Talanta 76 (2008) 166–171

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Flow injection spectrofluorimetric determination of carvedilol mediated by micelles

Raúl A. Silva[a], Chien Chun Wang[d], Liliana P. Fernández[b,d], Adriana N. Masi[c,d,*]

[a] Área de Farmacotecnia, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, 5700 San Luis, Argentina
[b] Área de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, 5700 San Luis, Argentina
[c] Área de Bromatología-Ensayo y Valoración de Medicamentos, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, 5700 San Luis, Argentina
[d] CONICET, Chacabuco y Pedernera, 5700 San Luis, Argentina

ARTICLE INFO

Article history:
Received 28 December 2007
Received in revised form 15 February 2008
Accepted 18 February 2008
Available online 29 February 2008

Keywords:
Carvedilol determination
Flow injection spectrofluorimetry
Micellar enhancement
Pharmaceuticals

ABSTRACT

A novel flow injection (FI)-spectrofluorimetric methodology for the determination of carvedilol in micro-heterogeneous medium has been developed. In the sodium dodecyl sulfate (SDS) surfactant medium, an additional fluorescence enhancement was produced by the electrolyte NaCl. A total enhancement of 3.1-fold in the native fluorescent response was achieved respect to aqueous medium. Using an excitation and emission wavelength of 286 and 341 nm, respectively, a good linear relationship was obtained in the range of 9×10^{-8} to 1×10^{-6} mol L^{-1} with a detection limit of 3.63×10^{-9} mol L^{-1} ($S/N = 3$). This method was applied to determine carvedilol in commercial pharmaceutical formulations. Good concordance was found between the nominal (6.25, 12.5 and 25.0 mg) and experimental values. The new methodology developed showed high selectivity respect to the common excipients used in pharmaceuticals. The sampling rate was 30 samples h^{-1}. From the fluorescent properties, binding constant for carvedilol–SDS determined was 3.2×10^{2} L mol^{-1}.

1. Introduction

Carvedilol (1-(9H-carbazol-4-yloxy)-3-[2-(2-methoxyphenoxy)ethylamino]propan-2-ol, Fig. 1) is a nonselective β-adrenergic blocking agent with α_1-blocking activity, indicated for the treatment of hypertension and mild or moderate heart failure of ischemic or cardiomyopathic origin. Relative to other beta blockers, carvedilol has minimal inverse agonist activity; the use of carvedilol has been shown to provide additional morbidity and mortality benefits in congestive heart failure [1].

Since its use for pharmaceutical purposes is relatively recent, literature reveals that methods available for carvedilol determination are scarce. Different analytical techniques have been employed for the determination of carvedilol in biological fluids [2,3], specially those applied to the analysis of plasma [4–8] and urine [9] should be highlighted. Some chemists have developed methods for determining carvedilol by HPLC with high sensitivity, but the procedures for sample preparing were tedious and time consuming [2–8,10–12], with poor reproducibility and recovery. Also spectrophotometric methods have been reported [13,14], but in these cases sensitivities obtained were low. A differential pulse voltammetric procedure using a glassy carbon electrode was developed for the analysis of tablets [15]. However, this method presented various limitations, including time-consuming sample clean-up and laborious extraction steps, low sensitivity and long run times, being then less suitable for routine analysis.

Some luminescent methods have been proposed for the determination of carvedilol in pharmaceutical drugs and biological samples [16–18], using chemioluminometry and sinchronofluorescence. Table 1 resumes the main characteristics of the reported methodologies for carvedilol determination.

For routine laboratory quality control of final products, for research tasks and/or for rapid screening of biological samples, development of fast, simple, reliable, rugged and automatized analytical procedures are required. High quality chemical data collected at run-time are essential for the control of modern chemical manufacturing facilities.

It is widely known the ability of organized media to provide an appropriate microenvironment able to modify the catalytic and luminescence properties of reactants and products [19]; the effect of organized media over the carvedilol has not yet been broadly studied.

This paper reports a rapid spectrofluorimetric method for determining the content of carvedilol in pharmaceuticals. Effects of pH,

* Corresponding author at: Área de Bromatología-Ensayo y Valoración de Medicamentos, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, 5700 San Luis, Argentina. Tel.: +54 2652425385; fax: +54 2652430224.
E-mail address: amasi@unsl.edu.ar (A.N. Masi).

0039-9140/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2008.02.029

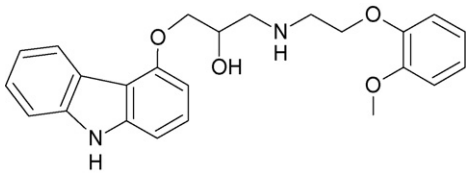

Fig. 1. Chemical structure of carvedilol.

presence of different surfactant agents and ionic strength on the relative fluorescent intensity and fluorescent spectrum of carvedilol were examined. The method has a wide linear range and low detection limit. It was successfully applied for determining carvedilol in tablets without interferences from pharmaceuticals excipients. In addition, sample preparation is easy, fast and without prior separation steps.

2. Experimental

2.1. Instruments

A Shimadzu RF-5301PC spectrofluorimeter (Shimadzu Corporation, Analytical Instrument Division, Kyoto Japan), equipped with a Xenon discharge lamp and 1 cm quartz cells was used for the fluorescence measurements. For flow measurements a LC flow cell unit (12 μL cell) was used.

A pH meter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA), model EA 940 with combined glass electrode was used for monitoring pH adjustment.

2.2. Reagents

Carvedilol was kindly provided by Gador S.A. (Buenos Aires, Argentina). Chemicals of analytical grade were used: sodium dodecyl sulfate (SDS), Triton® X-100 and hexadecyl trimethylammonium bromide (HTAB) were purchased from Tokyo Kasei Industries. Chuo-Ku, Tokyo, Japan. High-purity water was obtained from a Millipore (Milford, MA, USA) Milli-Q Plus System.

The pH values in optimization stage were adjusted by the addition of solutions of NaOH 0.01 mol L^{-1}, NaOH (c), HCl 0.01 mol L^{-1} or HCl (c) until the target pH value was reached.

2.2.1. Solutions

Carvedilol standard solution containing 1 mg mL^{-1} was prepared dissolving the reagent in ethanol. During the experiments, this solution was found to be stable for several weeks when was kept in dark at 5 °C. Standard working solution of 1 μg mL^{-1} was prepared daily by dilution of stock standard solution with ultra pure water and stored in a dark bottle at 5 °C. In these conditions, carvedilol was stable for almost 4 weeks.

A 0.1 mol L^{-1} SDS, was prepared with an adequate weight of SDS and dissolving in ultra pure water. A 2 mol L^{-1} NaCl solution was prepared dissolving an adequate weight of the salt in ultra pure water. A 0.1 mol L^{-1} HCl solution was prepared mixing an adequate volume of concentrated acid with ultra pure water.

2.2.2. Sample solutions

Ten tablets containing 6.25 mg carvedilol each were weighed and finely powdered. A portion of the powder, equivalent to 6.25 mg of carvedilol, was weighed and treated with 10 mL of ethanol, shaken for 15 min, centrifuged during 10 min. The supernatant was separated and the residue was treated with another portion of 10 mL ethanol. The two portions were then joined and filtrated through Millipore membranes of 0.45 μm pore size. Two hundred milliliters of the filtered solution were transferred to a 100 mL volumetric flask and taken to volume with ultra pure water. The same procedure was applied with tablets containing 12.5 and 25 mg carvedilol. The final concentrations were 0.625, 1.25 and 2.5 μg mL^{-1}, respectively.

2.3. FIA configuration

In Fig. 2, a schematic representation of the FIA system used for the on line spectrofluorimetric determination of carvedilol is shown. The manifold used was built using a four-channel Gilson Minipuls-3 peristaltic pumps fitted with rate selectors; a Rheodyne Model 5041 injection valve, acting as selecting valve, and PVC tubing of 0.8 mm i.d.

Under the conditions described in Table 1, a stream of SDS/NaCl (position 3 in Fig. 2), was mixed in reaction coil (R) with a stream of water (position 4) as reagent blank for producing the baseline. After changing the valve position a stream of carvedilol/HCl (position 1) was mixed in reaction coil (R) with a stream of SDS/NaCl and impelled then through the spectrofluorimeter for measurement.

2.4. General procedure

A stream of sample or standards solutions containing carvedilol at pH 2 was combined with the carrier stream. The carrier stream consisted of a solution prepared with SDS (0.04 mol L^{-1}) and sodium chloride (0.4 mol L^{-1}) to obtain the optimal conditions for carvedilol fluorescent emission. The drug contained in the sample/standards and the carrier stream interacted in reactor (R) and flowed to the fluorescence detector. The valve was switched in such manner that allowed, in one position, to pass the carrier stream and ultra pure water, and in the second position allowed to pass the sample/standards and carrier solution. In this way the fiagram had always the same background produced by the same concentration of carrier solution.

2.5. Method validation procedure

In order to demonstrate the validity of this method 10 tablets containing 6.25 mg carvedilol each, were weighed and finely powder. The powder was divided into 10 equal portions. The proposed method was applied to six portions and the average quantity of carvedilol obtained was taken as a base value. Then, increasing quantities of carvedilol were added to the other five aliquots of sample and carvedilol was determined applying the same method.

3. Results and discussion

3.1. Spectral characteristics of carvedilol

3.1.1. Fluorescence characteristics of carvedilol in aqueous media

Fig. 3 shows the excitation and emission spectra obtained for a 1 μg mL^{-1} aqueous solution of carvedilol at pH 2. As can be seen, the drug showed a maximum emission at 341 nm when was excited at 286 nm. These wavelengths were selected for the following assays to measure the fluorescence intensity.

Carvedilol showed a strong native fluorescence signal at acid or extremely alkaline pHs, but showed a decrease in fluorescent emission at intermediate pHs. Fig. 4 resumes the effect of pH value in the fluorescence signal. Analysis of spectrofluorimetric data for carvedilol in water shows that the intensity increase at pH 2–3 decrease between 4 and 8, and increase again at pH 10–11. The working pH selected was 2 due to the higher intensity obtained and the additional advantage of preparing systems without adding buffer solutions. Thus, an HCl 0.01 mol L^{-1} medium was chosen for future studies.

Table 1
Comparative table for carvedilol determination

Instrumental methodology	Experimental detail	LOD	LOQ	LOL	Samples	Ref.
HPLC-fluorimetry	SPE. Column: Spherisorb C_6. Mobile phase: 65% ACN, 35% potassium acetate buffer (0.25 M, pH 4)	WD	0.40 ng mL^{-1}	242 ng mL^{-1}	Human plasma	[2]
HPLC-fluorimetry	Ether extraction	WD	WD	WD	Serum	[3]
HPLC-fluorimetry	Monolithic column. Isocratic mobile phase: 0.01 M disodium hydrogen phosphate buffer–ACN (40:60, v/v) pH 3.5	WD	1 ng mL^{-1}	80 ng mL^{-1}	Human plasma	[4]
HILIC–MS/MS	Extraction methyl *tert*-butyl ether, basic pH. Mobile phase: ACN–ammonium form-ate (50 mM, pH 4.5) (90:10, v/v)	WD	0.1 ng mL^{-1}	200 ng mL^{-1}	Human plasma	[5]
HPLC	Brownlee C8 column, isocratic elution, on-line deproteination	WD	0.8 ng mL^{-1}	WD	Human plasma	[6]
HPLC-fluorimetry	Protein precipitation with methanol. Column: Develosil 3 μm ODS 100 × 4.6 mm i.d. Mobile phase: ACN–30 mM potassium dihydrogen-phosphate buffer, pH 2	1.3 ng mL^{-1}	WD	WD	Human plasma	[7]
HPLC-ECD	Mobile phase: 53% (v/v) methanol, 47% (v/v) phosphate buffer (pH 3.8)	WD	0.10 ng mL^{-1}	WD	Human plasma	[8]
LC-MS	ESI. Liquid–liquid extraction with ethyl acetate	–	WD	WD	Human urine	[9]
HPLC-fluorimetry	SPE: reversed-phase octadecyl silica column	3.6 ng mL^{-1}	WD	1000 ng mL^{-1}.	Rat plasma	[10]
HPLC	Extracted with acetone. Internal Standard: naftopidil. pH 3.5. Samples clean-up: SPE columns	WD	0.01 ng mg^{-1}	0.35 ng mg^{-1} (wet weight)	Human Cardiac Tissue	[11]
HPLC–MS/MS	Internal standard (IS): metoprolol. LLE: die-thylether	WD	0.1 ng mL^{-1}	200 ng mL^{-1}	Human plasma	[12]
Spectrophotometry	Apparent molar absorptivity 15.4×10^3 L mol^{-1} cm^{-1}. λ = 285 nm. Solvent: methanol	WD	4 μg mL^{-1}	36 μg mL^{-1}	Bulk and formulations	[13]
Spectrophotometry	λ = 244 nm. Solvent: ethanol	WD	2 μg mL^{-1}	7 μg mL^{-1}	Tablets and compounded capsules	[14]
Nonaqueous volumetry	Medium: 0.01 M perchloric acid. Indicator: 1% violet crystal					
Differential pulse voltammetry	pH: 2.0–11.0 (glassy carbon electrode)	0.10 μg mL^{-1}	0.25 μg mL^{-1}	10.00 μg mL^{-1}	Tablets dosage form	[15]
Fluorimetry	λ_{em} = 356 nm, λ_{ex} = 254 nm	0.19 ng mL^{-1}	0.50 ng mL^{-1}	270 ng mL^{-1}	Tablets	[16]
Synchronous fluorimetry	λ_{em} = 356 nm, λ_{ex} = 254 nm, Δλ = 80 nm. Sensing reagent: isopropanol	1 ng mL^{-1}	0.005 μg mL^{-1}	0.1 μg mL^{-1}	Medicine dosage	[17]
Chemiluminometry	Reaction: oxidation of luminol by hypochlorite. Multi-pumping flow system multiple solenoid actuated μ-pumps	8.7×10^{-9} mol L^{-1}	1.2×10^{-7} mol L^{-1}	3.0×10^{-6} mol L^{-1}	Pharmaceuticals	[18]
FI-fluorimetry	λ_{em} = 341 nm, λ_{ex} = 286 nm. pH 2.0. Ionic strength: 0.1 mol L^{-1} SDS: 1.10^{-2} mol L^{-1}. Flow rate: 35 rpm. $K_B = 3.2 \times 10^2$ L mol^{-1}. Sampling rate: 30 samples h^{-1}	3.63×10^{-9} mol L^{-1}	9×10^{-8} mol L^{-1}	1×10^{-6} mol L^{-1}	Pharmaceuticals	This method

HILIC–MS/MS: hydrophilic interaction liquid chromatography with tandem mass spectrometry. WD: without datum. ACN: acetonitrile. ESI: electrospray ionization. SPE: solid phase extraction. LLE: liquid–liquid extraction.

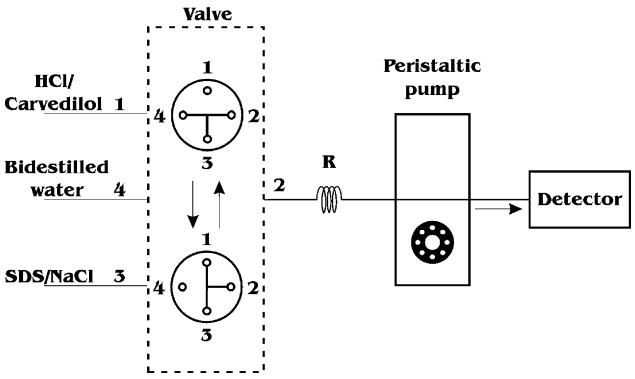

Fig. 2. FIA configuration.

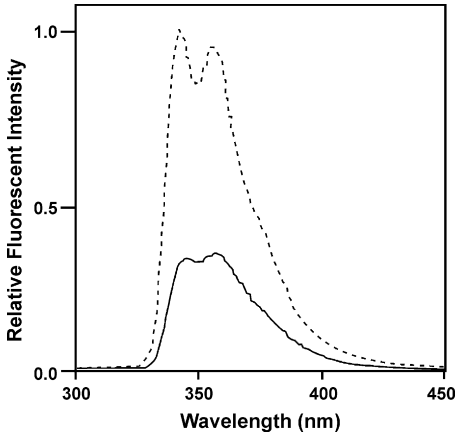

Fig. 3. Emission spectrum of carvedilol at pH 2 (λ_{exc} = 286 nm). (—) Carvedilol 0.1 μg mL^{-1}; (- - -) carvedilol 0.1 μg mL^{-1}, NaCl 0.1 mol L^{-1} and SDS 0.01 mol L^{-1}.

3.1.2. Fluorescence characteristics of carvedilol in micellar media

3.1.2.1. Nature and concentration of surfactant agent. In order to perform the luminescent emission, the fluorescence properties of carvedilol in various surfactant media were studied: anionic surfactant (SDS, 0–9 × 10^{-3} mol L^{-1}), cationic surfactant (CTAB, 0–5 × 10^{-2} mol L^{-1}) and non-ionic surfactant (TX-100, 0–1 × 10^{-3} mol L^{-1}). Experimental data showed that the enhancement factor for carvedilol–SDS system (2.5-fold respect to carvedilol fluorescence in water medium) was higher than carvedilol–CTAB; for TX-100, an important spectrum interference was observed; thus, the anionic surfactant SDS was chosen for further work.

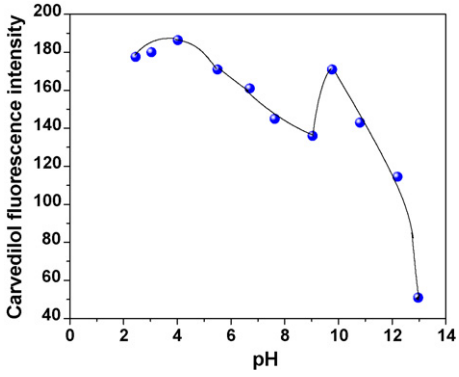

Fig. 4. Effect of pH on cavedilol fluorescence intensity.

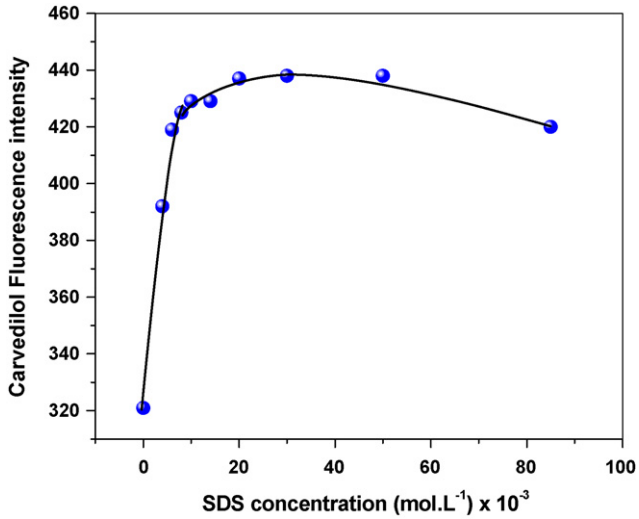

Fig. 5. Effect of surfactant concentration on carvedilol fluorescence intensity.

The fluorescence spectrum of carvedilol in ultra pure water and aqueous SDS revealed that the fluorescence intensity increased, above the cmc, with SDS concentration, and that this increase was more evident at 10 mmol L^{-1} (Fig. 5). The fluorescence increase in micellar media was attributed to a stabilization/protection of the excited state singlet, that hinders decay by quenching and other non-radiative deactivation processes [20,21].

3.1.2.2. Binding constant for the SDS–carvedilol system. The binding constant value (K_B) was obtained from fluorescence data of carvedilol as a function of SDS surfactant concentration using Eq. (1) [22,23]:

$$\frac{I_\alpha - I_0}{I_S - I_0} = 1 + \frac{1}{K_B[M]} \quad (1)$$

where I_α is the emission intensity at infinite micellar concentration; I_0 the emission intensity without micelles; I_S the emission intensity at intermedia micellar concentration; K_B the binding constant; [M] the micellar concentration in mol L^{-1}.

The concentration of the micelles [M] can be determined using the relation below [24]:

$$[M] = \frac{[\text{surfactant}] - \text{CMC}}{N_{av}} \quad (2)$$

where [surfactant] = total surfactant concentration; N_{av} = aggregation number. N_{av} is ca. 62 [25].

According to this model, the solubilization process is considered as an addition reaction of solute molecules (S) in the micellar aggregations (M), giving MS_i adducts (a micelle containing i molecules of solute). From the slope of the plot of $(I_\alpha - I_0)/(I_S - I_0)$ versus inverse micellar concentration, the binding constant K_B was determined, giving a value of 3.2 × 10^2 L mol^{-1}.

3.1.3. Effects of electrolytes on the fluorescence intensity of carvedilol

In aqueous surfactant media, the role of NaCl is to push the organic compounds inside the micelle. In this work it was found that in the presence of 0.1 mol L^{-1} NaCl, the fluorescence signal of carvedilol in surfactant media increased almost 3.1-fold respect to the same in absence of salt. The effect produced by the addition of inert salts to the system is shown in Fig. 6. The working concentration chosen was 0.1 mol L^{-1}.

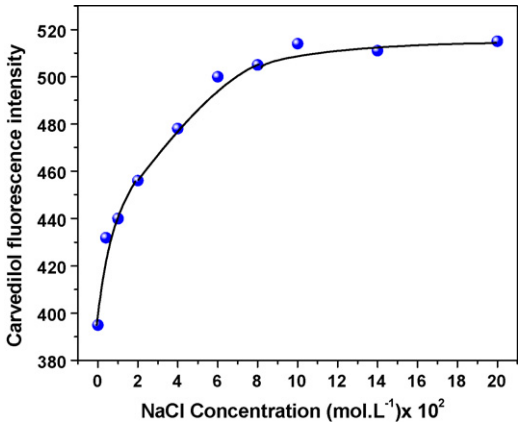

Fig. 6. Effect of ionic strength on carvedilol fluorescence intensity. SDS concentration 0.01 mol L^{-1}.

3.2. Effect of flow rate

The effect of flow rate of FIA system on fluorescent signal was studied. Although the fluorescent signal was highest for 45 rpm, from 40 rpm a great turbulence was observed due to the introduction of bubbles into the flow system, the flow selected was 35 rpm. Under these optimal conditions the sampling rate was 30 samples h^{-1}.

3.3. Validation method

3.3.1. Linearity and sensitivity

Calibration curve was constructed covering a concentration range from 9×10^{-8} to 2×10^{-6} mol L^{-1}. Fig. 7 shows the fiagram obtained with different standards of carvedilol. The triplicate signals demonstrated good reproducibility. Equation for calibration graph was obtained by least-square linear regression analysis of the areas of analyte standard fluorescent signals versus analyte concentrations: $F = 2030x + 100.7C$. Where F is the relative fluorescence intensity and C the concentration of carvedilol. The method was linear up to 1×10^{-6} mol L^{-1} of carvedilol. Correlation coefficient was 0.9998. The LOD was defined as the compound concentration that produced a signal-to-noise ratio greater than three, while the limit of quantitation of the assay was evaluated as the concentration equal to 10 times the value of the signal to-noise ratio. LOD and LOQ values for this method based upon these criteria are shown in Table 1.

3.3.2. Precision and accuracy

The precision of the method based on repeatability was performed, by replicating injections ($n = 6$) of four standard solutions prepared by the standard addition method covering different concentration levels. Accuracy was determined and expressed by percentual relative error which was always under 1.5%.

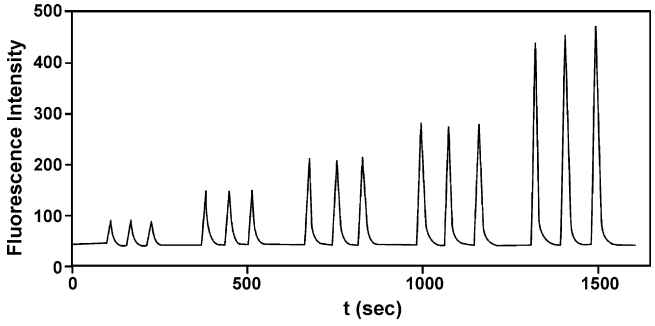

Fig. 7. Carvedilol fiagram for calibration curve.

Table 2
Validation of the method for the determination of carvedilol in commercial pharmaceutical formulae

Sample ($n = 6$)	Base value (mg)	Added (mg)	Found (mg)	E%
A	6.29	1	7.40	1.50
B	6.29	2	8.22	0.84
C	6.29	3	9.18	1.10
D	6.29	4	10.31	0.19

Table 3
Analysis of carvedilol tablets

Sample[a]	Nominal quantity (mg)	Carvedilol found (mg)	E%
1	6.25	6.29	0.64
2	12.50	12.40	0.80
3	25.00	25.30	1.20

[a] Rotiaz from Richmond Lab. ($n = 6$).

The optimum working conditions for the on line fluorimetric determination of carvedilol are resumed in Table 1. The validation method results are shown in Table 2.

3.3.3. Analysis of pharmaceuticals

The developed method was applied to the determination of carvedilol in commercial pharmaceutical samples containing 6.25, 12.5 and 25 mg of carvedilol, respectively. The results are shown in Table 3.

4. Conclusions

The FIA spectrofluorimetric method proposed for the determination of carvedilol in pharmaceuticals samples has the advantages of simplicity, speed, accuracy and the use of inexpensive equipment and reagents. The fluorescent detection gives a special selectivity without interference from the common excipients found in commercial pharmaceutical forms. The use of SDS micellar system provides a simple means to enhance the fluorescence of carvedilol. This phenomenon can be explained by the protection of lowest excited state of fluorophore in micellar microenvironment from non-radiative processes that normally readily occur in bulk aqueous solutions. The association constant for carvedilol–SDS system was determined using the adduct model. The addition of SDS/NaCl gives a 3.1-fold increase in sensitivity and improves the limit of detection without further sample manipulation. Additionally, it can be remarked the wide range linearity obtained in the calibration curve, with high sensitivity and high sampling rate results adequate for the quality control and routine analysis of tablets.

Acknowledgments

The authors wish to thank CONICET (Consejo Nacional de Investigaciones Científicas y Tecnológicas), FONCYT (Fondo Nacional de Ciencia y Tecnología), National University of San Luis (Project 22/Q528) for the financial support.

References

[1] M. Packer, M.B. Fowler, E.B. Roecker, Circulation 106 (2002) 2194.
[2] F. Behn, S. Läer, T.S. Mir, H. Scholz, Chromatographia 53 (2001) 641.
[3] F. Varin, L.X. Cubeddu, J.R. Powell, J. Pharm. Sci. 75 (1986) 1195.
[4] A. Zarghi, S.M. Foroutan, A. Shafaati, A. Khoddam, J. Pharm. Biomed. Anal. 44 (2007) 250.
[5] D.W. Jeong, Y.H. Kim, H.Y. Ji, Y.S. Youn, K.C. Lee, H.S. Lee, J. Pharm. Biomed. Anal. 44 (2007) 547.

[6] G. Lamprecht, K. Stoschitzky, Chromatographia 59 (2004) 551.
[7] P. Ptacek, J. Macek, L. Klima, J. Chromatogr. B 789 (2003) 405.
[8] M. Machida, M. Watanabe, S. Takechi, S. Kakinoki, A. Nomura, J. Chromatogr. B. 798 (2003) 187.
[9] K. Deventer, P. Van Eenoo, F.T. Delbeke, Rapid Comm. Mass Spectrom. 19 (2005) 90.
[10] N. Hokama, N. Hobara, H. Kameya, S. Ohshiro, M. Sakanashi, J. Chromatogr. B: Biomed. Sci. Appl. 732 (1999) 233.
[11] F. Behn, S. Läer, H. Scholz, J. Chromatogr. Sci. 30 (2001) 121.
[12] N.C do C. Borges, G. Duarte Mendes, D. de Oliveira Silva, V. Marcondes Rezende, R. Barrientos-Astigarraga, G. De Nucci, J. Chromatogr. B 822 (2005) 253.
[13] P.S. Jain, G.S. Talele, S.G. Talele, S.J. Surana, Indian J. Pharm. Sci. 67 (2005) 358.
[14] C. Viana Silva Ieggli, S. Gonçalves Cardoso, L. Potrich Belle, J. AOAC Int. 88 (2005) 1299.
[15] A. Radi, T. Elmogy, Il Farmaco 60 (2005) 43.
[16] L.X. Xu, N. Hui, L.Y. Ma, H.Y. Wang, Spectrochim. Acta A: Mol. Biomol. Spectrosc. 61 (2005) 855.
[17] Y. Xiao, H.Y. Wang, J. Han, Spectrochim. Acta A: Mol. Biomol. Spectrosc. 61 (2005) 567.
[18] C.K. Pires, K.L. Marques, J.L.M. Santos, R.A.S. Lapa, J.L.F.C. Lima, E.A.G. Zagatto, Talanta 68 (2005) 239.
[19] W.L. Hinze, K.L. In:, Mittal (Eds.), Use of Surfactant and Micellar Systems in Analytical Chemistry in Solution Chemistry Surfactants, vol. 1, Plenum Press, New York, 1979, p. 79.
[20] C.D. Tran, T.A. Van Fleet, Anal. Chem. 60 (1988) 2478.
[21] H. Singh, W.L. Hinze, Anal. Lett. 15 (1982) 221.
[22] S. De, A. Girigoswami, S. Mandal, Spectrochim. Acta Part A 58 (2002) 2547.
[23] M. Almgren, F. Greiser, J.K. Thomas, J. Am. Chem. Soc. 101 (1979) 279.
[24] F.H. Quina, V.G. Toscano, J. Phys. Chem. 81 (1977) 1750.
[25] W. Hinze, In: W.L. Hinze, D.W. Armstrong (Eds.), Ordered Media in Chemical Separations, ACS Symposium Series 342, American Chemical Society, Washington, DC, 1987, p. 4.