Alkyne-Mediated Approach to the Synthesis of (4*R*,5*R*)-5-Hydroxy-4-decanolide and (−)-Muricatacin

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The asymmetric synthesis of two naturally occurring 5-hydroxy-γ-butyrolactones, (4*R*,5*R*)-5-hydroxy-4-decanolide (**1a**) and (−)-muricatacin (**2**), is described using a general alkyne-mediated strategy. The key steps involved are *Sonogashira* coupling for the desired carbon-chain extension followed by *Sharpless* asymmetric dihydroxylation to construct the hydroxy-lactone framework.

Introduction. – Chiral 5-hydroxy-γ-butyrolactones constitute an important class of natural products and have received considerable attention due to their interesting wide range of biological activities [1]. These compounds have found applications as insect anti-feedants [2], cytotoxic agents [3], and flavor constituents in wine, sherry, and tobacco smoke [4]. They also serve as important precursors for the synthesis of bioactive natural products [5] and other compounds, such as HIV-1 protease inhibitors [6]. (4*R*,5*R*)-5-Hydroxy-4-decanolide (**1a**; *Fig.*) is one such γ-butyrolactone which was recently found in male *Nasonia vitripennis* as an additional pheromone compound differing only in its configuration from the previously described (4*R*,5*S*)-5-hydroxy-4-decanolide (**1b**) [7]. The enantiomers of these two compounds, (4*S*,5*S*)- and (4*S*,5*R*)-isomers **1c** and **1d**, were also natural compounds, named as L-factors, isolated from the cultures of *Streptomyces griseus*, which reveal autoregulatory properties [8]. Due to their notable bioactivity, the synthesis of L-factors has received attention of organic chemists and accordingly various strategies have been developed [9]. In few cases, (4*R*,5*R*)- and (4*R*,5*S*)-isomers were also synthesized [10]. In continuation of our interest in the synthesis of bioactive lactones using alkyne-assisted approaches [11],

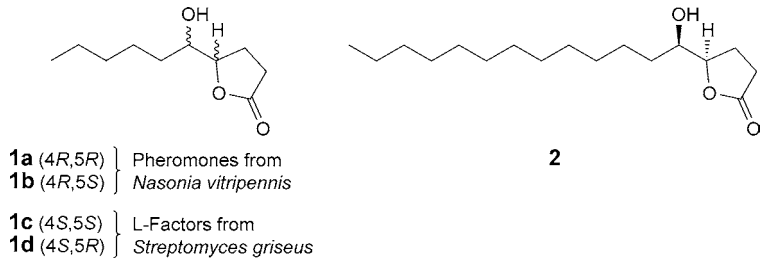
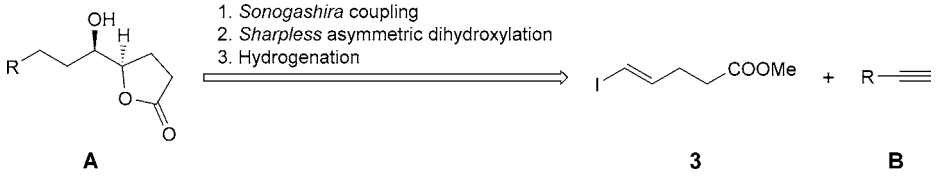


Figure. *Structures of 5-hydroxy-4-decanolides,* **1a**–**1d**, *and (−)-muricatacin* (**2**)

herein, we describe a different strategy to access the pheromone, (4*R*,5*R*)-5-hydroxy-4-decanolide (**1a**), *via* an alkyne-based convergent route. This has various advantages, such as the easy accessibility of the desired alkynes, the coupling of which can be accomplished under mild reaction conditions, and generation of the desired stereogenic centers using alkyne functionality.

We considered that the construction of the required carbon chain would be possible through *Sonogashira* coupling of alkyne **B** with vinyl iodide **3** to give an enyne, which will undergo *Sharpless* asymmetric dihydroxylation followed by hydrogenation to achieve the desired hydroxy-lactone **A**. The above mentioned reaction sequence involving *Sonogashira* coupling has not been utilized for the synthesis of 5-hydroxy-γ-butyrolactones **1a** and **2** before. Furthermore, this strategy will also be the general procedure to prepare diversely alkylated 5-hydroxy-γ-butyrolactones (*Scheme 1*) having different side chains. This was demonstrated by the synthesis of (−)-muricatacin (**2**), a natural lactone isolated from the seeds of *Annona muricata* [12]. Since its isolation in 1991, several syntheses of muricatacin and its analogs have been described [13]. Typically, the alkyl side chain was introduced by using *Grignard* reaction or *Wittig* olefination, and in few cases by other methods, such as cross metathesis.

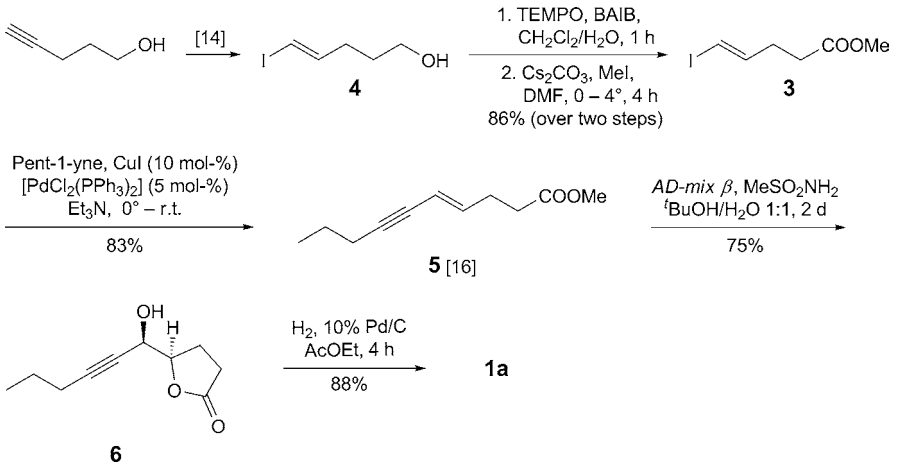
Scheme 1. *Retrosynthetic Analysis of 5-Hydroxy-γ-butyrolactones*



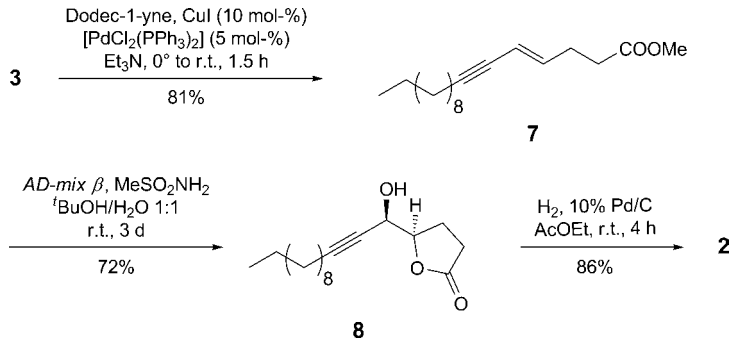
Results and Discussion. – The synthesis of (4*R*,5*R*)-5-hydroxy-4-decanolide (**1a**) is shown in *Scheme 2*. The synthesis started with the known (4*E*)-5-iodopent-4-en-1-ol (**4**), which was obtained readily in one step from pent-4-yn-1-ol following the reported protocol [14]. Firstly, the oxidation of alcohol **4** in the presence of [bis(acetyloxy)iodo]benzene (BAIB)/TEMPO in CH_2Cl_2/H_2O provided the corresponding acid, which was esterified using Cs_2CO_3/MeI to get vinyl iodide **3** in 86% yield over two steps. *Sonogashira* coupling [15] of **3** with pent-1-yne under standard conditions ($[PdCl_2(PPh_3)_2]$, CuI, Et_3N) afforded enyne ester **5** [16] in 83% yield. In the next step, enantioselective *Sharpless* asymmetric dihydroxylation [5e][17] of **5** was carried out with *AD-mix β* in ^{t}BuOH/H_2O 1:1, which resulted in hydroxy-lactone **6** in 75% yield *via* dihydroxylation followed by *in situ* lactone formation. Finally, exhaustive hydrogenation of the acetylenic functionality to saturation was achieved using 10% Pd/C in AcOEt to give the desired target compound, (4*R*,5*R*)-5-hydroxy-4-decanolide (**1a**), in 88% yield. The spectroscopic data (IR, ^{1}H- and ^{13}C-NMR) of **1a** were identical and the observed optical rotation, $[\alpha]_D = -32.8$ ($c = 1.54$, $CHCl_3$), was comparable with the data reported in [9h] ($[\alpha]_D = -33.1$ ($c = 1.64$, $CHCl_3$)).

Encouraged by the successful accomplishment of **1a**, we continued to explore the generality of the above mentioned strategy by the synthesis of another naturally occurring 5-hydroxy-γ-butyrolactone, (−)-muricatacin (**2**; *Scheme 3*). The structural

Scheme 2. *Synthesis of (4*R*,5*R*)-5-Hydroxy-4-decanolide* (**1a**)



Scheme 3. *Synthesis of (−)-Muricatacin* (**2**)



difference in **2** is the side chain ($Me(CH_2)_{11}$) at C(5) when compared with **1a** ($Me(CH_2)_4$). Thus, vinyl iodide **3** was coupled with dodec-1-yne under *Sonogashira* reaction conditions to obtain enyne **7** in 81% yield. Next, **7** was transformed to (−)-muricatacin (**2**) following a similar sequence of reactions as used for **1a**, *i.e.*, *Sharpless* asymmetric dihydroxylation followed by hydrogenation. The spectroscopic data of **2** were identical with those reported previously, and the optical rotation, $[\alpha]_D = -22.6$ ($c = 1.0$, $CHCl_3$), was comparable to the data reported in [13l][13m] ($[\alpha]_D = -23.3$ ($c = 1.8$, $CHCl_3$)).

Conclusions. – The stereoselective total syntheses of (4*R*,5*R*)-5-hydroxy-4-decanolide (**1a**) and (−)-muricatacin starting (**2**) from two alkyne substrates have been accomplished in six steps. This strategy relies on the use of the alkyne functionality, which allows the desired chain extension and provides the necessary platform for the construction of the asymmetric diol function followed by lactonization. The present route offers a useful showcase of an alkyne-assisted approach through *Sonogashira*

coupling and *Sharpless* asymmetric dihydroxylation to the synthesis of 5-hydroxyalkyl-γ-butyrolactones. The reaction sequence is new and unique, and might find application to access diversely alkylated 5-hydroxy-γ-butyrolactones.

D. S. and *N. N. R.* thank the *Council of Scientific and Industrial Research* (CSIR), New Delhi, for the award of a research fellowship. *C. R. R.* is grateful to *CSIR*, New Delhi, for financial support as part of XII-five year plan project under *ORIGIN* (CSC-108).

Experimental Part

General. All reagents and solvents were of reagent grade and used without further purification unless specified otherwise. Technical grade of AcOEt and hexanes used for column chromatography were distilled prior to use. All reactions were performed under N_2 atmosphere in flame-dried or oven-dried glassware with magnetic stirring. Thin-layer chromatography (TLC): silica gel *60 F_{254}* (*Merck KGaA*). Column chromatography (CC) and flash column chromatography (FC): silica gel (SiO_2; 60–120 mesh) packed in glass columns. FT-IR Spectra: *PerkinElmer 683* infrared spectrophotometer; neat or KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker Avance-300* spectrometer (300 and 75 MHz, resp.); in $CDCl_3$; at ambient temp.; δ in ppm rel. to Me_4Si as internal standard, J in Hz. ESI-and HR-ESI-MS: *Agilent Technologies LC-MSD trap SL* spectrometer; in m/z. Elemental analyses: *Vario Micro Cube Elementar*; in %.

*Methyl (4*E*)-5-Iodopent-4-enoate* (**3**). To a soln. of (4*E*)-5-iodopent-4-en-1-ol (**4**; 780 mg, 3.67 mmol) in H_2O/CH_2Cl_2 1:1 (3 ml) were added TEMPO (165 mg, 0.51 mmol) and BAIB (1.65 g, 11.0 mmol) at 0°. After stirring at r.t. for 1 h, the mixture was diluted with CH_2Cl_2 (3 ml). The resulting soln. was washed with a sat. aq. $Na_2S_2O_3$ soln. (5 ml). The org. layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated under reduced pressure to give the crude carboxylic acid. Without further purification, the crude acid (0.765 g, 3.38 mmol) was subjected to esterification with MeI (0.31 ml, 5.0 mmol) and successively added to a suspension of Cs_2CO_3 (1.21 g, 3.71 mmol) in DMF (7 ml). After stirring at 0–4° for 4 h, the mixture was poured into cold H_2O and extracted with AcOEt (2 × 5 ml), dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was separated by FC (SiO_2; hexanes/AcOEt) to afford **3** (720 mg, 86%) as colorless oil. IR (KBr): 2950, 1737, 1437, 1198. ^{1}H-NMR: 6.52 (*dd*, J = 6.7, 14.3, 1 H); 6.03 (*d*, J = 14.3, 1 H); 3.68 (*s*, 3 H); 2.48–2.31 (*m*, 4 H). ^{13}C-NMR: 172.6; 144.0; 76.1; 51.6; 32.5; 31.0. ESI-MS: 263 ($[M+Na]^+$). Anal. calc. for $C_6H_9IO_2$ (240.04): C 30.02, H 3.78; found: C 30.14, H 3.66.

*Methyl (4*E*)-Dec-4-en-6-ynoate* (**5**) [16]. To a soln. of **3** (150 mg, 0.62 mmol) and pent-1-yne (590 mg, 3.46 mmol) in Et_3N (5 ml) was added $[PdCl_2(PPh_3)_2]$ (43 mg, 0.06 mmol) at 0°. The mixture was stirred at 0° for 15 min, then CuI (23 mg, 0.12 mmol) was added. After stirring at 0° for 10 min, the mixture was warmed to r.t. and further stirred for 1 h. After completion, the mixture was concentrated under reduced pressure. The residue was separated by FC (SiO_2; hexanes/AcOEt) to afford enyne **5** (93 mg, 83%) as light yellow liquid. IR (KBr): 2925, 2853, 1758, 1622, 1437, 770. ^{1}H-NMR: 6.02 (*dd*, J = 6.8, 15.8, 1 H); 5.52 (*d*, J = 15.8, 1 H); 3.67 (*s*, 3 H); 2.42–2.39 (*m*, 2 H); 2.33–2.22 (*m*, 4 H); 1.58–1.48 (*m*, 2 H); 0.88 (*t*, J = 6.7, 3 H). ^{13}C-NMR: 173.0; 140.3; 111.3; 89.5; 84.4; 51.4; 31.9; 30.9; 29.3; 22.6; 14.1. ESI-MS: 203 ($[M+Na]^+$). Anal. calc. for $C_{11}H_{16}O_2$ (180.25): C 73.30, H 8.95; found: C 73.39, H 8.86.

*(5*R*)-Dihydro-5-[(1*R*)-1-hydroxyhex-2-yn-1-yl]furan-2(3*H*)-one* (**6**). Compound **5** (100 mg, 0.55 mmol) was dissolved in a 1:1 mixture of ^{t}BuOH (2.7 ml) and H_2O (2.7 ml) and cooled to 0°. To this mixture was added $MeSO_2NH_2$ (105 mg, 1.11 mmol) followed by *AD-mix* β (777 mg), and the resulting mixture was stirred for 72 h at 0°. After completion of the reaction (monitored by TLC), the reaction was quenched by adding solid Na_2SO_3 (15 mg), the mixture was stirred for l h, and then diluted with H_2O (5 ml) and extracted with AcOEt (3 × 5 ml). The combined org. layer was dried (Na_2SO_4) and evaporated to dryness under reduced pressure. The residue was subjected to CC (SiO_2; hexanes/AcOEt) to give **6** (77 mg, 75%) as yellow liquid. $[\alpha]_D^{20} = -8.59$ (c = 1.28, $CHCl_3$). IR (KBr): 3443, 2925, 2854, 1774, 1609, 1183. ^{1}H-NMR: 4.54 (*q*, J = 7.4, 1 H); 4.45 (*dd*, J = 5.4, 7.4, 1 H); 2.65–2.47 (*m*, 2 H); 2.37–

2.26 (*m*, 1 H); 2.24–2.14 (*m*, 4 H); 1.55–1.47 (*m*, 2 H); 0.95 (*t*, *J* = 7.3, 3 H). ^{13}C-NMR: 177.0; 87.8; 81.7; 76.4; 64.6; 30.8; 23.2; 21.7; 20.5; 13.3. HR-ESI-MS: 205.2128 ($[M+Na]^+$, $C_{10}H_{14}NaO_3^+$; calc. 205.0835).

*(4*R*,5*R*)-5-Hydroxy-4-decanolide* (= *(5*R*)-Dihydro-5-[(1*R*)-1-hydroxyhexyl]furan-2(3*H*)-one*; **1a**) [9h]. To a soln. of **6** (50 mg, 0.27 mmol) in EtOH (3 ml), 10% Pd/C (15 mg) was added, and the heterogeneous mixture was stirred overnight under H_2 atmosphere at r.t. After completion of the reaction, the mixture was filtered through a small pad of *Celite*, and the resulting filtrate was concentrated under reduced pressure. The crude product was subjected to FC (SiO_2; hexanes/AcOEt) to give **1a** (45 mg, 88%) as white solid. M.p. 45–48°. $[\alpha]_D^{20} = -32.8$ (*c* = 1.54, $CHCl_3$). IR (KBr): 3444, 2926, 2854, 1627, 1188. ^{1}H-NMR: 4.42 (*ddd*, *J* = 4.5, 7.3, 11.9, 1 H); 3.57 (*dt*, *J* = 4.5, 9.0, 1 H); 2.60 (*ddd*, *J* = 5.0, 9.9, 17.8, 1 H); 2.50 (*ddd*, *J* = 6.1, 9.6, 13.2, 1 H); 2.24 (*ddd*, *J* = 5.0, 9.9, 12.6, 1 H); 2.12 (*dddd*, *J* = 7.7, 8.4, 11.2, 12.8, 1 H); 1.65–1.47 (*m*, 3 H); 1.44–1.26 (*m*, 5 H); 0.88 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR: 177.3; 82.9; 73.6; 32.8; 31.6; 28.6; 25.0; 24.0; 22.5; 13.9. HR-ESI-MS: 209.2553 ($[M+Na]^+$, $C_{10}H_{18}NaO_3^+$; calc. 209.1148).

*Methyl (4*E*)-Heptadec-4-en-6-ynoate* (**7**). To a soln. of **3** (200 mg, 0.83 mmol) and dodec-1-yne (207 mg, 1.24 mmol) in Et_3N (7 ml) was added $[PdCl_2(PPh_3)_2]$ (58 mg, 0.082 mmol) at 0°. The mixture was stirred at 0° for 15 min, then CuI (38 mg, 0.19 mmol) was added. After stirring at 0° for 10 min, the mixture was warmed to r.t. and further stirred for 1 h. After completion, the mixture was concentrated under reduced pressure. The residue was separated by FC (SiO_2; hexanes/AcOEt) to afford **7** (188 mg, 81%) as light yellow liquid. IR (KBr): 2926, 2854, 1742, 1438, 1252, 1164, 955. ^{1}H-NMR: 6.02 (*dd*, *J* = 6.8, 15.8, 1 H); 5.51 (*d*, *J* = 15.8, 1 H); 3.67 (*s*, 3 H); 2.48–2.38 (*m*, 4 H); 2.31–2.22 (*m*, 2 H); 1.58–1.44 (*m*, 2 H); 1.39–1.22 (*m*, 14 H); 0.87 (*t*, *J* = 6.7, 3 H). ^{13}C-NMR: 173.0; 140.3; 111.3; 89.7; 78.6; 51.6; 33.2; 31.9; 29.5; 29.3; 29.1; 28.9; 28.7; 28.0; 22.6; 19.3; 14.0. HR-ESI-MS: 301.2133 ($[M+Na]^+$, $C_{18}H_{30}NaO_2^+$; calc. 301.2138).

*(5*R*)-Dihydro-5-[(1*R*)-1-hydroxytridec-2-yn-1-yl]furan-2(3*H*)-one* (**8**). To a soln. of **7** (160 mg, 0.57 mmol) in a 1:1 mixture of ^{t}BuOH (2.8 ml) and H_2O (2.8 ml), cooled to 0°, was added $MeSO_2NH_2$ (105 mg, 1.11 mmol) followed by *AD-mix β* (804 mg), and the resulting mixture was stirred for 72 h at 0°. After completion of the reaction (monitored by TLC), the reaction was quenched by adding solid Na_2SO_3 (25 mg), the mixture was stirred for l h, then diluted with H_2O (5 ml), and extracted with AcOEt (3 × 10 ml). The combined org. layer was dried (Na_2SO_4) and evaporated to dryness under reduced pressure. The residue was subjected to CC (SiO_2; hexanes/AcOEt) to give **8** (117 mg, 72%) as yellow liquid. $[\alpha]_D^{20} = -10.77$ (*c* = 1.04, $CHCl_3$). IR (KBr): 3416, 2925, 2854, 2233, 1777, 1461, 1185, 1044, 1016. ^{1}H-NMR: 4.53 (*q*, *J* = 6.0, 1 H); 4.44 (*d*, *J* = 6.0, 1 H); 2.69–2.44 (*m*, 2 H); 2.40–2.23 (*m*, 2 H); 2.23–2.13 (*m*, 2 H); 1.55–1.41 (*m*, 2 H); 1.38–1.20 (*m*, 14 H); 0.86 (*t*, *J* = 6.7, 3 H). ^{13}C-NMR: 176.8; 88.1; 81.7; 76.1; 64.7; 31.8; 29.5; 29.4; 29.2; 29.0; 28.8; 28.3; 28.1; 23.3; 22.6; 18.6; 14.0. HR-ESI-MS: 303.3421 ($[M+Na]^+$, $C_{17}H_{28}NaO_3^+$; calc. 303.1931).

(−)-Muricatacin (= *(5*R*)-Dihydro-5-[(1*R*)-1-hydroxytridecyl]furan-2(3*H*)-one*; **2**) [13l][13m]. To a soln. of **8** (100 mg, 0.35 mmol) in EtOH (5 ml), 10% Pd/C (30 mg) was added, and the heterogeneous mixture was stirred overnight under H_2 atmosphere at r.t. After completion of the reaction, the mixture was filtered through a small pad of *Celite*, and the resulting filtrate was concentrated under reduced pressure. The crude product was purified by FC (SiO_2; hexanes/AcOEt) to give **2** (86 mg, 86%) as white solid. M.p. 74–76°. $[\alpha]_D^{20} = -22.6$ (*c* = 1.0, $CHCl_3$). IR (KBr): 3445, 2916, 2845, 1746, 1463. ^{1}H-NMR: 4.42 (*dd*, *J* = 7.1, 11.9, 1 H); 3.57 (*dd*, *J* = 4.9, 9.6, 1 H); 2.70–2.47 (*m*, 2 H); 2.42–2.04 (*m*, 2 H); 1.63–1.16 (*m*, 22 H); 0.88 (*t*, *J* = 6.7, 3 H). ^{13}C-NMR: 177.3; 82.9; 73.5; 32.9; 31.8; 29.6; 29.5; 29.4; 29.3; 28.6; 25.4; 24.0; 22.6; 14.0. HR-ESI-MS: 285.2426 ($[M+H]^+$, $C_{17}H_{33}O_3^+$; calc. 285.2424).

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Received November 14, 2014