Aerobic Oxidation of Isosorbide and Isomannide employing TEMPO/Laccase

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Supporting information

1. Materials and Methods

Chemicals

Substrates **6-8** as well as product-references and TEMPO were purchased from Sigma Aldrich; Substrates **1** and **2** and corresponding mono- and diketones were obtained from Evonik Industries AG; TEMPO-derivatives were obtained from BASF Schweiz AG. All other chemicals were purchased from Sigma Aldrich or Fluka and used as received. Solvents were obtained from Roth.

Enzymes

Enzymes were purchased from Sigma-Aldrich.
Since the provider does not give the amino sequence of the enzymes, the alignment below is based on two published sequences.[1,2]

Laccase from *Agaricus bisporus*, NCBI: AAA17035, GI: 166334, 520 amino acids
Laccase from *Trametes versicolor*, NCBI: AAC49828.1, GI: 1172163, 519 amino acids

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Alignment:
47.7% identity in 520 residues overlap; Score: 1106.0; Gap frequency: 4.8%

FVLVAACISSVLADTKTFNFDLVNTRLAPDGFERDTVVINGEFPGTLVQVNKGDSVRIPV
FVTLALVARSLAAIGPVASLVVANAPVSPDGFLRDAIVVNGVVPSPLITGKKGDRFQLNV
**  *    *  *          *    **** **  * **  *  *    ***     *

NNKLTSSTMRRSVSIHWHGFFQARTSGQDGPAFVNQCPQPPNTTFTYEFSVADESGTFWY
VDTLTNHSMLKSTSIHWHGFFQAGTNWADGPAFVNQCPIASGHSFLYDFHVPDQAGTFWY
   **   *  * ********** *   **********      * * * * *  *****

HSHLSTQYCDGLRGAFVVYDPEDPLGHLYDVDDETTVITLAEWYHVLAPDINNEFFSSGI
HSHLSTQYCDGLRGPFVVYDPKDPHASRYDVDNESTVITLTDWYHTAAR--LGPRFPLGA
************** ****** **    **** * *****  ***  *       *  *

IPVQDSGLINGKGRFNGGPETPFAVVNVEQGKRYRFRVIAISCRPFFTFSVDNHNLTFME
----DATLINGLGRSASTPTAALAVINVQHGKRYRFRLVSISCDPNYTFSIDGHNLTVIE
    *  **** **    *    ** **  *******   *** *  *** * ****  *

ADSVEHDPVEIQNVDIYAAQRVSVILNANQPVDNYWMRAPMTGGNPDRNPNLNISLTLAI
VDGINSQPLLVDSIQIFAAQRYSFVLNANQTVGNYWVRANPNFGTVGFAGGIN----SAI
 *     *       * **** *  ***** * *** **    *        *     **

LRYKGAPEVEPTTVNVPGH-KLLDQEMHPIAQEG-PGKLGDGPPDKHITLNIAQPNAPFF
LRYQGAPVAEPTTTQTTSVIPLIETNLHPLARMPVPGSPTPGGVDKALNLAFNFNGTNFF
*** ***  ****        *     ** *    **    *  **   *        **

DINGISYISPTVPVLLQILSGAKRPEDVLPSEQIFFVPKNSLIEVNIPGEGA-----HPF
-INNATFTPPTVPVLLQILSGAQTAQDLLPAGSVYPLPAHSTIEITLPATALAPGAPHPF
 **      *************    * **       *  * **   *         ***

HLHGHNFDVVLASNDDTFNFVNPPRRDVY----PINGGNTTFRFFTDNPGAWFLHCHIDW
HLHGHAFAVVRSAGSTTYNYNDPIFRDVVSTGTPAAGDNVTIRFQTDNPGPWFLHCHIDF
***** * **      * *   *  ***     *  * * * ** ***** ********
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HLEAGLAIVFAEAPEDNVSGPQSQITPQDWLDLCPEYNAI
HLDAGFAIVFAE---DVADVKAANPVPKAWSDLCPIYDGL
** ** ******   *          *  * **** *
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2. Oxidation under O_2-pressure

Since the reaction is oxygen dependent, increased oxygen pressure was expected to accelerate the reaction. However, running the reaction under an atmosphere of air and under pure oxygen pressure of 2 bar gave essentially the same conversions as tested for substrate **1**, **2**, **6** and **7**.

3. Analytics

Determination of Conversion

The determination of the conversion was carried out on a Varian 3900 gas chromatograph equipped with FID and a 14 % cyanopropyl-phenyl phase capillary column (J&W Scientific DB-1701; 30 m x 0.25 mm, 0.25 µm film), with an injection and detection temperature of 220 and 250 °C respectively, and a 20:1 split ratio.

Temperature program for **1** and **2**: 80°C hold 2 min, 10°C/min to 160°C, hold for 10 min.

H 6) S1 Achiral GC-FID: Retention times of substrates, intermediates and products.

substrate	retention times [min]		
	diol	monoketone	diketone
1	14.8	16.2 (*exo*-hydoxyketone) 12.9 (*endo*-hydroxyketone)	11.9
2	11.2	12.9 (*endo*-hydroxyketone)	11.9

Alcohols and ketones were identified by co-injection with commercially available reference material.

GC/MS analyses were carried out on an Agilent Technologies 7890A GC-System equipped with FID and an Agilent Mass Selective Detector 5975C and a HP 5 capillary column (30m, 0.25mm, 0.25µm film). Helium was used as carrier gas.

Temperature program for **3** and **5**: 40°C hold 2 min, 20°C/min to 180°C, hold for 1 min.

Table S2 Achiral GC-MS: Retention times of substrates and products.

substrate	retention times [min]	
	alcohol	ketone
6	9.1	9.5
7	9.3	9.5
8	5.4	5.6

Alcohols and Ketones were identified by co-injection with commercially available reference material.

4. Computational Details

All structures were optimized using the MP2/cc-pVDZ procedure[3,4] and characterized as true minima by frequency calculations, followed by MP2/cc-pVTZ single point calculations. Solvent effects (aqueous solution) were taken into account by the IEF-PCM model.[5] All structures resulting from staggered conformation of the hydroxy groups were included. Relative energies of oxidations of alcohols were obtained by isodesmic reaction with acetone to yield the ketone and 2-propanol, e.g. **1** + acetone → **3** + 2-propanol. Similarly, relative energies of hydrates were obtained from the reaction with water, e.g. **3** + H_2O → **3**(H_2O)

Gibbs free energies were obtained by the standard rigid rotor-harmonic oscillator approximations. Frequencies and zero point energy are unscaled. All calculations were done by the Gaussian 03 program.[6]

References

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