

First Asymmetry Synthesis and Stereochemistry of Glutinone

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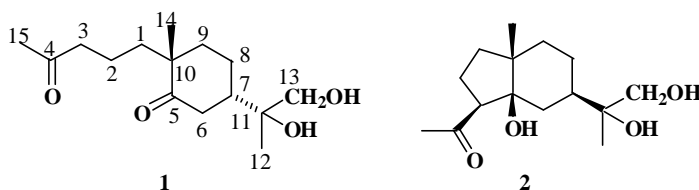
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Abstract: The first asymmetry synthesis of glutinone and its three diastereoisomers were carried out in 8 steps and the stereochemistry of this natural product was given out.

Keywords: Asymmetry synthesis, asymmetry dihydroxylation, sesquiterpenoid.

Recently, two new sesquiterpenoids, glutinone **1** and lucinone **2**, were isolated from the aerial parts of traditional medicine *Jasania glutinosa*¹ by Castillo and co-workers³. However, Castillo only gave the structure of glutinone, but its absolute configuration is still unknown. Here, we wish to report our stereoselective construction of the four possible diastereoisomers (**9a**, **9b**, **9c** & **9d**) of glutinone. By comparing the spectrum data with that of the natural product, we outlined the stereochemistry of glutinone **1**.

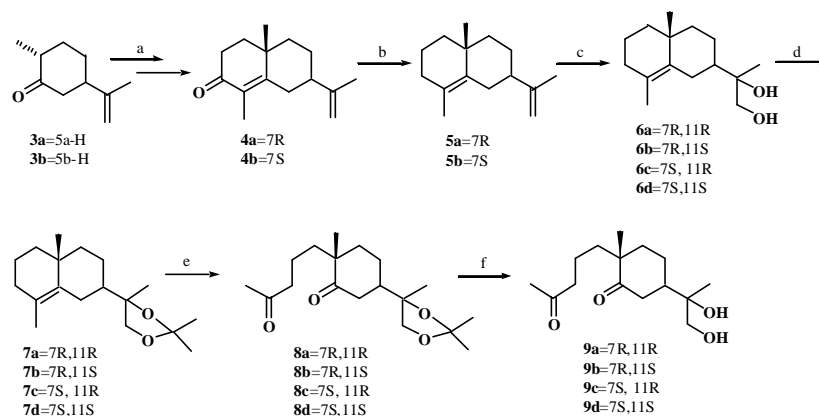
Scheme 1



Starting from (+)-dihydrocarvone **3a**, we got α -cyperone **4a** in three steps⁴. Deoxygenation⁵ of **4a** with AlCl_2H gave the diene **5a**. According to Sharpless' method⁶, **5a** was treated with commercially available AD-mix- β in *t*-BuOH- H_2O to afford diols **6a** in 90% yield. After **6a** was protected by its acetonide, which was oxidized by O_3 to give dione **8a**. Deprotection in 60% HOAc, one of the four possible diastereoisomers of glutinone **9a** was obtained. Again, **9b** was obtained in the similar way when AD-mix- α was used. Next, same reactions were carried out from (-)-dihydrocarvone **3b**, we got the other two isomers **9c** & **9d**. Confirmed by the spectrum data with that of the natural product, so we found that **9a** has the absolute configuration as shown for the natural compound **1**⁷.

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Scheme 2



Reagents and conditions: a. ref 4, 70% ; b. AlCl_3H , ether, 92%; c. AD-mix- α & β , $\text{Bu}^i\text{OH-H}_2\text{O}$, 0°C , over 85%; d. cat. TsOH, acetone, 88%; e. O_3 , Py, CH_2Cl_2 , 56%; f. 60% HAc, reflux, 90%.

Acknowledgments

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Reference and Notes

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7. Compound **9a**: $[\alpha]_D^{17} = +64.3$ (c=1.0, CHCl_3); ^1H NMR (CDCl_3 , 400M): δ ppm 1.11 (s, 3H, CH_3 -14), 1.12 (s, 3H, CH_3 -12), 2.11 (s, 3H, CH_3 -15), 3.40, 3.55 (AB quartet, 2H, J=10.7 Hz, CH_2 -13); ^{13}C NMR (CDCl_3 , 400M): δ ppm 18.28, 20.49, 22.34, 23.23, 30.01, 36.42, 37.34, 38.91, 44.35, 45.23, 47.39, 68.24, 73.90, 209.24, 215.77; MS (EI, 70ev), m/z : 252 ($\text{M}^+ - \text{H}_2\text{O}$).

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