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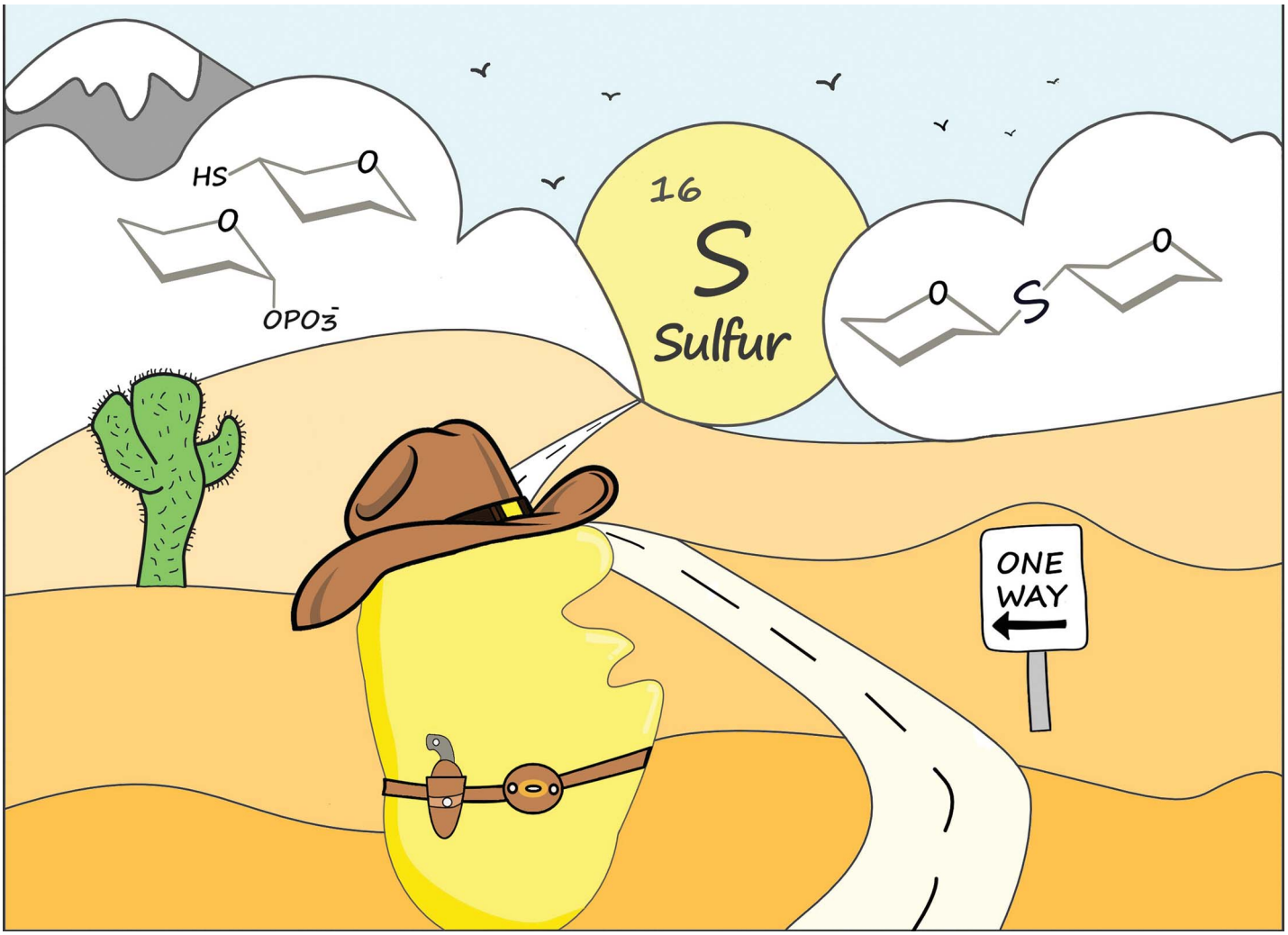

Showcasing research from Dr Martin Fascione's laboratory, Department of Chemistry, University of York, UK, and Prof Gavin Miller's laboratory, School of Chemical and Physical Sciences, Keele University, UK.

Reverse thiophosphorylase activity of a glycoside phosphorylase in the synthesis of an unnatural Manβ1,4GlcNAc library

β-Mannosides are ubiquitous in nature, with diverse roles in many biological processes. Notably, Manβ1,4GlcNAc a constituent of the core *N*-glycan in eukaryotes was recently identified as an immune activator, highlighting its potential for use in immunotherapy. Here we present a chemoenzymatic strategy that affords a series of novel unnatural Manβ1,4GlcNAc analogues using a carbohydrate phosphorylase enzyme. We also pioneer "reverse thiophosphorylase" enzymatic activity, favouring the synthesis of longer glycans by catalysing the formation of a phosphorolysis-stable thioglycoside linkage, an approach that may be generally applicable to other phosphorylases.

As featured in:

See Gavin J. Miller, Martin A. Fascione *et al.*, *Chem. Sci.*, 2023, **14**, 11638.

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