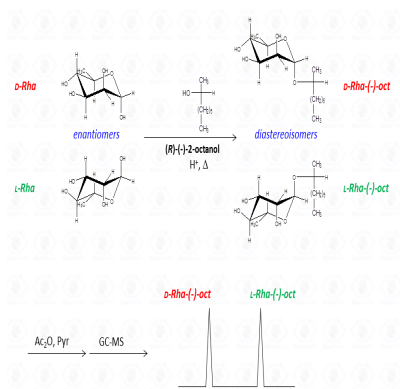




Acetylated Octyl Glycosides

Description

Analysis of these derivatives is a way to assess the absolute configuration of a monosaccharide unit. In nature, many monosaccharides such as rhamnose, fucose, or arabinose, occur with both D and L configurations. None of the three methods discussed so far, is capable of assessing the absolute configuration. For example in the case of acetylated methyl glycosides of D and L rhamnose, methylglycosides are enantiomers and they cannot be separated on the chromatographic column usually used in GC-MS and they are eluted as a single peak.

The common way to resolve the enantiomeric mixture is to transform it in a mixture of diastereoisomers (Fig. 34) by using an optically pure alcohol (as 2-octanol or 2-butanol) that can be resolved by the GC-MS chromatographic conditions used.

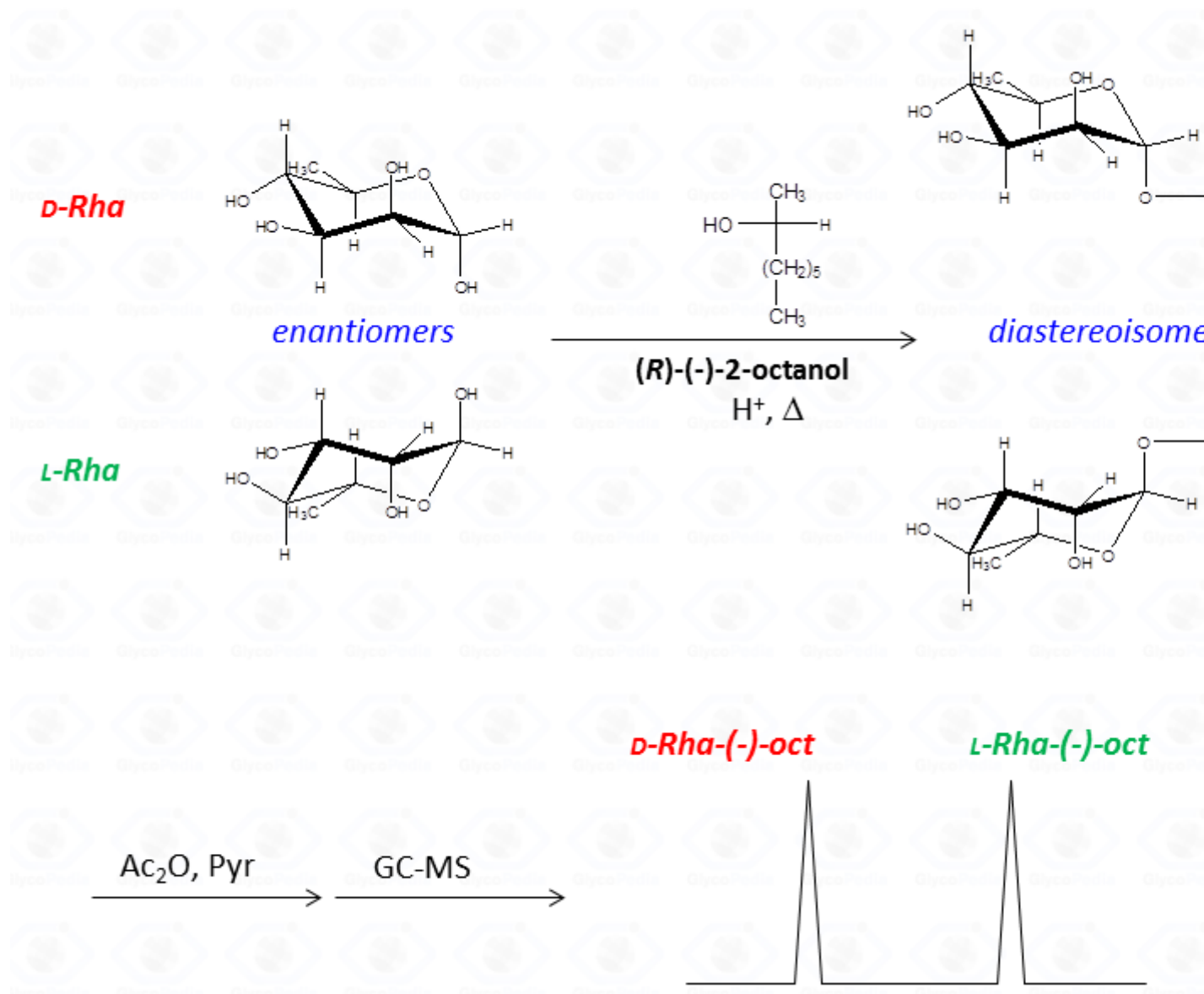


Figure 34: Scheme of solvolysis of an enantiomeric mixture of rhamnose using chiral (*R*)-(-)-2-octanol.

Recognition of the two diastereoisomers is performed by comparing their retention time with that of the reference compounds. With regard to standard preparation only one of the two possible configurations of the monosaccharide is used, whereas it is necessary to use the optically active alcohol in both its racemic and enantiomeric pure form.

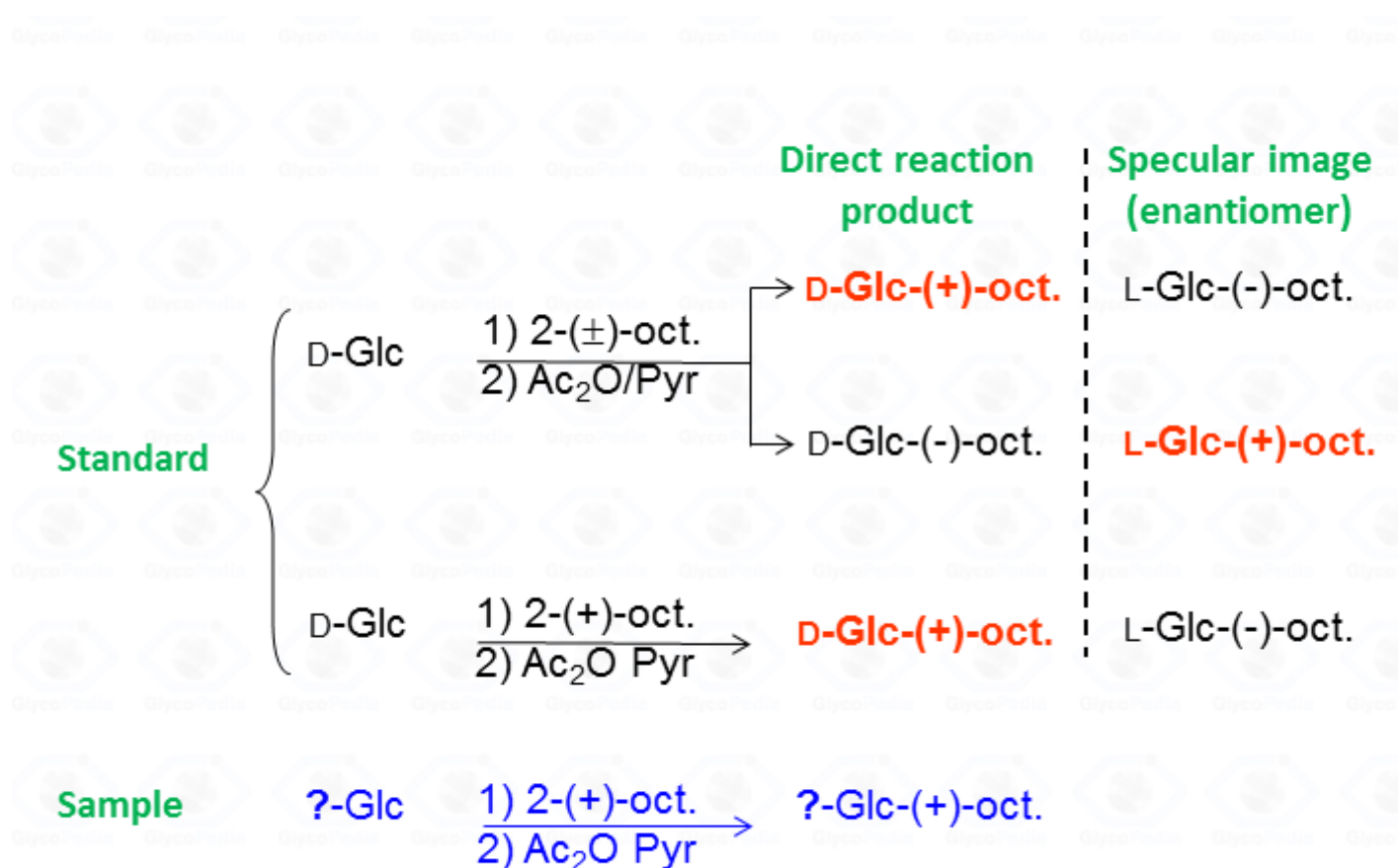


Figure 35: Strategy used to prepare 2-octylglucoside standards.

Following the example given in Fig. 35, the reaction between D-glucose and racemic octanol yields to sets of diastereoisomers, D-Glc-(+)-oct and D-Glc-(-)-oct. Each set differs from the other for the absolute configuration of octanol. Within each set, glucosides can be either α or β and either in the pyranose or furanose form. Each component of the two sets displays the same EI-MS spectrum (Fig. 36) which is very similar to that of the corresponding acetylated methyl glycosides (Fig. 13). Actually, the fragmentation rules discussed for methylglycosides apply to octylglycosides and the main difference between the spectra of the two derivatives is given by the signals originated by the fragmentation of the 2-octanol lipophilic tail.

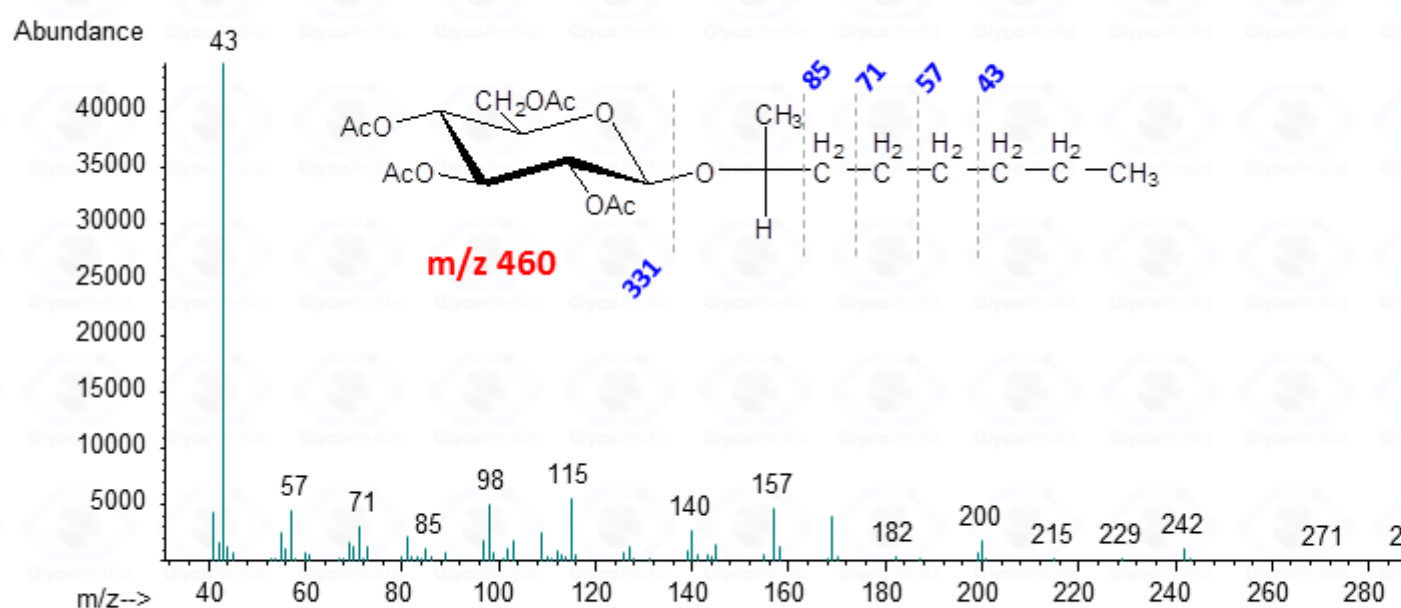


Figure 36: EI-MS spectrum of 2-octylglucoside.

The diastereoisomeric mixture is resolved by the GC-MS column and the chromatographic profile presents a series of peaks, for which the attribution to a specific set is accomplished by comparison with the chromatogram resulting from the glucoside reacted with the enantiopure 2-octanol. It must be noted that by this procedure, isomers from L-glucose are not produced but their retention time are deduced indirectly: in fact, retention time of D-Glc-(+)-oct corresponds to that of its enantiomer, L-Glc-(-)-oct, and that of D-Glc-(-)-oct is the same of L-Glc-(+)-oct. By these considerations, the assignment of the chromatogram reporting both D- and L-2-octylglucosides retention times, is performed, so that determination of the absolute configuration of an unknown sample is made possible. The rationale shown for 2-octylglycosides applies to 2-butylglycoside, as well. Both types of derivatives are equally performing so that the choice of the chiral alcohol depends more on which is more routinely used in the laboratory.

In conclusion, both 2-octyl- and 2-butylglycosides are efficient derivatives to elucidate the absolute configuration of a monosaccharide, providing that the appropriate reference is available. These derivatives are stable and can be stored for several years and their EI-MS spectra resemble closely those of the parent methyl glycosides.

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