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Novel reagents for quantitative analysis of valiolamine in biological samples by high-performance liquid chromatography with pre-column UV derivatization

Chengyin Wang[a,b,*], Yujie Sun[a], Qunyin Wen[a], Guoxiu Wang[c,**], Yang Wang[a], Qishu Qu[a,b], Gongjun Yang[a,b], Xiaoya Hu[a,b]

[a] Department of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China
[b] Jiangsu Key Laboratory of Environmental Engineering and Monitoring, Yangzhou 225002, China
[c] Department of Chemistry and Forensic Science, University of Technology, City campus, Broadway, Sydney, NSW 2007, Australia

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ABSTRACT

A rapid, low-cost, high sensitive and quantitative method to detect valiolamine in a medium for microbial culture, involving derivatization with a new labeling reagent, 4-methoxybenzenesulfonyl fluoride (MOBS-F), followed by reverse-phase high-performance liquid chromatography with ultraviolet (UV) detection with simple operation procedure. 4-Methoxybenzenesulfonyl chloride (MOBS-Cl) and 2-nitrobenzenesulfonyl chloride (NBS-Cl) were compared with MOBS-F as novel reagents in this paper, and the MOBS-F was chosen as the most suitable derivatization reagent. The column was thermostatic at 35 °C, the mobile phase flow-rate was 1.0 mL/min and the detection wavelength was 240 nm. For a biological sample, the separation of the derivatives was achieved using a gradient mobile system. The elution program is 88% phosphate buffer (50 mM; pH = 3.0) and 12% methanol for 23 min, then 70% of phosphate buffer and 30% methanol for another 15 min and finally 88% of phosphate buffer and 12% of methanol for 5 min to re-equilibrate the column. The optimized conditions of the derivatization were as follows: derivatization reaction temperature 30 °C; derivatization reaction pH value 11.0, reaction time 10 min and MOBS-F concentration higher than 1.5 mg/mL for standard solutions and higher than 5.0 mg/mL for the biological sample. Calibration curves were linear in the range of 0.050–25 μg/mL for the standard solutions and 1.0–75 μg/mL for the biological sample. The sensitive analytical method is helpful to control the biotechnological process of voglibose production and product quality control.

1. Introduction

Voglibose, one of the most important alpha-glucosidase inhibitors, delays the digestion and absorption of carbohydrates, thereby inhibiting postprandial hyperglycemia and hyperinsulinemia, and is an aid in the treatment of diabetes [1]. It can be synthesized by chemical modification of valiolamine [2]. Although the chemical synthesis of valienamine can be accomplished, but the most of chemical synthesis methods have some disadvantages, including multiple steps, low yield, harsh reaction conditions (high-temperature and high-pressure), environmental pollution (plenty of by-products and waste water). Valiolamine was first obtained from a fermentation broth of Streptomyces hygroscopicus [3]. Mixtures of validamine and valienamine could be prepared from biodegradation of validamycin, and then be chemically converted into valiolamine [4]. The sensitive analytical method is helpful to control the biotechnological process. As one of the most important chemical intermediates for the production of voglibose, valiolamine is crucial for developing a reliable and sensitive method for quantitative analysis of valiolamine in a microbial culture medium [5].

Analytical methods to detect valiolamine have seldom been reported. Currently one of the most used analytical methods to detect valiolamine is thin layer chromatography (TLC) [6]. However, its sensitivity was shown to be comparatively poor and this cannot provide an accurately quantitative measure [7]. Just recently, Kim and co-workers reported a quantitative analysis of valiolamine through pre-column derivatization with phenylisocyanate (PITC) using high-performance liquid chromatography (HPLC) with UV detection [8], and the calibration curves were linear in the range of 0.99–19.95 μg/mL for the standard solutions and 24.9–99.7 μg/mL for the spiked sample. By now, this is only one paper reporting the use of HPLC method for the quantitative analysis of valiolamine as an amino compound.

* Corresponding author at: Department of Chemistry and Chemical Engineering, Yangzhou University, 180 Si-Wang-Ting Road, Yangzhou, Jiangsu, 225002, China. Tel.: +86 61 0401185990; fax: +86 514 87975244.
** Corresponding author at: Department of Chemistry and Forensic Science, University of Technology, City campus, Broadway, Sydney, NSW 2007, Australia.
E-mail addresses: wangcy@yzu.edu.cn (C. Wang), gwang@uow.edu.au (G. Wang).

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For HPLC with conventional detection systems, such as UV–vis or florescence detectors, valiolamine needs to be derivatized because an aqueous solution of valienamine without chromophore or fluorophore does not show any characteristic absorption maximum in the region of 200–360 nm, except for end absorption. Several derivatization agents have been employed in HPLC with spectrophotometric detection of amino or amino-glycoside compounds, such as o-phthaldiadehyde (OPA) [9–12], phenylisothiocyanate [13–15], 1-dimethylaminonaphthalene-5-sulphonyl chloride (Dansyl-Cl) [16–18] and 1-fluoro-2,4-dinitrobenzene (FDNB) [19–21]. Despite the popularity of these UV labeling reagents, various disadvantages have been reported. For the common OPA detection, instability of the derivatives lowers the reproducibility of the analysis results when using a manual derivatization process [22]. Although Dansyl-Cl can label both primary and secondary amino acids, it suffers from the limitations that the reaction must proceed in dark and that the possible by-products may affect the following separation process. The reaction conditions of FDNB with amino acids are facile, but previously reported data have indicated that this reagent undergoes decomposition in a methanol–water solution (about 30–50% in 25 min) when exposed to daylight [23]. Among these reagents, PITC can label both primary and secondary amino acids quickly, but it is highly toxic and the derivatization reaction conditions are very harsh [24]. We are interested in developing stable, economical derivatization reagents that can be reacted with a wide range of amino compounds under facile conditions. Previously, our research group has developed such a derivatization reagent, 4-acetamidobenzenesulfonyl fluoride (PAABS-F) [25]. In this study, we attempted to develop a new confirmation method to detect valiolamine in biologic samples, and focused our efforts on developing new amino function derivatization reagents with ultraviolet detection.

In this work, we aimed at development of a rapid, low-cost, high sensitive and quantitative method to detect valiolamine in biologic samples by HPLC and using a new derivatization reagent with facile conditions and simple operation procedure. 4-Methoxybenzenesulfonyl fluoride (MOBS-F), 4-methoxybenzenesulfonyl chloride (MOBS-Cl), 2-nitrobenzenesulfonyl chloride (NBS-Cl) are three stable, economical compounds with chromophore and strong ultraviolet absorption. MOBS-F as a derivatization reagent is reported firstly in a valid HPLC detection in this work, and there were few literatures about applications of MOBS-Cl and NBS-Cl in HPLC detection. Experimental results indicated three above mentioned derivatization reagents were reacted rapidly with valiolamine. Some optimizations of derivatization and separation conditions have been investigated. MOBS-F was chosen as the optimal derivatization reagent for the determination of valiolamine in a medium for microbial culture. Calibration curves were linear in the range of 0.050–25 μg/mL for the standard solutions and 1.0–75 μg/mL for the biological sample. A wider linear range was obtained for the determination, and the detection limit was 2 orders of magnitude lower than that reported in the literature [8], MOBS-F is much cheaper than PHI so as to reduce the detection cost. This present method is helpful to provide value reference to instruct voglibose production, such as utilization ratio of reactant, reclaiming valuable materials, product quality control and environmental monitoring for industrial wastewater discharge and treatment. The proposed method also will provide a new strategy for the separation and detection of other amino compounds.

2. Experimental

2.1. Apparatus

The HPLC system consisted of two LC-10A VP HPLC pumps (Shimadzu, Kyoto, Japan), a CTO-10AS VP column oven (Shimadzu), a DGU-12A on-line degasser (Shimadzu), a 7725i manual injector (Shimadzu), a SPD-10A VP UV–visible (UV–Vis) detector (Shimadzu, Tokyo, Japan), and a CLASS-VP LC work-station (Shimadzu) with a SCL-10A VP system controller (Shimadzu). The analytical column was a reversed-phase ODS column (150 mm × 4.6 mm interior diameter (I.D.), 5 μm, Shimadzu). A TDL 80-2B table-top high-speed centrifuge was used.

2.2. Reagents

All chemicals were of analytical reagent grade, unless stated otherwise. Phosphate acid, sodium hydroxide, potassium dihydrogen phosphate, disodium hydrogen phosphate, acetonitrile (HPLC-grade) and methanol (HPLC-grade) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Valiolamine was pro-

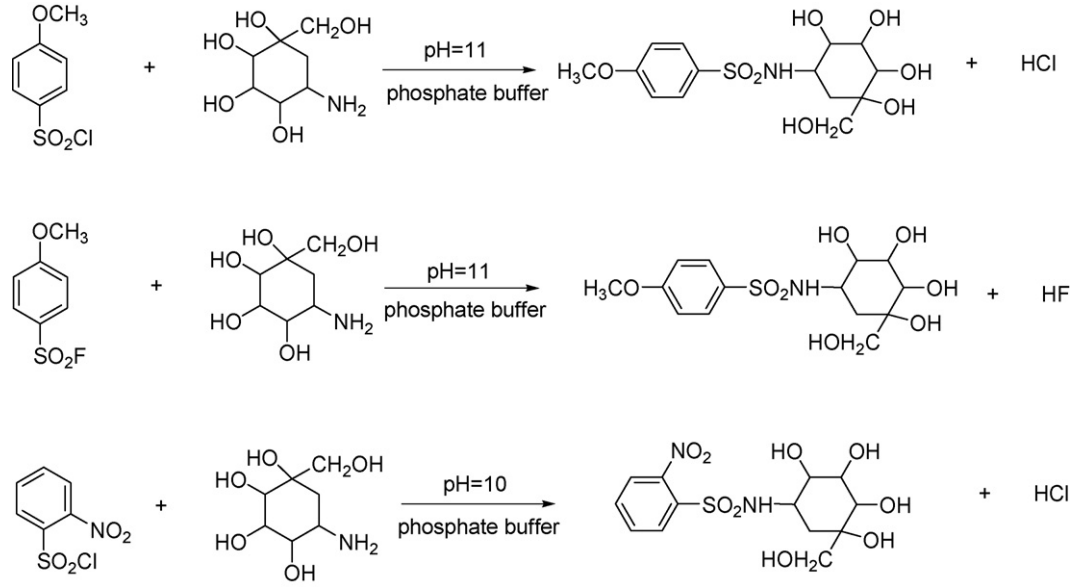

Fig. 1. Putative reaction scheme for the derivatization reaction of valiolamine with MOBS-Cl, MOBS-F and NBS-Cl.

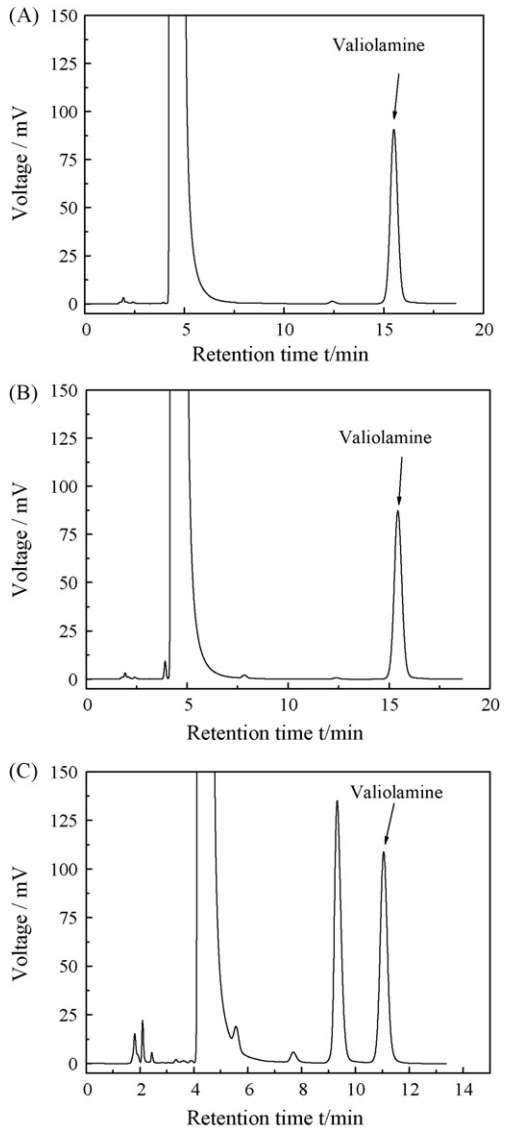

Fig. 2. (A) Chromatogram of 25 μg/mL valiolamine standard derivatized with MOBS-F. Chromatographic conditions: the elution program is an isocratic elution of 85% A and 15% B with UV detection at 240 nm (A: 50 mM, pH = 3.0 phosphate buffer; B: methanol). (B) Chromatogram of 25 μg/mL valiolamine standard derivatized with MOBS-Cl. Chromatographic conditions: the elution program is an isocratic elution of 85% A and 15% B with UV detection at 240 nm (A: 50 mM, pH = 3.0 phosphate buffer; B: methanol). (C) Chromatogram of 25 μg/mL valiolamine standard derivatized with NBS-Cl. Chromatographic conditions: the elution program is an isocratic elution of 88% A and 12% B with UV detection at 205 nm (A: 50 mM, pH = 3.5 phosphate buffer; B: methanol). *X*-axis represents retention time and *Y*-axis represents chromatographic response signal.

vided by Yaoxin Pharmaceutical Technology Co., Ltd. (Wuxi, China). MOBS-Cl was purchased from Jin Chun reagents Co., Ltd. (Shanghai, China). MOBS-F and NBS-Cl were provided by the Institute of Chemistry, Nanjing Zhongyi. Ultra-pure water was prepared with a Milli-Q system (Millipore, Milford, MA, USA).

2.3. Sample preparation and derivatization procedure

A microbial culture medium consisting of glucose (50 mg/mL), soybean flour (36 mg/mL), peptone (5 mg/mL) and calcium carbonate (4 mg/mL) [7] was sterilized, and then centrifuged at 9000 × *g* for 10 min to remove insoluble materials. The supernatant was used for further experiments. Standard stock solutions of valiolamine were prepared in water to give a accurate concentration of 10 mg/mL. This solution was then successively diluted with water to obtain the standard solution and diluted with the culture medium to obtain spiked samples (concentration under calibration graphs). Valiolamine standard solution was placed in a screw-capped glass vial in an appropriate volume, and Na_2HPO_4 (200 mM, 500 μL) and MOBS-F (25 mg/mL in acetonitrile, 100 μL) were successively added and mixed well. The mixture was kept reacting at 30 °C for 10 min. After being filtered through a 0.22 μm membrane, the mixture was injected into the analysis system. An equal volume of acetonitrile was added to each sample solution. After shaking, the mixture was centrifuged at 9000 × *g* for 10 min to remove most of the proteins present. The supernatant was transferred into a 1.0 mL vial for further derivatization procedures as for the standard solution above. The derivatization reaction process is shown in Fig. 1.

2.4. HPLC analysis

2.4.1. Mobile phase preparation

The mobile phase was prepared with (A) phosphate buffer (50 mM, pH = 3.0) and (B) methanol. All solutions were filtered through a 0.22 μm membrane filter before use.

2.4.2. Chromatographic conditions

The column was thermostatic at 35 °C, the mobile phase flow-rate was 1.0 mL/min, and the detection wavelength was 240 nm. Separation was achieved using a gradient mobile system. The elution program is 88% phosphate buffer (50 mM; pH = 3.0) and 12% methanol for 23 min, then 70% of phosphate buffer and 30% methanol for another 15 min, and finally 88% of phosphate buffer and 12% of methanol for 5 min to re-equilibrate the column.

The treatment of a biological sample last approximately 30 min. The derivatization reaction time was less than 10 min, and the determination time by HPLC was about 50 min. The real time applicability for valiolamine detection is about 1.5 h.

3. Results and discussion

3.1. Optimization of reaction conditions for the derivatization

3.1.1. Chromatographic separation conditions

The effect of different ratios of elution mixture was investigated. The experimental results indicated that the retention time of all responses was rapid with increasing a rate of the methanol and decreasing another rate of the phosphate buffer. For example, after the elution mixture of 20% phosphate buffer + 80% methanol was selected, all responses were finished in 2 min so that the separation for the determination of valiolamine was not good. With increasing the rate of the phosphate buffer, the retention time of all responses was extended. It was not good enough for the separation of the chromatograph peaks of valiolamine derivative from the hydrolyzates of derivatization reagents (MOBS-F or MOBS-Cl) until the elution mixture of 85% phosphate buffer (pH 3.0) +15% methanol was selected with UV detection at 240 nm. The separation conditions of MOBS-Cl valiolamine derivative were the same as those for MOBS-F valiolamine derivative. For using NCB-Cl as the derivatization reagent, a much higher rate of the phosphate buffer (88%) had to be selected because of separation of the chromatograph peaks of valiolamine derivative from an unknown chromatograph peak with UV detection at 205 nm.

In general, C18 ODS columns are stable within a pH range of 2–8. However, since silica dissolves at high pH it is not recommended to use solvents that exceed pH 7. Extremes of pH can be especially damaging to the column. Best lifetimes are obtained between pH 2.0 and 6.8. The acid mobile phase is used to improve the chromatographic peak shape and to provide a source of protons

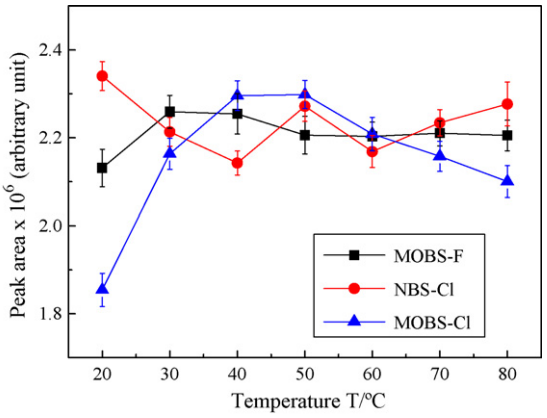

Fig. 3. The effect of temperature on the formation of valiolamine derivative. Chromatogram conditions were the same as in Fig. 2. *X*-axis represents temperature and *Y*-axis represents chromatographic peak area.

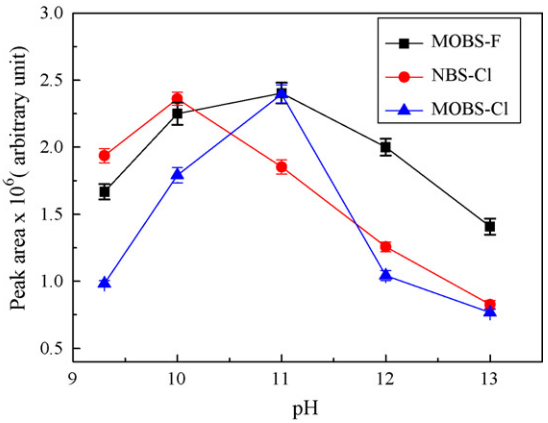

Fig. 4. The effect of pH of the phosphate buffer (0.2 M) on the formation of valiolamine derivative. Chromatogram conditions were the same as in Fig. 2. *X*-axis represents pH value of phosphate buffer and *Y*-axis represents chromatographic peak area.

in reverse-phase HPLC. Our experimental results indicated that the derivative retention time decreased with the increase of pH value of the mobile phase selected, and the separation of the chromatograph peak of valiolamine derivative from the hydrolyzates of derivatization reagents was not satisfactory. When 3.0–3.5 of mobile phase pH value was selected, the chromatographic peak shape and the separation were good.

Considering the reason that high concentration of phosphate buffer was especially damaging to the column, 50 mM molar concentrations of phosphate buffer was chosen in an elution solution. The column flow-rate was always set at 1.0 mL/min. Fig. 2 displays chromatograms of the valiolamine standard derivatized with MOBS-F, MOBS-Cl and NBS-Cl.

3.1.2. The effect of temperature on derivatization reaction

The effects of temperature on the derivatization reaction were investigated for valiolamine within the temperature range of 20–80 °C with a 10 °C increment. Valiolamine and derivatization reagents were mixed, and then reacted in a water bath for 10 min at different temperatures. The mixture was then cooled to room temperature for HPLC separation. As from Fig. 3, there were small differences in derivatization of MOBS-F and MOBS-Cl at 30, 40 and 50 °C. The optimum temperature for MOBS-F, MOBS-Cl and NBS-Cl derivatization reaction of valiolamine was 30, 40, 20 °C, respectively, based on chromatographic peak area data by contrast, indicating derivatization reactions could be carried out under moderate temperature.

3.1.3. The effect of phosphate buffer pH on derivatization reactions

As the choice of high pH phosphate buffer for the derivitaztion reaction is based upon the Hinsberg reaction under the alkaline condition, Experimental results (Fig. 4) shows the chromatograph peak of valiolamine is small when pH value of the phosphate buffer is low than 11 by using MOBS-F and MOBS-Cl, which indicated derivitaztion reaction incomplete. Contrarily, the chromatograph peak decreased because the reaction rate of derivatization reagent with valiolamine is less than the hydrolyzation rate of derivatization reagent. As from the data of chromatographic peak areas of valiolamine derivative in Fig. 4, there was small difference between an area (2.2×10^6) at pH 10 and the other (2.4×10^6) at pH 11 in the derivatization of valiolamine by MOBS-F, so pH 11 as the optimum pH was selected because of the highest sensitive response to valiolamine. Similarly, pH 11 and 10 was chosen as the optimum pH value of the phosphate buffer by MOBS-Cl and NBS-Cl, respectively, according to the experimental results.

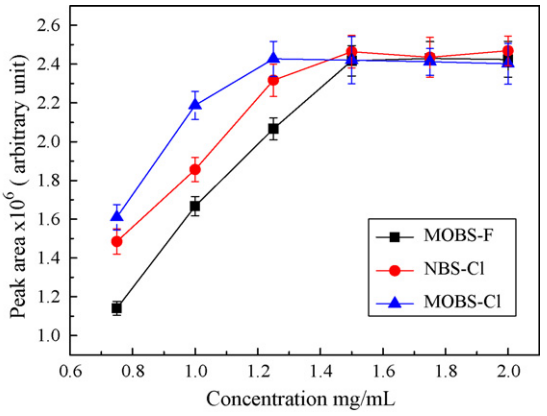

Fig. 5. The effect of concentration of MOBS-F, MOBS-Cl and NBS-Cl on the formation of valiolamine derivative. Chromatogram conditions were the same as in Fig. 2. *X*-axis represents concentration of derivatization reagents and *Y*-axis represents chromatographic peak area.

The effect of different molar concentrations of phosphate buffer on derivatization reaction was investigated, and then experimental results indicated that when the molar concentration of phosphate buffer is more than 200 mM, the buffer capacity is high enough to keep pH at a nearly constant value for the derivatization reaction, and steady chromatographic peak areas of valiolamine derivative were obtained.

3.1.4. The effect of derivatization reagent concentration on derivatization reactions

For developing MOBS-F, MOBS-Cl and NBS-Cl for derivatization and separation of the corresponding derivative, it was important to assess the effects of MOBS-F, MOBS-Cl and NBS-Cl concentration. According to Fig. 5, the yield of each corresponding derivative increases to reach a plateau at concentrations of MOBS-F, MOBS-Cl and NBS-Cl of about 1.5, 1.25 and 1.5 mg/mL, respectively. That is, the reactions of MOBS-F, MOBS-Cl and NBS-Cl with valiolamine have been basically completed when the concentration of MOBS-F, MOBS-Cl and NBS-Cl is about 60, 50, and 60 times higher than the concentration of valiolamine, respectively.

3.1.5. The effect of derivatization time on derivatization reactions

The effect of the reaction time on the derivatization reactions was examined under the optimized condition above. We tried to investigate the statistical difference in derivatization rate at vari-

Table 1
Regression analysis of calibration graphs and other quantitative data for valiolamine derivatives (standard valiolamine).

Derivatization reagent	Regression equation[a]	Correlation coefficient	Linear range (μg/mL)	LODs[b] (μg/mL)
MOBS-F	$Y = 18349.87597 + 100297.79939X$	0.9997	0.050–25	0.01
MOBS-Cl	$Y = 13469.28272 + 98757.35813X$	0.9997	0.050–25	0.01
NBS-Cl	$Y = 16823.47188 + 96302.88893X$	0.9997	0.25–25	0.25

[a] *X*, concentration of valiolamine (μg/mL); *Y*, peak area of valiolamine (arbitrary unit).
[b] LODs, concentration detection limit.

ous temperatures, however, found chromatographic peak areas of valiolamine derivative did not change after 5 min, indicated all of derivatization reaction was rapidly completed in 5 min. We thought 10 min time was enough as for a conservative selection of the derivatization reactions. In order to investigate the stability of the derivatives, the derivation reaction solutions were placed directly under light at room temperature. After 1 month, they were separated by HPLC, and then, no decrease in the peak area was observed. This indicated that the valiolamine derivatives were very stable at room temperature and could be stored directly under natural daylight.

3.2. Linearity and detection limits

To obtain calibration curves, valiolamine at different concentrations was derived with the three reagents and separated under the above optimal conditions. In our experiments, the lowest detection limits (LODs) were obtained on the basis of the minimum analyte concentration, which showed a three times higher peak than the baseline noise and the results are listed in Table 1. As can be seen, the LODs for MOBS-F and MOBS-Cl derivatives are 0.01 μg/mL, and for the NBS-Cl derivative, the LOD is 0.25 μg/mL.

3.3. Determination of valiolamine in medium for microbial culture

The optimized conditions for the formation of MOBS-F valiolamine derivative were as follows: reaction temperature 30 °C, pH value 11 and reaction time 10 min. For MOBS-Cl, the reaction temperature is 40 °C, the pH value 11, and the reaction time 10 min. For NBS-Cl, the reaction temperature is 10 °C, the pH value 10, and the reaction time 10 min. So, the NBS-Cl conditions were the mildest, followed by the MOBS-F conditions, and finally the MOBS-Cl conditions. However, the LOD of NBS-Cl valiolamine derivative was higher than for MOBS-F and MOBS-Cl. Considering peak area, peak sharpness, mild reaction conditions, and LODs, MOBS-F was chosen as the optimum derivatization reagent for the determination of valiolamine in a medium for microbial culture.

The medium for cultivation of microorganisms contained a number of compounds with amino groups, including proteins and amino acids, which can react with MOBS-F. Most proteins in the medium were already removed by precipitation with acetonitrile. However, amino acids possibly existed in the reaction mixtures, which might have contributed to further consumption of MOBS-F. Therefore, an additional amount of MOBS-F could be required to compensate for possible consumption of the derivatizing reagent by these amino compounds. A spike sample of valiolamine (75 μg/mL) was used to determine the most suitable concentration of MOBS-F. As is shown in Fig. 6, valiolamine (75 μg/mL) in the spike sample is completely converted to valiolamine derivative when the concentration of MOBS-F is 5 mg/mL. Therefore, all reactions were carried out in the presence of 5 mg/mL MOBS-F and less than 75 μg/mL of spiked valiolamine in the following experiments.

Despite the fact that the medium for microbial culture samples was very complex, good results were obtained and are shown in

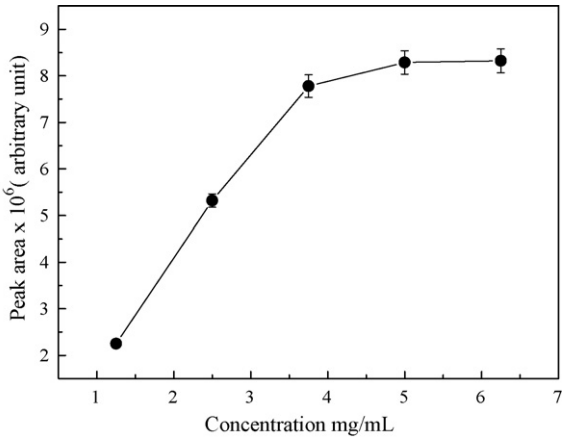

Fig. 6. The effect of concentration of MOBS-F on the formation of valiolamine derivative (medium spiked with valiolamine). Chromatogram conditions: the elution program is a gradient mobile system, 88% of A and 12% of B for 23 min, then 70% of A and 30% of B for another 15 min, and finally 88% of A and 12% of B for 5 min to re-equilibrate the column (A: 50 mM, pH = 3.0 phosphate buffer; B: methanol). *X*-axis represents concentration of derivatization reagent and *Y*-axis represents chromatographic peak area.

Table 2, indicating the good selectivity of MOBS-F for valiolamine analysis. Two spike samples contained 30 and 70 μg/mL valiolamine respectively were selected to detect valiolamine by using the published method [8], and the results were in accord with our proposed method. Nevertheless, a small peak in the blank medium was observed at the retention time of valiolamine, indicating possible interference of endogenous substances in the samples with the analysis of valiolamine. Therefore, for the quantitative analysis of valiolamine, the blank peak area at the retention time of valiolamine was subtracted from the peak area of the spiked medium [8]. Fig. 7 shows a representative chromatogram of the MOBS-F derivative of valiolamine.

According to present method, the linear regression evaluation of the peak area (*Y*) versus concentration (*X*) relationship for intra-day assay, as an example, gave $Y = 227519.2123 + 103162.11883X$ for spiked samples. Calibration curves were linear in the range of 1.0–75 μg/mL for spiked samples. The correlation coefficient of the calibration curve was 0.9983. The lowest concentration used in the construction of the calibration curve for the spiked sample was 0.05 μg/mL, and this limit is attributed to the interference of the blank peak at lower concentrations.

3.4. Reproducibility of HPLC analysis

As shown in Table 3, relative standard deviations (RSDs) of the within-day and between-day retention time precisions were

Table 2
Recoveries of valiolamine in medium for microbial culture ($n = 5$).

Compounds	Amount added (μg/mL)	Average recovery (%)	RSD[a] (%)
valiolamine	2.0	124.5	4.55
	30.0	100.05	2.19
	70.0	92.9	2.31

[a] RSD, relative standard deviation.

Table 3
Reproducibility of the studied MOBS-F derivative of valiolamine for spiked samples by reversed-phase HPLC ($n = 5$)[a].

Compounds	RSDs (%)											
	Retention time						Integrated area					
	Run-to-run			Day-to-day			Run-to-run			Day-to-day		
	A	B	C	A	B	C	A	B	C	A	B	C
Valiolamine	0.18	0.23	0.17	0.61	0.38	0.16	6.26	3.19	1.27	8.28	3.39	3.01

[a] The result was obtained from 2.0 (A), 30.0 (B) to 70.0 μg/mL (C) of valiolamine.

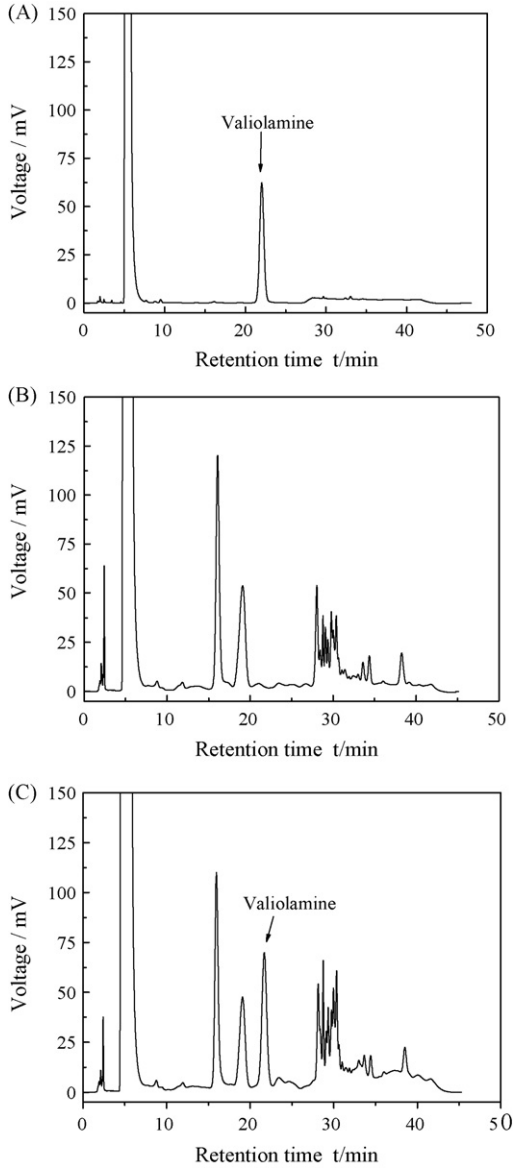

Fig. 7. (A) Representative chromatogram of MOBS-F derivative of valiolamine (standard valiolamine 25 μg/mL). (B) Representative chromatogram of MOBS-F derivative of valiolamine (blank medium). (C) Representative chromatogram of MOBS-F derivative of valiolamine (medium spiked with valiolamine 25 μg/mL). Chromatogram conditions were the same as in Fig. 6. *X*-axis represents retention time and *Y*-axis represents chromatographic response signal.

0.17–0.23% and 0.16–0.61%, respectively. RSDs of the within-day and between-day integrated area precisions were 1.27–6.26% and 3.01–8.28%, respectively. This indicates that the method has good precision and reproducibility.

4. Conclusions

This is the first demonstration that gives a comparison between the derivatization performances of MOBS-Cl, MOBS-F and NBS-Cl. The present work has shown that MOBS-Cl, MOBS-F and NBS-Cl formed effective derivative reagents. The method that we have developed, which is based on pre-column derivatization with MOBS-F, was found to be very sensitive and reliable for the HPLC determination of valiolamine in a medium for microbial culture. It can be applied for analysis of the valiolamine production process, as well as analysis of other amino-glycoside compounds in the pharmaceutical industry, and it also provides a new method for the separation and detection of amino compounds.

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