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Review Article

Liquid Chromatographic Investigation of Spontaneous Oscillatory *In Vitro* Chiral Conversion and Spontaneous Oscillatory Condensation of Simple Carboxylic Acids in Aqueous and Nonaqueous Media

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Oscillatory reactions are a narrow reaction type among the entity of chemical reactions and those involving purely organic compounds make a small contribution to an overall number of all known oscillatory reactions. The most abundant type is purely inorganic and mixed inorganic-organic oxidation-reduction reactions, basically because monitoring them is relatively easy (e.g., with use of potentiometric measurements). Investigation of the organic reactions can be more demanding, and then chromatography is an analytical technique of choice. In this paper, we provide an overview of chromatographic evidence with oscillatory reactions discovered in our laboratory in the course of the last several years that involve the low-molecular-weight carboxylic acids (profen drugs, amino acids, and hydroxy acids). The investigated processes comprise the oscillatory chiral conversion and the oscillatory condensation, spontaneously running in the aqueous and nonaqueous abiotic media, and they were traced with use of TLC and HPLC coupled with different detector types.

1. Introduction

An ability of profen drugs to undergo chiral conversion in biological systems has been recognized several decades ago, and it was considered a result of chemical reactions running in living organisms as reported, for example, in [1, 2]. This has been the matter of a serious concern in pharmacology and a subject of detailed biochemical investigations also, because most profen drugs are believed to have a high curative potential as the *S* enantiomers only. Chiral conversion of amino acids and hydroxy acids in biological systems has also been recognized as caused by various different racemases, but prior to our own research, none of these reactions was reported in the purely abiotic systems. This is rather understandable that none of these reactions running in biological systems has been recognized as an oscillatory reaction either, because recurrence and periodicity inherent of a given reaction become evident only in the course of the continuous or semicontinuous measurements performed in a simple model environment, free from the influence of the accompanying compounds that are present in complex natural systems.

2. Step One: Spontaneous Oscillatory *In Vitro* Chiral Conversion of Profen Drugs, Amino Acids, and Hydroxy Acids

An ability of 2-phenylpropionic acid and certain profen drugs to undergo a spontaneous oscillatory *in vitro* chiral conversion was discovered accidentally, when we have been working on enantioseparation of the 2-phenylpropionic acid, ibuprofen, and naproxen antimers by means of the chiral thin-layer chromatography (TLC) with densitometric detection [3]. Due to a substantial cost of the optically pure

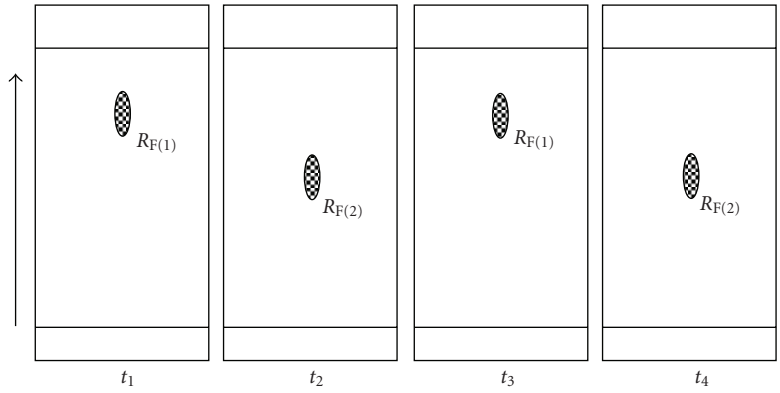


FIGURE 1: Schematic presentation of the oscillatory changes of the R_F values (valid for each investigated aryl substituted 2-propionic acid as a function of storage time in the solution. Stationary phase: silica gel impregnated with *L*-arginine; mobile phase: ternary liquid mixture composed of ACN, MeOH, and H_2O plus several drops of glacial acetic acid (originally published in [3]).

reagents, each day, we used to chromatograph the same samples of *S*(+)-ibuprofen and *S*(+)-naproxen solutions in 70% aqueous ethanol, respectively, and to our great surprise, each day, both the retardation parameter (R_F) values and the concentration profiles of the investigated samples considerably differed. The dispersion of the observed numerical data considerably surpassed the experimental error and yet the periodic oscillatory recurrence of these data was observed, which can simply be illustrated by Figure 1. Then, for the sake of comparison, we analyzed the *rac*-2-phenylpropionic acid sample in 70% aqueous ethanol and the same instability of the R_F values and the concentration profiles was discovered (Figure 2). The analogous results were obtained for the same compounds, when dissolved in the purely aqueous medium (i.e., in physiological salt [6]), and in the purely non-aqueous medium (i.e., dichloromethane [7]).

With time, the number of the similarly investigated profen drugs grew and the analogous phenomena of the unstable retention parameter values and the unstable concentration profiles proved characteristic of *S*(+)-ketoprofen, *rac*-ketoprofen, *S*(+)-flurbiprofen, and *R*(-)-flurbiprofen also [10–13]. This extraordinary behavior of the aryl-substituted propionic acids instigated our interest in other chiral propionic acid derivatives from the classes of amino acids and hydroxy acids. To this effect, we performed the analogous chromatographic investigations with the organic-aqueous solutions of *L*-alanine [14], *L*-*α*-phenylalanine [15], and tyrosine [4], using the chiral TLC with densitometric detection as the primary analytical tool to trace instabilities of the respective retardation parameter (R_F) values and those of the concentration profile intensities and shapes. With amino acids, once again these two striking instabilities were confirmed (as shown, e.g., in Figures 3 and 4).

The third class of chemical compounds that we have tested was hydroxy acids. The hydroxy acid that we have examined first (again, using 70% aqueous ethanol solution and the chiral TLC with densitometric detection) was *L*-lactic acids. The obtained results gave clear evidence that *L*-lactic acid also produces recurrently changing concentration profiles of chromatographic bands, as documented in papers [16–18].

In the course of our study, several general ideas were practically tested in our experiments. One such idea regarded chemical structure of the investigated chiral compounds, as initially all of them have been derived from propionic acid. Then, we decided to test some new low-molecular-weight carboxylic acids with the chirality center in the *α* position, but derived from acetic acid (the shorter aliphatic carbon chain) and butyric acid (the longer aliphatic carbon chain than that of propionic acid) as well. To this effect, we selected two amino acids (*R*- and *S*-phenylglycine), two hydroxy acids (*R*- and *S*-mandelic acid) derived from acetic acid, and also two hydroxy acids (*R*- and *S*-*α*-hydroxybutyric acid) derived from butyric acid. The chromatographic results valid for chiral compounds derived from acetic acid and *α*-substituted butyric acid, again confirmed a striking instability of the respective concentration profiles [5, 19], irrespective of the examined carbon chain length. Finally, we investigated two antimers of *β*-hydroxybutyric acid and again, we found that the *β* position of the asymmetry center does not prevent the two antimers of *β*-hydroxybutyric acid from the recurrent changing of their concentration profiles, thus indicating that the increased distance between carboxylic group and the chirality center does not eliminate the phenomenon previously observed with so many other chiral compounds [20].

Another practical idea was to choose a most adequate analytical technique able to disclose the true physicochemical nature of the phenomenon responsible for the recurrent changes of the retardation parameter (R_F) values and/or the changing concentration profiles of the respective chromatographic bands. We supposed that the reason could be the spontaneous oscillatory chiral conversion of all the examined compounds and in that case, the analytical technique of choice would be polarimetry, and more precisely, polarimetric measurement of the investigated compound's

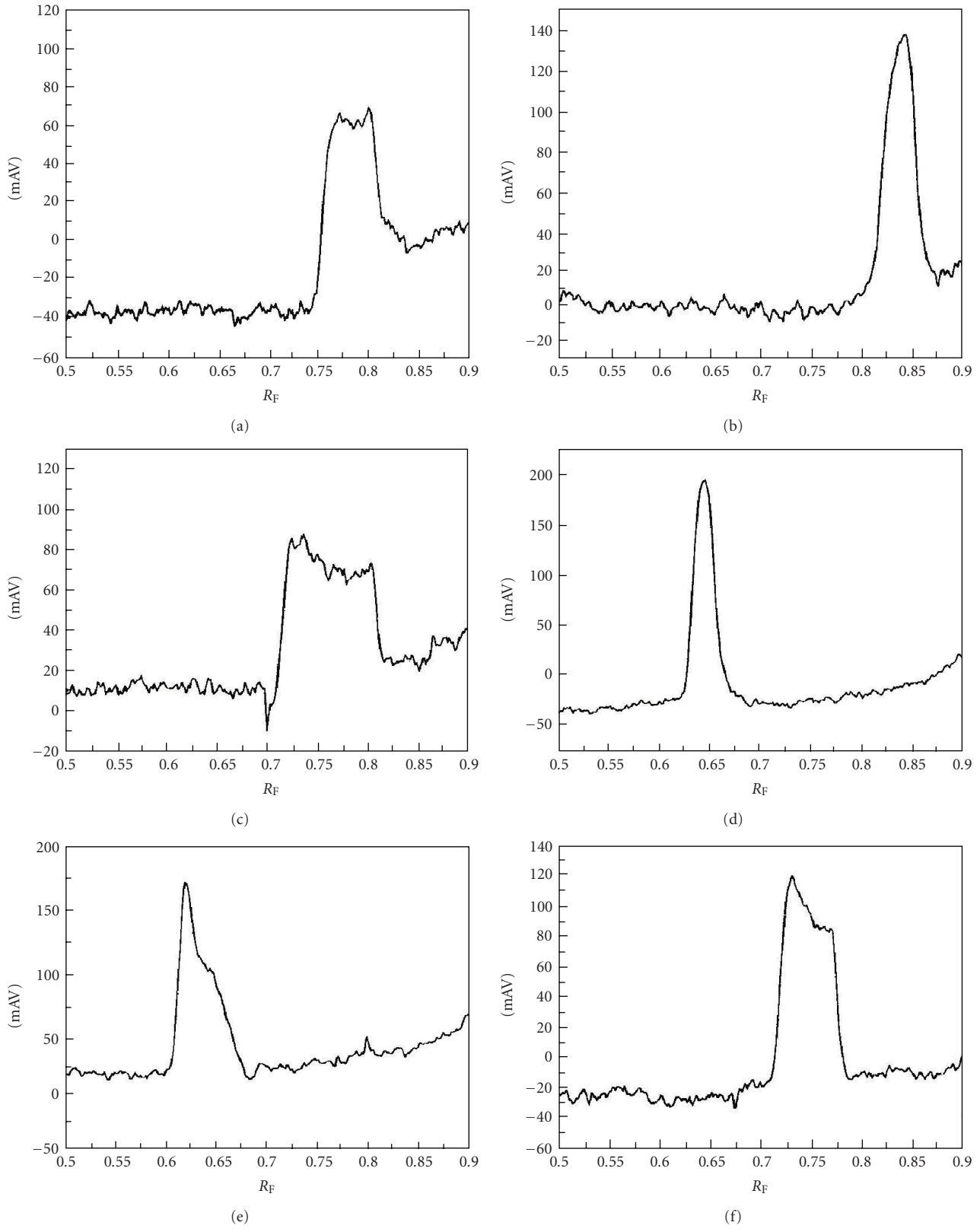


Figure 2: Sequence of the densitometrically recorded concentration profiles of 2-phenylpropionic acid after: (a) 0 h (racemic mixture), (b) 22.5 h (*S*-(+) form), (c) 27.5 h (racemic mixture), (d) 46.5 h (*R*-(−) form), (e) 51.5 h (shift from *R*-(−) form to racemic mixture), and (f) 70.5 h (racemic mixture), storage time at ambient temperature (22 ± 2°C). Changes of the peaks' concentration profiles are accompanied by the changing R_F values (originally published in [3]).

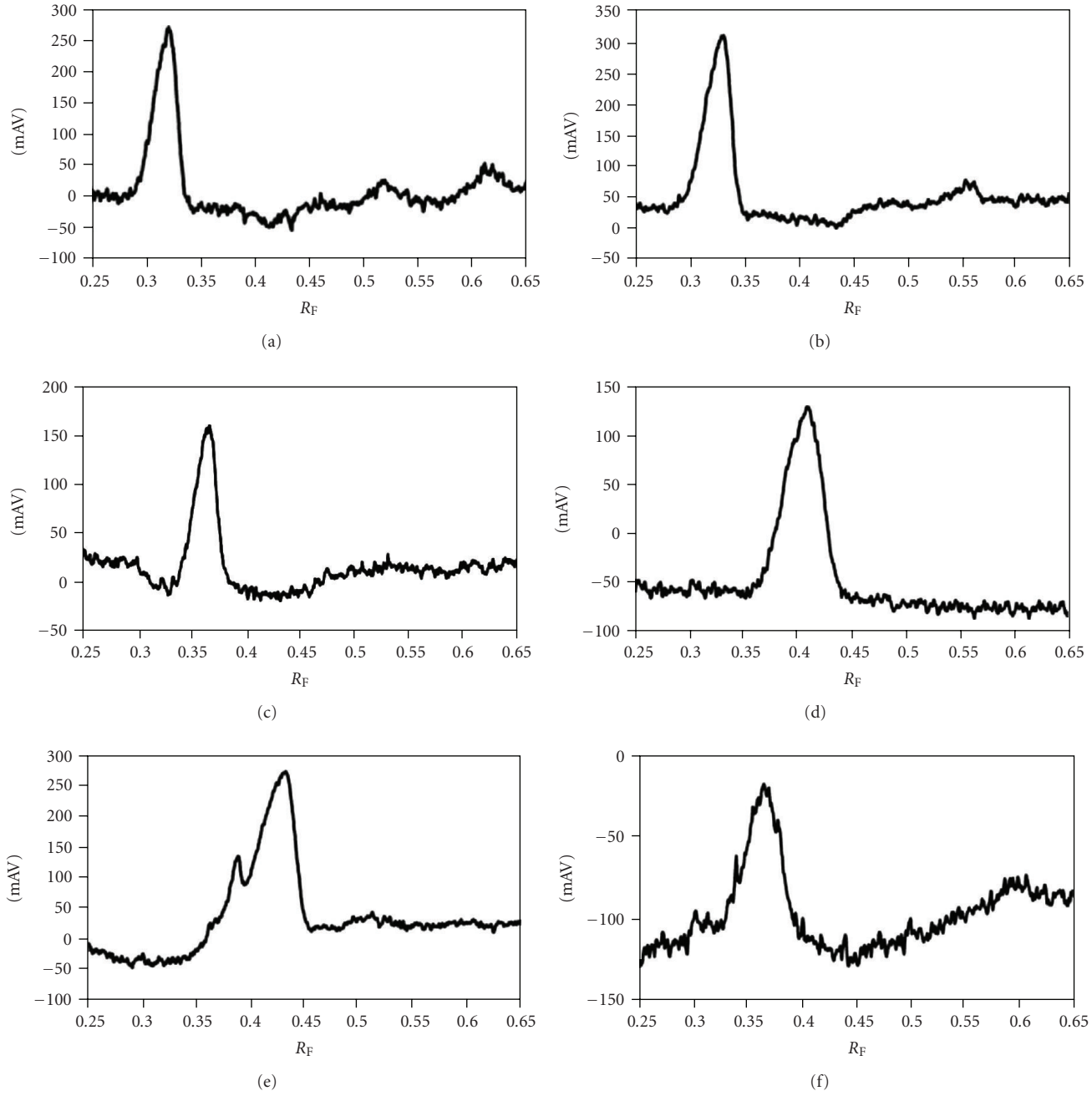


Figure 3: Sequence of the densitometrically recorded concentration profiles for *L*-tyrosine solution in ethanol—1 M hydrochloric acid, 7 : 3 (v/v) after (a) 1.3 h, (b) 5 h, (c) 25 h, (d) 28 h, (e) 120 h, and (f) 123 h storage time at ambient temperature (22 ± 2°C). (originally published in [4]).

specific rotation ($[\alpha]_D$) in the function of time

$$[\alpha]_D = \frac{100\alpha}{cd}, \tag{1}$$

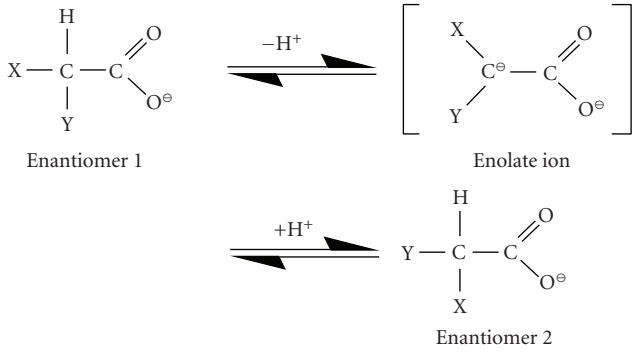
where α is the measured rotation (in angle degrees), D is the wavelength used (589 nm, which corresponds to the sodium D line), c is the concentration of the compound in g $(100\,\text{mL})^{-1}$ solution, and d is the measured sample thickness in dm.

In fact, with the most examined solutions, the polarimetric evidence of the changing specific rotation ($[\alpha]_D$) values in the function of time was provided in papers [3–7, 10–20]. However, in most cases, the respective measurements have been carried out pointwise with use of a simple noncontinuous polarimetric registration. Later, all polarimetric measurements have been repeated in the continuous registration mode and the selected examples of the changing specific rotation ($[\alpha]_D$) values valid for a typical profen, amino acid, and hydroxy acid are given in Figure 5.

Upon abundant experimental evidence originating from the chromatographic and polarimetric measurements, we drew a conclusion that the phenomenon observed with various different profen drugs, amino acids, and hydroxy acids was the oscillatory chiral conversion which can simply be summarized as

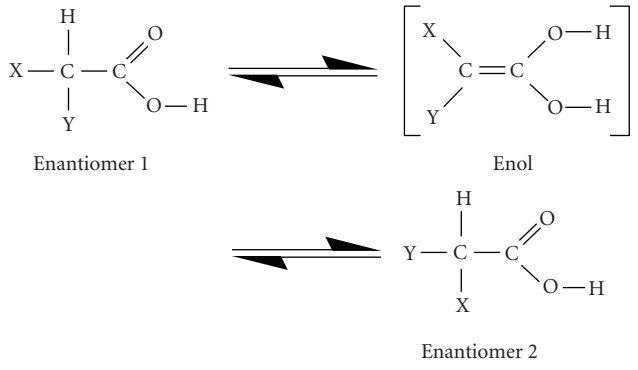
$$\text{Enantiomer}\,(+) \rightleftharpoons \text{Enol} \rightleftharpoons \text{Enantiomer}\,(-) \quad (2)$$

If we consider chiral conversion of selected carboxylic acids in aqueous solution in greater detail, then (2) can be written as [21]



(3)

In anhydrous media and in the presence of the trace amounts of water, the probable mechanism of chiral conversion is given by (4) [22]



(4)

where X = −NH_2, −OH, −Ar, and so forth, and Y = −R and so forth.

Summing up, at the first step of our study a conclusion could be drawn that the low-molecular-weight chiral carboxylic acids dissolved in the aqueous, organic-aqueous, and non-aqueous abiotic media characterize with an ability to spontaneously undergo a repeated chiral conversion which we named the oscillatory chiral conversion (in spite of the fact that the observed amplitudes of oscillations with the R_F and/or $[\alpha]_D$ values were relatively shallow and the periodicity rather irregular).

3. Step Two: Spontaneous Condensation of Profen Drugs, Amino Acids, and Hydroxy Acids

In the course of investigating the oscillatory chiral conversion of profens, amino acids, and hydroxy acids, we have been testing our samples stored for several days, weeks, or even months (and with time apparently ageing) with use of the nonchiral high-performance liquid chromatography with diode array detection (HPLC-DAD). In that way, after certain period of time, we detected new peaks on the chromatograms with all the investigated compounds, and yet one and the same UV spectrum was observed for all the peaks valid for a given compound. This made us anticipate that all investigated carboxylic acids most probably undergo spontaneous condensation, in that way yielding certain amounts of the covalently bonded condensates (dimers, trimers, and the higher condensates also), and that at each condensation step, one water molecule is split from each pair of the coupled molecular units.

Then, we decided to collect a valid experimental confirmation regarding this spontaneous condensation. With amino acids, we simply used the well-known biuret test to demonstrate very rapid spontaneous peptidization with all the compounds considered in our project. In Figure 6, we show a spectacular outcome of biuret test with *R*-, *S*-, and *rac*-phenylglycine, yielding visual evidence of peptidization with all three investigated species [5]. In that way, we came to a conclusion that with amino acids, the process of ageing consists of the two parallel reactions. The first is the oscillatory chiral conversion of a given amino acid to its antipode and the second is peptidization.

In the case of profen drugs and hydroxy acids, we provided experimental evidence of condensation with use of the ^{13}C NMR spectroscopy. Comparing the ^{13}C NMR spectra of the fresh prepared profen and hydroxy acid samples with those of the aged ones, and additionally making use of the programs simulating the ^{13}C NMR spectra, we could attribute certain NMR signals absent from the spectra of the fresh samples and appearing in the spectra of the aged samples to carbon atoms in the covalently bonded condensation products [8, 23]. Selected examples valid for the two hydroxy acids are shown in Figures 7 and 8. The analogous results were obtained for the profens as well. Thus, we came to a conclusion that with profen drugs and hydroxy acids, the process of ageing also consists of the two parallel reactions. One of them is the oscillatory chiral conversion of a given compound to its antipode and parallel to it, the condensation is running.

We searched for extra evidence with use of an analytical technique different from biuret test or liquid chromatography, in order to additionally document the phenomenon of spontaneous condensation with profen drugs, amino acids, and hydroxy acids. Thus, we used mass spectrometry in the electrospray ionization mode (MS-ESI), and recorded mass spectra of the freshly prepared samples and of those after

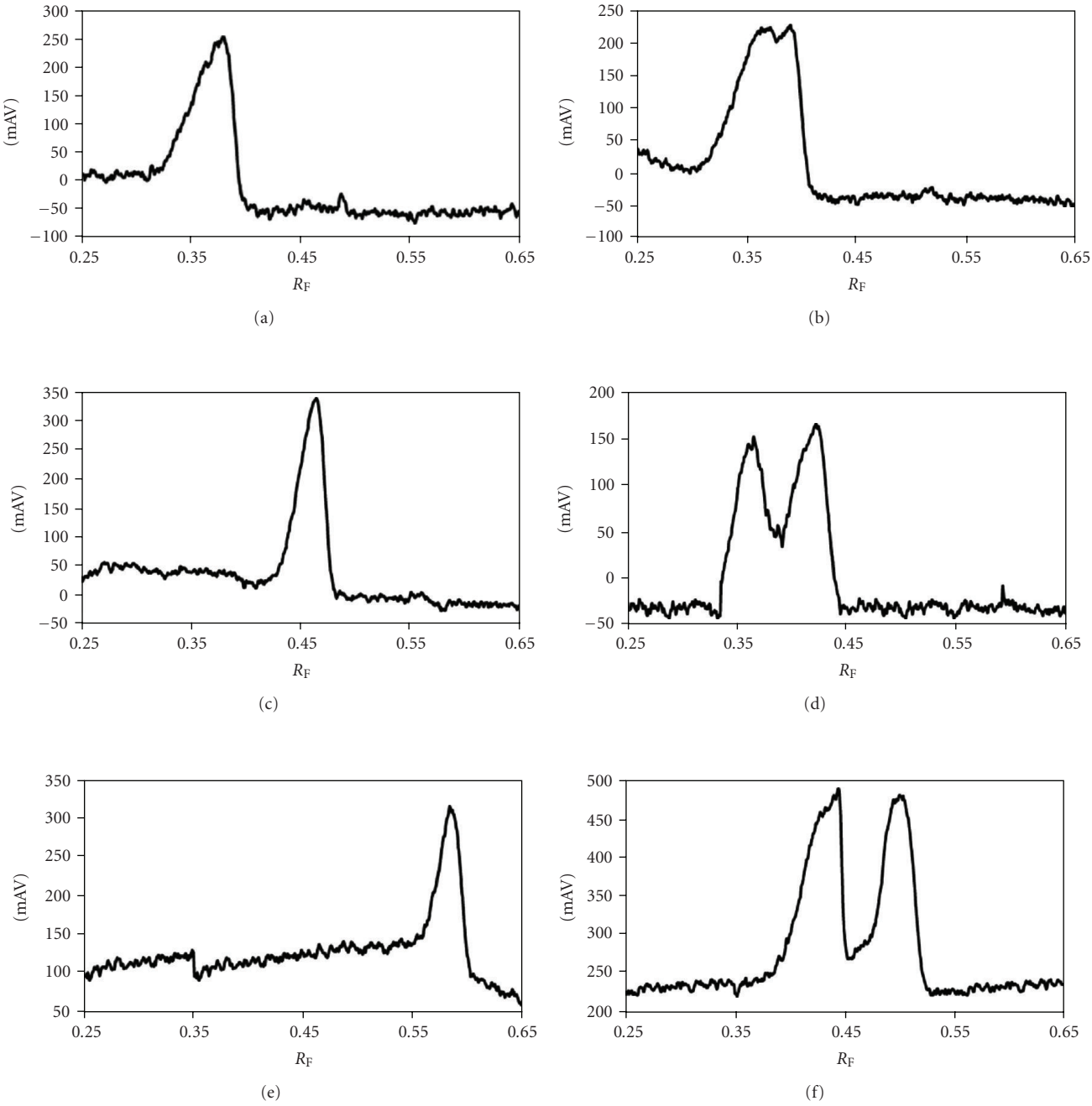


Figure 4: Sequence of densitometrically recorded concentration profiles for *L*-tyrosine solution in ethanol—1 M sodium hydroxide, 7 : 3 (v/v) after (a) 1 h, (b) 4.6 h, (c) 28 h, (d) 100.5 h, (e) 124.5 h, and (f) 168 h storage time at ambient temperature (22 ± 2°C) (originally published in [4]).

a certain storage period. As a result, we gathered pairs of the mass spectra showing much simpler patterns of signals with the fresh samples than with the aged one. Moreover, the mass spectra of the aged samples showed signals in the m/z range much higher than those valid for molecular ions of the starting compounds, which served as an additional proof of the condensation process taking place in the course of the sample storage. An example of the mass spectrometric evidence of condensation with the 70% aqueous ethanol solution of *S*-mandelic acid stored for the period of one year is given in Figure 9.

Summing up, at step two we collected sufficient experimental evidence to propose the general scheme of the parallel spontaneous oscillatory *in vitro* chiral conversion and spontaneous condensation of the low-molecular-weight carboxylic acids from the groups of profen drugs, amino acids, and hydroxy acids. An example of such parallel process valid for profens is given below [23]:

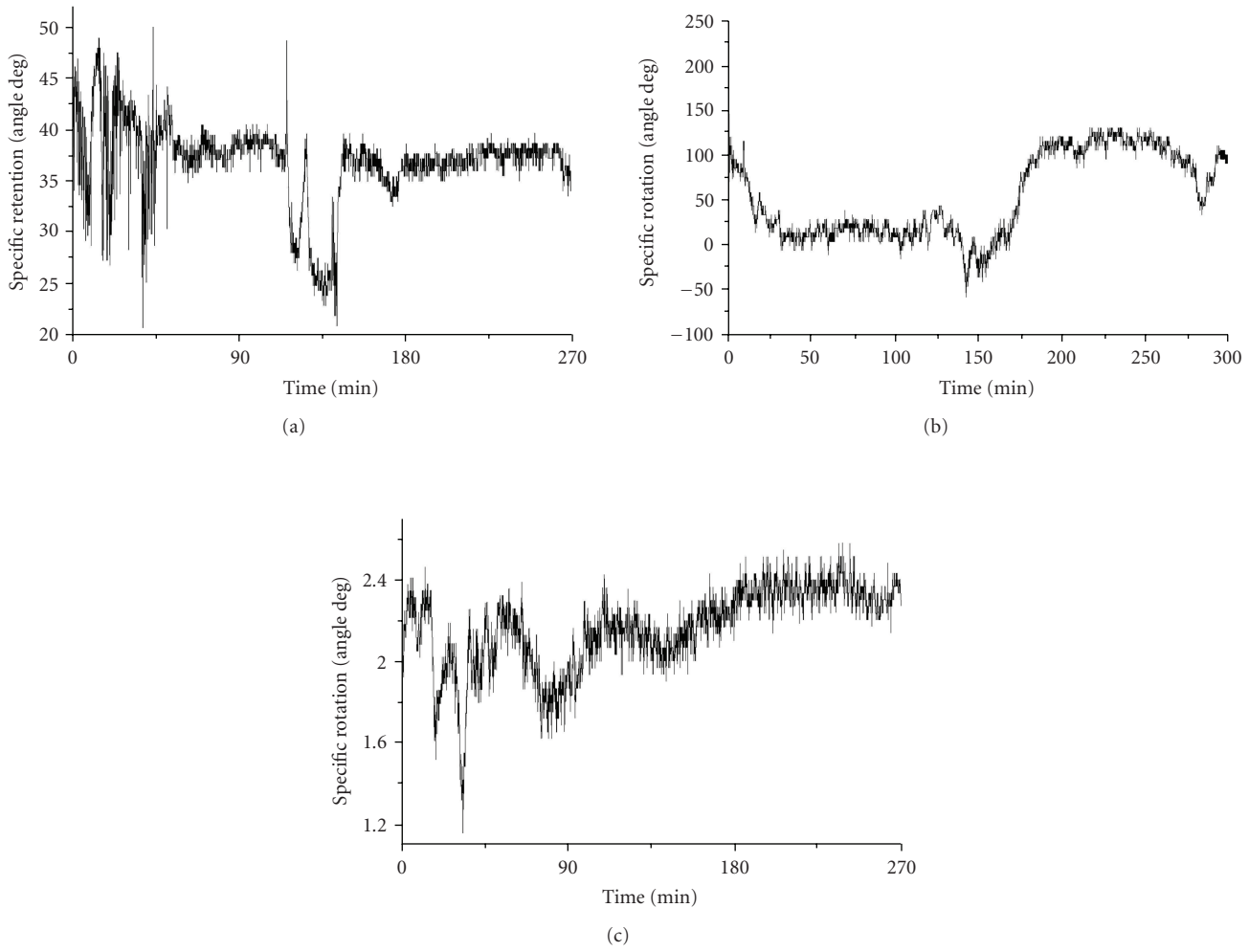
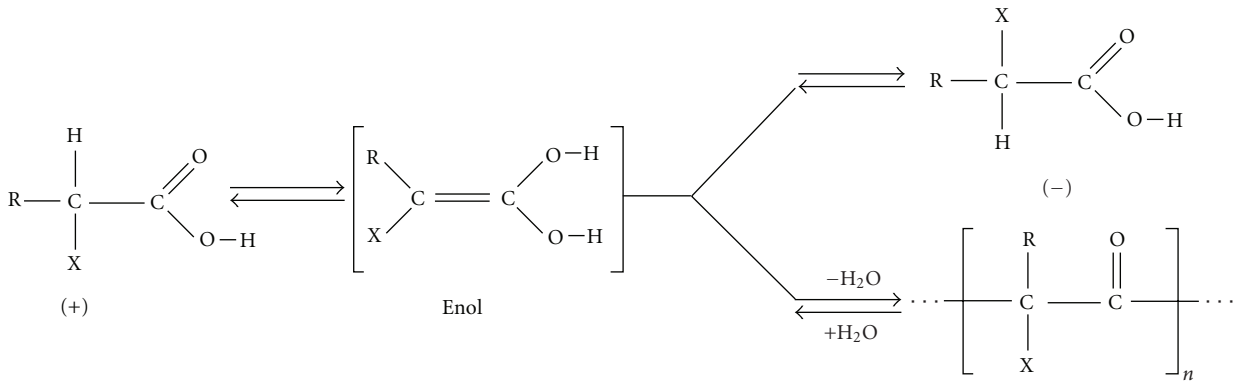


FIGURE 5: Continuous polarimetric registration at ambient temperature ($22 \pm 2^{\circ}$C) of the specific rotation ($[\alpha]_D$) values for (a) *S*-ketoprofen, (b) *S*-phenylglycine, and (c) *L*-lactic acid solutions in 70% aqueous ethanol (unpublished data).



(5)

where R: $-CH_3$, and X: –Ar.

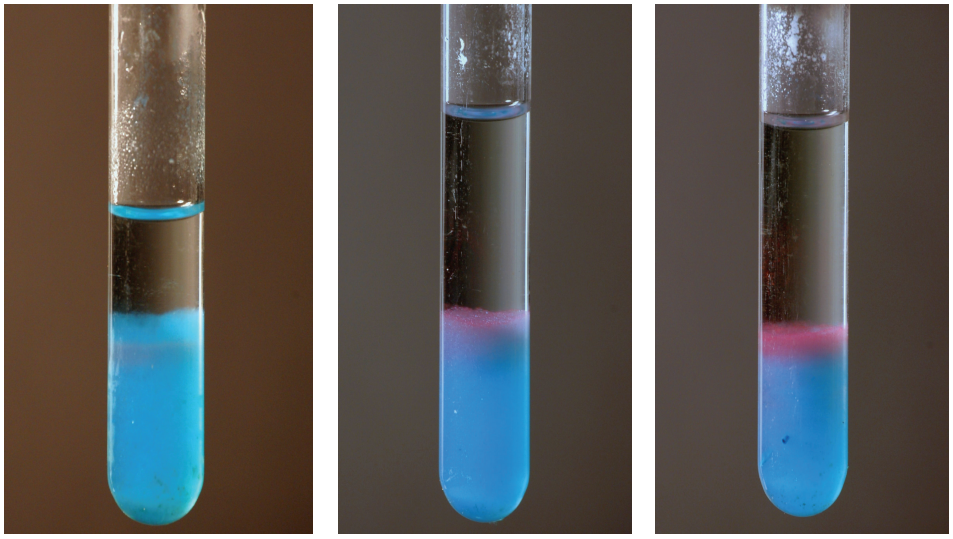


Figure 6: Test tubes showing the color outcome of the biuret test on 70% ethanol solutions of (a) *R*-phenylglycine, (b) *S*-phenylglycine, and (c) racemic *RS*-phenylglycine after storage for three days (originally published in [5]).

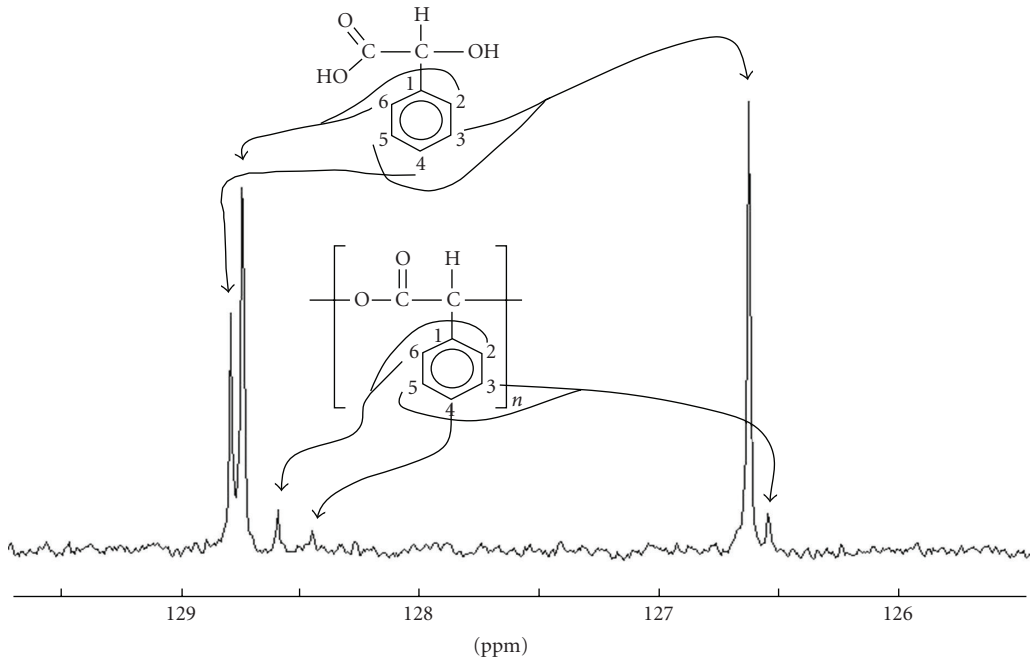


Figure 7: 100 MHz ^{13}C NMR spectrum of *S*-(+)-mandelic acid first dissolved and stored for ten days in pure ethanol, and then recorded in $CDCl_3$ at 25°C (originally published in [8]).

4. Step Three: Spontaneous Oscillatory Condensation of Profen Drugs, Amino Acids, and Hydroxy Acids

Some time after having discovered that the chiral low-molecular-weight carboxylic acids can in parallel undergo chiral conversion and condensation, we accidentally came across the reports in the literature [24, 25] on the phenomenon of the oscillatory condensation with the selected organic-silicon compounds (some of them chiral and structurally resembling our own compounds of interest), and the experimental evidence presented by the authors originated from the nonchiral TLC. These reports made us revisit the issue of condensation with the profen drugs, amino acids, and hydroxy acids, this time scrutinizing the dynamics of these processes in order to reveal, if they are really oscillatory or not. Step three of our study was accomplished largely with aid of the nonchiral HPLC-DAD.

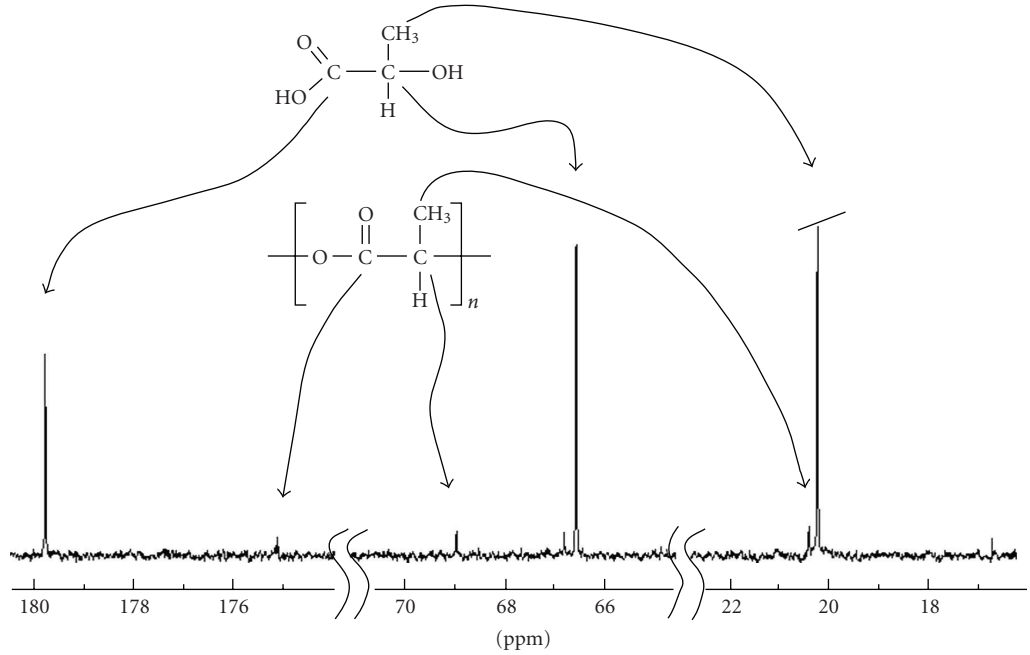


Figure 8: 100 MHz ^{13}C NMR spectrum of *L*-(+)-lactic acid first dissolved and stored for ten days in pure ethanol, and then recorded in $CDCl_3$ at 25°C (originally published in [8]).

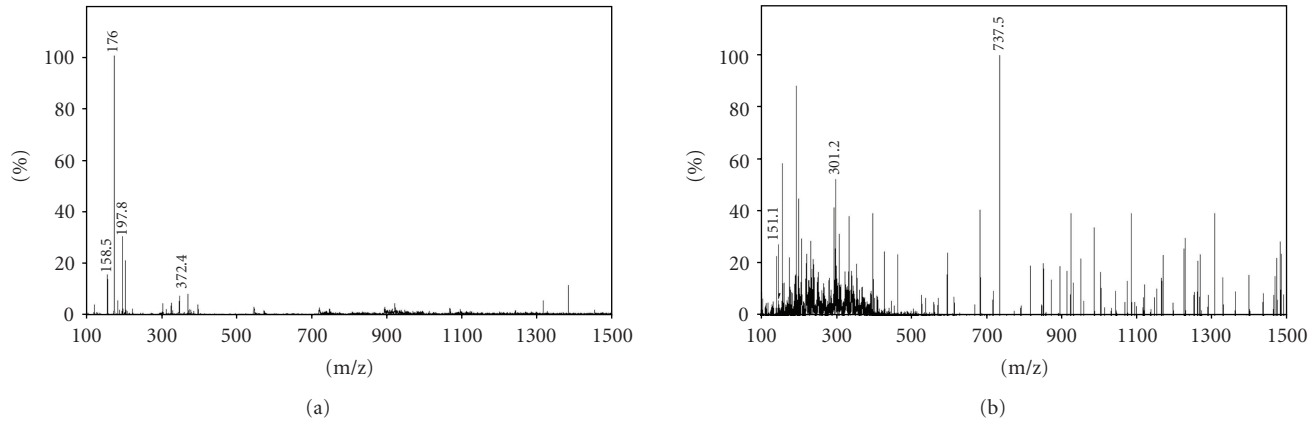


Figure 9: Mass spectra of the (a) freshly prepared and (b) stored for one year *S*-mandelic acid sample in the positive MS-ESI ionization mode [9].

The idea standing behind the experiments performed within the framework of step three consisted of the liquid chromatographic separation of the starting carboxylic acid (appearing in a given chromatographic band as an optically pure compound, or—due to the chiral inversion progressing with the storage time as a mixture of the two antimers) from the condensation products separated into the individual chromatographic bands. These analyses were carried out in the even time intervals with use of an autosampler. The peak height was considered as equivalent to the respective concentration of a given species. Ultimately, the peak heights were plotted against the sample storage time, and for all the low-molecular-weight carboxylic acids investigated in this study, the oscillatory nature of the quantitative changes with all the separated peaks was demonstrated. For the sake of illustration, in Figure 10, we show a selection of the results referring to the condensation products of *L*-lactic acid [26].

Summing up, at step three, we collected sufficient experimental evidence to propose the general scheme of the parallel spontaneous oscillatory *in vitro* chiral conversion and spontaneous oscillatory condensation of the low-molecular-weight carboxylic acids from the groups of profen drugs, amino acids, and hydroxy acids. Finally, it can be stated that each of the two parallel processes (and not only the chiral conversion) is oscillatory in nature.

Last not least, we have to add that the successful attempts have been undertaken to theoretically model the oscillatory phenomena presented in this study. These theoretical considerations are given in papers [15, 27–29].

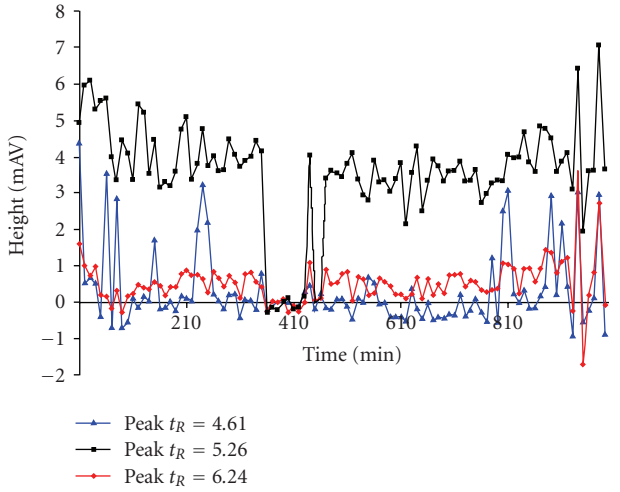


FIGURE 10: Time changes of the chromatographic peak heights (the retention times, t_R, of the peaks equal to 4.61, 5.26, and 6.24 min, resp.) for the *L*-lactic acid solution in ACN stored at 22°C for 900 minutes. Registration of the chromatograms by means of the DAD detector at the wavelength $\lambda = 220$ nm [26].

The results of our studies on the spontaneous oscillatory chiral conversion of the selected chiral low-molecular-weight carboxylic acids have already been adapted to elucidation of certain oscillatory phenomena (i.e., the keto-enol isomerization) observed in the aerosol particles rich in the organic matter and originating from the atmosphere surrounding the Earth [30].

5. General Conclusion

The contents of this paper provide a convincing evidence of the fact that liquid chromatography (both in the TLC and HPLC mode) can serve as an analytical tool of choice for as challenging research, as studying the reaction mechanisms (and kinetics) with the rarely occurring chemical processes (i.e., with the spontaneous nonlinear chiral conversion and the nonlinear condensation of the low-molecular-weight carboxylic acids running in vitro both in the non-aqueous and the aqueous media). A particular attention should be paid to the fact that such simple analytical tool as the chiral TLC can prove particularly helpful in assessing dynamics of nonlinear reactions with certain classes of chiral substrates undergoing steric conversion at the asymmetry center.

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