STUDY OF 3-(5-X-2-FURYL)ACRYLIC ACIDS AND THEIR METHYL ESTERS BY GAS CHROMATOGRAPHY

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Received November 24th, 1977

The Kovats's indices and homomorphous factors of 3-(5-substituted-2-furyl)acrylic acids and their methyl esters were determined on stationary phases UCW 98 and OV 17 at 180°C. It was found that the values of both chromatographic parameters increase with increasing polarity of the molecule.

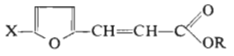
Compounds containing 2-furylethylene grouping in the molecule are arousing increased interest today, both from the point of view of the reactions which they undergo, and from the point of view of their possible biological activity. In connection with our previous paper[1] dealing with the study of the relationships between the structure and some physico-chemical properties of 3-(5-substituted-2-furyl)-acrylic acids and their methyl esters in this paper we study chromatographic parameters of the mentioned compounds by gas chromatography.

Chromatographic data, expressed as Kovats indices[2], are one of the best eharacteristics of the chromatographic behaviour of various compounds, as they reflect some relationships between the elution data obtained and the structure of the compounds under investigation, and enable the prediction to a certain extent, of the structure from known elution data.

In the present paper retention indices as well as homomorphous factors are given for 3-(5-X-2-furyl)acrylic acids and their methyl esters (*I*–*XVI*) of general formula sown behlow, chromatographed in two different polar phases. Retention indices and homomorphous factors of the compounds discussed are presented in Table I and II.

From Table I it is evident that the retention indices of the mentioned acids increase on both stationary phases with increasing polarity of the molecule; on the phase OV 17 the values of *I* are averagely 300 units higher than on the column where UCW 98 was the stationary phase, which is in agreement with the increased interaction of the more polar substances with the phase in which the possibility of induced interaction of the compounds studied with the electron cloud of the

* Part CXXI in the series Furan Derivatives; Part CXX: This Journal *44*, 420 (1979).



	X	R		X	R
I	H	H	*IX*	Br	CH_3
II	Br	H	*X*	I	CH_3
III	I	H	*XI*	NO_2	CH_3
IV	CH_3	H	*XII*	CH_3	CH_3
V	SCH_3	H	*XIII*	SCH_3	CH_3
VI	$COCH_3$	H	*XIV*	$COCH_3$	CH_3
VII	$COOCH_3$	H	*XV*	$COOCH_3$	CH_3
VIII	H	CH_3	*XVI*	$N(CH_3)_2$	CH_3

aromatic rings of this phase (polymethylphenylsiloxane) is increased. The lower values of ΔI in the case of compounds *I* and *IV* are a consequence of this fact.

With increasing acidity of the acids *I*–*VII* their retention indices also increase. The correlation of pK_A values with the retention indices is good in both cases: for the column with UCW 98 the correlation coefficient is $r = 0{\cdot}90$, and for that with OV 17 $r = 0{\cdot}91$.

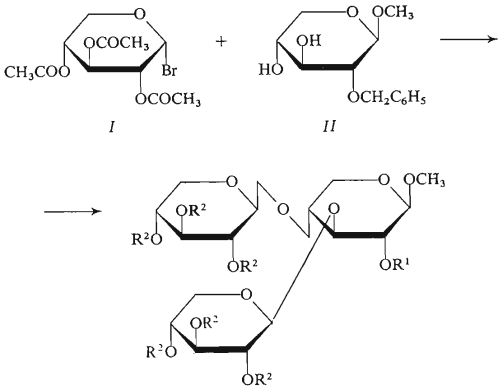
The change in the polarity of the molecule can be characterized with advantage by the factor *H* (see[3,4]). In Table I the homomorphous factors relative to 3-(2-furyl)-acrylic acid are given. On both phases the *H* values increase proportionally with increasing acidity of the compound and they correlate with the pK_A values[1] of the acids *I*–*VII*, with the exception of derivative *V*. For both stationary phases the correlation coefficient is 0·97. 3-(5-Nitro-2-furyl)acrylic acid could not be included into the group of the investigated acids, owing to its thermolability.

TABLE I

Retention Indices *I* and *H*-Factors[a] of 3-(5-X-2-Furyl)acrylic Acids

Compound (X)	Column				ΔI
	UCW 98		OV 17		
	I	*H*	*I*	*H*	
I (H)	1 254	—	1 479	—	225
II (Br)	1 488	234	1 767	288	279
III (I)	1 599	345	1 929	450	330
IV (CH_3)	1 344	90	1 563	84	219
V (SCH_3)	1 625	371	1 934	455	309
VI ($COCH_3$)	1 620	366	1 945	466	325
VII ($COOCH_3$)	1 666	412	1 980	501	314

[a] $H = I$[3-(5-X-2-furyl)acrylic acid] $- I$[3-(2-furyl)acrylic acid].



I *II*

III; $R^1 = CH_2C_6H_5$, $R^2 = COCH_3$
IV; $R^1 = H$, $R^2 = COCH_3$
V; $R^1 = H$, $R^2 = H$
VI; $R^1 = COCH_3$, $R^2 = COCH_3$
VII; $R^1 = CH_3$, $R^2 = CH_3$

SCHEME 1

The retention indices and the homomorphous factors of the methyl esters of 3-(5-X--2-furyl)acrylic acids are given in Table II. Equally as in the case of the acids discussed it can be stated that both the retention indices and the *H* values increese with increasing polarity of the ester. The unsubstituted derivative *VIII* and derivative *XII* with a methyl group in the position 5 of the furan ring are again an exception.

The effect of the increase in the polarity of the molecule on the increase of the *I* values is evident not only in the series of the acids, or their esters, but as it is also evident from the data in Table I and II, the values of the retention indices of the acids are about 30–70 units higher than in the corresponding esters, which is in agreement with the polarity of both compared groups.

EXPERIMENTAL

The chromatographic data of the discussed compounds were measured with a Hewlett–Packard gas chromatograph 7620 A, with a dual FID, using stainless steel columns of 2 mm diameter and 1·8 m long. The column A was packed with Chromosorb W-AW-DMCS 80–100 mesh with 10% of stationary phase (silicone elastomer UCW 98; Hewlett–Packard), while the column B contained Chromosorb W-AW-DMCS 80–100 mesh with 10% of OV 17 (Hewlett–Packard) as stationary phase. The flow rate of the carrier gas (nitrogen) was 35 ml/min. The temperature of the injection and the FID was 230°C, temperature of the column was 180°C.

TABLE II

Retention Indices *I* and *H*-Factors[a] of Methyl Esters of 3-(5-X-2-Furyl)acrylic Acids

Compound	Column				ΔI
	UCW 98		OV 17		
	I	*H*	*I*	*H*	
VIII (H)	1 198	—	1 420	—	222
IX (Br)	1 438	240	1 692	272	254
X (I)	1 551	353	1 862	442	311
XI (NO_2)	1 593	395	1 941	521	348
XII (CH_3)	1 321	123	1 543	123	222
XIII (SCH_3)	1 580	382	1 888	468	308
XIV (CH_3CO)	1 542	344	1 864	444	322
XV (CH_3COO)	1 606	408	1 923	503	317
XVI $(CH_3)_2N$	1 657	459	1 975	555	318

[a] $H = I$[Methyl 3-(5-X-2-furyl)acrylate] $- I$[methyl 3-(2-furyl)acrylate].

Synthesis of the investigated compounds: Compounds *IV*, *V VII* were prepared by the Doebner method[5], compounds *I*—*II* by the Perkin synthesis[6-8]. Acetylation of *I* gave the corresponding substituted acid[9] *VI*. Ethyl esters *VIII*, *XIII* (ref.[10]; *IX*, (ref. [9]); *XI*, *XIV*, *XVI* (ref.[11]) were obtained by esterification with methanol, *XVI* (ref.[12]) was obtained directly from the aldehyde using Wittig's method.

We thank Miss E. Hájniková, Department of Organic Chemistry, Faculty of Chemical Technology, Slovak Institute of Technology, Bratislava, for accurate technical assistance.

REFERENCES

1. Kováč J., Štetinová J., Surá J., Špaček F., Brežný R.: This Journal *42*, 1871 (1977).
2. Kovats E.: Helv. Chim. Acta *41*, 1915 (1958).
3. Schomburg G.: J. Chromatogr. *23*, 1 (1966).
4. Schomburg G.: J. Chromatogr. *23*, 28 (1966).
5. Taylor P. A. H.: J. Chem. Soc. *2767* (1959).
6. Ragajopalan S., Raman P. V.: *Organic Synthesis*, Vol. 3, p. 425. Wiley, Interscience, New York 1967.
7. Nazarova Z. N.: Zh. Obshch. Khim. *25*, 539 (1955).
8. Nazarova Z. N., Pimenova A. N.: Zh. Obshch. Khim. *27*, 2842 (1957).
9. Dorofeenko G. N., Karban V. J., Dulenko L. V., Novikov V. Z.: Izv. Vysh. Ucheb. Zav. Khim. Tekhnol. *7*, 432 (1964).
10. Reese J.: Ger. 851; Chem. Abstr. *50*, 8738 (1956).
11. Natt M. P.: U.S. 2 890 982; Chem. Abstr. *53*, 20 089 (1959).
12. Nazarova Z. N., Popov O. O.: USSR 382 616; Chem. Abstr. *50*, 8730 (1956).

Translated by Ž. Procházka.