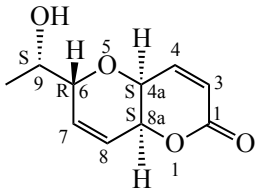
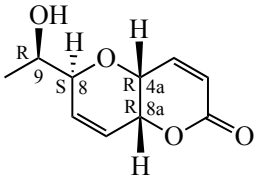
C-Glycosides: Synthesis of Enantiomeric (-)-Diplopyrones

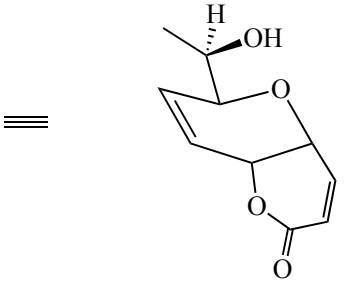
(+)-Diplopyrone is a toxin isolated from the fungus *Diplodia mutilaa*, and it is responsible for cork oak decline in parts of southern Europe, where the disease has a large and negative economic and environmental impact. We are investigating the asymmetric synthesis of enantiomeric (-)-diplopyrone, its desmethyl analog, and isomeric diplopyrones using *C*-glycosides, which are compounds in which the *exo*-glycosidic carbon-oxygen bond of a carbohydrate has been replaced with a carbon-carbon bond. Viewing (-)-diplopyrone as a "*C*-glycoside problem" means that the required stereochemistry at C6 and C9 will need to be established by synthesis and that the ring junction chirality centers will come from the starting carbohydrate. A partial retrosynthesis of one of targets currently being pursued in our lab is shown below.

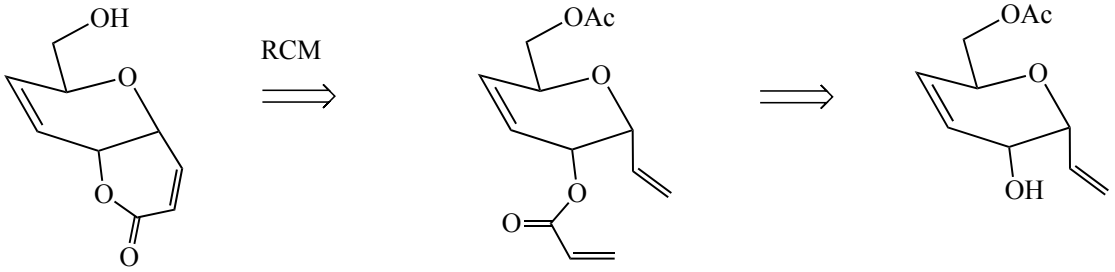


(+)-Diplopyrone-(natural)



(-)-Diplopyrone





Relevant publications from our lab:

P. P. Vagadia,[#] S. P. Brown,[#] D. L. Zubris, N. A. Piro, W. J. Boyko, W. S. Kassel, and R. M. Giuliano, "Stereoselective Synthesis of 7-Deoxy-1,2;3,4-Di-*O*-Isopropylidene-D-*glycero*-α-D- *galacto*-Heptopyranose," *Carbohydrate Chemistry: Proven Methods* **2015**, *3*, 245-253.

V. Basava, B. Flores, M. Giovine, T. Licisyn, K. Walck, W. Boyko, and R. M. Giuliano, "Addition Reactions of Benzenesulfinic Acid with Glycals and 1,2-Dibromosugars," *Journal of Carbohydrate Chemistry* **2008***, 27*, 389-400.