

The Total Synthesis of Salvinolone

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Salvinolone **1** is synthesized in seven steps starting from the readily available enone **3**.

Based on our previous studies on the syntheses of tricyclic diterpenes we now report the total synthesis of salvinolone **1**¹ which is a natural abietane-type diterpene.

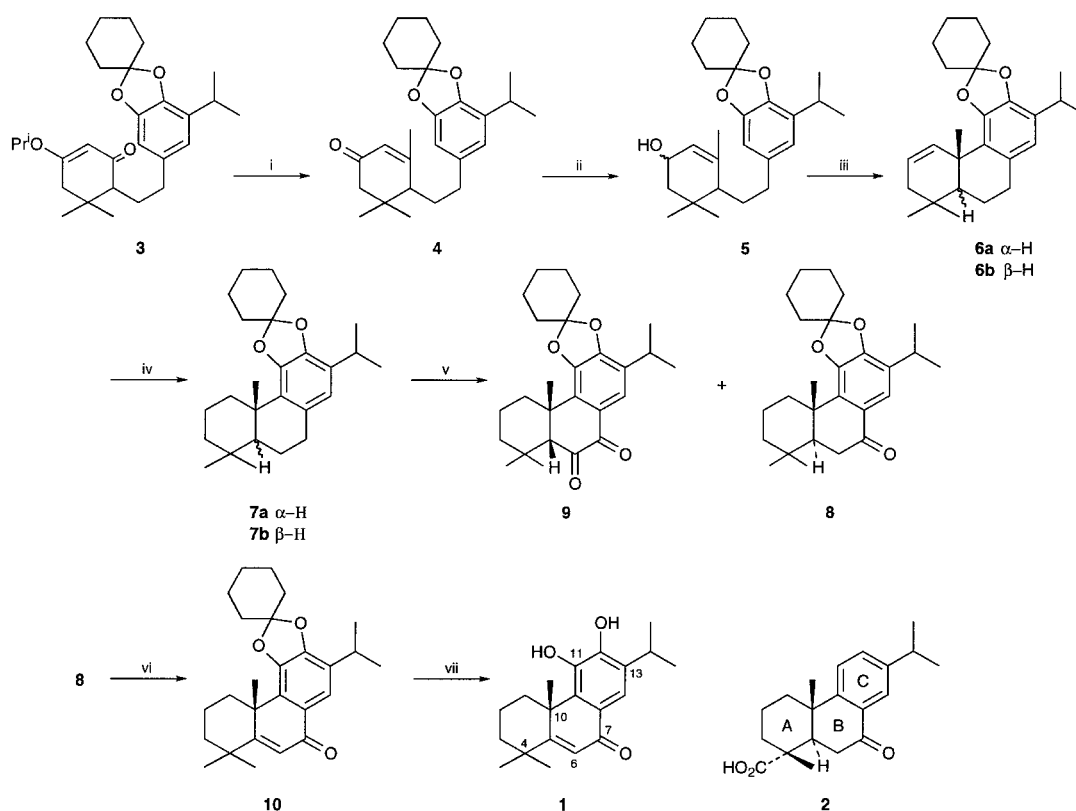
As shown in Scheme 1, the known³ enone **3** was methylated by MeLi to afford compound **4** which was reduced by NaBH₄ in the presence of CeCl₃·7H₂O⁴ to afford the corresponding unsaturated alcohol **5**. Stereoselective cyclization of **5** with a solution of phosphorus pentoxide in methanesulfonic acid⁵

Techniques used: IR, ¹H NMR, MS, column chromatography, TLC

References: 11

Schemes: 3

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Scheme 1 Reagents and conditions: i, MeLi (100%); ii, NaBH₄, CeCl₃·7H₂O (80%); iii, P₂O₅, MeSO₃H (95%); iv, H₂, 5% Pd–C (100%); v, CrO₃–HOAc–H₂O (22 and 70%); vi, DDQ, MeOH (87%); vii, BBr₃ (33%)

gave an inseparable mixture of diastereoisomers. A 3:1 ratio of *trans*-isomer **6a** to *cis*-isomer **6b** was shown in the ¹H NMR spectrum. The stereochemistry of the *cis*-fused AB rings in **6b** was indicated by characteristic signals at 0.85 ppm.⁶ Catalytic hydrogenation of **6** by 5% Pd–C afforded a mixture of **7a** and **7b** which was directly oxidized with CrO₃–HOAc–H₂O.⁷ In this oxidation, the *trans*-fused **7a** was converted into the monoketone **8** and the *cis*-fused **7b** was converted into the diketone **9**. Then, **8** was refluxed with DDQ¹⁰ in methanol to give α,β-unsaturated ketone **10**. Conversion of **10** into the target compound **1** was achieved by deprotection with BBr₃.¹¹

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