35. **Kyosuke Tsuda*** and **Masao Maruyama****: Studies on the Coal Tar Bases. IV[1]. Infrared Spectra of Polymethylpyridines.

(*Pharmaceutical Institute, Medical Faculty, University of Kyushu,**
*and Takamine Research Laboratory, Sankyo Co., Ltd.***)

Recently, Densham and others[2] adopted the infrared absorption spectrum for the analyses of β- and γ-picoline and 2,6-lutidine in the b.p. 140~145° fraction of coal tar bases. Nisbet[3] also described the infrared spectra of 2,3,4,6- and 2,3,5,6-tetramethylpyridines isolated from coal tar bases.

The present paper gives the data of infrared absorption spectra measured with 18 kinds of methyl derivatives of pyridine, with the exception of 3,4,5-trimethylpyridine, and with pyridine itself[4]. The samples used for the measurement were the ones synthesized by the author[5] and those isolated from coal tar bases[6]. The absorption curves in a range of 5~16 μ are shown in Figs. 1~19.

All the measurements were made with carbon disulfide solution of the samples so that the absorption of carbon disulfide appears in the wavelength range of 6~7 μ, and the absorption of stretching vibration of >C=N- and >C=C< which usually appear in this range is not clear.

The absorptions in the range of 10~16 μ wavelength can be utilized for both qualitative and quantitative analyses and show specific absorption of the sample, i.e. chiefly the absorption due to skeletal vibration of the molecule. Specific absorptions of pyridines are summarized in Table I, in which the position of specific absorptions is indicated by a line whose length denotes the intensity.

As can be seen from Table I, the position of the specific absorption tends gradually to move towards the shorter wavelength range in the order of pyridine, monomethyl-, dimethyl-, trimethyl-, and tetramethylpyridines, and the intensity of absorption also becomes weaker in that order.

The fact that the position and intensity are the same in the absorption bands of 2,3,5,6-tetramethylpyridine (Fig. 18) and pentamethylpyridin (Fig. 19) is to be noted.

The absorption curves of the synthetic produt and the one isolated from coal tar were compared with 2,3,6-collidine and 2,3,5,6-tetramethylpyridine[7] and in both cases the two samples gave identical results.

The authors take this opportunity in expressing their gratitude to Prof. Takayuki Sohmiya and Mr. Hitoshi Kamata of the Technological Faculty, University of Tokyo, for their kind guidance and help during the course of this study.

Experimental

Apparatus—Baird Double-beam Infrared Recording Spectrophotometer was used, with NaCl prism. Thickness of cell, 0.1 mm.

Solvent—Carbon Disulfide.

Samples—Following 8 kinds were isolated from coal tar: Pyridine, α-, β- and γ-picoline, and 2,6-, 2,4-, 2,3-, and 3,5-lutidine. Pyridine and α-picoline were purified by fractional distillation, β-

---

* Hakata, Fukuoka (津田恭介).

** Nishi-Shinagawa, Shinagawa-ku, Tokyo (丸山正生).

1) Part III: This Bulletin, **1**, 142 (1953).

2) A. B. Densham, D. J. Langston, G. Gough: J. Chem. Soc., **1952**, 2433.

3) H. B. Nisbet, A. M. Pryde: Nature, **167**, 862 (1951); **168**, 832 (1951).

4) H. M. Randall, *et al.*: "Infrared Determination of Organic Structures", (1949). Van Nostrand & Co., New York, U.S.A.

5) K. Tsuda, *et al.*: Cf. foregoing papers.

6) Part V: This Bulletin, **1**, 149 (1953).

7) This sample isolated from coal tar bases was kindly sent by Prof. H. B. Nisbet of the Heriot-Watt College, for which the authors express their gratitude.

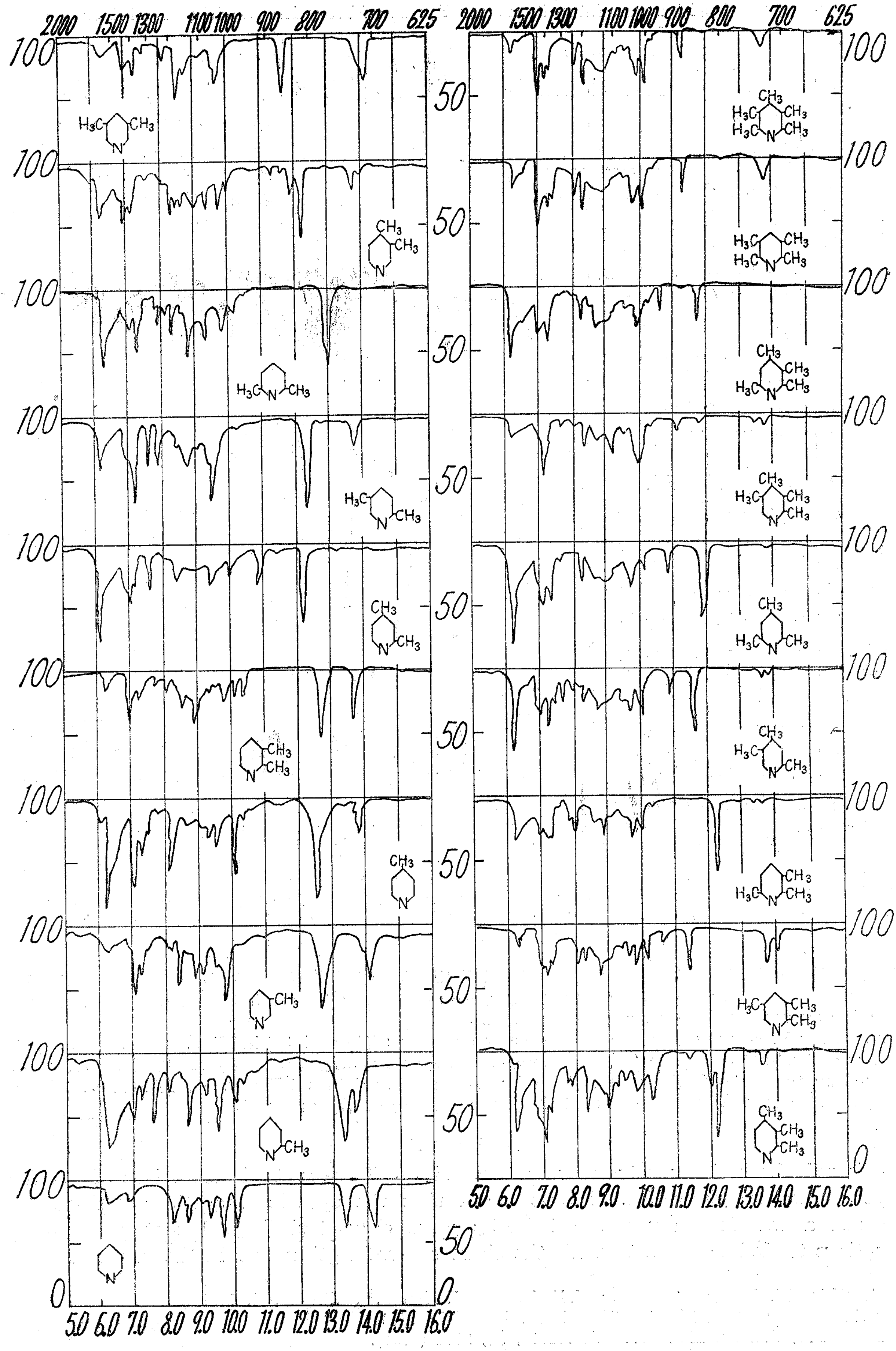
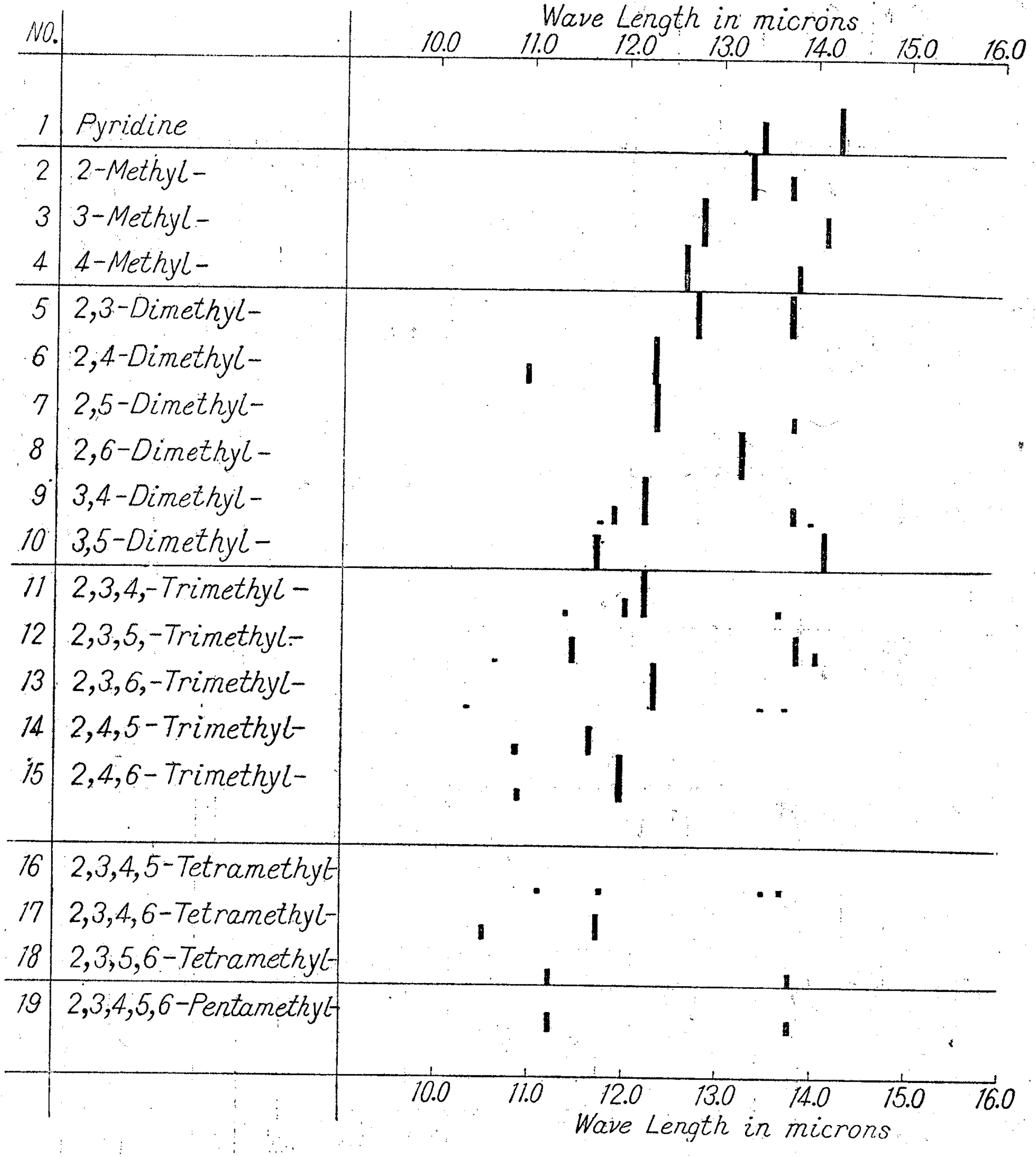

2000 1500 1300 1100 1000 900 800 700 625
100
50
0
5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0
H₃C CH₃ N
CH₃ CH₃ N
H₃C N CH₃
CH₃ N
H₃C CH₃ N CH₃

Table I Position and Intensity of the Specific Absorption Bands of Pyridines



and γ-picoline and 2,6-lutidine by the fractional distillation of their N-oxides[8] and recrystallizations as oxalates and hydrochlorides, and the purification of 2,4-, 2,3- and 3,5-lutidine by the N-oxide method[6] and recrystallization of their picrates[6].

Following 11 compounds were synthetically prepared: 2,5- and 3,4-lutidine, 2,4,6-, 2,3,6-, 2,3,5-, 2,4,5-, and 2,3,4-collidine, and 2,3,4,6-, 2,3,4,5-, and 2,3,5,6-tetramethylpyridine. 2,4,6-Collidine was prepared by the method of Hantzsch[9] and pentamethylpyridines by that of Karrer[10]. Others were prepared by the method elaborated by one (Tsuda) of the authors[5].

Summary

Infrared absorption spectra were measured of all the methyl derivatives of pyridine, except 3,4,5-trimethylpyridine. It was found that the specific absorptions of these compounds in a wavelength range of 10~16 μ were characteristic, and that these specific absorptions tended to move towards the shorter wavelength range in the order of mono-

---

[8] E. Ochiai, M. Ikehara, T. Katoh, N. Ikekawa: J. Pharm. Soc. Japan, 71, 1385 (1951).
[9] A. Hantzsch: Ann., 215, 1 (1882); Ber., 18, 1744 (1885).
[10] P. Karrer, S. Mainoni: Helv. Chim. Acta, 34, 2151 (1951).

methyl-, dimethyl-, trimethyl-, and tetramethylpyridines with their intensity becoming weaker in that order. These studies were made in order to utilize the data for analyses of pyridines in coal tar bases.

(Received April 16, 1953)

---

36. **Nobuo Ikekawa:** Studies on the Coal Tar Bases. V[1]. Pyridine Bases from Low-Temperature Coking Tar (1).

(Pharmaceutical Institute, Medical Faculty, University of Kyushu)*

Some time ago, the author took part in a study[2], in collaboration with others, on the constituent of a fraction below 150° of pyridine bases contained in the coal tar of low-temperature coking. The present paper discusses the pyridine bases contained in the fraction of b.p. 150∼190° from the same tar.

There are some references to the pyridine bases in the fraction of b.p. 150∼190° from coal tar bases[3], California cracked gasoline[4], and shale tar[5]. In these studies, the bases were isolated as picrates or mercuric chloride double salts from which the bases were isolated and oxidized to pyridine-carboxylic acids to determine their structures. In a majority of cases, the melting points of picrates were compared with those described in literature.

In the present series of experiments, all the methyl derivatives of pyridine, except 3,4,5-trimethylpyridine, were synthesized[6] for comparison, and direct comparisons were made by the mixed fusion of picrates or other salts. This seemed to offer a more conclusive evidence and also need only a small amount of material.

Separation of bases from the light oil of low-temperature coking tar with sulfuric acid yields about 0.2% of bases, which are acetylated to remove primary and secondary amines. This

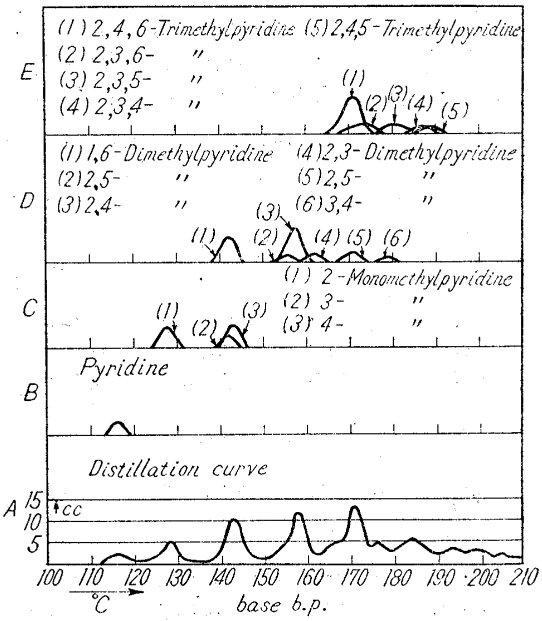


Fig. 1 Distribution of Pyridines in Fraction of 110∼190° in Low-Temperature Coking Tar

Abscissa: Distillation temperature

Ordinate: Unit showing quantitative relationship: No. of cc. in A, amount of base calculated from the amount of picrate in B, C, D, and E. Total amount of each pyridine compound is indicated by the area bound within the curve.

---

* Hakata, Fukuoka (池川信夫).

1) Part IV: This Bulletin, **1**, 146 (1953).

2) E. Ochiai, M. Ikehara, T. Kato, N. Ikekawa: J. Pharm. Soc. Japan, **71**, 1385 (1951).

3) F. B. Ahrens: Ber., **28**, 795 (1895), **29**, 2996 (1896), **37**, 2062 (1904); A. Eckert, S. Loria: Monatsch., **38**, 225 (1917); F. Schütz, W. Buschmann, H. Wissebach: Ber., **56**, 1967 (1923); W. Gollmer: Brennstoffchemie, **4**, 1 (1928); M. P. Oparina: Ber., **56**, 562 (1931).

4) A. C. Bratton, J. R. Bailey: J. Am. Chem. Soc., **59**, 175 (1937); J. T. Hackmann, J. P. Wibaut, H. P. Gitsels: Rec. trav. chim., **62**, 229 (1943) (C. A., **38**, 3117 (1944)).

5) F. C. Garrett, J. A. Smyth: J. Chem. Soc., **81**, 449 (1902), **83**, 763 (1903); T. Eguchi: Bull. Chem. Soc. Japan, **2**, 176 (1927), **3**, 227, 235 (1928).

6) K. Tsuda, N. Ikekawa, *et al.*: This Bulletin, **1**, 122, 126, 142 (1953).