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A chiron approach to the total synthesis of cytotoxic (+)-muricatacin and (+)-5-*epi*-muricatacin from D-ribose ☆

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ABSTRACT

A chiron approach strategy toward the total synthesis of (+)-muricatacin and (+)-5-*epi*-muricatacin starting from commercially available and inexpensive D-ribose through the key intermediate (*S*)-5-((*R*)-1-hydroxyallyl)furan-2(5*H*)-one has been disclosed.

1. Introduction

The naturally occurring γ-butenolides are an emerging class of compounds with potent antitumor, antiparasitic, and pesticidalactivities. Muricatacin (**1**, Fig. 1), which was isolated in 1991 from the seeds of *Annona muricata*, is the structural prototype.[1] It shows cytotoxic activity on tumor cell lines (A-549 (lung carcinoma) with ED_{50} = 23.3 μg/mL, MCF-7 (breast carcinoma) with ED_{50} => 9.8 μg/mL, and HT-29 (colon adenocarcinoma) with ED_{50} = 14.0 μg/mL). Because of its simple structure and potent biological activity, muricatacin (**1**) has garnered much attention from the synthetic community. Several groups have reported the total synthesis of (+) or (−)-muricatacin or both and also their epimers.[2–29] Cyclization of L-glutamic acid by nitrous acid deamination,[2] Sharpless asymmetric dihydroxylation,[3,26] epoxidation,[6] acetylene–vinylidene rearrangement,[8] photo-induced rearrangement of epoxy diazomethyl ketones,[10] enantioselective *cis*-dihydroxylation of double bond using chiral auxiliary,[14] enantioselective 1,2-addition of 2-[(trimethylsilyl)oxy]furan to aldehydes,[15] ruthenium-catalyzed cycloisomerization oxidation of homopropargyl alcohols,[18] Lewis acid-catalyzed ring-opening of vinyl epoxide,[19] stereoselective addition of a Grignard reagent to a suitably protected α-hydroxy aldehyde,[21] and α- and α′-C–H bond functionalization of tetrahydrofuran[24] were the major strategies used in the total synthesis of this class of natural products. Moreover, syntheses of 7-oxamuricatacin, β-substituted derivatives,[30] and aza-analogues[31–33] have also been reported. Recently Barros et al. reported total synthesis of (−)-muricatacin by desymmetrization of dienedioate.[34]

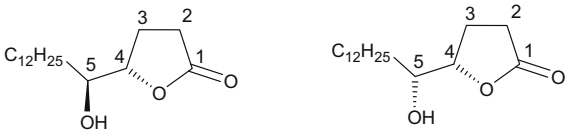

Figure 1.

In addition, muricatacin has also been used as the starting material for the total synthesis of various natural products.[35–42] Thus, simple structural features of muricatacin and its analogues, along with their biological activity, motivated us to develop an efficient total synthesis of this interesting natural product.

The chiron approach is one of the most widely used approaches toward the total synthesis of natural products in which chiral templates such as amino acids, carbohydrates, hydroxy acids, and terpenes are used as the starting materials.[43] Over the last few years we have been working on the synthetic development of enantiomerically pure scaffolds by the chiron approach from commercially available inexpensive sugars and their utilization toward the total synthesis of natural products or natural product-like molecules.[44–49] In this endeavor we herein wish to report a simple and efficient chiron approach synthesis of (+)-muricatacin (**1**) and (+)-5-*epi*-muricatacin (**2**) starting from commercially available and inexpensive D-ribose via 5-(1-hydroxyallyl)furan-2(5*H*)-one (**7**), a key intermediate.

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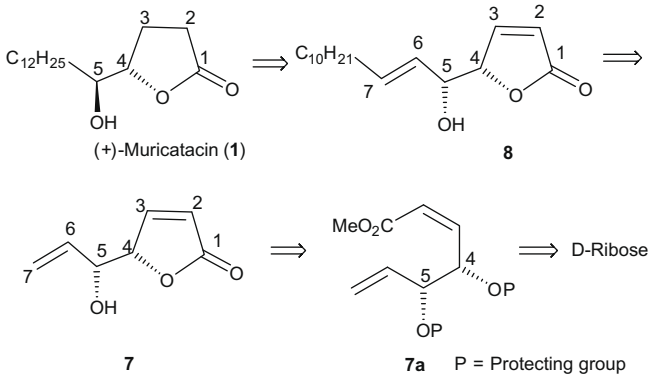


Scheme 1. Retrosynthesis of (+)-muricatacin.

2. Results and discussion

The retrosynthetic strategy for (+)-muricatacin (**1**) is depicted in Scheme 1. We envisaged that **1** could be elaborated from lactone **8** by hydrogenation of the double bonds, followed by epimerization at C-5. The lactone **8** was expected to be obtained from **7** by cross metathesis with the required olefin counterpart. The synthesis of compound **7** could be possible from diene **7a** by deprotection of protecting groups that leads to cyclization. The stereochemistry at C4 and C5 in all these intermediates and those at C2 and C3 in D-ribose are similar. Therefore, D-ribose is the starting material of choice for the chiron approach synthesis of both **1** and **2**.

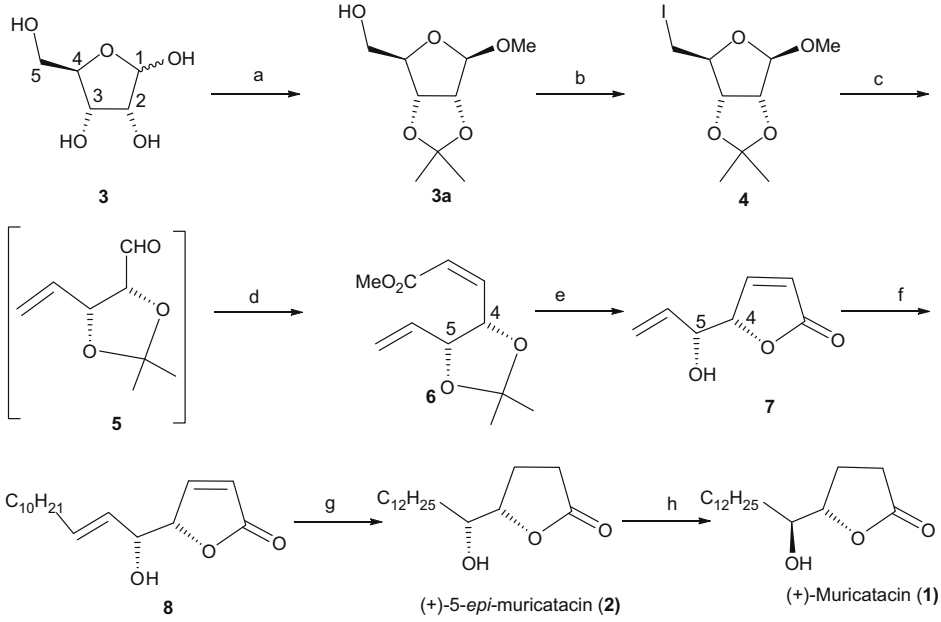
As per the retrosynthesis shown above, the synthesis of (+)-muricatacin began with acetonide-protected methyl furanoside **4** derived from D-ribose (**3**) in two steps.[50,51] The acetonide protection was essential here as it gives a good *Z*-selective Wittig product.[34,52] Zinc dust-mediated ring-opening of compound **4** under sonication[53] afforded aldehyde **5**, which was used as such without further purification. *Z*-Selective Wittig reaction[34,52] of this crude aldehyde with methyl (triphenylphosphoranylidene)acetate furnished α,β-unsaturated ester **6** with 8.2:1 *Z*/*E* selectivity. Isopropylidene deprotection of compound **6** with trifluoroacetic acid[34] gave rise to cyclized α,β-unsaturated γ-lactone **7** in 79% yield (Scheme 2). It is worth mentioning here that the enantiomerically pure lactone **7** is an integral structural component of an ever increasing number of biologically and chemically significant natural products, including many members of the annonaceous acetogenins (family Annonaceae).[35–42]

The cross-metathesis[25] of lactone **7** with 1-dodecene in the presence of Grubb's 2nd generation catalyst delivered compound **8** that was the precursor of (+)-5-*epi*-muricatacin (**2**). It was observed that by increasing equivalent of 1-dodecene the yield of cross-metathesis product was enhanced. Thus, by using 10 equiv of 1-dodecene, the cross product **8** was obtained in 95% yield (Table 1).

Hydrogenation of compound **8** in the presence of 10% Pd/C gave (+)-5-*epi*-muricatacin (**2**) in 92% yield. In order to synthesize compound **1**, the stereochemistry of the hydroxyl group at C-5 in compound **2** had to be inverted. In spite of performing hydrogenation reaction prior to the inversion of C-5 under Mitsunobu[26] conditions to prevent elimination,[54] the inversion was futile. Therefore, in order to obtain the natural product **1** from **2**, the latter was subjected to oxidation with Dess–Martin periodinane (DMP) to deliver the ketone which, on reduction with K-selectride, furnished compound **1** with >99% selectivity and in 90% yield after two steps (Scheme 2). The spectral data for synthetic **1** and **2** (^{1}H and ^{13}C NMR, see Supplementary data) were consistent with those previously reported, and the optical rotation for compound **1** ($[\alpha]_D^{28}$ +22.4 (*c* 0.42, $CHCl_3$, lit. $[\alpha]_D^{20}$ +23.0 (*c* 1.6, $CHCl_3$) for (+)-muricatacin[13]) and that for compound **2** ($[\alpha]_D^{28}$ +16.4 (*c* 0.3, $CHCl_3$), lit. $[\alpha]_D^{25}$ +14.3 (*c* 7.4, $CHCl_3$) for (+)-5-*epi*-muricatacin[16]) were comparable to that reported in the literature.

Table 1
Optimization of cross-metathesis of compound **7** with 1-dodecene

Entry	Equivalent of 1-dodecene	Time (h)	Yield of **8** (%)
1	3	8	72
2	6	8	84
3	10	8	95



Scheme 2. Reagents and conditions: (a) MeOH, acetone, HCl, 55 °C, 1h (Ref. 50 or 51); (b) I_2, PPh_3, imidazole, PhMe–CH_3CN, 0–100 °C, 5 min (Ref. 51); (c) activated Zn, THF, H_2O, sonication, 50 °C, 3 h; (d) Ph_3PCHCO_2Me, dry MeOH, 0 °C, 12 h, 62% over two steps; (e) TFA, THF, H_2O, 65 °C, 2 h, 79%; (f) Grubbs 2nd generation catalyst, 1-dodecene (10 equiv), dry DCM, 12 h, 95%; (g) H_2, Pd/C, MeOH, 6 h, 92%; and (h) (i) DMP, dry DCM, 0 °C to rt; (ii) K-Selectride, THF, −78 °C, 2 h, 90%.

3. Conclusions

In summary, we have achieved a short and efficient route for the total synthesis of (+)-muricatacin and (+)-5-*epi*-muricatacin starting from D-ribose through a key intermediate, lactone **7**. The stereochemistry inherited from C2 and C3 of D-ribose at C4 and C5 was translated to the desired stereochemistry of the C_{12} side chain of **2**. The highly functionalized stereochemically pure lactone **7** should find wide applications as a scaffold toward the syntheses of simple and complex oxygenated alkylbutyrolactone natural products in general and acetogenin derivatives in particular. It has been reported that the activity of this natural product is affected by the side chain;[55] therefore, by using different cross olefin counterparts, various analogues of muricatacin might be synthesized. Work in this direction is underway in our laboratory.

4. Experimental

4.1. General

Organic solvents were dried by standard methods. All the products were characterized by ^{1}H, ^{13}C, two-dimensional homonuclear COSY (correlation spectroscopy), IR, and ESIMS. Analytical TLC was performed using 2.5 × 5 cm plates coated with a 0.25 mm thickness of silica gel (60F-254), and visualization was accomplished with $CeSO_4$ (1% in 2 N H_2SO_4) and subsequent charring over a hot plate. Column chromatography was performed using silica gel (100–200 and 230–400 mesh). NMR spectra were recorded on Bruker Avance DPX 200FT, Bruker Robotics, and Bruker DRX 300 Spectrometers at 200 and 300 MHz (^{1}H) and 50 and 75 MHz (^{13}C), respectively. Experiments were recorded in $CDCl_3$ and CD_3OD at 25 °C. Chemical shifts are given on the δ scale and are referenced to the TMS at 0.00 ppm for ^{1}H and 0.00 ppm for ^{13}C. For ^{13}C NMR reference $CDCl_3$ appeared at 77.4 ppm. IR spectra were recorded on Perkin–Elmer 881 and FTIR-8210 PC Shimadzu spectrophotometers. Mass spectra were recorded on a JEOLJMS-600H high-resolution spectrometer in the electron-impact (EI) mode at 70 eV, or on a JEOL Accutof-DART instrument in the electrospray-ionization (ESI, positive-ion) DART mode. Optical rotations were determined on an Autopol III polarimeter using a 1-dm cell at 28 °C in chloroform as the solvent; concentrations indicated are in g/100 mL.

4.2. (*Z*)-Methyl 3-((4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)acrylate (6)

To a solution of the iodofuranoside **4** (1.0 g, 3.18 mmol) in 10 mL of THF (with two drops of water) was added 2.0 g of zinc preactivated with 2 N HCl. The reaction mixture was sonicated at 50 °C for 3 h. After completion of the reaction, it was filtered through a Celite pad, washed twice with EtOAc, and the filtrate was concentrated under reduced pressure at low temperature to give the labile aldehyde **5**, which was immediately used for the next step without further purification. The crude aldehyde **5** was dissolved in 50 mL of dry MeOH under an argon atmosphere and cooled to 0 °C. Methyl (triphenylphosphoranylidene)acetate (1.67 g, 5 mmol) was added portionwise to aldehyde **5**, and the reaction mixture was stirred at 0 °C for 12 h. After completion of the reaction, the organic solvent was evaporated to give a residue that was purified by flash column chromatography to furnish compound **6** (420 mg, 62% over two steps).

Eluent for column chromatography: 1:4 EtOAc–hexane (v/v); $[\alpha]_D^{28}$ +224 (*c* 0.16, $CHCl_3$); R_f 0.59 (1:9, EtOAc–hexane); IR (Neat, cm^{-1}): 3021, 2360, 1720, 1601, 1216, 1046; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.38 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 4.84 (t, 1H, *J* 7.0 Hz), 5.08–5.29 (m, 2H), 5.54–5.71 (m, 2H), 5.86 (dd, 1H, *J* 1.5, 11.6 Hz), 6.17 (dd, 1H, *J* 7.5, 11.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.5 (CH_3), 28.2 (CH_3), 51.8 (CH_3), 76.0 (CH), 80.0 (CH), 109.5 (qC), 118.1 (CH_2), 121.3 (CH), 134.3 (CH), 147.1 (CH), 166.3 (C=O); DART–HRESIMS: Calcd for $C_{11}H_{17}O_4$ $[M-H]^+$: *m*/*z* 213.1127; found *m*/*z* 213.1143.

4.3. (5*S*)-5-((*R*)-1-Hydroxyallyl)furan-2(5*H*)-one (7)

Compound **6** (800 mg, 3.77 mmol) dissolved in 15 mL of 4:1 THF–H_2O was heated at 65 °C with 3 mL of CF_3CO_2H. After completion of reaction (TLC, 2 h), the reaction was quenched with satd aq $NaHCO_3$, and the product was extracted with EtOAc (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a residue that was purified by flash column chromatography to afford compound **7** (418 mg, 79%) as a light-yellow oil. Eluent for column chromatography: 1:14 EtOAc–hexane (v/v); $[\alpha]_D^{28}$ −488 (*c* 0.53, $CHCl_3$); R_f 0.38 (1:1 EtOAc–hexane); IR (Neat, cm^{-1}): 3449, 3021, 2359, 1756, 1597, 1216, and 1042; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (br s, 1H), 4.44 (t, 1H, *J* 4.4 Hz), 4.99–5.02 (m, 1H), 5.23–5.29 (m, 1H), 5.37–5.43 (m, 1H), 5.79–5.93 (m, 1H), 6.13 (dd, 1H, *J* 2.0, 5.8 Hz), 7.47 (dd, 1H, *J* 1.4, 5.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4): δ 72.0 (CH), 86.2 (CH), 118.4 (CH_2), 123.3 (CH), 135.2 (CH), 153.9 (CH), 173.7 (C=O); HREIMS: Calcd for $C_7H_9O_3$ $[M-H]^+$: *m*/*z* 141.0552; found *m*/*z* 141.0525.

4.4. (5*S*)-5-((*R*, *Z*)-1-Hydroxytridec-2-enyl)furan-2(5*H*)-one (8)

To a 50-mL two-necked oven-dried round-bottomed flask fitted with a reflux condenser and septum was added Grubbs 2nd generation catalyst (16 mg, 0.018 mmol) under an argon atmosphere. Dry degassed CH_2Cl_2 (5 mL) was then added to the above-mentioned solution through a syringe, and the solution was kept stirring. Compound **7** (100 mg, 0.71 mmol) and **1**-dodecene (1.2 g, 7.1 mmol) in DCM (2 mL each) were added through a syringe to the stirring solution. The septum was replaced with a glass stopper while the stirring was continued. The solution was refluxed for 12 h. The mixture was cooled slowly to room temperature. The organic solvent was then evaporated under reduced pressure to give a black residue that was purified by column chromatography to give **8** as a semisolid compound (195 mg, 95%). Eluent for column chromatography: 1:7 EtOAc–hexane (v/v); $[\alpha]_D^{28}$ −154 (*c* 0.43, $CHCl_3$); R_f 0.50 (1:1 EtOAc–hexane); IR (KBr, cm^{-1}): 3442, 3021, 2927, 2858, 2362, 1755, 1604, 1217, 1042; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J* 6.0 Hz), 1.26 (m, 14H), 1.32–1.38 (m, 2H), 2.06 (dd, 2H, *J* 6.8, 13.7 Hz), 4.37 (t, 1H, *J* 5.2 Hz), 4.94–4.97 (m, 1H), 5.47 (dd, 1H, *J* 6.2, 15.5 Hz), 5.79–5.86 (m, 1H), 6.16 (dd, 1H, *J* 1.9, 5.7 Hz), 7.47(dd, 1H, *J* 1.4, 5.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4): δ 14.6 (CH_3), 23.2 (CH_2), 29.4–30.1 (6 × CH_2), 32.4 (CH_2), 32.8 (CH_2), 72.3 (CH), 86.3 (CH), 123.5 (CH), 126.8 (CH), 135.9 (CH), 153.6 (CH), 173.1 (C=O); HREIMS: Calcd for $C_{17}H_{27}O_3$ $[M-H]^+$: *m*/*z* 279.1960; found *m*/*z* 279.1946.

4.5. (+)-5-*epi*-Muricatacin (2)

A catalytic amount of 10% Pd/C (20 mg) was added to a solution of **8** (195 mg, 0.696 mmol) in MeOH (10 mL). A vacuum was created in a round-bottomed flask containing the above-mentioned reaction mixture with the help of a pump, and the mixture was left stirring under H_2 in a balloon at 1 atmosphere. After completion of the reaction (TLC control, 6 h), the catalyst was removed by filtration, washed twice with MeOH and the combined filtrate was concentrated to afford a solid residue that was purified by column chromatography to give **2** (182 mg, 0.64 mmol, 92%) as a white solid: (mp 71–73 °C), (lit. mp 70–72 °C).[26] Eluent for column chromatography: 1:7 EtOAc–hexane (v/v); $[\alpha]_D^{28}$ +16.6 (*c* 0.078, $CHCl_3$), lit. $[\alpha]_D^{25}$ +14.3 (*c* 7.4, $CHCl_3$);[16] R_f 0.5 (1:1 EtOAc–hexane); IR (KBr,

cm^{-1}): 3401, 3021, 2926, 2359, 1768, 1598, 1216, 1040; ^1H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, 3H, J 13.2 Hz), 1.25 (m, 19H), 1.38–1.42 (m, 2H), 1.50 (d, 1H, J 6.8 Hz), 2.10–2.30 (m, 2H), 2.49–2.60 (m, 2H), 3.89–3.94 (m, 1H), 4.40–4.46 (m, 1H); ^{13}C NMR (75 MHz. $CDCl_3$): δ 14.0 (CH_3), 20.9 (CH_2), 22.6 (CH_2), 25.5 (CH_2), 28.6 (CH_2), 29.2 (CH_2), 29.4–29.5 (6 × CH_2), 31.8 (2 × CH_2), 71.2 (CH), 82.8 (CH), 177.4 (C=O); DART–HRESIMS: Calcd for $C_{17}H_{33}O_3$ $[M+H]^+$: m/z 285.2429; found m/z 285.2425.

4.6. (+)-Muricatacin (1)

To an ice cooled solution of **2** (51 mg, 0.18 mmol) in dry DCM (6 mL) was added Dess–Martin periodinane (115 mg, 0.27 mmol), and the reaction mixture was allowed to stir for 1.5 h. The resulting mixture was diluted with satd aq $NaHCO_3$ and 10% aq $Na_2S_2O_3$. It was stirred for another 30 min and then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to afford the desired ketolactone, a solid residue. The solid, without further purification was taken in a 50-mL two-necked oven-dried round-bottomed flask in dry THF (5 mL) at −78 °C, and the keto group was selectively reduced by K-Selectride (0.2 mL 1 N solution in THF, 1.1 equiv) under an argon atmosphere. After completion of reaction (TLC control, 2 h), satd aq NH_4Cl was added, and the resulting solution was extracted with EtOAc (3 × 15 mL). The combined organic layer was dried (Na_2SO_4) and concentrated in vacuo to a residue that was purified by column chromatography to give pure compound **1** as a white solid material (46 mg, 0.16 mmol, 90%): mp 68–70 °C, (lit. mp 68–70 °C).[26] Eluent for column chromatography: 1:7 EtOAc–hexane (v/v); $[\alpha]_D^{28}$ +22.4 (c 0.42, $CHCl_3$), lit. $[\alpha]_D^{20}$ +23.0 (c 1.6, $CHCl_3$)[13]; R_f 0.46 (1:1 EtOAc–hexane); IR (KBr, cm^{-1}): 3417, 2925, 2855, 2360, 1751, 1664, 1596, 1197, 1101; ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, J 6.3 Hz.), 1.26 (m, 19H) 1.52 (s, 3H), 2.04–2.29 (m, 2H), 2.46–2.67 (m, 2H), 3.52–3.58 (m, 1H), 4.38–4.44 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.6 (CH_2), 24.1 (CH_2), 25.4 (CH_2), 28.7 (CH_2), 29.3 (CH_2), 29.5–29.6 (6 × CH_2), 31.9 (CH_2), 32.9 (CH_2), 73.6 (CH), 82.9 (CH), 177.2 (C=O); DART–HRESIMS: Calcd for $C_{17}H_{33}O_3$ $[M+H]^+$: m/z 285.2430; found m/z 285.2399.

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Supplementary data

Supplementary data (^1H and ^{13}C NMR spectra of all compounds) associated with this article can be found, in the online version, at doi:10.1016/j.carres.2009.09.021.

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