Synlett C. Mayer et al. Letter

Synthesis of (+)-Methyl Dihydropalustramate and of the Pyrido-[1,2-*a*]azepine Core of *Stemona* Alkaloids

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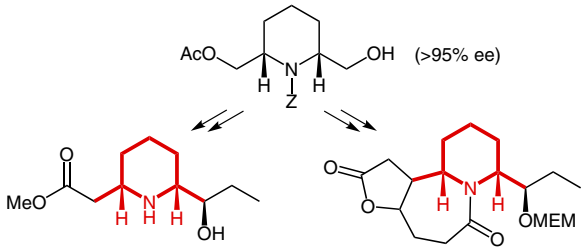
Dedicated to Professor K. Peter C. Vollhardt



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Abstract Starting from a readily available, enantiomerically pure 2,6-disubstituted piperidine the synthesis of pyrido[1,2-*a*]azepines was accomplished. Key reactions for the ring closure were a photochemically induced acyl radical addition or a SmI_2-promoted ketyl radical addition to an α,β-unsaturated ester. *En route* to the cyclization precursor an epoxidation/ring opening sequence led to an undesired oxazolidinone which turned out to be useful for the configuration assignment. The compound was successfully converted into (+)-methyl dihydropalustramate.

Key words alkaloids, cyclization, piperidines, radical reaction, total synthesis

While *Stemona* alkaloids with a pyrrolo[1,2-*a*]azepine core have received wide synthetic attention,[1,2] the homologous alkaloids with a pyrido[1,2-*a*]azepine core (**A**, Figure 1) have not been intensively investigated.[3] Indeed, they are smaller in number than the former compound class and represent only a fractional subset of known *Stemona* alkaloids.[4] According to a classification suggested by Pilli et al.,[5] only one out of eight *Stemona* alkaloid groups contains a pyrido[1,2-*a*]azepine core. Still, the reported biological activity of several naturally occurring pyrido[1,2-*a*]azepines is remarkable[6] and warrants synthetic studies.[7] We have been interested particularly in a possible route to *Stemona* alkaloids, which could be derived from a potential intermediate **B**, in which the piperidine ring is not further oxygenated but in which the stereogenic hydroxypropyl group is properly attached to position C4 of the pyrido[1,2-*a*]azepine core.

Our approach to target compounds of structure **B** was planned to commence with chiral piperidine **1** (Figure 1), which is readily available in enantiomerically pure form by

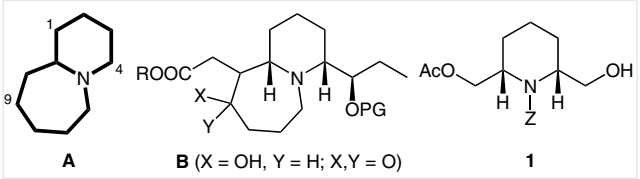
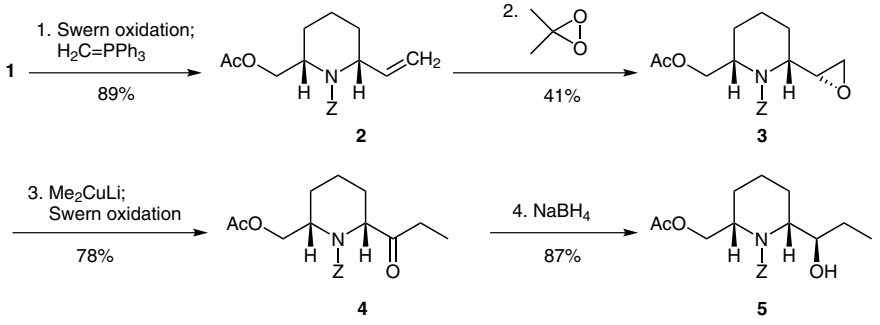


Figure 1 General structure **A** of the pyrido[1,2-*a*]azepine core in *Stemona* alkaloids, general structure **B** (PG = protecting group) of target compounds, and structure of enantiomerically pure alcohol **1** (Z = benzyloxycarbonyl)

an enantioselective lipase-catalyzed acetylation of the respective *meso*-diol.[8] It was attempted to close the azepine ring by a reductive cyclization reaction upon installation of the appropriate substituents on the piperidine core. In this communication, we present the preliminary results of our synthetic studies, including the enantioselective preparation of dihydropalustramic acid, a key degradation product of palustrine.

Due to 1,3-allylic strain, the carbon substituents of piperidine **1** ($AcOCH_2$, CH_2OH) are likely forced in axial positions by the Z protecting group at the nitrogen.[9] This arrangement renders reactions at these substituents capricious and leads to unexpected side reactions. The stereoselective conversion of the primary hydroxymethyl (CH_2OH) into the hydroxypropyl group has not yet proven feasible by an oxidation/ethyl addition sequence. Despite literature precedence for related pyrrolidine aldehydes,[10] attempted addition reactions to the intermediary formed piperidine aldehyde gave low yields and produced, if at all, mainly the undesired product diastereoisomer. An alternative route was found to start with Wittig reaction of the aldehyde to olefin **2**, which could be oxidized with dimethyldioxirane[11] to a diastereomeric mixture (dr = 48:52) of epoxides, from which product **3** was isolated in 41% yield (Scheme 1). Ring opening with dimethyl cuprate[12] and Swern oxidation[13] de-

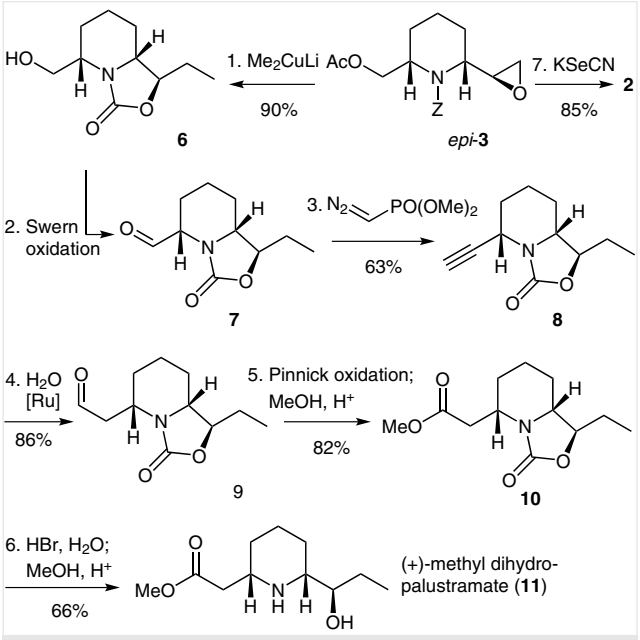


Scheme 1 Preparation of secondary alcohol **5** from primary alcohol **1**. *Reagents and conditions*: (1) (a) $(COCl)_2$ (2.0 equiv), DMSO (3.0 equiv), Et_3N (4.0 equiv), CH_2Cl_2, −78 °C → r.t., 2 h; (b) *t*-BuOK (3.0 equiv), Ph_3PMeBr (3.0 equiv), toluene, r.t., 30 min, 89%; (2) Oxone® (7.5 equiv), $NaHCO_3$ (22 equiv), acetone–H_2O = 2:1, r.t., 48 h, **3** (41%), *epi*-**3** (45%); (3) (a) CuI (3.0 equiv), MeLi (6.0 equiv), Et_2O, −35 °C, 15 min; (b) $(COCl)_2$ (2.0 equiv), DMSO (3.0 equiv), Et_3N (4.0 equiv), CH_2Cl_2, −78 °C → r.t., 2 h, 78%; (4) $NaBH_4$ (1.5 equiv), THF–MeOH, 0 °C → r.t., 1 h, 87%; Oxone® = $KHSO_5{\cdot}0.5KHSO_4{\cdot}0.5K_2SO_4$.

livered ketone **4**, which underwent in the anticipated fashion a diastereoselective reduction to secondary alcohol **5**. Following this route, we could obtain the desired product **5** in an overall yield of 25% from primary alcohol **1**.

Attempts to convert the epimeric epoxide *epi*-**3** into alcohol **5** failed because the intermediate of the dimethyl cuprate ring opening cyclized readily to oxazolidinone **6** (Scheme 2). The relative configuration of oxazolidinone **6** was initially established by NMR data.[14] We noted, however, that the compound could be nicely employed for the synthesis of dihydropalustramic acid, which in turn would unambiguously prove its absolute and relative configuration. To this end, Swern oxidation of the primary alcohol group to aldehyde **7** was followed by alkynylation with the Seyferth–Gilbert reagent.[15] Although conversion of terminal alkynes into aldehydes and carboxylic acids has been described via hydroboration methods,[16] we found the direct *anti*-Markovnikov addition of water based on the Hintermann procedure[17] superior. In the event, alkyne **8** was treated in an acetone–water mixture with ruthenium catalyst $CpRuCl(PPh_3)_2$ ligated by 2-(diphenylphosphino)-6-(2,4,6-triisopropylphenyl)pyridine yielding the desired aldehyde **9** in 86% yield. Further conversion into the known ester **10** was performed by a Pinnick-Lindgren oxidation[18] followed by esterification. Product **10** was in all scalar properties identical to its enantiomer *ent*-**10**, which has been previously reported and which has been successfully converted into (−)-dihydropalustramic acid and (−)-methyl dihydropalustramate.[19] In an analogous fashion we employed the same set of reaction conditions[19a] to prepare the enantiomeric product (+)-methyl dihydropalustramate (**11**) via (+)-dihydropalustramic acid.

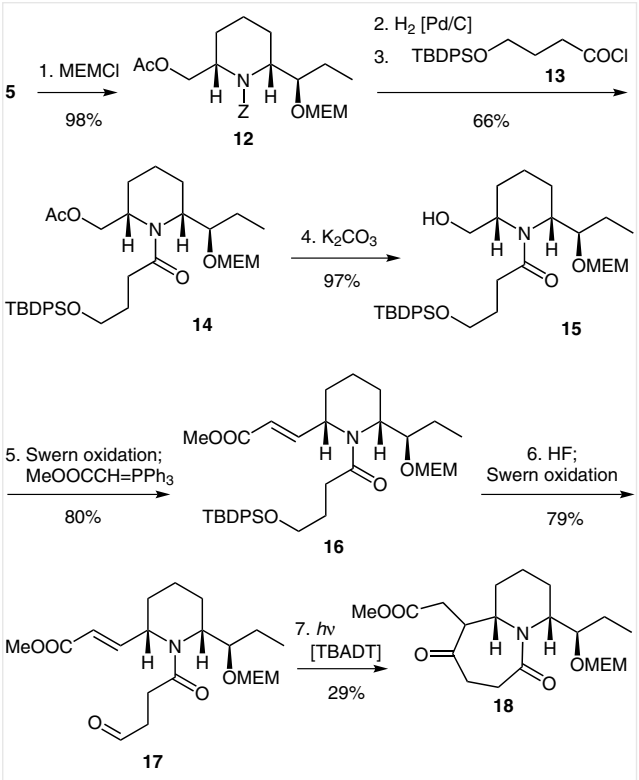
Gratifyingly, it was found that epoxide *epi*-**3** could be converted into the starting material **2** of the epoxidation by treatment with KSeCN[20] (Scheme 2). Based on this recycling step, the overall yield of the transformation **2** → **5** (Scheme 1) could be significantly improved and gram quantities of



Scheme 2 Conversion of epoxide *epi*-**3** into (+)-methyl dihydropalustramate and into olefinic precursor **2**. *Reagents and conditions*: (1) CuI (6.0 equiv), MeLi (12 equiv), THF, 0 °C, 3 h, 90%; (2) $(COCl)_2$ (3.0 equiv), DMSO (4.0 equiv), Et_3N (5.0 equiv), CH_2Cl_2, −78 °C → r.t., 2 h; (3) N_2CH-$PO(OMe)_2$ (2.0 equiv), *t*-BuOK (2.0 equiv), THF, −78 °C → r.t., 16 h, 63%, two steps; (4) $CpRuCl(PPh_3)_2$ (0.05 equiv), (dpp)(tpp)py (0.05 equiv), acetone–H_2O = 4:1, 65 °C, 43 h, 86%; (5) (a) $NaClO_2$ (10 equiv), KH_2PO_4 (7.0 equiv), *t*-BuOH–2-methyl-2-butene–H_2O = 3:1:2, r.t., 16 h; (b) H_2SO_4 (1.5 equiv), MeOH, 65 °C, 3 h, 82%; (6) (a) HBr–H_2O–DME = 2:1:1, 110 °C, 3 d; (b) H_2SO (2.0 equiv), MeOH, 55 °C, 3 h, 66%; (7) KSeCN (3.0 equiv), *t*-BuOH–H_2O, r.t., 3 d, 85%; Cp = cyclopentadienyl, (dpp)(tpp)py = 2-(diphenylphosphino)-6-(2,4,6-triisopropylphenyl)pyridine.

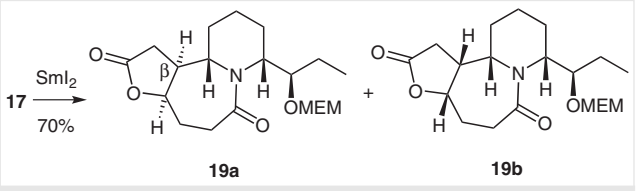
the desired alcohol **5** became available. The further conversion of alcohol **5** into an appropriate precursor for reductive cyclization turned out to proceed uneventfully (Scheme 3). Protection of the hydroxyl group in **5** with MEM chloride gave product **12**, from which the Z group was removed hydrogenolytically. An acylation of the resulting piperidine

with TBDPS-protected 4-hydroxybutanoyl chloride (**13**) delivered amide **14**. Saponification of the acetate led to primary alcohol **15**, which was oxidized to the respective aldehyde. A Wittig reaction delivered the α,β-unsaturated ester **16**, which was *E*-configured as expected. Removal of the TBDPS protecting group was accomplished by treatment with HF and the resulting alcohol was oxidized by Swern oxidation. Overall, aldehyde **17** was obtained from alcohol **5** in six steps and 40% overall yield.



Scheme 3 Synthesis of cyclization precursor **17** and photocyclization to product **18**. *Reagents and conditions*: (1) MEMCl (3.0 equiv), NEt*i*-Pr_2 (6.0 equiv), 1,2-DCE, 70 °C, 16 h, 98%; (2) H_2 (1 atm), $Pd(OH)_2/C$ (0.2 equiv), MeOH, r.t., 1 h, 83%; (3) $ClOC(CH_2)_3OTBDPS$ (2.0 equiv), DMAP (1.1 equiv), py–THF = 10:1, 80 °C, 3 d, 79%; (4) K_2CO_3 (3.0 equiv), MeOH–H_2O = 2:1, r.t., 97%; (5) (a) $(COCl)_2$ (2.0 equiv), DMSO (3.0 equiv), Et_3N (4.0 equiv), CH_2Cl_2, −78 °C → r.t., 2 h; (b) $Ph_3PCHCOOMe$ (3.0 equiv), toluene, 60 °C, 1 h, 80%; (6) (a) HF_{aq} (18 equiv), MeCN, r.t., 2 h, 82%; (b) $(COCl)_2$ (2.0 equiv), DMSO (3.0 equiv), Et_3N (4.0 equiv), CH_2Cl_2, −78 °C → r.t., 2 h, 96%; (7) hv (λ = 366 nm), TBADT (0.02 equiv), MeCN, r.t., 13 h, 29%; MEM = 2-methoxyethoxymethyl, 1,2-DCE = 1,2-dichloroethane, TBDPS = *tert*-butyldiphenylsilyl, DMAP = 4-dimethylaminopyridine, TBADT = tetrabutylammonium decatungstate.

Our original plan to induce the desired azepine ring closure was to employ a method established by the group of A. Albini and M. Fagnoni. They had found that tetrabutylammonium decatungstate, $[NBu_4]_4[W_{10}O_{32}]$,[21] was an excellent catalyst for the photochemical generation of acyl radicals from aldehydes, which in turn underwent smooth addition to appropriate Michael acceptors.[22] The photoactivated decatungstate was suggested to abstract a hydrogen atom from the aldehyde and to transfer it back after Michael addition to the respective acceptor-substituted radical. While yields for this reaction were reported to exceed 70%, if unfunctionalized aldehydes and simple Michael acceptors (e.g. methyl acrylate) were employed,[22] preliminary experiments with *tert*-butyl 4-oxobutanoate and a piperidine-substituted α,β-unsaturated ester resulted only in yields below 40%. Likewise, the attempted cyclization of aldehyde **17** could not be optimized to a synthetically useful level. Both substrate (0.04–0.1 M) and catalyst (2–10 mol%) concentrations had little influence on the reaction outcome with yields varying slightly between 26% and 30%. It appears likely that intramolecular hydrogen abstraction reactions are competing reaction pathways, which lead to degradation of the substrate. Remarkably, product **18** was isolated as a single diastereoisomer but its relative configuration could not be unambiguously assigned. Given the low yields of the cyclization, further work with product **18** was not performed, but rather other cyclization conditions, which could be applicable to aldehyde **17**, were evaluated.



Scheme 4 Reductive cyclization of aldehyde **16**. *Reagents and conditions*: SmI_2 (5.0 equiv), HMPA (20 equiv), THF, r.t., 1 h, dr = **19a**/**19b** = 77/23, 70%; HMPA = hexamethylphosphoramide.

In this context, previous work by Honda et al. seemed particularly promising.[2b] They had employed a SmI_2-promoted reductive cyclization[23] of an appropriate aldehyde to an α,β-unsaturated ester as the key step in the total synthesis of the pyrrolo[1,2-*a*]azepine alkaloid (−)-stemoamide. The reaction was suggested to proceed by a ketyl radical which adds intramolecularly to the Michael acceptor leading to formation of the pyrrolo[1,2-α]azepine skeleton. The resulting γ-hydroxyester was found to form in situ the respective γ-lactone. The vicinal stereogenic centers at the pyrrolidine carbon atom and the lactone β-carbon atom were found to be *trans* (60% yield) if the reaction was performed in MeOH–THF but *cis* (55% yield) if performed in the presence of hexamethylphosphoramide (HMPA). The effect of the double bond configuration at the α,β-unsaturated ester on the relative product configuration was found to be marginal. Although it was clear that these results could not be expected to apply similarly to a pyrido[1,2-*a*]azepine cyclization, we subjected aldehyde **17** to the reaction conditions of the SmI_2-promoted cyclization. No ring closure was observed in the absence of HMPA and aldehyde **17** was instead almost quantitatively reduced to the respective alco-

hol (90% yield). However, we were pleased to find that HMPA conditions allowed for a smooth cyclization to the desired azepine ring (Scheme 4). Addition of MeOH proved in this case detrimental to the success of the reaction and the cyclization was performed with 20 equivalents of HMPA in THF under strict exclusion of air and moisture.

Products **19** were impossible to separate and turned out to be oils, which were difficult to obtain completely pure from solvent. Satisfactory NMR data could still be obtained for the major diastereoisomer **19a**. The relative configuration was tentatively assigned to both diastereoisomers **19a** and **19b** based on NOESY experiments. Although the relative configuration at the β-carbon atom of the γ-lactone ring in **19a** may need adjustment for further work, it is believed that compounds **19** hold great promise for further synthetic work towards the synthesis of pyrido[1,2-*a*]azepines.

In summary, it was shown that enantiomerically pure piperidine **1** can serve as a useful building block for the construction of the pyrido[1,2-*a*]azepine core of *Stemona* alkaloids. While it turned out to be more problematic than expected to establish the hydroxypropyl group at carbon C4 of the core, the further reaction sequence proceeded smoothly and delivered with aldehyde **17** a suitable precursor for subsequent cyclization reactions. Upon treatment with SmI_2 in HMPA/THF, the desired skeleton **B** could be accessed, which seems to be a reasonable starting point for further synthetic studies. It became obvious, though, that those reactions, which proceed readily with pyrrolidines, do not always work similarly with related piperidines. It is therefore necessary to modify the existing protocols for the construction of pyrrolo[1,2-*a*]azepines when applied to pyrido[1,2-*a*]azepines or to develop completely new synthetic strategies for the preparation of the latter.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380685. Included are procedures and analytical data for all new compounds.

Primary Data

Primary data for this article are available online at http://www.thieme-connect.com/products/ejournals/journal/ 10.1055/s-00000083 and can be cited using the following DOI: 10.4125/pd0066th.

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