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gem-Dibromocyclopropanes and enzymatically derived *cis*-1,2-dihydrocatechols as building blocks in alkaloid synthesis*

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Abstract: The application of the title building blocks, the 6,6-dibromobicyclo[3.1.0]hexanes and the *cis*-1,2-dihydrocatechols, to the total synthesis of crinine and lycorinine alkaloids is described.

Keywords: alkaloids; clividine; crinines; *cis*-1,2-dihydrocatechols; *gem*-dibromocyclopropanes; haemultine; hamayne; intramolecular Alder-ene reaction; lycorinines.

INTRODUCTION

During the course of a program concerned with establishing new methods for the total synthesis of various Amaryllidaceae alkaloids we have identified two structural motifs that seem particularly well suited to this purpose [1]. These are the 6,6-dibromobicyclo[3.1.0]hexanes (**1**) [2] and the enantiomerically pure *cis*-1,2-dihydrocatechols (**2**) [3]. The cyclopropanes **1** are readily prepared by dibromocarbene addition to the relevant cyclopentene [2] while the latter compounds can be generated by dihydroxylation of the corresponding aromatic compound using genetically engineered microorganisms that overexpress the enzyme toluene dioxygenase [3]. Both of these types of processes can be conducted on multigram scales meaning that compounds of the general forms **1** and **2** are readily available ones. There is an interesting structural relationship between the two systems because ring-fused *gem*-dibromocyclopropanes such as **1** are rather strained species capable of undergoing, often in a readily controlled and well-defined manner, electrocyclic ring-opening in the presence of nucleophiles (Nu^- or NuH) to give bromo-substituted cyclohexenes of the general form **3** [2b,d–f]. As such, the first system can be viewed as a latent form of the second that is able to be "revealed" at an appropriate point in a reaction sequence.

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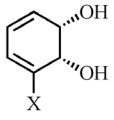

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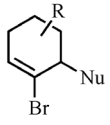
(X = Cl, Br, I, Me, CN, $CH{=}CH_2$....)



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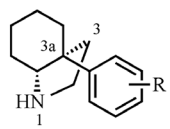
Given the prevalence of substituted cyclohexene and cyclohexane substructures within many of the Amaryllidaceae alkaloids of interest to us, we have found compounds of the general form **1** or **2** to be especially useful building blocks for the construction of these often highly biologically active natural products [1]. The following sections detail some of our recent efforts to deploy them in the synthesis of crinine and lycorinine alkaloids.

6,6-DIBROMOBICYCLO[3.1.0]HEXANES AS PRECURSORS TO CRININE ALKALOIDS

The crinine-type alkaloids are a prominent group of natural products embodying the *cis*-C3a-arylhexahydroindole unit **4** as the key structural motif [4]. They display a rather fascinating array of biological properties including immuno-stimulatory, antimalarial, anticholinergic, and apoptosis-inducing behaviors [4–7]. For example, crinine {**5** [8], m.p. = 207–209 °C, $[\alpha]_D = -26.1°$ (c = 0.26, $CHCl_3$)} displays antimalarial properties [9] while the enantiomerically related vittatine {**6** [10], m.p. = 207–208 °C, $[\alpha]_D = +26°$ (c = 0.5, $CHCl_3$)} inhibits the production of NO in lipopolysaccharide (LPS)-activated mouse peritoneal macrophages [11].



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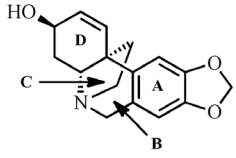

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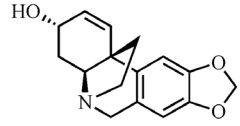

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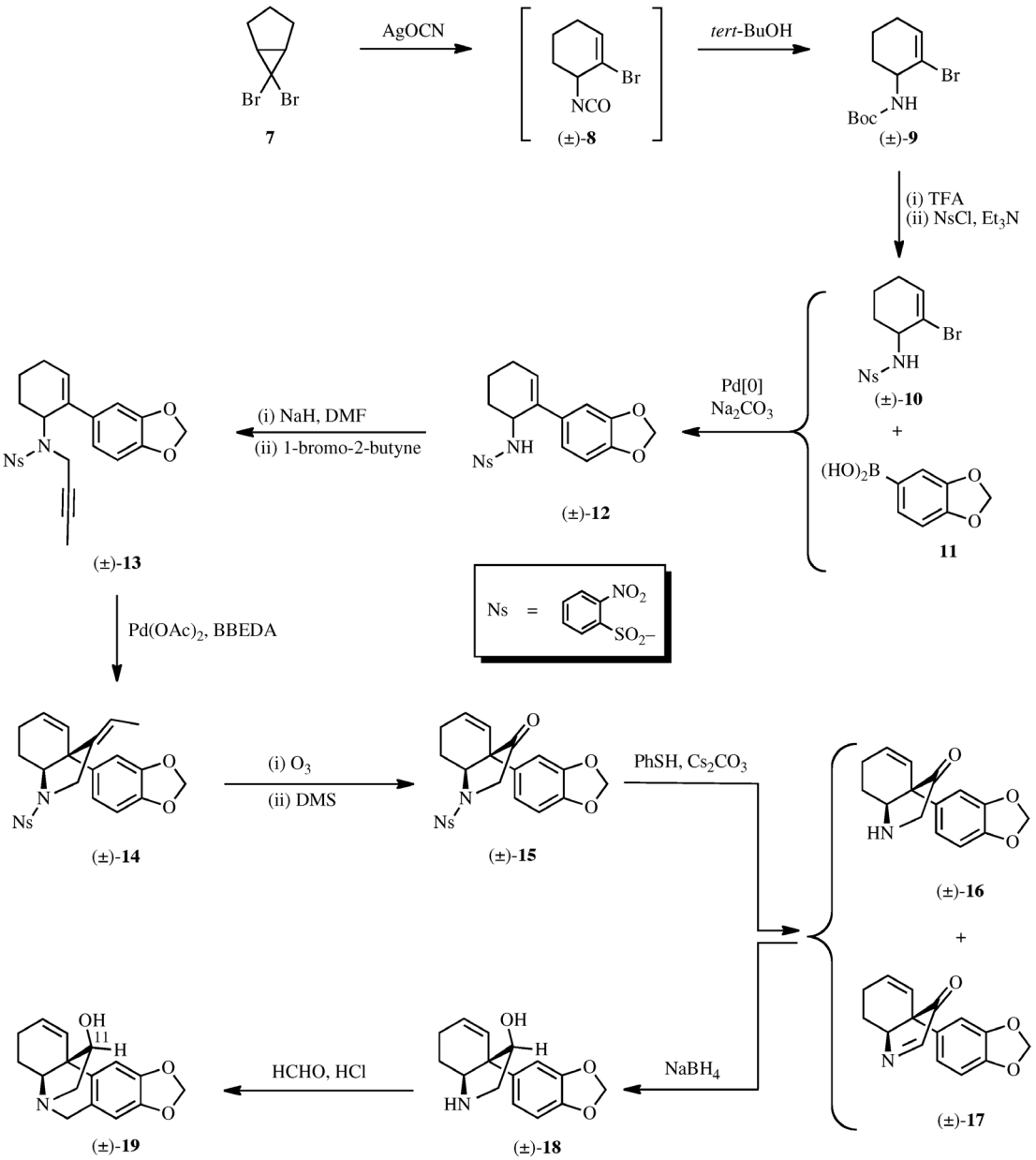
A range of approaches to the crinine alkaloids has been reported [4,5,8,10,12], but a particularly effective one involves subjecting the relevant *cis*-C3a-arylhexahydroindole (**4**) to a Pictet–Spengler reaction and thereby installing, in the closing stages of the synthesis, the constituent B-ring [12]. Accordingly, the identification of concise routes to compounds of the general form **4**, which already incorporates the quaternary carbon (C3a) of the target alkaloids, has been a popular area of research and one in which we have been involved and now describe.

The details of our approach to the racemic form of the biogenetically unusual alkaloid haemultine [13] are shown in Scheme 1 and the opening stages involved treating the parent and well-known [14] 6,6-dibromobicyclo[3.1.0]hexane (**7**) with silver cyanate so as to induce electrocyclic ring-opening of the cyclopropane and thereby generating an intermediate π-allyl cation that is captured by the silver counterion to give allylic isocyanate (±)-**8** [15]. This last species is itself intercepted by added *tert*-butanol and so forming the isolable compound (±)-**9** which was obtained in 79 % yield. It was anticipated that a subsequent and stereochemically demanding cyclization process would not be accommodated by the planar geometry imposed at nitrogen by the associated carbamate residue. Accordingly, this was cleaved using trifluoroacetic acid, and the 1°-amine so formed immediately protected as the nosylate (±)-**10** [16] (87 %) through reaction with nosyl chloride in the presence of triethylamine. Suzuki–Miyaura cross-coupling of compound (±)-**10** with the commercially available aryl boronic acid **11** afforded the anticipated product (±)-**12** (77 %) that upon treatment with sodium hydride then 1-bromo-2-butyne gave the doubly N-alkylated sulfonamide (±)-**13** (86 %). In the pivotal step of the reaction sequence, compound (±)-**13** was treated with $Pd(OAc)_2$ and the strongly σ-donating ligand *N*,*N*′-bis(benzylidene)ethylenediamine (BBEDA) in refluxing benzene and thus effecting an intramolecular Alder-ene (IMAE) reaction [16,17] and so-forming, in a completely stereoselective process, the *cis*-C3a-arylhexahydroindole (±)-**14** [15] in 94 % yield.

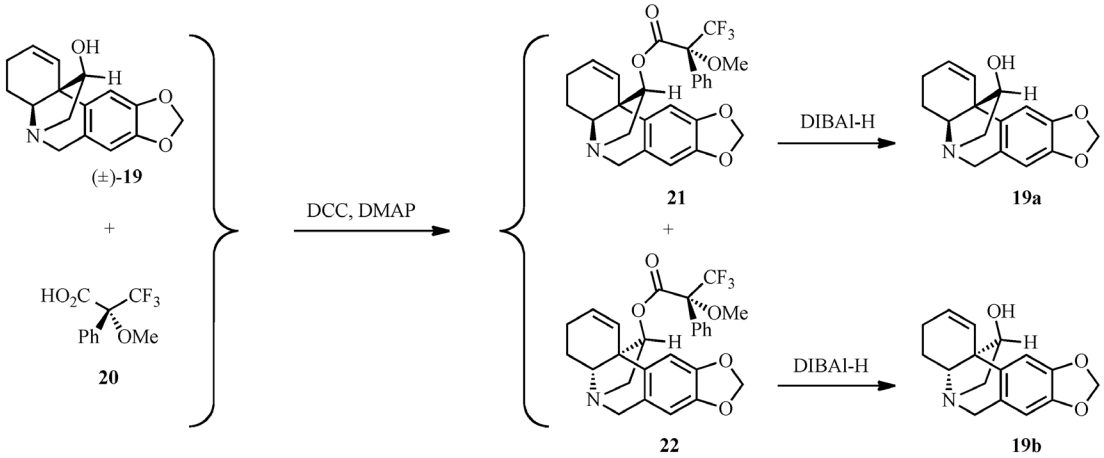


Scheme 1

As a prelude to installing the C11-hydroxyl group in the target alkaloid, diene (±)-**14** was briefly exposed to ozone at –78 °C and after reductive work-up with dimethyl sulfide the ketone (±)-**15** was obtained, albeit in only 38 % yield (at 88 % conversion) because of complications arising from competitive cleavage of the *endo*-cyclic double bond within the substrate. The structure of this ketone was confirmed by single-crystal X-ray analysis. In anticipation of carrying out a Pictet–Spengler reaction to install the B-ring associated with haemultine, compound (±)-**15** was treated with a mixture of thiophenol and caesium carbonate in order to cleave the nosyl group [18] and thus reveal the corresponding 2°-amine. As a result, a chromatographically separable mixture of the anticipated product (±)-**16** (61 %)

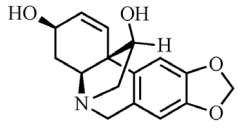
and its dehydro-analogue (±)-**17** (19 %) was obtained. Presumably, the latter compound arises via an E1cb process that also produces the *o*-nitrobenzenesulfinic acid anion. Treatment of compounds (±)-**16** and (±)-**17**, either as a mixture or separately, with an excess of sodium borohydride in tetrahydrofuran (THF)/methanol resulted in a stereoselective reduction process and formation of the anticipated alcohol (±)-**18** that was obtained in 92 % yield. Finally, subjection of compound (±)-**18** to reaction with formaldehyde in the presence of HCl gave the racemic modification, (±)-**19** (92 %), of the target crinine alkaloid haemultine. The structure of compound (±)-**19** was also confirmed by single-crystal X-ray analysis.

Our initial efforts to isolate the constituent enantiomeric forms of compound (±)-**19** involved treating this with L-(+)-tartaric acid but, despite various attempts, the ensuing diastereoisomeric salts could not be separated from one another. In contrast, coupling of the racemic material with acid **20** gave the expected mixture of Mosher esters **21** and **22** (Scheme 2) that could be separated using high-performance liquid chromatography (HPLC) techniques [19]. These were then cleaved using diisobutylaluminum hydride (DIBAl-H) to give the corresponding and now enantiomerically pure forms, **19a** and **19b**, of haemultine, the absolute configurations of which are currently being confirmed.



Scheme 2

The work detailed in Scheme 1 serves to establish the capacity of the IMAE/Pictet–Spengler reaction sequence to provide crinine alkaloids, especially those bearing oxygen-containing functionality in the C-ring. Since almost all of the crinine alkaloids contain oxygenation in the D-ring we have sought to adapt the above-mentioned protocols so as to allow for the synthesis of natural products such as hamayne (**23**) [20], a compound that has been isolated from various sources including the bulbs of *Crinum jagus* and *Crinum glaucum*. Extracts of these are used in traditional medicine in southern Nigeria for memory loss and other mental symptoms associated with aging. Furthermore, it has been shown [21] that compound **23** itself results in 100 % inhibition of acetylcholinesterase (AChE) at 50 mg/mL.



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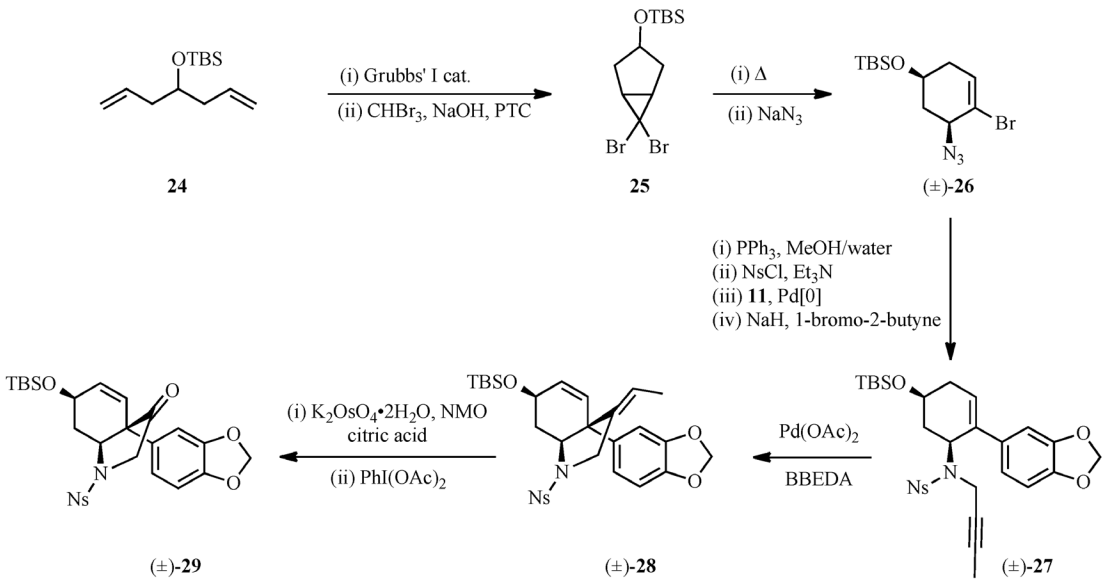
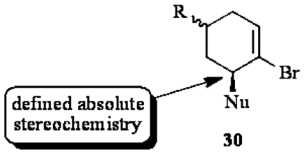
The reaction sequence being used to prepare target **23**, which has not been the subject of any reported synthetic studies, starts with the ring-closing metathesis of the OTBS ether, **24**, of commercially available diallyl alcohol (Scheme 3). The product cyclopentene (90 %) is then subjected to reaction with dibromocarbene generated under the Makosza conditions [2a] from bromoform and sodium hydroxide in the presence of a phase-transfer catalyst (PTC). The major diastereoisomeric form of the ensuing 6,6-dibromobicyclo[3.1.0]hexane **25** was subjected to thermally induced rearrangement in chlorobenzene and the product 2,3-dibromocyclohexene treated with sodium azide. The allylic azide (±)-**26** so-formed (in 90 % yield) was then subjected to Staudinger reduction with triphenylphosphine in methanol/water and the ensuing 1°-amine treated with nosyl chloride. Suzuki–Miyaura cross-coupling of the product sulfonamide with boronic acid **11** and reaction of the ensuing arylated cyclohexene (78 %) with sodium hydride then 1-bromo-2-butyne afforded the dialkylated sulfonamide (±)-**27** (95 %) the structure of which was confirmed by single-crystal X-ray analysis. While the last compound failed to engage in an efficient IMAE reaction when this was effected thermally, subjection of a benzene solution of it containing $Pd(OAc)_2$ and BBEDA to microwave irradiation at 120 °C afforded the anticipated product (±)-**28** in 75 % yield. Treatment of this compound under the Upjohn dihydroxylation conditions in the presence of citric acid, followed by reaction of the crude product mixture with phenyliodonium diacetate in dichloromethane gave the ketone (±)-**29** in 50–60 % yield. Efforts are now underway to complete the synthesis of the racemic form of hamayne (**23**) by removing the nosyl-group within compound (±)-**29**, reducing the ketone carbonyl moiety in a stereocontrolled manner and then engaging the ensuing amino-alcohol in a Pictet–Spengler reaction. Treatment of the expected tetracyclic compound with a fluoride ion source, so as to cleave the OTBS ether, should then deliver the racemic modification of hamayne, viz. (±)-**23**.



Scheme 3

Given the symmetrical nature of the 6,6-dibromobicyclo[3.1.0]hexanes **7** and **25** used as starting materials in the above-mentioned reaction sequences (they are both meso-compounds), it is tempting to contemplate how they might be converted, in a completely enantioselective manner, into the corresponding ring-expanded products of the general form **30**. Studies directed towards such ends are now underway in our laboratories.



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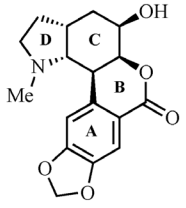
cis-1,2-DIHYDROCATECHOLS AS PRECURSORS TO LYCORININE ALKALOIDS

It has been demonstrated, over the last three decades or so, that the enzymatically derived and enantiomerically pure *cis*-1,2-dihydrocatechols of the general form **2** are exceptionally useful starting materials for the synthesis of a wide range of natural products [3]. Their utility arises, in part at least, because the halogenated forms (X = Cl, Br or I) of these compounds embody strongly differentiated functionalities that can be manipulated in quite selective ways and thereby allowing for their conversion into a striking array of versatile derivatives. Our own very positive experiences of these systems [3b,d,f] prompted us to consider exploiting them in developing routes to the lycorinine alkaloids [4b,22], of which (–)-clividine (**31**) and (+)-clivonine (**32**) are representative members and which mostly just differ in terms of the stereochemical disposition of the substituents attached to the cyclohexane C-ring.



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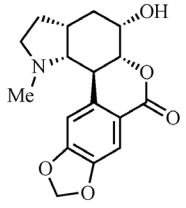

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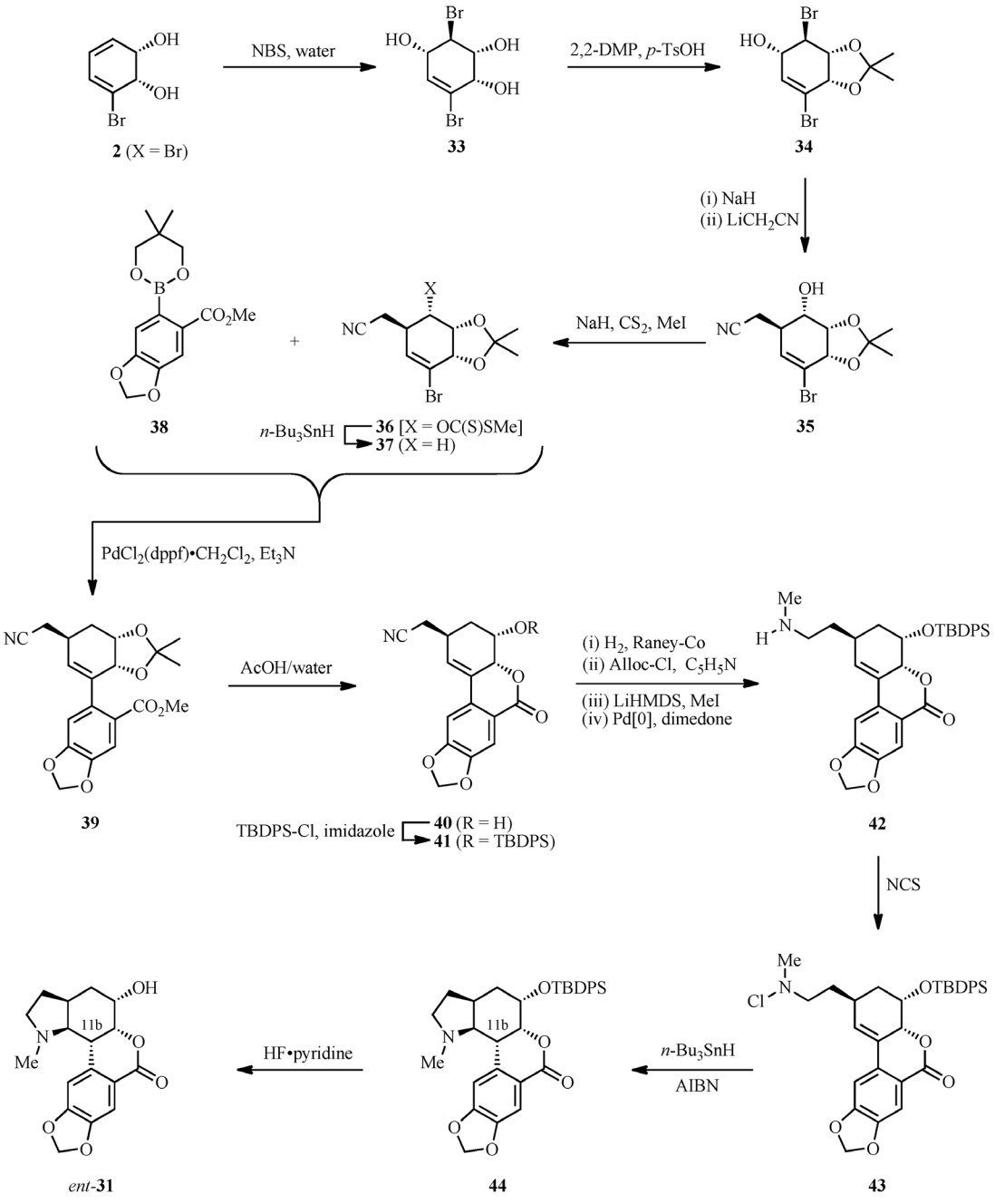
Given the presence of this motif and its obvious structural resemblance to the *cis*-1,2-dihydrocatechols **2**, we sought to exploit this situation. As a result, we were able to establish a synthesis of *ent*- or (+)-clividine (*ent*-**31**) using the reaction sequence shown in Scheme 4 [23]. Thus, the *cis*-1,2-dihydrocatechol **2** (X = Br) derived from bromobenzene was treated with *N*-bromosuccinimide (NBS) in aqueous THF and the ensuing bromohydrin **33** converted into the corresponding acetonide (**34**) [92 % from **2** (X = Br)] under standard conditions. Sequential treatment of the latter compound with sodium hydride then the conjugate base of acetonitrile afforded the γ-hydroxynitrile **35** in 87 % yield. Presumably, this conversion involves initial ring-closure of the *trans*-bromohydrin **34** to give the corresponding epoxide that reacts with acetonitrile anion at the allylic position to afford, via a *trans*-selective ring-opening process, the observed product. Barton–McCombie deoxygenation of alcohol **35** was accomplished via the derived xanthate ester **36** and thus affording compound **37** (81 %) that engaged in a Suzuki–Miyaura cross-coupling reaction with the readily prepared aryl boronate **38** and so giving the arylated cyclohexene **39** (95 %) which embodies the A- and C-rings of the target *ent*-**31**. Treatment of compound **39** with aqueous acetic acid effected hydrolytic cleavage of the acetonide unit

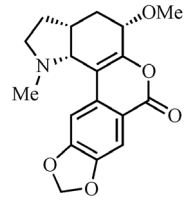


Scheme 4

and subsequent lactonization and thereby generating the tricyclic product **40** (84 %) now also incorporating the B-ring ring of the target and thus leaving just the D-ring needing to be formed. To such ends, and in anticipation of ensuring appropriate levels of stereocontrol (vide infra), compound **40** was converted into the corresponding *t*-butyldiphenylsilyl (TBDPS) ether **41** (80 %) and the nitrile residue within the latter was then reduced to the corresponding 1°-amine (82 %) using dihydrogen in the pres-

ence of Raney cobalt. The readily obtained Alloc-protected derivative (90 %) was N-methylated using lithium hexamethyldisilazide (LiHMDS) and methyl iodide, and the *N*-methyl carbamate (84 %) so-formed was deprotected using $Pd(PPh_3)_4$ and an excess of dimedone and thus affording the 2°-amine **42** (89 %). As a prelude to carrying out a nitrogen-centered radical cyclization reaction [24], compound **42** was treated with *N*-chlorosuccinimide (NCS) and the resulting *N*-chloroamine **43** (93 %) then subjected to reaction with tri-*n*-butyltin hydride in the presence of the free radical initiator AIBN. As a result, the TBDPS ether, **44**, of *ent*-clividine was formed in a completely diastereoselective manner and in 83 % yield. Clearly, then, the intermediate benzylic radical formed at C11b after the initial *cis*-selective cyclization reacts preferentially at its β-face with tri-*n*-butyltin hydride to generate the observed product **44**. Presumably, this preference reflects the greater steric demands imposed by the 1,3-related OTBDPS-group than by the flanking D-ring. The completion of the synthesis simply involved deprotection of compound **44** using HF·pyridine and *ent*-clividine (*ent*-**31**) was thereby obtained in 99 % yield and its structure confirmed by single-crystal X-ray analysis of the corresponding picrate salt. Given that the enantiomer of the starting diol **2** (X = Br) is available [25], the illustrated reaction sequence will also allow access to (–)-clividine and its congeners.

In some related studies we have been able to establish a synthesis of narseronine (**45**), an alkaloid isolated recently from the flowering plant *Narcissus serotinus* L. that grows in dry coastal regions of many parts of the Mediterranean [26]. Perhaps the most notable structural feature of the compound is the presence of an unsaturated δ-lactone residue within the B-ring. Interestingly, no biological evaluation of narseronine appears to have been reported although, given its structural resemblance to active systems, it is reasonable to expect that it will display some fascinating properties.



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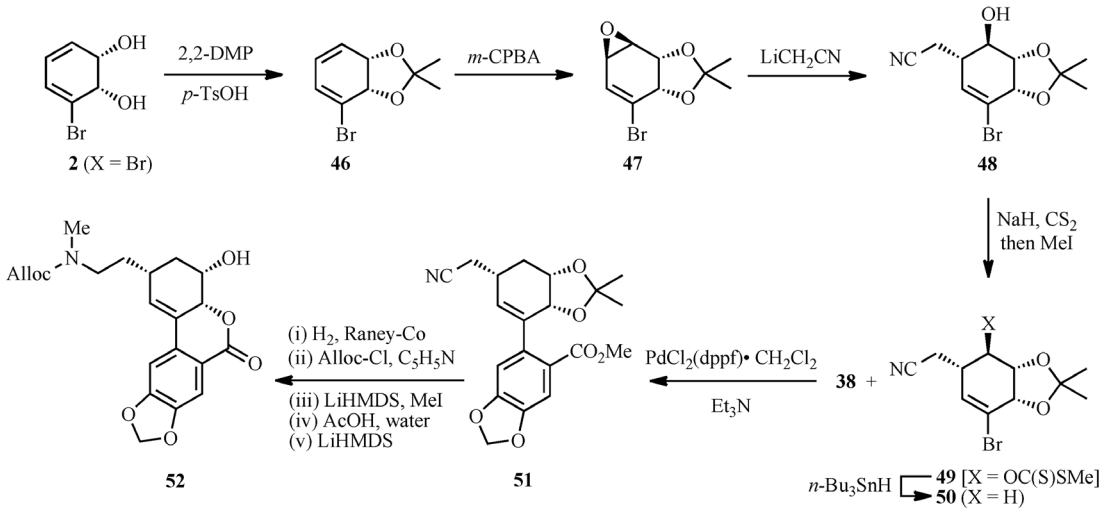
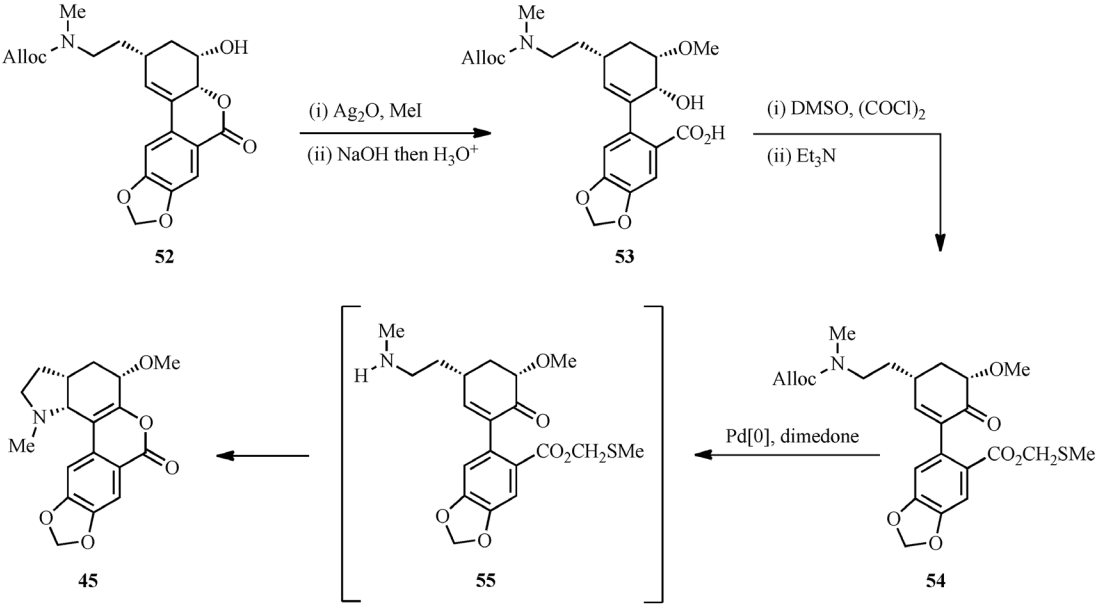
In the opening stages (Scheme 5) of our synthesis [27], *cis*-1,2-dihydrocatechol **2** (X = Br) was converted into the corresponding and well-known acetonide **46** [28] (93 %), which was then subjected to reaction with *m*-chloroperbenzoic acid (*m*-CPBA) and so giving the epoxide **47** [28] in 95 % yield. Reaction of epoxide **47** with the lithium anion of acetonitrile resulted in a regio- and stereo-selective ring-opening reaction to give compound **48** (96 %) that was subjected to a xanthate-ester mediated Barton–McCombie deoxygenation sequence and thus giving, via ester **49**, nitrile **50** (82 %), the epimer of compound **37**, a key intermediate associated with the above-mentioned synthesis of *ent*-clividine. Suzuki–Miyaura cross-coupling of compound **50** with aryl boronate **38** gave cyclohexene **51** (75 %), which was subjected with reaction with dihydrogen in the presence of Raney cobalt. The ensuing 1°-amine was protected as the corresponding Alloc carbamate that was then subjected to an N-methylation/acetonide cleavage/lactonization sequence and thus affording compound **52** (66 % from **51**).



Scheme 5

In the closing stages of our naseronine synthesis (Scheme 6), hydroxylactone **52**, which embodies all but the D-ring of the final target, was subjected to a Purdie–Irvine methylation reaction using silver oxide and methyl iodide and then to a lactone ring-cleavage process using sodium hydroxide. The hydroxyacid **53** (68 %) obtained after acidic work-up was subjected to reaction with DMSO/oxalyl chloride then triethylamine. This not only effected a Swern oxidation of the hydroxy group but also converted the acid residue into the corresponding methylthiomethyl ester and thus giving compound **54** in 48 % yield together with the starting lactone *O*-methyl ether (29 %). In the final and pivotal step of the reaction sequence, carbamate **54** was treated with $Pd(PPh_3)_4$ in the presence of dimedone and thus affording narseronine (**45**) in 82 % yield. Presumably, this pleasing conversion involves initial cleavage



Scheme 6

of the Alloc group and the resulting 2°-amine **55** then engages in an intramolecular and stereoselective hetero-Michael addition reaction to establish the D-ring. The enolate so-formed then reacts with the pendant methylthiomethyl ester residue in an intramolecular acylation process to give the observed product **45**, the structure of which was confirmed by single-crystal X-ray analysis.

The spectral data obtained on the synthetically derived sample of narseronine were in good agreement with those reported by Bastida et al. [26] Since the optical rotation of the natural product has not been reported, its absolute configuration remains unclear at the present time.

The synthetic utility of the title building blocks seems clear, and we are continuing to use them as starting materials for the synthesis of a wide range of natural products. Results of these studies as well as the outcomes of the biological evaluation of compounds such as (±)-**19**, (±)-**23**, *ent*-**31**, and **45** will be reported in due course.

ACKNOWLEDGMENTS

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