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# Stereoselective Synthesis of Dehydrobaimuxinol

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### STEREOSELECTIVE SYNTHESIS OF DEHYDROBAIMUXINOL

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**ABSTRACT:** A stereoselective synthesis of dehydrobaimuxinol (1) is reported by employing an allylic oxidation as a key step.

Dehydrobaimuxinol (1), a new natural sesquiterpenoid, was isolated from *Aquilaria Sinensis* (Lour.) Golg.<sup>1</sup> This compound, as well as its naturally occurring derivatives, exhibits a number of interesting biological and pharmacological activities, such as anesthesia, muscular relaxation and analgesia<sup>1,2</sup> We now wish to report the first stereoselective synthesis of 1.

10-Epieudesm-4-ene-3, 11-diols 2 was prepared from (+) dihydrocarvone<sup>3</sup>.

The cyclization of diols 2 to  $\alpha$ -agarofuran (3) has been investigated in detail.<sup>3,4</sup> Huffman<sup>4</sup> claimed that among the more convenient procedures of the cyclization was the direct conversion of 2 to 3 upon either mild acids or Jones reagent. But in our hands the cyclization could be proceeded quickly on treatment of 2 with concentrated sulfuric acid.

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In general, oxidation of an allylic methyl group by selenium dioxide resulted in a complex mixture of oxidation products and yield was poor.<sup>5</sup> We



Reagents and conditions: a. conc.  $H_2SO_4$ , benzene, rt; b. 5% SeO<sub>2</sub>on silica gel, dioxane, reflux; c. NaBH<sub>4</sub>, MeOH, 0-25°C.

found that, by treatment with 5% selenium dioxide supported on silica gel<sup>6</sup> in dioxane, 3 was oxidized regioselectively at C-15 to afford the corresponding allylic  $\alpha,\beta$ -unsaturated aldehyde 4, a new compound, and primary alcohol 1 in a 83% combined yield. Probably when selenium dioxide is absorbed on silica gel, it would attack selectively the maximum exposed or least hindered methyl group in 3. Reduction of 4 with sodium borohydride exclusively gave 1, whose spectral data agree well with those reported.<sup>1</sup>

#### EXPERIMENTAL

#### a-Agarofuran 3

Diols 2 (120 mg) was dissolved in redistilled benzene (15 mL) and treated with conc.  $H_2SO_4$  (2 drops) at room temperature for 10 min. The pink solution was washed successively with saturated aqueous NaHCO<sub>3</sub>, water and brine prior to drying (MgSO<sub>4</sub>). The crude products were purified by silica gel chromatography (ether / petroleum ether) to give 48 mg (43%) of 3 as a colorless oil. The spectral data of 3 were identical with those of  $\alpha$ -agarofuran isolated from *Alpinia japonica*.<sup>7</sup>

### Dehydrobaimuxinol 1

(a) From 3 A mixture of 3 (44 mg) in dioxane (5 mL) and 5%  $SeO_2$  on silica gel (400 mg) was stirred at room temperature for 1 h, then heated at reflux for an additional 4 h. The cooled suspension was filtered, the filtrate

was evaporated to dryness, and the residue was dissolved in ether, washed (saturated aqueous NaHCO<sub>3</sub>, water and brine), dried (MgSO<sub>4</sub>), and finally separated by column chromatography (1 / 4, ether / petroleum ether) to afford 4 (22 mg, 48%) followed by 1 (17 mg, 35%). 1:  $v_{max}$ (film) 3380 cm<sup>-1</sup>;  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 0.94 (3H, s, C<sub>10</sub>-CH<sub>3</sub>), 1.27 (3H, s, C<sub>11</sub>-CH<sub>3</sub>), 1.38 (3H, s, C<sub>11</sub>-CH<sub>3</sub>), 4.05 (1H, J<sub>AB</sub> = 14.2Hz, 15-H), 4.25 (1H, J<sub>AB</sub> = 14.2 Hz, 15-H), 5.95 (1H, t, J = 2.9Hz, HC = C) ppm. 4:  $v_{max}$ (film) 1695cm<sup>-1</sup>;  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 0.92(3H, s, C<sub>10</sub>-CH<sub>3</sub>), 1.38 (6H, s, C<sub>11</sub>-CH<sub>3</sub>), 6.91 (1H, t, J = 2.88Hz, HC = C), 9.49(1H, s, CHO) ppm.

(b)From 4 To a well-stirred solution of 4 (15 mg) in dry methanol (2 mL) at 0°C was added slowly NaBH<sub>4</sub> (20 mg) over a period of 30 min. The mixture was then warmed to room temperature and stirred for an additional 3.5 h. The excess NaBH<sub>4</sub> was destroyed by addition of 5% aqueous HCl at 0°C, and the resulting solution was extracted with ether. The dried organic phase was concentrated to yield 14 mg (97%) of 1.

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