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Direct observation of the target cell for jasmonate-type leaf-closing factor: genus-specific binding of leaf-movement factors to the plant motor cell

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Abstract—We report the synthesis of the novel fluorescence-labeled jasmonate glycoside **2** based on β-D-glucopyranosyl 12-hydroxyjasmonate **1**, which is a leaf-closing substance of *Albizzia julibrissin* Durazz. The fluorescence study using **2** revealed that the target cell for **1** is a motor cell. Probe **2** bound to the motor cells of two plants belonging to genus *Albizzia*. This result suggested that a receptor for **2**, which is common among genus *Albizzia* would be involved in the nyctinastic leaf movement.

Most leguminous plants close their leaves in the evening, as if to sleep, and open them in the morning according to the circadian rhythm controlled by a biological clock. Charles Darwin, well known for his theory of evolution, carried out the pioneering work on this field.[1] And in the 1970s, physiological studies, especially those using *Albizzia saman*, revealed that nyctinastic leaf movement is induced by the swelling and shrinking of motor cells in the pulvini, a small organ located in the joint of the leaf to the stem.[2] Flux of potassium ions across the plasma membranes of the motor cells is followed by massive water flux, which results in swelling and shrinking of these cells. We revealed that nyctinasty is controlled by a pair of leaf-movement factors: leaf-opening and leaf-closing substances.[3] And, we have also revealed that the target cell of the leaf-opening substance of the *Cassia* plant is a motor cell.[4]

However, most of the physiological studies on nyctinasty were carried out using plants belonging to genus *Albizzia*. Considering that each nyctinastic plant has a pair of leaf-movement factors whose bioactivities are specific to the plant genus,[5] bioorganic studies of nyctinasty using *Albizzia* plants would be important for the connection of results between bioorganic and physiological studies. We have already revealed that the target cell of the leaf-opening factor of genus *Albizzia* is a motor cell by using fluorescence-labeled leaf-opening factor.[6] And we isolated potassium β-D-glucopyranosyl 12-hydroxyjasmonate (**1**) as a leaf-closing substance among genus *Albizzia*.[7] Bioactivity of **1** was not effective for plants belonging to other genus, such as *Cassia mimosoides*, *Phyllnathus urinaria*, and *Mimosa pudica*. However, no bioorganic study was carried out using **1**. Thus, it will be important to clarify whether the genus-specific bioactivity of the leaf-movement factors could be due to the involvement of a genus-specific receptor. In this paper, we synthesized probe **2** to identify the target cell of **1**, and carried out fluorescence studies using **2** to address this issue.

We developed a novel fluorescent probe (**2**) based on the structure of **1**, a leaf-closing substance of genus *Albizzia*. From our previous study, it was already shown that potassium β-D-glucopyranosyl tuberonate (**3**),[8] a cis-isomer of **1**, had no leaf-closing activity for *Albizzia* plant. This result strongly suggested that an aglycon moiety of **1** would be important for leaf-closing activity. Then, we synthesized potassium β-D-galactopyranosyl 12-hydroxyjasmonate (**4**) for a structure–activity relationship study of **1** (Scheme 1). Aglycon (**5**) was synthesized from commercially available (±)-methyl

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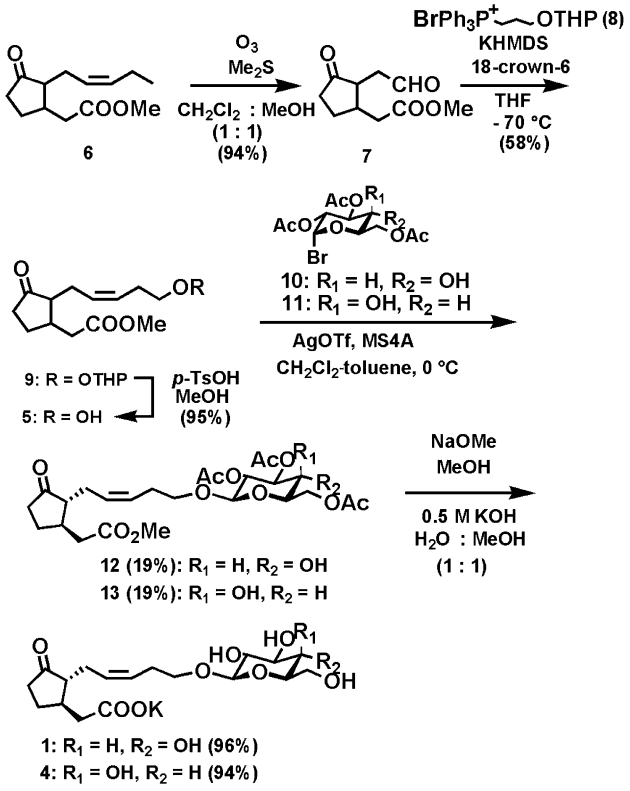
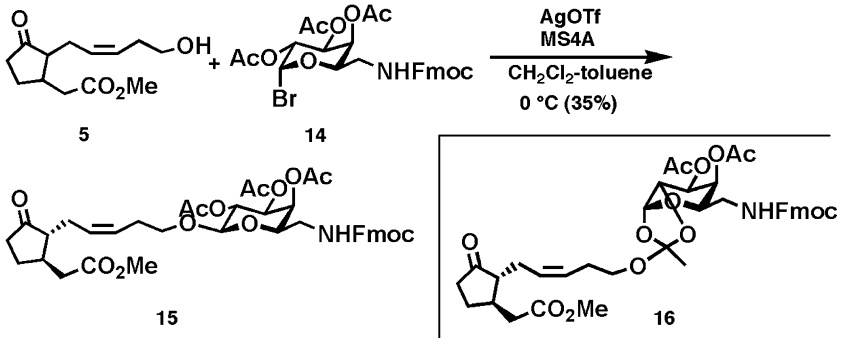


Scheme 1. Synthesis of the glycosides of 12-hydroxyjasmonate.

jasmonate (**6**).[9] Ozonolysis of **6** gave aldehyde **7**. Then, Wittig reaction of **7** with **8** gave THP-protected aglycon of (±)-**2** (**9**). The reaction was carried out with excess amount of 18-crown-6 to give the (*Z*)-isomer predominantly. The resulting **9** was deprotected by *p*-TsOH to give (±)-methyl 12-hydroxyjasmonate (**5**), which was used in the glycosidation reaction with **10** or **11**. Glycosidation of **5** with **11** and successive deprotection gave β-D-galactopyranosyl 12-hydroxyjasmonate (**4**)[10] as a mixture of diastereomers in 19% yield with 39% of acetylated **5**. And glycosidation conditions recently developed by Schmidt and co-workers[11] and Suzuki et al.[12] gave almost no coupling product. The resulting **4** showed leaf-closing activity for *Albizzia julibrissin* at 1×10^{-5} M. Similar to other glycoside-type leaf-movement factors, these results showed that the leaf-closing activity of **1** was not affected by the structure modification in the sugar moiety. Thus, probe **2** was designed according to the molecular design of a previously developed probe.[13] FITC was introduced on the 6′-position of the sugar moiety with a glycylglycylglycyl linker connecting **4** and FITC by an amide linkage. AMCA, which was a fluorescent dye used in our preceding fluorescence study, cannot be used because of intrinsic blue auto fluorescence in the section of *Albizzia* plants.

Probe **2** was synthesized from **5** and Fmoc-protected 6′-aminogalactosyl bromide (**14**) as shown in Schemes 2 and 3. Under normal Königs–Knorr condition, coupling product **15** was obtained in 35% yield (Scheme 2) with 28% of acetylated aglycon. The low yield would be due to the decomposition of the substrate under acidic reaction condition. However, the addition of 2,6-lutidine to keep the reaction media neutral resulted in no improvement in the yield of glycosidation product: 59% of the corresponding orthoester (**16**)[14] was obtained



Scheme 2. Glycosidation of **5**.