Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Asymmetric Synthesis of Rupestonic Acid and Pechueloic Acid

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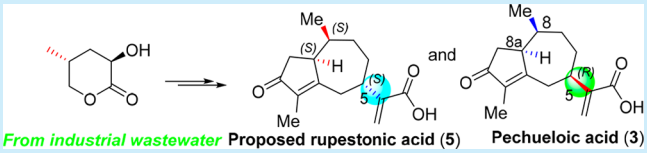
Supporting Information

ABSTRACT: In this report, the originally proposed rupestonic acid (**5**) and pechueloic acid (**3**) were efficiently synthesized. The chiral lactone **13**, recycled from the degradation of saponin glycosides, was utilized to prepare the key chiral fragment **11**. During the exploration of this convergent assembly strategy, the ring-closing metathesis (RCM), SmI_2-prompted intermolecular addition, and [2,3]-Wittig rearrangement proved to be effective transformations for the synthesis of subunits.



Natural sesquiterpenes are a promising class of compounds for drug discovery due to their interesting biological activities.[1] Guaianes and guaianolides in this family have attracted significant attention in recent years. As shown in Figure 1,

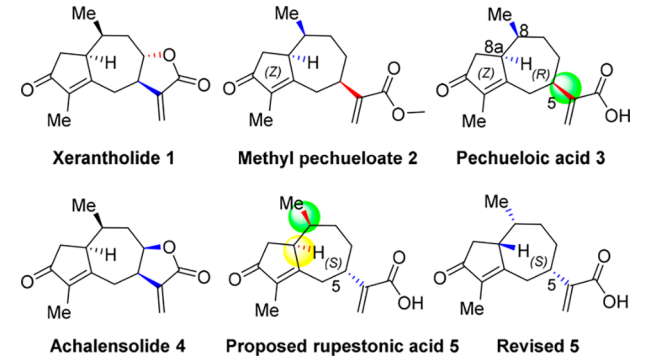


Figure 1. Several structures of guaianes and guaianolides.

xerantholide[2a] (**1**) was first isolated in 1977 from *Pechuel-Loeschea leibnitziane*, and the absolute configuration was confirmed in 1982.[2b] From the same plant, another natural product (+)-methyl pechueloate[2c] (**2**) was subsequently isolated in 1982. Later, pechueloic acid (**3**) and its methyl ester (**2**), as well as achalensolide (**4**), were isolated in 1987 from *Decachaeta scabrella*.[2c,3] In 1988, rupestonic acid (**5**), as the main active ingredient, was isolated from *Artemisia rupestris L*,[4] a well-known traditional Chinese medicinal plant (Yizhihao in Chinese) in Xinjiang. Rupestonic acid demonstrated potential use in detoxification, antihypersusceptibility, antibacterial, antitumor, antivirus as well as liver protection.[5] In addition, rupestonic acid is chosen as the "marker compound" for the chemical evaluation or standardization of *A. rupestris* L. Although many interesting approaches to such [5,7]-skeletons have been reported in recent years,[6] it is difficult to apply them in asymmetric synthesis of these natural products. Therefore, an efficient asymmetric method to these important chemical series is still challenging (Figure 1).

Structurally, the absolute configuration of rupestonic acid (**5**) was first proposed as (5*S*,8*S*,8a*S*) form[4] and was later revised to (5*S*,8*R*,8a*R*).[7] Surprisingly, the originally proposed structure (5*S*,8*S*,8a*S*)-**5** is still being used in scientific publications without any explanation.[8,9] Due to its remarkable bioactivities, especially against influenza viruses, rupestonic acid (**5**) and the scarce pechueloic acid (**3**) attracted considerable attention in structural modifications and activity evaluations.[8,9] A few groups reported their total syntheses; for example, optically pure pechueloic acid (**3**) was first synthesized from (+)-dihydrocarvone by Pedro,[10] and the racemate was prepared by Deprés in 2009.[8e] (+)-Achalensolide (**4**) was asymmetrically synthesized by Mukai and co-workers using a Rh(I)-catalyzed Pauson−Khand-type reaction as the key step to construct the bicyclo[5.3.0]decane skeleton.[11] The above synthetic routes applied excellent chemical transformations except imperfect stereochemistry control for some chiral centers. In 2009, Deprés and co-workers reported a synthetic method to (±)-rupestonic acid (**5**).[8e] However, the ^1H and ^{13}C NMR spectroscopic data of synthetic *rac*-**5** were not identical to those reported in the original literature for the rupestonic acid (**5**) isolation[4] or to the later revised (5*S*,8*R*,8a*R*) form. As a continuation of our interest in developing divergent syntheses of natural products,[12] we decided to confirm the absolute structure of natural rupestonic acid (**5**) through an asymmetric method. We herein present an asymmetric approach to synthesizing the original rupestonic acid (**5**) and pechueloic acid (**3**) using the recovered material **13** from industrial waste.[13]

Our retrosynthetic analysis of the originally proposed rupestonic acid (**5**) is outlined in Figure 2, with high stereocontrol of each chiral center as our focus in constructing

Received: November 7, 2017

DOI: 10.1021/acs.orglett.7b03459
Org. Lett. XXXX, XXX, XXX−XXX

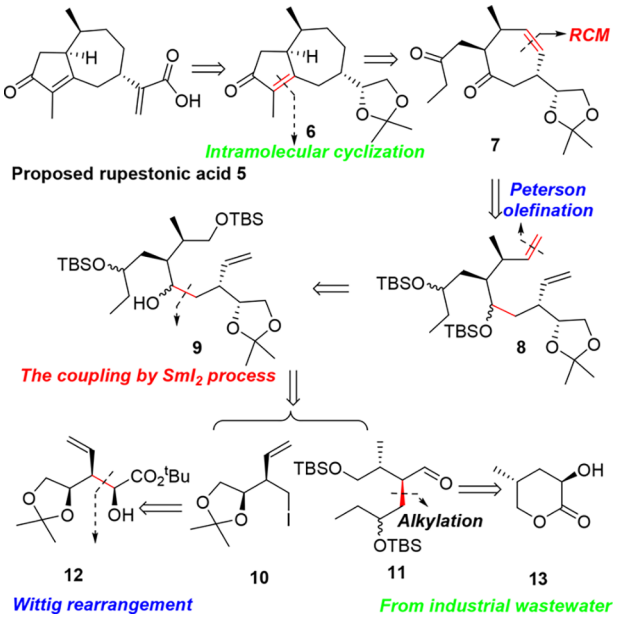
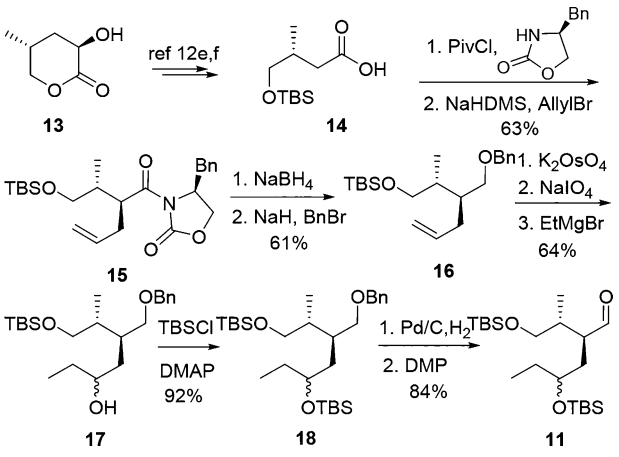


Figure 2. Our strategy to access rupestonic acid (**5**).

this target molecule. The key intermediate **6** could be obtained through intramolecular aldol condensation.[14] As for the formation of the seven-membered ring **7**, we proposed to use a ring-closing metathesis (RCM)[15] reaction from compound **8**. One terminal olefin was formed through Peterson olefination,[16] and the other key chiral center was generated using [2,3]-Wittig rearrangement.[17] The key intermediate **9** could be obtained through SmI_2-promoted coupling of iodide **10** and aldehyde **11**.[18] Moreover, the concept of "*from nature to nature*" was applied in our asymmetric synthesis of chiral fragment **11**, specifically that the intermediate **11** could be prepared from industrial waste **13**.[13]

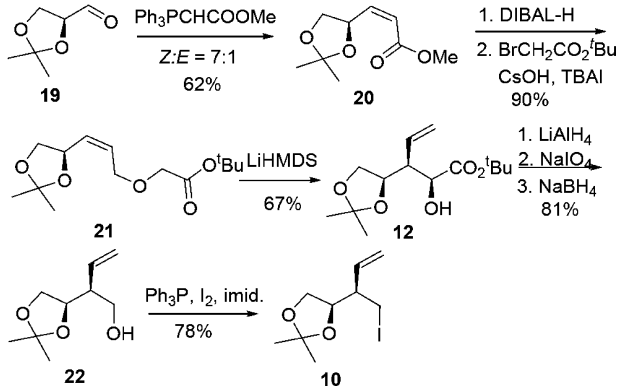
The chiral lactone **13**, recycled from the degradation of saponin glycosides,[13] was easily converted to the key chiral acid **14** in 41% overall yield[12e,f] (Scheme 1). After the introduction of chiral auxililary oxazolidinone,[19] the subsequent allylation gave **15** in 63% yield with high diastereoselectivity (dr > 98:2). Reduction ($NaBH_4$) of **15** and the following protection produced ether **16** in 61% yield. Dihydroxylation (K_2OsO_4, NMO)[20] of **16** and subsequent cleavage ($NaIO_4$) gave crude aldehyde, which was treated with ethylmagnesium bromide to give a mixture of two inseparable alcohols **17** in 64% combined yield. Notably, this new chiral center from Grignard addition would be eliminated at a later stage, therefore the diastereomeric mixture was used in the following steps. Protection (TBSCl) and debenzylation ($Pd/C, H_2$) gave the primary alcohol, which could be oxidized to the corresponding aldehyde **11** in 77% overall yield.

Scheme 1. Preparation of Aldehyde 11



As shown in Scheme 2, chiral iodide **10** was conveniently prepared through a key [2,3]-Wittig rearrangement.[17] The

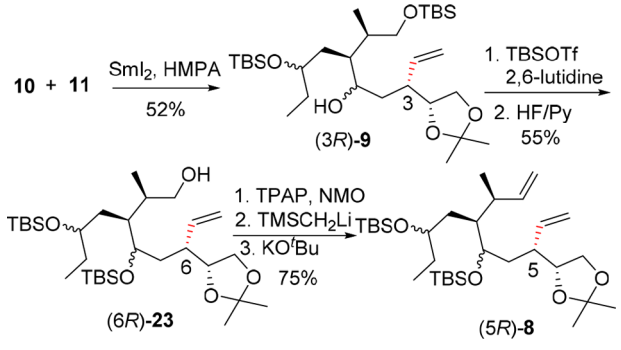
Scheme 2. Preparation of Chiral Iodide 10



conversion of chiral aldehyde **19** to the desired chiral iodide **10** was achieved according to the following synthetic sequence: Wittig reaction gave olefin **20** with 88:12 selectivity (*Z*/*E*), and the pure Z isomer was obtained in 62% yield. Reduction (DIBAL-H) and subsequent etherification ($BrCH_2COOMe$) gave ether **21** in 90% overall yield. The following key step, [2,3]-Wittig rearrangement of **21**, was accomplished by treatment with lithium bis(trimethylsilyl)amide (LiHMDS), smoothly producing the desired chiral product **12** with high diastereoselectivity (dr > 99:1) in 67% yield. Reduction ($LiAlH_4$) of **12** and subsequent cleavage ($NaIO_4$) gave crude aldehyde, which was directly reduced with sodium borohydride ($NaBH_4$) to give alcohol **22** in 81% overall yield. Finally, iodination (Ph_3P/I_2, imidazole) of **22** resulted in the desired chiral iodide **10** in 78% yield.

Next, we turned our attention to the preparation of diene **8** (Scheme 3). Different conditions were surveyed for the coupling of iodide **10** and aldehyde **11** (see Supporting Information). When the reaction was conducted using SmI_2[17] in the presence of hexamethylphosphoric triamide (HMPA) at −50 °C to room temperature overnight, the desired adduct (3*R*)-**9** was obtained in 52% yield. Again, this new chiral center from SmI_2-promoted

Scheme 3. Preparation of Terminal Olefin (5*R*)-8

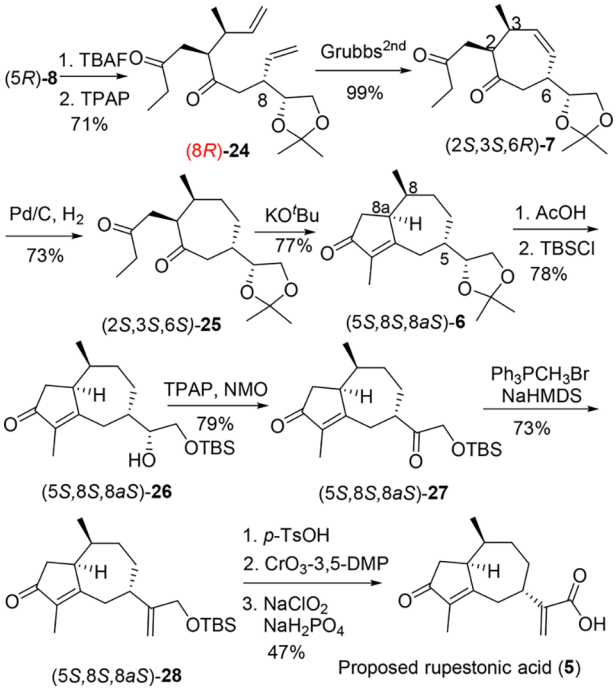


DOI: 10.1021/acs.orglett.7b03459
Org. Lett. XXXX, XXX, XXX−XXX

addition would be eliminated at a later stage, therefore the diastereomeric mixture was used in the following steps. After the protection (TBSOTf) of alcohol (3*R*)-**9**, selective release of the primary hydroxyl group was achieved with HF/Pyridine to give (6*R*)-**23** in 55% yield. Oxidation of alcohol (6*R*)-**23** with tetrapropylammonium perruthenate (TPAP) in the presence of NMO gave an aldehyde, which underwent Peterson olefination to afford the desired diene (5*R*)-**8** in 75% yield.

With the diene (5*R*)-**8** in hand, the initial attempt of ring-closing metathesis (RCM)[15] reaction failed when Grubbs second-generation catalyst was used, most likely due to the steric hindrance. Thus, deprotection (TBAF) of (5*R*)-**8** and subsequent oxidation (TPAP) were conducted to give diketone (8*R*)-**24** in 71% overall yield (Scheme 4). Fortunately, the

Scheme 4. Preparation of Proposed Rupestonic Acid 5



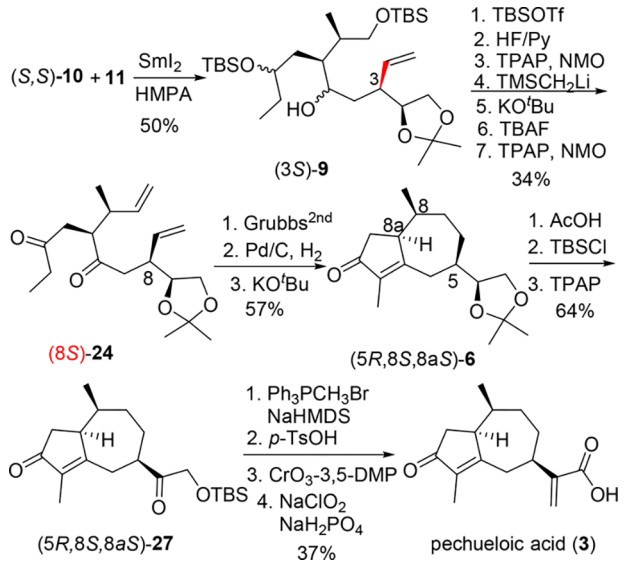
subsequent ring closure using Grubbs second-generation catalyst successfully afforded the seven membered (2*S*,3*S*,6*R*)-7 in 99% yield. Upon the reduction of carbon−carbon double bond in (2*S*,3*S*,6*R*)-7 by hydrogenation (Pd/C, H_2) in 73% yield, the intramolecular aldol condensation of the resulting (2*S*,3*S*,6*S*)- **25** was achieved by treatment with *t*-BuOK to afford the desired bicyclic skeleton (5*S*,8*S*,8a*S*)-**6** in 77% yield.

Deprotection (80% AcOH) and subsequent selective protection of the primary hydroxy group with TBSCl afforded (5*S*,8*S*,8a*S*)-**26** in 78% yield. Oxidation of (5*S*,8*S*,8a*S*)-**26** with TPAP afforded ketone (5*S*,8*S*,8a*S*)-**27** in 79% yield, which was converted to the olefin product using standard Wittig condition (NaHMDS, Ph_3PCH_3Br) in 73% yield. Upon cleavage of O-TBS protection group, the resulting alcohol was subjected to sequential Jones oxidation, Pinnic oxidation, affording proposed rupestonic acid [(5*S*,8*S*,8a*S*)-**5**][$[\alpha]_D^{23}$ = +49.6 (*c* 0.357, EtOH), lit.[4] $[\alpha]_D^{26}$ = +150 (*c* 0.176, EtOH)] in 47% isolated yield. The stereochemistry of synthetic (5*S*,8*S*,8a*S*)-**5** was confirmed by X-ray crystallography (see the SI).

To our surprise, the analytical data of optical rotation and NMR spectra generated from synthetic (5*S*,8*S*,8a*S*)-**5** were substantially different from those reported for rupestonic acid.[4] Moreover, in analytical reversed-phase HPLC (see the SI), synthetic (5*S*,8*S*,8a*S*)-**5** showed a different retention time from the isolated natural product. By comparison of the respective NMR data of synthetic (5*S*,8*S*,8a*S*)-**5** with the natural product, the perceptible differences in the signals of the C-5 position suggested that the stereochemistry assigned to C-5 position might be incorrect.

To confirm our hypothesis, we synthesized a diastereomeric compound, pechueloic acid (**3**) (Scheme 5). The (*S*,*S*)-**10** was

Scheme 5. Preparation of Pechueloic Acid 3



prepared from the (*R*)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde. Following the similar synthetic sequence described above, pechueloic acid (**3**) was obtained and the stereochemistry was confirmed by X-ray crystallography (see the SI).

To our delight, the optical rotations [$[\alpha]_D^{24}$ = +115.0 (*c* 0.814, EtOH)] and the NMR data of synthetic pechueloic acid (**3**) (see SI) were in excellent agreement with those reported for isolated **3**[3c] and the originally proposed natural rupestonic acid **5**.[4] As mentioned previously, the synthetic rupestonic acid (**5**) showed a different retention time compared to authentic rupestonic acid in analytical reversed phase HPLC (see the SI). However, synthetic pechueloic acid (**3**) and the authentic rupestonic acid displayed an identical retention time, and coeluted under two different HPLC conditions. Therefore, we conclude that the absolute structure of natural rupestonic acid isolated from the traditional Chinese medicinal plant (Yizhihao in Chinese) in Xinjiang in 1988[4] is the same as the pechueloic acid (**3**) isolated from *Decachaeta scabrella* in 1987.[3c]

In summary, the first asymmetric approach to rupestonic acid (**5**) and pechueloic acid (**3**) has been accomplished using our previously proposed "*from nature to nature*" strategy. It is worth mentioning that this convergent assembly process provided an efficient approach to synthesize both (5*R*,8*S*,8a*S*)-**5** and pechueloic acid (**3**). Peterson olefination, SmI_2 prompted intermolecular addition and [2,3]-Wittig rearrangement offered an effective method for the synthesis of subunits to rupestonic acid. Moreover, the absolute stereochemistry of natural rupestonic acid (**5**) is the same as that of the pechueloic acid (**3**).

DOI: 10.1021/acs.orglett.7b03459
Org. Lett. XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03459.

Experimental procedure and characterization of all new compounds (PDF)

Accession Codes

CCDC 1584456−1584457 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (21772027, 21472022 to B.-G.W., 21702032 to C.-M.S.) for financial support. We thank the National Natural Science Foundation of China and Xinjiang Joint Foundation (U1303224 to Z.-Y.G.) for financial support. We thank Prof. Wei-Sheng Tian (SIOC) for providing the lactone **13**. We thank Dr. Han-Qing Dong (Arvinas, Inc.) for helpful suggestions. We also thank Prof. Haji Akber Aisa (XTIPC.CAS) for providing isolated rupestonic acid.

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DOI: 10.1021/acs.orglett.7b03459
Org. Lett. XXXX, XXX, XXX−XXX