Pergamon

Tetrahedron Letters 40 (1999) 7823–7826

TETRAHEDRON LETTERS

Potassium β-D-glucopyranosyl 11-hydroxyjasmonate, a leaf-closing substance of *Albizzia julibrissin* Durazz

Minoru Ueda and Shosuke Yamamura *

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama 223-8522, Japan

Received 23 July 1999; revised 16 August 1999; accepted 20 August 1999

Abstract

Potassium β-D-glucopyranosyl 11-hydroxyjasmonate (**1**) was isolated as a leaf-closing substance of a nyctinastic plant, *Albizzia julibrissin* Durazz. Compound **1** was quite effective for the leaf-closing of *A. julibrissin* at 2×10^{-5} M, and was proved to be a *trans*-isomer of β-D-glucopyranosyl tuberonic acid previously isolated from potato as a tuber-inducing stimulus.

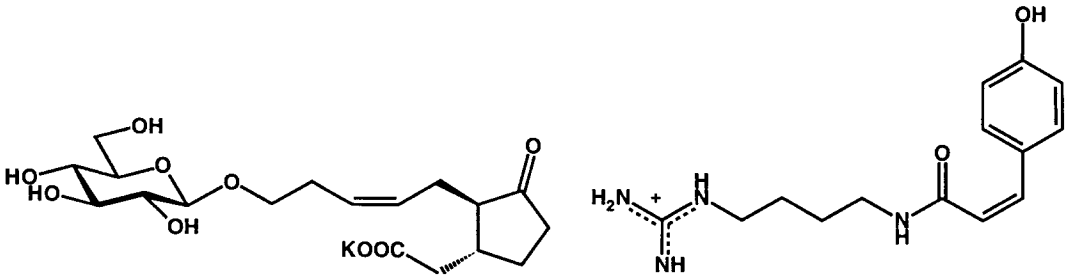
Keywords: plants; natural products; biologically active compounds.

Most leguminosae plants close their leaves in the evening, as if to sleep, and open them in the morning.[1] This rhythmic movement of the leaves is called nyctinasty, which is known to be controlled by an internal biological clock.[2] Among them, the nyctinastic leaf-movement of *Albizzia julibrissin* Durazz (nemu-no-ki in Japanese) is the most well-known.

Recently, we have identified several bioactive substances that regulate this leaf-movement,[3–16] and revealed that nyctinastic movement of the plants is controlled by the interaction between leaf-closing and -opening substances.[11–14] From *A. julibrissin*, we had already isolated a leaf-opening substance, *cis-p*-coumaroylagmatine (**2**). However, the counterpart of **2**, a leaf-closing substance, remained unidentified. We have now isolated potassium β-D-glucopyranosyl 11-hydroxyjasmonate (**1**) as a leaf-closing substance of *A. julibrissin*.

* Corresponding author. Fax: 81 45 563 5967; e-mail: yamamura@chem.keio.ac.jp

0040-4039/99/$ - see front matter
PII: S0040-4039(99)01628-7



Potassium β-D-glucopyranosyl 11-hydroxyjasmonate (1)

cis-p-coumaroylagmatine (2)

Isolation of the leaf-opening substance was carried out based on a bioassay using a leaf of *A. julibrissin*. The status of the leaf of *A. julibrissin* is easily affected by the prolonged radiation of sunlight. Under the radiation of sunlight, the leaf did not close. Thus, our bioassay previously established could not be used in the case of *A. julibrissin*. We, therefore, developed a new method that could be carried out over a short period of time. The most important problem lies in the difficulty for the leaf to pump up the sample solution through the vessel. To circumvent this difficulty, we developed the suction method: the leaf immersed in the sample solution is put in a bell funnel, and decompressed using an aspirator. The sample solution is pumped up through the vessel to the stomata by compulsion. The bioactive fraction makes the leaf close within a few minutes in this bioassay.

The fresh whole plant of *A. julibrissin* (2.6 kg) was extracted with MeOH:H_2O (8:2) (22.5 L) for 2 weeks and concentrated in vacuo. The concentrated extract was partitioned with ethyl acetate, then with *n*-butanol. The bioactive aqueous layer was carefully separated by Amberlite XAD-7 column chromatography eluted with MeOH:H_2O (0:100, 10:90, 30:70, 50:50 and 100:0), and the 30% MeOH aqueous fraction showed weak leaf-closing activity. The 30% MeOH aqueous fraction was further purified by gel filtration column chromatography using Toyopearl HW-40S with 30% MeOH aqueous, and then HPLC using preparative Cosmosil 5C18AR column with 20% MeOH aqueous repeatedly to give potassium β-D-glucopyranosyl 11-hydroxyjasmonate (**1**, 1.8 mg).

The structural determination of **1** was carried out by means of NMR and HR FABMS (negative) experiments.[17] The strong molecular ion corresponding to **1** was observed at *m/z* 411 in the positive mode FABMS, that suggested **1** exists as a potassium salt. HMQC, HMBC, and HOHAHA experiments gave the planar structure of **1** (Fig. 1).[17] NOE (5.6%) between $H_{1'}$ and H_{12} and HMBC correlation between H_1 and C_{12} suggested that the hydroxy group at the C_{12} position is glycosilated. The stereochemical relationship between H_3 and H_7 was determined to be *anti* from the coupling constant (J=10 Hz), and also no NOE was observed between H_3 and H_7. Compound **1** is a *trans*-isomer of the previously identified potato-tuber inducing stimulus, β-D-glucopyranosyl tuberonic acid (**3**), in which the stereochemical relationship between H_3 and H_7 is *syn*.[18] The ^{1}H NMR spectrum of **1** is slightly different from that of **3** on the signals assigned to the five-membered ring.

Potassium β-D-glucopyranosyl 11-hydroxyjasmonate (**1**) was effective for the leaf-closing of *A. julibrissin* at 2×10^{-5} M, and not effective for the leaf of other nyctinastic plants, such as *Phyllanthus urinaria* L., *Mimosa pudica* L., and *Aeshynomene indica* L. even at 1×10^{-4} M.

Yoshihara et al. reported that, in the process of isolation, β-D-glucopyranosyl tuberonic acid (**3**) readily changed another biologically inactive compound, β-D-glucopyranosyl 11-hydroxyjasmonate (**1**), through epimerization at C_7.[18] However, in our case, it was interesting that the thermodynamically stable *trans*-form was the bioactive compound.

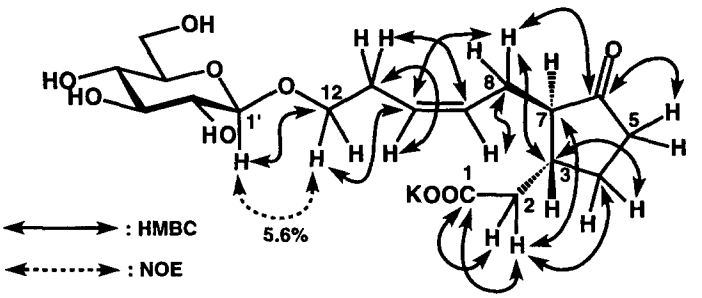
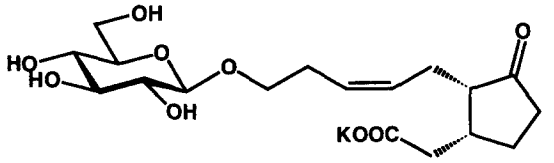
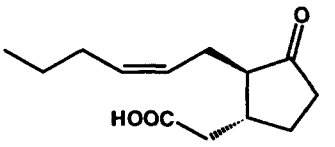


Figure 1. HMBC and NOE correlations in potassium β-D-glucopyranosyl 11-hydroxyjasmonate (**1**)



Potassium β-D-glucopyranosyl tuberonate (3)



Jasmonic acid (4)

Jasmonic acid (**4**) was known to be effective for the inhibition of the IAA-induced opening of the pulvinules.[19] However, **4** was effective for the leaf-closing of *A. julibrissin* even at as high as 1×10^{-4} M. Thus, **4** would not be a genuine leaf-closing substance of *A. julibrissin*.

In a previous paper, we advanced a universal mechanism for the chemical control of nyctinasty, namely, that either the leaf-closing or -opening substance is a glycoside, and the glycoside is hydrolyzed into its aglycon, the bioactivity of which is much weaker than that of the original glycoside, by a β-glucosidase whose activity is controlled by a biological clock.[12] In the case of *A. julibrissin*, the leaf-closing substance has also been identified as a glycoside, which would be hydrolyzed into its aglycon by β-glucosidase activated in the morning. These results suggest that our 'β-glucosidase mechanism' would be universally applicable to all nyctinastic plants. Our examination of the time-course change of **1**, and the β-glucosidase activity in the plant body of *A. julibrissin* will be reported in a later paper.

Acknowledgements

We are indebted to the Ministry of Education, Science, Sports and Culture (Japan) for Grant-in-Aid for Scientific Research on Special Promotion Research No. 09101001, the Asahi Glass Foundation, and Pioneering Research Project in Biotechnology given by the Ministry of Agriculture, Forestry and Fisheries for financial support. And we wish to thank Prof. Teruhiko Yoshihara (Hokkaido University) for sending us a sample of β-D-glucopyranosyl tuberonic acid. We also wish to thank Mr. Yuichiro Shibasaki (Keio University) for the collection of the plant.

References

1. Darwin, C. *The Power of Movement in Plants. Third Thousand*; John Murray: London, 1882.
2. Bünning, E. *The Physiological Clock. Third Edition*; English University Press: London, 1973.
3. Miyoshi, E.; Shizuri, Y.; Yamamura, S. *Chem. Lett.* **1987**, 511.
4. Shigemori, H.; Sakai, N.; Miyoshi, E.; Shizuri, Y.; Yamamura, S. *Tetrahedron Lett.* **1989**, *30*, 3991.
5. Shigemori, H.; Sakai, N.; Miyoshi, E.; Shizuri, Y.; Yamamura, S. *Tetrahedron* **1990**, *46*, 383.

6. Ueda, M.; Niwa, M.; Yamamura, S. *Phytochemistry* **1995**, *39*, 817.
7. Ueda, M.; Shigemori-Suzuki, T.; Yamamura, S. *Tetrahedron Lett.* **1995**, *36*, 6267.
8. Ueda, M.; Ohnuki, T.; Yamamura, S. *Tetrahedron Lett.* **1997**, *38*, 2497.
9. Ueda, M.; Tashiro, C.; Yamamura, S. *Tetrahedron Lett.* **1997**, *38*, 3253.
10. Ueda, M.; Ohnuki, T.; Yamamura, S. *Phytochemistry* **1998**, *49*, 633.
11. Ueda, M.; Asano, M.; Yamamura, S. *Tetrahedron Lett.* **1998**, *49*, 9731.
12. Ueda, M.; Asano, M.; Sawai, Y.; Yamamura, S. *Tetrahedron* **1999**, *55*, 5781.
13. Ueda, M.; Ohnuki, T.; Yamamura, S. *Chem. Lett.* **1998**, 179.
14. Ohnuki, T.; Ueda, M.; Yamamura, S. *Tetrahedron* **1998**, *54*, 12173.
15. Ueda, M.; Yamamura, S. *Tetrahedron Lett.* **1999**, *40*, 353.
16. Ueda, M.; Yamamura, S. *Tetrahedron Lett.* **1999**, *40*, 2981.
17. Potassium β-D-glucopyranosyl 11-hydroxyjasmonate (**1**): ^{1}H NMR (400 MHz, D_2O, rt): 5.67 (1H, td, J=7, 11 Hz, H_{10}), 5.61 (1H, td, J=7, 11 Hz, H_9), 4.47 (1H, d, J=8 Hz, $H_{1'}$), 4.02 (1H, d, J=10 Hz, H_{12a}), 3.91 (1H, dd, J=2, 12 Hz, $H_{6'a}$), 3.82 (1H, td, J=7, 10 Hz, H_{12b}), 3.72 (1H, dd, J=6, 12 Hz, $H_{6'b}$), 3.49 (1H, t, J=9 Hz, $H_{3'}$), 3.45 (1H, dd, J=2, 6 Hz, $H_{5'}$), 3.38 (1H, t, J=9 Hz, $H_{4'}$), 3.26 (1H, dd, J=8, 9 Hz, $H_{2'}$), 2.68 (1H, dd, J=5, 14 Hz, H_{2a}), 2.56 (2H, q, J=7 Hz, H_8), 2.52 (2H, q, J=7 Hz, H_{11}), 2.43–2.41 (1H, m, H_3), 2.32 (1H, td, J=9, 18 Hz, H_{4a}), 2.30 (1H, dd, J=9, 14 Hz, H_{2b}), 2.22 (1H, td, J=7, 10 Hz, H_7), 1.52 (1H, m, H_{4b}) ppm; ^{13}C NMR (100 MHz, D_2O, 35°C): 228.7 (C_6), 184.0 (C_1), 129.43 (C_{10}), 128.5 (C_9), 103.2 ($C_{1'}$), 76.8 ($C_{3'}$), 76.7 ($C_{5'}$), 74.1 ($C_{2'}$), 70.6 ($C_{4'}$), 70.7 (C_{12}), 62.0 ($C_{6'}$), 55.0 (C_7), 39.4 (C_3), 39.0 (C_5), 28.2 (C_8), 27.7 (C_4), 25.8 (C_{11}) ppm. FABMS (positive): $[M]^+$ *m/z*: 411; HR FABMS (negative): $[M-K]^-$. Found *m/z*: 387.1687; $C_{18}H_{27}O_9$ requires *m/z*: 387.1655.
18. Yoshihara, T.; Omer, E.-S.; Koshino, H.; Sakamura, S.; Kikuta, Y.; Koda, Y. *Agric. Biol. Chem.* **1989**, *53*, 2835.
19. Tanada, T. *Physiol. Plant.* **1983**, *57*, 42.