Regio- and Stereoselective Fungal Oxyfunctionalisation of Limonenes

Rüdiger Kaspera^a, Ulrich Krings^a, Michael Pescheck^b, Dieter Sell^b, Jens Schrader^b, and Ralf G. Berger^{a,*}

- ^a Zentrum für Angewandte Chemie der Universität Hannover, Institut für Lebensmittelchemie, Wunstorfer Str. 14, D-30453 Hannover, Germany. Fax: +49-511-762-4547. E-mail: rg.berger@lci.uni-hannover.de
 - b Karl-Winnacker-Institut der DECHEMA e.V., Theodor-Heuss-Allee 25, D-60486 Frankfurt am Main, Germany
 - * Author for correspondence and reprint requests

Z. Naturforsch. **60 c**, 459–466 (2005); received November 23/December 23, 2004

Selective transformations of limonene by asco- and basidiomycetes were investigated. On the shake flask scale, *Penicillium citrinum* hydrated R-(+)-limonene to α -terpineol [83% regioselectivity (rs), more than 80 mg l⁻¹ product yield], and *Gongronella butleri* catalysed the terminal oxidation to yield perillyl alcohol (60% rs, 16 mg l⁻¹). On the laboratory bioreactor scale, *Penicillium digitatum* produced a peak concentration of 506 mg α -terpineol l⁻¹ in the fed-batch mode, equivalent to a theoretical yield of 67%, and no volatile by-products were

found. Fusarium proliferatum transformed R-(+)-limonene enantiospecifically to cis-(+)-

carveol (98.6% ee, more than 35 mg l⁻¹ product yield) and S-(-)-limonene predominantly to trans-(-)-carveol (96.3% ee). Pleurotus sapidus selectively dehydrogenised the accumulating trans-(-)-carveol to the corresponding enantiopure R-(-)-carvone. The results show that a careful selection of strain and bioprocess parameters may improve both the yield and the optical purity of a desired product.

Key words: Limonene, Oxyfunctionalisation, Stereoselectivity