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New methods for amlodipine and valsartan native spectrofluorimetric determination, with factors optimization study

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ABSTRACT

Four native fluorescence methods were suggested for simultaneous determination of amlodipine (AML) and valsartan (VAL). These methods were based on excitation of both drugs at λ_{ex} 300 nm, in one step, to give maximum emission at λ_{em} 378 and 496 nm for AML and VAL, respectively. The first method, single λ_{ex} method, was used without any additions. The sensitivity of this method was further increased by the addition of hydroxy propylmethyl cellulose (HPMC) surfactant, β-cyclodextrin, or ferric oxide magnetite nanoparticles, in the other three methods. Different types of surfactants, and different concentration levels of both β-cyclodextrin and ferric oxide nanoparticles, were scanned to determine the optimum conditions for enhancing the sensitivity. Some factors affecting the fluorescence intensity of both cited drugs, like the type and volume of the added solvent (to be used as a sensing agent), and pH of measurement were studied and optimized. The proposed methods could be used in determination of AML and VAL in bulk powder, their laboratory prepared mixtures and pharmaceutical formulations. The obtained results were statistically compared to each other and to that of some reported methods. The specificity of the developed methods was investigated, and the methods were validated according to ICH guidelines.

1. Introduction

Amlodipine besylate (AML) (Fig. 1a), chemically known as 3-ethyl 5-methyl (4RS)-2-[(2-aminoethoxy) methyl]-4-(2-chlorophenyl)-6-methyl-1, 4-dihydropyridine-3, 5-dicarboxylate benzenesulphonate [1], is a dihydropyridine calcium channel blocker, used in the management of hypertension, chronic stable angina pectoris, and Prinzmetal's variant angina [2].

Valsartan (VAL) (Fig. 1b), chemically known as N-[p-(o-1 H tetrazol-5-ylphenyl)benzyl]-N-valeryl-L-valine [1], is a potent and specific angiotensin II receptor antagonist, used for treatment of hypertension, heart failure, and post-myocardial infarction [2].

The official method for AML and VAL analysis in USP, 2012 and BP, 2010 [3,4] was high-performance liquid chromatography (HPLC) procedure for the assay of bulk powder. The scientific literature revealed several analytical methods for AML and VAL detection in various matrices including pharmaceutical formulations and/or biological fluids, either together or in different combinations. These methods included densitometry, video scanning and capillary electrophoresis comparative study [5], various spectrophotometric techniques [6–11], and fractional wavelet transform with chemometric calibration [12]. Few spectrofluorimetric methods had been reported for AML detection, after derivatization of the drug with fluorogenic reagents, and measuring its fluorescence [13]. The native fluorescence of AML was studied and applied for its determination in its combined dosage form [14–16]. Reversed phase high-performance liquid chromatography (RP-HPLC), high performance thin layer chromatography (HPTLC) and spectrophotometric methods were also developed [9]. RP-HPLC [17,18], HPLC photodiode array detection [19], ion-pair LC [20], HPLC with fluorescence detection after chemical derivatization [21,22], HPLC with amperometric detection [23], liquid chromatography–mass spectrometry (LC–MS) [24–27], HPTLC [28], ultra-performance liquid chromatography (UPLC) [29–31], capillary electrophoresis [32], and micellar electrokinetic chromatography [33] were other separation techniques. Other electrochemical methods were studied for determination of various amlodipine matrices e.g. anodic stripping voltammetry [34–38], boron-doped diamond electrode technique [39], and ion

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selective electrode technique, either in combination with VAL [40], or alone using a novel approach introduced by authors' team [41].

Herein, screening of the studied factors for optimization purposes to enhance spectrofluorimetric native response of AML and VAL for rapid, simultaneous, and sensitive detection of the combination mixture in bulk powder matrix, as well as pharmaceutical formulation, were presented. A new method was introduced using a single excitation wavelength for simultaneous determination of both drugs in one step. The addition of surfactant, β-cyclodextrin, and nanoparticles were studied to enhance the sensitivity in the other three methods. The proposed methods were further compared to other different reported techniques used for simultaneous determination of AML and VAL in various matrices (Table 1). It was found that their LODs, LOQs and linearity ranges were better

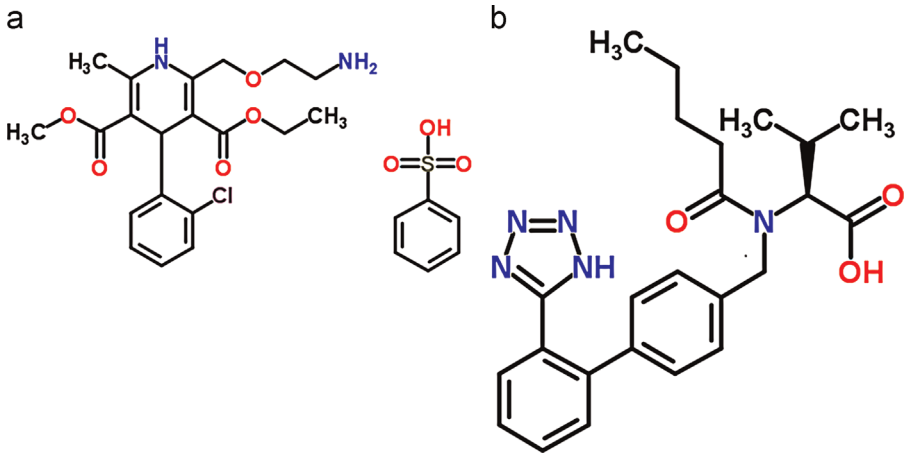

Fig. 1. AML and VAL chemical structures.

Table 1
Comparison between the suggested methods and other reported methods with various approaches for determination of AML and VAL in various matrices.

Method	Linearity range		Mean ± SD		LOD	
	AML	VAL	AML	VAL	AML	VAL
Single λ_{ex} method (μg mL^{-1})	0.1–0.5	0.05–0.45	99.86 ± 1.174	100.5 ± 2.04	0.002	0.017
After HPMC addition (μg mL^{-1})	0.05–0.5	0.01–0.45	100.27 ± 1.386	99.94 ± 2.664	0.003	0.003
After β-CD addition (μg mL^{-1})	0.1–0.5	0.03–0.27	99.9 ± 0.765	99.3 ± 2.588	0.004	0.008
After nanoparticles addition (μg mL^{-1})[a]	0.1–0.5	0.03–0.27	99.88 ± 0.858	99.92 ± 1.333	0.009	0.004
Densitometry (μg/spot)	0.02–0.14	0.4–2.8			0.006	0.04
Video-scanning (μg/spot)	0.02–0.14	0.4–2.8			0.008	0.06
Capillary electrophoresis (mg mL^{-1}) [5][b]	0.005–0.03	0.1–0.6			0.001	0.008
Spectrophotometry (μg mL^{-1}) [10]	10–80	20–180	100.19 ± 0.76	99.91 ± 0.55	8.5	12
Successive spectrum subtraction-constant multiplication (μg mL^{-1})	2–32	4–40	100.24 ± 0.65	100.08 ± 1.03		
Successive derivative subtraction-constant multiplication (μg mL^{-1})	2–32	4–40	100.24 ± 0.48	99.89 ± 0.49		
Absorbance subtraction-absorptivity factor (μg mL^{-1})	2–32	1.5–26	100.39 ± 0.24	99.22 ± 0.39		
Amplitude modulation (μg mL^{-1}) [11]	2–32	1.5–6	99.96 ± 0.26	99.90 ± 0.36		
PLS-1 (μg mL^{-1})	2–10	24–40	100.2 ± 0.9	99.9 ± 1.0		
GA-PLS (μg mL^{-1})	2–10	24–40	100.1 ± 0.9	100.0 ± 0.8		
ANN (μg mL^{-1})	2–10	24–40	100.0 ± 1.0	100.1 ± 0.7		
GA-ANN (μg mL^{-1})	2–10	24–40	100.0 ± 0.8	100.0 ± 0.8		
PCA-ANN (μg mL^{-1}) [8]	2–10	24–40	100.1 ± 0.9	99.8 ± 0.9		
Fractional wavelet transform (μg mL^{-1}) [12]	1.08–17.27	3.00–35.00				
Spectrofluorimetry (μg mL^{-1}) [14]	0.2–3.6	0.008–0.8	98.96 ± 0.91	99.27 ± 0.94	0.025	0.012
RP-HPLC (μg mL^{-1})	2–25	20–150	99.57 + 1.33 to 101.42 + 0.75	99.69 + 0.63 to 1002.01 + 0.07	0.23	1.1
HPTLC (ng/spot)	100–600	1200–3200	99.44 + 0.74 to 100.14 + 1.32	99.30 + 0.70 to 101.40 + 0.77	2.95	70.9
Spectrophotometry (μg mL^{-1}) [9]	2–20	10–50	98.4 + 1.21 to 100.5 + 1.30	98.53 + 1.42 to 99.67 + 1.65	0.03	0.03
HPLC with fluorescence detector (μg mL^{-1}) [22]	0.8–5.6	12–84	101.27 ± 1.09	101.05 ± 0.86		
RP-HPLC (ng mL^{-1}) [18]	6–200	50–4000			2	7
RP-LC (μg mL^{-1}) [17]	5–50	10–160			1.35	3.22
UPLC (μg mL^{-1}) [31]	0.1–0.3	0.05–0.3			0.093	0.047
UPLC (μg mL^{-1}) [30]	5.0–12.0	76.5–178.5			0.023	0.06
Boron-doped diamond electrode (mol L^{-1}) [39]	4.9×10^{-7}–7.2×10^{-6}	9.7×10^{-6}–1.3×10^{-4}			2.3×10^{-7}	6.2×10^{-6}
Voltammetry (μM) [37]	1.00–35.00	1.50–32.00			0.31	0.36

[a] The suggested methods.
[b] The reported methods for comparison.