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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 known[3] enone **3** was methylated by MeLi to afford compound **4** which was reduced by $NaBH_4$ in the presence of $CeCl_3{\cdot}7H_2O$[4] to afford the corresponding unsaturated alcohol **5**. Stereoselective cyclization of **5** with a solution of phosphorus pentoxide in methanesulfonic acid[5] 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 CrO_3–HOAc–H_2O.[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 DDQ[10] in methanol to give α,β-unsaturated ketone **10**. Conversion of **10** into the target compound **1** was achieved by deprotection with BBr_3.[11]

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

References: 11

Schemes: 3

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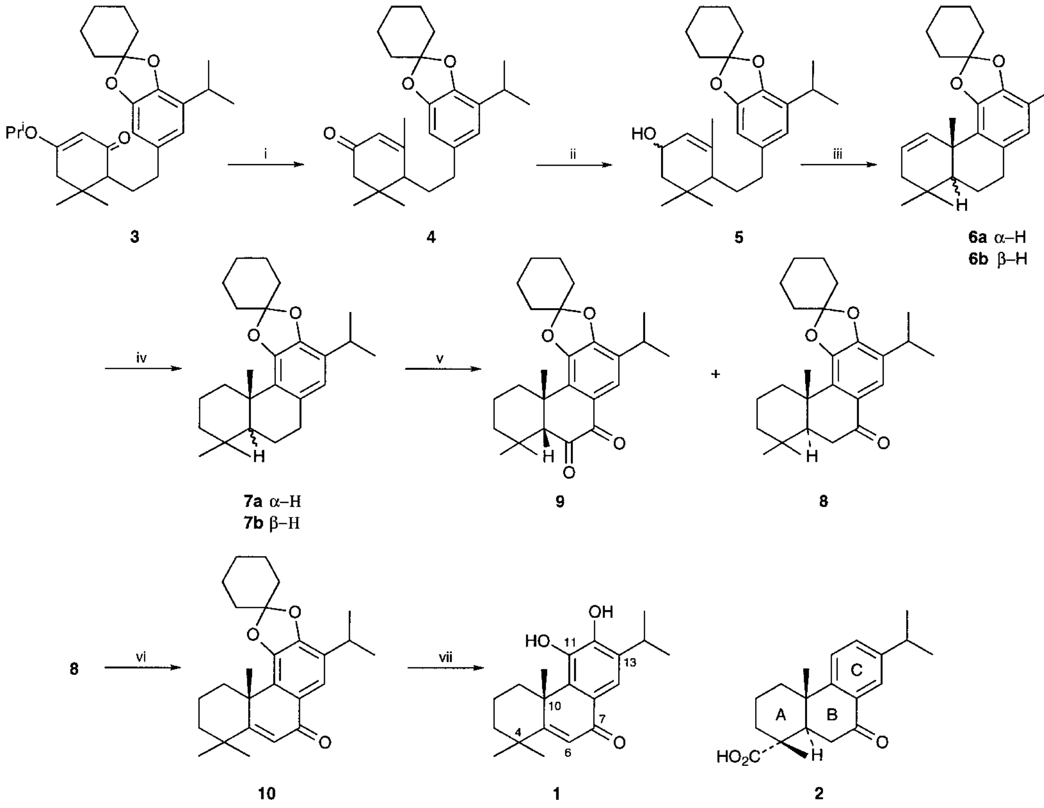

Scheme 1 *Reagents and conditions:* i, MeLi (100%); ii, $NaBH_4$, $CeCl_3{\cdot}7H_2O$ (80%); iii, P_2O_5, $MeSO_3H$ (95%); iv, H_2, 5% Pd–C (100%); v, CrO_3–HOAc–H_2O (22 and 70%); vi, DDQ, MeOH (87%); vii, BBr_3 (33%)

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