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Total Synthesis of Ileabethoxazole, Pseudopteroxazole, and *seco*-Pseudopteroxazole

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Dedicated to Professor K. C. Nicolaou on the occasion of his 70th birthday

Abstract: *The total syntheses of ileabethoxazole, pseudopteroxazole, and seco-pseudopteroxazole, three antituberculosis diterpenoids that had been isolated from Pseudopterogorgia elisabethae, were accomplished in a collective fashion. A cascade alkyne carbopalladation/Stille reaction was exploited to construct a triene precursor with suitable geometry. A fully substituted arene was then assembled through a key 6π electrocyclization/aromatization sequence, and served as an advanced common intermediate. Two radical cyclizations led to the formation of the five- and six-membered rings of ileabethoxazole and pseudopteroxazole, respectively, with the desired stereochemistry, and a straightforward side-chain elongation delivered seco-pseudopteroxazole.*

Tuberculosis (TB) has long been a severe threat to human health.[1] In recent years, the rapid increase in multidrug-resistant and extensively drug-resistant TB infections and TB/HIV co-infection raises the demand for more effective chemotherapeutics.[2] Natural products provide an unparalleled source of lead compounds for anti-TB drug development.[3] Ileabethoxazole, pseudopteroxazole, and *seco*-pseudopteroxazole (**1**–**3**, Figure 1) are benzoxazole alkaloids that were isolated by Rodríguez and co-workers from the Caribbean sea whip *Pseudopterogorgia elisabethae* and display promising inhibitory activity against *Mycobacterium tuberculosis*.[4] From structural and biosynthetic perspectives, these molecules belong to a large and diverse diterpenoid family isolated from the same species,[5] and some of their congeners (**4**–**6**) are shown in Figure 1. Notably, a significant number of the family members possess multisubstituted aromatic cores, which enhances the difficulty of their chemical synthesis.[6] Corey and co-workers reported the first total syntheses of the originally proposed and revised structures of **2**[7] by employing an intramolecular Diels–Alder and a Robinson annulation strategy, respectively. The Harmata group then disclosed a synthesis of **2** based on benzothiazine chemistry.[8] Recently, Williams and Shah accomplished the first total synthesis of **1** with a congested five-membered ring, which featured an elegant Pauson–Khand strategy.[9] Herein, we report collective total syntheses of **1**–**3** that are based on an electrocyclization/aromatization strategy.

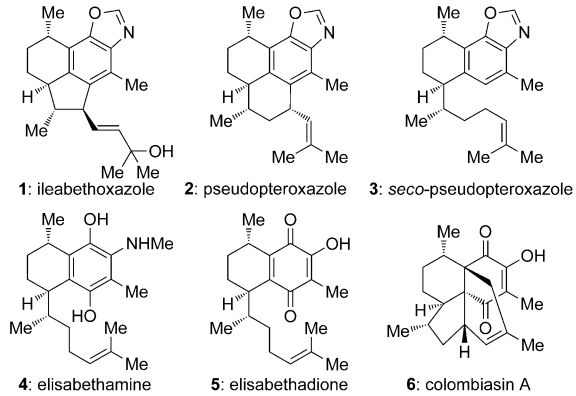
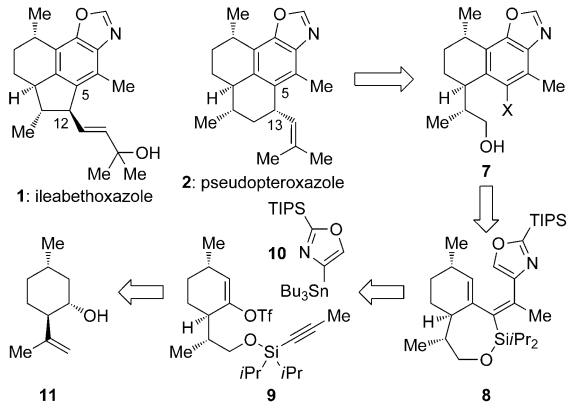


Figure 1. Benzoxazole-containing diterpenoids **1**–**3** and biogenetically related natural products **4**–**6**.

We first undertook a retrosynthetic analysis of ileabethoxazole (**1**) and pseudopteroxazole (**2**; Scheme 1). The initial disconnections at the C5–C12 and C5–C13 bonds of the five- and six-membered rings, respectively, generate arene **7**



Scheme 1. Retrosynthetic analysis of **1** and **2**.

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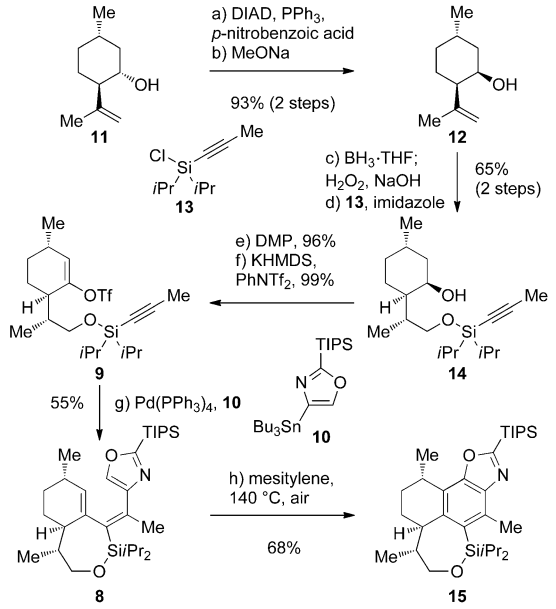
as a common intermediate. Metal-mediated or free-radical cyclization could be used to effect the ring closures. Inspired by Nicolaou's seminal synthesis of the endiandric acids[10] as well as other elegant work in the electrocyclization area,[11–13] we envisioned a one-pot 6π electrocyclization/aromatization process to forge the aromatic core of **7**. Similar strategies were exploited to build tetra- and pentasubstituted arenes in our synthesis of daphenylline, rubriflordilactone A, tubingensin A, xiamycin A, and oridamycins A and B.[14] However, examples of assembling fully substituted arenes by such strategies are rare, presumably owing to the difficulty associated with preparing geometrically suitable hexasubstituted triene substrates. To construct a triene such as **8**, we envisioned to take advantage of a tandem alkyne carbopalladation/Stille reaction between alkynyl triflate **9** and oxazolyl stannane **10**, based on the pioneering work of Suffert and others.[15] The geometry of the central C=C bond of **8** would be secured by a mechanism of oxidative addition/*cis* alkyne insertion/transmetalation/reductive elimination. Compound **9** was traced back to commercially available (+)-isopulegol (**11**). Notably, a series of analogues could be flexibly obtained from the common intermediate **7**.

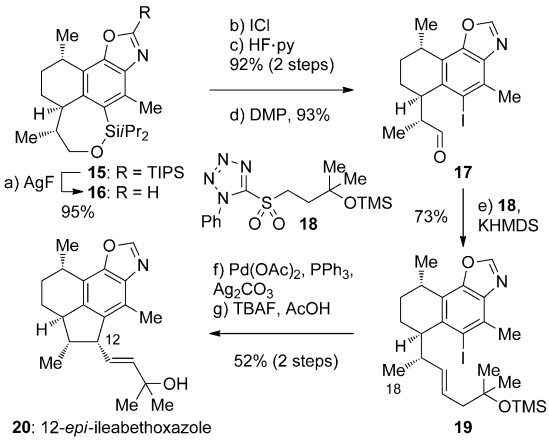
The synthesis commenced with the assembly of fully substituted arene intermediate **15** (Scheme 2). (+)-Isopulegol (**11**) was subjected to a Mitsunobu reaction (DIAD, PPh_3, *para*-nitrobenzoic acid) followed by basic hydrolysis to obtain alcohol **12** (93% yield over two steps) with an inverted secondary hydroxy group. This hydroxy group was essential to direct the hydroboration/peroxide cleavage process in a diastereoselective manner (ca. 2.3:1).[16] Monosilylation (chloride **13**,[17] imidazole) of the resultant mixture of diols afforded compound **14** (a single diastereomer was obtained after column chromatography, 65% yield over two steps).



Scheme 2. Construction of common intermediate **15**. DIAD = diisopropyl azodicarboxylate, DMF = *N*,*N*-dimethyl formamide, KHMDS = potassium bis(trimethylsilyl)amide, Tf = trifluoromethanesulfonyl, TIPS = triisopropylsilyl.

DMP oxidation and subsequent triflate formation (KHMDS, $PhNTf_2$) furnished compound **9** with good overall efficiency. The following alkyne carbopalladation/Stille cascade reaction was crucial not only for the formation of the two C–C bonds but also for the geometric control of the central C=C bond of **8**. Although THF, benzene, and toluene have been reported to be suitable solvents for similar transformations,[15] in this case, we only observed trace amounts of the cascade product when these solvents were used; gradual decomposition of the starting materials was predominant. DMF turned out to be a favorable solvent for the formation of the desired product **8**, whereas the direct Stille–Migita coupling between triflate **9** and stannane **10** and homodimerization of **10** were competitive side reactions. Under the optimized conditions [Pd(PPh_3)$_4$ (10 mol%), **10** (1.1 equiv), 80°C], **8** was obtained in an acceptable yield (55%) as a single geometric isomer. Notably, LiCl was found to promote the direct coupling over the cascade reaction. Exposure of **8** to air at 140°C smoothly provided the fully substituted arene **15** in 68% yield.

With **15** in hand, we investigated the formation of the five-membered ring for the synthesis of ileabethoxazole by a Heck-type cyclization strategy (Scheme 3). Treatment of

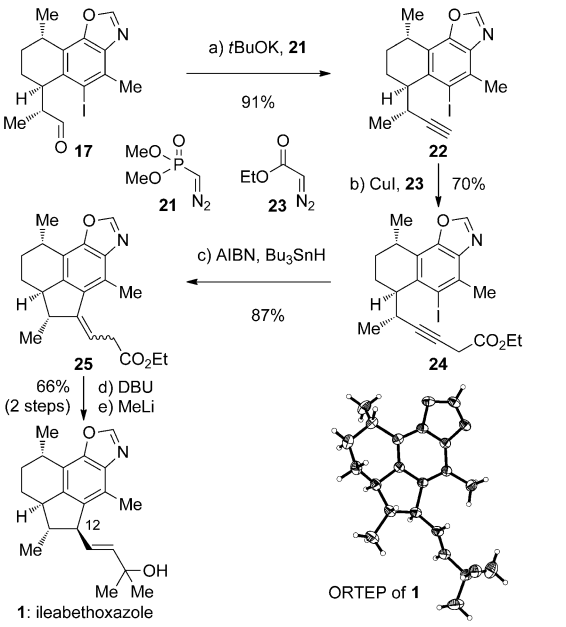


Scheme 3. Synthesis of 12-*epi*-ileabethoxazole. TBAF = tetrabutylammonium fluoride.

15 with AgF selectively removed the oxazole TIPS group to give **16** in 95% yield.[18] Cleavage of the C–Si bond of **16** with ICl,[19] followed by release of the primary hydroxy group with HF·py, afforded the corresponding iodine-substituted alcohol, which then underwent DMP oxidation, yielding aldehyde **17** with good overall efficiency. An olefinic side chain was elaborated by Julia–Kocienski olefination[20] with tetrazolyl sulfone **18** and KHMDS at −55°C, leading to *trans* alkene **19** (73% yield) as a single geometric isomer. We examined a variety of Heck reaction conditions for the 5-*exo*-trig cyclization of **19**; $Pd(OAc)_2$, PPh_3, and Ag_2CO_3 as a crucial additive at 70°C turned out to be an optimal combination.[21] Desilylation (TBAF, AcOH) of the cyclization product provided compound **20** (52% over two steps) as a single diastereomer, which was confirmed to be 12-*epi*-ileabethoxazole by NMR spectroscopy. The orientation of the C18 methyl group may influence the transition state of the Heck-

type cyclization, resulting in a non-epimerizable tertiary C12 center. We postulated that the desired stereochemistry at C12 could be established by thermodynamic control, according to the *trans* orientation of the methyl and alkenyl substituents in the natural product.

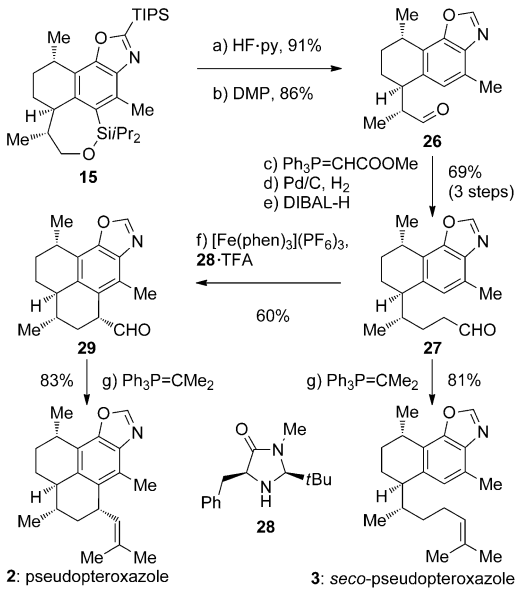
We then turned our attention to an alternative cyclization strategy for ileabethoxazole synthesis (Scheme 4). Treatment



Scheme 4. Synthesis of ileabethoxazole. AIBN = 2,2′-azobis(2-methylpropionitrile), DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

of aldehyde **17** with Seyferth–Gilbert reagent **21** and *t*BuOK gave terminal alkyne **22** in 91% yield.[22] Notably, under Bestmann conditions (Ohira–Bestmann reagent, K_2CO_3, MeOH),[23] epimerization at the carbonyl α-position occurred rapidly. Elongation of **22** with a two-carbon unit was effected according to Fu's method (**23**, CuI) with good efficiency.[24] The resultant compound **24** was first subjected to reductive Heck conditions;[25] however, 6-*endo*-dig cyclization products were obtained predominately. Fortunately, under conventional radical conditions (AIBN, Bu_3SnH, 80 °C), 5-*exo*-dig cyclization proceeded smoothly to afford **25** (87% yield) as an inconsequential geometric mixture. Exposure of this compound to DBU at 40 °C migrated the exocyclic C=C bond to a thermodynamically more favorable position, which meanwhile established the C12 stereochemistry (12:1 d.r.). Treatment of the resultant α,β-unsaturated ester with an excess of MeLi provided ileabethoxazole (**1**) in 66% yield over two steps; its structure was confirmed by X-ray crystallography (see Scheme 4).[26] The spectroscopic and physical properties of this synthetic sample were consistent with those reported for the natural product and Williams' synthetic sample.

We completed the syntheses of pseudopteroxazole (**2**) and *seco*-pseudopteroxazole (**3**) from the common intermediate **15** (Scheme 5). Exposure of **15** to HF·py broke the two C–Si bonds and generated the primary alcohol in 91% yield, which underwent DMP oxidation to aldehyde **26** (86% yield). The



Scheme 5. Syntheses of pseudopteroxazole and *seco*-pseudopteroxazole. DIBAL-H = diisobutylaluminum hydride, phen = 1,10-phenanthroline.

key closure of the six-membered ring relied on a radical cyclization by organocatalytic SOMO catalysis.[27] The two-carbon side chain was installed through a three-step sequence (Wittig reaction, hydrogenation, and DIBAL-H reduction), giving aldehyde **27** in 69% overall yield. This compound was subjected to the MacMillan conditions[27a] [secondary amine **28** (30 mol%), $[Fe(phen)_3](PF_6)_3$ (2.6 equiv), −20 °C] to provide tetracycle **29** in 60% yield as a single diastereomer. Wittig olefination with $Ph_3P{=}CMe_2$ afforded **2**. *seco*-Pseudopteroxazole (**3**) was obtained from **27** by a similar olefination method. The spectroscopic and physical properties of synthetic **2** and **3** are identical to those reported for the natural products.

In summary, we have accomplished the total syntheses of ileabethoxazole, pseudopteroxazole, and *seco*-pseudopteroxazole (**1**–**3**) in a collective manner. The key step was a one-pot 6π electrocyclization/aromatization sequence, which efficiently constructed the multisubstituted arene scaffold from a geometry-defined hexasubstituted triene. This work provides a versatile synthetic approach to analogues of benzoxazole diterpenoids and may facilitate their biological studies.

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Keywords: arenes · diterpenoids · electrocyclization · radical reactions · total synthesis

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