**New chemical transformations of pinolidoxin and the origin of its artifacts**

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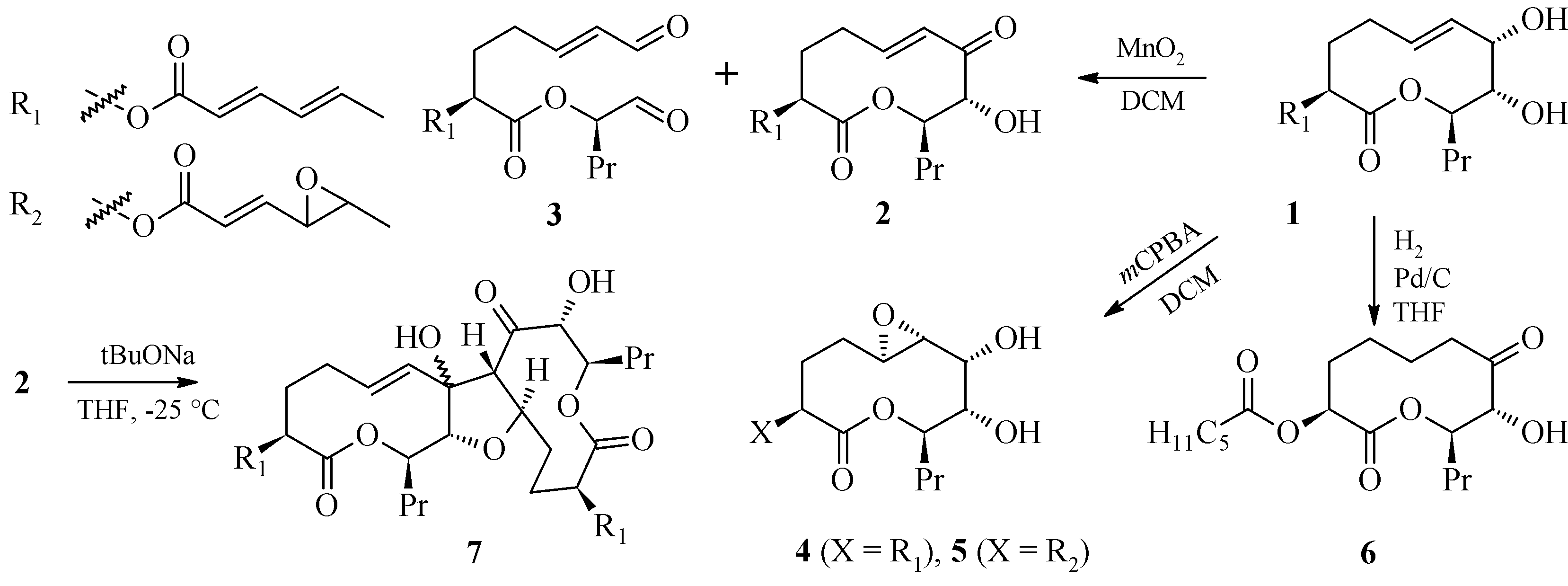
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The ten-membered lactones (nonenolides) represent significant potential as models for the development of pesticides with low-toxic activity for non-target organisms. Pinolidoxin **1**, first isolated from *Ascochyta pinodes*, is a representative of this extensive class due to its substantial phytotoxic activity [1]. In our study **1** was biotechnologically obtained from pea’s pathogen *Didymella sp*. Further chemical modification of **1** allows to obtain semi-synthetic derivatives as potential herbicides with mechanisms of action different from those of commonly used agrochemicals. Although there are several derivatives of **1** being published up to date chemical stability and reactivity of these type substances were not investigated. During the search for new phytotoxic derivatives of pinolidoxin **1** its unusual chemical behavior was discovered and described in our work.

Scheme 1. Chemical modification of pinolidoxin



The oxidation of compound **1** using MnO2 gives C7-oxidized alpha-ketol **2** alongside with dialdehyde **3** formed by C7-C8 cleavage with the yield ratios of 35 and 44% respectively. The epoxidation **1** with m-CPBA involves two regions: lactone cycle and sorbic acid residue of the molecule. The major 5,6-epoxide **4** was isolated in 56% yield. It is noteworthy that ring epoxidation gives only 5R,6R diastereomers (NMR NOESY confirmed). Hence previously reported absolute configuration of substance **4** isolated from *A. pinodes* and *P. bellidis* should be revised [1-2]. Furthermore, compounds **2** and **4** appeared to be the products of pinolidoxin **1** autoxidation (HPLC-MS confirmed) thus previously reported epoxide **4** suspected to be an artifact rather than compound of natural origin. Hydrogenation of **1** in a presence of Pd/C occurs with allylic alcohol moiety transposition into the saturated ketone **6**. Interestingly, under sodium tert-butoxide compound **2** undergoes dimerization through Baylis-Hillman type reaction into dimer **7** with 62 % yield. Structures and composition of derivatives **2**-**7** was confirmed by spectral methods (1D/2D NMR and ESI-MS).

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**References**

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