*Ultraviolet Spectra of β-Furyl Ketone and its Derivatives**

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Koltzin and Bulfson[1] have reported that β-furyl ketones of the A and B types have an ultraviolet absorption maximum at 240~270 mμ and 442~460 mμ respectively. Since these types of compounds possess another chromophoric group which is unconjugated or conjugated to the β-furoyl group, the present authors hoped to examine the ultraviolet spectrum of simple β-furyl ketones. For the present paper, the ultraviolet spectra of fifteen β-furyl ketones and their derivatives, which have been isolated from natural sources or have been synthesized in this laboratory, have been examined; the results are listed in the Table I.

Simple β-furyl ketones (I–V) have a broad absorption maximum at 205~208 mμ which is regarded as due to the furan nucleus[2], and also a considerably sharp maximum at 251~255 mμ (ε 3000~8000). The latter maximum, in the longer wave length region, is considered to be usable for analytical purposes as the maximum characteristic of a β-furyl ketone. The β-furyl ketone band of the VI acid appears as a shoulder under the influence of the strong band of the α, β-unsaturated acid group at 218 mμ.

The longest wavelength bands of the semicarbazones (VII–IX) at 265 mμ and of the 2, 4-dinitrophenylhydrazones (X–XII) at about 380 mμ are located at almost the same position as those of the semicarbazone and the

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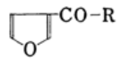
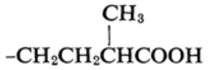
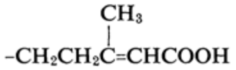
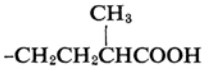
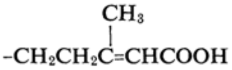
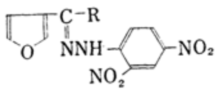
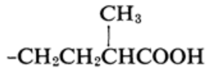
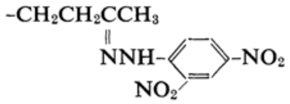
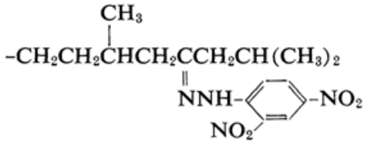
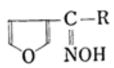
* Natural Furan Derivatives, Part XII. Part XI: T. Tokoroyama and T. Matsuura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 630 (1962).

[1] V. E. Koltzin and N. S. Bulfsone, *J. Gen. Chem., U. S. S. R.*, **30**, 3091 (1960).

[2] T. Kamikawa and T. Kubota, *Tetrahedron*, **12**, 262 (1961) and cited references.

TABLE I

Type of compound	No.	R	λ_{max}^{EtOH}, mμ	ε_{max}
	I[8]	$-CH_2CH_2CH(CH_3)_2$	207 253	14100 5800
	II[9]	$-CH_2CH_2COCH_3$	208 251	16600 7700
	III[10]	 $-CH_2CH_2\overset{CH_3}{\overset{\vert}{C}}HCH_2COCH_2CH(CH_3)_2$	207 251	14100 6200
	IV[11]	 $-CH_2CH_2\overset{CH_3}{\overset{\vert}{C}}HCOOH$	ca. 205 252	7400 3100
	V[12]	$-CH_2CH_2N(CH_3)_2 \cdot HCl$	ca. 205 255	8000 3600
	VI[13]	 $-CH_2CH_2\overset{CH_3}{\overset{\vert}{C}}=CHCOOH$	218 255(infl.)	19400 4100
	VII[12]	$-CH_3$	218 264	7900 17700
	VIII[12]	 $-CH_2CH_2\overset{CH_3}{\overset{\vert}{C}}HCOOH$	218 265	8400 20000
	IX	 $-CH_2CH_2\overset{CH_3}{\overset{\vert}{C}}=CHCOOH$	216 265	22400 19600
	X	$-CH_3$	251[a] 380[a]	14900 26600
	XI[11]	 $-CH_2CH_2\overset{CH_3}{\overset{\vert}{C}}HCOOH$	251[a] 380[a]	13400 25600
	XII[8]	$-CH_2CH_2CH(CH_3)_2$	ca. 253[a] 382	11200 21300
	XIII[9]		241[a] 369[a]	30500 39000
	XIV[10]		ca. 260[a] 373[a]	24200 47800
	XV[8]	$-CH_2CH_2CH(CH_3)_2$	209 229	6300 5000

a) Determined in chloroform

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[3] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", 2nd Ed., Edward Arnold Ltd., London (1957), p. 114 ff.

[4] K. Hirayama, in "Jikken Kagaku Koza", Ed. by the Chemical Society of Japan, Maruzen Co., Tokyo (1957)., Vol. 1, p. 85 ff.

[5] Ibid., p. 57.

[6] A. E. Gilliam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", 2nd Ed., Edward Arnold Ltd., London (1957), p. 57.

[7] T. Ueda and Y. Fujita, 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1961.

[8] T. Matsuura, This Bulletin, **30**, 430 (1957).

[9] T. Kubota and N. Ichikawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 450 (1954).

[10] T. Kubota and T. Matsuura, This Bulletin, **31**, 492 (1958).

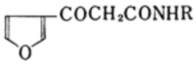
[11] T. Kubota and K. Naya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 86 (1956).

[12] K. Naya, ibid., **77**, 759 (1956).

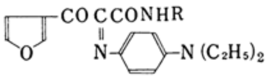
[13] T. Matsuura, ibid., **78**, 389 (1957).

2, 4-dinitrophenylhydrazone of α, β-unsaturated ketones[3,4]. On the other hand, the bis-2, 4-dinitrophenylhydrazones, XIII and XIV, which have the additional 2, 4-dinitrophenylhydrazone group of a saturated ketone in the molecule, show a maximum at about 370 mμ with twice the absorption intensity. This hypsochromic shift is apparently due to the overlapping of the band of the unsaturated ketone derivative with the band of the saturated ketone derivative[5,6].

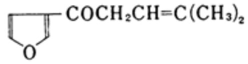
The ultraviolet absorption maxima[7] of egomaketone (β-dehydroperillaketone) (XVI) and of its ketonic derivatives show a good agreement with those discussed above.



A (R=Aryl)



B (R=Aryl)



XVI

Experimental

The ultraviolet spectra were determined with a Hitachi recording spectrophotometer, model EPS 2.

Semicarbazone IX of 2-Methyl-4-(β-furoyl)-1-butene-1-carboxylic Acid.—The acid[13] (0.1 g.) was treated with semicarbazide hydrochloride (0.1 g.) and potassium acetate (0.1 g.) in dilute ethanol for two days. The crystals which separated were collected (0.12 g.) and recrystallized from dioxane to give colorless plates; m. p., 200~201°C (decomp.).

Found: C, 54.40; H, 6.11; N, 14.49. Calcd. for $C_{12}H_{15}O_4N_3 \cdot 1/4\ (C_4H_8O_2)$: C, 54.35; H, 5.97; N, 14.63%.

2,4-Dinitrophenylhydrazone (X) of 3-Acetylfuran.—3-Acetylfuran[12] was treated with 2, 4-dinitrophenylhydrazine-sulfuric acid in ethanol. Recrystallization from ethyl acetate gave orange needles; m. p., 227~228°C.

Found: C, 49.97; H, 3.57; N, 19.45. Calcd. for $C_{12}H_{10}O_5N_4$: C, 49.66; H, 3.47; N, 19.31%.

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