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Validation of a LC-fluorescence method for determination of free captopril in human plasma, using a pre-column derivatization reaction with monobromobimane

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Abstract

Both derivatization of free captopril in human plasma samples using monobromobimane as fluorescent label and the corresponding HPLC-fluorescence detection (FLD) method were validated. Calibration curve for the fluorescent captopril derivative in plasma samples is linear in the ppb–ppm range with a detection limit of 4 ppb and an identification limit of 10 ppb ($P\%$: 90; $v \geq 5$). These methods were successfully applied on bioequivalence studies carried out on some marketed pharmaceutical formulations. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Free captopril; Human plasma; Pre-column derivatization; Monobromobimane; HPLC-FLD

1. Introduction

Captopril, (2*S*)-1-1[(2*S*)-3-mercapto-2-methyl-propanoyl] pyrolidine-2 carboxylic acid, is an inhibitor of angiotensin—converting enzyme, acting directly on the adrenal gland to stimulate the release of aldosterone [1]. The enthalpy of captopril–angiotensin I converting enzyme binding was recently evaluated [2].

First approaches for captopril determination in biological matrix were made by GC [3–5] and GC–MS [6–13].

HPLC is far from a method of choice for captopril determination in blood, plasma and urine. However, the low concentration levels and the relative sensitivity of captopril to oxidation determine the liquid chromatograph (LC) methods to follow three different directions,

(i) the use of electrochemical detection, as a more sensitive alternative detection compared with UV, without any derivatization of the analyte of interest [11–17];
(ii) the UV or the fluorescent detection of a derivatization product of captopril, while labeling is made prior or after the chromatographic separation;
(iii) the use of pre-concentration techniques such as liquid–liquid extraction [18] or multicolumn switching set-up [19].

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With concern to the derivatization reagents frequently used for captopril labeling, the following list can be considered: (a) *N*-(4-benzoylphenyl) aleimide [20,34], (b) 1-benzyl-2-chloropyridinium bromide [21–23], (c) 2,4′-dibromoacetophenone [24–29], (d) *N*-(4-dimethylamino-3,5-dinitrophenyl)maleimide [29], (e) *N*-(4-dimethylaminophenyl) maleimide [30], (f) *N*-(1-pyrenyl)maleimide [31], (g) 7-fluorobenzofurozan-4-sulphonic acid [32], (h) *N*-(7-dimethylamino-4-methyl(coumarin 3-yl)maleimide [33], (i) 5,5′-dithio-(bis-2-nitrobenzoic acid) [35].

Some other separation techniques such as electrophoresis [36], capillary zone electrophoresis [37], capillary izotachophoresis [38] and LC-chemiluminiscence based detection [39] were also used.

A special attention should be paid to the publication of Kok and all [40], which is describing a comparative study between free captopril determination in plasma samples as fluorescent monobromobimane derivative and the total captopril content using OPA as post column derivatization reagent. The ingenious post column derivatization method is using captopril as ternary reagent for giving the fluorescent glycine-*o*-phtalaldehyde derivative.

We have considered that a very attentive approach to the monobromobimane derivatization method proposed by Kok, including optimization and validation procedures for both labeling and HPLC-fluorescence detection (FLD) method could be useful for large-scale bioequivalence studies.

It is the major aim of the present work, which is responding to the high actual interest over validation of bioanalytical chromatographic methods having as target bioavailability and bioequivalence studies [41].

2. Experimental

A Hewlett–Packard 1100 series LC was used during the experimental session, each module (G1312 A-binary pump, R-7725i-manual injector, G1316 A-Peltier column thermostat and G1315 A-diode array detector) have been subjected to operational qualification accordingly to the built-in procedures. The fluorescence detector Hewlett–Packard 1046 series was also qualified before experiments.

The chromatographic column, Inertsil 5 ODS-2 (Chrompack, Varian, Cat. No. 4363 (serial no. 358i77, Batch 28 406), 150 mm L × 4,6 mm i.d. × 5 μm d.p. was tested initially with a mixture of benzene, toluene, xylene, using isocratic elution with H_2O/acetonitrile (ACN) = 30/70. The constructed Van Deemter curve made for xylene revealed a maximal efficiency of 14 232 theoretical plates for an averaged mobile phase flow speed of 5.45 cm/s. (corresponding to a flow rate of 0.8 ml/min) and a reduced plate height of 2.27. It is to mention that after the method validation procedures and after ending of a whole bioequivalence study for captopril (consisting in more than 1200 samples), the same column behave with a third of its initial efficiency (∼ 5000 theoretical plates) and a reduced plate height of 6.2.

The column was fitted with HPLC Chromguard SS Reversed Phase 10 mm (L) × 3 mm i.d. guard column.

The column was operated at 60 °C.

The mobile phase consists in a mixture of 0.1% aqueous trifluoracetic acid (TFA)/ACN = 85/15 used in the isocratic elution mode at a flow rate of 1.5 ml/min.

In the early stages of the method development, serial diode array detection was achieved, using an analytical wavelength of 381 nm and a spectral width of 4 nm (ref. wavelength 560 ± 20 nm). FLD uses a 400 nm excitation wavelength and a 480 nm emission wavelength. The Xe lamp was set to a nominal power of 5 W and a frequency of 220 Hz; the cut off filter was set to 280 nm, the excitation slit was 2 × 2 mm and the emission slit 4 × 4 mm. The response time was 1 s and the PMT gain interval was set between 16 and 18. For real plasma samples obtained during the bioequivalence studies on pharmaceutical products containing captopril, a 250 μl injection loop was used.

Water and all the other organic solvents used during experiments were HPLC grade. Special attention was paid for ACN, which was HPLC gradient grade. Solvents were obtained from Merck and Fluka. Sodium phosphates, boric acid,

phosphoric acid, sodium hydroxide were p.a. grade from Merck. Monobromobimane ($C_{10}H_{11}N_2O_2Br$) was purchased from Sigma (Cat. No. B4380).

3. Results and discussion

Fluorescent labeling of captopril using monobromobimane (m-BBr) is made according to the following reaction (Fig. 1).

Several considerations have to be done from the very beginning: (a) the derivatization reagent (m-BBr) has low fluorescent activity (as long as the bromine atom still exists in the chemical structure), (b) m-BBr is acting selectively on thiol groups. Reactions with hydroxyl groups are not achieved. This means that: (i) captopril in its oxidized form—captopril disulfide—is not reacting with m-BBr, (ii) plasma matrix is relatively rich in thiolic compounds, so the expected interfering pattern can be substantial, (c) generally, decomposition products of m-BBr and especially those, which are resulting after bromine elimination, are characterized by a highly fluorescent yield. On the other hand, if the derivatization is carried out immediately after the sample is collected from volunteers, it prevents the competition between time-consuming oxidation mechanism and fast derivatization reaction. The derivative once formed is stable towards the oxidation reaction, due to the fact that the –SH group is no more available.

The validation of the derivatization process was made via de following consecutive steps.

3.1. Appropriate solvent used for m-BBr solutions

Solutions of m-BBr (4 mg/m) in water, water/ACN = 1/1 and ACN were kept 24 h at room temperature in amber vials. Solutions were injected on the analytical column, and were subjected to the chromatographic analysis according to the following conditions: column temperature 60 °C, mobile phase MeOH/ACN/aqueous 0.1% TFA = 35/35/30, flow rate 1 ml/min, analytical wavelength $\lambda = 381 \pm 2$ nm (ref. wavelength $\lambda = 560 \pm 20$ nm).

The sum of the areas of the secondary peaks appearing in the chromatograms was expressed as percentage from the m-BBr peak obtained in the chromatogram of a freshly prepared solution of m-BBr, having the same concentration as the initial solutions.

There are no major differentiation between the stability of m-BBr in the three solvating solutions (1.75% decomposition products in water, 2.1% in water/ACN = 1/1 and 1.5% in pure ACN.

3.2. Stability of m-BBr in acidic conditions

To three aliquots of m-BBr solution (4 mg/ml) in ACN, TFA was added in the proportions: 0.1, 1, 10%. The resulting solutions were kept for 24 h at room temperature in amber vials. Procedure

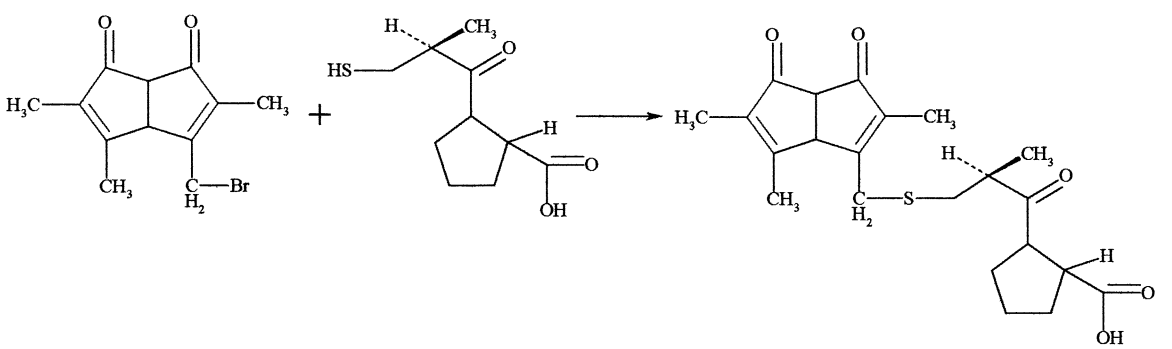

Fig. 1. Derivatization reaction of captopril with the thiol group selective coupling reagent m-BBr.

for observing degradation products was similar to the previous series of experiments. The results (1.6 for 0.1% TFA, 1.68 for 1% TFA and 1.72 for 10% TFA) clearly demonstrates that the reagent is stable in acidic conditions.

3.3. Stability of m-BBr in alkaline conditions

To three aliquots of m-BBr solution (4 mg/ml) in ACN, triethylamine (TEA) was added in the proportions: 0.1, 1, 5%. Solutions were allowed to stand 10 min before injection to the chromatographic system.

Some other experiments were carried out on solutions containing m-BBr dissolved in water/ACN = 1/1.

The observation of the degradative processes was expressed as in the previous sections. After 10 min, degradation products are 4.6 formed in the 0.1% TEA containing solution, 7.2 when 1% TEA was added and about 18 for 5% TEA.

When water exists in the solvating media, the decomposition process is accelerated (about seven for 0.1% TEA, 17 for 1% TEA and 38 for 5% TEA).

3.4. pH optimization for captopril–m-BBr reaction

About 1 ml aliquots of a freshly prepared captopril solution in water (500 μg/ml) were mixed with 0.5 ml aliquots of 0.1 M phosphate (pH 3.0 and 7.5) and borate (pH 9) buffers and with 0.5 ml aliquots of m-BBr solution in ACN (2 mg/ml). Chromatographic separations were performed for each sample, 2 and 30 min after mixing.

The percentage of the captopril–m-BBr derivative was expressed in an indirect way, according to the residual peak area of the unreactioned captopril. At pH 3, no derivatization occurs, regardless of the reaction period. At pH 7.5, 75% of the sampled captopril was labeled after 2 min, and reaction was fully completed after 30 min. At pH 9, 95% of sampled captopril was labeled after 2 min and reaction was quantitative after 30 min. However, with alkaline conditions, chromatograms were crowded with the reagent decomposition products and the fluorescent derivative of interest can hardly be separated from degradation interfering products. Longer the reaction time is, higher will be the interfering pattern.

3.5. Optimization of the concentration of the reagent solution

About 1 ml aliquots of freshly prepared captopril solution in water (500 μg/ml) were mixed with 0.5 ml aliquots of 0.1 M phosphate buffer pH 7.5 and 0.5 ml aliquots of m-BBr solutions in ACN having concentrations of 2.5, 5.0 and 20 mg/ml. The prepared samples were injected 2 min after mixing. Formation of the captopril–m-BBr derivative was evaluated considering the integrated peak area and comparing the values with the derivative peak area resulted in the previous experiment (for pH 7.5).

The resulting formation yields (100.6, 104.4 and 110.3%, respectively) clearly indicate that the choice of a moderate excess of the derivatization reagent is a better solution. It is also important to underline that higher the concentration of m-BBr is, higher will be the interfering pattern in the resulting chromatograms, due to its degradation.

3.6. Stability of captopril–m-BBr derivative in acidic conditions

To a freshly prepared 1 ml captopril solution in water (500 μg/ml) addition of 0.5 ml phosphate buffer pH 7.5 and 0.5 ml m-BBr solution in ACN (4 mg/ml) was done. The sample was allowed to stand for 30 min and 0.5 ml of an aqueous 70% (w/v) trichloracetic acid (TCA) were added.

The resulting mixture was subject to chromatographic separation immediately after mixing and 2, 24 and 240 h later. Peaks areas recorded for captopril–m-BBr derivative exhibits a relative standard deviation (R.S.D.) below 2%, meaning that the labeled captopril derivative is stable in acidic media. Between analyses, the sample was kept in a freezer at −40 °C. According to our results the m-BBr solutions are very stable for at least 3 months, if they are kept at a refrigerator. Plasma samples subjected to the derivatization procedure can be stored for at least 6 months at −40 °C.

Table 1
Recovery of captopril–m-BBr derivative from spiked plasma samples

Concentration (ng/ml)	Peak area in spiked water samples	Peak area in spiked plasma samples	Calculated recovery (%)
12.5	116.0	66.4	57.2
25	235.2	140.7	59.8
100	868.8	494.5	57.0
250	2078	1284.5	61.8
500	4314	2429	56.3
1000	8769	5021	57.3
2000	17405	9824	56.5
Averaged recovery	58.00		
S.D.	2.04		
R.S.D. (%)	3.5		

3.7. Recovery of captopril–m-BBr derivatized in spiked human plasma samples

Two series of captopril solutions were made. The first one contains spiked water samples of captopril having concentrations of 2000, 1000, 500, 250, 100, 25 and 12.5 ng/ml. The second one contains spiked plasma samples of captopril with identical concentrations.

To 1 ml of each of the analyte spiked water solutions, 0.5 ml of phosphate buffer pH 7.5 and 50 μl of 4 mg/ml m-BBr solution in ACN were added. Samples were allowed to stand for 30 min and addition of 0.15 ml aliquot of aqueous 70% (w/v) TCA was made.

Same operations were achieved on captopril spiked plasma samples. After TCA addition, samples were centrifuged at 7000 rpm for 5 min and supernatant was isolated.

All samples were subjected to chromatographic analysis.

Peak areas of the captopril–m-BBr derivative in chromatograms obtained after injection of spiked plasma samples are expressed as percentages towards peak areas integrated in the corresponding chromatograms resulting after spiked water samples injections. Results are enlisted in Table 1.

One can conclude that over the protein precipitation step, captopril–m-BBr derivative is lost (probably due to adsorption over precipitated proteins). Recovery is, however, reproducible over a large concentration interval.

The validation of the chromatographic method used for separation of captopril–m-BBr from plasma samples was made with respect to the following algorithm.

3.8. Selectivity of the method

Blank plasma samples and the corresponding captopril spiked plasma samples were subjected to derivatization with m-BBr and protein precipitation with TCA. A typical resulting chromatogram is given in Fig. 2.

No interference was observed resulting from plasma matrix or from the derivatization reagent degradation pattern. It is worthwhile to note that over five different bioequivalence studies carried out on more than 120 healthy volunteers, no interference occurring from plasma was observed.

3.9. Reproducibility of retention and detector response

Reproducibility of retention and detector response was carried out on both captopril spiked water and plasma samples, at concentration levels of 100 ng/ml, considering inter-day and intra-day experiments and ten successive trials.

Inter-day experiments are made at 24 h distance. Sample solutions were kept at deep freeze (-40 °C) between the experimental sessions. Results are given in Table 2.

3.10. Calibration

Calibration graph was made on captopril spiked plasma samples having concentrations of 12.5, 25, 50, 75, 100, 125 and, respectively, 150 ng/ml.

The linear regression is characterized by a correlation coefficient of 0.9992, a slope of 3.231 (with R.S.D. = 0.45%) and an ordinate to origin of − 1.642 (R.S.D. = 2.62%).

The calculated LOQ for a precision of 90% and 5 degrees of freedom was 8.7 ng/ml. Detection limit for a ratio signal-to-noise = 3 was 4 ng/ml.

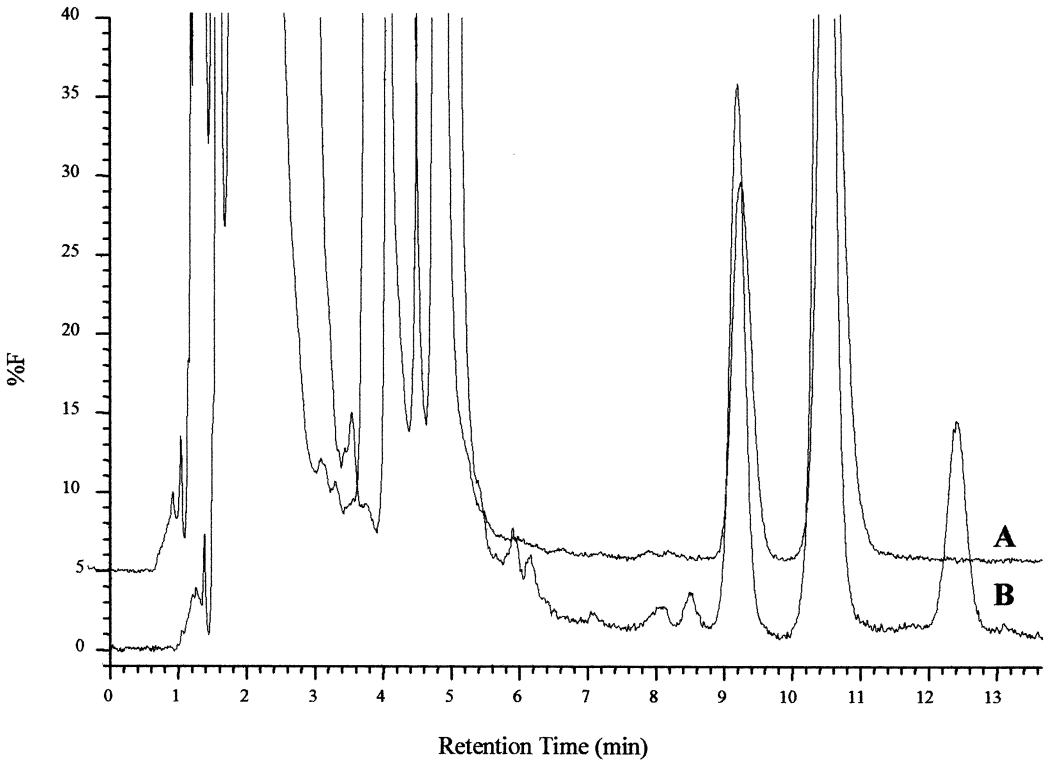

Fig. 2. Resulting chromatograms (FLD trace) from blank (A) and 25 ng/ml captopril spiked (B) plasma sample (the sample preparation procedure is given in Fig. 3, the chromatographic conditions are given in Section 2). t_R for captopril–m-BBr derivative is 12.35 min.

Table 2
Reproducibility of retention times and detector responses for captopril–m-BBr derivative separated from spiked water and plasma samples

Matrix	Experimental series	Parameter	Mean value	S.D.	R.S.D. (%)
Spiked water	Intra-day	Peak area	505.7	6.1	1.2
Spiked water	Inter-day	Peak area	506.0	8.9	1.8
Spiked water	Intra-day	t_R (min)	12.164	0.016	0.13
Spiked water	Inter-day	t_R (min)	12.259	0.064	0.52
Spike plasma	Intra-day	Peak area	300.5	9.0	3.03
Spike plasma	Inter-day	Peak area	302.2	12.8	4.2
Spike plasma	Intra-day	t_R (min)	12.350	0.07	0.57
Spike plasma	Inter-day	t_R (min)	12.362	0.116	0.94

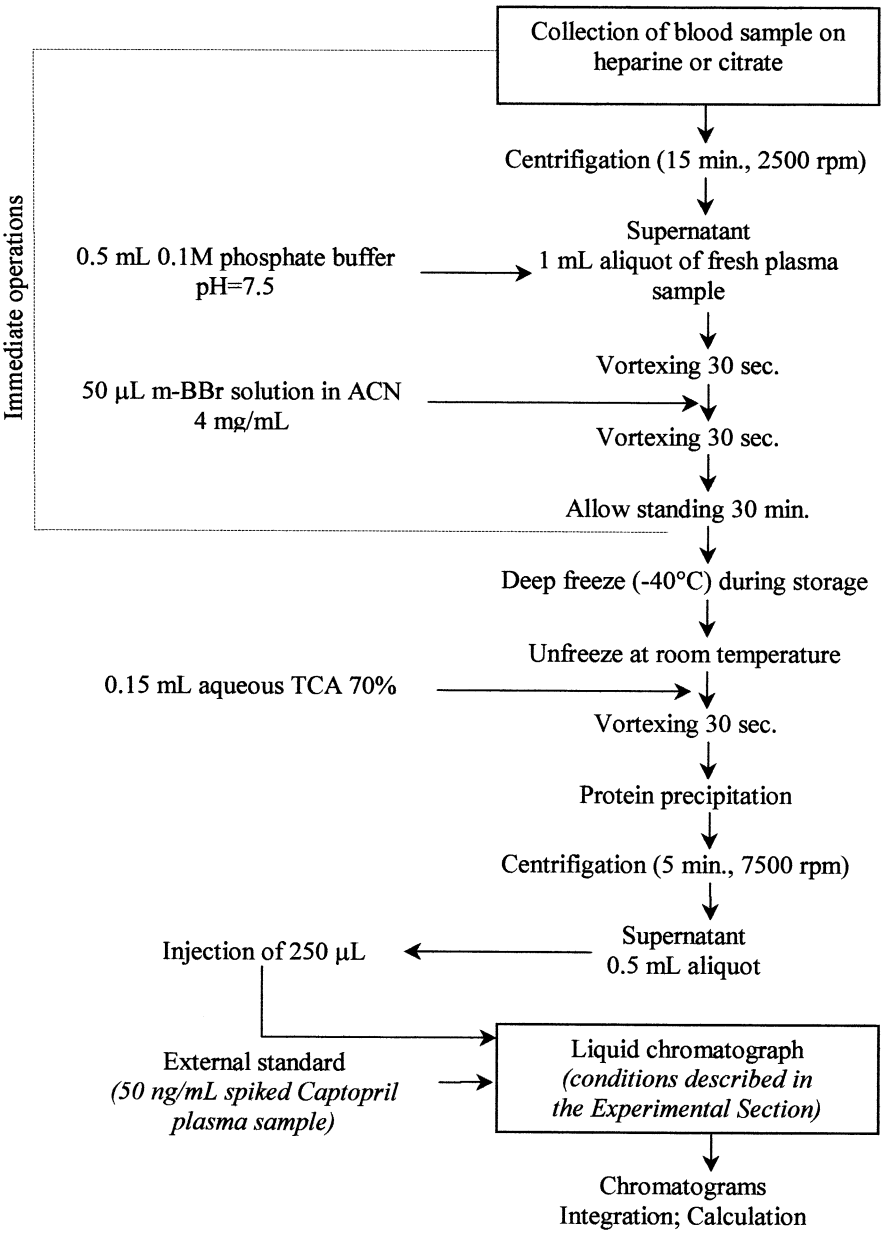

Fig. 3. Operational flow chart for the sample preparation method for determination of free captopril in human plasma samples.

3.11. Accuracy of the method

The accuracy of the method was carried out on three captopril spiked plasma samples at nominal concentrations of 10, 100 and 200 ng/ml. Experimental peak areas were interpolated in the linear regression equation given in the previous section. The mean recoveries were 95.1% (10 ng/ml, three trials), 100.7% (100 ng/ml, three trials) and 98.6% (200 ng/ml, three trials).

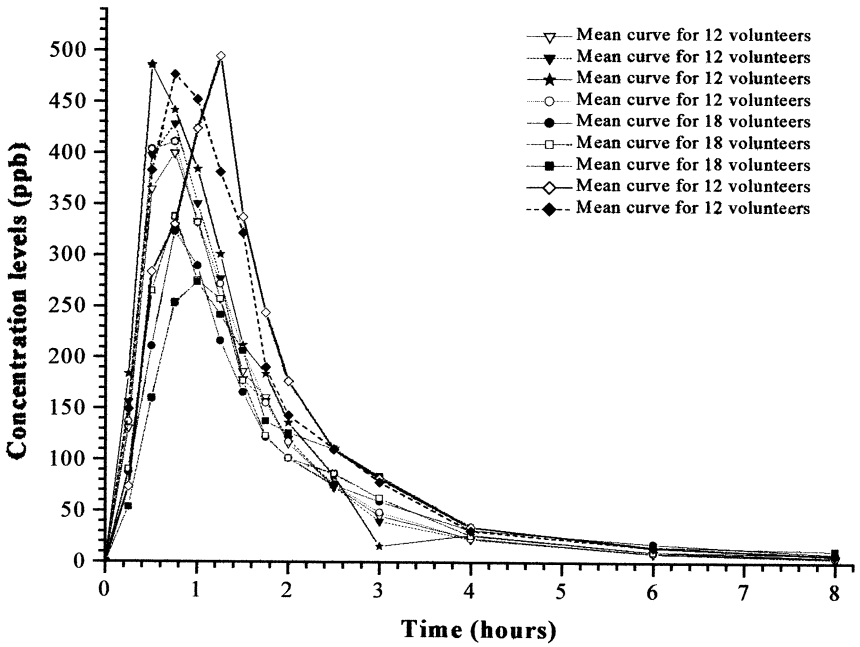

Fig. 4. Mean profiles of free captopril concentration in human plasma samples collected during several bioequivalence studies carried out on some marketed drug formulations.

3.12. Ruggedness of the chromatographic method

Modification of the ration between organic and aqueous components of the mobile phase was first tested. Experimental values of 10/90, 17.5/83.5 and 80/20 were applied. For the first case, retention of the labeled captopril is increased to almost 18 min, and no interfering effects were observed. For the second case, retention of the derivative is reduced to 10.8 min, but baseline separation from the other m-BBr degradation products is still achieved. In the third case, the retention time of the derivative is decreased to 9.8 min and some interference with m-BBr degradation product was observed. Considering these results, the method could be considered rugged enough towards mobile phase composition.

The use of different other C_{18} columns was taken into discussion. A Chromspher C_{18} 150 mm (L) × 4.6 mm (i.d.) × 5 μm (d.p.) and a Nucleosil C_{18} AB (Macherey–Nagel) 250 mm (L) × 4.6 mm (i.d.) × 5 μm (d.p.) columns were considered. Both columns behave well, but retention of the derivative is considerably increased (about 20 min in the first case, more than 22 min for the second one).

A column temperature variation in the range of 50–65 °C is not essentially affecting separation process. At temperatures lower than 45 °C, a peak shape degradation become obvious.

Addition of TFA in the mobile phase is essential. Without the acidic additive, elution is not possible anymore. The whole procedure for captopril analysis in plasma samples using m-BBr labeling and FLD detection can be summarized as in Fig. 3.

In order to demonstrate that the exposed method is really rugged, in Fig. 4, some overlaid mean profiles of captopril concentration obtained during bioequivalence studies carried out on drugs marketed on Romanian market are given.

Experiments were carried out on 12 or 18 healthy volunteers series during a 3 years period, using two different HP 1100 chromatographic systems and two analytical working teams.

4. Conclusions

A method for free captopril determination in plasma samples is proposed and validated. Sam-

ple preparation consists in captopril derivatization using the fluorescent m-BBr reagent, followed by protein precipitation with TCA. The chromatographic method is developed on a C18 double end-capped stationary phase, using isocratic elution and an CAN/aqueous 0.1% TFA binary mobile phase. Fluorescence detection was used. Detection and identification limits are in the low ng/ml concentration range. The reliability of the validated sample preparation and chromatographic methods was sustained by the successfully bioequivalence studies carried out on different marketed drugs, made on more than 120 volunteers. Several advantages of this method over the liquid–liquid methods known from the literature can be mentioned, it is not a time-consuming and expensive method, and mostly, it eliminates a main source of random errors. By the optimization and validation of the original paper [40], it became an useful tool for bioequivalence studies.

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