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ORIGINAL PAPER

Aminohydroxylation of divinylcarbinol and its application to the synthesis of bicyclic hydroxypyrrolidine and aminotetrahydrofuran building blocks

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Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

Aminohydroxylation of prochiral divinylcarbinol and subsequent Pd(II)-catalysed oxy-/amidocarbonylation of aminopentenediols is reported. The method was applied to the preparation of useful building blocks for syntheses of cytotoxic jaspines and glycosidase inhibitor DLX-homologues. The key intermediates, tetrahydrofuranolactones (L-*arabino-II*) and pyrrolidinolactones (L-*arabino-IX* and L-*xylo-IX*), were prepared in a short 2-step sequence from divinylcarbinol.
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Introduction

Pachastrissamine (jaspine B, *I*) (Fig. 1), the first naturally occurring anhydrophytosphingosine derivative, is a metabolite isolated from the Okinawa marine sponge *Pachastrissa* sp. (Kuroda et al., 2002). The Debitus research group reported isolation of the same natural product from a different marine sponge *Jaspis* sp. (Ledroit et al., 2003). In anti-cancer assays, this novel sphingosine derivative proved to be the most potent compound against the A549 human lung carcinoma cell line isolated from the *Jaspis* genus. The combination of potent biological properties and relatively straightforward molecular structures has led to the development of a number of its synthetic preparations (Llaveria et al., 2011; Passiniemi & Koskinen, 2011; Yoshimitsu et al., 2011; Srinivas Rao & Venkateswara Rao, 2011; Urano et al., 2010; Salma et al., 2010; Inuki et al., 2009, 2010; Yoshimitsu et al., 2010; Vichare & Chattopadhyay, 2010; Canals et al., 2009; Enders et al., 2008; Abraham et al., 2008, and the articles cited in their review). The biological activities of numerous synthetic analogues and epimers have also been prepared and tested.

Previous investigations in our laboratory have demonstrated that the Pd(II)-catalysed oxy- and amidocarbonylation of unsaturated polyols and amino polyols represent an efficient entry to *cis*-fused 5-membered bicyclic lactones (Gracza et al., 1991; Jäger et al., 1997; Hümmer et al., 1997). This methodology has been used as the key step in a number of natural product syntheses (Gracza & Jäger, 1992, 1994; Dixon et al., 1999; Babjak et al., 2002, 2005; Karlubíková et al., 2011). Here we report on a further application of this versatile methodology to encompass the asymmetric syntheses of the 3,6-anhydro-2,5-dideoxy-5-R-amino-L-*arabino*-1,4-hexonolactones (L-*arabino-IIa*, L-*arabino-IIb*, *N*-R-2,3,6-trideoxy-3,6-imino-L-*arabino*-1,4-hexonolactones (L-*arabino-IXa*, L-*arabino-IXb*), and *N*-R-2,3,6-trideoxy-3,6-imino-L-*xylo*-1,4-hexonolactones (L-*xylo-IXa*, L-*xylo-IXb*).

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