

Conductimetric and Potentiometric Titration of Some Hydroxylated Cinnamic Acids with Tetrabutylammonium Hydroxide in Non-Aqueous Media*

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In this study, four hydroxycinnamic acids, namely 3,4-dihydroxycinnamic acid, 4-hydroxycinnamic acid, 4-hydroxy-3-methoxycinnamic acid and 4-hydroxy-3,5-dimethoxycinnamic acid, were titrated conductimetrically and potentiometrically using triethylamine and tetrabutylammonium hydroxide in acetonitrile, 2-propanol, and pyridine solvents under a nitrogen atmosphere at 25°C.

In conductimetric titration with tetrabutylammonium hydroxide all of the compounds exhibited conventional stoichiometric titration curves in 2-propanol . As is evident from the titration curves, all these compounds gave two well-defined end points. The first end point corresponds to exactly one equivalent and the second one to the two equivalents of the base. In conductimetric titration with tetrabutylammonium hydroxide, all of the acids (except caffeic acid) show two end points in pyridine solvent. These compounds were titrated conductimetrically in acetonitrile and gave only one end point.

Potentiometric titration curves of these phenolic acids with tetrabutylammonium hydroxide in pyridine solvent look very much like the titration curves of weak diprotic acids obtained in an aqueous media with a strong base. In addition, equilibrium is attained very rapidly after each addition of the titrant. However, a second end point cannot be easily observed in the case of 2-propanol.

None of the compounds cited above gave meaningful conductimetric and potentiometric titration curves upon titration with triethylamine, which is a weaker base than tetrabutylammonium hydroxide.

Introduction

Hydroxycinnamic acids are commonly found in foods such as fruits, vegetables and grains. The highest concentrations of these phenolics are typically found in the surface layers. Accordingly, it has been speculated that these compounds play some role in the natural fungal resistance¹ of these foods. These phenolic acids have also been associated with sour, bitter and astringent flavors found in vegetable proteins². A

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specific cinnamic acid, ferulic acid, has been identified as the odorless precursor to the highly malodorous p-vinyguaiacol (PVG)^{3,4}. Hydroxycinnamic acids have also been associated with accelerated browning^{5,6}. Because these acids can influence both the color and flavor of a variety of food products, many analytical procedures have been developed.

There are a number of publications on the titrations of carboxylic acids and phenolics in non-aqueous media⁷⁻²¹, but no reports dealing with the titration of cinnamic acids in non-aqueous media have appeared so far.

In this study, solutions of 3,4-dihydroxycinnamic acid, 4-hydroxycinnamic acid, 4-hydroxy-3-methoxycinnamic acid and 4-hydroxy-3,5-dimethoxycinnamic acid in pyridine, acetonitrile and 2-propanol solvents were titrated conductimetrically and potentiometrically with triethylamine and tetrabutylammonium hydroxide under a nitrogen atmosphere, at 25°C.

Experimental

Apparatus

An Orion Model 101 conductivity meter equipped with an Orion Cat. No. 99.01.01 conductivity cell was used.

Electrode potentials were measured using a Hanna HI 9321 Microprocessor pH meter. A glass-silver-silver chloride electrode system was used and the silver-silver chloride electrode was modified by replacing the saturated aqueous KCl solution with a saturated solution of KCl in methanol.

Chemicals

Analytical reagent grade chemicals were used unless indicated otherwise.

3,4-dihydroxycinnamic acid (caffeic acid), 4-hydroxycinnamic acid (p-coumaric acid), 4-hydroxy-3-methoxycinnamic acid (ferulic acid) and 4-hydroxy-3,5-dimethoxycinnamic acid (sinapinic acid) were purchased from Sigma (99% pure) and used without further purification.

Tetrabutylammonium hydroxide (TBAOH) was purchased from Merck as a 0.100 M solution in 2-propanol/methanol and was diluted with pure, dry 2-propanol to give an approximately 0.020 M solution. Triethylamine was purchased from Fluka (98% purity). Triethylamine solutions were prepared with about a 0.020 M concentration. These solutions were standardized against primary standard benzoic acid (with five runs). The reservoir for the titrant was fitted with a drying tube containing ascarite and magnesium perchlorate to prevent the absorption of carbon dioxide and moisture from the atmosphere.

The solutions were kept in a dark-colored ground glass stoppered flask in a refrigerator. The solutions, prepared and kept under these conditions, were found to be stable for at least 6 months.

Benzoic acid (sublimed) was purchased from Merck.

Pyridine was purchased from Merck and used after further purification²². Acetonitrile and 2-propanol were purchased from Merck (HPLC grade) and used as received.

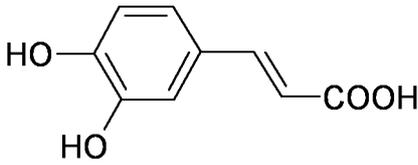
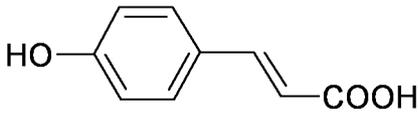
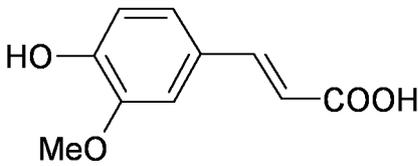
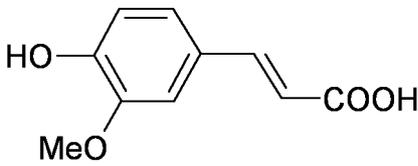
Throughout the work ca. $2.0 \cdot 10^{-3}$ M solutions of the phenolic compounds were titrated (five runs) with 0.0200 M solutions of titrants.

Results and Discussion

The following conclusions can be drawn from the conductimetric and potentiometric titration curves obtained for solutions of four hydroxy cinnamic acids with tetrabutylammonium hydroxide in pyridine ($\epsilon = 13.6$), 2-propanol ($\epsilon = 19.4$) and acetonitrile ($\epsilon = 36$).

The conductimetric titration of acids in non-aqueous solvents, using tetrabutylammonium hydroxide as titrant, yields conductance curves of various shape, depending on the acid as well as on the solvent employed. In the conductimetric titration with tetrabutylammonium hydroxide, all of the compounds exhibited conventional stoichiometric titration curves in 2-propanol. There are one carboxylic acid group and two phenolic groups in caffeic acid and there are one carboxylic acid group and one phenolic group in the other three cinnamic acids (Table 1). As is evident from the titration curve (Figure 1), all these compounds give well-defined two end points. The first end point corresponds to exactly one equivalent and the second one to the two equivalents of the base. Beyond the first end point, the conductivity of the solution increases further, but generally with a smaller slope. The slopes for the phenolate ions are definitely smaller than that for carboxylate ions. Caffeic acid shows similar titration curves, only its specific conductivity increases more sharply after the second end point. The slopes of the titration curves in the 2-propanol medium for phenolic acids before the first end point were practically identical (Figure 1). After the second end points, the slopes of the titration curves are also in the same manner as found in the titration before the first end point.

Table 1. Studied Hydroxycinnamic Acids

Private Nouns	Systematic Nouns	Formulas
Caffeic Acid (C ₉ H ₈ O ₄)	3,4-Dihydroxycinnamic acid	
p-Coumaric Acid (C ₉ H ₈ O ₃)	4-Hydroxycinnamic acid	
Ferrulic Acid (C ₁₀ H ₁₀ O ₄)	4-Hydroxy -3-methoxycinnamic acid	
Sinapinic Acid (C ₁₁ H ₁₂ O ₅)	3,5-Dimethoxy -4-hydroxycinnamic acid	

In the conductimetric titration with tetrabutylammonium hydroxide, all of the acids (except caffeic

acid) show two end points in pyridine solvent. Caffeic acid cannot be titrated in this medium because of the formation of precipitate. The slopes of the titration curves in the pyridine medium for the phenolic acids are twice as much as in the 2-propanol medium. Figure 2 clearly shows that cinnamic acids can be titrated in media with dielectric constants as low as 13.6.

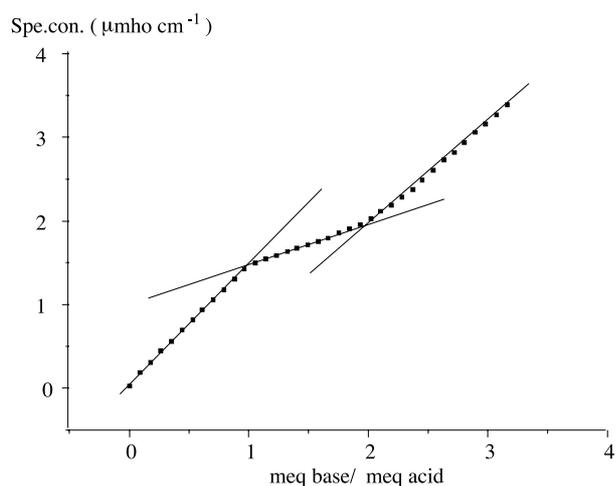


Figure 1. Conductimetric titration curve of 4-hydroxy – 3,5-dimethoxycinnamic acid in 2-propanol with tetrabutylammonium hydroxide.

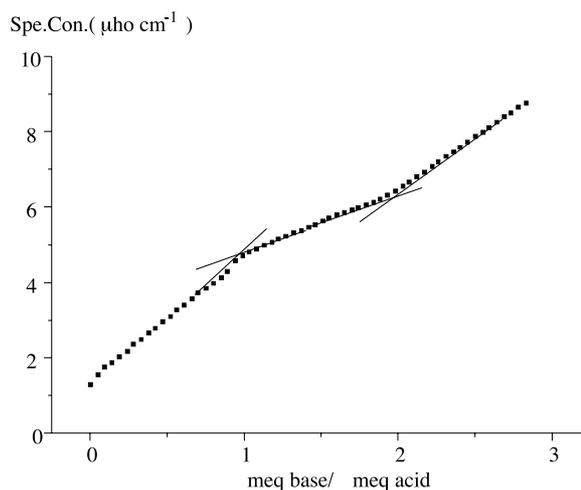


Figure 2. Conductimetric titration curve of 3,5-dimethoxycinnamic acid in pyridine with tetrabutylammonium hydroxide

Acetonitrile is a dipolar aprotic solvent. From a practical point of view, it is one of the best solvents for the titration of phenolic acids, because it dissolves these acids in sufficient amounts at room temperature. So this solvent was selected as the titration medium. Hydroxycinnamic acids have been titrated in acetonitrile using TBAOH conductimetrically. In these titrations, all acids show single and distinct stoichiometric end points. This means that these compounds cannot be determined stepwise when they are dissolved in acetonitrile solvent. The conductimetric titration curve of 4-hydroxycinnamic acid in acetonitrile with tetrabutylammonium hydroxide is shown in Figure 3. In the titration, until equivalence is reached, tetrabutylammonium and carboxylate ions are present in the medium. After the equivalence point, tetrabutylammonium and phenolate ions are present in the medium and the specific conductivity increases very slowly through the addition of hydroxyl ions into the medium. The mobilities of these ions in dipolar aprotic solvents are very limited and very close to each other. Hence, conductimetry is not an appropriate method for determining cinnamic acids with tetrabutylammonium hydroxide in dipolar aprotic solvents such as acetonitrile.

The potentiometric titration curves of these phenolic acids with tetrabutylammonium hydroxide in 2-propanol solvent look very much like the titration curves of weak diprotic acids obtained in the aqueous media with strong bases. In addition, equilibrium is attained very rapidly after each addition of the titrant. But, the second end point can not be easily observed in the case of 2-propanol. The potential jumps of these compounds at the first end points are over 150 mV. While at the second end points, the jumps are about 30-40 mV. Caffeic acid behaves differently from the others. In the potentiometric titration of caffeic acid, the second end point corresponding to two equivalent phenolic protons is observed in this solvent (Figure 4).

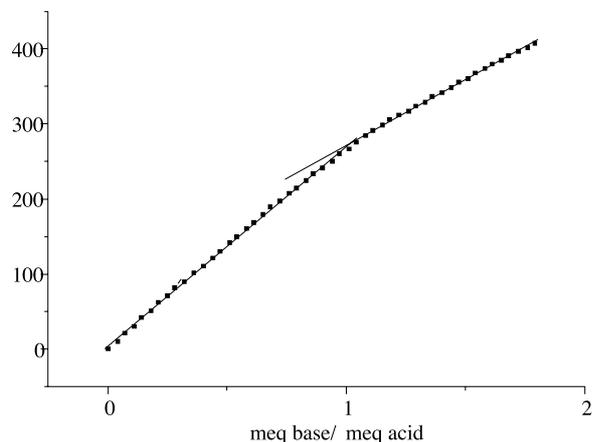
Spe.Con. ($\mu\text{mho cm}^{-1}$)

Figure 3. Conductimetric titration curve of 4-hydroxycinnamic acid in acetonitrile with tetrabutylammonium hydroxide

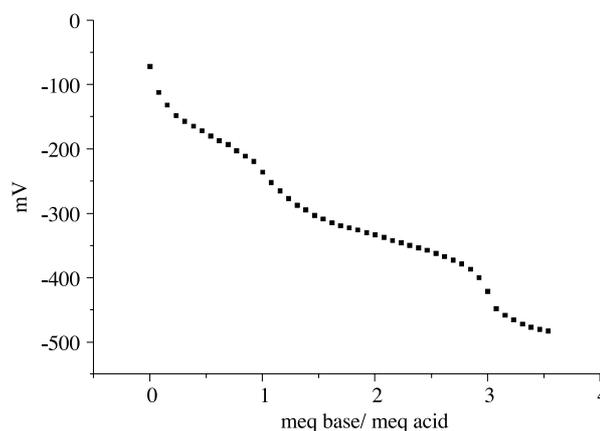


Figure 4. Potentiometric titration of caffeic acid in 2-propanol with tetrabutylammonium hydroxide

Pyridine was found to be a good basic solvent for use with tetrabutylammonium hydroxide as a titrant (Figure 5). Constant potentials were reached rapidly, remained steady and were reproducible. In the potentiometric titration with tetrabutylammonium hydroxide, all of the three (except caffeic acid) show two end points in pyridine. The potential jumps of these compounds at the first end points are over 50 mV. At the second end points, they are approximately 80-100 mV. None of the cinnamic acids (Table 1) exhibited conventional potentiometric titration curves when titrated with tetrabutylammonium hydroxide in acetonitrile under a nitrogen atmosphere at 25°C.

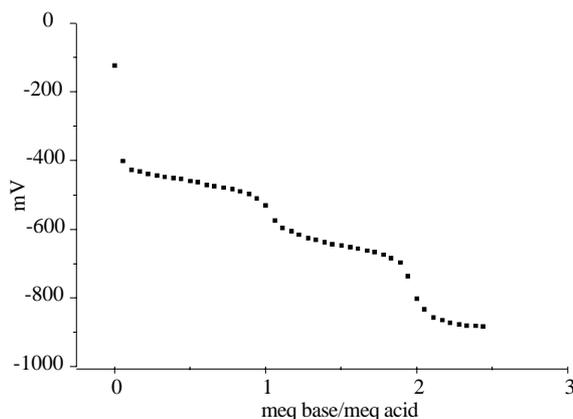


Figure 5. Potentiometric titration of p-coumaric acid in pyridine with tetrabutylammonium hydroxide

It is clear that 2-propanol is to be preferred for the conductimetric titration of cinnamic acids, especially when tetrabutylammonium hydroxide is used as a titrant. These compounds can be determined stepwise when they are dissolved in 2-propanol in concentrations as low as $2.0 \cdot 10^{-3}$ M. Therefore, only the results obtained in this medium were evaluated statistically. The titration of each compound was performed five times (Table 2). In conclusion, it can be said that four cinnamic acids can be analyzed in 2-propanol medium using conductimetry with rather small RSD and the recovery values obtained are sufficient.

These phenolics have been titrated with triethylamine under the same conditions in 2-propanol, pyridine and acetonitrile medium. None of the compounds gave a meaningful conductimetric and potentiometric titration curve on titration with triethylamine.

Table 2. Conductimetric analysis of cinnamic acids in 2-propanol medium with TBAOH (0.0200 M) (n=5)

Compounds	Results, 95% confidence	Taken M	Recovery %
3,4-dihydroxycinnamic acid	$1.72 \cdot 10^{-3} \pm 6.09 \cdot 10^{-5}$	$1.80 \cdot 10^{-3}$	95.6
4-hydroxycinnamic acid	$1.61 \cdot 10^{-3} \pm 2.86 \cdot 10^{-5}$	$1.64 \cdot 10^{-3}$	98.4
4-hydroxy-3-methoxycinnamic acid	$1.96 \cdot 10^{-3} \pm 2.86 \cdot 10^{-5}$	$1.94 \cdot 10^{-3}$	99.0
3,5-dimethoxy-4-hydroxycinnamic acid	$2.26 \cdot 10^{-3} \pm 2.86 \cdot 10^{-5}$	$2.24 \cdot 10^{-3}$	99.1

References

1. D.H. Hahn, J.M. Faubion, L.W. Rooney, **Cereal. Chem.** **60:4**, 255, (1983).
2. C.J. Huang, J.F. Zayas, **J. Food. Sci.** **56**, 1308 (1991).
3. M. Naim, B.J. Striem, J. Kanner, H. Peleg, **J. Food. Sci.** **53**, 500 (1988).
4. H. Peleg, B.J. Streim, M. Naim, V. Zehavi, **Proc. Int. Soc. Citric.** **4**, 1743 (1988).
5. H.E. Chen, **J. Chin. Agric. Chem. Soc.** **26:1**, 69 (1988).
6. J.L. Cilliers, V.L. Singleton, **J. Agric. Food Chem.** **37**, 890 (1989).
7. R.H. Cundiff, P.C. Markunas, **Anal. Chem.**, **28:5**, 792 (1956).
8. D.B. Bruss, G.A. Harlow, **Anal. Chem.**, **30:11**, 1836 (1958).
9. N.V. Meurs, A.M.F. Dahmen, **Anal. Chim. Acta.** **19**, 64 (1958).
10. N.V. Meurs, A.M.F. Dahmen, **Anal. Chim. Acta.** **21**, 10 (1959 a).
11. N.V. Meurs, A.M.F. Dahmen, **Anal. Chim. Acta.** **21**, 443 (1959 b).
12. C.A. Streuli, **Anal. Chem.**, **32:3**, 407-410 (1960).
13. R.R. Miron, D.M. Hercules, **Anal. Chem.**, **33:12**, 1770-1774 (1961).
14. L.W. Marple, J.S. Fritz, **Anal. Chem.**, **34:7**, 796 (1962).
15. T. Gündüz, E. Kılıç, G. Özkan, **Analyst**, **113**, 1017 (1988).
16. G. Franchini, A. Marchetti, C. Preti, L. Tassi, G. Tosi, **Anal. Chem.**, **61**, 177 (1989).
17. T. Gündüz, E. Kılıç, G. Özkan, M.F. Awaad, M. Taştekin, **Anal. Chim. Acta.** **234**, 339 (1990 a).
18. T. Gündüz, E. Kılıç, M. Taştekin, G. Özkan, **Can. J. Chem.** **68**, 431-434 (1990 b).
19. T. Gündüz, E. Kılıç, G. Özkan, M.F. Awaad, M. Taştekin, **Can. J. Chem.** **68**, 674 (1990 c).

20. A.G. Gonzalez, M.A. Herrador, A.G. Asuero, **Anal. Chim. Acta.** **281**,179 (1993).
21. M. Bos, W.E. Linden, **Anal. Chim. Acta.** **332**, 201-211 (1996).
22. D.D. Perrin, W.L.F. Armarego, D.R. Perrin, “**Purifications of Laboratory Chemicals**”. pp.79, 189 and 248 Pergamon Press, London 1966.