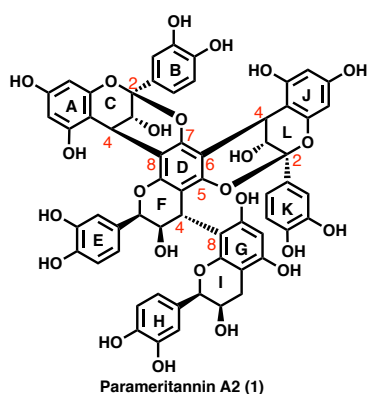


Total Synthesis of Tetrameric Epicatechin Parameritannin A2 via Cascade Pummerer-type Reaction.

(Department of Chemistry, Tokyo Institute of Technology)

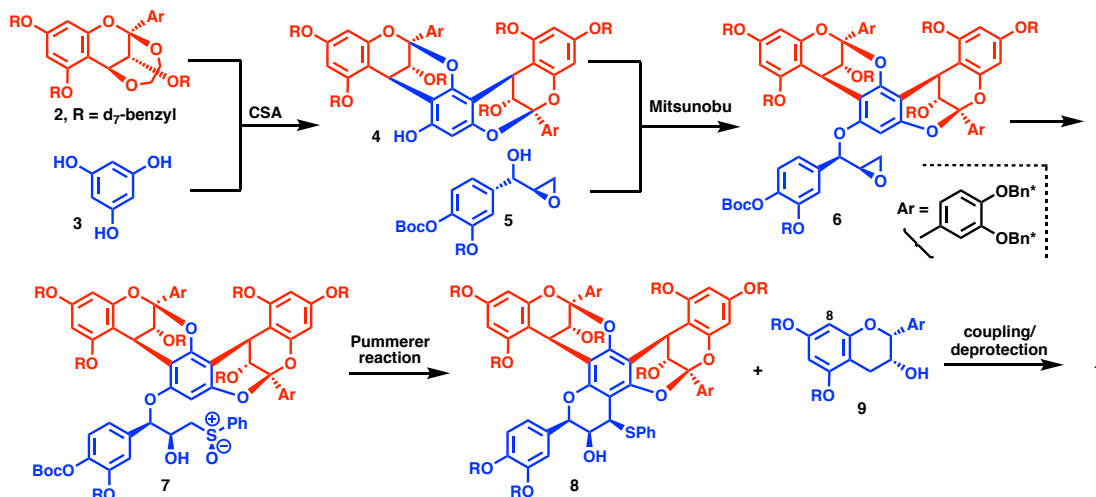
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Keywords: Total synthesis; Pummerer; Cascade reactions; Regioselective reactions



Parameritannin A2 (**1**), isolated from Indonesian folk medicinal plant *Parameria laevigata*,¹ is a tetrameric epicatechin derivative possessing two-fold double connection in the middle epicatechin unit, which is additionally connected to bottom epicatechin unit through single linkage. Biological study of **1** has been restricted by the scarcity, thus calling for the availability by organic synthesis.

Two molecules of dioxy compound **2** upon annulation with phloroglucinol **3** gave dioxabicyclo compound **4** as the sole product. Alcohol **5**, derived from (*S*)-glycidol, was then reacted with phenol **4** under the modified Mitsunobu conditions, and the resultant coupled product **6** was transformed to sulfoxide **7**.



The key pyran-ring cyclisation of sulfoxide **7** involving Pummerer reaction and intramolecular Friedel-Crafts reaction promoted by TMSOTf successfully delivered cyclized product **8**. Activation of sulfide **8** under soft Lewis acidic conditions followed by union with the flavan **9** attached the bottom epicatechin unit. Finally, removal of all protecting groups gave **1**.

1) Kamiya, K.; Watanabe, C.; Endang, H.; Umar, M.; Satake, T. *Chem. Pharm. Bull.* **2001**, *49*, 551-557.