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Determination of the absolute configuration of the cytotoxic natural product pericosine D

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This paper is dedicated to Professor Takushi Kurihara on the occasion of his retirement from Osaka University of Pharmaceutical Sciences

ABSTRACT

The synthesis of two diastereomers of pericosine A from (−)-quinic acid was achieved, thus enabling the confirmation of the relative configuration and elucidation of the absolute stereochemistry of cytotoxic natural product pericosine D assigned as methyl (3*R*,4*R*,5*S*,6*R*)-6-chloro-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate.

1. Introduction

In recent research of marine natural products, a new area has emerged, which involves studies of the metabolites of microorganisms from marine sources.[1,2] Over the course of such studies, Numata et al. isolated a series of unique and highly functionalized C-7 cyclohexenoid-type natural products designated pericosines A-D **1**–**4**, which are cytotoxic metabolites of the fungus *Periconia byssoides* OUPS-N133 originally separated from the sea hare *Aplysia kurodai*.[3–7] These compounds are expected to exhibit various biological activities, including antiviral, antifungal, and antitumor activities, because of the multi-functionalized carbasugar cyclohexenoid structure.

Synthetic studies of carbasugars have been actively pursued worldwide because of their importance in synthetic organic chemistry and natural products chemistry.[8,9] Over the course of our synthetic studies on bioactive natural products and their analogues, focusing on small molecules, we have been interested in the pericosines because of the reason described above.[10–15] The absolute stereostructures of pericosines A and B were determined by total syntheses.[14–16] However, the relative stereochemistry of **3** and **4** remained ambiguous when we had started this project.[4,5] The synthesis of pericosine D, a diastereoisomer of pericosine A **1**, was attempted in order to elucidate its relative and absolute stereostructures. The only certain information about the stereochemistry of pericosine D we were able to determine was the *cis*-configuration between H-3 and H-4.[5] There are four possible diastereoisomers with such relative chemistries, including **1** and **6**, both of which were synthesized in our previous studies and were different from pericosine D[12–15] (Fig. 1). Therefore, the relative configuration of pericosine D must be either **4** or **5**. Herein, we report the short total synthesis of **4** and **5**, which enabled confirmation of the relative stereochemistry and determination of the absolute configuration of pericosine D **4** as methyl (3*R*,4*R*,5*S*,6*R*)-6-chloro-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate.

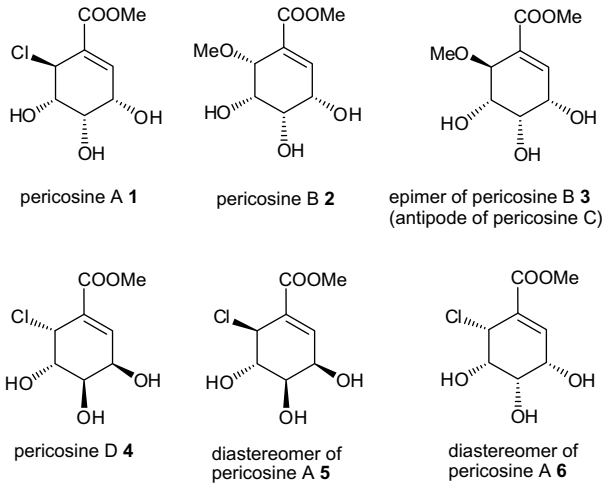

Figure 1. Structures of pericosines and related compounds.

2. Results and discussion

The synthesis of **4** and **5** was carried out as shown in Scheme 1. Diene **7**,[17] prepared from (−)-quinic acid, was oxidized with

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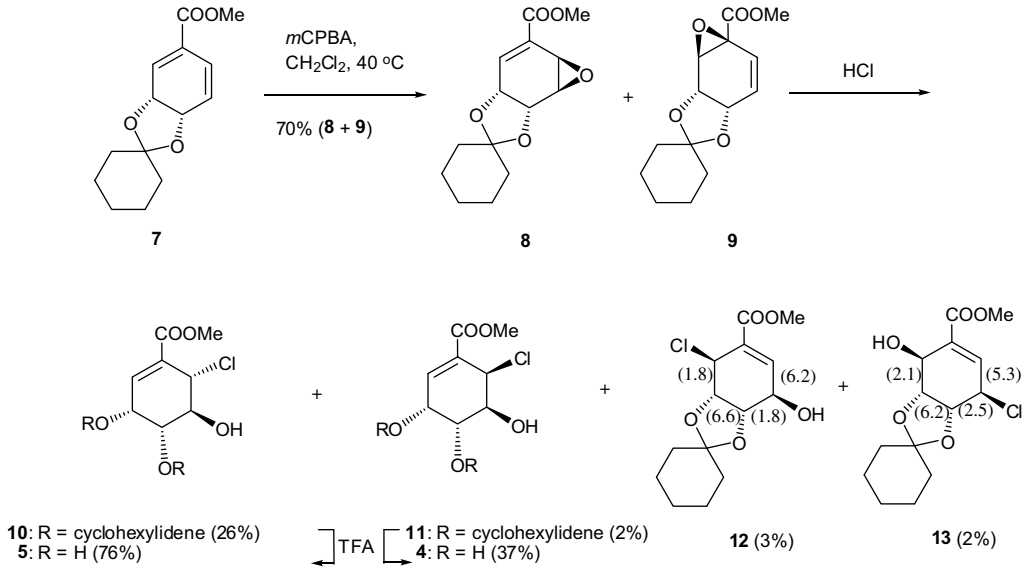

Scheme 1. Synthesis of **4** and **5**.

*m*CPBA at 40 °C to give an inseparable mixture of epoxides **8** and **9** in 70% combined yield in a ratio of ca. 3:2.[18,19] However, their stereochemical assignment was still ambiguous at this stage, even when detailed NMR analysis of the mixture of **8** and **9** was conducted. Our stereochemical deduction of **9** did not agree with acetonide **14** illustrated in Figure 2, which was reported to be formed via a similar synthesis.[18,19] The stereochemistry at C-6 in **9** will be determined later.

Treatment of a mixture of **8** and **9** with HCl in Et_2O afforded four chlorohydrins **10**–**13** in 26%, 2%, 3%, and 2% yields, respectively,[20] with the recovery of unreacted **9** (20%). The structures of these chlorohydrins were confirmed by 2D NMR analysis. The relative chemistry of major chlorohydrin **10** was assigned on the basis of NOESY cross peaks 5-OH/H-4, H-6. From this, the stereochemistry of the starting epoxide **8** was suggested, as shown in Scheme 1. COSY, HSQC, and HMBC analyses proved that the minor chlorohydrin **11** has the same planar structure as **10**, and thus **11** must have the desired relative configuration leading to **4** because it was thought to be derived from the same precursor **8**. The formation of chlorohydrin **12**, together with the migration of the double bond in **8**, was confirmed from HMBC cross peaks, C-2/H-3, H-4, H-6 and C-1/H-3, H-5, H-6, and quaternary carbon (δ 109.5 ppm)/H-4.

The stereochemistry at C-6 in **12** was determined by comparing with the closely related compound **15** synthesized previously by us (Fig. 2).[12,13] The planar structure of chlorohydrin **13** was determined on the basis of COSY, HSQC, and HMBC spectra. This was confirmed by an independent experiment in which a reaction of the recovered pure epoxide **9** with HCl afforded **13** in 3% yield with

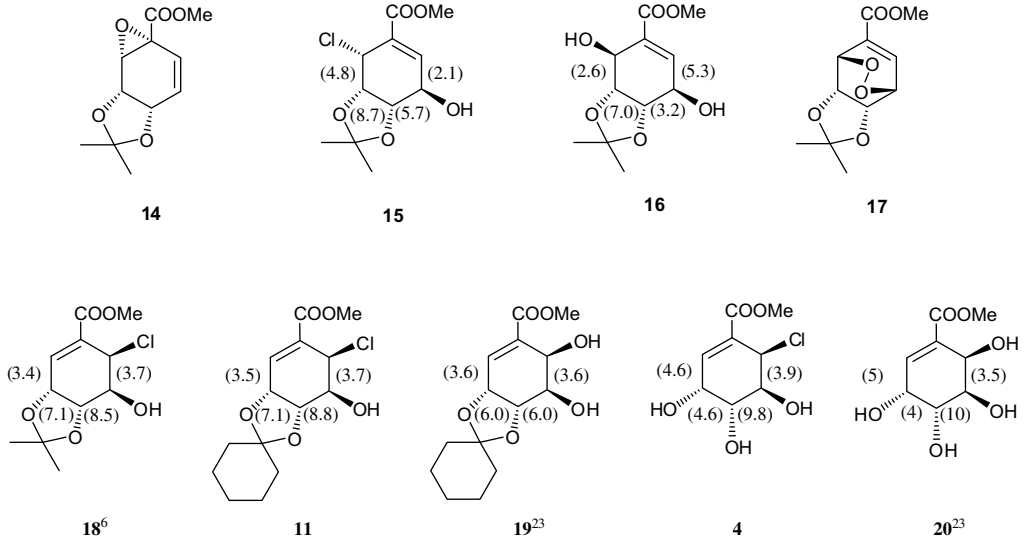

Figure 2. Structure and coupling constants of **4**, **11** and related compounds.

recovery of **9** in 78%. In the stereochemical inspection of **12** and **13**, the similarity of ^{1}H NMR coupling constants to those of known diol **16**, which was derived from peroxide **17**,[21] supported the relative chemistry of **12** and **13** shown in Scheme 1, as well as the stereochemistry of **8** and **9**.

Deprotection of **10** with TFA gave target compound **5**,[22] which was different from pericosine D, in 76% yield. From this result, the relative chemistry of pericosine D was confirmed as **4**.[6] Finally, **11**was deprotected in the same way to afford **4** in 37% yield with recovery of **11** in 23%. Since the spectral data of synthesized **4** agreed with those of natural **4**, including the specific rotation,[7] the absolute configuration of natural pericosine D was assigned as methyl (3*R*,4*R*,5*S*,6*R*)-6-chloro-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate. Similarity of coupling constants in ^{1}H NMR spectra of **4** and **11** to those of closely related compounds **18**–**20**[6,23]shown in Figure 2 also supported our conclusion for correction of the data of natural **4**.

3. Conclusion

We have synthesized two diastereomers of pericosine A thus confirming the relative chemistry of pericosine D. Our conclusion is in agreement with a recent report on natural pericosines.[6] Furthermore the undefined absolute stereochemistry of natural pericosine D **4** was elucidated to be methyl (3*R*,4*R*,5*S*,6*R*)-6-chloro-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate.

4. Experimental

4.1. General information

IR spectra were obtained with a JEOL FT/IR-680 Plus spectrometer. EIMS was determined with a JEOL JMS-700 (2) mass spectrometer. NMR spectra were recorded at 27 °C on Varian UNITY INOVA-500 and Mercury-300 spectrometers in $CDCl_3$ with tetramethylsilane (TMS) as internal reference. Specific rotations were measured using a JASCO model DIP181 spectrometer. Liquid column chromatography was conducted over silica gel (SILICYCLE, Silia Flash F60, mesh 230–400). Analytical TLC was performed on precoated Merck aluminum sheets (DC-Alufolien Kieselgel 60 F254), and compounds were detected by spraying an ethanol solution of phosphomolybdic acid followed by heating. Dry THF was distilled over sodium benzophenone ketyl under an argon atmosphere.

4.2. Methyl (3*R*,4*R*,5*S*,6*R*)-3,4-*O*-cyclohexylidene-5,6-epoxy-3,4-dihydroxy-1-cyclohexene-1-carboxylate 8 and methyl (1*S*,4*R*,5*S*,5*S*)-3,4-*O*-cyclohexylidene-1,6-epoxy-4,5-dihydroxy-2-cyclohexene-1-carboxylate 9

To a solution of diene **7** (113.1 mg, 0.45 mmol) in CH_2Cl_2 (10 mL) was added mCPBA (93.7 mg, 1.2 equiv). After stirring at 40 °C for 15 h, the reaction mixture was treated with aq $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and filtered, after which the solvent was removed under reduced pressure to give a crude residue that was purified by column chromatography (eluent: hexane–EtOAc = 10:1) to afford a mixture of **8** and **9** (85.1 mg, 70% in combined yield). Data for the mixture of **8** and **9**: IR (liquid film) ν_{max} 1723 (C=O), 1654 (C=C) cm^{-1}; HRMS *m*/*z* calcd for $C_{14}H_{18}O_5$ (M)$^+$ 266.1154, found 266.1158. Compound **8**: ^{1}H NMR ($CDCl_3$) δ 1.35–1.70 (10H, m), 3.69 (1H, ddd, *J* = 3.7, 2.1, 0.5 Hz, H-5), 3.84 (3H, s, COOMe), 3.99 (1H, ddd, *J* = 3.7, 1.6, 0.7 Hz, H-6), 4.58 (1H, dd, *J* = 6.9, 2.3 Hz, H-3), 4.81 (1H, ddt, *J* = 6.9,2.1,0.7 Hz, H-4), 6.83 (1H, ddd, *J* = 2.3, 1.6, 0.7 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ 23.7, 23.9, 24.8, 35.2, 37.4, 46.1, 49.3, 52.3, 70.0, 70.8, 111.6, 127.1, 140.2, 165.5. Compound **9**: ^{1}H NMR ($CDCl_3$) δ 1.35–1.70 (10H, m), 3.81 (3H, s, COOMe), 3.92 (1H, d, *J* = 1.8 Hz, H-6), 4.49 (1H, ddd, *J* = 7.1, 2.5, 1.8 Hz, H-4), 4.78 (1H, dd, *J* = 7.1, 1.8 Hz, H-5), 5.88 (1H, ddd, *J* = 10.2, 2.5, 0.7 Hz, H-3), 6.39 (1H, dd, *J* = 10.2, 1.8 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ 23.7, 23.9, 24.9, 35.3, 37.3, 51.8, 52.9, 55.0, 69.8, 70.3, 111.5, 121.0, 132.1, 168.9.

4.3. Methyl (3*R*,4*R*,5*S*,6*S*)-6-chloro-3,4-*O*-cyclohexylidene-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate 10, methyl (3*R*,4*R*,5*S*,6*R*)-6-chloro-3,4-*O*-cyclohexylidene-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate 11, methyl (3*R*,4*S*,5*R*,6*S*)-6-chloro-3,4-*O*-cyclohexylidene-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate 12 and methyl (3*R*,4*S*,5*R*,6*S*)-3-chloro-3,4-*O*-cyclohexylidene-4,5,6-trihydroxy-1-cyclo hexene-1-carboxylate 13

To a mixture of **8** and **9** (125.7 mg, combined amount) in Et_2O (40 mL) was added 1.0 M HCl in Et_2O (600 μL). After stirring overnight at rt, the reaction mixture was condensed under a reduced pressure to afford a crude residue which was purified by preparative TLC (eluent: 2% MeOH in CH_2Cl_2) to give **10** (37.0 mg, 26%), **11** (3.2 mg, 2%), **12** (3.7 mg, 3%), and **13** (2.6 mg, 2%) with recovery of **9** (24.6 mg, 20%).

Compound **10**: colorless oil; $[\alpha]_D^{25} = +4.1$ (*c* 1.65, $CHCl_3$); IR (liquid film) ν_{max} 3447 (OH), 1726 (C=O), 1653 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.37–1.76 (10H, m), 2.48 (1H, d, *J* = 4.1 Hz, 5-OH), 3.83 (3H, s, COOMe), 4.31 (1H, br dd, *J* = 5.7, 5.0 Hz, H-4), 4.43 (1H, br ddd, *J* = 5.0, 4.8, 4.1 Hz, H-5), 4.74 (1H, ddd, *J* = 4.8, 1.8, 0.9 Hz, H-6), 4.76 (1H, ddd, *J* = 5.7, 3.9, 1.1 Hz, H-3), 6.89 (1H, ddd, *J* = 3.9, 0.9, 0.7 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ 23.7, 23.8, 24.9, 35.4, 37.5, 52.4, 52.7, 70.3, 72.1, 74.4, 111.7, 130.1, 135.8, 165.4; HRMS *m*/*z* calcd for $C_{14}H_{19}O_5^{35}Cl$ (M)$^+$ 302.0921, found 302.0920, *m*/*z* calcd for $C_{14}H_{19}O_5^{37}Cl$ (M)$^+$ 304.0892, found 304.0891.

Compound **11**: oil; $[\alpha]_D^{25} = -121.3$ (*c* 0.2, $CHCl_3$); IR (liquid film) ν_{max} 3445 (OH), 1735 (C=O), 1644 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25–1.80 (10H, m), 2.39 (1H, d, *J* = 7.1 Hz, 5-OH), 3.83 (3H, s, COOMe), 3.83 (1H, m, H-5), 4.39 (1H, dd, *J* = 8.8, 7.1 Hz, H-4), 4.88 (1H, dd, *J* = 7.1, 3.5 Hz, H-3), 5.03 (1H, d, *J* = 3.7 Hz, H-6), 7.11 (1H, d, *J* = 3.5 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ 23.6, 24.4, 25.0, 34.4, 37.3, 52.6, 55.0, 71.4, 72.0, 75.3, 111.0, 132.4, 137.2, 164.2; HRMS *m*/*z* calcd for $C_{14}H_{19}O_5^{35}Cl$ (M)$^+$ 302.0921, found 302.0920, *m*/*z* calcd for $C_{14}H_{19}O_5^{37}Cl$ (M)$^+$ 304.0892, found 304.0897.

Compound **12**: oil; $[\alpha]_D^{25} = +18.1$ (*c* 0.14, $CHCl_3$); IR (liquid film) ν_{max} 3447 (OH), 1725 (C=O), 1653 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25–1.61 (10H, m), 2.19 (1H, d, *J* = 10.5 Hz, 3-OH), 3.85 (3H, s, COOMe), 4.41 (1H, ddd, *J* = 10.5, 6.2, 1.8 Hz, H-3), 4.65 (1H, ddd, *J* = 6.6, 1.8, 1.1 Hz, H-4), 4.84 (1H, dd, *J* = 6.6, 1.8 Hz, H-5), 5.07 (1H, dd, *J* = 1.8, 0.4 Hz, H-6), 7.33 (1H, br d, *J* = 6.2 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ 23.5, 23.8, 25.0, 33.8, 36.1, 49.1, 52.5, 66.1, 76.5, 77.7, 109.5, 132.7, 141.1, 164.8; HRMS *m*/*z* calcd for $C_{14}H_{19}O_5^{35}Cl$ (M)$^+$ 302.0921, found 302.0918, *m*/*z* calcd for $C_{14}H_{19}O_5^{37}Cl$ (M)$^+$ 304.0891, found 304.0892.

Compound **13**: oil; $[\alpha]_D^{25} = +302.8$ (*c* 0.009, $CHCl_3$); IR (liquid film) ν_{max} 3458 (OH), 1723 (C=O), 1652 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32–1.63 (10H, m), 3.00 (1H, d, *J* = 6.0 Hz, OH), 3.84 (3H, s, COOMe), 4.54-4.60 (3H, overlapped), 4.71 (1H, ddd, *J* = 5.8, 2.2, 0.9 Hz), 7.06 (1H, dd, *J* = 4.8, 1.1 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ 23.6 (t), 23.9 (t), 25.0 (t), 34.2 (t), 36.8 (t), 52.5 (q), 53.4 (d), 65.7 (d), 77.6 (d), 109.7 (s), 133.2 (s), 137.5 (d), 166.1 (s); ^{1}H NMR (acetone-d_6) δ 1.35–1.65 (10H, m), 3.79 (3H, s, COOMe), 4.55 (1H, dd, *J* = 6.2, 2.1, H-5), 4.62 (1H, ddd, *J* = 6.2, 2.5, 0.9 Hz, H-4) 4.70 (1H, dd, *J* = 5.3, 2.5 Hz, H-3), 4.76 (1H, d, *J* = 2.1 Hz, H-6), 6.99 (1H, dd, *J* = 5.3, 0.9 Hz, H-2); ^{13}C NMR (acetone-d_6) δ 24.4 (t), 24.7 (t), 25.7 (t), 35.0 (t), 37.6 (t), 52.4 (q), 55.1 (d), 64.4 (d), 78.1 (d), 78.9 (d), 109.8 (s), 134.4 (s), 137.0 (d), 166.6 (s); HRMS *m*/*z* calcd for

$C_{14}H_{19}O_5^{35}Cl$ $(M)^+$ 302.0921, found 302.0916, *m*/*z* calcd for $C_{14}H_{19}O_5^{37}Cl$ $(M)^+$ 304.0892, found 304.0898.

Data of pure **9**; $[\alpha]_D^{25} = +108.6$ (*c* 0.73, $CHCl_3$); oil; IR (liquid film) ν_{max} 1729 (C=O), 1652 (C=C) cm^{-1}; ^1H and ^{13}C NMR same as above; HRMS *m*/*z* calcd for $C_{14}H_{18}O_5$ $(M)^+$ 266.1154, found 266.1150.

4.4. Methyl (3*R*,4*R*,5*S*,6*S*)-6-chloro-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate 5

Chlorohydrin **10** (7.1 mg) was dissolved in MeOH (0.5 mL) and TFA (0.5 mL, excess). After stirring for 2 days at rt, the reaction mixture was condensed under reduced pressure to afford a crude residue which was purified by silica gel chromatography (eluent: 5% MeOH in CH_2Cl_2) to give **5** (3.9 mg, 76%). Compound **5**: oil; $[\alpha]_D^{25} = -101.0$ (*c* 0.20, EtOH); IR (liquid film) ν_{max} 3410 (OH), 1724 (C=O), 1668 (C=C) cm^{-1}; ^1H NMR (acetone-d_6) δ 3.74 (1H, br dd, *J* = 7.8, 4.1 Hz, H-4), 3.78 (3H, s, COOMe), 4.25 (1H, dd, *J* = 7.8, 5.0 Hz, H-5), 4.42 (1H, br dd, *J* = 4.3, 4.1 Hz, H-3), 4.66 (1H, ddd, *J* = 5.0, 1.1, 0.9 Hz, H-6), 6.81 (1H, dd, *J* = 4.3, 0.9 Hz, H-2); ^{13}C NMR (acetone-d_6) δ 52.2 (q), 57.9 (d), 66.1 (d), 71.2 (d), 74.1 (d), 132.2 (s), 139.8 (d), 166.2 (s); HRMS *m*/*z* calcd for $C_8H_{12}O_5^{35}Cl$ $(M+H)^+$ 223.0373, found 223.0377.

4.5. (−)-Pericosine D: methyl (3*R*,4*R*,5*S*,6*R*)-6-chloro-3,4,5-trihydroxy-1-cyclohexene-1-carboxylate 4

Chlorohydrin **11** (2.6 mg) was dissolved in MeOH (0.5 mL) and TFA (0.5 mL, excess). After stirring for 3 h at 0 °C, the reaction mixture was allowed to return to room temperature and condensed under reduced pressure to afford a crude residue that was purified by silica gel chromatography (eluent: 5% MeOH in CH_2Cl_2, then acetone) to give **4** (0.7 mg, 37%) with recovery of **11** (0.6 mg, 23%). Compound **4**: Oil; $[\alpha]_D^{25} = -275.4$ (*c* 0.04, EtOH); IR (liquid film) ν_{max} 3381 (OH), 1713 (C=O), 1654 (C=C) cm^{-1}; ^1H NMR (acetone-d_6) δ 3.78 (3H, s, COOMe), 3.95 (1H, dd, *J* = 9.8, 4.6, H-4), 4.06 (1H, dd, *J* = 9.8, 3.9 Hz, H-5), 4.48 (1H, t, *J* = 4.6 Hz, H-3), 5.07 (1H, d, *J* = 3.9 Hz, H-6), 6.90 (1H, d, *J* = 4.6 Hz, H-2); ^{13}C NMR (acetone-d_6) δ 52.5 (q), 58.9 (d), 66.4 (d), 68.4 (d), 69.2 (d), 132.3 (s), 140.7 (d), 165.7 (s); HRMS *m*/*z* calcd for $C_7H_{12}O_4^{35}Cl$ $(M-OMe)^+$ 191.0111, found 191.0102.[7]

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7. The spectral data of which appeared in the literature[6] are incorrect as well as those of another diastereomer of pericosine. The correct data of natural **4** were presented as follows from our independent deprotection experiment against **18**. Natural **4**: oil; $[\alpha]_D^{25} = -273.6$ (*c* 0.01, EtOH); IR (liquid film) ν_{max} 3382 (OH), 1712 (C=O), 1654 (C=C) cm^{-1}; ^1H NMR (acetone-d_6) δ 3.78 (3H, s, COOMe), 3.94 (1H, dd, *J* = 9.8, 4.6, H-4), 4.05 (1H, dd, *J* = 9.8, 3.9 Hz, H-5), 4.47 (1H, t, *J* = 4.6 Hz, H-3), 5.07 (1H, d, *J* = 3.9 Hz, H-6), 6.90 (1H, d, *J* = 4.6 Hz, H-2); ^{13}C NMR data could not be obtained due to a shortage of the material; HR-EIMS *m*/*z* calcd for $C_7H_8O_4^{35}Cl$ $(M-OMe)^+$ 191.0111, found 191.0100.
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