

Rate-Product Correlations for the Solvolysis of 5-Nitro-2-Furoyl Chloride

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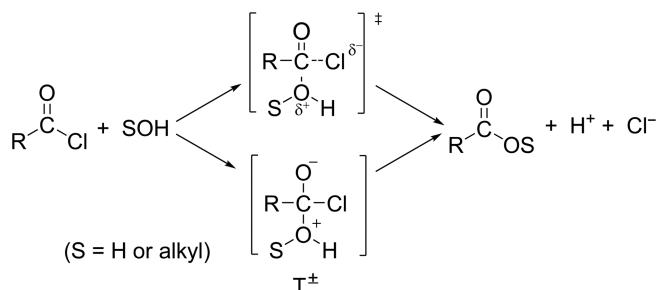
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The solvolysis rate constants of 5-nitro-2-furoyl chloride (5-NO₂(C₄H₂O)-2-COCl, **1**) in 27 different solvents are well correlated with the extended Grunwald-Winstein equation, using the *N_T* solvent nucleophilicity scale and *Y_{Cl}* solvent ionizing scale, with sensitivity values of 1.20 ± 0.05 and 0.37 ± 0.02 for *l* and *m*, respectively. The activation enthalpies (ΔH^\ddagger) were 5.63 to 13.0 kcal·mol⁻¹ and the activation entropies (ΔS^\ddagger) were -25.9 to -43.4 cal·mol⁻¹·K⁻¹, which is consistent with the proposed bimolecular reaction mechanism. The solvent kinetic isotope effect (SKIE, $k_{\text{MeOH}}/k_{\text{MeOD}}$) of 2.65 was also in accord with the S_N2 mechanism and was possibly assisted using a general-base catalysis. The product selectivity (*S*) for solvolysis of **1** in alcohol/water mixtures was 1.2 to 11, which is also consistent with the proposed bimolecular reaction mechanism.

Key Words : 5-Nitro-2-furoyl chloride, Extended grunwald-winstein equation, S_N2 mechanism, Solvent kinetic isotope effect, Product selectivity

Introduction

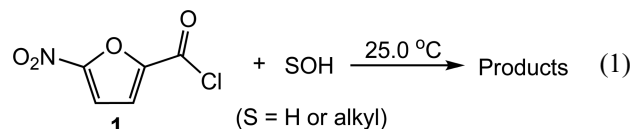
The mechanism of acyl-transfer reactions has been intensively investigated both experimentally¹ and theoretically for many years.² However, the mechanisms of most of these reactions remain not well established. The bimolecular solvolysis of acyl halides (RCOX) is believed to proceed either through a direct displacement mechanism (S_N2) or through an associative addition-elimination (A-E) mechanism involving a tetrahedral intermediate (Scheme 1).³ For acyl halides with a strong electron donating group, (R), a dissociative mechanism involving an acylium ion (RCO⁺) intermediate has also been involved.⁴ The two types of mechanism, (S_N2 and stepwise addition-elimination), are also common in the bimolecular aminolysis of acyl halides.



Scheme 1

In order to gain further understanding of the acyl transfer mechanism, a kinetic study was undertaken of the solvolysis of 5-nitro-2-furoyl chloride (**1**) in a variety of pure and binary solvents at 25.0 °C [Eq. (1)]. Furthermore, the *l* and *m* values were determined using the extended Grunwald-

Winstein equation⁵ [Eq. (2)], together with the enthalpies and entropies of activation, the solvent kinetic isotope effect (SKIE), and product selectivity (*S*).



$$\log(k/k_o) = l N_T + m Y_{Cl} + c \quad (2)$$

In Eq. (2), *k* and *k_o* represent the rate constants of the solvolysis in a given solvent and a standard solvent (80% ethanol), respectively; *l* represents the sensitivity to changes in the solvent nucleophilicity (*N_T*);⁶ and *m* represents the sensitivity to changes in the solvent ionizing power (*Y_X*, for a leaving group X), and *c* is a constant (residual) term.⁷

Results and Discussion

The rate constants (*k*) for the solvolysis of **1** were determined at 25.0 °C in 27 solvents. The solvents consisted of ethanol, methanol, and binary mixtures of water with ethanol, methanol, acetone, and 2,2,2-trifluoroethanol (TFE). These values are reported in Table 1, together with the solvent nucleophilicity (*N_T*)⁶ and solvent ionizing power (*Y_{Cl}*)⁷ values.

In the present study, the rate constants of the solvolysis represented in Eq. (1) were measured using an automatic conductivity apparatus. In most solvents, the reactions proceeded rapidly, which enabled the responses to be recorded as a function of time.⁸ In order to promote a rapid dissolution in the solvent, the substrate was added as a small volume of a concentrated stock solution in the acetonitrile in order that

Table 1. Rate constants for the solvolysis (k , s⁻¹) of 5-nitro-2-furoyl chloride (**1**)^a in binary solvent mixtures at 25 °C and the N_T and the Y_{Cl} values for the solvent

Solvent ^b (%)	N_T ^c	Y_{Cl} ^c	k
100EtOH	0.37	-2.52	3.21×10^{-2}
90EtOH	0.16	-0.94	8.68×10^{-2}
80EtOH	0.00	0.00	1.14×10^{-1}
70EtOH	-0.20	0.78	1.29×10^{-1}
60EtOH	-0.39	1.38	1.45×10^{-1}
50EtOH	-0.58	2.02	1.57×10^{-1}
40EtOH	-0.74	2.75	1.67×10^{-1}
30EtOH	-0.93	3.53	1.43×10^{-1}
20EtOH	-1.16	4.09	1.36×10^{-1}
100MeOH ^d	0.17	-1.17	9.84×10^{-2}
90MeOH	-0.01	-0.18	2.05×10^{-1}
80MeOH	-0.06	0.67	2.24×10^{-1}
70MeOH	-0.40	1.46	2.76×10^{-1}
60MeOH	-0.54	2.07	2.91×10^{-1}
50MeOH	-0.57	2.70	3.11×10^{-1}
40MeOH	-0.87	3.25	2.43×10^{-1}
30MeOH	-1.06	3.73	2.04×10^{-1}
20MeOH	-1.23	4.10	1.91×10^{-1}
87Acetone	-0.34	-1.81	9.95×10^{-3}
80Acetone	-0.37	-0.83	2.10×10^{-2}
75Acetone	-0.39	-0.28	2.91×10^{-2}
63Acetone	-0.54	0.62	4.61×10^{-2}
52Acetone	-0.68	1.45	6.23×10^{-2}
42Acetone	-0.81	2.21	7.15×10^{-2}
97TFE ^e	-3.30	2.83	3.73×10^{-4}
80TFE	-2.19	2.90	1.78×10^{-3}
50TFE	-1.73	3.16	1.36×10^{-2}

^aUnless otherwise indicated, a 1.0 mol dm⁻³ solution of the substrate in the indicated solvent, containing 0.1% CH₃CN. ^bOn a volume-volume content at 25.0 °C, and the other component is water. ^cValues from refs. 6, 7. ^dValues of $k = 3.72(\pm 0.03) \times 10^{-2}$ s⁻¹ in deuterated methanol (MeOD), corresponding to k_{MeOH}/k_{MeOD} value of 2.65 ± 0.04 (with associated standard error). ^eSolvent prepared on a weight-weight basis at 25.0 °C, and the other component is water.

the reaction solution contained approximately 0.1% acetonitrile.

The rate constants were increased as the amount of water in the binary solvent systems was increased as shown in Table 1; that is, faster solvolysis reactions in the nucleophilic solvent systems and slower reactions in the electrophilic solvent systems were observed. This phenomenon supports that the solvolysis of **1** is dominated by a bimolecular reaction mechanism.

The rate constant for the ethanolysis of **1** measured in this study was 3.21×10^{-2} s⁻¹ at 25.0 °C (Table 1), which is larger than that previously reported for 4-nitro-benzoyl chloride (4-NO₂C₆H₄COCl),⁹ $k = 1.35 \times 10^{-2}$ s⁻¹ at 25.0 °C. This suggests that the 5-nitro-2-furyl group (5-NO₂(C₄H₂O)) has greater electron-withdrawing power than the 4-nitro-benzene group (4-NO₂(C₆H₄)), and therefore it would be more favorable for nucleophilic attacks at the electron-deficient carbonyl carbons.

The activation parameters, (ΔH^\ddagger and ΔS^\ddagger), which are calculated from the k values at three different temperatures for solvolysis of **1** in pure EtOH and MeOH, and in 80% EtOH, 90% MeOH, 87% acetone, and 80% TFE are shown in Table 2. The values of ΔH^\ddagger were relatively low (5.63 to 13.0 kcal·mol⁻¹) and the values of ΔS were largely negative (-25.9 to -43.4 cal·mol⁻¹K⁻¹), but these were within the ranges of previously reported results for a normal S_N2 reaction.¹¹ In the deuterated methanol (MeOD), a SKIE (k_{MeOH}/k_{MeOD}) of 2.65 ± 0.04 was observed at 25.0 °C. Also, the values of $k = 3.11(\pm 0.01) \times 10^{-1}$ s⁻¹ in 50% MeOH-50% H₂O and $k = 1.10(\pm 0.03) \times 10^{-1}$ s⁻¹ in 50% MeOD-50% D₂O corresponded to SKIE values of 2.83 ± 0.03 . These are within the SKIE values of 1.58-2.90, which were reported for the corresponding methanolyses of *n*-propyl chloroformate and a series of benzenesulfonyl chlorides at 25.0 °C in which the reactions were believed to be S_N2 in character.¹²

The extended Grunwald-Winstein equation [Eq. (2)] is useful for determining the extent of nucleophilic participation using the solvent because the magnitudes of l and m in equation (2) are the indicators used to determine whether a nucleophilic substitution reaction proceeds through an unimolecular, S_N1 (*i.e.*, $l \approx 0$ and $m \approx 1$) or a bimolecular reaction, (S_N2, *i.e.*, $l \approx 1.3$ and $m \approx 0.5$) and an addition-elimination mechanism (*i.e.*, $l \approx 1.6$ and $m \approx 0.7$). Therefore, the determination of the l and m values would provide valuable information concerning the structure of the

Table 2. Rate constants and activation parameters for the solvolysis of 5-nitro-2-furoyl chloride^a (**1**) at various temperatures

Solvent (%)	T (°C)	k (s ⁻¹) ^b	ΔH^\ddagger (kcal/mol) ^c	$-\Delta S^\ddagger$ (cal/mol·K) ^c
100 EtOH	25	3.21×10^{-2}	11.8 ± 0.03	25.9 ± 0.1
	35	6.13×10^{-2}		
	45	1.12×10^{-1}		
80 EtOH ^d	25	1.14×10^{-1}	5.63 ± 0.1	43.4 ± 0.3
	35	1.98×10^{-1}		
	45	2.62×10^{-1}		
100 MeOH	25	9.84×10^{-2}	10.2 ± 0.9	28.7 ± 3.0
	35	1.87×10^{-1}		
	45	2.91×10^{-1}		
90 MeOH ^d	25	2.05×10^{-1}	7.57 ± 1.4	36.1 ± 4.8
	35	3.54×10^{-1}		
	45	4.57×10^{-1}		
87 Acetone ^d	25	9.95×10^{-3}	12.4 ± 1.1	26.0 ± 3.7
	35	2.17×10^{-2}		
	45	3.71×10^{-2}		
80 TFE ^e	25	1.78×10^{-3}	13.0 ± 0.3	27.3 ± 1.1
	35	3.53×10^{-3}		
	45	7.12×10^{-3}		

^aA 1.0 mol dm⁻³ solution of the substrate in the indicated solvent, also containing 0.1% CH₃CN. ^bAverages of three or more runs. ^cThe activation parameters are accompanied by the standard error. ^dOn a volume-volume content at 25.0 °C, and the other component is water. ^eSolvent prepared on a weight-weight basis at 25.0 °C, and the other component is water.

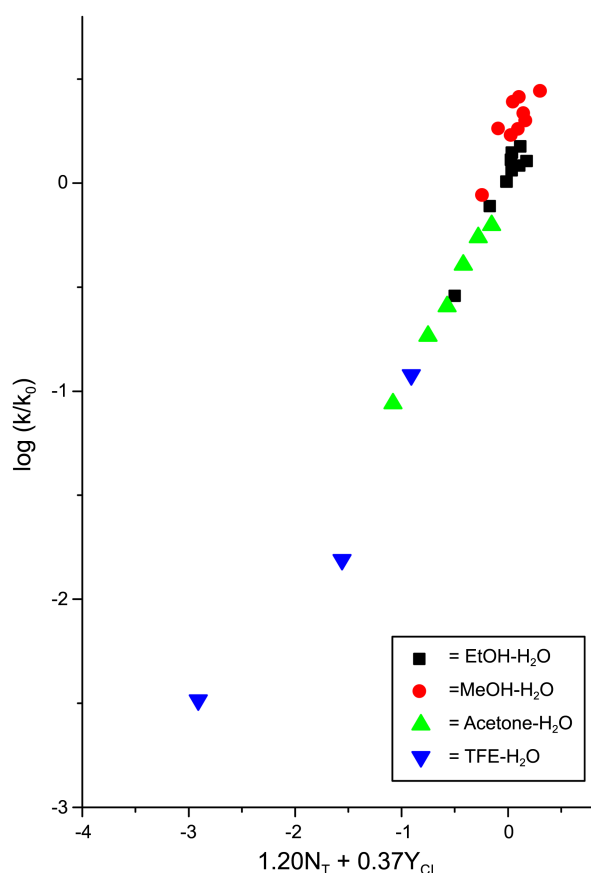


Figure 1. Extended Grunwald-Winstein plot the solvolysis of 5-nitro-2-furoyl chloride (**1**) at 25.0 °C against ($1.20 N_T + 0.37 Y_{Cl}$).

transition state for the solvolyses.^{3,5,9}

The application of the extended Grunwald-Winstein equation⁵ to the rate constants of the solvolysis of **1** (from

Table 1) leads to good correlation with N_T and Y_{Cl} (correlation coefficient of 0.955 for 27 solvents) with values of 1.20 ± 0.05 for l , 0.37 ± 0.02 for m , and 0.06 ± 0.04 for c . This relationship is presented graphically in Figure 1. The sensitivity values, (l and m), are reported in Table 3, where they are compared with the values from literature for related substrates.

The l value of 1.20 and m value of 0.37 for **1** were smaller than those recently reported for reactions that proceed through an addition-elimination mechanism ($l = 1.56$ – 1.68 and $m = 0.55$ – 0.76), whereas these values were similar to those previously reported for the bimolecular solvolyses of other substrates (Table 3). This suggests that there is an S_N2 mechanism involving a nucleophilic attack by the solvent at the carbonyl carbon atom of **1**. The solvolysis of **1**, where the bond making ($l = 1.20$) is more progressed than the bond breaking ($m = 0.37$), and the values are still in the range of S_N2 mechanism, reflects the degree of the nucleophilic assistance based on the measure of the solvent nucleophile.¹⁹

The lower m value ($m = 0.37$) for the solvolysis of **1**, compared with that of *n*-octyl chloroformate ($m = 0.76$),²¹ phenyl chloroformate ($m = 0.53$),¹⁹ methyl chloroformate ($m = 0.58$),¹⁷ and ethyl chloroformate ($m = 0.55$),²⁰ may reflect a reduced need for solvation of the developing negative charge on the carbonyl oxygen (see Table 3).

The l to m ratios have also been suggested as a useful mechanistic criteria. The l/m values from the extended Grunwald-Winstein equation could be classified into two classes of mechanism; l/m values of 1.2 to 3.5 for bimolecular mechanism (S_N2) or an addition-elimination pathway (A-E), and l/m values below 0.7 for an ionization pathway (I).⁵ For the solvolysis of **1**, the l/m value was 3.2 which is similar to those of previous studies investigating the solvolyses of 2,2,2-trichloro-1,1-dimethylethyl chloroformate,¹⁸

Table 3. Coefficients from the extended Grunwald-Winstein correlations of the specific rates for the solvolysis of 5-nitro-2-furoyl chloride at 25.0 °C and a comparison with coefficients from the correlations for other acyl chlorides

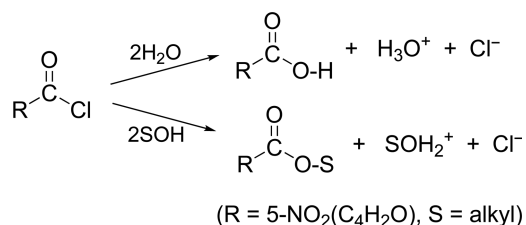
Substrate	n^a	l^b	m^b	l/m	R^c
2-AdOCOC ^d	19	~ 0	0.47 ± 0.03	~ 0	0.970
<i>i</i> -PrOCOC ^e	20	0.28 ± 0.05	0.52 ± 0.03	0.54	0.979
9-Fluorenyl-OCOC ^f	30	0.95 ± 0.07	0.38 ± 0.04	2.5	0.941
$((CH_3)_2N)_2POCg$	27	1.14 ± 0.05	0.63 ± 0.03	1.8	0.982
$CH_3SO_2Cl^h$	43	1.20 ± 0.05	0.52 ± 0.03	2.3	0.969
$(CH_3)_2NSO_2Cl^i$	32	1.20 ± 0.04	0.72 ± 0.03	1.7	0.985
$C_6H_5PCl^j$	25	1.25 ± 0.09	0.46 ± 0.06	2.7	0.954
$(C_6H_5O)_2POCl^k$	29	1.31 ± 0.10	0.61 ± 0.04	2.1	0.960
$(CH_3O)_2PSCl^l$	28	1.16 ± 0.08	0.55 ± 0.03	2.1	0.966
Cl_3CCH_2OCOCm	34	1.34 ± 0.07	0.50 ± 0.04	2.7	0.957
Cl_3CCH_2OCOCm	30	1.28 ± 0.06	0.46 ± 0.03	2.8	0.973
CH_3OCOCl	19	1.59 ± 0.09	0.58 ± 0.05	2.7	0.977
C_6H_5OCOCn	21	1.68 ± 0.10	0.57 ± 0.06	3.0	0.973
C_2H_5OCOCo	28	1.56 ± 0.09	0.55 ± 0.03	2.8	0.967
<i>n</i> -OctOCOC ^p	19	1.67 ± 0.07	0.76 ± 0.03	2.2	0.988
5-NO ₂ (C ₄ H ₂ O)-2-COC ^q	27	1.20 ± 0.05	0.37 ± 0.02	3.2	0.955

^aNumber of solvents. ^bFrom equation (2) and with associated standard error. ^cMultiple correlation coefficient. ^dRef. 3. ^eRef. 13. ^fRef. 14. ^gRef. 15. ^hRef. 12. ⁱRef. 16. ^jRef. 2. ^kRef. 16. ^lRef. 17. ^m18. ⁿRef. 19. ^oRef. 20. ^pRef. 21. ^qThis work.

phenyl chloroformate,¹⁹ and ethyl chloroformate,²⁰ and these similarities suggest the existence of a bimolecular mechanism (S_N2) or an addition-elimination pathway (A-E).

In addition, the $k_{80\%EtOH}/k_{100\%EtOH}$ ratio has also been suggested as a useful mechanistic criterion.^{12,16,20} The $k_{80\%EtOH}/k_{100\%EtOH}$ values of 95 to 320 are considered to represent the S_N1 reaction or ionization pathway.^{5a,d} In contrast, several $k_{80\%EtOH}/k_{100\%EtOH}$ values were reported for the proposed S_N2 reactions: the solvolyses of methyl chloroformate (4.0),¹⁷ ethyl chloroformate (3.2),²⁰ benzyl chloroformate (3.4),⁹ and *p*-methylbenzoyl chloride (5.3).¹² These values ($k_{80\%EtOH}/k_{100\%EtOH} = 3.2$ –5.3) had less sensitivity due to the solvent ionizing power. The $k_{80\%EtOH}/k_{100\%EtOH}$ value of 3.6 obtained for the solvolysis of **1** is similar to those obtained from the four substrates that are believed to proceed through the S_N2 mechanism.

The product formation through reactions with water produces two equivalents of strong acid and the reaction with an alcohol produces only one equivalent of strong acid. The situation is summarized in Scheme 2. If a water-alcohol solvent is used, the reaction, as presented in Scheme 2, is simplified in that the second solvent molecule, which is used to extract the proton from the molecule serving as the nucleophile, could be either water or alcohol. Furthermore, the amounts of each of the two protonated solvent species shown are determined *via* a rapid equilibration within the mixed solvent.



Scheme 2

The partitioning ratio ([ester]/[acid]) is used in conjunction with the molar composition ratio for the solvent involved ([H₂O]/[SOH]) in order to calculate the selectivity value (*S*), defined as in Eq. (3).

$$S = \frac{[\text{Ester in product}]/[\text{Acid in product}]}{\times ([\text{Water in solvent}]/[\text{Alcohol in solvent}])} \quad (3)$$

The values for the percentages of reactions proceeding with ester formation (x%) for solvolyses of **1**, at 25.0 °C, in mixtures of water with ethanol and methanol are reported in Table 4. The product ratios (x/100–x) were then used in Eq. (3) to provide the *S* values, which are also presented in Table 4.

The product selectivities (*S*, Table 4) reveal that for aqueous ethanol and methanol mixtures the selectivity increases with increases in the water content; thus, the reactivity-selectivity principle (RSP)²² is not followed in ethanol and methanol mixtures.

The greater value of *S* in the more aqueous media for **1** is a

Table 4. Selectivities (*S*) for the solvolyses of 5-nitro-2-furoyl chloride (**1**) in alcohol/water mixtures (after one half-life at 25.0 °C)^a

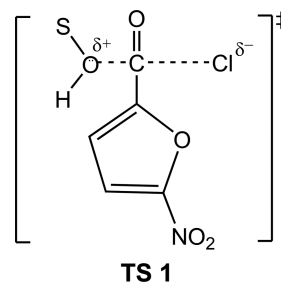
Alcohol ^b %(v/v)	[Ester]/[Acid]	<i>S</i>	[Ester]/[Acid]	<i>S</i>
	EtOH-H ₂ O		MeOH-H ₂ O	
90	3.33	1.2	8.32	2.1
80	2.37	1.9	6.34	3.6
70	1.79	2.5	5.04	4.9
60	1.45	3.1	4.17	6.3
50	1.15	3.7	3.27	7.4
40	0.843	4.1	2.35	7.9
30	0.542	4.5	1.65	8.7
20	0.311	4.3	1.05	9.5
10	0.131	4.1	0.555	11

^aDetermined by duplicate HPLC analyses of two solutions of each solvent composition; average deviation < ± 2%. ^bVolume/volume basis at 25.0 °C. ^cInjected 10 μL of a 1% solution of 5-nitro-2-furoyl chloride in dry acetonitrile into 3 mL of solvent.

strong indication that the role of alcohol as a nucleophile is important while the effect of the ionizing power is insignificant in the product-determining step of the reaction of **1**. Similar selectivity changes have been shown to be typical for a general bimolecular reaction mechanism channel in aqueous alcohol media.^{23,c,d}

Conclusions

The application of the extended Grunwald-Winstein Eq. (2) to the solvolysis of **1** led to an *l* value of 1.20 and an *m* value of 0.37. These values were smaller than those reported for reactions that proceed through an addition-elimination mechanism (*l* = 1.56–1.68 and *m* = 0.55–0.76, Table 3). Therefore, it can be concluded that the solvolysis of **1** proceeds through an S_N2 mechanism (TS 1), in which the bond making is more progressed than the bond breaking on the bases of the magnitudes of *l* and *m*.⁵ This conclusion can be further supported by reasonable activation parameters (*i.e.*, relatively small ΔH^\ddagger and large negative ΔS^\ddagger) and the solvent kinetic isotope effect (2.65). The selectivity values (*S*) obtained in the binary solvents were also consistent with the proposed mechanism.



Experimental

The solvents were purified as previously described.^{14,18} The 5-nitro-2-furoyl chloride (**1**, Aldrich, 98%) was used as

received. The kinetic experiments were performed by allowing a conductivity cell containing 12.5 mL of solvent to equilibrate, with stirring, in a constant-temperature water bath. Then, a 12 μ L portion of a 1.0 mol dm⁻³ stock solution of **1** in acetonitrile was added. The monitoring of the conductivity increases with time and the rate constant calculations were conducted as previously reported.^{14,18} Multiple regression analyses were performed using commercially available packages.^{14,18}

The solvolysis products, (ester and acid), are determined via the HPLC analysis as reported previously,²³ and the product selectivities, (*S*), are calculated using Eq. (3). The *S* values were calculated from the observed peak area ratios of the ester and acid, and divided by the appropriate response factor. For the response calibrations, the area ratios from the solvolyses of **1** in pure alcohol and in 40% acetonitrile-water mixtures were used. The eluent was a 60% methanol-water mixture and the flow rate adjusted to 1 mL min⁻¹. The HPLC system was a Hewlett-Packard 1050 Series instrument, with 250 \times 4 mm Spherisorb ODS reversed columns.

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