JOC Article

Total Synthesis of Flavocommelin, a Component of the Blue Supramolecular Pigment from *Commelina communis*, on the Basis of Direct 6-*C*-Glycosylation of Flavan

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Received March 31, 2004

We succeeded in a first total synthesis of flavocommelin (**1**), a component of the blue supramolecular pigment, commelinin (**2**), from *Commelina communis*, by direct 6-*C*-glycosylation of the flavan **4** using perbenzylglucosyl fluoride **8** in the presence of MS 5 Å in CH_2Cl_2 and a catalytic amount of $BF_3{\cdot}Et_2O$. After 6-*C*-glycosylation of **4**, oxidation with CAN to flavanone **18** and subsequent 4′-*O*-glycosylation, promoted with a combination of $BF_3{\cdot}Et_2O$ and DTBMP, afforded diglucosylflavanone **20**. DDQ oxidation of **20** and deprotection successively gave **1**.

Introduction

A variety of *C*-glycosylflavonoids are found widely distributed in the plant kingdom.[1] The *C*-glycosides are generally linked at C-6 and/or C-8 on the A-ring of the flavonoid nucleus. Their biological activities as antioxidants,[2] flower-color-development,[3] DNA binding,[4] hypotension,[5] and ovipositional[6] and feeding[7] stimulation for insects are well-known. Carthamin, a *C*-glucosylchalcone, is practically used as a red pigment.[8] Despite the attractive biological characteristics and commercial utility, only a few synthetic methods for *C*-glycosylflavonoids have been reported.[1,9,10] In fact, the synthesis of a flavone bearing both *O*- and *C*-glucosides has hitherto never been reported.

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We have focused our attention on flavocommelin (**1**), a 7-*O*-methylapigenin 6-*C*-,4′-*O*-di-β-D-glucoside, and one of the components of commelinin (**2**), a blue supramolecular pigment that is a metalloanthocyanin (a metal-complex anthocyanin) in *Commelina communis*.[3b] Commelinin (**2**), to our knowledge, is the most stable of the metalloanthocyanins due to the presence of *C*-glucosylflavone. Its structure has been established by X-ray crystallographic analysis[3b] and the pigment is a stoichiometric self-assembled supramolecule composed of six molecules of malonylawobanin (**3**), six molecules of **1**, and two atoms of magnesium ion (Figure 1). The components of **2** spatially self-assemble on the basis of very strict chiral molecular recognition. Recognition by self-association (itself) of **1** and **3**, and copigmentation between **1** and **3** might be caused by chiral hydrophobic $\pi-\pi$ interactions and some hydrogen bonding among the sugar residues.[3b,11] To elucidate the basis for molecular chiral recognition in the formation of commelinin (**2**), **1** and its analogues bearing various D- and/or L-glucose are necessary. We herein report the first successful synthesis of flavocommelin (**1**) using a newly developed approach for efficient *C*-glycosylation of flavan as a key reaction.

10.1021/jo0494681 CCC: $27.50
Published on Web 07/02/2004