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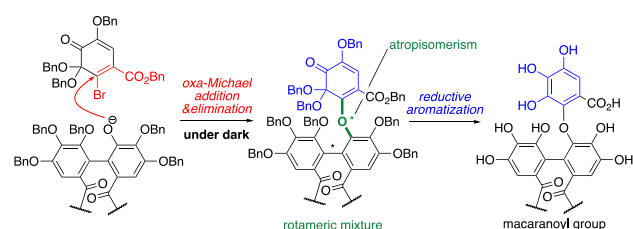
Synthesis of an Ellagitannin Component, the Macaranoyl Group with a tetra-*ortho*-Substituted Diaryl Ether Structure

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Supporting Information Placeholder



ABSTRACT: Herein, a practical synthesis of the macaranoyl group contained in ellagitannins, i.e., a C–O digallate structure with a tetra-*ortho*-substituted diaryl ether bond, is described. The methodology involved an oxa-Michael addition/elimination reaction between a brominated *ortho*-quinone monoketal and a phenol with a hexahydroxydiphenoyl moiety in the presence of 18-crown-6 under dark conditions, followed by reductive aromatization. The existence of rotamers originating from the constructed ether moiety is discussed as well.

Ellagitannins are a class of natural polyphenols. To date, more than a thousand ellagitannins have been isolated.¹ Their general structure comprises D-glucose esterified with galloyl and axially chiral hexahydroxydiphenoyl (HHDP) groups, biosynthesized via C–C coupling of two galloyl groups in pentagalloyl-D-glucose.² Ellagitannins additionally contain C–O

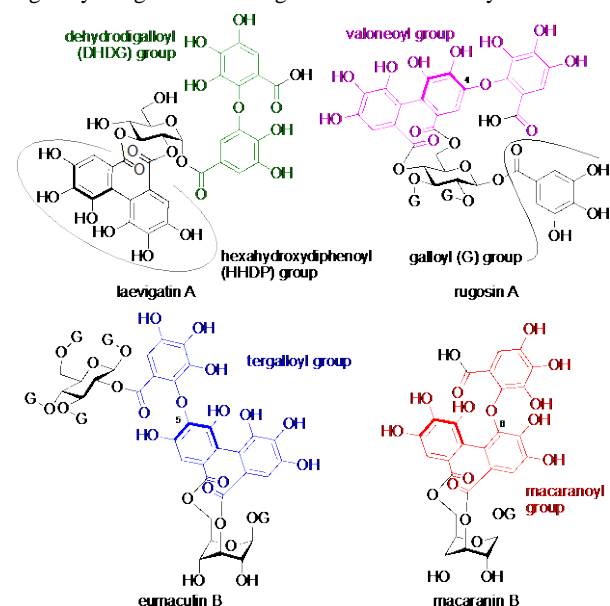


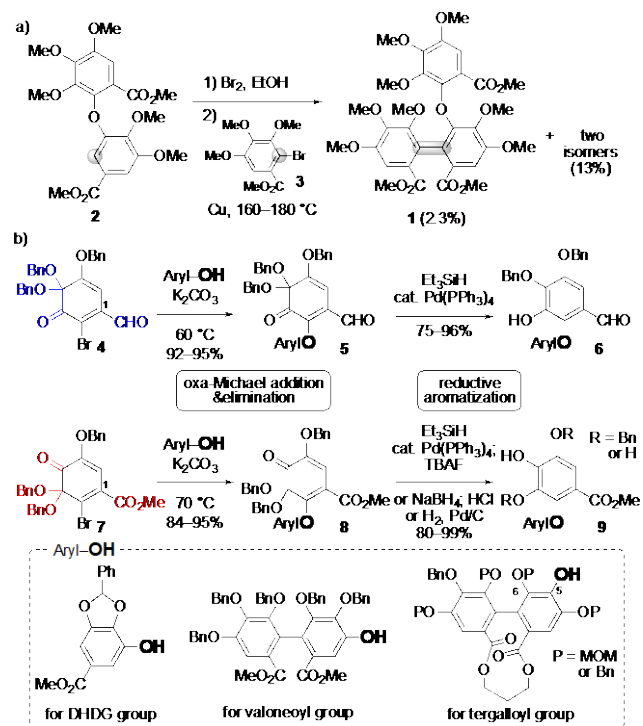
Figure 1. Ellagitannins with C–O digallate structures.

digallate moieties, comprising a diaryl ether structure wherein two galloyl groups are connected via a C–O bond. Etheral linkages between a galloyl group and other components, e.g. an HHDP group, have also been found in nature, and form more complicated C–O digallate structures.³ Dehydrodigalloyl (DHDG), valoneoyl, tergalloyl, and macaranoyl groups are representative components (Figure 1). As exemplified by eumaculin B, these components can oligomerize a monomeric ellagitannin via esterification of a carboxyl group in the motif with a hydroxy group of a glucose moiety in another ellagitannin, resulting in broad structural diversity of the ellagitannins.⁴

C–O Digallate structures have previously been constructed by three groups. Feldmann et al. and Abe et al. synthesized the DHDG group using independent strategies,^{5, 6} and Abe et al. additionally prepared the valoneoyl group.⁷ Recently, we reported a unified synthetic strategy for DHDG, valoneoyl, and tergalloyl groups.⁸ Nevertheless, their synthetic application to the macaranoyl group has not been explored as yet.

Nishioka and coworkers have previously synthesized a methylated macaranoyl analogue **1**, for the structural determination of this component of natural ellagitannins. They achieved this via Ullmann coupling between an aryl bromide, prepared from **2**, and a second aryl bromide **3** (Scheme 1a).⁹ However, the yield was low, and two isomers of **1**, derived from the undesired bromination products of **2**, were also generated. Herein, we describe a practical synthesis of the macaranoyl group achieved by adaption of our synthetic procedure for the C–O digallate structures.

Scheme 1. (a) Reported method for synthesizing the macaranoyl group. (b) Our synthetic method for C–O digallate structures.

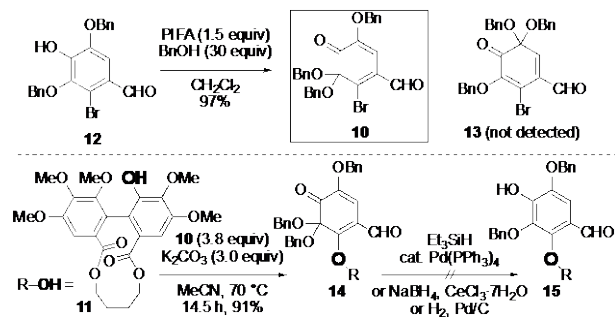


Our unified synthetic method for DHDG, valoneoyl, and tergalloyl groups is described in Scheme 1b.⁸ Orthoquinone monoketal (*o*-Qk) **4**^{8a} was used as an electrophile, and the oxa-Michael addition of a phenol bearing a galloyl or HHDP moiety to **4**, followed by elimination of the bromine atom gave **5**. Subsequent treatment of **5** with Et_3SiH and a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ resulted in reductive aromatization of **5** to form **6**. We further developed a novel *o*-Qk **7**,^{8b} wherein the ketone and ketal locations in **4** were reversed. Thus, the electrophilic carbon of **7** was more reactive than that of **4** by acquiring an additional conjugation effect from the ketone, which allowed the oxa-Michael/elimination reaction despite the replacement of the aldehyde at the 1-position of **4** with a methyl ester. This modification had further positive effects on the subsequent reaction; in addition to reductive conditions involving Et_3SiH and $\text{Pd}(\text{PPh}_3)_4$, NaBH_4 reduction followed by acidic workup, as well as hydrogenolysis, could both induce the reductive aromatization of **8** to supply **9**. As these two electrophiles enabled the formation of a tetra-*ortho*-substituted diaryl ether structure in the tergalloyl group, wherein the ethereal bond is located at the 5-oxygen of the HHDP group, this method may also form the corresponding bond in the macaranoyl group. However, this transformation appears challenging because the C–O bond must be constructed at a more crowded position (6-O), implying that steric repulsion may be problematic for the synthesis.

To construct the macaranoyl group, we initially used electrophile **10**, wherein the methyl ester of **7** was replaced with an aldehyde (Scheme 2). *o*-Qk **10** is more electrophilic than **7** owing to the strong inductive effect of the aldehyde and is hence expected to realize the desired reaction. To minimize steric hindrance at the reaction site, phenol **11**¹⁰ was selected as the nucleophile, wherein all the oxygen atoms of the HHDP group, except for 6–O, were methylated. *o*-Qk **10** was prepared in 97% yield via phenyliodine(III) bis(trifluoroacetate) (PIFA)-mediated oxidation¹¹ of phenol **12**¹⁰ in the presence of excess benzyl alcohol (BnOH). Although the synthesis of **7** also provided its regioisomer,^{8b} **13**, the corresponding regioisomer of **10**, was not formed. The reaction of **10** with **11**

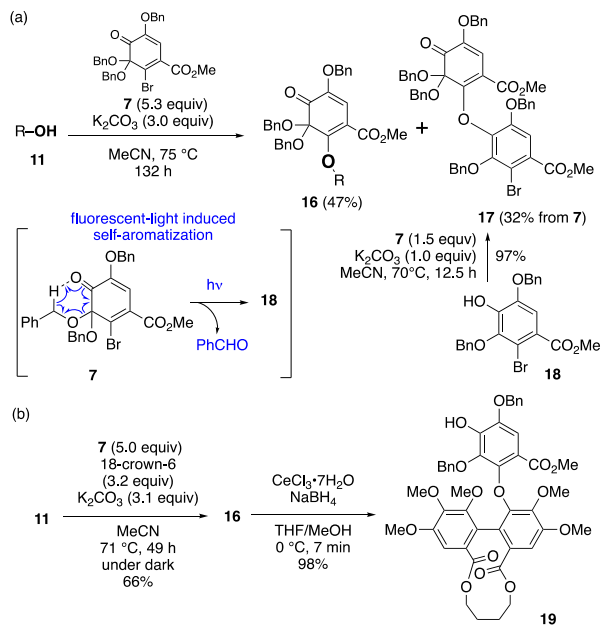
proceeded smoothly to furnish the desired product **14** in 91% yield. However, subsequent reductive aromatization using Et_3SiH and catalytic $\text{Pd}(\text{PPh}_3)_4$ to obtain **15** failed, instead affording **11** as the major product. Other reaction conditions such as Luche reduction¹² and hydrogenolysis were also attempted; while no desired product was obtained, **11** was generated (Supporting Information (SI)-S2). Hydride reduction failure may be explained by the high electrophilicity of the α,β -unsaturated aldehyde moiety of **14**, which preferred an attack by H^- on the β -carbon to eliminate **11**. Under hydrogenolysis conditions, in addition to reductive aromatization of **14** and removal of two Bn groups in **15**, the aldehyde function is likely being reduced. Thus, we assumed that the production of **11** was attributed to the oxidation of the 1-aryloxy-2,3,4-trihydroxy-6-methylbenzene ring in air.

Scheme 2. Attempt to synthesize the macaranoyl group using *o*-Qk **10**.



Therefore, we conducted experiments using *o*-Qk **7**, the reactivity of which was enhanced owing to the mesomeric effects between the ketone and ester. The oxa-Michael addition/elimination reaction between **7** and **11** gave the coupling product **16** in 47% yield (Scheme 3a).¹³ However, the reaction required over 5 days and various byproducts were detected by TLC and MS analysis. One of the major byproducts was identified as **17**; its structure was confirmed by comparing its spectral data with that of **17**, synthesized in 97% yield via oxa-Michael addition/elimination reaction of **7** and phenol **18**.^{8b} Because the isolated yield of **17** was 32%, it was expected that suppressing this side reaction would increase the yield of **16**. We established that **17** was generated via self-aromatization of **7** under light irradiation. The ^1H NMR spectrum of **7** in chloroform-*d* after irradiation with a fluorescent light (Panasonic, FL20SS-EX-N/18) for 24 h, displayed signals corresponding to benzaldehyde and phenol **18** along with those attributed to **7** (SI-S3). The amounts of these two products increased continually over time, with a disappearance of **7** observed after 4 days. The production of **17** involved the generation of **18** *in situ*, followed by its reaction with the remaining **7**. This side reaction was not detected in the previous study that utilized **7** because those reactions were complete within a shorter time (≤ 10 h).^{8b} Thus, prolonged reactions with **7** should be conducted under dark conditions. We further hypothesized that the addition of 18-crown-6 would enhance the reactivity of **11** because of the formation of the salt-free phenolate anion.¹⁴ Based on this consideration, we conducted the following experiment. To a suspension of **11** and K_2CO_3 in acetonitrile in a reaction flask wrapped with aluminum foil, **7** and 18-crown-6 were added, and the mixture was stirred at $71\text{ }^\circ\text{C}$. The desired reaction was complete within 49 h, which was 83 h shorter than the time required for reaction in Scheme 3a; **16** was obtained in 66% yield (Scheme 3b). Subsequent reductive aromatization of **16** proceeded smoothly under Luche reduction conditions¹² to supply phenol **19** with a macaranoyl structure in 98% yield.

Scheme 3. (a) Formation of byproduct **17** in the reaction of **11** with **7**. (b) Optimized oxa-Michael addition/elimination reaction using **7** and transformation into phenol **19**.



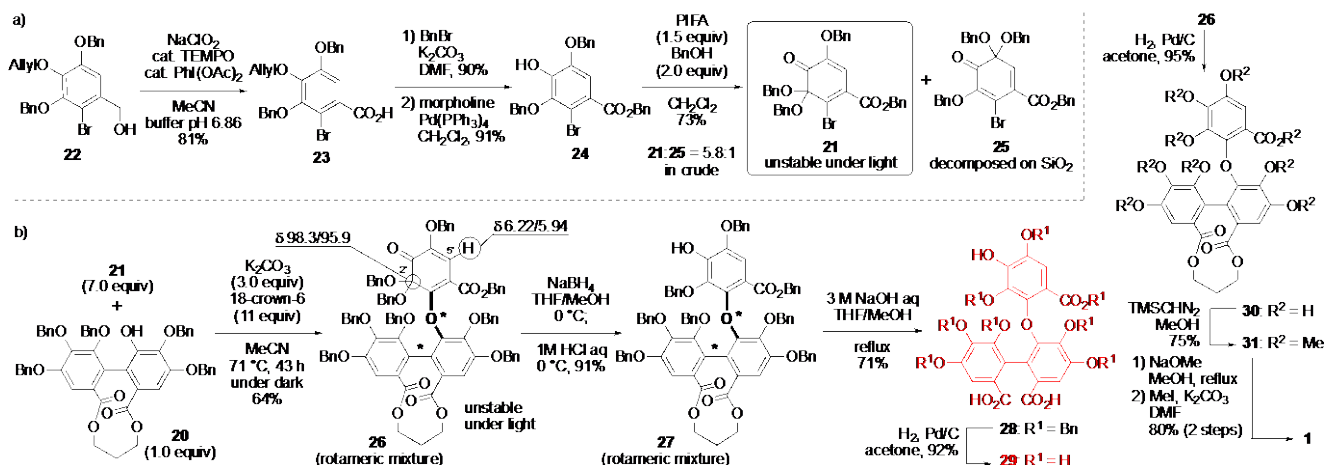
We next attempted a practical synthesis of the macaranoyl group. Because removal of methyl protecting groups of phenolic hydroxy groups is difficult, benzyl (Bn)-protecting groups are frequently used in ellagitannin synthesis owing to their tolerance of various reaction conditions and ease of removal via hydrogenolysis.^{8a, 15} Thus, an oxa-Michael addition/elimination reaction using an analogue of **11**, wherein its methyl groups were substituted by Bn groups, would be more practical. Additionally, we decided to change the ester moiety of **7** because selective hydrolysis of the methyl ester in the presence of other esters, formed between D-glucose and HHDP/galloyl groups, is difficult. Replacement with a benzyl ester would facilitate the release of the carboxylic group, which expedites the synthesis of oligomeric ellagitannins containing the macaranoyl group.¹⁶ Thus, we focused on the oxa-Michael addition/elimination reaction of phenol **20**¹⁰ and *o*-Qk **21**.

The synthetic method of **21** is shown in Scheme 4a. Transformation of alcohol **22**^{8b} into carboxylic acid **23** via 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)-mediated oxidation with $\text{PhI}(\text{OAc})_2$ and NaClO_2 ,¹⁷ benzylation of **23**, and removal

of the allyl group provided phenol **24**. PIFA-mediated oxidation of **24** into **21** was performed in the presence of 2.0 equiv of BnOH to generate a crude product mixture of **21** and **25** in a 5.8:1 ratio. Undesired **25** was decomposed during purification by silica gel chromatography, and **21** was isolated exclusively in 73% yield, suggesting that **25** possesses similar properties to the regioisomer of *o*-Qk **7**.^{8b} Similar to **7**, *o*-Qk **21** underwent light-mediated self-aromatization to afford **24** and benzaldehyde (SI-S4).

The oxa-Michael addition/elimination reaction of **20** and **21** proceeded under conditions analogous to those of the reaction between **11** and **7** (Scheme 4b). Even though the reaction site of **20** is more hindered than that of **11**, owing to the surrounding Bn groups, the reaction was completed within 43 h and gave the desired product **26** in 64% yield, illustrating the robust reactivity of **21**. While **26** also underwent self-aromatization under light to slowly degrade into phenol **27** and benzaldehyde, it remained stable for a month when kept in the dark (SI-S5). Interestingly, the ¹H and ¹³C NMR spectra of **26** in acetonitrile-*d*₃ at 24 °C displayed signal duplication. For example, the proton and carbon signals for the 5''- and 2''-positions were detected at δ 6.22/5.94 and 98.3/95.9, respectively. The four substituents located adjacent to the formed ether bond impart rigidity to it and impede bond rotation, appearing to generate a C–O chiral axis.¹⁸ Although **26** also contains a C–C chiral axis in the biphenyl structure, no examples exist of C–C chiral axis rotation in protected HHDP groups. Thus, we rationalized that the duplication of signals is attributed to the presence of rotamers, arising from the C–O chiral axis.¹⁹ No coalescence of the signals pairs was observed in the ¹H NMR spectrum despite elevating the temperature to 75 °C, which suggested that the rotation energy barrier was sufficiently high. As self-aromatization of **26** was observed in this experiment (SI-S6), we did not measure the ¹H NMR spectra at higher temperatures.

We next transformed **26** into the unprotected macaranoyl derivative (Scheme 4b). Treatment of **26** with NaBH_4 followed by 1 M aqueous HCl induced reductive aromatization, affording **27** in 91% yield. Selective hydrolysis of diester moieties bearing the propane tether, followed by the hydrogenolysis of obtained **28** provided the desired compound **29**. The macaranoyl structure of **29** was confirmed via the transformation of **26** into known compound **1**. Following the reductive aromatization of **26**, and removal of all the Bn groups via hydrogenolysis, the treatment of obtained **30** with TMS diazomethane²⁰ gave a nona-methylated compound **31**. Methanolysis to cleave the



propane tether of **31** using NaOMe in MeOH produced **1** and the product of partial hydrolysis, resulting from the presence of a small amount of water contained in the reaction mixture. Thus, the crude product was exposed to MeI and K₂CO₃ to afford **1**. The ¹H NMR spectrum of synthesized **1** was identical to the literature data for **1**,⁹ confirming the macaranoyl structure of **27–31**.

Diaryl ether **27** was also isolated as a rotameric mixture (Figure 2). The ¹H NMR spectrum of **27** in acetonitrile-*d*₃ at 24 °C contained signal pairs, which appeared broadened in the 3.6–5.3 ppm region. While some of the broad signals became sharp at 0 °C, almost all signals in that range were broadened at 50 °C. Coalescence of a pair of the broad signals was detected at 75 °C,²¹ indicating that the rotation barrier of **27** was lower than that of **26**. This difference was attributed a decrease in steric hindrance resulting from the transformation of the ketal moiety of **26** to the benzyloxy moiety of **27**. Although tri- or tetra-*o*-substituted diaryl ethers can exhibit atropisomerism,²² this feature was not observed in previously synthesized diaryl ether compounds.⁸ Rotamers of **28** were also detected in the ¹H/¹³C NMR spectra at 22 °C, indicating that the presence of rotamers is specific to the macaranoyl structure.

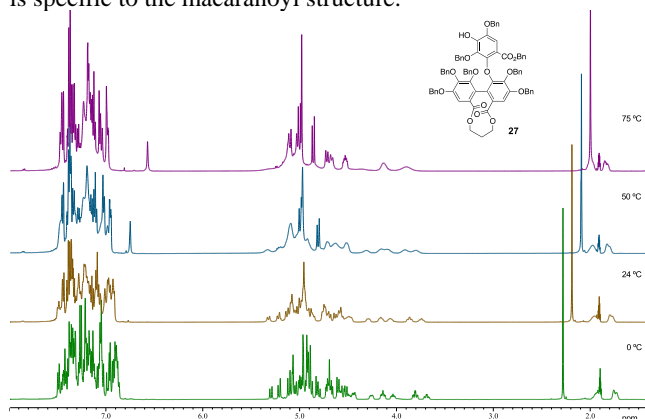


Figure 2. ¹H NMR spectra of **27** in acetonitrile-*d*₃ (500 MHz) at various temperatures.

In summary, we succeeded in a practical synthesis of the macaranoyl group by expanding our established synthetic procedures for the C–O digallate structure. The oxa-Michael addition/elimination reaction using phenol **20** and *o*-Qk **21** gave a satisfactory yield of **26** upon addition of 18-crown-6, which enhanced the reactivity of **20**, and by performing the reaction in the dark, the self-aromatization of **21** was suppressed. NaBH₄-mediated reductive aromatization of **26** provided diaryl ether **27**, which was readily transformed to **29**. We additionally discovered that **26** and **27** existed as rotational mixtures owing to the presence of the C–O chiral axis. This observation demonstrates the robustness of our method and suggests the possibility of its application to the synthesis of other C–O digallate structures. We intend to report the synthesis of ellagitannins with a macaranoyl group in the near future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, analytical data, and copies of the ¹H and ¹³C NMR spectra for all new products (PDF).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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- (19) Although **16** also appeared to be a rotameric mixture at 24 °C, **14** was not, suggesting that the ester moieties on the *o*-Qk ring of **16** and **26** are required to establish the C–O chiral axis. Dicarboxylic acid **29** was also isolated as a rotameric mixtures, indicating that the propane tether of **26** was not involved in the generation of the rotamers.
- (20) TMS diazomethane was used for the methylation to eliminate the risk of isomerization of the macaranoyl skeleton of **30** into the tergalloyl and valoneoyl skeletons via Smiles rearrangement. See Ref. 16a for details.
- (21) The ¹³C NMR spectrum of **27** also showed a pair of signals corresponding to **27** at ≤ 24 °C. These paired signals coalesced at 50–70 °C. See SI-S7 for details.
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