学位論文内容の要旨

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学位論文題名

Isolation, structure determination, and chemical synthesis of acyl glucoses from *Solanum pennellii* and investigation of their biological activities

(*Solanum pennellii*由来の新規アシルグルコースの単離、構造決定、化学合成、およびその生物活性の生物有機化学的研究)

Plants produce thousands of specialized metabolites called secondary metabolites for their defense, growth, and development. Acyl sugars are nonvolatile secondary metabolites produced and stored in a specific structure called trichomes. Acyl sugars have been reported as ingredients in several plant families including Solanaceae, Martyniaceae, Rosaceae, Geraniaceae, Caryophyllaceae, and Brassicaceae. *Solanum pennellii* is a wild-type tomato plant that belongs to the Solanaceae family. The basic core of the acyl sugars in *S. pennellii* is either a glucose or a sucrose moiety with mono-, di- or tri-fatty acids, whose carbon lengths are from two to twelve. These compounds play an important role in agriculture, medicine, and the food industry since they are found to be herbicides, microbial growth inhibitors, allelopathic compounds, antioxidants, anti-inflammation activities, and in some cases, used as components in food additives. However, the isolation and identification of acyl sugars are difficult due to the α and β anomerization at C-1 in the glucose moiety. Moreover, because of the availability of a wide diversity of acyl sugars, their chemical structures are complex and diverse. Thus, isolation and identification of acyl sugars were carried out in this study. In the present research, a new acyl sugar was isolated using a strategy to fix the α and β anomerization into either one of the isomers, and its chemical structure was elucidated by total synthesis and 1D and 2D NMR spectroscopy. The biological activity of the isolated compound was investigated. Additionally, the total synthesis of two acyl sugars that have been previously reported was carried out.

1. Isolation and identification of acyl sugars.

The isolations of acyl sugars were carried out according to the reported method

[Nakashima, T. et al., *J Nat Prod*, 2020, **83**, 2337-2346]. Anomerization in acyl sugars was fixed into either one of the isomers by treating the ethanol extract of S. *pennellii* with 2,4,6-tris(benzyloxy)-1,3,5-triazine to attach the benzyl groups to free hydroxyl groups present at the glucose moiety. Then separation was done by silica gel column chromatography followed by HPLC separation to yield a new benzylated derivative of pennelliiside D. The structural determination of dibenzyl pennelliiside D was done by 1D and 2D NMR spectroscopy, and it was revealed that the chemical structure of dibenzyl pennelliiside D was to be 1,6-*O*-dibenzyl-3,4-*O*-diisobutyryl-2-*O*-(2-methylbutyryl)-*β*-D-glucose. Then, benzyl groups were removed under a hydrogen gas atmosphere with palladium/carbon to yield pennelliiside D. Its structure was confirmed as 3,4-*O*-diisobutyryl-2-*O*-(2-methylbutyryl)-D-glucose based on the analysis of 1D and 2D NMR spectroscopy.

2. Synthesis of pennelliisides

Although the structure of pennelliiside D was determined as above, it was not performed to determine the absolute configuration of the 2-methylbutyryl fatty acid moiety in pennelliiside D. In previous studies, it has been reported some acyl sugars contain 2-methylbutyryl fatty acid, although its absolute configuration was unrevealed. Thus, the total syntheses of two possible isomers of *R* and *S* of 2-methylbutyryl fatty acid moiety in pennelliiside D were carried out starting from *β*-D-glucose pentaacetate. By comparing the spectroscopic data and the specific rotation values of natural with those of synthesized dibenzyl pennelliiside D, the absolute configuration of the acyl moiety in pennelliiside D was identified to be *S*. Then, deprotection of benzyloxy groups was carried out to yield pennelliiside D, 3,4-*O*-diisobutyryl-2-*O*-((*S*)-2-methylbutyryl)-D-glucose. Additionally, in this study, benzylated derivatives of two identified acyl sugars, dibenzyl pennelliiside A and B, were synthesized.

3. Biological activity of pennelliiside D

It has been reported that acyl sucroses show seed growth inhibition. Moreover, long-chain fatty acid moieties with isopropyl branches have been reported to show a more potent on inhibition of root growth in *Arabidopsis thaliana*. Therefore, the root growth activity of pennelliiside D and its constituent fatty acid moieties were examined using *A. thaliana*, which revealed that neither the compound nor the fatty acid moieties showed root growth-inhibitory activity at any tested concentration.