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Total syntheses and absolute stereochemistry of decarestrictines C_1 and C_2

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ABSTRACT

The total syntheses of decarestrictines C_1 and C_2 have been described. The synthetic strategy involves a practical and flexible approach using esterification and ring-closing metathesis to unite the acid and alcohol fragments. The acid fragments are enantiomers of each other and have been prepared from L-(−)-malic acid via similar transformations; in Sharpless asymmetric epoxidation, (+)-DET has been used for decarestrictine C_1 and (−)-DET for decarestrictine C_2. The alcohol fragment is identical for both decarestrictines C_1 and C_2 and has been accessed from D-(+)-mannitol. Comparison of the ^1H and ^{13}C NMR data combined with the computational studies predicts the presence of two conformations without and with hydrogen bonding (conformational isomers I and II for decarestrictine C_1), respectively. The ^1H and ^{13}C NMR data for decarestrictine C_2 completely agreed with the analytical data reported by Kibayashi et al.

Decarestrictines A–D, the first representatives of a new class of fungal metabolites,[1] isolated from *Penicillium simplicissium* and *Penicillium corylophilum*, are structurally related 10-membered lactones, with similar physio-chemical properties.[2] The structures of these secondary metabolites were established by spectroscopic analysis and confirmed by X-ray analysis. The carbon skeleton, forming the 10-membered lactone ring, varies in the oxygenation patterns ranging from C3–C7 and carries one *E*-configured double bond either at C4 or at C5. Tested via sodium acetate incorporation into cholesterol, the decarestrictines have revealed potent inhibitory effects on cholesterol biosynthesis in cell line tests with HEP-G2 liver cells and hence hold the promise of favorable effects on in vivo lipid metabolism. These appear to be more selective in that they exhibit no significant *anti*-bacterial, *anti*-fungal, *anti*-protozoal, or *anti*-viral activity. The interesting biological activity of decarestrictines has elicited recent synthetic endeavors, including the total syntheses of decarestrictines C_2 (**4**), D (**5**), J, and L (Fig. 1).[3]

In continuation of our interest[4] in exploring ring-closing metathesis for macrolides[5] synthesis and generalizing its substrate and protecting group-based selectivity, we planned to synthesize decarestrictines C_1 (**3**) and C_2 (**4**). Since both molecules contain a double bond and a lactone functionality, cross-metathesis followed by lactonization or esterification followed by ring-closing metathesis seemed to be the method of choice for an efficient convergent synthesis. As shown in Scheme 1, the retrosynthetic analysis suggested synthesis of an alcohol fragment **7** for both molecules and acid fragments **8** and *ent*-**8**. These fragments could be prepared from D-(+)-mannitol and L-(−)-malic acid, respectively.

Epoxy alcohol **13** was prepared following a known protocol taking commercially available L-(−)-malic acid as the starting material.[6] One-pot conversion of the alcohol to the *trans*-α,β-unsaturated ester was achieved by IBX oxidation in DMSO followed by treatment of the reaction mixture with (carboethoxymethylene)triphenylphosphorane.[7] The ester was selectively reduced to the allylic alcohol by DIBAL-H in CH_2Cl_2 at −78 °C. Incorporation of the required chirality was achieved by Sharpless asymmetric epoxidation.[8] Accordingly, the allylic alcohol was treated with $Ti(OiPr)_4$, (+)-DET, and *t*BuOOH to obtain the (*S*,*S*)-epoxide. The primary hydroxyl group of the epoxide was transformed to its corresponding iodo derivative. The opening of the epoxide ring of the iodo compound with Zn in refluxing ethanol[9] afforded secondary allylic alcohol **14** (Scheme 2), which was protected as its *p*-methoxybenzyl ether. The isopropylidine group was deprotected by treatment with catalytic amount of *p*-TSA in MeOH. The result-

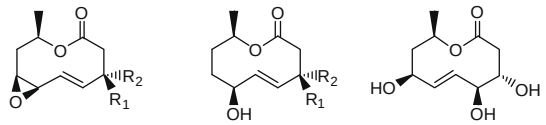

Figure 1. Representative members of decarestrictine family.

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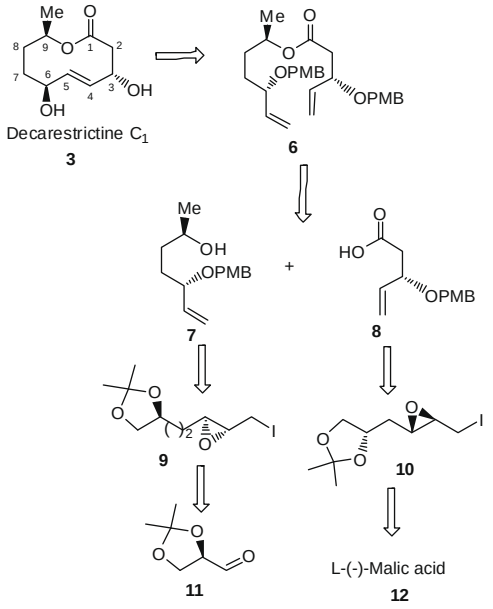
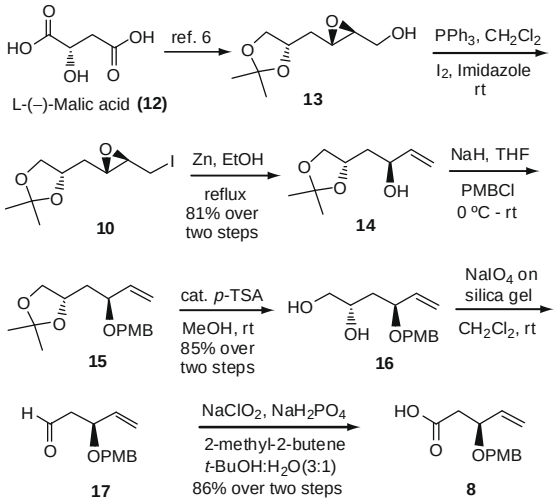


Scheme 1. Retrosynthetic analysis of decarestrictine C_1.

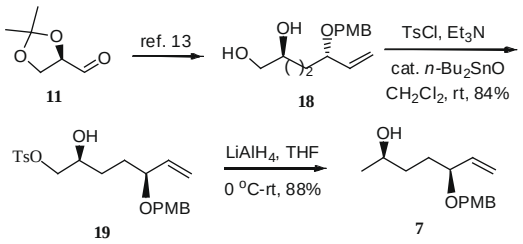


Scheme 2. Synthesis of fragment **8**.

ing diol was oxidatively cleaved with $NaIO_4$ impregnated over silica gel[10] followed by oxidation[11] with $NaClO_2$ to obtain the acid **8.**[12] Similarly, starting from **12** and following the same sequence of reactions using (−)-DET in place of (+)-DET led to the acid fragment *ent*-**8** for decarestrictine C_2.

The known aldehyde **11** synthesized from D-(+)-mannitol was converted to an intermediate **18**[13] followed by selective protection of the primary hydroxyl group with TsCl, Et_3N, and catalytic amount of nBu_2SnO[14] afforded compound **19** (Scheme 3). The resulting tosyl compound **19** was treated with $LiAlH_4$ to give the required alcohol fragment **7**[15] for both the decarestrictines C_1 and C_2.

The alcohol **7** and the (*S*)-acid fragment **8** were united under Yamaguchi conditions,[16] using 2,4,6-trichlorobenzoyl chloride to furnish the ester **6.**[17] The ester **6** underwent ring-closing metathesis with Grubb's 2nd generation catalyst[18] in CH_2Cl_2 at reflux to yield the single trans diastereomer **20**[19], which was characterized by the usual spectroscopic techniques. The coupling constant of 16.1 Hz between H4 and H5 clearly demonstrated the trans nature



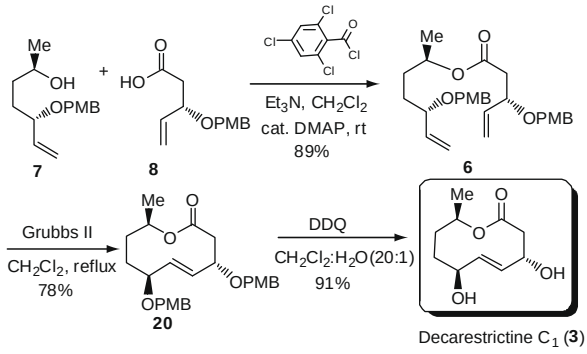
Scheme 3. Synthesis of alcohol fragment **7** for both decarestrictines C_1 and C_2.

of the double bond. Deprotection of the *p*-methoxybenzyl ethers was carried out with DDQ in aqueous methylene chloride to afford the natural product decarestrictine C_1 (**3**) (Scheme 4).[20] The spectral (^1H and ^{13}C NMR) and analytical data were in good agreement with the natural product (decarestrictine C).[1]

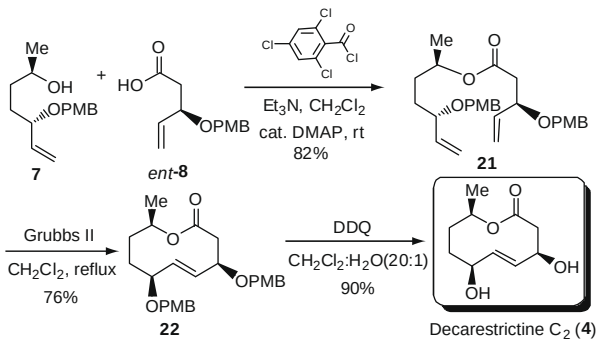
Similarly, the alcohol **7** was coupled with the (*R*)-acid fragment *ent*-**8** and the same sequence of reactions was performed to obtain the decarestrictine C_2 (**4**) (Scheme 5).[21] The ^1H, ^{13}C NMR, and analytical data were in good agreement with the reported values.[3b]

^1H NMR studies of decarestrictine C_1 revealed the presence of two distinct conformational isomers at room temperature and high temperature NMR spectroscopy at 110 °C, showed conversion of the isomeric mixture to a single compound (Fig. 2).

This prompted us to undertake a systematic computational conformational analysis of decarestrictine C_1. A careful analysis of the conformational geometries and their energetics reveals that the most stable conformation is the one which has intramolecular hydrogen bond between –OH and –C=O groups. Three other conformations are closer in energy (see Supplementary data for full details) but are so similar and difficult to be distinguished within NMR time scale.[22] Further, the observed features of two conforma-



Scheme 4. Synthesis of decarestrictine C_1.



Scheme 5. Synthesis of decarestrictine C_2.

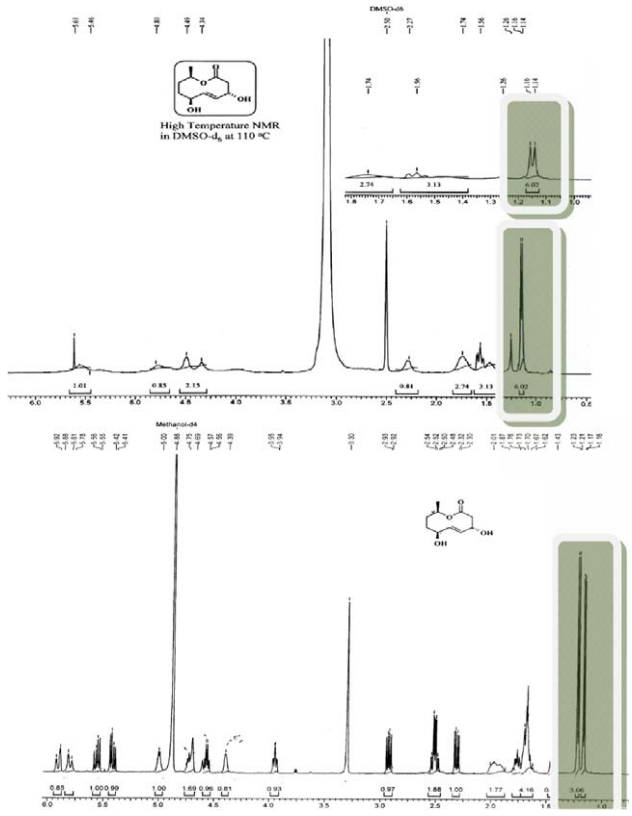


Figure 2. ^{1}H NMRs of decarestrictine C_1 in DMSO-d_6 at 110 °C and CD_3OD at ambient temperature.

tions collapsing to a single conformation may be traced to the existence of hydrogen bond in conformation II (Fig. 3) which upon heating collapses to conformation I.

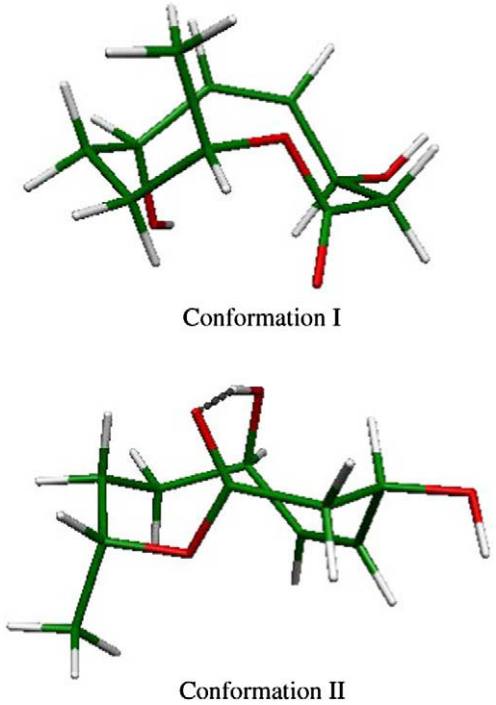


Figure 3. Two lowest energy conformations obtained at B3LYP/6-31G(d) level.

In conclusion, we have synthesized decarestrictines C_1 and C_2 in a convergent manner starting from easily available starting materials and demonstrated another application of our protecting group-directed ring-closing metathesis reaction. Earlier reports claimed the isolated decarestrictine C to be an inseparable diastereomeric mixture of decarestrictine C_1 and decarestrictine C_2. The ^{1}H and ^{13}C NMR data of the decarestrictine C_1 completely agree with those of the isolated decarestrictine C, showing a mixture of two conformers at room temperature. The spectral (^{1}H and ^{13}C NMR) and analytical data of decarestrictine C_2 were well matched with the data reported by Kibayashi et al. and were not well matched with the natural product data. Computational studies in conjunction with spectral data (high temperature NMR spectroscopy at 110 °C, showed conversion of the isomeric mixture to a single compound and cooling to room temperature again resulted in an isomeric mixture) predict the presence of an intramolecular hydrogen bonded conformation which is competitive with another conformation devoid of hydrogen bonding, thereby proving that decarestrictine C has two different conformations at room temperature in CD_3OD and not a mixture of C_1 and C_2.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.099.

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12. *Analytical and spectral data of* **8**: $[\alpha]_D^{25}$ −32.6 (*c* 1, $CHCl_3$); IR ($CHCl_3$, cm^{-1}) 3004, 2935, 2838, 2683, 1713, 1612, 1514, 1422, 1302, 1248, 1112, 1064, 1035, 993, 934, 822, 758, 693, 516; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.45–2.80 (ddd, 2H, *J* = 5.3, 8.1, 15.6 Hz), 3.80 (s, 3H), 4.25 (m, 1H), 4.34 (d, 1H, *J* = 11.2 Hz), 4.55 (d, 1H, *J* = 11.2 Hz), 5.28 (ddd, 1H, *J* = 0.9, 1.5, 10.5 Hz), 5.79 (ddd, 1H, *J* = 7.6, 10.1, 17.2 Hz), 6.85 (d, 2H, *J* = 8.8 Hz), 7.24 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 40.8 (t), 55.2 (q), 70.2 (t), 76.2 (d), 113.8 (d), 118.5 (t), 129.5 (d), 136.7 (d), 159.2 (s), 175.9 (s); Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.27; H, 6.69.
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15. *Analytical and spectral data of* **7**: $[\alpha]_D^{25}$ −61.4 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 3409, 3076, 3006, 2966, 2934, 1613, 1513, 1248, 1173, 1036, 994, 756. ^{1}H NMR

($CDCl_3$, 200 MHz): δ 1.15–1.18 (d, 3H, J = 6.2 Hz), 1.47–1.74 (m, 4H), 2.17 (br s, 1H) 3.69–3.77 (m, 2H), 3.80 (s, 3H), 4.28 (d, 1H, J = 11.4 Hz), 4.54 (d, 1H, J = 11.4 Hz), 5.17–5.26 (m, 2H), 5.75 (m, 1H), 6.85–6.89 (m, 2H), 7.23–7.27 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 23.3, 31.8, 35.0, 55.0, 67.4, 69.6, 80.1, 113.6, 117.1, 129.3, 130.3, 138.7, 158.9; Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.94; H, 8.72.

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17. *Analytical and spectral data of* **6**: $[\alpha]_D^{25}$ −36.5 (c 1.0, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 3076, 3005, 2978, 2935, 2864, 1729, 1642, 1613, 1513, 1464, 1248, 1036, 994, 822, 756. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.16–1.19 (d, 3H, J = 6.3 Hz), 1.49–1.75 (m, 4H), 2.44 (dd, 1H, J = 5.7, 14.9 Hz), 2.63 (dd, 1H, J = 8.0, 14.9 Hz), 3.69 (m, 1H), 3.79 (s, 3H), 3.81 (s, 3H), 4.21 (m, 1H), 4.32 (d, 2H, J = 11.4 Hz), 4.52 (d, 2H, J = 11.4 Hz), 4.90 (m, 1H), 5.14–5.35 (m, 4H), 5.60–5.86 (m, 2H), 6.82–6.88 (m, 4H), 7.20–7.26 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 19.9, 31.0, 31.4, 41.3, 55.0, 69.6, 70.0, 70.7, 76.7, 79.4, 113.6, 117.1, 117.8, 129.1, 130.2, 130.5, 137.3, 138.7, 159.0, 170.2; Anal. Calcd for $C_{28}H_{36}O_6$: C, 71.77; H, 7.74. Found: C, 71.68; H, 7.64.
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19. *Analytical and spectral data of* **20**: $[\alpha]_D^{25}$ −53.1 (c 1.0, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2978, 2932, 2864, 1612, 1513, 1459, 1247, 1172, 1086, 1035, 821, 756. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.14 (d, 3H, J = 6.6 Hz), 1.63–1.70 (m, 3H), 1.84 (m, 1H), 2.44 (dd, 1H, J = 7.3, 14.2 Hz), 2.91 (dd, 1H, J = 8.3, 14.2 Hz), 3.71 (m, 1H), 3.75 (2s, 6H), 4.24–4.29 (m, 2H), 4.35 (d, 1H, J = 11.5 Hz), 4.45 (d, 1H, J = 11.7 Hz), 4.50 (d, 1H, J = 11.5 Hz), 5.00 (m, 1H), 5.44 (dd, 1H, J = 8.5, 16.1 Hz), 5.61 (dd, 1H, J = 9.3, 16.1 Hz), 6.83–6.85 (m, 4H), 7.22–7.25 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.6, 27.9, 29.9, 42.3, 55.2, 70.2, 71.0, 76.2, 79.2, 113.7, 128.9, 129.2, 129.4, 130.0, 130.4, 138.9, 159.2, 170.3; Anal. Calcd for $C_{26}H_{32}O_6$: C, 70.89; H, 7.32. Found: C, 70.72; H, 7.28.
20. *Analytical and spectral data of* **3**: $[\alpha]_D^{25}$ −9.5 (c 1.0, MeOH). ^{1}H NMR (CD_3OD, 500 MHz) (conformational isomers) δ 1.16 (d, 1.5H, J = 6.6 Hz), 1.21 (d, 1.5H, J = 6.9 Hz), 1.43 (dd, 0.5H, J = 6.8, 15.7 Hz), 1.62–1.74 (m, 2H), 1.76 (m, 0.5H), 1.90–2.01 (m, 1H), 2.29 (dd, 0.5H, J = 5.6, 13.4 Hz), 2.47–2.54 (m, 1H), 2.90 (dd, 0.5H, J = 7.5, 13.4 Hz), 4.39 (m, 1H), 4.54 (m, 1H), 4.69–4.75 (m, 2H), 5.00 (m, 1H), 5.39 (dd, 0.5H, J = 7.5, 16.2 Hz), 5.53 (dd, 0.5H, J = 8.2, 16.2 Hz), 5.78 (dd, 0.5H, J = 15.9 Hz), 5.88 (dd, 0.5H, J = 15.9 Hz); ^{13}C NMR (CD_3OD, 125 MHz) (conformational isomers) δ 18.9, 22.1, 28.6. 29.2, 32.6, 45.4, 45.8, 68.7, 69.1, 70.4, 72.4, 74.2, 130.7, 131.9, 138.2, 172.0, 172.5. Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.15; H, 8.23.
21. *Analytical and spectral data of* **4**: $[\alpha]_D^{25}$ −38.0 (c 0.74, MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 1.16 (d, 3H, J = 6.5 Hz), 1.44 (dd, 1H, J = 7.0, 15.9 Hz), 1.67 (br t, 1H, J = 12.3 Hz), 1.83–1.95 (m, 2H), 2.32 (t, 1H, J = 10.4 Hz), 2.61 (dd, 1H, J = 5.2, 10.1 Hz), 4.32 (m, 1H), 4.35 (ddd, 1H, J = 5.2, 8.6, 10.6 Hz), 4.77 (m, 1H), 5.45 (br d, 1H, J = 15.9 Hz), 5.73 (ddd, 1H, J = 1.6, 8.6, 15.9 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 22.5, 29.5, 36.5, 47.6, 69.2, 74.3, 74.9, 131.9, 134.8, 173.0; MS (ESI) m/z: 223.22 (M^++Na).
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