The extract was washed with saturated NaCl, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexane : ethyl acetate=10 : 1) provide the desired iodohydrin as an oil (203 mg, 90%).

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11. Other Lewis acids instead of $BF_3 \cdot OEt_2$ could be used for the opening of cyclic ethers. In fact, we briefly tested this possibility with $SnCl_4$ using styrene oxide. Identical products to those shown in Table 1 were obtained, albeit in lower yields.
12. We have reported an example of iodination during our study on samarium(II) iodide-promoted reactions of epoxyalkanone hydrazones, although in this case the reactive species responsible for iodination might not be identical in nature to the reacting species for the iodination by SmI_2-benzene-HMPA and $BF_3 \cdot OEt_2$ reported here. See Kang, H.-Y.; Hong, W. S.; Lee, S. H.; Choi, K. I.; Koh, H. Y. *Synlett* **1997**, 33-34.
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Synthesis of Iridolactones *via* Stereoselective Favorskii Rearrangement: (+)-Dolicholactone, (+)-Alyxialactone, and (−)-4-*epi*-Alyxialactone

Eun Lee*, Cheol Hwan Yoon, Young Jin Lee, and Hak Joong Kim

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-742, Korea
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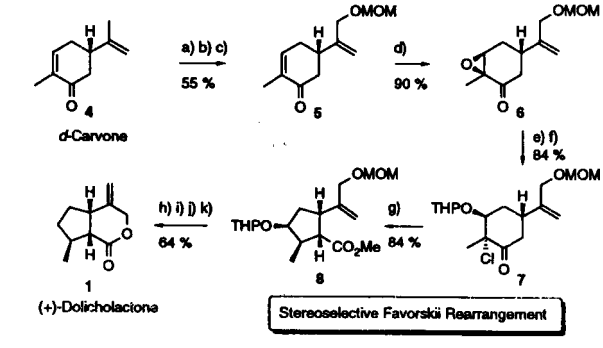
Recently, we reported expedient syntheses of (+)-dihydronepetalactone and (+)-iridomyrmecin from *d*-carvone chlorohydrin. In a key step of the synthesis, a cyclopentanecarboxylate intermediate was obtained *via* stereoselective Favorskii rearrangement.[1] This reaction is remarkable: the presence of a neighboring oxy substituent in the chloroketone substrate dictates the rate and the direction of the rearrangement. Using modified substrates, facile syntheses of a plethora of iridoid lactones[2] are possible, and this report concerns our recent efforts in the synthesis of (+)-dolicholactone (1),[3] (+)-alyxialactone (2),[4] and (−)-4-*epi*-alyxialactone (3).[4] Syntheses of these iridoid lactones have not been reported in literature.

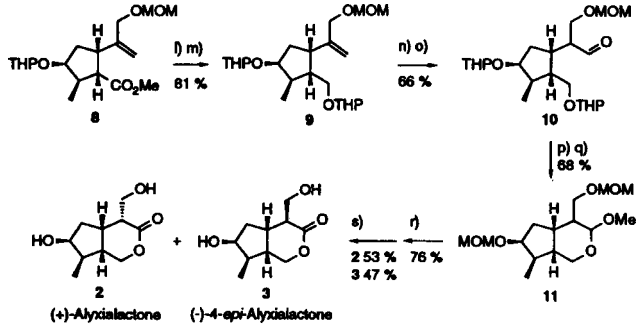
Allylic chlorination of *d*-carvone (**4**), hydroxide substitution, and protection with MOM chloride led to the preparation of the hydroxycarvone derivative **5**. The enone **5** was converted into the epoxyketone **6**, from which the chloroketone derivative **7** was obtained *via* epoxide ring opening by chloride and protection with DHP. The Favorskii rearrangement of **7** proceeded regio- and stereoselectively producing a cyclopentanecarboxylate derivative **8** in good yield (Scheme 1). (+)-Dolicholactone (**1**) was obtained from **8** *via* basic hydrolysis, MOM and THP deprotection, and radical-mediated deoxygenation.

The intermediate **8** was then used for the synthesis of **2** and **3**. It was converted into the triol derivative **9** *via* LAH reduction and DHP protection. Hydroboration with disiamylborane and oxidation of **9** yielded a mixture of epimeric primary alcohols, and they were converted into the corresponding aldehydes **10**. When **10** were treated with *p*-toluenesulfonic acid in methanol at room temperature, both THP protecting groups were removed and a mixture of bi-



a) $Ca(OCl)_2$, Dry ice, DCM-H_2O (10:1); b) K_2CO_3, NaI, H_2O, Reflux
c) MOMCl, DIPEA, cat. DMAP, DCM; d) H_2O_2, 2N NaOH, MeOH, r.t. 1 h
e) 1.5 eq. TMSCl, 1.5 eq. DMSO, MeCN, r.t. 40 min; f) DHP, cat. *p*-TsOH, DCM, r.t. 1 h
g) 1.5 eq. MeONa, MeOH, r.t. 10 min; h) aq. NaOH, Reflux
i) conc. HCl (pH 1), Reflux; j) NaH; CS_2; MeI; k) Bu_3SnH, cat. AIBN, Benzene, Reflux

Scheme 1.



l) LAH, Ether; m) DHP, DCM, cat. *p*-TsOH; n) Disiamylborane, Ether; H_2O_2, aq. NaOH
o) Swern Oxid.; p) cat. *p*-TsOH, MeOH, r.t.; q) MOMCl, DIPEA, cat. DMAP, DCM, 0 °C
r) Jones Reagent, Acetone, 0 °C; s) BCl_3, DCM, 0 °C, 30 min

Scheme 2.

cyclic methyl acetals with a secondary hydroxyl group was obtained. Jones oxidation of the corresponding MOM ethers **11** yielded a 1 : 1 mixture of epimeric lactones in 76% yield, which were separated by flash column chromatography (Scheme 2). (+)-Alyxialactone (**2**) and (−)-4-*epi*-alyxialactone (**3**) were obtained upon deprotection of the MOM groups of each isomer with boron trichloride.[5]

The present work demonstrates that regio- and stereoselective Favorskii rearrangement may be used for expedient syntheses of cyclopentanoid natural products. Further developments in this area of studies will be reported in due course.

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