

First Total Synthesis of 4,5-Secoeudesmane-type and Iphionane-type Compounds — Synthesis of 4,5-Dioxo-seco- γ -eudesmol and 5 β ,11-Dihydroxyiphionan-4-one

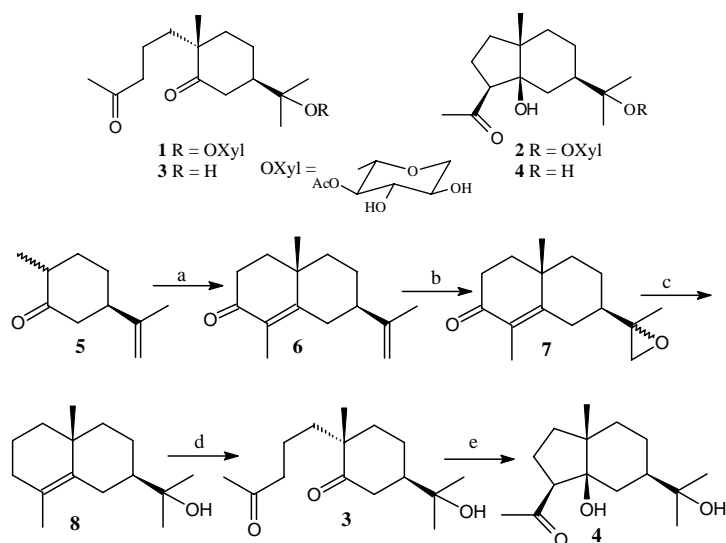
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4, 5-Secoeudesmane-type and iphionane-type compounds are sesquiterpenes with new carbon skeletons found in natural sources in recent years.¹⁻⁶ The co-occurrence of 4, 5-secoeudesmanes, iphionanes and eudesmanes as natural products suggests that 4, 5-secoeudesmanes, iphionanes most likely are generated biogenetically from eudesmanes, and iphionanes are formed biogenetically by aldol reaction of 4, 5-dioxosecoeudesmanes^{1,4,6,7}. The study on the synthesis of this two kind of new sesquiterpenes has not been reported in the literature.

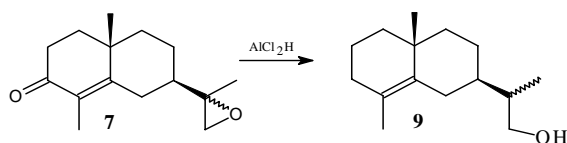
In 1987, Bohlman *et al.* reported the isolation of oxylpyranosides **1** and **2** from the North Eastern African plant *Iphiona scabra* and determination their structures by spectroscopic methods². This two compounds were also isolated from *Iphiona mutronata* by Ahmed *et al.* in 1990³. Herein, we reported the first synthesis of their aglycones **3** and **4** (scheme).

Scheme



a. ref 8; b. mCPBA, CH₂Cl₂, 0 °C, 90%; c. LiAlH₄, ether, r.t. 7h, then AlCl₂H, 0°C, 6h, 82%; d. O₃/O₂, pyridine, CH₂Cl₂, -78°C, 50%; e. *t*-BuOK, THF, -20°C, 5h, 70%.

By the published method,⁸ (+)- α -cyperone **6** was easily prepared from (+)-dihydrocarvone **5** in two steps using (R)-(+)-Phenylethylamines as chiral auxiliary. Epoxidation of **6** with mCPBA at 0°C gave epoxide **7**. Compound **7** was reduced first with LiAlH₄ and then with AlCl₂H⁹ in one pot to afford (+)- γ -eudesmol **8**¹⁰ in 80% yield. This result is remarkable, reduction of oxirane and deoxygenation at C-3 are accomplished in one step. AlCl₂H is usually used for deoxygenation of α,β -unsaturated carbonyl and allylic alcohols, and we found it also could reduce oxirane in a complementary way to LiAlH₄ to yield less substituted alcohol. Reduction of epoxide **7** only with AlCl₂H gave a epimeric mixture primary alcohol **9**. So it is necessary to cleave the oxirane in **7** first with LiAlH₄ (to give a tertiary alcohol) and then deoxygenate at C-3 by addition of AlCl₂H to the reaction mixture. Our synthetic route to (+)- γ -eudesmol is much more efficient than those described in the literature.¹¹ Ozonolysis of (+)- γ -eudesmol **8** gave 4, 5-dioxoseco- γ -eudesmol **3**. Dione **3** was treated with *t*-BuOK in THF to yield 3,11-dihydroxyiphionan-4-one **4**. The spectra data of **3** and **4** are consisted with their structure.



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References and Notes

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