# Ligand Chromatography on Asymmetric Complex-forming Sorbents as a New Method for Resolution of Racemates

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*Summary* Chromatography on an asymmetric complexating sorbent in the presence of transition-metal ions provides a method for quantitative resolution of racemates that are capable of forming complexes.

COMPLEXATION of a racemic mixture of multidentate ligands[1] is a highly stereoselective process, on account of the dense packing of the ligands into the complex co-ordination spheres and because the chelating ligand has several bondings participating in the formation of the asymmetric complex.

We have been working on the application of the stereoselective effects of such complex formation, in combination with chromatographic procedures, to the resolution of racemates. In such a process, one ligand (the optically active one) should be rigidly attached to a stationary phase, while the other (racemic) ligand should be able to move with the mobile phase. The metal atom forming the complex may be combined with either ligand. The important point is that the complex generated should be kinetically labile, *i.e.* readily decomposed and re-formed. On the basis of these concepts we have developed a novel procedure for the resolution of racemates of compounds capable of producing complexes. The procedure consists of the use of stereoselective phenomena involved in the formation of the complexes, and is effected by ligand chromatography on an asymmetric complexating stationary phase in the presence of transition-metal ions.

We have carried out the chromatographic separation of a number of racemates on asymmetric sorbents containing L-amino-acid ionogenic groups[2] in the presence of complex-generating metal ions. We have achieved exceptionally high stereoselectivity of sorption on these sorbents for a great number and variety of optically active compounds. In some cases, quantitative separation of optical isomers was possible during one chromatographic cycle.

An asymmetric sorbent was prepared by treatment of a chloromethylated styrene-*p*-divinylbenzene (0·8%) co-polymer with L-proline.[2] It had an analytical exchange capacity of 1·96 mg-equiv. per g.

12 g of this sorbent (granular diameter 0·03–0·05 mm) was treated with 0·1N-$CuSO_4$ solution in 1N-ammonia (taken in excess), washed with water, and loaded into a column of diameter 9 mm and length 50 cm.

A small column containing 2 g of the same sorbent (not treated with $Cu^{2+}$) was placed below the main column in order to trap the copper ions eluted.[3] A solution of DL-proline (0·5 g) in water (5 ml) was introduced into the main column and the system was washed with water (10 ml/h). Evaporation of the portion of the eluate which gave a positive reaction with Ninhydrin afforded L-proline (0·25 g), $[\alpha]_D^{20}$ −80·5° (*c* 1, $H_2O$). Next, 1N-ammonia solution (100 ml) was passed through the column; evaporation of the eluate afforded optically pure D-proline (0·25 g).

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