

Shunsaku Shiotani* and Hiroyuki Morita

College of Liberal Arts, University of Toyama,
Gofuku 3190, Toyama 930, Japan
Received March 20, 1991

The ^{13}C nmr spectra of 2- or 3-monosubstituted furo[2,3-*b*] **1a-1j**, furo[3,2-*b*] **2a-2j**, furo[2,3-*c*] **3a-3j** and furo[3,2-*c*]pyridine derivatives **4a-4j** are reported. Effects by change in annelation and substituent effects on ^{13}C chemical shifts and carbon-proton coupling constants are discussed. The spectra of benzo[*b*]furan derivatives **5a-5j** having the corresponding substituent are also reported for comparison.

J. Heterocyclic Chem., **28**, 1469 (1991).

During our research on the chemical properties of furopyridines, we synthesized several compounds having a substituent at 2- or 3-position. Their synthesis and ^1H nmr spectral data have been reported previously [2]. Since these compounds **1a-4j** represent a homogeneous and fairly complete set of compounds, we thought it of some interest to report and briefly comment on their ^{13}C nmr spectra. As a matter of fact, to our knowledge ^{13}C nmr data have been reported so far only for the parent structure of furo[2,3-*b*] **1a**, furo[3,2-*b*] **2a**, furo[2,3-*c*] **3a** and furo[3,2-*c*]pyridine (**4a**) by us [1] and for compound **2a** by Hickson *et al* [3].

Results and Discussion.

The furopyridines studied are listed in Chart 1, the corresponding ^{13}C chemical shifts in Table I, the substituent effects in Table II and the C-[H] coupling constants in Table III. The ^{13}C chemical shifts, the substituent effects and the coupling constants of benzo[*b*]furan derivatives **5a-5j** having the corresponding substituent at 2- or 3-position are also listed in Table I, Table II and Table III for comparison [4].

Spectral assignments were made on the basis of standard chemical shift theory [5], comparison with the data reported for derivatives of pyridine [6,7,8,9], monosubstituted furan derivatives [10] and the parent furopyridines for which the assignments of the chemical shift of CH groups were confirmed using the selected C-[H] spin decoupling method [1], and comparison of $^1J_{\text{CH}}$ values of the

corresponding carbon.

The signals of furanoid carbons C-2 and C-3 of the parent furopyridines appear at 144.41-148.50 and 104.52-107.89 ppm respectively, and are comparable to those of benzo[*b*]furan (144.72 and 106.42 ppm) and those of furan (143.6 and 110.4 ppm) [10]. These facts indicate that the electronic effect of pyridine and benzene ring in these fused systems upon C-2 and C-3 is small. It is worth indicating, however, that the difference of C-2 chemical shift of each furopyridine (+3.78, +2.88, +0.47 and -0.31 ppm for **2a**, **3a**, **4a** and **1a**, respectively) to that of benzo[*b*]furan reflect the difference in chemical shift of C-3a but not C-7a by change of the annelation: C-3a (δ 147.31 ppm) of furo[3,2-*b*]pyridine (**2a**) corresponds to the α -carbon (δ 149.9 ppm) of pyridine, furo[2,3-*c*] **3a** (δ 133.39 ppm) to the γ -carbon (δ 136.0 ppm) and furo[3,2-*c*] **4a** (δ 124.34 ppm) and furo[2,3-*b*] **1a** (δ 118.93 ppm) to the β -carbon (δ 123.8 ppm) [9]. Moreover, there is a good correlation between the chemical shift of C-2 of furopyridines and the electron density (q_r) (0.938, 0.940, 0.965 and 0.967 for C-2 of **2a**, **3a**, **4a** and **1a**) which also correlates to q_r of C-3a (0.979, 0.998, 1.035 and 1.036 for **2a**, **3a**, **4a** and **1a**) but not to that of C-7a (0.991, 0.994, 0.951 and 0.924 for **2a**, **3a**, **4a** and **1a**) calculated using simple HMO method [11,12], the lower chemical shift and electron density of C-2 corresponds to the lower chemical shift and electron density of C-3a. These facts imply that the electronic effect of the pyridine ring of C-2 is exerted mainly through the C-3 - C-3a link, as in the case of benzo[*b*]furan [13]. Con-

Chart 1

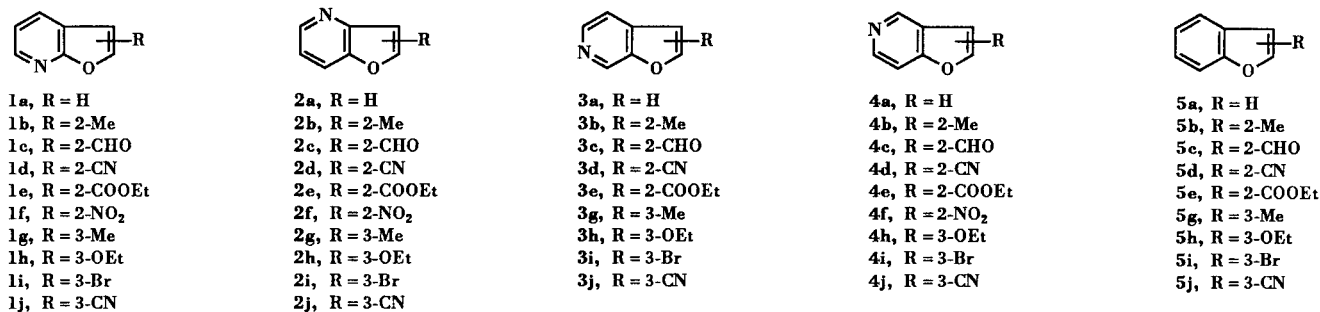


Table 1
¹³C Chemical Shifts of Furopyridine and Benz[*b*]furan Derivatives [a]

	C-2	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a	Others
Furo[2,3-<i>b</i>]pyridine									
Unsubstituted 1a	144.41	105.64	129.93	118.93	143.82	–	118.93	161.72	
2-Me 1b	155.30	101.55	128.37	118.71	142.36	–	121.05	161.69	13.99 (-Me)
2-CHO 1c	151.50	114.59	133.09	120.66	149.06	–	118.93	162.18	180.05 (-CHO)
2-CN 1d	126.96	117.44	132.10	120.91	148.53	–	117.44	161.42	110.96 (-CN)
2-COOEt 1e	144.58	112.03	131.78	119.83	147.09	–	118.66	161.33	158.38 (-CO) 61.15 (O-CH ₂ -) 13.69 (-CH ₃)
2-NO ₂ 1f	152.10	105.79	133.68	121.93	149.89	–	118.69	159.03	
3-Me 1g	140.92	115.13	128.39	118.54	143.73	–	120.86	162.08	7.94 (-Me)
3-OEt 1h	124.25	142.60	128.05	118.35	144.60	–	114.08	159.62	66.25 (O-CH ₂ -) 14.52 (-CH ₃)
3-Br 1i	142.33	96.60	128.88	119.69	145.24	–	119.27	160.55	
3-CN 1j	151.74	94.21	129.73	120.88	146.50	–	116.76	160.76	111.18 (CN)
Furo[3,2-<i>b</i>]pyridine									
Unsubstituted 2a	148.50	107.89	–	145.70	118.56	117.88	147.31	147.41	
2-Me 2b	159.57	103.94	–	144.99	117.47	116.69	149.04	147.33	14.16 (-Me)
2-CHO 2c	154.45	117.22	–	148.04	122.73	119.88	145.60	149.62	179.73 (-CHO)
2-CN 2d	130.27	118.86	–	148.21	122.22	119.03	144.31	148.87	110.72 (-CN)
2-COOEt 2e	148.19	113.57	–	147.04	121.20	119.00	145.72	148.58	158.32 (-CO) 61.37 (O-CH ₂ -) 13.74 (-CH ₃)
2-NO ₂ 2f	154.74	107.42	–	149.26	123.81	120.20	144.46	147.50	
3-Me 2g	145.09	116.71	–	145.09	118.44	117.79	147.80	147.80	6.53 (-Me)
3-OEt 2h	129.37	140.38	–	145.06	119.15	118.20	143.21	146.55	66.71 (O-CH ₂ -) 14.47 (-CH ₃)
3-Br 2i	146.26	99.38	–	146.63	119.91	118.74	144.65	147.28	
3-CN 2j	154.84	97.06	–	148.01	121.15	119.54	143.85	147.48	110.62 (-CN)
Furo[2,3-<i>c</i>]pyridine									
Unsubstituted 3a	147.60	105.60	115.66	141.99	–	133.58	133.39	151.84	
2-Me 3b	158.91	101.82	114.69	142.02	–	132.49	135.29	151.82	13.77 (-Me)
2-CHO 3c	153.82	114.37	117.23	143.14	–	135.90	132.36	152.16	180.10 (-CHO)
2-CN 3d	129.58	116.96	116.59	143.53	–	134.85	131.41	151.92	110.52 (-CN)
2-COOEt 3e	148.09	111.96	116.79	142.90	–	135.31	132.88	152.11	158.67 (-CO) 61.93 (O-CH ₂ -) 14.08 (-CH ₃)
3-Me 3g	144.24	115.05	114.15	141.72	–	133.49	135.82	152.23	7.31 (-Me)
3-OEt 3h	127.56	142.99	113.35	141.26	–	133.74	127.68	150.23	66.59 (O-CH ₂ -) 14.35 (-CH ₃)
3-Br 3i	145.41	97.11	114.27	143.04	–	134.24	133.41	151.53	
3-CN 3j	154.28	94.97	114.86	144.36	–	134.92	131.34	151.53	110.89 (-CN)
Furo[3,2-<i>c</i>]pyridine									
Unsubstituted 4a	145.19	104.52	143.97	–	144.11	106.74	124.34	158.88	
2-Me 4b	156.06	100.28	142.35	–	143.29	106.06	126.07	158.74	13.74 (-Me)
2-CHO 4c	152.87	114.86	147.02	–	147.94	107.89	123.90	159.94	179.22 (-CHO)
2-CN 4d	127.78	116.52	145.70	–	147.50	107.16	122.49	159.30	110.54 (-CN)
2-COOEt 4e	146.26	111.37	145.92	–	146.65	107.42	124.05	159.35	158.42 (-CO) 61.57 (O-CH ₂ -) 13.96 (-CH ₃)
2-NO ₂ 4f	153.22	105.06	147.23	–	148.72	107.64	122.93	157.13	
3-OEt 4h	124.98	142.77	142.24	–	144.75	106.99	119.32	157.59	66.74 (O-CH ₂ -) 14.45 (-CH ₃)
3-Br 4i	143.09	96.99	143.21	–	145.53	106.99	124.20	158.91	
3-CN 4j	152.55	93.70	143.46	–	146.60	107.52	121.73	158.77	110.84 (-CN)
Benzo[<i>b</i>]furan									
Unsubstituted 5a	144.72	106.42	121.08	122.64	124.12	111.30	127.39	154.96	
2-Me 5b	155.16	102.48	119.93	122.30	122.93	110.50	129.19	154.77	13.62 (-Me)
2-CHO 5c	152.28	117.47	123.27	123.71	128.68	112.03	126.24	155.69	179.24 (-CHO)
2-CN 5d	127.15	118.27	122.44	124.42	128.29	111.86	125.34	155.50	111.64 (-CN)
2-COOEt 5e	145.11	112.84	122.05	122.95	126.71	111.40	126.27	154.94	158.50 (-CO) 60.52 (O-CH ₂ -) 13.50 (-CH ₃)
3-Me 5g	141.24	115.47	119.25	122.10	123.95	111.18	128.98	155.30	7.53 (-Me)
3-OEt 5h	124.78	144.16	118.76	121.95	124.86	111.50	121.95	153.65	66.49 (O-CH ₂ -) 14.72 (-CH ₃)
3-Br 5i	142.51	97.89	119.69	123.32	125.62	111.62	127.05	154.35	
3-CN 5j	151.77	94.58	119.81	124.39	126.24	111.84	124.39	154.04	111.84 (-CN)

[a] δ in ppm from TMS.

Table II
Observed Substituent Effects on Carbon Chemical Shifts of Furopyridines and Benzo[*b*]furan [a]

		C-2	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a
2-Me	1b	+10.89	-4.09	-1.56	-0.22	-1.46	—	+2.12	-0.03
	2b	+11.07	-3.95	—	-0.71	-1.09	-1.19	+1.73	-0.08
	3b	+11.31	-3.78	-0.97	+0.03	—	-1.09	+1.90	-0.02
	4b	+10.87	-4.24	-1.62	—	-0.82	-0.68	+1.73	-0.14
	5b	+10.44	-3.94	-1.15	-0.34	-1.19	-0.80	+1.80	-0.19
3-Me	1g	-3.49	+9.49	-1.54	-0.39	-0.09	—	+1.93	+0.36
	2g	-3.41	+8.82	—	-0.61	-0.12	-0.09	+0.49	+0.39
	3g	-3.36	+9.45	-1.51	-0.27	—	-0.09	+2.43	+0.39
	5g	-3.48	+9.05	-1.83	-0.54	-0.17	-0.12	+1.59	+0.34
3-OEt	1h	-20.16	+39.96	-1.88	-0.58	+0.78	—	-4.85	-2.10
	2h	-19.13	+32.49	—	-0.64	+0.59	+0.32	-2.66	-0.86
	3h	-20.04	+37.39	-2.31	-0.73	—	+0.16	-5.71	-1.61
	4h	-20.21	+38.25	-1.73	—	+0.64	+0.25	-5.02	-1.19
	5h	-19.94	+37.74	-2.32	-0.69	+0.74	+0.20	-5.44	-1.31
2-CHO	1c	+7.09	+8.95	+3.16	+1.73	+5.24	—	±0.00	+0.46
	2c	+5.95	+9.33	—	+2.34	+4.17	+2.00	-1.71	+2.21
	3c	+6.22	+8.77	+1.57	+1.15	—	+2.32	-1.03	+0.32
	4c	+7.68	+10.34	+3.05	—	+3.83	+1.15	-0.44	+1.01
	5c	+7.56	+11.05	+2.19	+1.07	+4.56	+0.73	-1.15	+0.73
2-CN	1d	-17.45	+11.80	+2.17	+1.98	+4.71	—	-1.49	-0.30
	2d	-18.23	+10.97	—	+2.51	+3.66	+1.15	-3.00	+1.46
	3d	-18.02	+11.36	+0.93	+1.54	—	+1.27	-1.98	+0.08
	4d	-17.41	+12.00	+1.73	—	+3.39	+0.42	-1.85	+0.42
	5d	-17.57	+11.85	+1.36	+1.78	+4.17	+0.56	-2.05	+0.54
2-COOEt	1e	+0.17	+6.39	+1.85	+0.90	+3.27	—	-0.27	-0.39
	2e	-0.31	+5.68	—	+1.34	+2.64	+1.12	-1.59	+1.17
	3e	+0.49	+6.36	+1.13	+0.91	—	+1.73	-0.51	+0.27
	4e	+1.07	+6.85	+1.95	—	+2.54	+0.68	-0.29	+0.47
	5e	+0.39	+6.42	+0.97	+0.31	+2.59	+0.10	-1.12	-0.02
2-NO ₂	1f	+7.69	+0.15	+3.75	+3.00	+6.07	—	-0.24	-2.69
	2f	+6.24	-0.47	—	+3.56	+5.25	+2.32	-2.88	+0.09
	4f	+8.03	+0.54	+3.24	—	+4.61	+0.90	-1.41	-1.75
3-Br	1i	-2.08	-9.04	-1.05	+0.76	+1.42	—	+0.34	-1.17
	2i	-2.24	-8.51	—	+0.93	+1.35	+0.86	-2.66	-0.13
	3i	-2.19	-8.49	-1.39	+1.05	—	+0.66	+0.02	-0.31
	4i	-2.10	-7.53	-0.76	—	+1.42	+0.25	-0.14	+0.03
	5i	-2.21	-8.53	-1.39	+0.68	+1.50	+0.32	-0.34	-0.61
3-CN	1j	+7.33	-11.43	-0.20	+1.95	+2.68	—	-2.17	-0.96
	2j	+6.34	-10.83	—	+2.31	+2.59	+1.66	-3.46	+0.07
	3j	+6.68	-10.63	-0.81	+2.37	—	+1.34	-2.05	-0.31
	4j	+7.36	-10.82	-0.51	—	+2.49	+0.78	-2.61	-0.11
	5j	+7.05	-11.84	-1.27	+1.75	+2.12	+0.54	-3.00	-0.92

[a] Positive values indicate downfield shifts.

Table III
 ^1H - ^{13}C Coupling Constants of Furopyridine and Benzo[*b*]furan Derivatives [a] [b]

	C-2	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a	Others
Furo[2,3-<i>b</i>]pyridine									
Unsubstituted $^1\text{J}_{\text{CH}}$ 1a	204.3 9.9 (C2-H3)	178.51 12.6 (C3-H2) 2.8 (C3-H4)	165.3 7.7 (C4-H6)	164.2 8.8 (C5-H6)	180.2 7.1 (C6-H4) 4.4 (C6-H5)	-	- 5.5 (C3a-H5) 4.4 (q) (C3a-H2,3,6)	- 13.2 (C7a-H6) 8.3 (q) (C7a-H2,3,4)	-
2-Me $^1\text{J}_{\text{CH}}$	- 9.3 (C2-H3) 7.1 (q) (C2-Me)	176.9 3.3 (qm) (C3-H4, Me) (C4-H6)	163.7 6.6 (C4-H6)	163.7 8.8 (C5-H6)	179.6 8.0 (C6-H4) 5.5 (C6-H5)	-	- [c]	- [c]	129.1 (q) (Me) 1.1 (C-H3)
3-Me $^1\text{J}_{\text{CH}}$	201.6 6.6 (q) (C2-Me)	- [d]	164.3 7.7 (C4-H6)	163.7 8.8 (C5-H6)	179.6 7.5 (C6-H4) 5.0 (C6-H5)	-	- 9.2 (C3a-H5) 3.3 (C3a-H2)	- 14.3 (C7a-H6) 8.8 (t) (C7a-H2,4)	128.0 (q) (Me) 1.7 (C-H2)
3-OEt $^1\text{J}_{\text{CH}}$	203.8	- 9.3 (C3-H2) 2.8 (C3-H4)	167.0 7.7 (C4-H6)	164.8 8.8 (C5-H6)	180.7 7.7 (C6-H4) 4.9 (C6-H5)	-	- 8.2 (C3a-H5) 4.9 (C3a-H3)	- 13.7 (C7a-H6) 8.7 (t) (C7a-H2,4)	143.9 (t) (CH ₂) 4.4 (q) (C-H(Me)) 126.9 (q) (Me) 2.7 (t) (C-H(CH ₂))
2-CHO $^1\text{J}_{\text{CH}}$	- 31.3 (C2-H(CHO)) 8.8 (C2-H3)	180.7 2.8 (C3-H4)	167.5 7.1 (C4-H6) 1.1 (C4-H5)	165.9 8.9 (C5-H6)	181.8 7.1 (C6-H4) 4.4 (C6-H5)	-	- [d]	- 14.3 (7a-H6) 7.1 (t) (C7a-H3,4)	182.9 (CHO) 1.7 (C-H3)
2-CN $^1\text{J}_{\text{CH}}$	- 7.7 (C2-H3)	184.6 2.7 (C3-H4)	168.1 7.1 (C4-H6) 1.1 (C4-H5)	166.4 8.8 (C5-H6)	182.4 7.7 (C6-H4) 4.4 (C6-H5)	-	- 8.8 (C3a-H5) 3.8 (C3a-H3)	- 14.3 (C7a-H6) 8.8 (t) (C7a-H3,4)	- 1.7 (C(CN)-H3)
2-COOEt $^1\text{J}_{\text{CH}}$	- 7.7 (C2-H3)	182.9 2.8 (C3-H4)	167.5 7.1 (C4-H6) 1.1 (C4-H5)	165.4 8.8 (C5-H6)	181.3 7.7 (C6-H4) 4.4 (C6-H5)	-	- 8.2 (C3a-H5) 4.4 (C3a-H3)	- 14.8 (C7a-H6) 8.2 (C7a-H4)	148.3 (t) (CH ₂) 126.9 (q) (Me) 4.4 (q) (C-H(CH ₂)) 2.8 (t) (C-H(CH ₂)) 1.1 (C(CO)-H3)
2-NO ₂ $^1\text{J}_{\text{CH}}$	- [c]	189.0 3.3 (C3-H4)	168.6 7.1 (C4-H6) 1.1 (C4-H5)	167.0 8.8 (C5-H6)	182.9 7.7 (C6-H4) 4.4 (C6-H5)	-	- 9.7 (C3a-H5) 3.9 (C3a-H3)	- [c]	-

Table III (continued)

	C-2	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a	Others
3-Br	1i ¹ J _{CH} 209.8	-	167.0 8.8 (C3-H2) 7.1 (C4-H6) 3.9 (C3-H4)	164.8 8.8 (C5-H6) 7.7 (C6-H4) 5.5 (C6-H5)	180.7 7.7 (C6-H4) 5.5 (C6-H5)	-	-	-	-
3-CN	1j ¹ J _{CH} 211.5	-	168.6 10.8 (C3-H2) 7.7 (C4-H6) 2.8 (C3-H4)	165.9 8.8 (C5-H6) 7.7 (C6-H4) 5.0 (C6-H5)	182.4 7.7 (C6-H4) 5.0 (C6-H5)	-	-	-	-
Fuoro[3,2-b]pyridine									
Unsubstituted	¹ J _{CH} 203.8	179.6	-	178.5	164.8	166.4	-	-	-
2a	11.0 (C2-H3)	12.1 (C3-H2)	-	6.6 (C5-H7) 3.9 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.1 (C7-H5) 1.1 (C7-H6)	[d]	[d]	-
2-Me	2b ¹ J _{CN} -	177.4	-	178.0	164.2	166.4	[d]	[d]	129.1 (q) (Me)
	9.9 (C2-H3)	3.9(q) (C3-Me)	-	6.6 (C5-H7) 3.9 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.7 (C7-H5) 1.1 (C7-H6)	[d]	[d]	1.1 (C-H3)
	7.1(q) (C2-Me)	3.3 (C3-C4)	-	178.5	164.3	166.5	[d]	[d]	128.5 (q) (Me)
3-Me	2g ¹ J _{CN} 201.1	-	-	6.6 (C5-H7) 3.3 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.5 (C7-H5) 1.1 (C7-H6)	[d]	[d]	1.7 (C-H2)
	6.0(q) (C2-Me)	11.8 (C3-H2)	-	179.6	164.8	167.0	-	-	143.9 (t) (CH ₂)
	203.8	12.6 (C3-H2)	-	6.6 (C5-H7) 3.8 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.1 (C7-H5) 1.1 (C7-H6)	11.0 (C3a-H5)	7.1 (t) (C7a-H3,6)	4.4 (C-H(CH ₂))
3-OEt	2h ¹ J _{CH} 203.8	-	-	180.7	165.9	169.2	-	-	183.5 (CHO)
	33.0 (C2-H(CHO))	181.3	-	6.6 (C5-H7) 3.3 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.1 (C7-H5) 1.1 (C7-H6)	12.6 (C3a-H5)	7.7 (t) (C7a-H3,6)	1.7 (C-H3)
2-CHO	2c ¹ J _{CH} -	185.1	-	180.7	166.4	170.3	-	-	-
	8.8 (C2-H3)	185.1	-	6.6 (C5-H7) 3.9 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.1 (C7-H5) 1.1 (C7-H6)	13.0 (C3a-H5)	2.2 (C(CN)-H3)	2.2 (C(CN)-H3)
2-CN	2d ¹ J _{CH} -	185.1	-	180.7	166.4	170.3	-	-	-
	8.8 (C2-H3)	185.1	-	6.6 (C5-H7) 3.9 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.1 (C7-H5) 1.1 (C7-H6)	13.0 (C3a-H5)	2.2 (C(CN)-H3)	2.2 (C(CN)-H3)

Table III (continued)

	C-2	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a	Others
2-COOEt	-	183.3	-	180.2	165.4	169.2	-	-	-
2e ¹ J _{CH}	8.2 (C2-H3)			6.6 (C5-H7) 3.3 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.1 (C7-H5)	14.0 (C3a-H5) 3.9 (C3a-H3)	[d]	148.9 (t) (CH ₂) 4.4 (q) (C-H(CH ₃)) 127.4 (q) (Me) 2.7 (t) (C-H(CH ₂))
2-NO ₂	-	107.4	-	181.8	167.0	170.8	-	-	-
2f ¹ J _{CH}				6.6 (C5-H7) 3.3 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.1 (C7-H5)	13.2 (C3a-H5) 3.8 (C3a-H3)	9.3 (t) C7a-H3,6) 3.3 (C7a-H5)	
3-Br	209.3	-	-	180.2	164.8	168.1	-	-	-
2i ¹ J _{CH}				6.6 (C5-H7) 3.3 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.1 (C7-H5)	12.2 (C3a-H5) 6.6 (C3a-H7)	7.7 (t) (C7a-H2,6) 1.7 (C7a-H5)	
3-CN	210.9	-	-	181.8	164.4	169.7	-	-	-
2j ¹ J _{CH}				6.6 (C5-H7) 3.9 (C5-H6)	9.9 (C6-H5) 1.1 (C6-H7)	7.1 (C7-H5)	[d]	8.8 (t) (C7a-H2,6) 1.7 (C7a-H5)	1.1 (C-H2)
Furo[2,3-c]pyridine									
Unsubstituted	203.2	179.6	164.3	180.2	-	182.9	-	-	-
3a ¹ J _{CH}	11.0 (C2-H3)	13.2 (C3-H2) 2.7 (C3-H4)	9.9 (C4-H5)	11.0 (C5-H7) 2.2 (C5-H4)	-	12.1 (C7-H5)	8.8 (t) (C3a-H5,2) 4.4 (C3a-H3)	[d]	
2-Me	-	178.0	163.7	180.2	-	182.4	-	-	129.1 (q) (Me)
3b ¹ J _{CH}	10.4 (C2-H3)	3.3 (qn) (C3-H4, Me) 7.1 (q) (C2-Me)	9.9 (C4-H5)	10.4 (C5-H7)	-	12.1 (C7-H5)	8.2 (C3a-H5) 3.8 (C3a-H3)	[c]	1.1 (C-H3)
3-Me	200.1	-	163.7	181.0	-	182.9	-	-	128.5 (q) (Me)
3g ¹ J _{CH}	6.4 (q) (C2-Me)		9.3 (C4-H5) 1.1 (C4-H7)	11.0 (C5-H7)	-	12.1 (C7-H5)	[c]	1.2 (C-H2)	
3-OEt	202.7	-	163.1	179.6	-	183.5	-	-	143.4 (t) (CH ₂) 2.8 (t) (C-H(CH ₃))
3h ¹ J _{CH}		9.9 (C3-H2)	8.2 (C4-H5) 1.7 (C4-H7)	10.4 (C5-H7) 2.2 (C5-C4)	-	12.1 (C7-H5)	7.7 (C3a-H5) 5.5 (C3a-H2)	7.4 (t) (C7a-H4,7) 4.9 (C7a-H5)	

Table III (continued)

	C-2	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a	Others
2-CHO	3c ¹ J _{CH}	181.3 2.7 (C3-H4) (C2-H(CHO)) 9.3 (C2-H3)	168.6 7.2 (C4-H5) (C4-H7) (C5-H4)	181.3 11.5 (C5-H7) 1.7 (C5-H4)	-	186.2 12.1 (C7-H5) 1.1 (C7-H4)	- 7.7 (t) (C3a-H5,7) 3.3 (C3a-H3)	- 7.1 (t) (C7a-H4,7) 5.3 (C7a-H5)	184.6 1.7 (C-H3)
2-CN	3d ¹ J _{CH}	185.7 2.8 (C3-H4) (C2-H3)	165.9 11.5 (C4-H5) (C4-H7)	181.8 11.0 (C5-H7) 1.6 (C5-H4)	-	187.3 12.1 (C7-H5) 1.7 (C7-H4)	- 8.2 (C3a-H5) 3.8 (t) (C3a-H3,7)	- 7.1 (t) (C7a-H4,7) 4.9 (C7a-H5)	- 1.6 (C-H3)
2-COOEt	3e ¹ J _{CH}	183.4 2.8 (C3-H4) (C2-H3)	170.3 6.6 (C4-H5) (C4-H7)	181.3 11.0 (C5-H7) 1.7 (C5-H4)	-	186.2 12.1 (C7-H5) 1.7 (C7-H4)	- 8.2 (C3a-H5) 3.8 (t) (C3a-H3,7)	- 6.2 (t) (C7a-H4,7) 4.4 (C7a-H5)	148.3 (t) (CH ₂) 127.4 (q) (Me) 4.4 (q) 2.7 (t) (C-H(CH ₂)) 3.3 (t) (C(CO)-H(CH ₂)) 1.1 (q) (C(CO)-H(CH ₃))
3-Br	3f ¹ J _{CH}	209.3	167.0 9.3 (C4-H5) (C4-H7)	179.1 11.5 (C5-H7) 5.0 (C5-H4)	-	185.1 12.1 (C7-H5) 1.1 (C7-H4)	- 8.2 (C3a-H5) 3.9 (t) (C3a-H2,7)	- 7.7 (t) (C7a-H4,7) 4.7 (C7a-H5)	- 1.1 (C-H2)
3-CN	3j ¹ J _{CN}	209.8	167.0 11.5 (C3-H2) 2.8 (C3-H4)	183.5 11.0 (C5-H7) 1.6 (C5-H4)	-	187.3 12.6 (C7-H5) 1.1 (C7-H4)	- [d]	- [c]	- 1.1 (C-H2)
Furo[3,2-c]pyridine									
Unsubstituted	¹ J _{CH}	204.3	181.8	-	179.6	167.0	-	-	
4a	11.0 (C2-H3)	12.6 (C3-H2) 1.1 (C3-H4)	12.1 (C4-H6)	-	12.1 (C6-H4) 2.2 (C6-H7)	8.8 (C7-H6)	11.0 (C3a-H4) 4.4 (q) (C3a-H2,3,7)	9.3 (C7a-H6) 7.1 (q) (C7a-H2,3,4)	
2-Me	4b ¹ J _{CH}	177.3 3.8 (q) (C2-H3) 7.1 (q) (C2-Me)	180.2 12.6 (C4-H6)	-	179.1 12.1 (C6-H4) 2.2 (C6-H7)	166.4 8.8 (C7-H6) 1.1 (C7-H4)	- [c]	- [c]	129.1 (q) (Me) 1.1 (C-H3)
3-OEt	4h ¹ J _{CH}	203.8	182.9 12.6 (C4-H6)	-	179.6 12.1 (C6-H4) 2.2 (C6-H7)	167.6 8.8 (C7-H6)	- [c]	- [c]	143.4 (t) (CH ₂) 126.9 (q) (Me) 4.4 (q) 2.8 (t) (C-H(CH ₂))
2-CHO	4c ¹ J _{CH}	180.2 34.1 (C2-H(CHO)) 9.3 (C2-H3)	183.5 12.6 (C4-H6)	-	181.3 12.6 (C6-H4) 2.2 (C6-H7)	169.3 8.8 (C7-H6) 1.7 (C7-H4)	- 9.4 (C3a-H4) 3.9 (t) (C3a-H3,7)	- 9.9 (C7a-H6) 6.6 (t) (C7a-H3,4)	183.5 1.7 (C-H3)

Table III (continued)

	C-2	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a	Others
2-CN									
4d ¹ J _{CH}	-	185.7 (C3-H4)	184.6 (C4-H6)	-	181.8 (C6-H4)	170.3 (C7-H6)	-	-	-
	9.3 (C2-H3)	1.1 (C3-H4)	12.6 (C4-H6)		2.2 (C6-H7)	1.7 (C7-H4)	9.3 (C3a-H4)	10.4 (C7a-H6)	1.6 (C-H3)
2-COOEt									
4e ¹ J _{CH}	-	182.9 (C3-H4)	182.9 (C4-H6)	-	180.7 (C6-H7)	169.2 (C7-H4)	-	-	-
	8.8 (C2-H3)	1.1 (C3-H4)	12.6 (C4-H6)		2.2 (C6-H7)	1.7 (C7-H4)	8.8 (C3a-H4)	9.9 (C7a-H6)	2.8 (t) (C(CO)-H(CH ₂))
					148.3 (t) (CH ₂)				127.4 (q) (Me) 4.4 (q) (C-H(CH ₃)) 2.8 (t) (C-H(CH ₂))
2-NO ₂									
4f ¹ J _{CH}	-	189.5 (C3-H4)	185.6 (C4-H6)	-	182.9 (C6-H7)	171.4 (C7-H4)	-	-	-
	[c]	1.1 (C3-H4)	12.6 (C4-H6)		1.7 (C6-H7)	4.4 (t) (C7a-H3,7)	9.3 (C3a-H4)	9.9 (C7a-H6)	
3-Br									
4i ¹ J _{CH}	210.4	-	183.5 (C4-H6)	-	180.7 (C6-H7)	168.1 (C7-H4)	-	-	-
		12.1 (C2-H3)	12.6 (C4-H6)		2.2 (C6-H7)	8.8 (C7-H6)	[c]	[c]	
		1.1 (C3-H4)							
3-CN									
4j ¹ J _{CH}	211.5	-	185.1 (C4-H6)	-	181.8 (C6-H7)	170.3 (C7-H6)	-	-	-
		11.5 (C3-H2)	13.2 (C4-H6)		2.2 (C6-H7)	9.3 (C7-H6)	9.9 (C3a-H4)	9.9 (C7a-H7)	1.1 (C-H2)
		1.7 (C3-H4)					4.4 (t) (C3a-H2,7)	8.2 (t) (C7a-H2,4)	
Benzo[b]furan									
Unsubstituted									
¹ J _{CH}	201.1	176.9	162.0	159.8	161.0	163.7	-	-	-
5a	11.0 (C2-H3)	12.6 (C3-H2)	6.0	7.1	8.2	7.7	[c]	[c]	
		2.8 (C3-H4)	3.3		1.7	1.7			
2-Me									
¹ J _{CH}	-	174.7 (C2-H3)	159.8	164.3	161.0	163.2	-	-	-
	10.4 (C2-H3)	3.3 (C3-H4)	7.7	5.5	8.2	3.9	[c]	[c]	128.5 (q) (Me) 1.1 (C-H)
	7.1 (q) (C2-Me)		1.1	3.3	1.6	1.1			
3-Me									
¹ J _{CH}	198.9	-	160.4	160.4	161.0	164.2	-	-	-
	6.0 (q) (C2-Me)	[d]	6.6	7.1	8.2	7.1			127.4 (q) (Me) 1.1 (C-Me)
3-OEt									
¹ J _{CH}	201.1	-	160.4	160.4	161.0	163.2	-	-	-
		9.9 (C3-H2)	6.6	6.6	8.2	3.3	[c]	[c]	143.4 (t) (CH ₂) 4.4 (q) (C-H(CH ₃)) 2.8 (t) (C-H(CH ₂))

Table III (continued)

		C-2	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a	Others
2-CHO	5c ¹ J _{CH}	-	179.1 2.8 (C2-H3) (C3-H4)	164.8 3.8	162.1 6.0	162.1 8.2	166.5 7.7	- [c]	- [c]	181.3 1.7 (C-H3)
2-CN	5d ¹ J _{CH}	-	181.8 2.8 (C2-H3) (C3-H4)	163.2 6.4	162.1 5.5	162.6 8.2	165.9 6.6	- [c]	- [c]	- 1.7 (C-H3)
2-COOE	5e ¹ J _{CH}	-	180.2 2.8 (C2-H3) (C3-H4)	163.2 7.1	161.5 6.6	161.5 8.2	165.9 7.7	- [c]	- [c]	- 3.3 (t) (C(CO)-H(CH ₂))
3-Br	5i ¹ J _{CH}	207.6	-	164.3 2.8	161.0 7.1	161.5 8.2	164.8 5.5	- [c]	- [c]	147.8 (t) (CH ₂) 4.4 (q) (C-H(Me))
3-CN	5j ¹ J _{CH}	209.3	-	164.8 7.1	162.1 6.6	162.6 7.7	168.1 7.1	- [c]	- [c]	126.9 (q) (Me) 2.8 (t) (C-H(CH ₂))
				2.2	1.7	1.1	3.3			1.7 (C-H2)

[a] In Hz. [b] t: triplet, q: quartet, qn: quintet, couplings given no symbol are doublet. [c] Signals not well resolved from noise. [d] Overlapped by others signals.

trarily, the chemical shifts of the pyridinoid carbons C-4, C-5, C-6, C-7, C-3a and C-7a considerably vary depending on the annelation with furan ring, and the value of chemical shift of each carbon is compatible with the calculated value for each carbon in *o*-vinylmethoxy pyridines within ± 6.8 ppm, assuming that the substituent chemical shifts (SCS) of vinyl group and additivity in benzene derivatives are applicable for methoxy pyridines [14].

Overviewing the Table II, the substituent effects of each substituent upon the skeletal carbons (C-2-C-7a) at the same position are much similar with each other in sign and magnitude with very few exceptions. The substituent effect of an electron-withdrawing substituent at C-2 or C-3 on the carbon having the substituent and the *ortho* carbon is much similar in sign and magnitude to that of monosubstituted furans but somewhat different from that of benzene derivatives; the reported SCS values for formyl group on C_x and C_{ortho} in benzene are +9.0 and +1.2 ppm, methoxycarbonyl on C_x and C_{ortho} +1.3 and -0.5 ppm, cyano on C_x and C_{ortho} -19.6 and +1.4 ppm, bromo on C_x and C_{ortho} -5.4 and +3.3 ppm, and nitro on C_x and C_{ortho} +19.6 and -5.3 ppm [14], while the effects of 2-formyl group on C-2 and C-3 of furopyridines are +5.95 - +7.68 ppm and +8.77 - +10.34 ppm, 2-ethoxycarbonyl on C-2 and C-3 -0.31 - +1.07 ppm and +5.68 - +6.85 ppm, 2-cyano on C-2 and C-3 -17.41 - -18.23 ppm and +10.97 - +12.00 ppm, 3-cyano on C-3 and C-2 +6.34 - +7.36 ppm and -10.63 - -11.43 ppm, 3-bromo on C-3 and C-2 -2.08 - -2.24 ppm and -7.53 - -9.04 ppm, and 2-nitro on C-2 and C-3 +6.24 - +8.03 ppm and -0.15 - +0.54 ppm respectively. The substituent effects of electron-donating (Me and OEt) groups at 2- or 3-position in furopyridines are similar to those in benzene.

In respect to the substituent effects of 2- or 3-substituent on the chemical shifts of pyridine carbons, there is a small but characteristic influence depending on the electronic effect of the substituent. Thus, in all the compounds studied, the electron-withdrawing substituents cause a very small to small down-field shift on C-4, C-5, C-6 and C-7 with the exception of C-4 of compounds having bromo or cyano group at 3-position for which these signals are shifted up-field by 0.2-1.39 ppm. The electron-withdrawing substituents again cause a very small down-field shift on C-3a of **1i** and **3i** and C-7a of **1c-5c**, **1d-5d**, **2e-4e**, **2f**, **4i** and **2j**. The electron-withdrawing substituents also cause up-field shift on C-3a of **2c-5c**, **1d-5d**, **1e-5e**, **1f**, **2f**, **4f**, **1i**, **2i**, **4i**, **5i** and **1j-5j** and C-7a of **1d**, **1e**, **5e**, **1f**, **4f**, **1i-3i**, **5i**, **1j** and **3j-5j**. A methyl group at 2- or 3-position shifts the signals of C-4, C-5, C-6 and C-7 of furopyridines up-field. The signals of C-7a of 2-methylfuropyridines are shifted slightly up-field. The carbon C-4, C-5, C-3a and C-7a of 3-ethoxyfuropyridines are shifted also slightly up-field. The electron-donating substituents cause a very small to small

down-field shift on C-6 and C-7 of 3-ethoxyfuropyridines and C-3a of 2-methyl and 3-methyl derivatives and C-7a of 3-methyl derivatives of furopyridines.

Moreover, it is observed that an electron-donating (Me and OEt) and electron-withdrawing substituent (CN and Br) at C-3 causes shielding effect on C-4 by 0.2-2.3 ppm, which can be interpreted by the steric compression effect [15]. The same effect can be observed in the chemical shift of methyl groups at 3-position of furopyridines and benzo[*b*]furan: the methyl chemical shifts (7.94-6.53 ppm) are higher than that of 3-methylfuran (9.5 ppm) [10] by 1.6-3.0 ppm, while the shifts of 2-methyl groups (14.16-13.45 ppm) are almost the same as that of 2-methylfuran (13.3 ppm) [10].

The one-bond C-H couplings show quite significant differences depending on the position of the carbon atoms. In the parent structures of furopyridine, the C2-H2 and C3-H3 interactions are quite steady at 203.2-204.3 Hz and 178.5-179.6 Hz respectively, and are larger than those of benzo[*b*]furan by 2.1-3.2 Hz and 1.6-2.7 Hz. The C-H couplings of carbons in the pyridine-ring of parent compounds (¹J_{CH} for β- and γ-carbon: 164.2-167.0 Hz and for α-carbon: 178.5-182.9 Hz) are comparable to those for the corresponding carbons of pyridine (163, 161 and 179 Hz [9]). The difference between the ¹J_{CH} of α-carbons (C-6 (*m*-position to C-7a) (+1.2 Hz) of **1a**, C-5 (*o*) (-0.5 Hz) of **2a**, C-5 (*p*) (+0.1 Hz) and C-7 (*o*) (+4.5 Hz) of **3a** and C-4 (*m*) (+2.8 Hz) and C-6 (*m*) (+0.6 Hz) of **4a**) and that of the α-carbon of pyridine, between the ¹J_{CH} of β-carbons (C-5 (*p*) (+1.2 Hz) of **1a**, C-6 (*m*) (+1.8 Hz) of **2a** and C-4 (*m*) (+1.3 Hz) of **3a** and C-7 (*o*) (+4.0 Hz) of **4a**) and that of β-carbon of pyridine, and between the ¹J_{CH} of γ-carbons (C-4 (*m*) (+4.3 Hz) of **1a** and C-7 (*o*) (+5.4 Hz) of **2a**) and that of the γ-carbon of pyridine are affected by the position of the furanoid oxygen atom: the order of increasing differences in coupling constant is *ortho* (+4.0 - +5.4 Hz) > *meta* (+0.6 - +4.3 Hz) > *para* position (-0.5 - +1.2 Hz) to the oxygen atom.

In the presence of an electron-donating group (Me and OEt) in the adjacent position, the C-H interactions of furanoid carbons of furopyridines and benzo[*b*]furan slightly drop by 0.0-3.1 Hz for C2-H2 and 1.6-2.3 Hz for C3-H3, while the presence of an electron-withdrawing group in the adjacent position increases the coupling constant of C2-H2 or C3-H3 of both furopyridines and benzo[*b*]furan consistently: C3-H3 interactions are increased by 0.6-2.2 Hz, 4.9-6.1 Hz, 3.3-4.4 Hz and 9.9-10.5 Hz by the presence of 2-CHO, 2-CN, 2-COOEt and 2-NO₂, and C2-H2 by 5.5-6.5 Hz and 6.6-8.2 Hz by 3-Br and 3-CN group, respectively. The substituent effects of the groups above mentioned upon the ¹J_{CH} values of pyridinoid and benzenoid carbons in the derivatives of furopyridines and benzo[*b*]furan are similar to those on the furanoid carbons

in tendency and magnitude with exception of the 3-OEt group.

The two-bond C-H coupling is well observed in the furan moiety; C2-H3 and C3-H2 constants of the parent furo-pyridines and benzo[*b*]furan fall in 9.9-11.0 Hz and 12.1-13.2 Hz. The corresponding coupling of the monosubstituted derivatives studied are smaller than that of the parent compound. The carbons at 3-position of these compounds also interact with hydrogen at 4-position where possible by 2.7-3.9 Hz.

The long-range couplings observed for the pyridine carbons can be divided into four groups, (1) couplings of 1.1-5.5 Hz, (2) 8.8-11.5 Hz, (3) 5.5-10.4 Hz and (4) 10.4-14.0 Hz, which are correlated to $^2J_{CH}$ coupling between carbon and hydrogen at β - or γ -position, $^2J_{CH}$ coupling between carbon and hydrogen at α -position, $^3J_{CH}$ interaction through the carbon atoms and $^3J_{CH}$ interaction through the nitrogen atom of pyridine, respectively, comparing with the corresponding coupling of pyridine [16] and its derivatives [7]. Carbons C-3a and C-7a interact also with hydrogen at 2- and 3-position by 3.3-5.5 Hz for C3a-H2, 3.3-4.4 Hz for C3a-H3, 7.1-8.8 Hz for C7a-H2 and 7.1-9.3 Hz for C7a-H3 which are consistent with the values for the corresponding interactions of 2- or 3-monosubstituted furan derivatives [10] and are not affected by change of the annelation.

EXPERIMENTAL

NMR Measurements.

All ^{13}C spectra were obtained at *ca* 27° with a JEOL FX 90Q spectrometer at 22.50 MHz in deuteriochloroform solutions (25-30% w/v) using complete proton decoupling and fully proton coupling techniques. Chemical shifts were measured relative to the central peak of the solvent (77.00 ppm) and corrected to internal tetramethylsilane.

Conditions of Measurement.

Decoupled spectra: spectral width 4500 Hz with 16384 memory points; acquisition time 1.82 s; pulse width 5 μ s; number of pulses accumulated 200 to 1000. Coupled spectra: spectral width 4500 Hz with 16384 memory points; acquisition time 1.82 s; pulse width 5 μ s; number of pulses accumulated 2000 to 20000.

Materials.

Compounds **5a** and **5b** were commercially obtained reagents and were purified by distillation before use. Compound **5c** was prepared by the method of Bisagni [17], **5d** by Stoermer [18], **5e** by Hantzsch [19], **5g** by Boehme [20], **5h** by von Auwers [21], **5i** by Stoermer [22], **5j** by Martynoff [23], **4a** and **4b** by Eloy [24] and **4f** by McFarland [25]. Compounds **1a-1d**, **1f-1j**, **2a-2d**, **2f-2j**, **3a-3d**, **3g-3j**, **4c**, **4d**, **4h-4j** were synthesized as described elsewhere [2a-2f]. All compounds gave mp and spectral data (ir and 1H nmr) [2a-2f] in accord with their structures.

2-Ethoxycarbonyl derivatives **1e**, **2e**, **3e** and **4e** were prepared by esterification of the corresponding carboxylic acids [2d,2e] with ethanol as follows: a mixture of carboxylic acid (1.63 g, 10

mmoles), ethanol (50 ml) and sulfuric acid (2 g) was refluxed for 15 hours. After evaporation of the solvent under reduced pressure, the residual syrup was dissolved in water (100 ml) and basified with sodium hydrogen carbonate and extracted with chloroform. The residue of the dried chloroform layer was purified by recrystallization from ether or distillation under reduced pressure to give esters **1e**, **2e**, **3e** and **4e**.

Ethyl Furo[2,3-*b*]pyridine-2-carboxylate (**1e**).

This compound was obtained as a colorless syrup, bp 135-140° (5 mm Hg) which solidified on standing (mp 56-58°), in 85% yield. The ir and 1H nmr spectra were identical with those of the sample prepared by the method of McFarland [26].

Ethyl Furo[3,2-*b*]pyridine-2-carboxylate (**2e**).

This compound was obtained as colorless sandy crystals (ether), mp 80.5-82.5°, in 75% yield.

Anal. Calcd. for $C_{10}H_9NO_3$ (191.19): C, 62.82; H, 4.74; N, 7.33. Found: C, 63.16; H, 4.79; N, 7.27.

Ethyl Furo[2,3-*c*]pyridine-2-carboxylate (**3e**).

This compound was obtained as colorless crystals (ether), mp 78-79°, in 78% yield.

Anal. Calcd. for $C_{10}H_9NO_3$ (191.19): C, 62.82; H, 4.74; N, 7.33. Found: C, 63.00; H, 4.73; N, 7.29.

Ethyl Furo[3,2-*c*]pyridine-2-carboxylate (**4e**).

This compound was obtained as colorless needles (ether), mp 90-93°, in 70% yield.

Anal. Calcd. for $C_{10}H_9NO_3$ (191.19): C, 62.82; H, 4.74; N, 7.33. Found: C, 63.07; H, 4.83; N, 7.25.

Acknowledgements.

The authors are grateful to Dr. Tadashi Kometani of the Department of Chemistry, Toyama Technical College for his aid in measuring ^{13}C nmr spectra. We gratefully acknowledge support of this work by grant from Koshi Foundation for Scholarship.

REFERENCES AND NOTES

- [1] Part X. S. Shiotani and H. Morita, *J. Heterocyclic Chem.*, **27**, 637 (1990).
- [2a] S. Shiotani, H. Morita, M. Inoue, T. Ishida, Y. Iitaka and A. Itai, *J. Heterocyclic Chem.*, **21**, 725 (1984); [b] S. Shiotani and H. Morita, *ibid.*, **23**, 665 (1986); [c] H. Morita and S. Shiotani, *ibid.*, **23**, 549 (1986); [d] H. Morita and S. Shiotani, *ibid.*, **23**, 1465 (1986); [e] H. Morita and S. Shiotani, *ibid.*, **24**, 373 (1987); [f] S. Shiotani, H. Morita, T. Ishida and Y. In, *ibid.*, **25**, 1205 (1988).
- [3] C. L. Hickson and H. McNab, *Synthesis*, 464 (1981).
- [4] Though ^{13}C nmr spectral data of compounds **1a**, **2a**, **3a**, **4a** [1] and **5a**, **5b** and **5g** [13] had been reported separately, the data taken under the same condition with that for other compounds studied are also listed in Table I, II and III in order to compare the spectral data directly and accurately.
- [5] G. Levy and G. Nelson, Carbon-13 Nuclear Magnetic Resonance, John Wiley & Son, Interscience, New York, 1980.
- [6] U. Vögeli and W. von Philipsborn, *Org. Magn. Reson.*, **5**, 551 (1973).
- [7] Y. Takeuchi and N. Dannis, *Org. Magn. Reson.*, **7**, 144 (1975).
- [8] G. Miyajima, Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.*, **20**, 429 (1972).
- [9] F. A. L. Anet and I. Yavari, *J. Org. Chem.*, **41**, 3589 (1976).
- [10] S. Gronowitz, I. Johnson and A.-B. Hörnfeldt, *Chem. Scr.*, **7**, 211

- (1975).
- [11] W. Friedrichsen, *Comprehensive Heterocyclic Chemistry*, Vol 4, A. R. Katritzky, ed, Pergamon Press, Oxford, 1984, pp 974-975.
- [12] K. Yate, *Hückel Molecular Orbital Theory*, Academic Press, New York, 1978.
- [13] T. Okayama and T. Fueno, *Bull. Chem. Soc. Japan*, **47**, 1263 (1974).
- [14] J. B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972.
- [15] W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, **88**, 1496 (1966).
- [16] M. Hausen and H. J. Jacobsen, *J. Magn. Reson.*, **10**, 74 (1973).
- [17] M. Bisagni, N. P. Buu-Hoï and R. Royer, *J. Chem. Soc.*, 3688 (1955).
- [18] R. Stoermer and C. Calov, *Ber.*, **34**, 770 (1901).
- [19] A. Hantzsch, *Ber.*, **19**, 2400 (1886).
- [20] W. R. Hoehme, *Organic Synthesis*, Vol 33, C. C. Price, ed, John Wiley & Son, Inc., New York, 1953, p 43.
- [21] K. von Auwers, *Liebigs Ann. Chem.*, **393**, 338 (1912).
- [22] R. Stoermer and B. Kahlert, *Ber.*, **35**, 1633 (1902).
- [23] M. Martynoff, *Compt. Rend.*, **233**, 878 (1951).
- [24] F. Eloy and A. Deryckere, *J. Heterocyclic Chem.*, **8**, 57 (1971).
- [25] J. W. McFarland, W. A. Essary, I. Cilenti, W. Cozart and P. E. McFarland, *J. Heterocyclic Chem.*, **12**, 705 (1975).