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## Note

# Enantiomer separation of polyols and amines by enantioselective gas chromatography

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Polymers of the polysiloxane type can be modified to yield highly enantioselective chiral stationary phases for capillary gas chromatography (GC)[1–4]. After formation of suitable derivatives, enantiomeric mixtures of a large number of compound classes have been separated[5]. Chiral polymers derived from XE-60 by hydrolysis of the cyano groups in the side chains and by chemical binding of L-valine-(*S*)- or (*R*)-α-phenylethylamide can be used for the separation of amino acids[3], amino alcohols[6], α- and β-hydroxy acids[7,8], N-methylamino acids[8], chiral alcohols[9], amines[7], ketones[10], pentoses[11] and hexoses[6,12,13].

This work describes the enantiomer separation of trifluoroacetylated polyols, which have never been separated before, and an improved separation of trifluoroacetylated amines.

## EXPERIMENTAL

### *Materials*

D- and L-arabinitol were obtained from P-L Biochemicals (Milwaukee, WI, U.S.A.), D-mannitol from E. Merck (Darmstadt, F.R.G.). L-Mannitol and D- and L-fucitol were prepared by reduction of the corresponding sugars with $NaBH_4$ in methanol solution. The secondary amines used in this investigation are all commercially available.

### *Formation of derivatives*

The fully trifluoroacetylated derivatives of polyols were prepared by heating a 100-μg sample in 200 μl of dichloromethane and 100 μl of trifluoroacetic anhydride for 20 min at 100°C in Wheaton Micro Vials (Wheaton Scientific, Millville, NJ, U.S.A.). After removal of excess of reagent in a stream of dry nitrogen, the derivatives were dissolved in 200 μl benzene and used for GC.

### *Gas chromatography*

XE-60–L-valine-(*S*)-α-phenylethylamide and the diastereoisomeric (*R*)-α-phenylethylamide were prepared as described earlier[4]. Fused-silica capillary columns with these phases were supplied by Chrompack (Middelburg, The Netherlands). Glass capillary columns were prepared as described previously[14]. A Carlo Erba Model 2101 gas chromatograph with hydrogen as carrier gas was used.

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## RESULTS AND DISCUSSION

Polyols are widespread natural compounds derived from aldoses or ketoses by reduction. In some cases (ribitol, xylitol, galactitol), chirality is lost upon reduction and a symmetrical polyol is formed. Arabinitol and mannitol, however, are optically active and the separation of the enantiomers may be of interest. D-Arabinitol has recently been identified as a metabolite of *Candida albicans* and *Candida tropicalis* in leukaemia patients with fungal septicaemia[15]. The enantiomers of most of the common pentose and hexose isomers have been separated as trifluoroacetylated derivatives or trifluoroacetylated methyl glycosides[6,11–13]. This is a relatively rare case of chiral recognition with nitrogen-free compounds, because enantioselectivity has mainly been attritubed to the formation of association complexes caused by hydrogen bonding. Other effects, for instance dipole–dipole interaction[16] or the rigidity of the cyclic carbohydrate structures, may also contribute to enantioselectivity. However, the separation of some trifluoroacetylated polyols as shown in Figs. 1 and 2 clearly demonstrates that cyclic structures are not necessary for chiral recognition. As in the case of carbohydrates, trimethylsilylated polyols are not separated; the acyl residues seem to be essential.

The complementary properties of the two phases XE-60–L-valine-(*S*)-α-phenylethylamide and its diastereomer XE-60-L-valine-(*R*)-α-phenylethylamide are not only of advantage for the separation of polyols and carbohydrates. The (*R*)-phase also

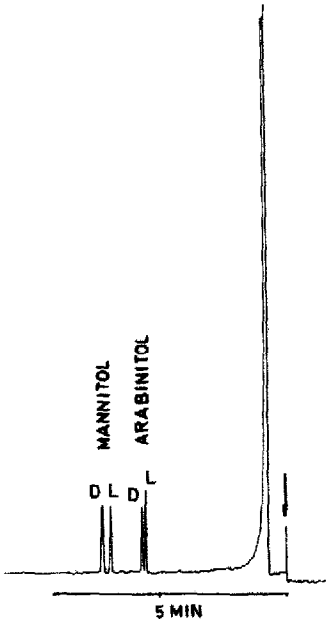



Fig. 1. Enantiomer separation of arabinitol and mannitol trifluoroacetates on a 15-m Pyrex glass capillary column coated with XE-60-L-valine-(*R*)-α-phenylethylamide. Column temperature: 145°C. Carrier gas: 0.7 bar hydrogen.

Fig. 2. Enantiomer separation of fucitol (6-deoxygalactitol) trifluoroacetate on a 50-m fused-silica capillary column coated with XE-60-L-valine-(*S*)-α-phenylethylamide (Chrompack). Column temperature: 140°C. Carrier gas: 1.2 bar hydrogen.

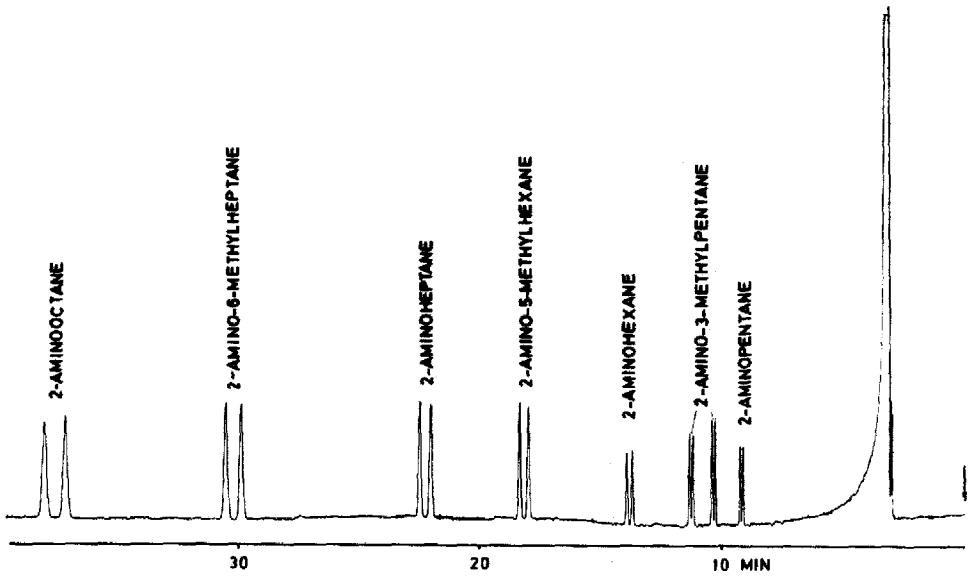


Fig. 3. Enantiomer separation of chiral amines as trifluoroacetyl derivatives on a 50-m fused-silica capillary column coated with XE-60-L-valine-(*R*)-α-phenylethylamide. Column temperature: 120°C. Carrier gas: 1.2 bar hydrogen.

displays high enantioselectivity for trifluoroacetylated amino alcohols[6] and chiral amines as shown in Fig. 3. The separation factors of 1.01–1.025 are sufficient for baseline separation. The (*R*)-enantiomers are eluted first. An equivalent separation of amines has recently been obtained on the (*S*)-phase after the formation of isopropylureido derivatives[7], but the higher volatility of trifluoroacetyl derivatives may be more convenient in practice.

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