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Note

A gas chromatographic study of substituted furancarboxylic and benzoic acids and their methyl esters

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In preceding papers[1–4], the preparation of substituted 5-phenyl-2-furancarboxylic acids and *p*-substituted (2-X-5-furyl) benzoic acids and their methyl esters was described. The 5-phenyl-2-furancarboxylic acids were prepared by modified Meerwein arylation of pyromucic acid. We applied this method successfully to pyromucic acid methyl ester using benzenediazonium salts with electron-accepting substituents. The 2-(4-carboxyphenyl)furan was prepared by aprotic arylation of furan with 4-aminobenzoic acid and isopentyl nitrite. The methyl esters were also prepared by reaction of the corresponding acid with diazomethane and also by esterification with methanol using sulphuric acid as catalyst. The pK_a values of the acids were determined and found to correlate with the Hammett constants[1,3].

According to the literature, the compounds studied have not been previously analyzed by gas chromatography (GC). These substituted 5-phenyl-2-furancarboxylic acids, *p*-substituted (2-X-5-furyl)benzoic acids and their methyl esters are interesting from the point of view of both physical chemistry and biological activity, so that chromatographic studies were thought to be useful. The main purpose of this work was to distinguish between these compounds, and we also studied the effect of substituents on their retention times.

EXPERIMENTAL

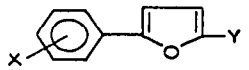
The appropriate compounds were prepared according to earlier work[1–4]. All analyses were carried out on a Hewlett-Packard 7620A research gas chromatograph with a dual hydrogen flame ionization detector using a steel column packed with 10% silicone gum UCW-98 on Chromosorb W AW DMCS, 80–100 mesh. The nitrogen carrier-gas flow-rate was 30 ml/min. The column temperature was 220° and the injector and detector temperatures were 270°. The retention times were calculated directly from the Hewlett-Packard 3370A integrator.

RESULTS

Retention times (t_R) for substituted 5-phenyl-2-furancarboxylic acids and their methyl esters are given in Table I, and t_R values for *p*-substituted (2-X-5-furyl)benzoic acids and their methyl esters in Table II. The results show that the t_R values, under the

TABLE I

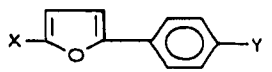
RETENTION TIMES (t_R) AND PHYSICAL CONSTANTS OF SUBSTITUTED 5-PHENYL-2-FURANCARBOXYLIC ACIDS AND THEIR METHYL ESTERS



No.	*X*	*Y*				*No.*
		COOH		*$COOCH_3$*		
		m.p. (°C)	*t_R (min)*	*m.p. (°C)*	*t_R (min)*	
1	H	149	3.67	64	3.63	14
2	3-F	150	4.08	75–76	3.33	15
3	2-Cl	173–176	1.65	68	5.52	16
4	3-Cl	158	4.65	75	6.20	17
5	3,4-Cl_2	232	2.26	110–112	10.65	18
6	3,5-Cl_2	232	2.04	131–134	9.20	19
7	3-CF_3	190	2.07	90	3.04	20
8	2-Br	167	2.18	55	7.03	21
9	2-NO_2	213–215	1.97	62–63	8.27	22
10	3-NO_2	244	8.69	146	11.06	23
11	4-NO_2	251–252	2.91	172–173	5.36	24
12	3-NO_2, 4-Cl	239	3.49	140–143	17.36	25
13	3-CF_3, 4-Cl	194	1.46	108–109	5.46	26

TABLE II

RETENTION TIMES (t_R) AND PHYSICAL CONSTANTS OF *p*-SUBSTITUTED (2-X-5-FURYL)BENZOIC ACIDS AND THEIR METHYL ESTERS

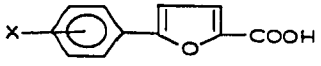


No.	*X*	*Y*				*No.*
		COOH		*$COOCH_3$*		
		m.p. (°C)	*t_R (min)*	*m.p. (°C)*	*t_R (min)*	
27	H	224	4.23	121	3.98	36
28	CH_3	226	5.57	77–78	4.90	37
29	C_2H_5	177–179	7.21	54–55	6.89	38
30	Br	256–258	7.80	132–133	8.44	39
31	I	207–210	4.31	108–111	10.78	40
32	CH_2OH	213–215	9.84	116–118	10.11	41
33	COH	205–206	7.43	152	9.02	42
34	$COCH_3$	240	2.13	156	11.04	43
35	CHNOH	248–250	8.74	156–158	7.56	44

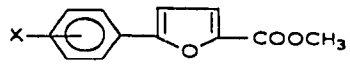
experimental conditions used, do not depend on the electron acceptor or electron donor character of the substituent which is bonded to the benzene or furan ring. In a more detailed study, we found that t_R depends on the effective radius of the molecule (for example, substances 27–36; 28–37; 29–38; 30–39; 31–40). The t_R value is also dependent on the position of the substituent on the benzene ring in the case of derivatives of 5-phenyl-2-furancarboxylic acids (Table III).

TABLE III

RETENTION TIMES (t_R) OF DERIVATIVES OF 5-PHENYL-2-FURANCARBOXYLIC ACIDS AND THEIR METHYL ESTERS



(A)



(B)

A		*B*	
X	t_R *(min)*	*X*	t_R *(min)*
2-Cl	1.65	2-Cl	5.52
3-Cl	4.89	3-Cl	6.20
2-NO_2	1.97	2-NO_2	8.27
3-NO_2	8.69	3-NO_2	11.06

It is possible to explain these unexpected results by using the chromatographic column with a non-polar stationary phase. The polar effect of substituents is probably less marked in comparison with their steric effects under the experimental conditions used.

The results in Tables I and II confirm that GC is a suitable method for the determination of substituted 5-phenyl-2-furancarboxylic acids and *p*-substituted (2-X-5-furyl)benzoic acids and their methyl esters.

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