

# Synthesis of Hypermodified Nucleosides Related to Phenylalanine Transfer Ribonucleic Acids.

メタデータ	言語: jpn 出版者: 公開日: 2022-05-27 キーワード (Ja): キーワード (En): 作成者: Itaya, Taisuke メールアドレス: 所属:
URL	<a href="https://doi.org/10.24517/00066020">https://doi.org/10.24517/00066020</a>

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# 1998 Fiscal Year Final Research Report Summary

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## Synthesis of Hypermodified Nucleosides Related to Phenylalanine Transfer Ribonucleic Acids.

Research Project

### Project/Area Number

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09672140

### Research Category

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Grant-in-Aid for Scientific Research (C)

### Allocation Type

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Single-year Grants

### Section

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一般

### Research Field

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Chemical pharmacy

### Research Institution

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Kanazawa University

### Principal Investigator

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### Project Period (FY)

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1997 - 1998

### Keywords

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tRNA modified base / tRNA modified nucleoside / Wittig reaction / Osmium oxidation / Cyclic carbonic acid diester / Imidazolidine linkage / Substituent effect / Hammett equation

### Research Abstract

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(1)An improved synthesis of the key intermediates for the synthesis of [R-(R\*, S\*)]- and [S-(R\*, R\*)]-beta-hydroxybutyryl-tRNAs, the most probable structures for the minor base from rat liver tRNA<sup>Phe</sup>, has been achieved by the Wittig reaction between 1-benzyl-7-formylbutyryl and the

phosphorane derived from (R)- 2-[(methoxycarbonyl)amino]-3-(triphenylphosphonio)- propanoate, followed by methylation, OsO<sub>4</sub> oxidation, and cyclo-condensation with COCl<sub>2</sub> in the presence of pyridine. (R\*, R\*)-beta-Hydroxywybutine and its diastereomer, which were required for the determination of the optical purity of the chiral bases by means of chiral HPLC, were conveniently prepared through pyrolysis of the cyclic carbonate followed by NaBH<sub>4</sub> reduction and catalytic hydrogenolysis. The samples of [R-(R\*, S\*)]- and [S-(R\*, R\*)]-beta-hydroxywybutines were thus shown to be optically pure.

(2)The synthesis at the nucleoside level started with the Vilsmeier reaction of 3-[2,3,5-tris-O-(tert-butylidimethylsilyl)-beta-D-ribofuranosyl]wye and proceeded through the Wittig reaction with (R)-2-[(methoxycarbonyl)-amino]-3-(triphenylphosphonio)propanoate, methylation with trimethylsilyldiazomethane, OsO<sub>4</sub> oxidation, cyclocondensation with triphosgene, and catalytic hydrogenolysis. Chromatographic separation of the resulting diastereomeric mixture and subsequent deprotection afforded the two desired nucleosides for the first time.

(3)it has been revealed that the rate of isomerization of l-benzyl-4-methyl-4,9-dihydro- 1H-imidazo[1 ; 2-alpha]purin-9-ones in 0.1 M MeONa-MeOH at .25°C increases with increasing electron-withdrawing nature of the 7-substituent and that the reactivity is further promoted by the intramolecular hydrogen bond between the carbonyl group at the 9-position and the 7-substituent.

## Research Products (2 results)

All Other

All Publications (2 results)

[Publications] Taisuke Itaya: "Studies towards the Synthesis of the Hypermodified Nucleoside of Rat Liver Phenylalanine Transfer Ribonucleic Acid: Improved Synthesis of the Based β-Hydroxywybutine" Chem.Phaim.Bull.46. 1220-1224 (1998) 

[Publications] T.Itaya: "Studies towards the Synthesis of the Hypermodified Nucleoside of Rat Liver Phenylalanine Transfer Ribonucleic Acid : Improved Synthesis of the Base beta-Hydroxywybutine" Chem.Pharm.Bull.46. 1220-1224 (1998) 

URL: [https://kaken.nii.ac.jp/report/KAKENHI-PROJECT-09672140/096721401998kenkyu\\_seika\\_hokoku\\_](https://kaken.nii.ac.jp/report/KAKENHI-PROJECT-09672140/096721401998kenkyu_seika_hokoku_)

Published: 1999-12-07