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42. Kan-ichi Ueda : Sulfur-containing Pyridine Derivatives. XLIX.* Ultraviolet Absorption Spectra of Thiazolopyridines.

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The ultraviolet absorption spectra of 2-aminothiazolopyridines of the [5,4-*b*] and [4,5-*b*] series were previously shown by Takahashi and Yamamoto[1] in comparison with those of pyridine and thiazole derivatives which are the components of bicyclic thiazolopyridine. In this report, the spectra were recorded only for the substituted thiazolopyridines and the fundamental relation of the spectral properties to the four isomeric thiazolopyridines was not shown.

The present paper describes the spectral properties of thiazolopyridines and its substitution products which fall chiefly under the [4,5-*c*] and [5,4-*c*] series, including the comparison with the spectrum of benzothiazole[2] itself.

The compounds examined, whose spectral data have not yet appeared in any literature, are listed in Table I.

TABLE I. Ultraviolet Spectral Data[a]

Compound	λ_{max} mμ	log ε
Thiazolo[5,4-*c*]pyridine[b]	(231)	3.73
	289	3.64
2-Methylthiazolo[5,4-*c*]pyridine[b]	212	4.38
	(242)	3.67
	286.5	3.61
Thiazolo[4,5-*c*]pyridine[c]	216	4.40
	(242)	3.68
	(268)	3.27
2-Methylthiazolo[4,5-*c*]pyridine[c]	216	4.49
	(240)	3.74
	(248)	3.71
	(270)	3.16
	(280)	2.82
5-Chlorothiazolo[5,4-*b*]pyridine[d]	218	4.35
	252	3.77
	287.5	3.79
	296	3.79
7-Bromothiazolo[4,5-*c*]pyridine[e]	253.3	3.79
2-Aminothiazolo[4,5-*c*]pyridine[f]	226	4.62
	266.5	4.06
2-Methylthiothiazolo[4,5-*c*]pyridine[g]	232	4.39
	279	4.18

a) All spectra were measured with the Beckman Model DU V spectrophotometer (dehyd. EtOH solution).
b) T. Takahashi, K. Ueda : This Bulletin, **4**, 216(1956).
c) T. Takahashi, K. Ueda, T. Ichimoto : *Ibid.*, **2**, 196(1954).
d) Colorless needles, m.p. 110°. Y. Yamamoto : J. Pharm. Soc. Japan, **71**, 920(1951).
e) T. Takahashi, O. Yamashita : This Bulletin, **4**, 20(1956).
f) T. Takahashi, K. Ueda : *Ibid.*, **2**, 34(1954).
g) T. Takahashi, K. Ueda, T. Ichimoto : *Ibid.*, **3**, 356(1955).

* This work is a part of a series entitled "Sulfur-containing Pyridine Derivatives" by Torizo Takahashi. Part XLVIII : This Bulletin, **4**, 216(1956).

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1) T. Takahashi, Y. Yamamoto : J. Pharm. Soc. Japan, **71**, 662(1951).
2) A. Cerniani, P. Passerini : J. Chem. Soc., **1954**, 2261.

Thiazolopyridine and 2-Methylthiazolopyridine (Figs. 1 and 2)

Apart from the different intensities of their spectra and those of benzothiazole, these spectra consist in general of three bands, identical with those of benzothiazole. The first absorption band lies in 268~290 mμ region, the second in 230~250 mμ region, and the third near 215 mμ. The second absorption band, however, appears as a shoulder in both thiazolopyridine and methylthiazolopyridine.

It is noteworthy that the intensity of the first band of the [5,4-*c*] series is higher than that of benzothiazole, although the wave length of absorption maximum does not change. If thiazolopyridine is regarded as azabenzothiazole, this phenomenon is in agreement with the generalization that the replacement of =CH- by =N- in simple monocyclic, as well as in bicyclic and tricyclic, compounds does not greatly alter the ultraviolet absorption, but the intensities in the longer wave lengths are often increased.

In the case of [5,4-*b*] series, the spectrum of 5-chlorothiazolo[5,4-*b*]pyridine was measured, which, as would be expected, was found to resemble that of the [5,4-*c*] series, apart from a small difference by the bathochromic and hyperchromic effect of chlorine atom, which are commonly found in the spectroscopic investigation. Moreover, the first band system has two absorption maxima, at 287.5 and 296 mμ.

On the contrary, the disappearence of the absorption maxima of the first band system in thiazolo[4,5-*c*]pyridine and its methyl derivatives, though their maxima still remain as a shoulder, is of considerable interest.

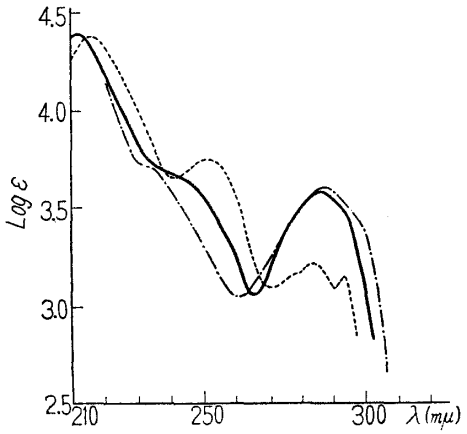

Fig. 1.
Ultraviolet Spectra of Thiazolopyridines and Benzothiazole (in EtOH)
——— 2-Methylthiazolo[5,4-*c*]pyridine
—·—· Thiazolo[5,4-*c*]pyridine
····· Benzothiazole

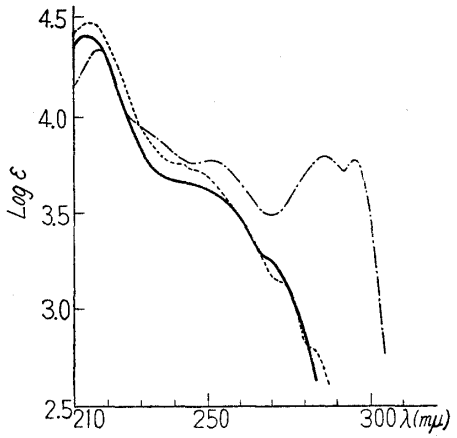

Fig. 2.
Ultraviolet Spectra of Thiazolopyridines (in EtOH)
——— Thiazolo[4,5-*c*]pyridine
····· 2-Methylthiazolo[4,5-*c*]pyridine
—·—· 5-Chlorothiazolo[5,4-*b*]pyridine

Substituted Thiazolopyridines (Fig. 3)

As shown by 7-bromothiazolo[4,5-*c*]pyridine, 2-methylthiothiazolo[4,5-*c*]pyridine, and 2-aminothiazolo[4,5-*c*]pyridine, substitution in the pyridine or thiazole ring of thiazolopyridines causes a shift of those bands toward a longer wave length and an increase in intensity, the effect of the groups being in the increasing order of Br, NH_2, and CH_3S.

In the case of 2,5-disubstituted thiazolopyridines, viz. 2,5-diamino-[1] and 2-amino-5-methylthiothiazolo[5,4-*b*]pyridine,[1] similar results were also observed, although additional one absorption band arising from the first band system appears.

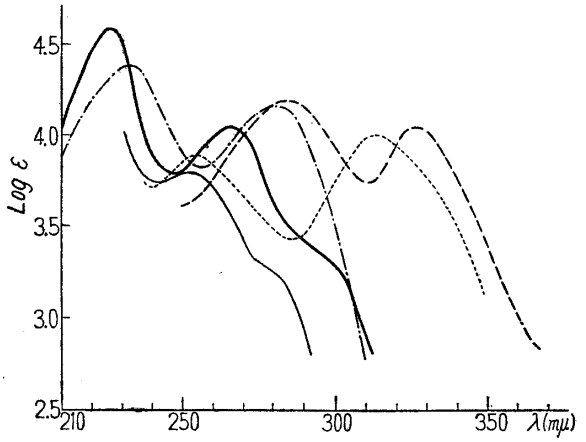

Fig. 3. Ultraviolet Spectra of Substituted Thiazolopyridines (in EtOH)

——— 2-Aminothiazolo[4,5-*c*]pyridine
——— 7-Bromothiazolo[4,5-*c*]pyridine
—·—· 2-Methylthiothiazolo[4,5-*c*]pyridine
····· 2,5-Diaminothiazolo[4,5-*b*]pyridine
– – – – 2-Amino-5-methylthiothiazolo[5,4-*b*]pyridine

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Summary

The ultraviolet absorption spectra of thiazolopyridine and its substitution products, and of benzothiazole were comparatively studied.

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Errata for Pharmaceutical Bulletin, Vol. 4, Nos. 1 and 2.

Page	Line	Error	Correction
41	25↑	diosgenin, $[\alpha]_D^{30}$: 110°	$[\alpha]_D^{30}$: −111
		Authors' Correction after Publication	
36	Footnote *1		
	2↓	at 10.18 μ	at 10.86 μ
41	7↓	(cf. Table I)	(cf. Table II)
127	10↓	(IX: R=H)	(VIII: R=H)
129	Experimental 5↑	(yield, 0.23 g.)	(yield, 0.023 g.)