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Significant fluorescence enhancement by supramolecular complex formation between berberine chloride and cucurbit(n = 7)uril and its analytical application

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ABSTRACT

The supramolecular interaction of cucurbit(n = 7)uril (Q[7]) with berberine chloride (BER) has been studied in aqueous solution at pH 2.0 and room temperature by spectro-fluorimetry. The association constant of the complex was 2.07×10^6 L mol^{-1} calculated by using a nonlinear least squares method. ^{1}H NMR spectra confirmed that a 1:1 stable complex is formed between Q[7] and BER. This work proposes a possible interaction mode, in which the guest BER is incorporated inside the hydrophobic cavity of the host Q[7] via the isoquinoline ring part of the guest molecule. Based on a significant enhancement of the fluorescence intensity of this supramolecular complex, a spectrofluorimetric method with high sensitivity and selectivity has been developed for the determination of BER in aqueous solution in the presence of Q[7]. The linear range of the method was from 7.43 to 11.2×10^3 ng mL^{-1} with the detection limit 4.2 ng mL^{-1}. There was no interference from the compounds normally used in tablets, serum or urine constituents. The proposed method was applied to the determination of BER in tablets, serum and urine samples with satisfactory results and good consistency with those obtained by the pharmacopoeia method. This shows that it has promising potential for therapeutic drug monitoring and pharmokinetics and for clinical application.

1. Introduction

Fluorescent sensors are advantageous for the analysis and detection of various organic and biological molecules due to their high sensitivity and selectivity [1,2]. Meanwhile, supramolecular transducing systems have attracted enormous research interest in recent years for the development of chemical sensors [3]. A variety of receptor molecules, such as cyclodextrin [4,5], crown ethers [6], calixarenes [7], and porphyrin [8], as typical host compounds, can selectively recognize organic species. Cucurbituril and its derivatives (Fig. 1) form a significant new kind of host compound, with a series of barrel-shaped molecules containing a hydrophobic cavity accessible through two identical carbonyl-fringed portals [9]. They are capable of interacting with a variety of organic or inorganic molecules through cavity encapsulation or portal ion–dipole interaction [10]. The encapsulation and release of guest molecules are controlled by the size of the carbonyl portal and cavity [11]. Noncovalent intermolecular forces, including van der Waals interaction, hydrophobic interaction, electrostatic interaction, hydrogen bonding, are believed to play a key role in the complex formation and its stabilization [12]. In addition, the formation of inclusion complexes is often able to effect enhancements or perturbations of the photophysical and photochemical properties of the included guest molecules [13].

Berberine chloride (BER), a kind of isoquinoline alkaloid, is the basic active ingredient of widely used traditional Chinese medicine *Coptis Chinensis* with antibacterial and anticonvulsant activities. It is commonly used for the treatment of diseases such as bacillary dysentery, lobar pneumonia and pertussis. At present, the analytical methods applied to the determination of BER are HPLC [14], capillary electrophoresis [15], electrochemical analysis [16], fluorophotometry [17] and chemiluminescence [18]. Most of the methods need a complicated extraction process [19], and also use organic solvents. BER can emit strong fluorescence in organic solvents but in aqueous solution, it possesses a low fluorescence quantum yield. Therefore, we need to develop a simple, highly sensitive and selective method, without an extraction process, for the determination of BER in aqueous solution.

In this paper, we report the supramolecular interaction between Q[7] and BER. A 1:1 stable complex and possible interaction model between host and guest were investigated by ^{1}H NMR. These investigations showed that the fluorescence intensity of BER was dramatically enhanced in the presence of Q[7], and was clearly associated with the formation of the inclusion complex between Q[7] and BER. To our knowledge, usage of Q[7] as the sensitiz-

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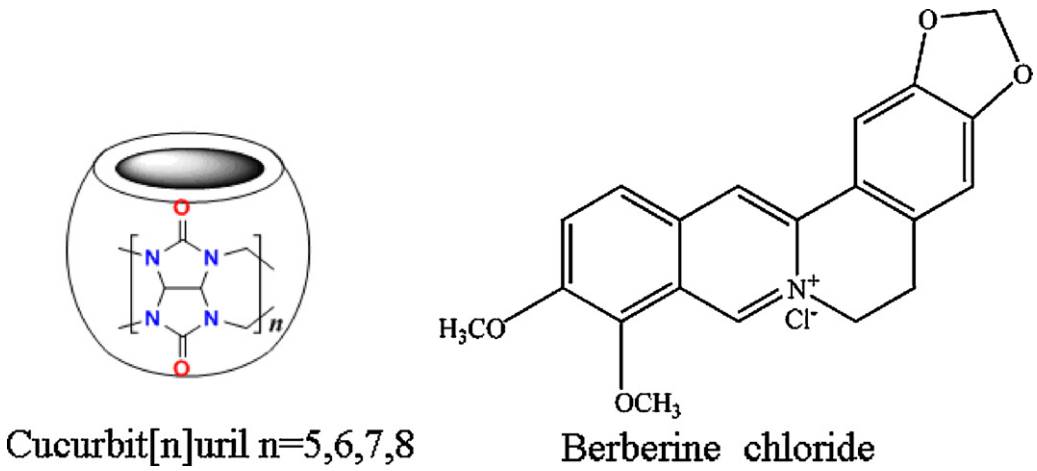


Fig. 1. The structures of cucurbit[*n*]uril and berberine chloride.

ing agent for the determination of BER in the aqueous solution by spectrofluorimetry has not previously been reported.

Based on the supramolecular interaction, the concentration of BER in aqueous solution was determined with high sensitivity and selectivity by spectrofluorimetry. The linear range of the method was from 7.43 to 11.2×10^3 ng mL^{-1} with a detection limit of 4.2 ng mL^{-1}. The proposed method has been applied to the determination of BER in tablets, serum and urine with satisfactory results consistent with those determined by the Chinese pharmacopoeia promulgation method. The method shows potential for therapeutic drug monitoring, pharmokinetics and for clinical applications.

2. Experimental

2.1. Apparatus and reagents

All the spectrofluorimetric measurements were carried out on a Cary Eclipse (Varian, Australia) spectrofluorimeter equipped with a xenon lamp and 1.0 cm quartz cells. Absorption spectra were obtained from a UV-1700 (Shimadzu) UV–vis spectrophotometer. pH measurements were made with a pH 3 digital pH-meter (Shanghai Lei Ci Device Works, Shanghai, China) with a combined glass-calomel electrode. ^{1}H NMR spectra were performed on a VARIAN INOVA-400 spectrometer in D_2O with DCl (pH = 2.0, 0.01 M). All ^{1}H MMR spectra are referenced in ppm with respect to a TMS standard.

BER (99%) (purchased from WuHan Yuancheng coll) was used as received without further purification. Q[7] was prepared at the Applied Chemistry Institute of Guizhou University, according to the literature [20]. Other chemicals used were analytical reagent grade. Doubly distilled water was used throughout.

2.2. Experimental procedure

2.2.1. Calibration graph

Into a series of 10 mL flasks were added different aliquots of the BER stock solution containing 0–11.2×10^3 ng mL^{-1} of BER and 0.9 mL of 1.00×10^{-3} mol L^{-1} Q[7]. The mixture was diluted to mark with 0.01 mol L^{-1} hydrochloric acid solution, shaken thoroughly and equilibrated at room temperature for 5 min. Then the fluorescent intensity of the solution was measured at 345/498 nm against a reagent blank. The excitation and emission band width were 5 nm.

2.2.2. Determination of the apparent association constant

Into a series of 10.0 mL flasks were added 0.1 mL of 1.00×10^{-4} mol L^{-1} BER and variable amounts of 2.00×10^{-4} mol L^{-1} Q[7]. The mixture was diluted to mark with 0.01 mol L^{-1} hydrochloric acid solution, shaken thoroughly and equilibrated at room temperature for 5 min. Then the fluorescent intensity of the solution was measured at 345/498 nm against a reagent blank. Again, the excitation and emission band width were 5 nm.

3. Results and discussion

3.1. Excitation and emission spectra

The excitation and emission spectra were scanned as described above (Fig. 2.). The maximum excitation and emission wavelengths of BER were 345 and 515 nm, respectively. However, when Q[7] was added to the aqueous solution of BER, a significant increase of the fluorescence intensity was observed, accompanied by a blue shift from 515 nm to 498 nm.

3.2. Influence of pH and reaction time

BER is a quaternary ammonium salt, so its fluorescence emission intensity should be unrelated to pH value in aqueous solution. The experimental results also indicated that there is no significant change of the fluorescence intensity over the pH range 1–7 for Q[7]-BER system. Considering that samples were prepared under acid condition (pH ≈ 2.0), a pH of 2.0 was fixed using 0.01 mol L^{-1} hydrochloric acid solution throughout experimental process.

In addition, the fluorescence intensity quickly reached a maximum after the reagents had been added and remained constant for at least 120 min. Hence, after the inclusive reaction was carried out for 5 min, the subsequent fluorescence measurement was made at room temperature.

3.3. Influence of Q[7] concentration

The influence of Q[7] concentration on the fluorescence intensity is shown in Fig. 3. In order to compare with Q[7], the influence of β-CD on the fluorescence intensity of BER was also tested. The results showed that with increasing concentration of Q[7], the fluorescence intensity of the complex increased and finally remained approximately constant. When the concentration of Q[7] was 3 times that of BER, the fluorescence intensity of BER was increased by a factor of nearly 140 compared to only a 3-fold increase of the fluorescence intensity with the same concentration of β-CD (Fig. 3). Thus, Q[7] shows a strong enhancement of the fluorescence inten-

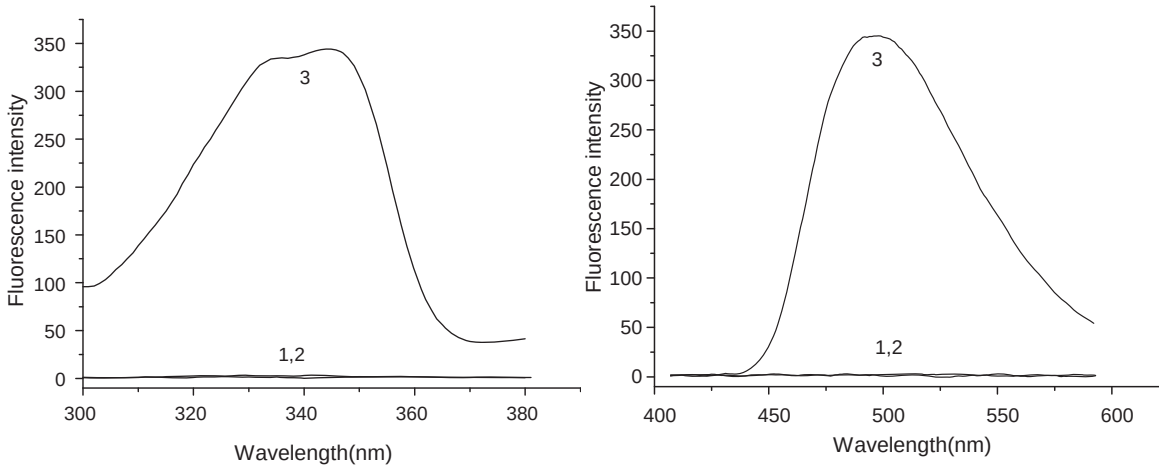


Fig. 2. Excitation and emission spectra: (1 and 2) reagent blank, berberine chloride; (3) berberine chloride + Q[7]; $C_{\text{berberine chloride}} = 1.0 \times 10^{-5}$ mol L^{-1}; pH = 2.0; $C_{Q[7]} = 3.0 \times 10^{-5}$ mol L^{-1}.

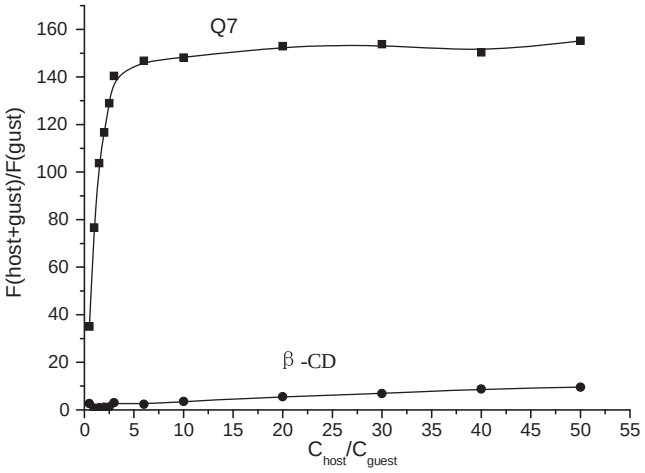


Fig. 3. Influence of Q[7] and β-CD on the fluorescence intensity. $C_{\text{berberine chloride}} = 1.0 \times 10^{-6}$ mol L^{-1}; pH = 2.0.

sity of BER and 3 times molar ratio of Q[7] vs. BER was used in the remainder of this investigation.

3.4. Apparent association constant

An apparent association constant value for the inclusion complex can be determined through the typical double reciprocal plots [21] or the nonlinear least squares method [22]. For the first method, the host should be present in a large excess with respect to the guest. Unlike cyclodextrin [21], the quantity of host Q[7] used in this work is not in excess of that of the guest, and therefore, the nonlinear least squares method was used to calculate the apparent association constant. With the assumption of a 1:1 stoichiometry, the inclusion complexation of the guest (G) with the host (H) is expressed by Eq. (1)

$$H + G \overset{K_S}{\rightleftharpoons} H - G \tag{1}$$

The stability constants (K_S) of the inclusion complex can be calculated using a nonlinear least squares method using the Curie fitting Eq. (2) [22]:

$$\Delta F = \frac{\alpha([H]_0 + [G]_0 + 1/K_S) \pm \sqrt{\alpha^2([H]_0 + [G]_0 + 1/K_S)^2 - 4\alpha^2[H]_0[G]_0}}{2} \tag{2}$$

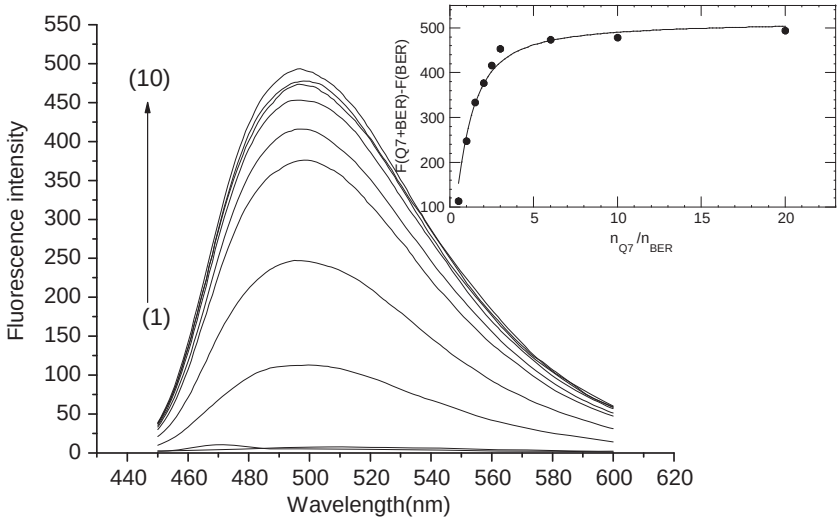


Fig. 4. Fluorescence spectra of BER in the presence of Q[7]: (1) 0 mM; (2) 0.5 μM; (3) 1 μM; (4) 1.5 μM; (5) 2.0 μM; (6) 2.5 μM; (7) 3 μM; (8) 6 μM; (9) 10 μM; (10) 20 μM. The inset shows curve-fitting plot for 1:1 stoichiometry. All emission spectra were obtained in 0.01 M HCl solution (pH = 2.0) of 1×10^{-6} M BER with excitation at 345 nm.

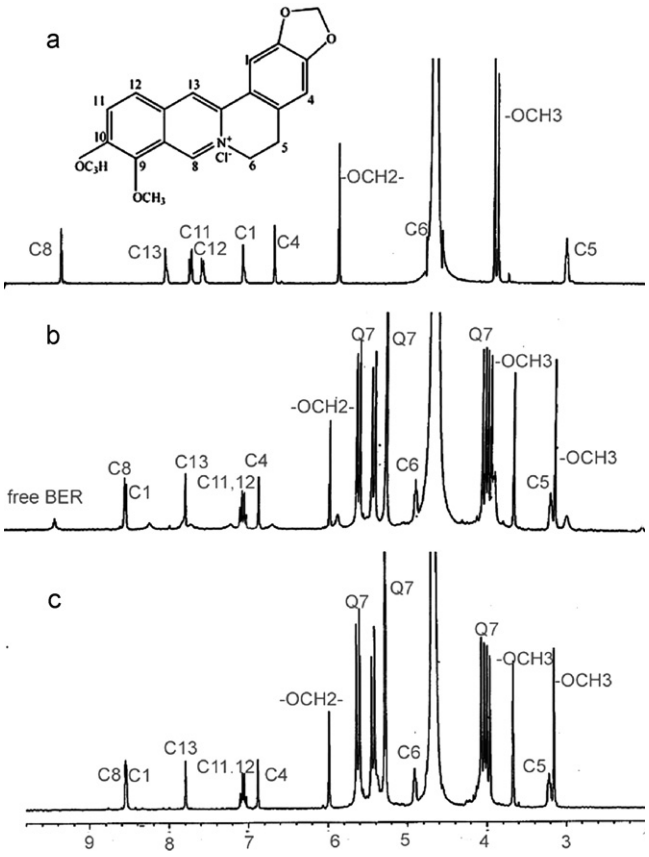
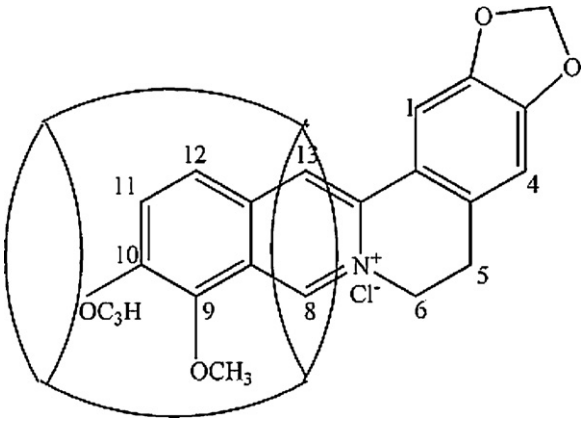


Fig. 5. ^{1}H NMR spectra of BER in the absence of Q[7] (a); after the addition of 0.5 equivalents of Q[7] (b); and the addition of 1 equivalent of Q[7] (c).

where $[H]_0$ and $[G]_0$ refer to the total concentration of host Q[7] and guest BER, respectively, $C_{Q[7]} = n_{Q[7]}/n_{BER} \times C_{BER}$, $n_{Q[7]}/n_{BER}$ refers to the molar ratio of Q[7] to BER. ΔF denotes the change in the fluorescence intensity of BER upon stepwise addition of the host Q[7], i.e. $\Delta F = F(\text{host}) - F(\text{without host})$, and α is the proportionality coefficient.

For BER, the plot of ΔF as a function of [Q[7]] gave a good fit ($r = 0.992$) (Fig. 4), verifying the validity of the 1:1 complex stoichiometry assumed above. The complex stability constant (K_S) obtained by the curve fitting is 2.07×10^6 L mol^{-1}.

The presence of a stable 1:1 host–guest complex between Q[7] and BER in aqueous solution was also confirmed by ^{1}H NMR. Fig. 5 shows the ^{1}H NMR spectra of BER as a function of Q[7] concentration. When the concentration of Q[7] is not in excess (Fig. 5(b)), there exist free BER and bound BER coexisting in the solution. However, the signals from the free BER disappeared with further addition of Q[7] (Fig. 5(c)), clearly indicating interaction between Q[7] and BER. Compared with the proton resonances of the unbound BER, the signals corresponding to the protons on C8, C11, C12, $-OCH_3$ of the bound BER exhibited an upfield shift, which is characteristic of this part of the molecule encapsulated in the Q[7] cavity [23], while the signals from the protons on C1, C4, C5, C6 of the bound BER experienced a downfield shift, which is characteristic of the protons of this part of molecule located just outside the carbonyl portal of the host Q[7] [24]. The signal attributed to the $-OCH_2-$ was essentially unchanged. Therefore, we deduced that the isoquinoline ring of the BER molecule could be encapsulated in the Q[7] cavity and this possible interaction model is shown in Scheme 1. Combination of hydrophobic interaction of the cavity of Q[7] as well as ion–dipole interaction between the carbonyl portal of Q[7] and N^+ ion of BER leads to the formation of host–guest



Scheme 1. The possible interaction model between Q[7] and BER.

inclusion complex [12]. The most noticeable effect is the host–guest interaction ratio. A comparison of the integrals of the protons of the bound BER with the protons of Q[7] revealed the complex Q[7]-BER to be a 1:1 host:guest species [25], which is in agreement with the results from the spectrofluorimetry.

It is important to rationalize physically the fluorescence enhancement and the blue shift of BER following the addition of Q[7]. Q[7] is basically spectroscopically inert. The absorption and fluorescence spectra of BER are mirror image with usual stokes' shift (see Fig. 2). We have confirmed no geometrical rearrangements or excited-state reactions for BER' s excited state by observing similar spectral features of BER upon changing BER concentrations, solutions temperatures and excitation wavelengths [24]. So, the fluorescence enhancement and the blue shift of BER after addition of Q[7] are probably explained by two aspects. The result of the ^{1}H NMR demonstrated that the isoquinoline ring of BER was enclosed in the cavity of Q[7], indicating that the Q[7] provides a less polar interior cavity and more protective hydrophobic micro-environment to accommodate the fluorophore, which should decrease the non-radiative deactivation pathways [24]. The other aspect, where the encapsulated BER reduced the rotational freedom of molecule, will reduce the opportunity for BER to collide with molecules in the solution [26]. In short, the proposed structure of the 1:1 inclusion complex would reduce the polarity of the BER fluorophore and the rotational freedom of the molecule, both by the hydrophobic interaction with the Q[7] interior wall and by shielding it from water molecules. The reduction in the polarity and rotational freedom of the molecule will lead to an increase in the energy gap between the excited

Table 1
Effect of interference (tolerance error ± 5.0%).

Interference	Tolerance (mol L^{-1})	Relative error (%)
K^+	1.5×10^{-3}	−3.36
Na^+	1.5×10^{-3}	−1.95
Ca^{2+}	3.0×10^{-4}	−2.65
Mg^{2+}	1.8×10^{-3}	−2.45
Zn^{2+}	3.0×10^{-3}	−4.82
Fe^{2+}	3.0×10^{-5}	−4.67
Polyethylene glycol	6.0×10^{-3}	0.56
Gelatin	1.5×10^{-4}	2.35
Methyl cellulose	9.0×10^{-3}	−3.48
Sodium carboxymethyl cellulose	1.2×10^{-3}	−0.42
Mannitol	6.0×10^{-3}	3.60
Sorbitol	6.0×10^{-3}	−1.38
Gum acacia power	1.2×10^{-3}	0.24
Lactose	9.0×10^{-3}	2.73
Sodium acetate	6.0×10^{-4}	−0.64
Casein	6.0×10^{-3}	−3.38

Table 2
Analytical characteristic compared with other spectrofluorimetry reported.

Methods	Medium	Linear range ($\mu g\,mL^{-1}$)	LOD ($ng\,mL^{-1}$)
Using 1,4-bis(1,3-Benzoxazol-2-yl)benzene (BBOB) as sensing material [28]	BBOB optode membrane	5.44–22.7	4435.2
Spectrofluorimetry with surfactant [29]	SDS solution	0.168–13.44	50.4
Resonance Rayleigh scattering with Fluorescence dyes [30]	Aqueous solution	0–1.68	14–215
Flow-injection analysis couples with liquid–liquid extraction [19] aqueous solution	Sodium perchlorate	0.001344–0.336	0.27
Using butylated-β-cyclodexin as sensing material [26]	PVC membrane	0.148–7.43	29.74
Using porphyrin-metalloporphyrin as sensing material [31]	PVC membrane	0.278–208.2	
Using supramolecular interaction of ethylenediamine linked β cyclodextrin dimer [32]	Aqueous solution	0.0128–10.0	3.6
The proposed method	Aqueous solution	0.00743–11.2	4.2

and ground state, result in emission enhancement and a blue shift [24].

3.5. Influence of interferences

The influence of the commonly used tablet excipients and the main constituents of serum on the quantitative determination of BER were investigated. The experiments were carried out by fixing the concentration of BER at $3.00 \times 10^{-6}\,mol\,L^{-1}$ in the presence of 3 equivalents of Q[7] and then recording the fluorescence intensity before and after adding the interferant to the BER-Q7 solution in $0.01\,mol\,L^{-1}$ hydrochloric acid solution (pH = 2.0). A foreign species was considered not to interfere with the measurement if the relative standard deviation caused by it was less than ±5% in the determination of the established level of BER. The results are shown in Table 1. It is clear that the determination was free from interference by the usual excipients and constituents of serum.

3.6. Analytical characteristic

Under the optimum experiment conditions, there was a linear relationship between the fluorescence intensity and the concentration of BER in the range covering from 7.43 to $11.2 \times 10^3\,ng\,mL^{-1}$ with a correlation coefficient of 0.9963. The regression equation was $\Delta F = 13.58 + 0.083$ [BER] ($ng\,mL^{-1}$). The detection limit, as defined by IUPAC [27], was determined to be $4.2\,ng\,mL^{-1}$ according to the formula $C = KS_0/S$, where the value of K was taken as 3, the standard deviation 0.116 was obtained from a series of 11 reagent blanks, and S was the slope of the standard curve. Compared with the other spectrofluorimetric method without the use of Q[7] [19,26,28–32], the proposed method has advantages, such as high sensitivity, wide linear range and also without any need for an extraction process (Table 2).

Table 3
Determination of berberine chloride in serum.

Sample no.	Added ($mol\,L^{-1}$)	Found ($mol\,L^{-1}$) Mean ± S.D.[a,b]	Recovery (%)	R.S.D.[c] (%)
1	8.00×10^{-7}	$(7.56 \pm 0.03) \times 10^{-7}$	94.50	0.40
	5.00×10^{-6}	$(5.32 \pm 0.05) \times 10^{-6}$	106.2	0.94
	8.00×10^{-6}	$(8.22 \pm 0.03) \times 10^{-6}$	102.8	0.36
2	8.00×10^{-7}	$(9.25 \pm 0.05) \times 10^{-7}$	115.7	0.54
	5.00×10^{-6}	$(5.13 \pm 0.05) \times 10^{-6}$	102.6	0.97
	8.00×10^{-6}	$(7.83 \pm 0.03) \times 10^{-6}$	97.87	0.38

Sample 1 serum was not deproteinized with acetonitrile.
Sample 2 serum was deproteinized with acetonitrile.
[a] Mean of three determinations.
[b] S.D.: standard deviation.
[c] R.S.D.: relative standard deviation.

3.7. Determination of BER in serum

The procedure for serum sample analysis was taken from Ref. [33]. Varying amounts of BER in the presence of 3 corresponding equivalents of Q[7] were added to the different kinds of diluted (25-fold) serum samples. Serum samples were divided into two groups; one was not deproteinized with acetonitrile and the other was mixed with acetonitrile according to the volume ratio of 1:2 to remove protein. The results of the recovery of BER are given in

Table 4
Determination of berberine chloride in commercial tablets.

Pharmaceutical preparation	Berberin of tablet ($mg\,tablet^{-1}$)				
	Label claim	Proposed method		Pharmacopoeia method	
		Mean ± S.D.[a,b]	R.S.D.[c] (%)	Mean ± S.D.[a,b]	R.S.D.[c] (%)
Berberine hydrochloride tablets	100	100.1 ± 0.94	0.94	104.9 ± 0.99	0.95
Fu fang huang lian su tablets	30	29.85 ± 0.36	1.22	29.83 ± 0.47	1.58

[a] Mean of six determinations.
[b] S.D.: standard deviation.
[c] R.S.D.: relative standard deviation.

Table 5
Determination of berberine chloride in urine.

Sample no	Added ($mol\,L^{-1}$)	Determination value ($mol\,L^{-1}$) Mean ± S.D.[a,b] (%)	Found ($mol\,L^{-1}$)	Recovery
1	–	$(13.87 \pm 0.76) \times 10^{-7}$	–	–
2	–	$(12.06 \pm 0.34) \times 10^{-7}$	–	–
3	–	$(11.58 \pm 0.41) \times 10^{-7}$	–	–
1	7.00×10^{-7}	$(20.57 \pm 0.25) \times 10^{-7}$	6.70×10^{-7}	95.71
1	14.00×10^{-7}	$(27.42 \pm 0.29) \times 10^{-7}$	13.55×10^{-7}	96.78
1	28.00×10^{-7}	$(41.11 \pm 0.51) \times 10^{-7}$	27.24×10^{-7}	97.29

[a] Mean of four determinations.
[b] S.D.: standard deviation.

Table 3. As can be seen, the proposed method can be used for the determination of BER with satisfactory recoveries of 94.50–115.7% and there was no interference from the serum constituents.

4. Application

4.1. Determination of BER in tablets

The samples were prepared according to the method described in reference [34]. Twenty tablets, with their sugarcoating peeled off, were finely powdered and the powder thoroughly mixed. An accurately weighed quantity of the powder equivalent to 6 mg of BER was dissolved in about 150 mL of boiling water, and added 1 mL 3 mol L^{-1} hydrochloride acid. The cooled solution with the residue was transferred to a 250 mL volumetric flask, diluted to mark with doubly distilled water, shaken thoroughly and equilibrated at room temperature for 15 min. A 10 mL sample of the mixture was centrifuged for 10 min. 2 mL of centrifugate and 2 mL of 2.00×10^{-4} mol L^{-1} Q[7] were transferred to a 25 mL flask and diluted with 0.01 mol L^{-1} hydrochloric acid solution. This solution was used for analytical determination. The results (Table 4) showed that the concentration of BER in commercial tablets determined by the proposed method was in good agreement with that claimed by the label and the pharmacopoeia method [35], indicating that the proposed method has high sensitivity, selectivity and accuracy.

4.2. Determination of BER in urine samples

Three healthy male volunteers participated in the study. Each volunteer took 200 mg of BER given in the form of two tablets of berberine hydrochloride. No other medication was taken during the experiments, which was confirmed by urine analyses. Food and (nonalcoholic) beverage intake was not regulated to obtain practical conditions within the experiments. According to Ref. [36], urine samples were collected after 3 h oral administration. 1 mL urine sample and 2 mL 2.00×10^{-4} mol L^{-1} Q[7] were transferred to a 10 mL flask and diluted to mark with 0.01 mol L^{-1} hydrochloric acid solution. This solution was used for analytical determination. Furthermore, one of urine samples was added with BER at different concentration levels to test in the recovery studies of BER. The results are summarized in Table 5 and show good recoveries, indicating that the proposed method is simple and accurate.

5. Conclusion

Based on the enhancement of the fluorescence intensity of BER, a spectrofluorimetric method for the determination of BER in aqueous solution in the presence of Q[7] has been developed. The supramolecular interaction of BER and Q[7] has been studied by spectrofluorimetry. The results showed that Q[7] reacted with BER to form a 1:1 complex with a apparent association constant of 2.07×10^6 L mol^{-1}. The possible interaction model of the inclusion complex was determined from ^{1}H NMR data, in which the guest BER was incorporated inside the hydrophobic cavity of the host Q[7] using the isoquinoline ring part of the guest molecule. The linear range of the method was from 7.43 to 11.2×10^3 ng mL^{-1} with a detection limit of 4.2 ng mL^{-1}. The method for the determination of the real samples was simple, precise and sensitive.

Acknowledgements

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