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Asymmetric amplification in amino acid sublimation involving racemic compound to conglomerate conversion†

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Supporting Information

Experimental Section

Sublimation protocol.

A hot stirring plate is set and kept constant to 430 °C. Then a screw caped bottle or flask (1000-mL volume) is placed and heating continues for 3 min. Such conditions do create an optimized temperature gradient.

Both DL-valine (0.03 g) and L-valine (0.02 g) (initial imbalance: 40% *ee*) or D-Valine (0.028 g) and L-Valine (0.012 g) (initial imbalance: 40% *ee*)were ground in a mortar and placed in the above-mentioned caped bottle. The sample was stirred for a few seconds to ensure maximum contact with the hot bottom. A sudden sublimation took place and a dense cloud of condensing valine microcrystals was observed for approximately 2 min. Such crystals were deposited on the inner walls and covered most of the flask with the exception of the hotter base (because of the high temperature on the plate). At this stage, analysis of an aliquot by powder X-ray diffraction revealed the complete transformation into a conglomerate system.

Once deposited, valine crystals underwent a slow sublimation (*ca*. 10 min) ascending the sublimation line up to 1/4 height. This process occurred without any further condensation from the inner atmosphere; the sublimed material was deposited on pre-existing crystals only.

After completion, the system was cooled to room temperature and crystals were dissolved in 0.01 M HCl, and the enantiomeric excess (whole sample) analyzed by HPLC. Alternatively, to assess the gradient-like distribution of *ees*, the solid was divided into three horizontal bands, carefully collected (inverted flask) to avoid contamination of the different fractions, dissolved in 0.01 M HCl, and used in HPLC analysis.

The same protocol and amounts of valine crystals apply to experiments conducted in open flasks.

Amino acid derivatization and chiral HPLC analysis.

D and L valine concentrations and ratios were quantified using HPLC analyses. Samples were rehydrated using 750 µl/mg 0.01 *M* HCl and were then injected into an Agilent HPLC-1100, equipped with a fluorescence detector. Excitation and emission wavelengths were programmed at 335 nm and 445, respectively. A Hypersil BDS C18 reverse-phase column (5 µm; 250 x 4 mm i.d.) was used for the analysis.

The derivatization takes place before injection by mixing the sample (2 µl) with the pre-column derivatization reagent (2.2 µl), which comprised 260 m*M* isobutyryl-L-cysteine (chiral thiol) and 170 mM *o*-phtaldialdehyde, dissolved in 1.0 *M* potassium borate buffer solution at pH 10.4. Eluent A consisted of 23 m*M* sodium acetate with 1.5 m*M* sodium azide and 1.3 m*M* EDTA, adjusted to pH 6.00 with 10 *M* sodium hydroxide and 10% acetic acid. Eluent B was HPLC-grade methanol and eluent C consisted of HPLC-grade acetonitrile. A linear gradient was performed at 1.0 ml/min and 25°C, from 95% eluent A and 5% eluent B upon injection to 76.6% eluent A, 23% eluent B, and 0.4% eluent C at min 31 and then at 1.07 ml/min to 56.6% eluent A, 40% eluent B, and 3.4% eluent C at min 73.

Retention times: L-Val, 61.5 min; D-Val, 68.5 min.