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# A Unified Strategy to *ent*-Kauranoid Natural Products: Total Syntheses of (−)-Trichorabdal A and (−)-Longikaurin E

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Supporting Information

**ABSTRACT:** The first total syntheses of (−)-trichorabdal A and (−)-longikaurin E are reported. A unified synthetic strategy is employed that relies on a Pd-mediated oxidative cyclization of a silyl ketene acetal to generate an all-carbon quaternary center and build the bicyclo[3.2.1]octane framework. These studies, taken together with our previous synthesis of (−)-maoecrystal Z, demonstrate that three architecturally distinct *ent*-kauranoids can be prepared from a common spirolactone intermediate.

Plants of the *Isodon* genus, long known in Asian traditional medicine for their curative properties, have been a rich source of bioactive natural products.[1] The vast majority of the more than 600 *Isodon* diterpenoids reported to date are *ent*-kauranoids, several of which are shown in Figure 1.[2] A number

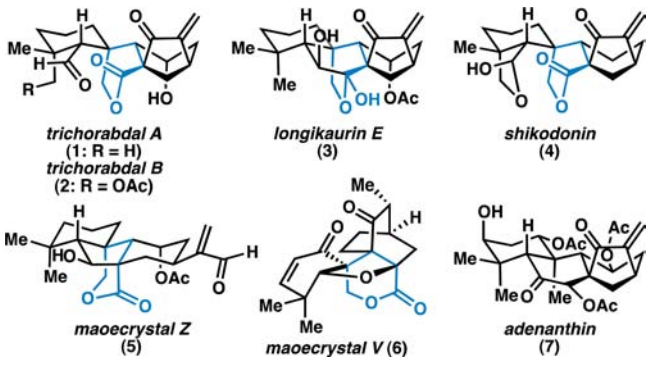
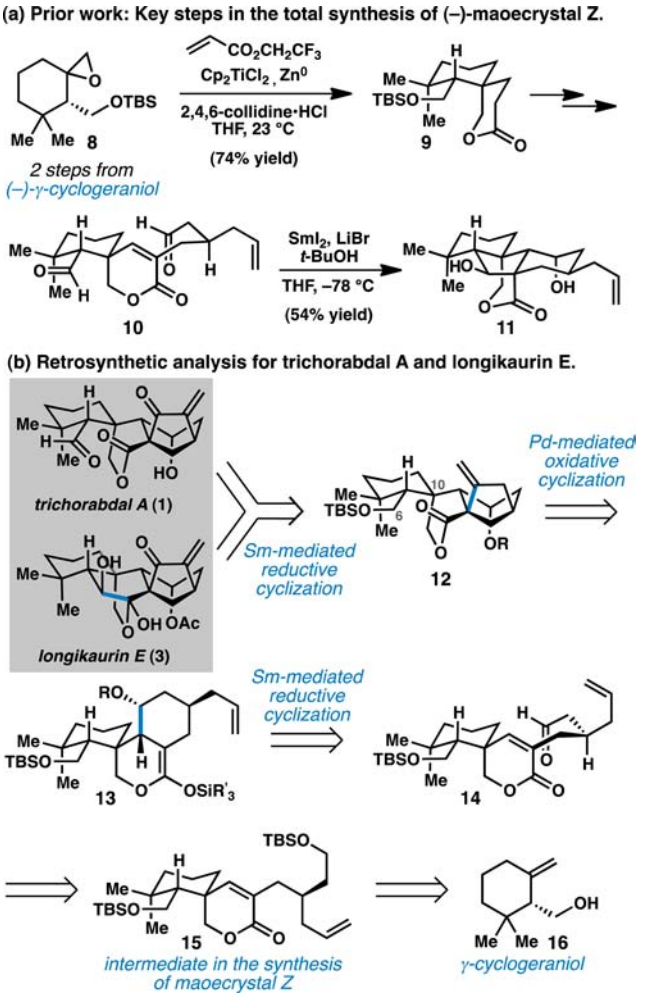



**Figure 1.** *Isodon* natural products.

of these compounds demonstrate potent antibacterial, anti-inflammatory, and anticancer properties. For example, compounds **1**, **2**, and **4** inhibit tumor growth *in vivo* in mice,[2d,3] while **3**, **5**, and **6** exhibit *in vitro* cytotoxicity against several human cancer cell lines.[2e,f,4] In addition, adenanthin (**7**) was recently found to selectively inhibit two isoforms of the peroxiredoxin enzymes, leading to differentiation of acute promyelocytic leukemia cells.[5] Cognizant of the structural similarities between many *Isodon* diterpenoids, particularly those possessing the *exo*-methylene cyclopentanone determined to be the active pharmacophore of **7**, we sought to develop a unified synthetic strategy that could enable access to several structurally distinct *ent*-kauranoid architectures.

As part of this program, we recently reported the first total synthesis of (−)-maoecrystal Z (**5**).[6] Key to our synthesis, we determined that spirolactone **9** could be prepared in good yield and excellent diastereoselectivity via a $Ti^{III}$-mediated reductive coupling reaction[7] of epoxide **8** and trifluoroethyl acrylate (Scheme 1a). Spirolactone **9** was elaborated to dialdehyde **10**, which upon exposure to a mixture of $SmI_2$[8] and LiBr[9]

**Scheme 1. Synthetic Considerations**

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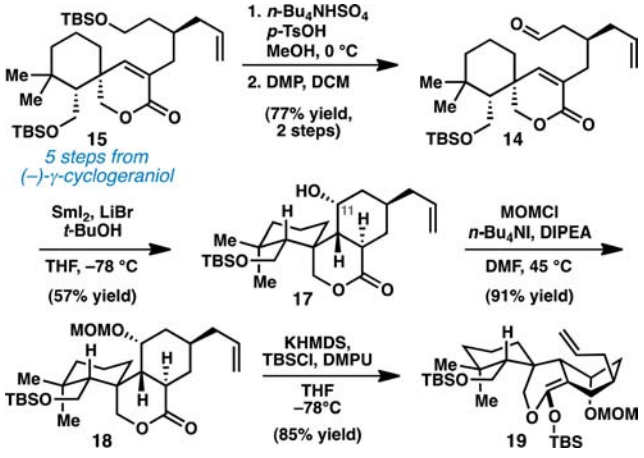
underwent a reductive cascade cyclization[10] to produce tetracyclic diol **11**. Diol **11** was advanced in four steps to **5**. Given that several bioactive *ent*-kauranoids possess the C10 spirocyclic quaternary center found in **5** (see Scheme 1b), we anticipated that spirocycle **9** could serve as a valuable synthon for the preparation of additional *ent*-kauranoid natural products, initially targeting (−)-trichorabdal A (**1**) and (−)-longikaurin E (**3**).

Retrosynthetically, we envisioned that both **1** and **3** could be accessible from *exo*-olefin **12** (Scheme 1b). Whereas the conversion of **12** to **1** was expected to require simple functional group manipulations, accessing the central 6-membered carbocycle of **3** would necessitate a nontrivial C−C bond formation. We hoped to forge this bond through a reductive cyclization of a substrate derived from **12**, which would possess a C6 aldehyde.[11] In a key synthetic step, the bicyclo[3.2.1]-octane of **12** would be constructed by a transition metal-mediated oxidative cyclization. Although this transformation is well established for silyl enol ether precursors,[12,13] we anticipated that use of silyl ketene acetal **13** might prove more challenging: prior to our studies there were no reported examples of transition metal-mediated oxidative cyclization reactions between silyl ketene acetals and simple olefins to generate all-carbon quaternary centers.[14] Nonetheless, this disconnection was appealing since **13** was presumed to be accessible following a $Sm^{II}$-mediated reductive cyclization of aldehyde **14**, which in turn could be derived from bis-silyl ether **15**, an intermediate in our total synthesis of (−)-maoecrystal Z (**5**).[6]

To this end, we set out to prepare a silyl ketene acetal substrate for the key Pd-mediated oxidative cyclization reaction. A survey of deprotection conditions revealed that treatment of bis-silyl ether **15** with *p*-TsOH and *n*-$Bu_4NHSO_4$ in MeOH at 0 °C[15] effected selective cleavage of the more accessible TBS ether, which was immediately subjected to oxidation with Dess−Martin periodinane[16] to give aldehyde **14** (Scheme 2).

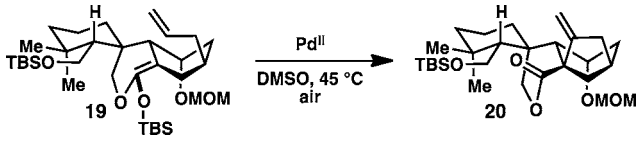
**Scheme 2. Synthesis of an Oxidative Cyclization Substrate**




Exposure of **14** to $SmI_2$ with LiBr and *t*-BuOH as additives afforded a single diastereomer of alcohol **17** in 57% yield. Efforts to simultaneously silylate the C11 alcohol and generate the silyl ketene acetal by treating **17** with excess base and a variety of silylating reagents were unfruitful. Fortunately, protection of the secondary alcohol as the MOM ether (**18**), followed by deprotonation with KHMDS and trapping with TBSCl at low temperature delivered silyl ketene acetal **19**; use of the MOM protecting group proved critical for this transformation.

We were pleased to find that subjection of **19** to 10 mol % $Pd(OAc)_2$ in DMSO at 45 °C under air furnished tetracycle **20**, albeit in poor yield (Table 1, entry 1). Whereas little difference

**Table 1. Reaction Optimization for the Formation of 20**




| entry | Pd source (equiv) | additive (equiv) | yield **20** (%)[a] |
|---|---|---|---|
| 1 | $Pd(OAc)_2$ (0.1) | – | 7 |
| 2 | $Pd(OAc)_2$ (1.0) | – | 35 |
| 3[b] | $Pd(OAc)_2$ (1.0) | – | 28[c] |
| 4 | $Pd(TFA)_2$ (1.0) | – | 19 |
| 5 | $PdCl_2$ (1.0) | – | 0 |
| 6 | $PdCl_2$ (1.0) | $AgBF_4$ (2.0) | 5[d] |
| 7[e] | $Pd(OAc)_2$ (1.0) | $H_2O$ (5.0) | 38 |
| 8 | $Pd(OAc)_2$ (1.0) | $K_2CO_3$ (5.0) | 0 |
| 9 | $Pd(OAc)_2$ (1.0) | AcOH (0.5) | 56 |
| 10 | $Pd(OAc)_2$ (0.1) | AcOH (0.5) | 7 |
| 11 | $Pd(OAc)_2$ (1.0) | AcOH (1.0) | 31 |
| 12 | $Pd(OAc)_2$ (1.0) | *p*-TsOH (0.5) | 46 |
| 13 | $Pd(OAc)_2$ (1.0) | BzOH (0.5) | 32 |
| 14 | $Pd(OAc)_2$ (1.0) | PivOH (0.5) | 40 |

[a]Isolated yield. [b]Reaction conducted in MeCN at 23 °C. [c]Product isolated as an inseparable 4.3:1 mixture with an olefin isomerization side product. [d]13% yield of a Wacker oxidation product was also isolated. See Supporting Information. [e]Run under a $N_2$ atmosphere.

was observed when the reaction was conducted under an air or oxygen atmosphere, the use of stoichiometric $Pd(OAc)_2$ (entry 2) substantially improved both conversion and the yield of **20**. In an effort to further improve the yield, a survey of reaction parameters was conducted. Although the desired transformation proceeds in MeCN at ambient temperature (entry 3), lower yields and increased side product formation are observed. All other solvents tested (e.g., PhMe, glyme, dioxane, *t*-BuOH, DMF) provided only trace quantities of **20**. Palladium sources bearing less coordinating counterions such as trifluoroacetate (TFA) and tetrafluoroborate (entries 4 and 6) also performed poorly, and $PdCl_2$ was ineffective (entry 5).

Over the course of these studies, we observed inconsistencies in both the yield and purity of **20** upon attempts to increase the scale of the reaction beyond a few milligrams, which led to the hypothesis that adventitious water or Brønsted acid might be playing an important role in the reaction. A series of control experiments revealed that water had little effect on product formation (entry 7), whereas bases such as $K_2CO_3$ inhibited the reaction (entry 8). However, the use of 0.5 equiv AcOH provided **20** in 56% yield (entry 9), and this finding was consistent on preparative scales. Neither an increased amount of AcOH nor the use of other acids examined further improved the yield. To the best of our knowledge, this is the first example of a Pd-mediated oxidative cyclization of a silyl ketene acetal to generate an all-carbon quaternary center.

With the carbon core in place, the remaining tasks in the synthesis of **1** included installation of the *exo*-enone and C6 aldehyde. β-Ketolactone **21** was obtained by ozonolytic cleavage of *exo*-olefin **20**, followed by α-methylenation using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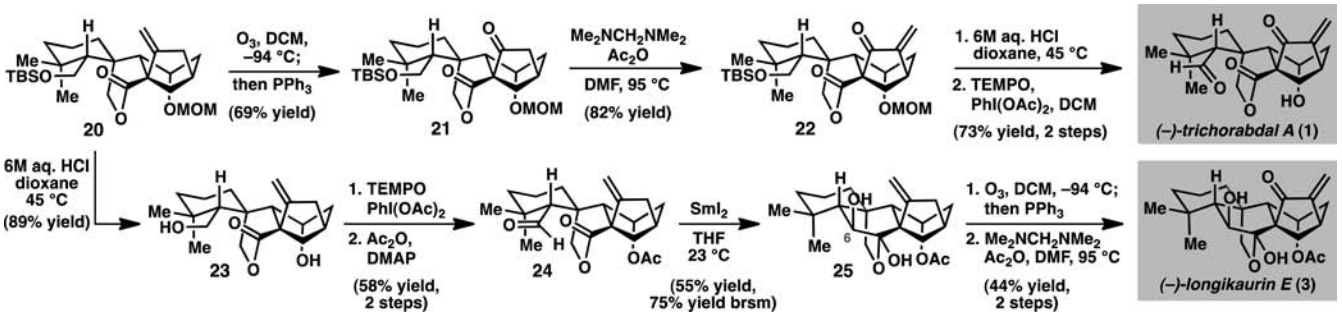
Scheme 3. Total Syntheses of (−)-Trichorabdal A (1) and (−)-Longikaurin E (3)




bis(dimethylamino)methane and acetic anhydride (Scheme 3).[17] Notably, the two-step protocol using Eschenmoser's salt[18] provided significantly diminished yields of **22**. Global deprotection proceeded cleanly with 6 M aqueous HCl in dioxane at 45 °C to give the diol. Selective oxidation of the C6 primary alcohol was accomplished using TEMPO and PhI(OAc)$_2$,[19] delivering (−)-trichorabdal A (**1**).[20]

Having completed our first objective, we turned our attention to the aldehyde-lactone coupling required for the synthesis of **3**. Global deprotection of **20** and selective oxidation of the primary alcohol proceeded under previously described conditions, and the resulting aldehyde was acetylated using $Ac_2O$ and DMAP to give **24** (Scheme 3). Gratifyingly, treatment of aldehyde **24** with $SmI_2$ in THF furnished a single diastereomer of lactol **25** in 55% yield, along with 27% yield of recovered starting material. Attempts to push this reaction to full conversion did not further improve the yield; instead, over-reduction of the product to the C6-deoxy lactol was observed.[21] Use of additives such as LiCl or LiBr resulted in direct reduction of the aldehyde to the primary alcohol. Ozonolysis of the alkene and $\alpha$-methylenation delivered (−)-longikaurin E (**3**).[22]

In conclusion, a unified synthetic strategy has enabled the first total syntheses of (−)-trichorabdal A (**1**) and (−)-longikaurin E (**3**) in 15 and 17 steps, respectively, from (−)-$\gamma$-cyclogeraniol.[23] Key to this strategy is a $Pd^{II}$-mediated oxidative cyclization reaction to generate the tetracyclic intermediate **20**, the divergence point of the synthetic route. A $Sm^{II}$-mediated pinacol-type coupling of an aldehyde-lactone was utilized in the elaboration of **20** to longikaurin E (**3**). These studies have identified a clear, non-biomimetic, synthetic relationship between several structurally distinct *ent*-kauranoid diterpenoids.

## ■ ASSOCIATED CONTENT

### Supporting Information

Detailed experimental procedures, compound characterization data, and $^1H$ and $^{13}C$ NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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