

**3-(5-SUBSTITUTED-2-FURYL)ACRYLIC ACIDS
AND THEIR METHYL ESTERS. TRANSFER
OF THE POLAR EFFECT OF THE SUBSTITUENT THROUGH
THE ETHYLENE GROUP***

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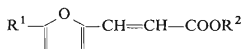
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Apparent dissociation constants were determined for twelve 3-(5-R-2-furyl)acrylic acids in 50% ethanol, 78% ethanol and 80% methyl cellosolve, as well as the constants of alkaline hydrolysis of ten methyl esters of 3-(5-R-2-furyl)acrylic acids in 60% aqueous acetone. The values obtained were correlated with σ_p and σ_m constants of substituents and the value of the transmission of polar effects through the ethylene group was determined.

In preceding papers we investigated the transfer of the polar effect of the substituent from benzene through the furan nucleus^{1,2}, from furan through the benzene nucleus^{3,4}, and from benzene through the furan nucleus and the ethylene group⁵. The aim of this paper is the establishment of the transfer effect of the influence of substituent from the furan through the ethylene group. The possibility of using Hammett's equation for five-membered heterocycles and the checking of its validity⁶⁻⁹ led to the determination of the ρ -constant for 5-substituted 2-furancarboxylic acids on the basis of the measured pK_A values and use of σ_p -constants of substituted benzoic acids ($\rho = 1.394$ (ref.⁶⁻⁸), 1.41 (ref.¹⁰). Similarly, for the correlation of σ_p and $\log k_h$ it was found that $\rho = 2.973$ (ref.⁶). In the series of 3-(5-R-2-furyl)acrylic acids, where the substituent R is directly on the furan nucleus no such study has been carried out.

We have synthesized 3-(5-R-2-furyl)acrylic acids and their esters I–XXVI (Table I). The synthesis of acids I (ref.¹¹), II, VIII, IX and XII was carried out by Doebner's method and III–VI (ref.^{12,5,13,14}) by Perkin's synthesis from corresponding aldehydes. Acetylation and nitration of 3-(2-furyl)acrylic acid (III) was used for the preparation of the corresponding 5-acetyl and 5-nitro derivative, VII (ref.¹⁵) and X (ref.¹⁶), respectively. Attempts at the preparation of 3-(5-benzazole derivatives-

* Part C in the series Furan Derivatives; Part XCIX: Chem. Zvesti, in press.

TABLE I
 3-(5-Substituted-2-furyl)acrylic Acids and Their Methyl Esters


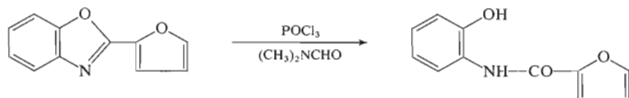
Compound ^a	R ¹ R ²	M.p., ^b °C yield, %	Formula (m.w.)	Calculated/Found		
				% C	% H	% N
<i>I</i>	CH ₃ H	154–155 84	C ₈ H ₈ O ₃ ^c (152.1)	—	—	—
<i>II</i>	SCH ₃ H	150–151 81	C ₈ H ₈ O ₃ S ^d (184.2)	52.12 52.23	4.34 4.42	— —
<i>III</i>	H H	140–141 65	C ₇ H ₆ O ₃ ^e (138.1)	—	—	—
<i>IV</i>	C ₆ H ₅ H	175–179 33	C ₁₃ H ₁₀ O ₃ ^f (214.2)	—	—	—
<i>V</i>	<i>I</i> H	159–60 64	C ₇ H ₅ IO ₃ ^g (264.0)	—	—	—
<i>VI</i>	Br H	178–179 67	C ₇ H ₅ BrO ₃ ^h (217.0)	—	—	—
<i>VII</i>	COCH ₃ H	190–191 30	C ₉ H ₈ O ₄ ⁱ (180.2)	—	—	—
<i>VIII</i>	COOCH ₃ H	208–210 66	C ₉ H ₈ O ₅ (196.2)	55.04 55.17	4.07 3.91	— —
<i>IX</i>	CN H	181–183 70	C ₈ H ₅ NO ₃ (163.1)	58.86 58.81	3.06 2.94	8.58 8.62
<i>X</i>	NO ₂ H	242–243 75	C ₇ H ₅ NO ₅ ^j (183.1)	—	—	—
<i>XI</i>	2-Benzothiazolyl H	243–244 37	C ₁₄ H ₉ NO ₃ S ^d (271.3)	61.92 61.87	3.31 3.49	5.11 5.11
<i>XII</i>	3-Pyridyl H	210–211 62	C ₁₂ H ₉ NO ₃ (212.2)	67.86 67.79	4.24 4.32	6.59 6.55
<i>XIII</i>	2-Benzoxazolyl H	163–164 8	C ₁₄ H ₉ NO ₄ (255.2)	65.83 65.91	3.52 3.65	5.48 5.45
<i>XIV</i>	CH ₃ CH ₃	36–38 34	C ₉ H ₁₀ O ₃ ^k (166.2)	—	—	—
<i>XV</i>	SCH ₃ CH ₃	36–37 120–121/0.566 ^l 64	C ₉ H ₁₀ O ₂ S ^d (198.2)	54.20 54.16	5.08 5.17	— —

TABLE I
(Continued)

Compound ^a	R ¹ R ²	M.p., ^b °C yield, %	Formula (m.w.)	Calculated/Found		
				% C	% H	% N
XVI	H CH ₃	87/0-566 ^e	C ₉ H ₁₀ O ₃ ^m (166·2)	—	—	—
XVII	C ₆ H ₅ CH ₃	106—108 69	C ₁₄ H ₁₂ O ₃ ⁿ (228·24)	—	—	—
XVIII	I CH ₃	81—82 61	C ₈ H ₇ IO ₃ ^o (277·0)	—	—	—
XIX	Br CH ₃	62—63 63	C ₈ H ₇ BrO ₃ ^p (231·1)	—	—	—
XX	COCH ₃ CH ₃	134—135 72	C ₁₀ H ₁₀ O ₄ (194·2)	61·79 61·69	5·15 5·27	—
XXI	COOCH ₃ CH ₃	144—145 77	C ₁₀ H ₁₀ O ₅ (210·2)	57·08 57·17	4·75 4·81	—
XXII	N(CH ₃) ₂ CH ₃	75—76 68	C ₁₀ H ₁₃ NO ₃ ^q (195·2)	61·47 61·54	6·66 6·73	7·17 7·11
XXIII	CN CH ₃	121—123 46	C ₉ H ₇ NO ₃ (177·2)	60·94 60·92	3·95 4·02	7·90 7·79
XXIV	NO ₂ CH ₃	146—148 60	C ₈ H ₇ NO ₅ ^r (197·2)	—	—	—
XXV	2-Benzothiazolyl CH ₃	142—143 26	C ₁₅ H ₁₁ NO ₃ S ^d (285·3)	63·09 63·18	3·85 3·94	4·90 4·82
XXVI	3-Pyridyl CH ₃	134—135 55	C ₁₃ H ₁₁ NO ₃ (229·2)	68·06 67·91	4·80 4·76	6·11 6·04

^a Compounds I, II, III, VI, VII, XX were crystallized from water, IV, VIII, IX, X, XII, XXII from ethanol, V, XVIII, XIX from 50% ethanol, XIII, XVII, XXI, XXIII, XXV, XXVI from methanol, XIV from 50% methanol, XXIV from 10% ethanol and compound XI was sublimated; ^b melting points were determined on a Kofler block and are uncorrected; ^c ref.¹¹ m.p. 152—153°C; ^d calculated/found II 17·40%, 17·36%; XI 11·79%, 11·42%; XV 16·18%, 15·83%; ^e ref.¹² m.p. 141°C; ^f ref.⁵ m.p. 175—179°C; ^g ref.¹³ m.p. 159—160°C; ^h ref.¹⁴ m.p. 177—178°C; ⁱ ref.¹⁵ m.p. 191°C; ^j ref.¹⁶ 241°C; ^k ref.¹⁷ m.p. 36—37°C; n.p. 65—70°C/0·266 kPa; ^l b.p. °C/kPa; ^m ref.¹⁸ b.p. 125—50/2·53 kPa; ⁿ ref.⁵ m.p. 106—108°C; ref.¹⁵ m.p. 82°C ^p ref.¹⁵ m.p. 62°C; ^q ref.²⁰, ^r ref.¹⁹.

-2-furyl)acrylic acids *via* the carbonylation of 2-(2-furyl)benzazoles were unsuccessful. 2-(2-Furyl)benzthiazole did not react under the conditions of the Vilsmeier reaction, while in 2-(2-furyl)benzoxazole the oxazole ring was opened in this reaction under formation of 2-hydroxyanilide-2-furancarboxylic acid (Scheme 1). 2-(2-



SCHEME 1

-Furyl)benzimidazole reacted with POCl_3 equally as other secondary amines, which prevented decarbonylation. For this reason we carried out the synthesis of 3-(5-benzazole derivatives-2-furyl)acrylic acid *XI* and *XIII* by reaction of 3-(5-cyano-2-furyl)-acrylic acid (*IX*) with 2-aminothiophenol and 2-aminophenol. With all acids the isomer *E* was obtained ($\nu(\text{CH}=\text{CH})$ 930 cm^{-1}). Esters *XIV* (ref.¹⁷), *XV*, *XVI* (ref.¹⁸), *XVII* (ref.⁵), *XVIII* (ref.¹⁵), *XIX* (ref.¹⁵), *XX*, *XXI*, *XXIV* (ref.¹⁹) were synthesized by esterification with methanol, while *XXV* was obtained with diazomethane. In the case of derivatives *XXII* (ref.²⁰), *XXIII* and *XXVI* the direct synthesis from aldehydes was carried out by Wittig's method.

Electron absorption spectra of the newly synthesized compounds are characterized by two absorption maxima in the 206–235 nm and 299–380 nm regions. In the case of the group of compound *II* λ_{max} at 249 nm is also observed, in the case of compounds *XIII* and *XV* the additional λ_{max} were at 298 and 500 nm, and 250 nm resp. In comparison with λ_{max} of 3-(2-furyl)acrylic acid (300 nm) it is evident that the bathochromic shift of the *K* band correspond to the distribution of electrons along a longer conjugated system (Table II). Among the most distinct absorption bands of the IR spectra are those of $\nu(\text{C}=\text{O})$ in the $1730\text{--}1690\text{ cm}^{-1}$ region for acids, and $1741\text{--}1704\text{ cm}^{-1}$ for esters, as well as $\nu(\text{C}=\text{C})$ at $1668\text{--}1630\text{ cm}^{-1}$ (stretching vibrations of the ethylene bond) and at $1645\text{--}1560$ (stretching vibrations of $\text{C}=\text{C}$ in the ring). The band $946\text{--}925\text{ cm}^{-1}$ belongs to the deforming vibrations of the $\gamma(\text{C}\text{--}\text{H})$ bonds in a *trans* arrangement.

pK_A -Values of the acids were measured in 50% and 78% aqueous ethanol and 80% methyl cellosolve (also used in the preceding paper⁵), due to the poor solubility of the majority of them in water. Kinetic measurements were carried out in 60% aqueous acetone. For the correlation of the results obtained σ_p and σ_m values of substituents^{21–23} were used. From the correlation of the constants of hydrolysis the value of the constant of hydrolysis for the methyl ester of 3-(5-methoxycarbonyl-2-furyl)acrylic acid (*XXI*) was excluded. This is several times higher than the assumed one (Table III) and it correlates well in the series of 5-X-2-furancarboxylic acids, *i.e.* when the pos-

sibility of hydrolysis at two sites in the molecules existed, the hydrolysis of the methoxycarbonyl group on the furan nucleus took place preferentially. The high correlation coefficient (0.985) of the correlation of apparent pK_A values of 3-(5-R-2-furyl)-acrylic acids and the logarithms of the constants of hydrolysis of their esters (Table IV) with a gradient $\rho = -0.525$ confirms that the use of Hammett's equation is substantiated for the acids mentioned. During a statistical treatment of apparent pK_A values for single acids, as well as of the logarithms of the constants of hydrolysis of their ester a good correlatability of substituents both with the σ_p and with

TABLE II
IR and UV Characteristics of New 3-(5-Substituted-2-furyl)acrylic Acids and Their Methyl Esters; λ_{\max} (nm); $\tilde{\nu}$ cm^{-1}

Compound	λ_{\max}	$\log \epsilon$	λ_{\max}	$\log \epsilon$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{CH}=\text{CH})$
<i>II</i>	223	3.76	316	4.17	1 690	1 631	930
	249	3.75				1 560	
<i>VIII</i>	217	4.42	304	4.42	1 730	1 636	926
					1 703	1 580	
<i>IX</i>	211	4.06	299	4.31	1 700	1 650	932
						1 590	
<i>XI</i>	227	3.92	362	4.33	1 720	1 645	934
						1 625	
<i>XII</i>	235	3.97	342	4.26	1 702	1 630	930
						1 606	
<i>XIII</i>	206	3.92	380	4.06	1 705	1 640	932
	298	3.70	500	2.64		1 625	
<i>XV</i>	225	3.85	333	4.19	1 723	1 636	922
	250	3.74				1 559	
<i>XX</i>	225	4.10	324	4.37	1 737	1 668	925
					1 720	1 645	
<i>XXI</i>	217	4.09	308	4.42	1 741	1 648	928
					1 724		
<i>XXIII</i>	208	4.27	225	4.18	1 726	1 630	946
						1 600	
<i>XXV</i>	227	4.19	360	4.33	1 720	1 650	936
						1 590	
<i>XXVI</i>	208	4.40	322	4.36	1 704	1 664	938
						1 592	

TABLE III

The Apparent pK_A Constants of 3-(5-R-2-Furyl)acrylic Acids in Different Solvents and Rate Constants for the Hydrolysis of Their Methyl Esters (k_h , $l \text{ mol}^{-1} \text{ s}^{-1}$)

Compound	pK_{A1}^a	pK_{A2}^b	pK_{A3}^c	$k_h \cdot 10^3$
<i>I</i>	5.98	6.65	7.01	1.4
<i>II</i>	5.78	6.46	6.67	3.0
<i>III</i>	5.76	6.45	6.65	2.9
<i>IV</i>	5.75	6.47	6.67	2.8
<i>V</i>	5.60	6.05	6.38	8.6
<i>VI</i>	5.46	6.11	6.21	10.3
<i>VII</i>	5.45	5.75	6.43	21.2
<i>VIII</i>	5.28	5.60	6.12	121.5
<i>IX</i>	5.15	5.72	5.98	53.8
<i>X</i>	4.88	5.44	5.82	114.5
<i>XI</i>	—	—	6.41	—
<i>XII</i>	—	—	5.90	—

^a 50% Ethanol; ^b 78% ethanol; ^c 80% methyl cellosolve.

TABLE IV

Statistics of the Hammett Correlation of σ_p and σ_m Substituent Constants and the Apparent pK_A Values for 3-(5-R-2-Furyl)acrylic Acids or of the Rate Constants of Hydrolysis of Their Methyl Esters

Correlation	n^a	r^b	ρ^c	s_p^d	q^e	q^f	s^g	$\pi_{C=C}^h$
$pK_{A1}-\sigma_p$	10	0.981	-1.040	0.073	5.786	0.021	0.070	0.737
$pK_{A1}-\sigma_m$	10	0.957	-1.245	0.102	5.864	0.073	0.078	0.835
$pK_{A2}-\sigma_p$	10	0.973	-1.254	0.082	6.424	0.016	0.091	0.889
$pK_{A2}-\sigma_m$	10	0.939	-1.485	0.094	6.513	0.063	0.092	0.996
$pK_{A3}-\sigma_p$	10	0.937	-1.069	0.081	6.688	0.038	0.053	0.758
$pK_{A3}-\sigma_m$	10	0.975	-1.364	0.107	6.691	0.047	0.084	0.915
$\log(3 + k_h)-\sigma_p$	9	0.995	1.957	0.074	0.468	0.005	0.069	0.966
$\log(3 + k_h)-\sigma_m$	9	0.972	2.279	0.106	0.313	0.092	0.082	0.999
$pK_{A1}-(\log 3 + k_h)$	9	0.985	-0.525	0.033	6.035	0.125	0.062	—

^a Number of derivatives; ^b correlation coefficient; ^c slope; ^d slope error; ^e calculated value for the unsubstituted derivative; ^f error of q ; ^g standard deviation from the regression line; ^h transmission factor for the ethene bond calculated with the ρ values from¹⁰ and^{6,7}.

σ_m values is observed. Up to now this fact has been observed in 5-X-2-furancarboxylic acids^{6,7} and therefore two ρ -values for 5-substituted furancarboxylic acids¹⁰ were calculated. The scatter of the ρ -values in the case of 3-(5-R-2-furyl)acrylic acids, caused by a change of solvent, is relatively small in comparison with analogous values in the benzene series²².

The calculation of the transmission factor of the C=C bond from the relation $\pi_{C=C} = \rho_{Fu/C=C}/\rho_{Fu}$ and the application of ρ_{Fu} -values obtained under the same working conditions for 5-X-2-furancarboxylic acids, gave the values 0.737–0.889 for σ_p and 0.835–0.996 for σ_m which considerably exceeded $\pi_{C=C}$ in the benzene series (for cinnamic acids $\pi_{C=C} = 0.508$ (ref.²²)). The same transmission factor can also be determined from preceding results in 3-(5-phenyl-2-furyl)acrylic acids⁵ where from the relation $\pi_{C=C} = \rho_{Bz/Fu/C=C}/\rho_{Bz/Fu}$ the values $\pi_{C=C} = 0.829$ or 0.739 are obtained. Approximately equal transmission value of the substituent determined in both directions^{1–4} indicate that the direct effect of the oxygen atom on the carboxyl group in close proximity is negligible and that the large differences in pK_A values of 2-furancarboxylic acids and 3-(2-furyl)acrylic acids should be sought in the influence on the ethylene bond by the heteroatom. According to the data of the ¹H-NMR spectroscopy *E*-[3-(2-furyl)]acrylic acid exists in *s-trans* conformation²⁴, which brings the ethylene group into close proximity of the furan nucleus oxygen that may affect its π -electron system directly. This can explain the decreased acidity of 3-(2-furyl)acrylic acids and the higher transmission factor of the C=C bond. From the measured values of the dissociation constants of 3-[5-(3-pyridyl)-2-furyl]acrylic acid the value $\sigma_p = 0.743$ for 3-pyridyl group and analogously the value $\sigma_p = 0.26$ for the 2-benzthiazolyl group were worked out.

EXPERIMENTAL

3(5-R-2-furyl)acrylic Acids

A) A mixture of 0.1 mol of 5-R-2-furaldehyde and 20.8 g (0.2 mol) of malonic acid in 50 ml of pyridine was heated on a boiling water bath for 3 hours. After the cessation of the CO₂ escape the mixture was poured onto 250 g of ice acidified with hydrochloric acid. The precipitated mixture was filtered off under suction and crystallized from a suitable solvent. In this manner acids *I*, *II*, *VIII*, *IX* and *XII* were prepared.

B) A mixture of 0.1 mol of 5-R-2-furaldehyde, 0.25 mol of anhydrous potassium acetate and 0.7 mol of acetic anhydride was heated at 140–150°C for 4 h. After cooling the mixture was poured onto 250 g of ice, the precipitated product was filtered off under suction, and crystallized from a suitable solvent. In this manner acids *III*–*VI* were prepared.

3-[5-(2-Benzthiazolyl)-2-furyl]acrylic Acid (*XI*)

A mixture of 16.3 g (0.1 mol) of 3-(5-cyano-2-furyl)acrylic acid (*IX*) and 12.5 g (0.1 mol) of 2-aminothiophenol was refluxed in 30 ml of toluene until the escape of ammonia ceased. The mixture was allowed to cool and the separated precipitate was filtered off, washed with water and sublimated in a vacuum.

3-[5-(2-Benzoxazolyl)-2-furyl]acrylic Acid (XIII)

A mixture of 16.3 g (0.1 mol) of 3-(5-cyano-2-furyl)acrylic acid (IX) and 10.1 g (0.1 mol) of 2-aminophenol was heated at 200°C until the escape of ammonia ceased. The melt was extracted with warm benzene, the extract was treated with charcoal and evaporated and the residue dissolved in a benzene-ether mixture and separated chromatographically on an alumina column. The strongly fluorescing fraction was collected and the solid substance was obtained by evaporation of the solution.

Methyl Esters of 3-(5-R-2-Furyl)acrylic Acids

A) A mixture of 0.1 mol of 3-(5-R-2-furyl)acrylic acid (I–VIII, X), 100 ml of methanol and 3 ml of concentrated H_2SO_4 , was refluxed for 3 h. Methanol was distilled off (60 ml), the mixture was poured onto ice and neutralized, and the precipitated ester (XIV–XXI, XXIV) was filtered off under suction, dissolved in chloroform, washed with a $NaHCO_3$ solution, dried and evaporated. The residue was purified by crystallization.

B) An ethereal diazomethane solution (0.02 mol) was added under stirring to a suspension of 2.7 g (0.01 mol) of 3-[5-(2-benzthiazolyl)-2-furyl]acrylic acid (XI) in 200 ml of ether and the mixture was allowed to stand at room temperature for 4 h. Ether was evaporated, the residue was treated with a $NaHCO_3$ solution in order to eliminate the acid, and the remaining ester XXV was crystallized from methanol.

C) 3.4 g (0.01 mol) of methoxycarbonylmethylidetriphenylphosphorane, 0.01 mol of 5-R-2-furaldehyde and 50 ml of benzene were refluxed for 20 h, benzene was evaporated and the reaction mixture separated by column chromatography on alumina. In this manner esters XXI, XXIII and XXIV were prepared.

Measurements

Electron absorption spectra were measured in the 200–480 nm region with a registration spectrophotometer UV VIS (Zeiss) at room temperature in ethanol using 1 cm cells and $3 \cdot 10^{-5} M$ concentration of the substances. The measurement of the infrared spectra was carried out with a two-beam spectrophotometer UR-20 (Zeiss) using the KBr technique (2 mg of substance per 1 g of KBr). The calibration of the apparatus was carried out with a polystyrene foil.

Apparent dissociation constants were determined by potentiometric titration of $5 \cdot 10^{-3} M$ solutions of corresponding acids in 50% and 78% aqueous ethanol and 80% aqueous methyl cellosolve with a 0.1M tetramethylammonium hydroxide solution under nitrogen. For measurement Radiometer pHM 4d with a glass electrode was used, also Radiometer G 200 B and a calomel electrode K 100, and an automatic burette Radiometer ABU 1c. The accuracy of the measurement was 0.02 pH. For checking the working conditions the following values were measured: for benzoic acid in 78% ethanol $pK_A = 6.36$ (lit.²⁵ 6.37) and for 3-(2-furyl)acrylic acid $pK_A = 6.50$ (lit.²⁵ 6.49). Statistical parameters and correlation dependences with σ_m , σ_p and the logarithm of the constants of hydrolysis of esters are given in Table IV.

Kinetic measurements: 50 ml of a $5 \cdot 10^{-5} M$ solution of ester in 60% aqueous acetone (v/v) and 50 ml of a 0.01M-KOH solution in 60% aqueous acetone were mixed and stirred in a thermostat for 30 min at 25°C. At selected time intervals (15 min) samples (10 ml) of the solution were withdrawn, then poured into 0.01M HCl (10 ml) and excess acid was determined by titration with 0.01M-KOH using a TTT 1c titrator (Radiometer). The accuracy of the measurement was checked by blank experiments before measurement. Constants of hydrolysis were calculated from the equation for the second order reaction and they were worked up by the least squares

method using a Hewlett Packard 9810 A calculator. Statistical parameters and the correlations are listed in Table IV.

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