Synthesis of 2-deoxybrassinosteroids analogs with 24-nor, 22(s)-23-dihydroxy-type side chains from hyodeoxycholic acid

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Natural brassinosteroids are widespread in the plant kingdom and it is known that they play an important role in regulating plant growth. In this study, two new brassinosteroid analogs with shorter side chains but keeping the diol function were synthesized. Thus, the synthesis of 2-deoxybrassinosteroids analogs of the 3?-hydroxy-24-nor, 22,23-dihydroxy-5?-cholestane side chain type is described. The starting material is a derivative from hyodeoxycholic acid (4), which was obtained with an overall yield of 59% following a previously reported five step route. The side chain of this intermediate was modified by oxidative decarboxylation to get a terminal olefin at the C22-C23 position (compound 20) and subsequent dihydroxylation of the olefin. The resulting epimeric mixture of 21a, 21b was separated and the absolute configuration at the C22 carbon for the main product 21a was elucidated by single crystal X-ray diffraction analysis of the benzoylated derivative 22. Finally, lactonization of 21a through a Baeyer-Villiger oxidation of triacetylated derivative 23, using CF3CO3H/CHCl3 as oxidant system, leads to lactones 24 and 25 in 35% and 14% yields, respectively. Deacetylation of these compounds leads to 2-deoxybrassinosteroids 18 and 19 in 86% and 81% yields. Full structural characterization of all synthesized compounds was achieved using their 1D, 2D NMR, and HRMS data.

2-deoxybrassinosteroids

Brassinosteroid analogs

Hyodeoxycholic acid

Short side chain

Synthesis

brassinosteroid

deoxycholic acid

hyodeoxycholic acid

lactone

decarboxylation

hydroxylation

nuclear magnetic resonance spectroscopy

oxidation reduction reaction

stereoisomerism

synthesis

X ray crystallography

Brassinosteroids

Chemistry Techniques, Synthetic

Crystallography, X-Ray

Decarboxylation

Deoxycholic Acid

Hydroxylation

Lactones

Magnetic Resonance Spectroscopy

Oxidation-Reduction

Stereoisomerism