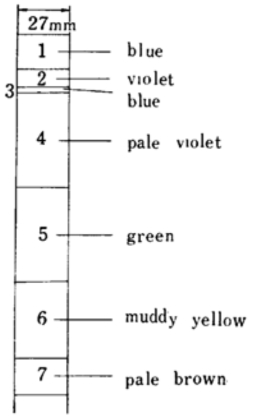

Fig. 9

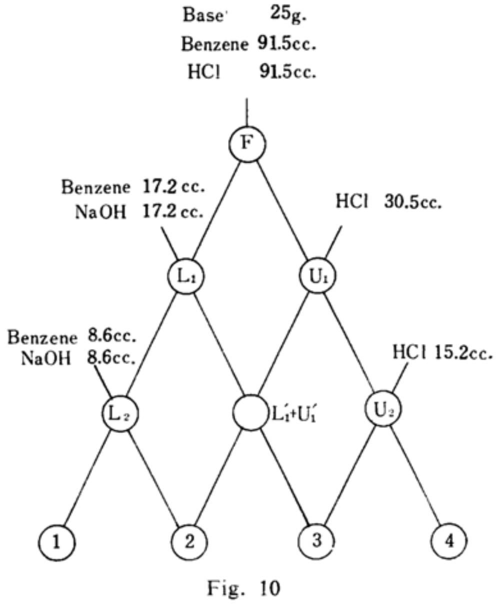

Fig. 10

cc.) was fractionated through a column 2 m. in height and packed with single turn helices, and a fraction boiling at 168∼171°C (534 cc.) was obtained. When a 50% aqueous solution of zinc chloride was stirred into this fraction, a white adduct was precipitated which was washed with benzene to remove free bases and then steam-distilled. The distillate, on treatment with an aqueous solution of picric acid, gave crude picrates, m. p. 240°C, in about a 4% yield based on the fraction. The crude picrate (49 g.) was refluxed with 700 cc. of ethanol, yielding 42 g. of pure picrate, which was decomposed to give pure 3,5-lutidine.

**Separation by Urea-adduct.**—*Separation of 2,3,6-Collidine.*—One kilogram of Industrial grade collidine grade 1 (Sample B) was distilled into the following fractions:

| Fraction | up to 165°C | 165∼167°C | 170∼175°C |
|---|---|---|---|
| Amount, g. | 515 | 107 | 326 |

To the fraction boiling at 170∼175°C (80 g.), a 50% aqueous solution of urea was added, and the resulting white adduct of m. p. 128∼132°C was decomposed by steam distillation. A picrate (12 g.) melting at 147.4∼148.4°C was obtained from the distillate. After being recrystallized once from ethanol, the picrate was decomposed, yielding 3.1 g. of pure 2,3,6-collidine.

*2,3,4,6-Tetramethylpyridine.*—To 16 g. of the fraction ($T_3$) boiling at 200∼201°C, 43 g. of a 50% aqueous solution of urea was added, and the resulting adduct was washed with ether and decomposed by steam distillation to give a base (4.5 g.) boiling at 198°C. The picrate of this base, after three recrystallizations from ethanol, melted at 122∼122.5°C. The base was also confirmed by picrolonate and ultraviolet absorption spectrum.

*2,3-Cyclopentenopyridine.*—To 36 g. of No. 3 fraction of $X_3$, a solution of urea (112 g.) in 50 cc. of water was added to form urea adduct, m. p. 124∼132°C, which was decomposed, yielding 18 g. of basic material showing $n_D^{25}$ 1.5200. This was next purified as picrate, and after a recrystallization from ethanol picrate of 2,3-cyclopentenopyridine (21 g.) which melted at 178∼179°C (uncorr.) was obtained. From the filtrate of urea adduct, 10 g. of the picrate of the base was recovered.

*2,3-Cyclopenteno-6-methylpyridine.*—To 5 g. of Nos. 8 and 9 fractions of $S_4$, 1 g. of a 60% aqueous solution of urea was added to yield an adduct from which 2,3-cyclopenteno-6-methylpyridine was recovered as picrate. The purified picrate did not show a melting point depression when admixed with an authentic sample. The results are shown in Table IX.

Similarly, from 50 g. of No. 9 fraction of $S_4$, 19.8 g. of picrate was obtained. The combined picrates were decomposed, yielding 7.45 g. of the free base with $n_D^{35}$ 1.5280. Bases which were recovered from the filtrate of the adduct boiled at 214°C and had $n_D^{20}$ 1.5270, and N content 10.31%.

**Chromatographic Separation.**—*Separation of 3,4,5-Collidine and 2,3-Cyclopenteno-6-methylpyridine.*—As Vignes used for the separation of pyridine, picolines and 2,6-lutidine[6], a mixture of cupric chloride (2 parts), aluminum chloride (25 parts), glycerol (6 parts) and distilled water (2 parts) was ground, dried at 50°C, and then used as an adsorbent in a chromatographic column. The adsorbent (190 g.) was packed in a column as shown in Fig. 9. No. 7 fraction (10.02 g.) from $X_3$, in Table VIII, was placed on a column and developed with 280 cc. of ether. After 5 hr., development was complete, giving various zones as shown in Fig. 9. From each zone, bases were recovered by the addition of an alkali, followed by steam distillation. While examining these bases as picrates, the author found that the bases of Nos. 4 and 5 mainly consisted of 2,3-cyclopenteno-6-methylpyridine, and a base of Nos. 1 and 2 whose picrate melted at 171∼172°C (uncorr.) was identified as 3,4,5-collidine (Table X). A comparison of the properties of the base with those of the synthetic sample used in the identification of coal tar bases[10] is as follows: b.p. 210.3∼210.8°C (reported 205∼207°C), melting point of the picrate 173.6∼174.3°C (reported 174°C), N content found 11.25% (Calcd. for $C_8H_{11}N$, 11.52%), molecular weight found 118 (Calcd. 121), and molar refractivity calculated from $d_4^{35}$ 0.9552 and $n_D^{35}$ 1.5115 38.1 (which is very close to the calculated values for collidines 38.6∼38.8). The infrared spectrum in carbon disulfide and the ultraviolet spectrum in cyclohexane agreed with those of the literature cited. The base (0.4954 g.) was oxidized with 3.91 g. of potassium permanganate (used as a 2% aqueous solution) at 90°C over a period of 32 hr. Pyridine carboxylic acid was recovered as its copper salt; this was then decomposed by hydrogen sulfide to give the crude acid (0.0874 g.). After a recrystallization from water, pyridine carboxylic acid was obtained which melted with decomposition at 262.5°C (corr.).

Found: N, 5.8. Calcd. for $C_8H_5O_6N\cdot 3H_2O$: N, 5.3%.

*Separation of 2,3,5-Collidine.*—Separation of this base by picrate formation was reported in the literature, but the procedure of recrystallization was time-consuming. By using the chromatographic column described above, 2,3,5-collidine was separated easily. Bases of the fraction boiling at 183∼190°C which remained in the solution after the solid urea adduct was removed were placed on the column and developed. A green zone was obtained, and from this zone was recovered a base whose picrate melted at 184∼185°C and proved to be 2,3,5-collidine by the mixed melting point. Colors developed by other bases in this procedure are as follows: 3,5-lutidine (blue), 2,4,5-collidine (violet), 2,3,6-collidine (blue) and 2,3-cyclopentenopyridine (blue).

**Separation of 2,3-Cyclopentenopyridine by Countercurrent Extraction.**—2,3-Cyclopentenopyridine which was separated as urea adduct could also be separated by countercurrent extraction. The scheme of extraction, shown in Fig. 10, was similar to that described in the literature[11] using benzene and hydrochloric acid.

Using No. 2 fraction of $S_1$ as a feed, 2,3-cyclopentenopyridine was found to be concentrated in a fraction which was only with great difficulty soluble in the acid phase. The extraction was conducted

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[11] S. Tanaka et al., *Japan Analyst* (*Bunseki Kagaku*), 5, 455, 513 (1956).

as shown in Fig. 10; bases were distributed between benzene and hydrochloric acid by shaking for 5 min. in a separatory funnel. The upper benzene layer $U_1$ was separated, hydrochloric acid (1 N) was added, and the extraction was repeated, forming upper $U_2$ and lower layer $U_1'$. To $L_1$, which was the lower layer of $U_1$, benzene and 1 N sodium hydroxide were added, and extraction was conducted to give $L_1'$ and $L_2$. $L_1'$ and $U_1'$ were combined and distributed between themselves. The extraction was continued until the 4 fractions shown in Fig. 10 were obtained. The amount, the refractive index and the melting point of the picrate of the base recovered from each fraction are shown in Table XI.

The basicity of the base was expected to decrease gradually from No. 1 to No. 4. From fraction No. 4 the picrate of 2,3-cyclopentenopyridine (4.5 g.) was separated and identified by mixed melting point with an authentic sample.

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