Conversion of Steroidal Vicinal Diols to the Corresponding Olefinic Compounds

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Abstract : The wide applicability of two-step conversion of a vicinal diol group to carbon-carbon double bond developed by Corey and Winter was examined for various steroids with vicinal diol(s). By refluxing with triethyl phosphite, cyclic thionocarbonates derived from the vicinal diol steroids were converted to the corresponding olefinic steroids in high yields. Using this two-step conversion as a key step, brassinosteroid-related compounds, (22*R*,23*R*,24*S*)- and (22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-diepoxy-*B*-homo-7-oxa-5 α -stigmastan-6-ones produced more efficiently than reported to date.

Key words : steroid, vicinal diol, thionocarbonate, triethyl phosphite, brassinosteroid

1 Introduction

Among the reactions to convert vicinal diol group to carbon-carbon double bond¹⁾, a two-step reaction developed by Corey and Winter seems to be useful to many types of vicinal diol compounds, because the elimination of cyclic thionocarbonate is *syn* type and olefinic product is sterically controlled^{2,3)}. However, the two step conversion has not been used widely so far. In the fields of steroids, we have recently applied the reaction to the conversion of 2 α ,3 α -diol to Δ^2 -steroidal compound and we have synthesized stereoisomers of a phytohormone brassinolide⁴⁾.

By epoxidation and lactonization of 2,22-dien-6-one **1** with *m*-chloroperbenzoic acid or molecular oxygen and aldehyde, Brosa and Miro have reported the synthesis of two brassinosteroid-related diepoxylactones **2** and **3**, which showed an interesting plant growth promoting activity in the rice lamina inclination test⁵⁾. However, their synthesis is not suited for obtaining enough amount for more detailed biological evaluation, because of the extremely low (3.4 and 2.3 %) yields of **2** and **3**. We have examined the wide applicability of the two-step reaction to more several kinds of steroidal vicinal diol compounds.

Further, we have examined a more efficient synthesis of the diepoxylactones **2** and **3**, using this reaction as a key step. In this paper, we wish to report these results.

2 Experimental

2.1 Analytical Methods

Melting points were determined under a hot-stage microscope (Yanaco micro melting point apparatus) and not corrected. ¹H (300 MHz)- and ¹³C (75 MHz)-NMR spectra were recorded on a Varian XL-VXR 300 spectrometer in a deuteriochloroform solution with tetramethylsilane as an internal standard. HR-FAB-MS were recorded on a JEOL HX-110 mass spectrometer. Silica gel (Merck, Kieselgel 60, 70~230 mesh) was used for column chromatography. Reactions were monitored by TLC on silica gel plate (Merck, Kieselgel 60F₂₅₄, 0.25 mm thickness). Spots were visualized with 10% H₂SO₄, followed by heating. All purified

Fig. 1 Structures of (22*E*,24*S*)-5 α -Stigmasta-2,22-dien-6-one **1**, (22*R*,23*R*,24*S*)- and (22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-diepoxy-*B*-homo-7-oxa-5 α -stigmastan-6-ones **2** and **3**.

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compounds showed a single spot by TLC analysis.

2.2 Steroids

(22*S*,23*S*,24*S*)-22,23-Dihydroxy-5 α -stigmast-2-en-6-one **9**, (22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-tetrahydroxy-5 α -stigmastan-6-one **11**, and (22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-tetrahydroxy-*B*-homo-7-oxa-5 α -stigmastan-6-one **13** were prepared according to the reported methods^{6,7}). (22*E*,24*S*)-2 β ,3 β -Dihydroxy-5 α -stigmast-22-en-6-one **4** and (22*E*,24*S*)-2 β ,3 β -dihydroxy-5 β -stigmast-22-en-6-one **6** were prepared by saponification of a known (22*E*,24*S*)-2 β ,3 β -dipropionyloxy-5 α -stigmast-22-en-6-one⁸) followed by chromatographic separation and their structures were confirmed by spectral data and also by the reported data⁹.

2.3 Typical Procedure for Preparation of Thionocarbonates with Thiophosgene

A solution of thiophosgene (30 μ L, 0.39 mmol) in dichloromethane (CH₂Cl₂) (3 mL) was added dropwise to a solution of (22*E*,24*S*)-2 β ,3 β -dihydroxy-5 α -stigmast-22-en-6-one **4** (119.7 mg, 0.270 mmol) and 4-dimethylaminopyridine (150 mg) in CH₂Cl₂ (10 mL) at 0°C and the mixture was stirred at 0°C for 1 h. The reaction was quenched by addition of water and the mixture was extracted with CH₂Cl₂. The organic phase was successively washed with 2*M* HCl, sat. NaHCO₃ and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. A residue was applied to a column of silica gel (1.0 cm i.d. $\times$ 10 cm). Elution with hexane-ethyl acetate (10 : 1, vol/vol) provided (22*E*,24*S*)-2 β ,3 β -dihydroxy-5 α -stigmast-22-en-6-one 2,3-thionocarbonate **5** (130.6 mg, 99%), mp 242~244°C (from hexane), ¹H-NMR δ : 0.69 (3H, s, 18-H₃), 0.79 (3H, d, *J*=6 Hz, 26-H₃), 0.80 (3H, t, *J*=7 Hz, 29-H₃), 0.84 (3H, d, *J*=6.5 Hz, 27-H₃), 0.90 (3H, s, 19-H₃), 1.02 (3H, d, *J*=6.5 Hz, 21-H₃), 2.54 (1H, d, *J*=10 Hz, 5 α -H), 4.88 (2H, m, 2 α -H and 3 α -H), 5.02 (1H, dd, *J*=15 and 8.5 Hz, 22-H), and 5.12 (1H, dd, *J*=15 and 8 Hz, 23-H). ¹³C-NMR δ : 12.2 ($\times$ 2), 14.2, 19.0, 21.0, 21.1, 21.2, 22.7, 24.0, 25.3, 28.6, 31.8, 37.0, 37.9, 39.1, 39.7, 40.3, 42.7, 46.5, 51.3, 52.8, 54.3, 55.9, 56.7, 79.5, 80.1, 129.8, 137.7, 191.4, and 208.1. HR-FAB-MS *m/z* : Calcd. for C₃₀H₄₇O₃S ([M+H]⁺) : 487.3246. Found : 487.3261.

(22*E*,24*S*)-2 β ,3 β -Dihydroxy-5 β -stigmast-22-en-6-one 2,3-thionocarbonate **7** (99%, 749.3 mg from 690 mg of **6**), mp 202~204°C (from hexane), ¹H-NMR δ : 0.69 (3H, s, 18-H₃), 0.79 (3H, d, *J*=6

Hz, 26-H₃), 0.80 (3H, t, *J*=7 Hz, 29-H₃), 0.84 (3H, d, *J*=6.5 Hz, 27-H₃), 1.00 (3H, s, 19-H₃), 1.02 (3H, d, *J*=6 Hz, 21-H₃), 2.34 (1H, dd, *J*=4 and 12.5 Hz, 5 β -H), 4.96 (2H, m, 2 α -H and 3 α -H), 5.02 (1H, dd, *J*=15 and 8.5 Hz, 22-H), and 5.12 (1H, dd, *J*=15 and 8 Hz, 23-H). ¹³C-NMR δ : 12.2 ($\times$ 2), 19.0, 21.1, 21.2, 21.7, 23.3, 23.9, 25.4, 26.2, 28.7, 31.8, 35.8, 36.2, 38.6, 39.3, 40.3, 42.6, 42.8, 43.2, 51.2, 52.6, 55.9, 56.8, 78.2, 78.6, 129.9, 137.7, 191.2, and 211.3. HR-FAB-MS *m/z* : Calcd. for C₃₀H₄₇O₃S ([M+H]⁺) : 487.3246. Found : 487.3239.

(22*S*,23*S*,24*S*)-22,23-Dihydroxy-5 α -stigmast-2-en-6-one 22,23-thionocarbonate **10** (93%, 543.2 mg from 535.4 mg of **9**), mp 238~240°C (from hexane), ¹H-NMR δ : 0.71 (3H, s, 18-H₃), 0.73 (3H, s, 19-H₃), 0.96 (3H, d, *J*=6.5 Hz, 26-H₃), 0.99 (3H, d, *J*=6.5 Hz, 27-H₃), 1.00 (3H, d, *J*=6 Hz, 21-H₃), 1.02 (3H, t, *J*=7 Hz, 29-H₃), 2.36 (1H, dd, *J*=12.5 and 4 Hz, 5 α -H), 4.66 (1H, m, 23-H), 4.72 (1H, m, 22-H), and 5.52-5.72 (2H, m, 2-H and 3-H). ¹³C-NMR δ : 11.8, 12.2, 13.1, 13.5, 18.3, 18.7, 21.0, 21.7, 22.1, 24.1, 26.4, 27.9, 37.5, 39.3, 39.6, 39.9, 43.5, 46.8, 49.4, 51.0, 53.2, 53.9, 56.2, 77.2, 83.1, 87.1, 124.4, 125.0, 191.5, and 211.3. HR-FAB-MS *m/z* : Calcd. for C₃₀H₄₇O₃S ([M+H]⁺) : 487.3246. Found : 487.3247.

(22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-Tetrahydroxy-5 α -stigmastan-6-one 2,3- and 22,23-bisthionocarbonate **12** (91%, 165.5 mg from 167.7 mg of **11**), mp 316~318°C (from hexane-CH₂Cl₂), ¹H-NMR δ : 0.72 (6H, s $\times$ 2, 18-H₃ and 19-H₃), 0.98 (3H, d, *J*=6.5 Hz, 26-H₃), 1.00 (6H, d $\times$ 2, *J*=6.5 Hz, 21-H₃ and 27-H₃), 1.10 (3H, t, *J*=7 Hz, 29-H₃), 2.53 (1H, dd, *J*=12.5 and 4 Hz, 5 α -H), 4.64 (1H, m, 23-H), 4.72 (1H, m, 22-H), 4.90 (1H, m, 2 β -H), and 4.95 (1H, m, 3 β -H). ¹³C-NMR δ : 11.8, 12.3, 12.8, 13.2, 18.3, 18.8, 21.0, 21.5, 22.1, 24.1, 26.4, 27.9, 37.2, 38.6, 39.0, 39.6, 41.1, 43.5, 46.4, 49.5, 50.6, 51.0, 52.5, 56.0, 78.1, 79.7, 83.2, 87.0, 191.4, 191.5, and 208.6. HR-FAB-MS *m/z* : Calcd. for C₃₁H₄₇O₅S₂ ([M+H]⁺) : 563.2865. Found : 563.2856.

(22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-Tetrahydroxy-*B*-homo-7-oxa-5 α -stigmastan-6-one 2,3- and 22,23-bisthionocarbonate **14** (69%, 523.5 mg from 649.6 mg of **13**), mp 148~150°C (from MeOH), ¹H-NMR (500 MHz) δ : 0.78 (3H, s, 18-H₃), 0.97 (3H, d, *J*=6.9 Hz, 26-H₃), 0.97 (3H, s, 19-H₃), 0.99 (3H, d, *J*=6.9 Hz, 27-H₃), 1.01 (3H, d, *J*=7.4 Hz,

21-H₃), 1.04 (3H, t, $J=7.4$ Hz, 29-H₃), 2.56 (1H, dd, $J=16.3$ and 4.4 Hz), 2.94 (1H, dd, $J=12.4$ and 2.8 Hz, 5 α -H), 4.07 (1H, dd, $J=12.8$ and 10.1 Hz, 7 β -H), 4.14 (1H, dd, $J=13.1$ and 2.1 Hz, 7 α -H), 4.56 (1H, dd, $J=4.2$ and 4.2 Hz, 23-H), 4.71 (1H, dd, $J=5.1$ and 5.1 Hz, 22-H), 5.11 (1H, m, 2 β -H), and 5.20 (1H, m, 3 β -H). HR-FAB-MS m/z : Calcd. for C₃₁H₄₇O₆S₂ ($[M+H]^+$): 579.2814. Found: 579.2811.

2.4 Preparation of Thionocarbonate with 1,1-Thiocarbonyldiimidazole

A mixture of a known (22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-tetrahydroxy-*B*-homo-7-oxa-5 α -stigmastan-6-one **13**⁷⁾ (66.1 mg, 0.134 mmol), 1,1-thiocarbonyldiimidazole²⁾ (198.3 mg, 1.11 mmol), and dry toluene (7 mL) was heated at reflux temperature under argon atmosphere for 3 h. The solvent was evaporated and the residue was applied to a column of silica gel (2.0 cm i.d. $\times$ 20 cm). Elution with hexane-ethyl acetate (3 : 1, vol/vol) afforded (22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-tetrahydroxy-*B*-homo-7-oxa-5 α -stigmastan-6-one **2**, 3- and 22,23-bisthionocarbonate **12** (23.6 mg, 45.4 μ mol) were respectively converted to (22*E*,24*S*)-5 α -stigmasta-2,22-dien-6-one **1** (382 and 17.0 mg, 94 and 91%, respectively).

2.5 Typical Procedure for the Reaction of a Thionocarbonate with Triethyl Phosphite

(22*E*,24*S*)-2 β ,3 β -Dihydroxy-5 α -stigmast-22-en-6-one **2**,3-thionocarbonate **5** (18.6 mg, 38.3 μ mol) was treated with triethyl phosphite (3 mL) at reflux temperature under argon for 5 h. The reaction mixture was cooled and then extracted with toluene. The organic phase was washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was applied to a column of silica gel (1.0 cm i.d. $\times$ 5.0 cm). Elution with toluene provided (22*E*,24*S*)-5 α -stigmasta-2,22-dien-6-one **1** (17.1 mg, 92%), mp 117~118°C (from MeOH) [lit.¹⁰⁾, mp 114~115°C (MeOH)]. Its spectral data were identical with those of an authentic sample¹⁰⁾.

In the same manner, (22*E*,24*S*)-2 β ,3 β -dihydroxy-5 β -stigmast-22-en-6-one **2**,3-thionocarbonate **7** (22.6 mg, 46.5 μ mol) was converted to (22*E*,24*S*)-5 β -stigmasta-2,22-dien-6-one **8** (20.8 mg, 99%), mp 133~134°C (from MeOH), ¹H-NMR δ : 0.68 (3H, s, 18-H₃), 0.79 (3H, d, $J=6$ Hz, 26-H₃), 0.80 (3H, t, $J=7$ Hz, 29-H₃), 0.84 (3H, d, $J=6.5$ Hz, 27-H₃), 0.89 (3H, s, 19-H₃), 1.01 (3H, d, $J=6.5$

Hz, 21-H₃), 5.02 (1H, dd, $J=15$ and 8.5 Hz, 22-H), 5.14 (1H, dd, $J=15$ and 8 Hz, 23-H), and 5.64 (2H, m, 2-H and 3-H). ¹³C-NMR δ : 12.2, 12.3, 19.0, 21.0, 21.2, 21.9, 23.1, 24.0, 25.4, 26.7, 28.8, 31.9, 34.3, 37.0, 37.2, 39.6, 40.4 ($\times 2$), 41.8, 43.0, 51.2, 56.0, 56.5, 57.0, 123.7, 124.2, 129.6, 138.0, and 215.1. HR-FAB-MS m/z : Calcd. for C₂₉H₄₇O ($[M+H]^+$): 411.3640. Found: 411.3625.

In the same manner, (22*S*,23*S*,24*S*)-22,23-dihydroxy-5 α -stigmast-2-en-6-one **22**,23-thionocarbonate **10** (479.9 mg, 0.987 mmol) and (22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-tetrahydroxy-5 α -stigmastan-6-one **2**, 3- and 22,23-bisthionocarbonate **12** (23.6 mg, 45.4 μ mol) were respectively converted to (22*E*,24*S*)-5 α -stigmasta-2,22-dien-6-one **1** (382 and 17.0 mg, 94 and 91%, respectively).

In the same manner, (22*S*,23*S*,24*S*)-2 α ,3 α ,22,23-tetrahydroxy-*B*-homo-7-oxa-5 α -stigmastan-6-one **2**,3- and 22,23-bisthionocarbonate **14** (162.8 mg, 0.281 mmol) was converted to (22*E*,24*S*)-*B*-homo-7-oxa-5 α -stigmasta-2,22-dien-6-one **15** (106.9 mg, 89%), mp 98~99°C (from MeOH) [lit.⁴⁾, mp 99~101°C (MeOH)]. Its spectral data were identical with those of an authentic sample⁹⁾.

2.6 Epimerization of (22*E*,24*S*)-5 β -Stigmasta-2,22-dien-6-one **8**

A mixture of (22*E*,24*S*)-5 β -stigmasta-2,22-dien-6-one **8** (18.3 mg, 45.0 μ mol), pyridinium *p*-toluenesulfonate (5 mg), and *N,N*-dimethylacetamide (3 mL) was heated at 150°C for 3 h. The reaction mixture was cooled and extracted with ethyl acetate. The extract was washed successively with 2*M* HCl, *sat.* NaHCO₃, and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was applied to a column of silica gel (1.0 cm i.d. $\times$ 5.0 cm). Elution with toluene afforded (22*E*,24*S*)-5 α -stigmasta-2,22-dien-6-one **1** (17.7 mg, 97%). Its spectral data were identical with those of an authentic sample¹⁰⁾.

2.7 Epoxidation of (22*E*,24*S*)-*B*-Homo-7-oxa-5 α -stigmasta-2,22-dien-6-one **15**

A solution of (22*E*,24*S*)-*B*-homo-7-oxa-5 α -stigmasta-2,22-dien-6-one **15** (61.4 mg, 0.144 mmol) in CH₂Cl₂ (10 mL) was treated with *m*-chloroperbenzoic acid (250 mg) at 0°C to room temperature for 3 h. A solution of NaHSO₃ (0.5 g) in water (5 mL) was added dropwise to the reaction mixture and the whole was stirred at 0°C for 1 h before extraction with CH₂Cl₂. The organic phase was washed with *sat.* NaHCO₃ and brine, dried over

anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The residue was applied to a column of silica gel (2.0 cm i.d. $\times$ 25 cm). Elution with CH_2Cl_2 -acetone (50 : 1, vol/vol) provided (22*R*, 23*R*, 24*S*)-2 α ,3 α ,22,23-diepoxy-*B*-homo-7-oxa-5 α -stigmastan-6-one **2** (31.9 mg, 48%) : mp 157~158°C (from MeOH) [lit.⁵], mp 104~107°C (solvent was not specified), R_F =0.69 (CH_2Cl_2 -acetone, 20 : 1, vol/vol). Its spectral data were identical with the reported data⁵.

Further elution with the same solvent gave (22*S*, 23*S*, 24*S*)-2 α ,3 α ,22,23-diepoxy-*B*-homo-7-oxa-5 α -stigmastan-6-one **3** (24.9 mg, 38%) : mp 162~164°C (from acetone) [lit.⁵], mp 159~163°C (solvent was not specified), R_F =0.65 (CH_2Cl_2 -acetone, 20 : 1, vol/vol). Its spectral data were identical with the reported data⁵.

3 Results and Discussion

The two-step reaction developed by Corey and Winter was at first applied to steroids with 2 β ,3 β -diol, in order to test the mildness of the reaction condition. 5 α -Steroidal 2 β ,3 β -diol **4** was reacted with thiophosgene in dichloromethane in the presence of 4-dimethylaminopyridine to form a cyclic thionocarbonate **5**. Treatment of **5** with triethyl phosphite under reflux provided, after chromatographic purification, the known 2,22-dien-6-one **1**¹⁰ in 91% yield from the 2 β ,3 β -diol **4**. The same procedure was applied to the 5 β -steroidal 2 β ,3 β -diol **6**. A high yield (98%) of 5 β -steroidal dienone **8** was attained with retention of the stereochemistry at the C-5 position. It should be noted that no epimerized product **1** was detected under the reaction condition. Epimerization at the C-5 position of **8** was easily effected by treatment with pyridinium *p*-toluenesulfonate and the 5 α -isomer **1** was obtained in 97% yield. Thus, the mildness of the reaction was confirmed based on the production of the compound **8**, which is both acid- and base-labile.

The procedure was then applied to brassinosteroid-related compounds with a vicinal diol in the side chain. The cyclic thionocarbonates **10** and **12**, derived from 22,23-diol compound **9** and 2 α ,3 α ,22,23-tetraol compound **11**, were respectively subjected to the two-step reaction and the known 2,22*E*-dien-6-one **1**¹⁰ was obtained in 88 and 83% yields, respectively. It is thus confirmed that formation of carbon-carbon double bond is

sterically controlled with *syn*-elimination. It has been reported that brassinosteroid-related compounds with an unnatural (22*S*,23*S*)-vicinal diol in the side chain were produced as by-products (*ca.* 40%), even by employing osmium-catalyzed asymmetric dihydroxylation of the steroidal 22-ene compounds, such as the 2,22-dien-6-one **1** or its related compounds¹¹. Thus, the present data show that the two-step reaction is useful for converting the unnatural stereoisomers to the 22-ene compounds, which, in turn, can be re-subjected to the osmium-catalyzed asymmetric dihydroxylation, eventually, increasing the overall yield of brassinosteroids with natural (22*R*,23*R*)-configuration, such as 28-homocastasterone and 28-homobrassinolide.

We next investigated an efficient synthesis of the diepoxylactones **2** and **3** using the above-mentioned conversion as a key step. The reported method has a drawback of extremely low yield of the diepoxylactones **2** and **3**⁹. Both epoxidation and lactonization of the 2,22-dien-6-one **1** were carried out in one step and epoxidation proceeded faster than lactonization⁹. This may be the reason for the low yield. Thus, we planned to carry out at first the lactonization and then the epoxidation at both the A-ring and the side chain. Previously, Mori *et al.* reported a short-step preparation of the steroid **13** from stigmasterol⁷. Thus, we now applied the two-step conversion to this steroid **13**. Following the method by Mori *et al.*⁷ and our isomerization reaction of 3 α ,5-cyclopropyl 5 α -steroidal 6-one to Δ^2 -5 α -steroid¹⁰, the steroid **13** was obtained in 24% yield by nine step reaction from a commercial stigmasterol. The steroid **13** was converted to the bithionocarbonate **14** in 69% yield by treatment with thiophosgene. When the steroid **13** was reacted with 1,1-thiocarbonyldiimidazole², the same bithionocarbonate **14** was obtained in 91% yield. The bithionocarbonate **14** thus obtained was then treated with triethyl phosphite to give a known lactonic diene **15**⁹ in 89% yield. Epoxidation of **15** with *m*-chloroperbenzoic acid provided, after chromatographic separation, (22*R*,23*R*)-diepoxylactone **2** and its (22*S*,23*S*)-isomer **3** in 48 and 38% yields, respectively.

In summary, we have achieved in a high yield the two-step conversion of the several kinds of steroids with vicinal diol group(s) to the corre-

Scheme Reagent and conditions : i, thiophosgene, DMAP, CH_2Cl_2 , 0°C , 1 h ; ii, triethyl phosphite, reflux, 5 h ; iii, PPTS, DMA, 150°C , 3 h ; iv, *m*CPBA, CH_2Cl_2 , 0°C , 1 h ; v, 1,1-thiocarbonyldiimidazole, toluene, reflux, 3 h.

sponding olefinic compounds. Using the reaction as a key step, we have developed a more efficient route to the brassinosteroid-related diepoxylactones 2 and 3.

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[ノート] ステロイド系ビシナルジオールの オレフィン化合物への変換

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Corey および Winter によって開発されたビシナルジオール基の炭素-炭素二重結合への2工程による変換反応の適応性について、いくつかのタイプ別にビシナルジオールを有するステロイドについて検討した。ビシナルジオールを有するステロイドから誘導された環状チオノカーボネートをトリエチルフォスファイトと加熱環流することにより、対応するオレフィン系ステロイドへ高収率で変換された。この2工程変換反応を鍵反応に用いて、ブラシノステロイド関連化合物である (22R,23R,24S) - and (22S,23S,24S) -2 α ,3 α ,22,23-diepoxy-B-homo-7-oxa-5 α -stigmastan-6-ones を既に報告されている方法よりもより効率的に合成した。

(連絡者:高津戸 秀) Vol.49, No.2, 163 (2000)

[ノート] ガンピョウの種子中に含まれるカスタステロン およびステロールの同定

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カンピョウ (*Lagenaria siceraria*, ウリ科) の種子よりイネ葉身屈曲試験において活性な物質を抽出・分画し、誘導体化後 GC-MS 分析を行ったところ、ブラシノステロイドの一種であるカスタステロンを同定した。また、種子中のステロールについても GC-MS 分析を行った。標品との直接比較により、3種の 24-アルキル- Δ^5 -ステロールと5種の 24-アルキル- Δ^7 -ステロールを同定した。

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[ノート] Stigmasta-5,25-dien-3 β -ol および stigmasta-5,24(25)-dien-3 β -ol の sitosterol からの簡便合成

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Stigmasta-5,25-dien-3 β -ol の sitosterol からの合成について検討した。Sitosterol 側鎖の methyl (trifluoromethyl) dioxirane による直接水酸化および 25 位水酸化化合物の phosphorus oxychloride による脱水反応を鍵反応に用いた。Stigmasta-5,25-dien-3 β -ol および stigmasta-5,24(25)-dien-3 β -ol を sitosterol から簡便に合成した。それらは逆相カラムを用いる HPLC により単離することができた。

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