FACILE SYNTHESIS OF (+)- AND (-)-GEISSMAN-WAISS LACTONES

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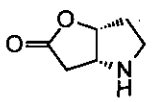
Abstract - (+)- and (-)- Geissman-Waiss lactones (**1**), were prepared from the readily accessible (4*R*, 5*R*)- and (4*S*, 5*S*)-5-allyl-4-methoxy-2-oxazolidinones [(+)- and (-)-**7**], respectively, in a highly stereocontrolled manner from the previously reported building block, 3-[(1*S*)-2-*exo*-alkoxy-1-apocamphanecarbonyl]-2-oxazolones (**4**).

Necine bases such as retronecine (**2**) and platynecine (**3**) have attracted considerable synthetic interest because they represent parent skeletons of a family of biologically active pyrrolizidine alkaloids.[1] The (+)- or (-)- Geissman-Waiss lactone[2] (**1**) serves as a versatile intermediate for the total synthetic routes to such necine bases.[3,4] Several groups have reported lengthy and multistep syntheses of chiral lactones (**1**) starting from optically active prolines and readily accessible natural carboxylic acids.[5,6] In this paper, we wish to report an entirely different approach to the optically pure Geissman-Waiss lactones (**1**) which involves considerable fewer steps than have been previously reported.



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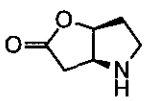

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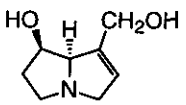

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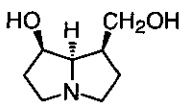

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In an earlier paper, we reported promising methodology for the versatile synthesis of 2-amino alcohols with

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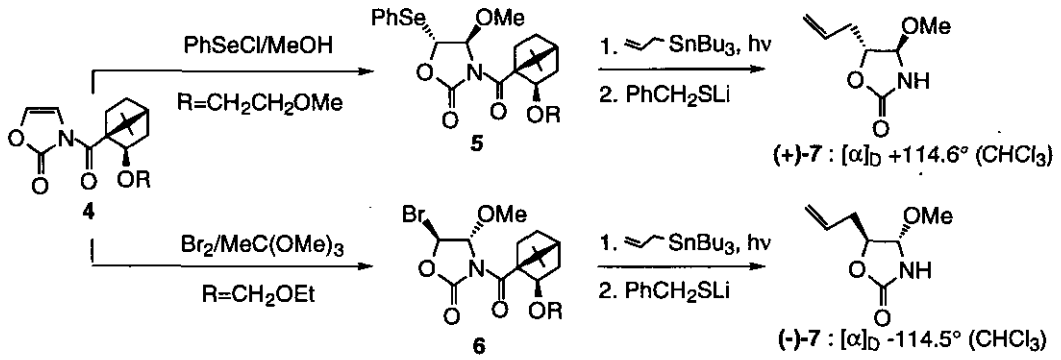
* Dedicated to Dr. Shigeru Oae, Professor Emeritus Tsukuba University, on the occasion of his 77th birthday.

adjacent stereogenic centers, starting with the simple heterocyclic 2-oxazolone as a building block.[7] Thus, (4*R*, 5*R*)- and (4*S*, 5*S*)-5-allyl-4-methoxy-2-oxazolidinones [(+)- and (-)-**7**] were readily prepared from 3-[(1*S*)-2-*exo*-alkoxy-1-apocamphanecarbonyl]-2-oxazolones (**4**) by highly stereocontrolled functionalizations which proceeded with opposite diastereoselection to provide 5-phenylseleno-4-methoxy- and 5-bromo-4-methoxy-2-oxazolidinones (**5** and **6**), respectively, as outlined in Scheme 1.

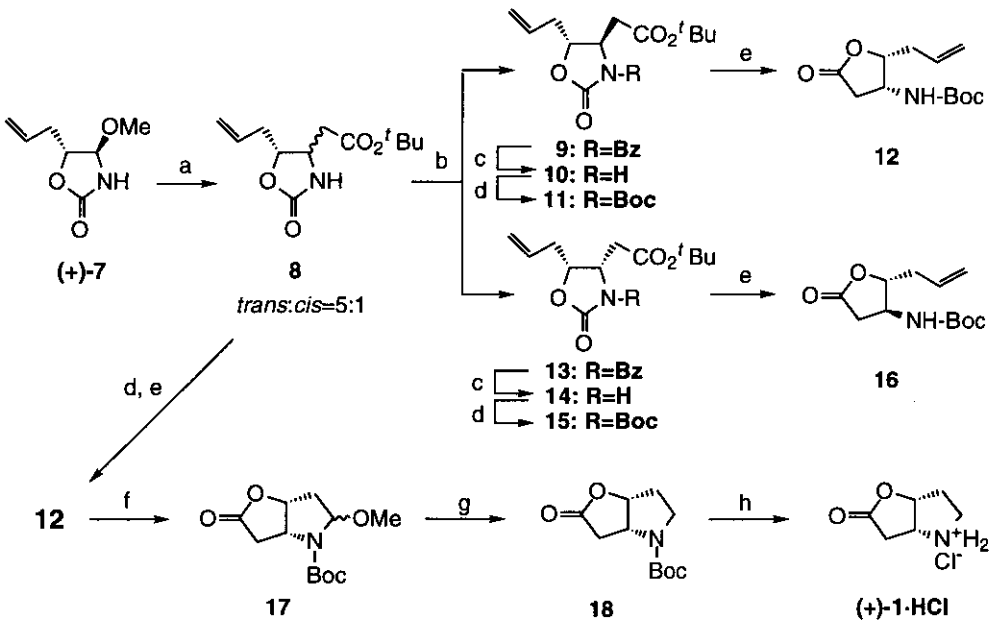


Scheme 1[7]

In the presence of $BF_3{\cdot}OEt_2$, treatment of (+)-**7** with the lithium acetyl enolates, prepared *in situ* from *sec*-BuLi and *tert*-butyl acetate at -78 °C, gave 4-*tert*-butoxycarbonylmethyl-5-allyl-2-oxazolidinone (**8**) in 98% yield as a mixture of *trans*- and *cis*- isomers in a ratio of 5:1. After conversion to the *N*-benzoyl-2-oxazolidinones (**9** and **13**) the compounds were cleanly purified by chromatography on silica gel. Conversion of each isomer to the *N*-Boc-derivatives (**11** and **15**) followed by treatment with Cs_2CO_3 in MeOH[8] resulted in the facile formation of *cis*- and *trans*-lactones (**12** and **16**), respectively, whose stereochemical assignments were made based on NOE analysis. The use of BuLi as an enolizing agent in place of *sec*-BuLi resulted in a complex mixture which included small amounts of **8**. Ozonolysis of optically pure **12**, followed by treatment with dimethyl sulfide gave the azabicyclic derivative (**17**) in 91% yield. Similar treatment of the *trans*-isomer (**16**) failed to give the bicyclic compounds. Treatment of **17** with triethylsilane in the presence of $BF_3{\cdot}OEt_2$ at 0 °C smoothly generated the (+)-*N*-Boc Geissman-Waiss lactone (**18**), which, after deprotection with HCl gave (+)-**1** as the hydrochloride (Scheme 2). Spectral and physical data were in good agreement with those reported for the Geissman-Waiss lactone.[6] The *cis*-lactone (**12**) could be routinely prepared from the mixed *trans*- and *cis*-2-oxazolidinones (**8**) by a convenient alternative route without diastereomeric separation. Thus, *tert*-butoxycarbonylation of **8**, followed by ring-opening with Cs_2CO_3 gave the diastereomeric mixture of lactones (**12** and **16**) from which the *cis*-lactone

(**12**) was purely isolated in 80% yield by a single recrystallization from hexane.

Similarly the enantiomeric Geissman-Waiss lactone [(-)-**1**] was synthesized from (4*S*, 5*S*)-5-allyl-4-methoxy-2-oxazolidinone [(-)-**7**] in an overall yield of 46%.



a: *t*-butyl acetate, *s*-BuLi, $BF_3{\cdot}OEt_2$; b: PhCOCl, NEt_3, DMAP; c: Cs_2CO_3/MeOH; d: $(Boc)_2O$, NEt_3, DMAP
e: i) Cs_2CO_3/MeOH, ii) NaH/THF; f: O_3/MeOH, Me_2S; g: Et_3SiH, $BF_3{\cdot}OEt_2$; h: HCl/Et_2O

Scheme 2

EXPERIMENTAL

Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP 370 polarimeter. ^{1}H-Nmr spectra were recorded in $CDCl_3$, unless otherwise stated, with tetramethylsilane as an internal standard at 500 MHz on a JEOL ALPHA-500 spectrometer. Infrared spectra were measured with a JASCO ir Report-100 spectrophotometer. Column chromatography was performed using silica gel 60 (70-230 mesh, Merck). All solvents were distilled before use; THF over Na/benzophenone, Et_2O over $LiAlH_4$, CH_2Cl_2 over CaH_2, MeOH over NaOMe and benzene over CaH_2.

(5*R*)-5-Allyl-4-*tert*-butoxycarbonylmethyl-2-oxazolidinones (8)

To a solution of *tert*-butyl acetate (0.70 g, 6 mmol) in THF (10 ml) was added *sec*-BuLi (1.14M in cyclohexane; 5.26 ml, 6 mmol) dropwise at -78 °C under an argon atmosphere, and was then stirred for 30

min. (4*R*, 5*R*)-5-Allyl-4-methoxy-2-oxazolidinone[7] [(+)-**7**] (0.31 g, 2 mmol) in THF (5 ml) and BF_3·OEt_2 (0.43 g, 3 mmol) were added successively and the mixture was stirred at -78 °C for 2 h. The usual work-up, followed by chromatography on silica gel (Hexane:EtOAc = 7:3) gave a mixture of *trans*- and *cis*-5-allyl-4-*tert*-butoxycarbonylmethyl-2-oxazolidinones (**8**) (0.47 g, 98%) as a colorless oil in a ratio of 82:18. The ratio was determined based on the ^{1}H-nmr peaks attributable to 4-position protons.

(4*R*, 5*R*)- and (4*S*, 5*R*)-5-Allyl-3-benzoyl-4-*tert*-butoxycarbonylmethyl-2-oxazolidinone (9 and 13)

A mixture of **8** (1.34 g, 5.6 mmol), triethylamine (2.24 g, 22.1 mmol), benzoyl chloride (1.63 g, 11.6 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (0.34 g, 2.8 mmol) was refluxed in THF (50 ml) for 8 h. The solution was passed through a silica gel-pad (EtOAc as eluent) followed by the usual work-up. Chromatographic separation on silica gel (hexane:CH_2Cl_2 = 3:2) gave **9** (1.47 g, 77%) and **13** (0.12 g, 6%) as colorless crystals.

(4*R*, 5*R*)-Isomer (9): mp 105 °C (from hexane); $[\alpha]_D^{26}$ -61.2 ° (c 1.00, $CHCl_3$); ^{1}H-nmr δ: 1.47 (9H, s), 2.56-2.66 (2H, m), 2.78 (1H, dd, J=7.9, 16.5 Hz), 2.98 (1H, dd, J=2.4, 16.5 Hz), 4.55-4.59 (2H, m), 5.26-5.32 (2H, m), 5.85 (1H, ddt, J=7.3, 10.4, 17.7 Hz), 7.42 (2H, t, J=7.9 Hz), 7.53 (1H, t, J=7.9 Hz), 7.61 (2H, d, J=7.9 Hz). Anal. Calcd for $C_{19}H_{23}NO_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 66.36; H, 6.98; N, 4.19.

(4*S*, 5*R*)-Isomer(13): mp 76 °C (from hexane); $[\alpha]_D^{27}$ +127.0 ° (c 1.00, $CHCl_3$); ^{1}H-nmr δ: 1.47 (9H, s), 2.50-2.69 (2H, m), 2.78 (1H, dd, J=9.2, 16.5 Hz), 3.05 (1H, dd, J=3.7, 16.5 Hz), 4.81 (1H, dt, J=3.7, 7.4 Hz), 4.94 (1H, dt, J=4.5, 7.4 Hz), 5.23 (1H, dd, J=1.2, 10.4 Hz), 5.26 (1H, dd, J=1.2, 16.5 Hz), 5.88 (1H, ddt, J=7.4, 10.4, 16.5 Hz), 7.42 (2H, t, J=7.9 Hz), 7.54 (1H, t, J=7.9 Hz), 7.63 (2H, d, J=7.9 Hz). Anal. Calcd for $C_{19}H_{23}NO_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 66.16; H, 6.95; N, 4.24.

(4*R*, 5*R*)-5-Allyl-4-*tert*-butoxycarbonylmethyl-2-oxazolidinone (10)

A solution of **9** (5.42 g, 15.7 mmol) and Cs_2CO_3 (10.22 g, 31.4 mmol) in MeOH (150 ml) was stirred at room temperature for 1 h and the reaction was quenched by addition of citric acid (6.25 g, 31.4 mmol). The mixture was passed through a silica gel-pad (EtOAc as eluent) and the filtrate concentrated *in vacuo*. Chromatography on silica gel (hexane:EtOAc = 7:3) gave **10** (3.49 g, 92%) as a colorless oil: $[\alpha]_D^{27}$ +89.4 ° (c 1.02, $CHCl_3$); ^{1}H-nmr δ: 1.46 (9H, s), 2.44-2.55 (4H, m), 3.81 (1H, dt, J=6.1, 7.3 Hz), 4.24 (1H, dd, J=6.1, 11.6 Hz), 5.20-5.24 (2H, m), 5.57 (1H, br s), 5.79 (1H, ddt, J=7.3, 10.4, 17.1 Hz).

(4*S*, 5*R*)-5-Allyl-4-*tert*-butoxycarbonylmethyl-2-oxazolidinone (14)

In an analogous manner, **13** (0.71 g, 2.1 mmol) was deacylated to give **14** (0.50 g, quant.) as colorless crystals; mp 58 °C (from hexane); $[\alpha]_D^{26}$ -53.5 ° (c 1.01, $CHCl_3$); ^{1}H-nmr δ: 1.46 (9H, s), 2.29-2.35 (1H, m), 2.49-2.56 (3H, m), 4.11 (1H, q, J=7.3 Hz), 4.69 (1H, dt, J=6.1, 7.9 Hz), 5.17-5.21 (2H, m), 5.58 (1H, br s), 5.77-5.85 (1H, m). Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81. Found: C, 59.51; H, 7.90; N, 5.84.

(4*R*, 5*R*)-5-Allyl-3-*tert*-butoxycarbonyl-4-*tert*-butoxycarbonylmethyl-2-oxazolidinone (11)

A mixture of **10** (0.48 g, 2 mmol), triethylamine (0.30 g, 3 mmol), di-*tert*-butyl dicarbonate (0.65 g, 3 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (0.12 g, 1 mmol) in THF (20 ml) was stirred at room temperature for 8 h. Flash evaporation followed by chromatography on silica gel (CH_2Cl_2) gave **11** (0.78 g, quant.) as colorless crystals; mp 62 °C (from hexane); $[\alpha]_D^{26}$ -18.1 ° (c 1.01, $CHCl_3$); ^{1}H-nmr δ: 1.46 (9H, s), 1.55 (9H, s), 2.45-2.55 (2H, m), 2.64 (1H, dd, J=9.2, 15.9 Hz), 2.82 (1H, dd, J=3.1, 15.9 Hz), 4.20 (1H, ddd, J=2.5, 3.1, 9.2 Hz), 4.37 (1H, dt, J=2.5, 6.1 Hz), 5.21 (1H, dd, J=1.2, 10.4 Hz), 5.24 (1H, dd, J=1.2, 17.1 Hz), 5.79 (2H, ddt, J=7.2, 10.4, 17.1 Hz). Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.81; H, 7.97; N, 4.10. Found: C, 59.73; H, 8.08; N, 4.21.

(4*S*, 5*R*)-5-Allyl-3-*tert*-butoxycarbonyl-4-*tert*-butoxycarbonylmethyl-2-oxazolidinone (15)

Using the same procedure as above, **14** (0.07 g, 0.3 mmol) was butoxycarbonylated to give **15** (0.10 g, 97%) as colorless crystals; mp 80 °C (from hexane); $[\alpha]_D^{26}$ +73.3 ° (c 0.50, $CHCl_3$); ^{1}H-nmr δ: 1.46 (9H, s), 1.55 (9H, s), 2.43-2.55 (2H, m), 2.69-2.77 (2H, m), 4.57-4.63 (2H, m), 5.17 (1H, dd, J=1.8, 10.4 Hz), 5.19 (1H, dd, J=1.8, 17.1 Hz), 5.82 (2H, ddt, J=6.7, 10.4, 17.1 Hz). Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.81; H, 7.97; N, 4.10. Found: C, 59.54; H, 7.98; N, 4.29.

(4*R*, 5*R*)-5-Allyl-4-(*tert*-butoxycarbonyl)aminotetrahydrofuran-2-one (12)

A solution of **11** (1.53g, 4.5 mmol) in MeOH (50 ml) was treated with Cs_2CO_3 (0.44 g, 1.4 mmol) at room temperature for 4 h and the reaction was quenched by the addition of citric acid (0.26 g, 1.4 mmol). The mixture was filtered through a celite-pad (EtOAc as eluent) and the filtrate was evaporated *in vacuo*. The residue was washed (brine) in EtOAc (100 ml) and the solvent was removed *in vacuo*. The residue was dissolved in THF (50 ml) and after the addition of NaH (60% in oil; 49 mg, 2.2 mmol) at 0 °C, it was stirred at room temperature for 5 min. The mixture was then passed through a silica gel-pad (EtOAc as eluent), the filtrate concentrated, and the oil chromatographed on silica gel (CH_2Cl_2:EtOAc = 9:1) to give

12 (0.94 g, 87%) as colorless crystals; mp 112 °C (from hexane); $[\alpha]_D^{27}$ +89.2 ° (c 1.00, $CHCl_3$); ir (nujol, cm^{-1}) 3360, 1765, 1675; ^{1}H-nmr δ: 1.45 (9H, s), 2.44-2.51 (3H, m), 2.89 (1H, dd, J=7.3, 17.7 Hz), 4.55-4.59 (2H, m), 4.87 (1H, br s), 5.16 (1H, d, J=10.4 Hz), 5.20 (1H, d, J=17.1 Hz), 5.84 (2H, ddt, J=7.3, 10.4, 17.1 Hz). Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81. Found: C, 59.47; H, 8.03; N, 5.83.

Using the alternative procedure, the *cis*-lactone could be obtained in pure form by a single recrystallization (hexane) of the mixed *cis*- and *trans*-lactones (**12** and **16**) (in a ratio of 5:1), which were obtained from the diastereomeric mixture of **8**.

(4*S*, 5*R*)-5-Allyl-4-(*tert*-butoxycarbonyl)aminotetrahydrofuran-2-one (16)

Using procedures analogous to those for the preparation of **12**, **15** (0.47 g, 1.4 mmol) was treated successively with Cs_2CO_3 (0.14 g, 0.4 mmol) and NaH (60% in oil; 15 mg, 0.7 mmol) to give **16** (0.23 g, 68%) as colorless crystals; mp 83 °C (from hexane); $[\alpha]_D^{28}$ +8.7 ° (c 0.51, $CHCl_3$); ^{1}H-nmr δ: 1.45 (9H, s), 2.43-2.56 (3H, m), 2.88 (1H, dd, J=8.6, 18.3 Hz), 4.11-4.17 (1H, m), 4.37 (1H, q, J=5.5 Hz), 4.98 (1H, br s), 5.19 (1H, d, J=10.4 Hz), 5.22 (1H, d, J=17.1 Hz), 5.81 (2H, ddt, J=7.3, 10.4, 17.1 Hz). Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81. Found: C, 59.48; H, 7.95; N, 5.69.

(1*R*,5*R*)-6-*tert*-Butoxycarbonyl-7-methoxy-2-oxa-6-azabicyclo[3.3.0]octan-3-one (17)

Ozone was passed through a solution of **12** (0.24 g, 1 mmol) in MeOH (20 ml) at -78 °C until the color of the solution became slightly blue. The solution was then flushed with oxygen for 2 min before the addition of dimethyl sulfide (0.29 ml, 3 mmol) and the resulting solution was then stirred at room temperature for 8 h. Evaporation under reduced pressure, followed by chromatography on silica gel (hexane:EtOAc = 7:3) gave crystalline **17** (0.23 g, 91%) as a mixture of (7*S*)- and (7*R*)-forms in a ratio of 5:1; mp 79 °C (from hexane); ^{1}H-nmr (DMSO-d_6 at 70 °C) δ: 1.43 (9×1/6H, s), 1.44 (9×5/6H, s), 2.03-2.15 (2H, m), 2.38 (5/6H, d, J=18.3 Hz), 2.45 (1/6H, d, J=18.3 Hz), 2.91-2.99 (1H, m), 3.18 (3×1/6H, s), 3.20 (9×5/6H, s), 4.43 (1/6H, t, J=6.7 Hz), 4.52 (5/6H, t, J=6.7 Hz), 5.07-5.10 (1H, m), 5.16-5.22 (5/6H, m), 5.47 (1/6H, d, J=5.5 Hz). Anal. Calcd for $C_{12}H_{19}NO_5$: C, 56.02; H, 7.44; N, 5.44. Found: C, 55.78; H, 7.58; N, 5.43.

(1*R*, 5*R*)-6-*tert*-Butoxycarbonyl-2-oxa-6-azabicyclo[3.3.0]octan-3-one (18)

A solution of **17** (0.26 g, 1 mmol) in CH_2Cl_2 (10 ml) was treated with triethylsilane (0.38 g, 3.3 mmol) in the presence of $BF_3{\cdot}OEt_2$ (0.14 g, 1 mmol) at 0 °C for 5 min. The usual work-up followed by chromatography on silica gel (CH_2Cl_2:EtOAc = 9:1) gave **18** (0.21 g, 91%) as colorless crystals; mp 111

°C (from hexane); $[\alpha]_D^{27}$ -131.1 ° (c 1.00, $CHCl_3$); ir (nujol, cm^{-1}) 1765, 1700; ^{1}H-nmr (DMSO-d_6 at 70 °C) δ: 1.41 (9H, s), 2.02-2.12 (2H, m), 2.51 (1H, d, J=18.9 Hz), 2.92 (1H, dd, J=6.7, 18.3 Hz), 3.20 (1H, dt, J=6.7, 10.4 Hz), 3.59 (1H, ddd, J=2.5, 7.9, 10.4 Hz), 4.34 (1H, t, J=5.5 Hz), 5.09 (1H, dt, J=1.8, 5.5 Hz). Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.13; H, 7.54; N, 6.16. Found: C, 58.18; H, 7.29; N, 6.16.

(1*R*, 5*R*)-2-Oxa-6-azabicyclo[3.3.0]octan-3-one Hydrochloride [(+)-1·HCl]

A solution of **18** (0.10 g, 0.46 mmol) in Et_2O (20 ml) was treated with Et_2O saturated with hydrochloric acid (40 ml) at room temperature for 8 h. The solution was evaporated to dryness *in vacuo* to give **(+)-1·HCl** (0.07 g, 98%) as colorless crystals; mp 185-186.5 °C (from EtOH); $[\alpha]_D^{26}$ +48.8 ° (c 0.20, MeOH) (lit.,[6] $[\alpha]_D$ +48.8 ° (MeOH)); ^{1}H-nmr (D_2O) δ: 2.22-2.30 (1H, m), 2.36-2.39 (1H, m), 2.90 (1H, d, J=19.5 Hz), 3.20 (1H, dd, J=9.2, 19.5 Hz), 3.36 (1H, dt, J=6.7, 11.6 Hz), 3.47 (1H, dt, J=3.7, 7.9, 11.6 Hz), 4.58 (1H, dd, J=5.5, 9.2 Hz), 5.32 (1H, t, J=5.5 Hz).

(1*S*, 5*S*)-2-Oxa-6-azabicyclo[3.3.0]octan-3-one Hydrochloride [(-)-1·HCl]

The title compound was synthesized from (4*S*, 5*S*)-5-allyl-4-methoxy-2-oxazolidinone[7] [(-)-7] using the same procedures as for **(+)-1·HCl**, which was obtained in an overall yield of 46% as colorless crystals, mp 186 °C (from EtOH); $[\alpha]_D^{26}$ -48.3 ° (c 0.20, MeOH). The ^{1}H-Nmr spectrum (D_2O) was identical to that of **(+)-1·HCl**.

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