NATURAL PRODUCT SYNTHESES UTILIZING 4-ALKOXYCARBONYLOXAZOLES AS β-HYDROXY-α-AMINO ACID SYNTHONS

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Abstract —— The utility of 4-alkoxycarbonyloxazoles as latent β-hydroxy-α-amino acids in the synthesis of amino sugars and amino acids is described.

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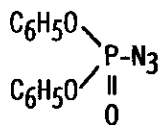
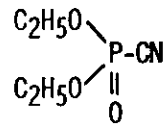
1. Introduction

Diphenyl phosphorazidate (DPPA)[1] and diethyl phosphorocyanidate (DEPC)[2] have been well proven to be versatile reagents for organic synthesis.[3,4]

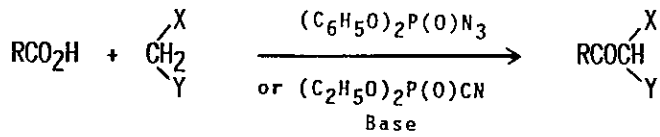


(DPPA)



(DEPC)

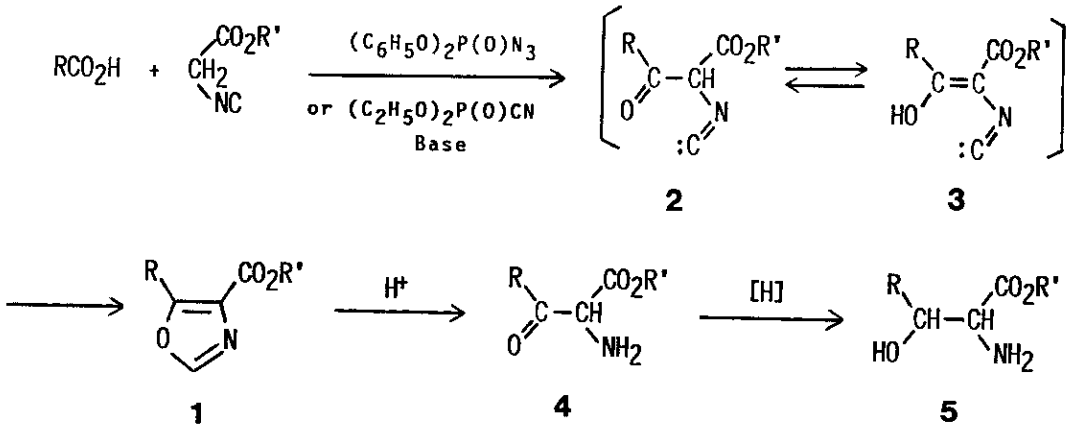
These reagents can be used for the direct C-acylation of active methylene compounds with carboxylic acids in the presence of bases.[5-8]



X and/or Y = electron-withdrawing groups

When isocyanoacetic acid esters are used as active methylene compounds in the above C-acylation, 4-alkoxycarbonyl-5-substituted oxazole derivatives **1** are obtained in good yields. The obvious intermediate is the C-acylated product **2**, which is cyclized via the enol **3** to give **1**.

The C-acylation of isocyanoacetates has been usually carried out by use of acid chlorides, acid anhydrides, benzoxazines, selenol esters, and so on. Very few reports have been concerned with the C-acylation by the direct use of carboxylic acids without prior isolation of activated intermediates. DPPA and DEPC in combination with base, however, allow the direct C-acylation of isocyanoacetates with carboxylic acids to give the oxazole derivatives **1**.



Acid treatment of **1** easily affords β-keto-α-amino acid derivatives **4**, which are readily reduced to give β-hydroxy-α-amino acid derivatives **5**. Various natural products including amino sugars can be prepared from **5**. Thus, 4-alkoxycarbonyl-5-substituted oxazoles **1** are regarded as β-hydroxy-α-amino acid **5** synthons. This was pioneered by Matsumoto and co-workers, who have developed a number of interesting synthetic works using isocyanoacetates.[9]

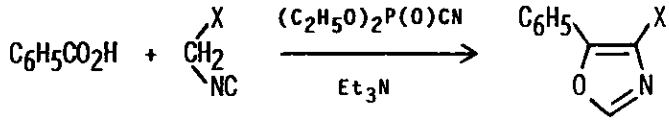
This review focuses on our own works concerning syntheses of natural products utilizing 4-alkoxycarbonyl-5-substituted oxazoles as β-hydroxy-α-amino acid synthons.

1 5

2. Construction of the Oxazole Skeletons

2.1 With DEPC

Our works on the oxazole synthesis started from the reaction of benzoic acid with tosylmethyl isocyanide. The desired oxazole **6a** was readily formed by use of DEPC-triethylamine.[5]



in DMF

6a : X = CH_3-C$_6$H$_4$-SO_2- , 81%
b : X = CH_3OCO- , 81%

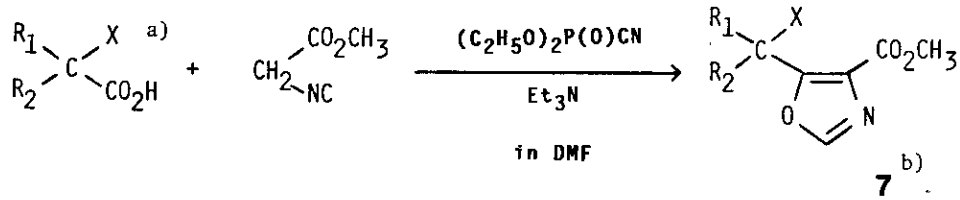
Methyl isocyanoacetate, analogously as tosylmethyl isocyanide, smoothly underwent the C-acylation by use of DEPC to give 4-methoxycarbonyl-5-phenyloxazole (**6b**). When O-protected α-hydroxy acids or N-protected α-amino acids were used in the C-acylation, 4 equivalents of triethylamine were required to conduct the oxazole synthesis smoothly[10] while 3 equivalents of the base were usually enough for the direct C-acylation using DEPC.[5-8] The use of an excess of the base causes a considerable racemization when optically active starting acids are used for the oxazole synthesis and the racemization would occur in the stage of the acylated intermediates 2. The results are summarized in Table I.[10]

To suppress the racemization, several reaction conditions were explored using Boc-L-Phe-OH.[11,12] Sodium hydride was found to be a much better base than triethylamine, and the optical purity of the resulting oxazole was 94%. However, the use of DEPC was not promising since the yield of the oxazole was so poor (18%). This led us to explore the possibility of DPPA in the C-acylation.

2.2 With DPPA

In the oxazole synthesis from Boc-L-Phe-OH and methyl isocyanoacetate using DPPA, similar reaction conditions to those when DEPC and triethylamine were used

Table I. The Oxazole Synthesis Using Diethyl Phosphorocyanidate (DEPC)



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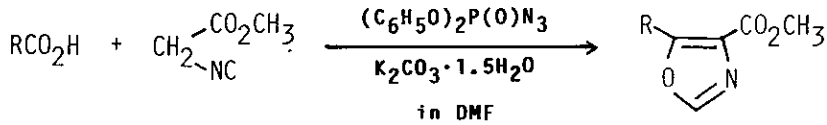
R_1	R_2	X	Yield, %
CH_3	H	OCH_2OCH_3	50
CH_3CH_2	H	OCH_2OCH_3	43
CH_3	CH_3	OCH_2OCH_3	28
C_6H_5	H	OCH_2OCH_3	42
H	H	$NHCO_2C(CH_3)_3$	41
CH_3	H	$NHCO_2C(CH_3)_3$	73
$(CH_3)_2CH$	H	$NHCO_2C(CH_3)_3$	76
$(CH_3)_2CHCH_2$	H	$NHCO_2C(CH_3)_3$	56
$C_6H_5CH_2$	H	$NHCO_2C(CH_3)_3$	45
$C_6H_5CH_2$	H	$NHCO_2CH_2C_6H_5$	35.5

a) Racemic O-methoxymethyl-α-hydroxy acids and Boc- or Z-L-α-amino acids are used.

b) Racemic oxazoles are obtained.

resulted in a poor yield (21%) of the oxazole.[11] However, the use of potassium carbonate afforded the oxazole in 60% yield. The best result (70%) was obtained by use of potassium carbonate sesquihydrate. The oxazole obtained almost retained the optical purity. This oxazole synthesis using DPPA has been proven to be quite general, and the results are summarized in Table II.[13] In the preferred procedure, 2 Mol. equivalents of potassium carbonate sesquihydrate together with 4 equivalents of methyl isocyanoacetate are used in dimethylformamide at or below room temperature.[13] Interestingly, when DEPC was used in the preferred procedure using DPPA, the isolated yield as well as the optical purity of the product was much inferior. This striking difference in the optical purity may be due to the fact that the cyanide anion (HCN, pKa 9.2) is a stronger base than the azide anion (HN_3, pKa 4.59). Since the C-acylation with achiral acids proceeds straightforwardly, a slight excess (1.2 equivalents) of methyl isocyanoacetate is enough to conduct the reaction.

Table II. The Oxazole Synthesis Using Diphenyl Phosphorazidate (DPPA)



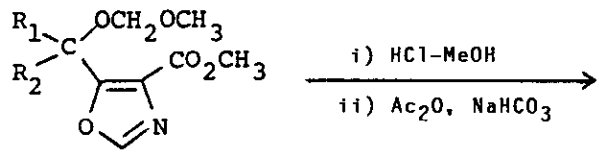
RCO_2H	Isolated yield,% a)	RCO_2H	Isolated yield,% a)
$C_6H_5CO_2H$	77	Boc-L-Tyr(Bzl)-OH	70 (53)
$C_6H_5CH_2CH_2CO_2H$	(85)	Boc-L-Trp-OH	78 (52)
Boc-Gly-OH	95 (76)	(S) $C_6H_5CHCO_2H$ OCH_2OCH_3	72
Boc-L-Ala-OH	80 (61)	(S) $C_6H_5CHCO_2H$ OCH_2OCH_3	70 (66) b)
Boc-L-Val-OH	78 (51)		
Boc-L-Leu-OH	78 (54)		
Boc-L-Met-OH	57 (40)	(R,R)	79 c) (54)
Boc-L-Phe-OH	70		
Boc-L-Phe-OH	60		

a) Numbers in parentheses are yields after recrystallization or distillation.
b) Sodium hydride was used as a base.
c) Diisopropylethylamine was used as a base.

3. Cleavage of the Oxazole Nucleus

Although oxazoles are generally quite stable to acid, the oxazole nucleus of 4-alkoxycarbonyloxazoles **1** are activated with the electron-withdrawing function and known[9] to undergo the acidic cleavage, giving β-keto-α-amino acid derivatives **4** with expulsion of one carbon fragment. In fact, treatment of 4-methoxycarbonyl-5-substituted oxazoles **7**, obtained from α-methoxymethyloxycarboxylic acids as shown

Table III. Preparation of 3-Amino-4-hydroxytetrones



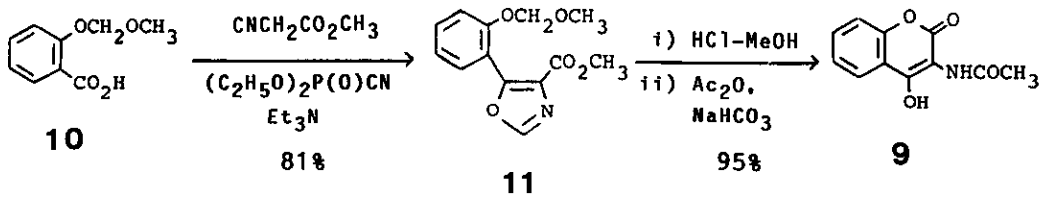
7

R_1	R_2	Yield of 8b, %
CH_3	H	91
CH_3CH_2	H	80
CH_3	CH_3	96
C_6H_5	H	90

8a: R_3=H
b: R_3=$COCH_3$

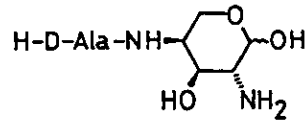
in Table I, readily underwent the cleavage of their oxazole nucleus by the action of 10% methanolic hydrogen chloride. Removal of the methoxymethyl group followed by lactonization simultaneously occurred to give 3-amino-4-hydroxytetrones **8a**, a class of furanose amino reductones, in excellent yields. Since amino reductones **8a** were very susceptible to air oxidation just like ascorbic acid, a representative of reductones, they were immediately converted to stable N-acetyl derivatives **8b**, as shown in Table III.

Using similar reaction sequences, 3-acetamido-4-hydroxycoumarin (**9**) was efficiently prepared from 2-methoxymethyloxybenzoic acid (**10**) by the C-acylation, acid treatment of the oxazole **11**, and then acetylation,[10] as shown below.



4. Synthesis of Prumycin

Prumycin (**12**)[14] is an antifungal antibiotic and has an interesting antitumor activity. To date, the synthesis of this interesting compounds has been reported by four laboratories including ours. Three of them[15-17] started from sugar derivatives. Our approach[18] started from L-serine and isocyanoacetic acid derivatives as shown in Chart 1.



Prumycin **12**

The direct C-acylation of methyl isocyanoacetate with Z-L-Ser(Bu^t)-OH using DPPA and potassium carbonate sesquihydrate in dimethylformamide afforded the key intermediate oxazole **13**, containing the requisite function of the 2,4-diaminosugar. Treatment of **13** with trifluoroacetic acid followed by acylation of the resulting alcohol **14** with pivaloyl chloride gave the oxazole **15**, which was recrystallized from ethyl acetate-hexane to give the optically pure oxazole **15**. Ring cleavage of **15** with 7% methanolic hydrogen chloride smoothly proceeded to give an equilibrium mixture of the hydrochlorides of C-acylamino acid esters **16a** and **16b**, which were neutralized and reduced with sodium borohydride in ethanol to

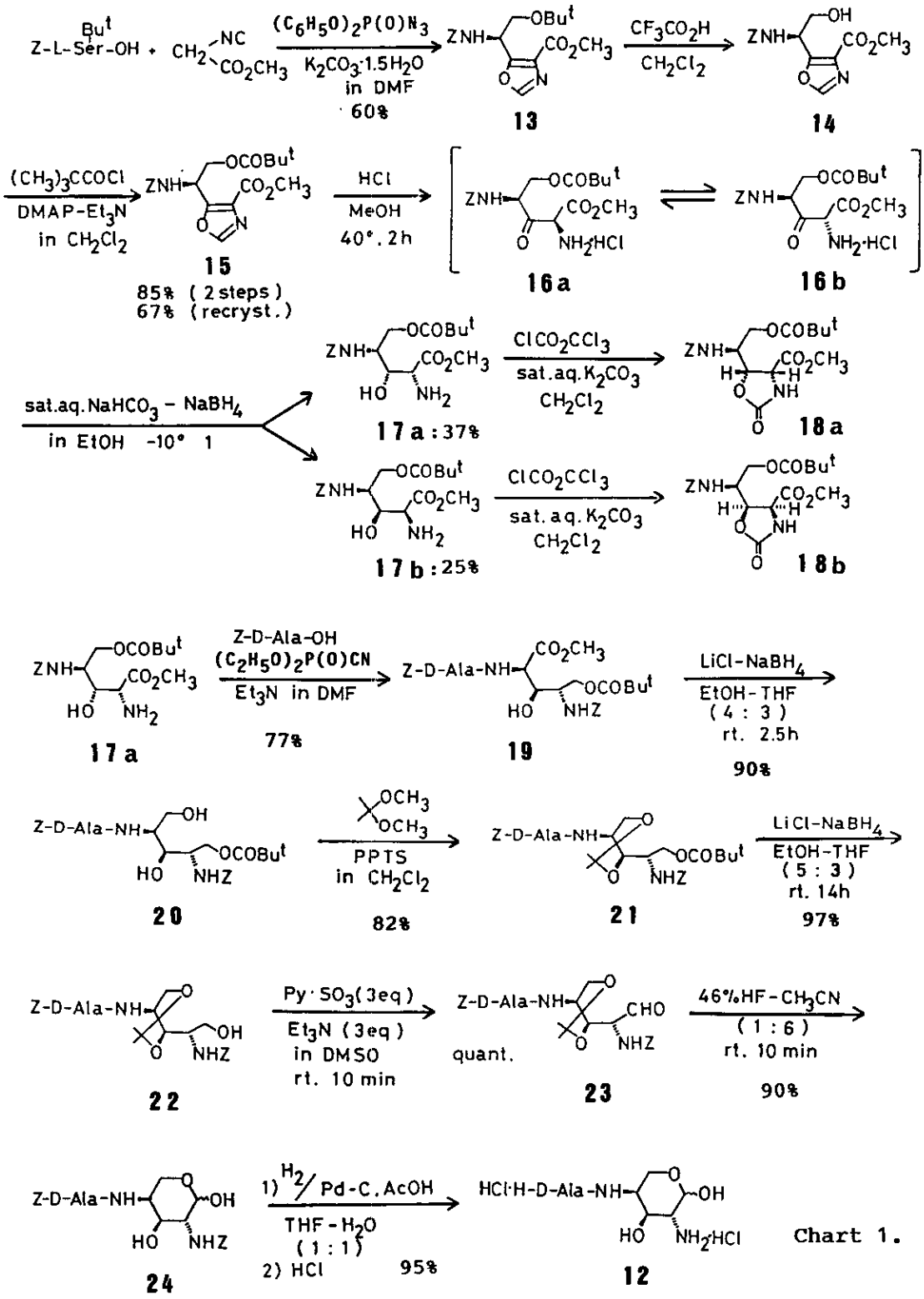

Z-L-Ser-OH
$(C_6H_5O)_2P(O)N_3$
$K_2CO_3 \cdot 1.5H_2O$
in DMF
60%
13
CF_3CO_2H
CH_2Cl_2
14
$(CH_3)_3CCOCl$
DMAP-Et_3N
in CH_2Cl_2
15
85% (2 steps)
67% (recryst.)
HCl
MeOH
40°, 2h
16a
16b
sat.aq.$NaHCO_3$ – $NaBH_4$
in EtOH -10° 1
17a : 37%
17b : 25%
$ClCO_2CCl_3$
sat.aq.K_2CO_3
CH_2Cl_2
18a
18b
Z-D-Ala-OH
$(C_2H_5O)_2P(O)CN$
Et_3N in DMF
77%
19
LiCl-$NaBH_4$
EtOH-THF
(4 : 3)
rt. 2.5h
90%
20
PPTS
in CH_2Cl_2
82%
21
LiCl-$NaBH_4$
EtOH-THF
(5 : 3)
rt. 14h
97%
22
Py·SO_3(3eq)
Et_3N (3eq)
in DMSO
rt. 10 min
quant.
23
46%HF-CH_3CN
(1 : 6)
rt. 10 min
90%
24
1) H_2 / Pd-C, AcOH
THF-H_2O
(1 : 1)
2) HCl
95%
12

Chart 1.

give a mixture of two erythro amino alcohols **17a** and **17b** in a 3:2 ratio. Erythro configurations at C-2 and C-3 of **17a** and **17b** were proven by $J_{2,3}$-values of the NMR spectra of the corresponding oxazolidone derivatives **18a** ($J_{2,3}$=9.6 Hz) and **18b** ($J_{2,3}$=8 Hz). The major isomer **17a** was coupled with Z-D-Ala-OH using DEPC to give the amido alcohol **19**. The methyl ester function of **19** was selectively reduced with lithium chloride-sodium borohydride in ethanol-tetrahydrofuran to give the 1,3-diol **20**. After conversion to the isopropylidene derivative **21**, treatment with an excess of lithium chloride-sodium borohydride yielded the β-amino alcohol **22**. Oxidation of **22** with sulfur trioxide pyridine complex-triethylamine-dimethyl sulfoxide[19,20] rapidly proceeded to give the α-amino aldehyde **23**, which on treatment with aqueous hydrogen fluoride-acetonitrile afforded N,N'-dibenzyloxycarbonylprumycin (**24**) in high yield. Catalytic removal of the benzyloxycarbonyl functions followed by treatment with hydrochloric acid yielded prumycin (**12**) as its hydrochloride. The above reaction sequences comprise a facile synthesis of prumycin (**12**) in 12 steps from Z-L-Ser(Bu^t)-OH with an overall yield of 7.5%.

5. L-Lyxonolactone

As described earlier (section 3), the oxazole derivatives **7** are easily transformed to the amino reductones **8**. Reduction of the carbon-carbon double bond in **8** will give the saturated lactone, which are suitable starting materials for the preparation of some amino sugars. In fact, we have succeeded the efficient syntheses of three 2,3,6-trideoxy-3-amino sugars,[21] L-daunosamine (**25**),[22] L-vancosamine (**26**),[23] and D-ristosamine (**27**),[24] starting from L-lactic acid (**28a**) and its ethyl ester (**28b**) via the oxazole **29**, the amino reductone **30**, and the L-lyxonolactone **31**. The overall strategy is outlined in Chart 2 .

L-Lactic acid (**28a**) was treated with chloromethyl methyl ether to give the bis-methoxymethyl derivative **32a**. Lithium L-methoxymethyllactate obtained by alkaline hydrolysis of **32a** was treated with DPPA, followed by the addition of the sodium salt of methyl isocyanoacetate afforded the oxazole **29a**, whose configurational homogeneity was ascertained by the NMR spectral study using the chiral shift reagent, $Eu(facam)_3$.

Alternatively, ethyl L-lactate (**28b**) was analogously treated with chloromethyl methyl ether to yield the methoxymethyl derivative **32b**, as shown in Chart 3. Successive treatment of **32b** with lithium hydroxide, DPPA, and the sodium salt of ethyl isocyanoacetate as above afforded the oxazole **29b**. Cleavage of the oxazole

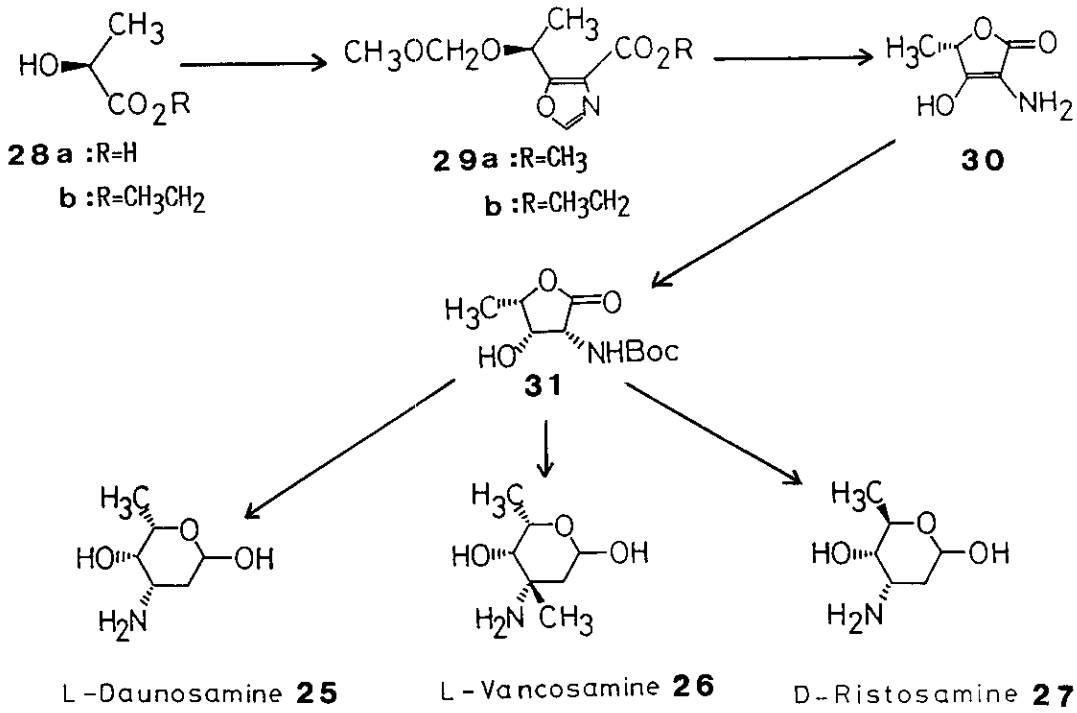
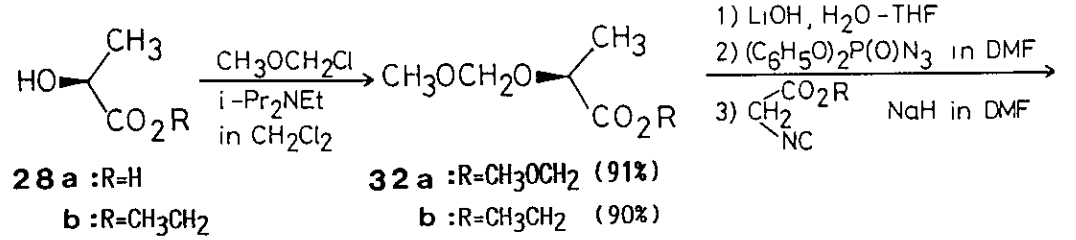
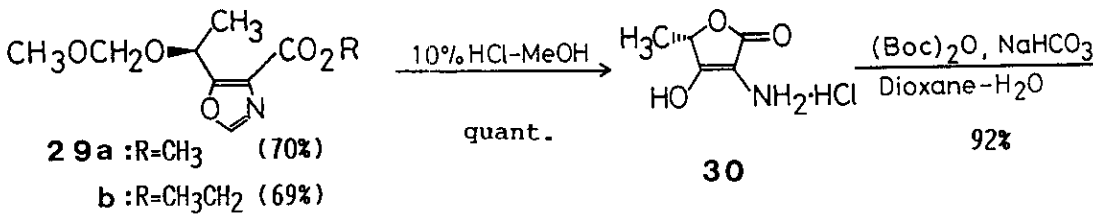


Chart 2.





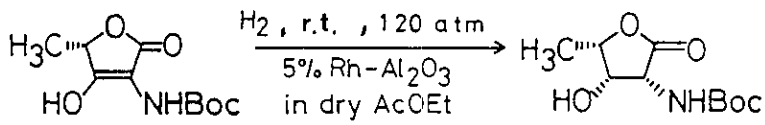
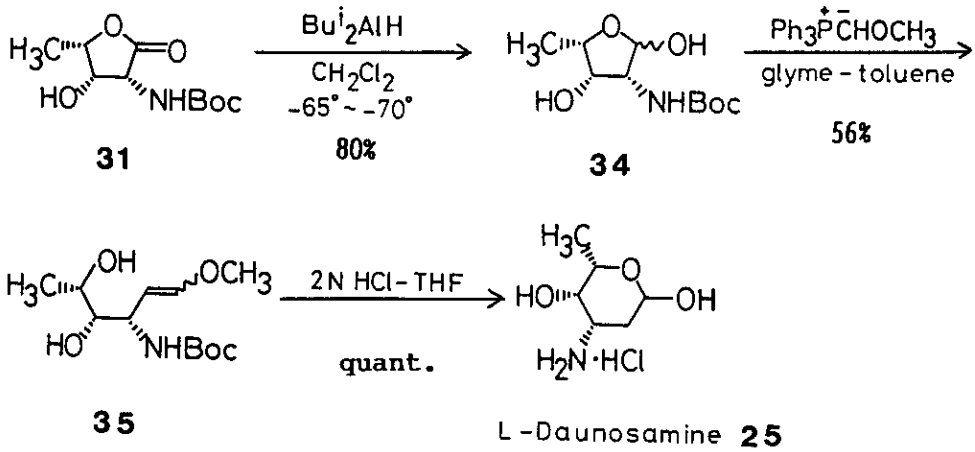


Chart 3.

nucleus of **29** was easily achieved with methanolic hydrogen chloride to give the amino reductone **30** as its hydrochloride, which was immediately converted to its Boc derivative **33**. Catalytic hydrogenation of **33** completely stereoselectively proceeded by use of rhodium alumina catalyst, to give the L-lyxonolactone **31** as a sole product. This is due to the presence of the methyl group at C-4 on the α-side, which prevents the approach of the catalyst from the α-side. The lactone **31**, obtained in 52% yield from ethyl L-lactate (**28b**), has been proven to be a versatile intermediate for the preparation of some amino sugars.

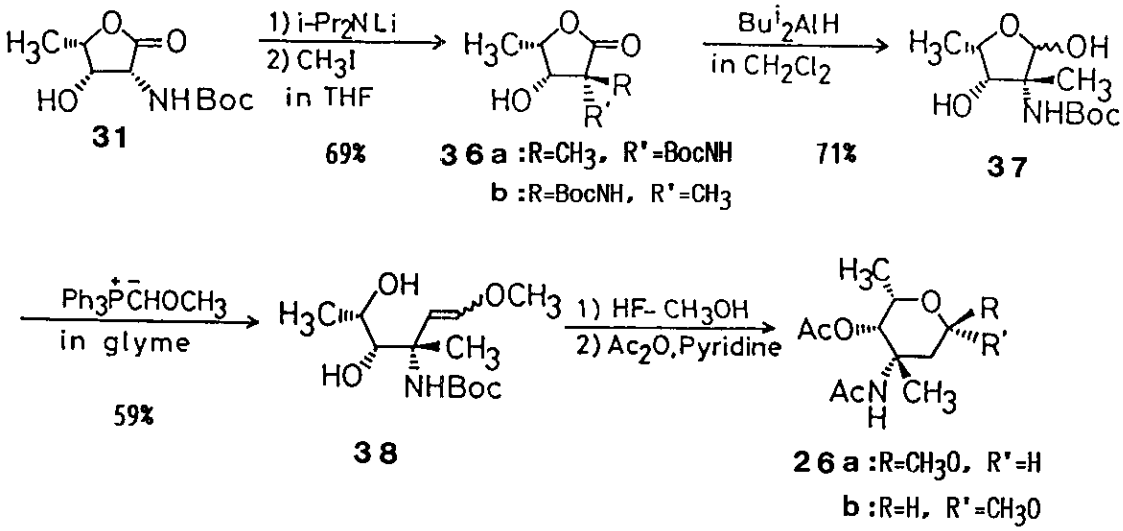
6. L-Daunosamine

L-Daunosamine (**25**) is the carbohydrate component of a group of important anticancer anthracycline antibiotics such as adriamycin, daunomycin, and carminomycin. To construct the daunosamine skeleton, attachment of the C_1-unit to the L-lyxonolactone **31** was required. Reduction of **31** with diisobutylaluminum hydride gave the lactol **34**. Introduction of the C_1-unit to **34** was achieved by the Wittig reaction of **34** with methoxymethylenetriphenylphosphorane, giving the methyl enol ether **35**. Treatment of **35** with hydrochloric acid in tetrahydrofuran finally gave L-daunosamine (**25**) as its hydrochloride. The above procedure is completely stereoselective, and the overall yield of the hydrochloride of **25** from ethyl L-lactate (**28b**) is 27% in 9 steps.



7. L-Vancosamine

L-Vancosamine (**26**) was isolated as a carbohydrate component of the antibiotics vancomycin and sporaviridin. Since L-vancosamine (**26**) is the 3β-C-methyl derivative of L-daunosamine (**25**), the stereoselective introduction of the methyl group is an only extra process, compared with the daunosamine synthesis. Treatment of the L-lyxonolactone **31** with lithium diisopropylamide followed by the addition of methyl iodide afforded an epimeric mixture of the C-methylated lactones **36a** and **36b** in a ratio of 96:4.[23] Obviously, the methylation preferentially occurs from the less hindered side of the molecule. Conversion of **36** to a vancosamine derivative analogously proceeded as in the L-daunosamine synthesis. Reduction of the epimeric mixture of **36** with diisobutylaluminum hydride afforded the pure lactol **37** after chromatographic separation. The Wittig extension of the C_1-unit was carried out with methoxymethylenetriphenylphosphorane to give the enol ether **38**. The enol ether **38** was unexpectedly labile and failed to give the vancosamine skeleton under various acidic conditions. Finally, we found that aqueous hydrofluoric acid-methanol was suitable to cyclize **38**. L-Vancosamine (**26**) was thus isolated as a separable anomeric mixture of its N,O-diacetyl methyl glycosides **26a** and **26b**.



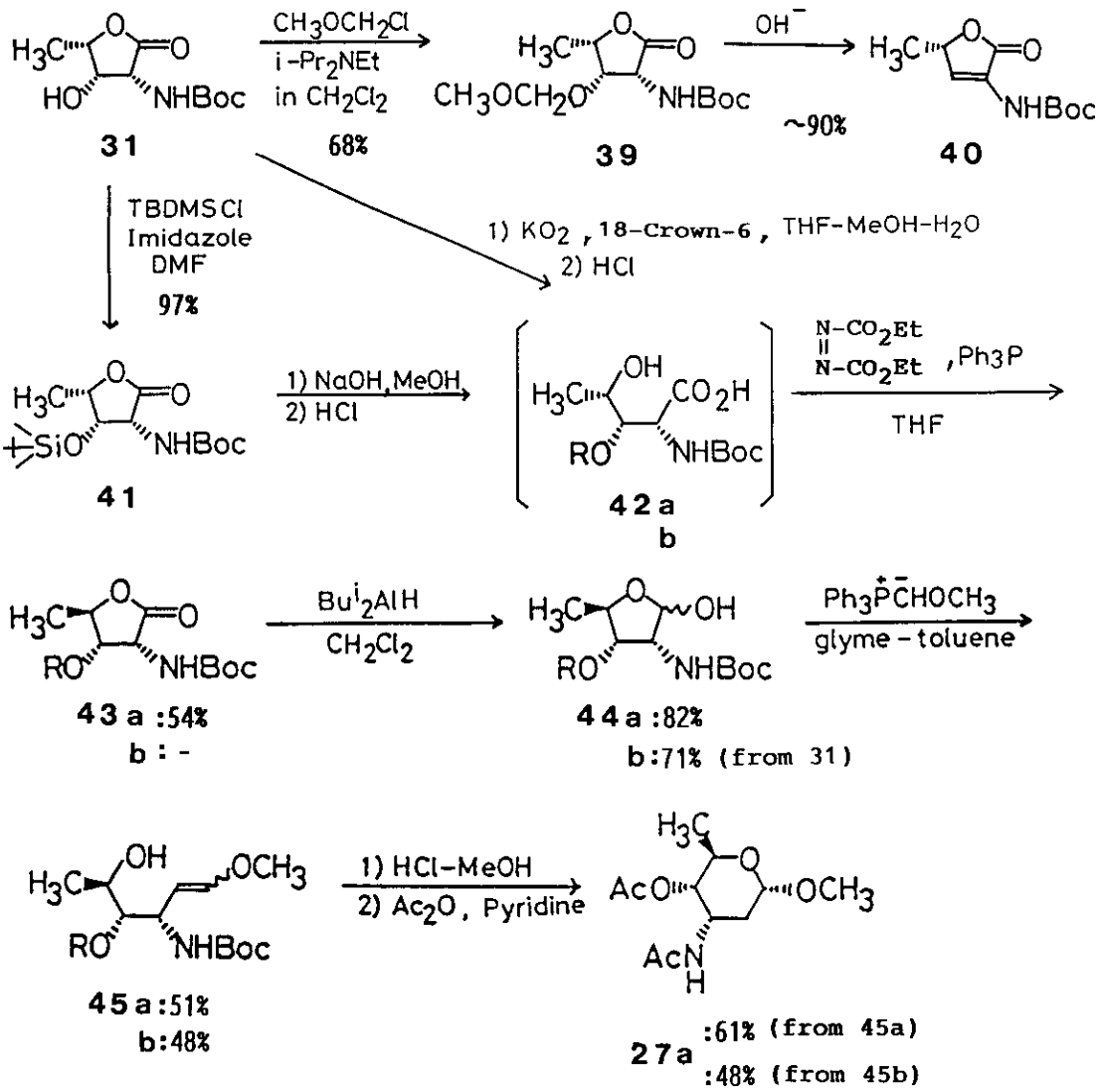
31 **36a** :R=CH_3, R'=BocNH; **b** :R=BocNH, R'=CH_3 **37** **38**

26a :R=CH_3O, R'=H; **b** :R=H, R'=CH_3O

8. D-Ristosamine

D-Ristosamine (**27**), the enantiomer of the carbohydrate component of the antibiotic ristomycin, only differs from L-daunosamine (**25**) at the configuration of the 5-

methyl group. If the methyl group of the L-lyxonolactone **31** can be inverted, the resulting D-ribonolactone can be easily converted to D-ristosamine analogously as the conversion of **31** to **25**. Our first attempt in the inversion of the methyl group was hydrolytic ring-opening of the L-lyxonolactone or its derivatives, followed by the Mitsunobu reaction. However, alkaline treatment of the methoxymethyl derivative **39** unexpectedly yielded the elimination product **40**. On the other hand, the corresponding tert-butyldimethylsilyl derivative **41** furnished



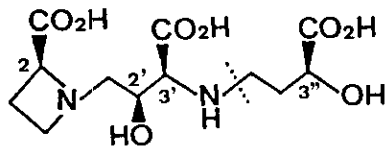
a: R = TBDMS
b: R = H

the ring-opened hydroxycarboxylic acid **42a** by alkaline hydrolysis followed by neutralization. The Mitsunobu reaction of **42a** afforded the D-ribonolactone **43a.** Successive treatment of **43a** with diisobutylaluminum hydride, methoxymethylene-triphenylphosphorane, hydrochloric acid in methanol, and acetic anhydride gave D-ristosamine as its N,O-diacetyl methyl glycoside **27a** via **44a** and **45a.**

Since the inversion of the methyl group in the above route was not effective, we further investigated a more efficient route without protection of the C-3 hydroxyl function of **31.** Hydrolysis of **31** was achieved with potassium superoxide in the presence of 18-crown-6. After acidification to pH 4, the crude product **42b** was subjected to the Mitsunobu reaction to give a mixture of D-ribonolactone **43b** and diethyl hydrazinedicarboxylate. Reduction of this mixture with diisobutylaluminum hydride afforded the pure D-ribonolactol **44b.** Sequential Wittig reaction, acid treatment, and acetylation gave the D-ristosamine derivative **27a** via **45b.**

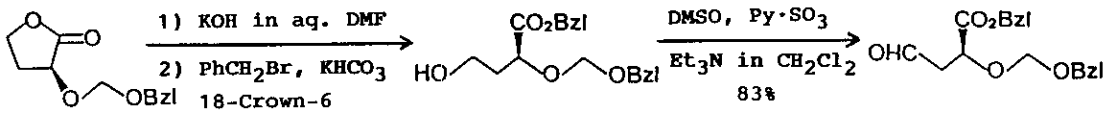
9. Mugineic Acid

Mugineic acid (**46**) is a typical phytosiderophore, which promotes uptake and transport of iron, excreted from roots of barley.[25] The first synthesis of mugineic acid[26] was achieved from two building blocks.



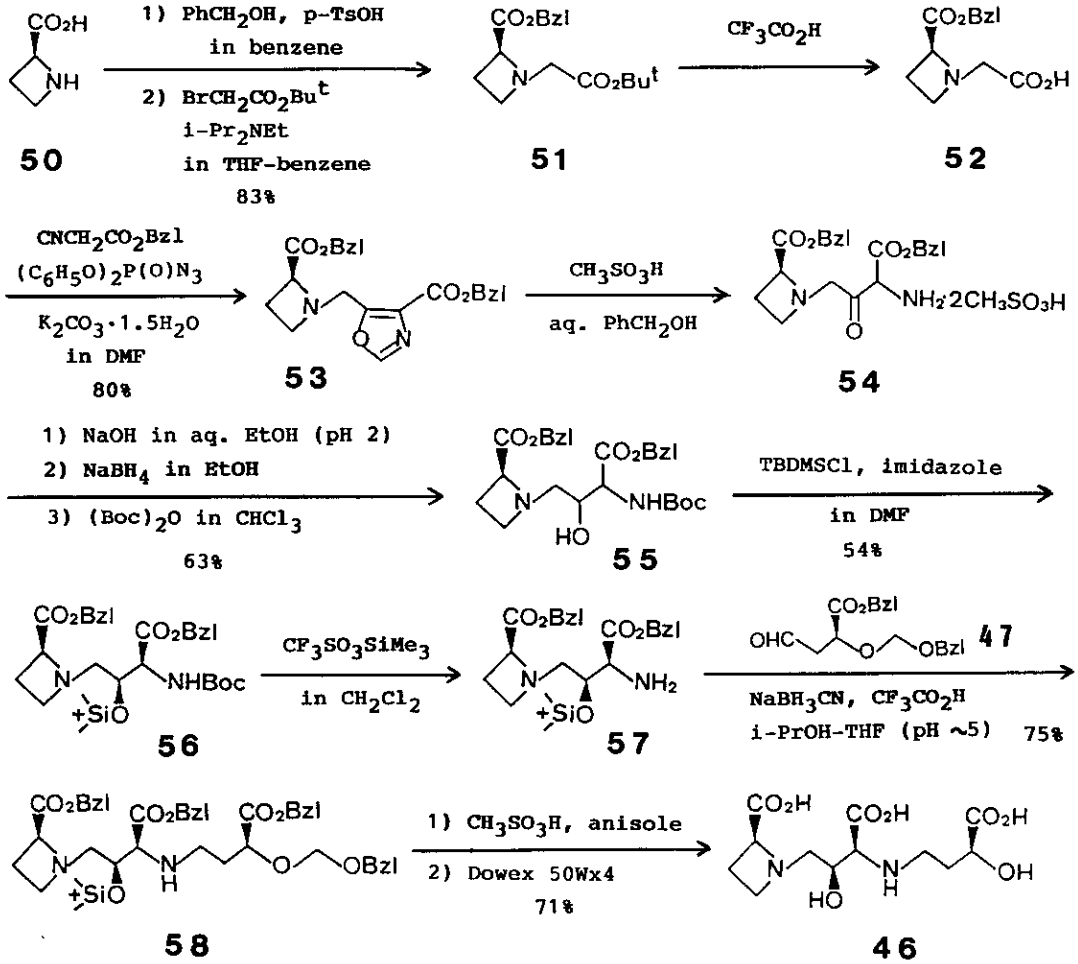
Mugineic Acid 46

Synthesis of the right-half fragment **47** started from the known γ-lactone **48**[27] obtained from L-malic acid in 4 steps. Alkaline hydrolysis of **48** followed by esterification afforded the benzyl ester **49**, which was oxidized with sulfur trioxide pyridine complex-dimethyl sulfoxide to give the aldehyde **47.**



48 **49** **47**

The left-half fragment of **46** was constructed from (S)-azetidine-2-carboxylic acid (**50**). Esterification of **50** with benzyl alcohol, followed by alkylation with tert-butyl bromoacetate afforded the diester **51**, which was subjected to acid treatment to give the amino acid **52**. Direct C-acylation of benzyl isocyanoacetate with the amino acid **52** smoothly proceeded by use of DPPA and potassium carbonate sesquihydrate to give the oxazole **53**. Conversion of the oxazole function to the β-hydroxy-α-amino acid was achieved analogously to our prumycin synthesis (section 4). Cleavage of the oxazole nucleus of **53** was easily accomplished with methanesulfonic acid to give the methanesulfonate of the α-amino ketone **54**. Ethanolic solution of the crude **54** was adjusted to pH 2, and treated with sodium borohydride to give a diastereoisomeric mixture of the amino alcohols. Chromatographic separation of the products was carried out as their Boc derivatives **55** to give two fractions. The major fraction was further separated as its tert-butyldimethyl-



silyl derivatives **56** and its isomer in a ratio of 2:1. Selective deprotection of the Boc group of the major isomer **56** with trimethylsilyl trifluoromethanesulfonate gave the left-half fragment **57**. Coupling of the right (**47**) and left (**57**) fragments was achieved with sodium cyanoborohydride to give the fully protected mugineic acid **58**, which was converted to mugineic acid (**46**) with methanesulfonic acid. Thus, mugineic acid was synthesized from (S)-azetidine-2-carboxylic acid (**50**) in 11 steps with an overall yield of 8.4%.

10. Conclusion

In summary, 4-alkoxycarbonyl-5-substituted oxazoles are quite a useful synthon of β-hydroxy-α-amino acids. Construction and cleavage of the oxazole nucleus will be conveniently accomplished by use of organophosphorus reagents, especially DPPA, and acids, respectively. Stereoselective reduction of the cleavage products gives β-hydroxy-α-amino acids, which will become versatile starting materials for a variety of natural products. The strategies outlined here have considerable synthetic applicability, but much more remains to be done!

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