Electronic Supplementary Material (ESI) for RSC Advances.

Electronic supplementary information (ESI)

Molecularly imprinted solid phase extraction in an efficient analytical protocol for indole-3-methanol determination in artificial gastric juice

Dorota Klejn, Piotr Luliński, Dorota Maciejewska*

Department of Organic Chemistry, Faculty of Pharmacy, Medical University of Warsaw,

Banacha 1, 02-097 Warsaw, Poland

* Corresponding author.

E-mail address: dorota.maciejewska@wum.edu.pl (D. Maciejewska).

Section S.1 Preparation of polymers and simulated pre-polymerization systems

Briefly, the appropriate template, the functional monomer – allylamine, and the selected cross-linker were dissolved in the porogen, carbon tetrachloride. A volume of 1.5 mL of the porogen to 1 mL of sum of the monomer and the cross-linker were put into a thick-walled glass tubes. *Notice*: Due to safety reasons the neccessary precautions should be made while working with carbon tetrachloride. The molar ratio of the template to the functional monomer and the cross-linker was equal to 1:4:20. Next, the initiator (AIBN) was added. The homogeneous solutions were purged with nitrogen for ca. 5 min and then the glass tubes were sealed. Subsequently, the polymerization was carried out under a nitrogen atmosphere for 24 h at 64 ^{o}C in thermostatic bath. After the synthesis, the polymers were ground, sieved and fine particles were removed by decantation. Next, the template was removed from the polymer with continuous extraction using methanol in a Soxhlet apparatus (24-36 h, 100 mL) and the process was controlled by HPLC-UV (if it was necessary, the additional washing step containing a 1 % acetic acid in methanol was carried out). Finally, the particles were dried at elevated temperature (60 ^{o}C, 6 h) and were left in exicator for further analysis. As a control, the non-imprinted polymers were prepared and treated in the same way, except that the template molecule was omitted from the polymerization step.

The so-called ‘false’ polymerization was carried out in order to monitor the template transformations during the imprinting process. The selected template (I3C or DIM), the porogen and the initiator were put into the vial but the monomer and the cross-linker were not added. The same amounts of each reagent were used in experiments. The solutions were purged with nitrogen, sealed and incubated at 64 ^{o}C by thermostatic bath for 1 h. Then, the solutions was cooled to room temperature and filtered through 0.45 μm membranes. Then, the aliquot of 20 μL was collected and diluted prior to HPLC-UV analysis.

Section S.2 Preparation and handling of stock solutions

The stock solutions of I3C, DIM, IAA, I3E, ICA, IAL were prepared by weighting the appropriate amount of each compound and dissolving it in dimethyl sulfoxide to obtain the concentration of 10 mmol L^{-1}, and were stored in the dark at lowered temperature. The standard solutions were prepared prior to use by dilution of the stock solutions with methanol – water (85:15 v/v) to obtain the required concentrations.

Section S.3 Calculation of binding parameters

The binding capacities (B, μmol g^{-1}) of MIPs and NIPs were calculated according to equation (1):

$$B = \frac{(c_i - c_f)V}{m} \quad (1)$$

followed by the calculation of distribution coefficients (K_D, L g^{-1}) for MIPs and NIPs, according to equation (2):

$$K_D = \frac{(c_i - c_f)V}{c_f m} \quad (2)$$

where V represents the volume of the solution (L), c_i represents the initial solution concentration (μmol L^{-1}), c_f represents the solution concentration after adsorption (μmol L^{-1}) and m is the mass of particles (g). The IF/AF for $_{\mathbf{IND}}$MIP**,** $_{\mathbf{I3C}}$MIP**,** and $_{\mathbf{DIM}}$MIP (series **E** or **P**) were calculated according to equation (3):

$$\mathrm{IF / AF} = \frac{K_D\ (\mathrm{MIP})}{K_D\ (\mathrm{NIP})} \quad (3)$$

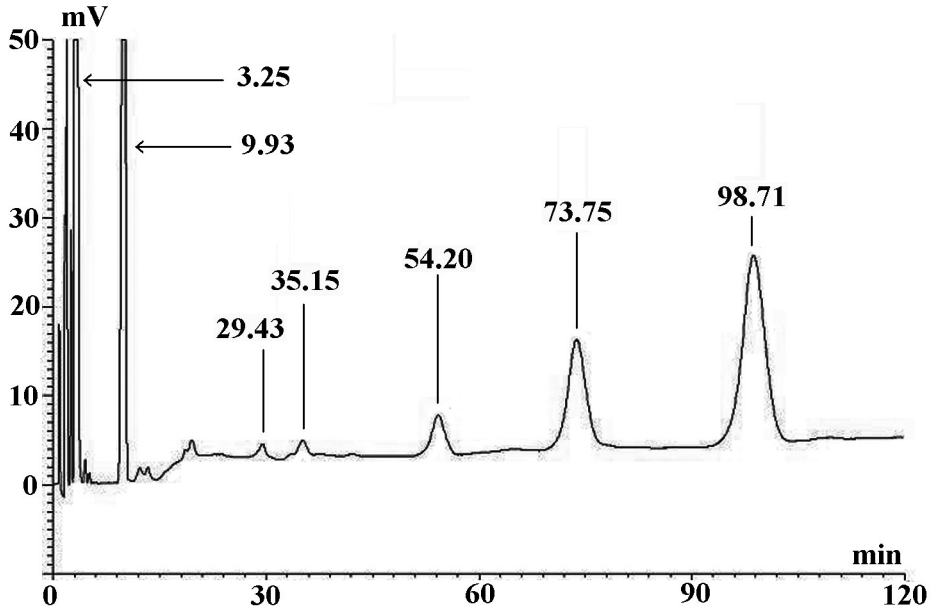

Fig. S1. Chromatogram of products fraction after the synthesis of indole cyclic trimer and indole cyclic tetramer. The retension time of: indole-3-carboxaldehyde is 3.25, 3,3'-diindolylmethane is 9.93. The assigment of peaks of indole linear trimer – 35.15, indole cyclic trimer – 73.75, and indole cyclic tetramer – 98.71 min based on literature data.[17,31] The peaks at 29.43 and 54.20 min are unidentified.

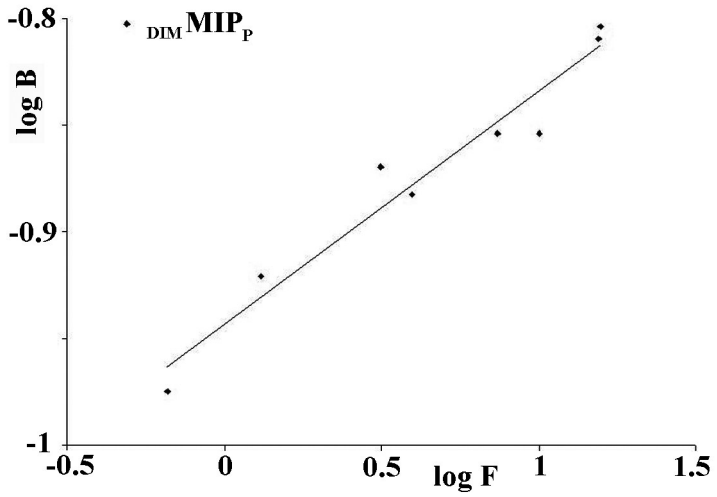

Fig. S2. The Freundlich isotherm of I3C on $_{DIM}MIP_P$ polymer.

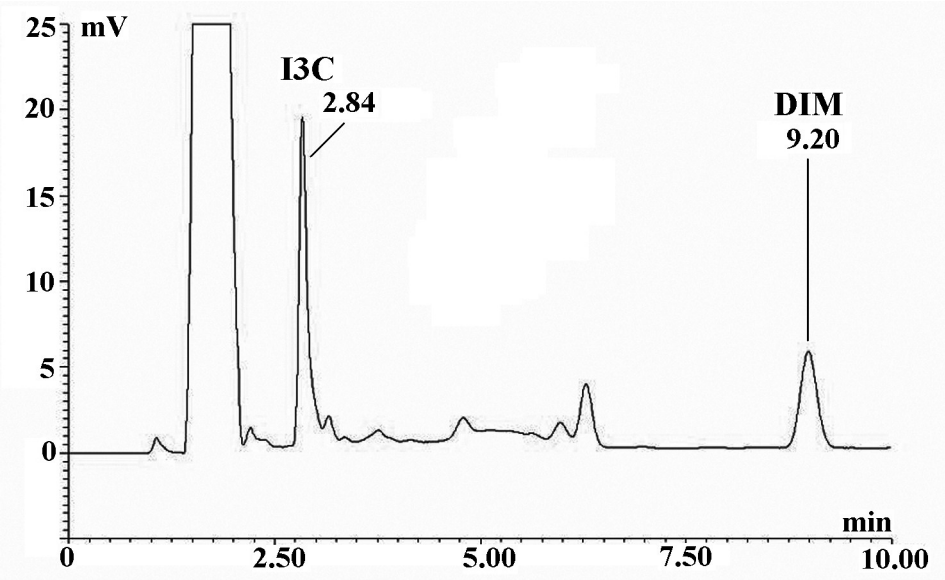

Fig. S3. Chromatogram of the fractions collected during the template removal step from $_{DIM}MIP_{P}$.