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Zr-Catalyzed Cycloalumination of 1,2-Dienes in the Synthesis of Lyngbioic Acid Derivatives†

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Abstract: Using at the key stage of the synthesis the reaction of catalytic cycloalumination of 1,2-dienes with Et_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 (Dzhemilev reaction), an original method for the preparation of analogs of natural Lyngbioic acid with high yields and stereoselectivity was developed, which are key synthons in the preparation of derivatives natural Grenadamide.

Keywords: 1,2-dienes; Cycloalumination; Lyngbioic acid derivatives

1. Introduction

Natural fatty acids containing a cyclopropane ring in their structure are found in the composition of phospholipids of the cell wall of various types of bacteria, as well as in the seed oil of subtropical plants[1]. It has been shown that cyclopropane-containing fatty acids isolated from marine cyanobacteria are able to inhibit quorum sensing (QS), thus inhibiting the growth of bacteria and fungi[2].

Studies on the development of effective methods for the synthesis of cyclopropane-containing fatty acids remain in demand due to the lack of universal approaches to the preparation of these compounds, since in most cases the known synthesis schemes are multistage (7-9 steps) and require the use of expensive and hard-to-find starting reagents[3-5].

2. Results and discussion

Based on our earlier results on the complete stereoselective synthesis of grenadamide and its precursor lingbioic acid using catalytic cycloalumination of 1.2-dienes[6-17], a number of cyclopropane-containing acids have been synthesized.

The reaction of cycloalumination of 1,2-dienes **1a-d** with Et_3Al catalyzed by Cp_2ZrCl_2 (5 mol%) under the conditions [1,2-diene: $AlEt_3$: Cp_2ZrCl_2 = 10: 13: 0.5, ~ 20^{0}C, 5 h, CH_2Cl_2], leading to obtain 1-ethyl-2-alkylidene(phenylidene)alumacyclopentanes **2a-d**, the oxidation of which with atmospheric oxygen in situ followed by acid hydrolysis in one preparative stage synthesized alcohols containing cis-double bonds **3a-d** in 87-91% yields and selectivity> 98%. After protecting the hydroxyl groups of alcohols **3a-d** with a tetrahydropyranyl group to obtain tetrahydropyran ethers **4a-d**, we carried out cyclopropanation reactions with aluminum carbenoids[18,19] generated in the Et_3Al-CH_2I_2 system (~ 20^{0}C, 6 h, $AlEt_3$: CH_2I_2 = 13:10, CH_2Cl_2) deprotection of hydroxyl groups

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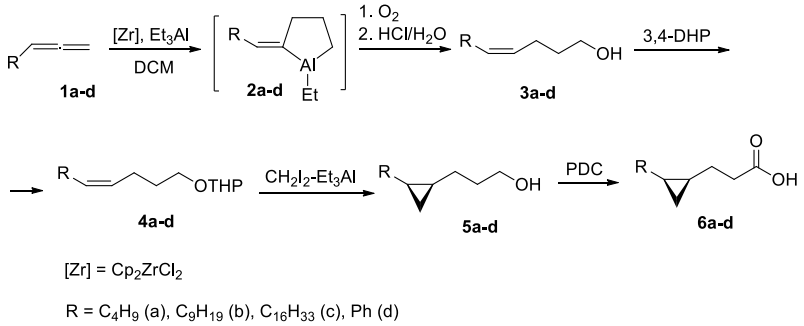
during the reaction, which led to the production of the corresponding alcohols containing in their structure cyclopropane fragments **5a-d** in yields of ~ 77-89%. Lingbioic acid derivatives were synthesized by oxidation with **5a-d** pyridinium dichromate in ~ 82-86% yields (Scheme 1).



Scheme 1. Synthesis of lingbioic acid derivatives.

3. Conclusions

Thus, we have developed an effective method for the preparation of derivatives of lingbioic acid, using at the key stage of the synthesis the reaction of catalytic cycloalumination of 1,2-dienes (the Dzhemilev reaction). These compounds, in our opinion, are of exceptional interest as objects for the development of anticancer and antibacterial drugs on their basis.

4. Experimental Part

Commercially available reagents (Sigma-Aldrich and Acros) were used. Reactions with organoaluminum compounds were carried out under dried argon atmosphere. Dichloromethane was distilled over P_2O_5. 1,2-dienes was prepared according to the known procedure[20]. Reaction products were analyzed on a Carlo Erba chromatograph. TLC was performed on Silufol UV-254 plates. Elemental composition of compounds was determined using a Carlo Erba-1106 instrument. Mass spectra were obtained using a Bruker MALDI-TOF/TOF Autoflex III instrument. 1H and 13C NMR spectra were recorded on a Bruker Avance 400 spectrometer (100.62 MHz for 13C and 400.13 MHz for 1H). Chemical shifts of 1H and 13C nuclei (δ) are given relative to the residual signals of the deuterated solvent (δ 7.28 for protons and 77.2 for carbon nuclei).

Synthesis of alcohol (3a-d). Dichloromethane (10 mL), 1,2-diene (10 mmol), Et_3Al (1.95 mL, 13 mmol) (*caution: organoaluminum compounds are pyrophoric and can ignite on contact with air, water, or any oxidizing agent*), and Cp_2ZrCl_2 (0.146 g, 0.5 mmol) were placed into a glass reactor under dry argon at 0°C with stirring and the stirring was continued for 4 h at room temperature (20°C). Then, the reaction mixture was oxidized for 8–10 h with atmospheric oxygen, which was additionally purified from traces of moisture by passing through a column containing molecular sieves (4 Å). After hydrolysis of the reaction mixture, the reaction product was isolated by column chromatography (5:1 petroleum ether/ethyl acetate). **(Z)-non-4-en-1-ol (3a).** Yield: 87 %. R_f =0.51 (5:1 petroleum ether/ethyl acetate**).** NMR ^{1}H (400 MHz, $CDCl_3$) δ 5.45–5.34 (m, 2H), 3.66 (t, J = 6.7 Hz, 2H), 2.16–2.11 (m, 4H), 2.08–2.03 (m, 2H), 1.36-1.32 (m, 4H), 0.91 (t,

J = 6.6 Hz, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 130.74, 128.83, 62.60, 32.64, 31.88, 26.90, 23.58, 22.34, 13.98. MS (MALDI TOF) m/z 142.24 $[M]^+$. Calcd for $C_9H_{18}O$: C 76.00; H 12.76. Found: C 76.07; H 12.70. **(Z)-tetradec-4-en-1-ol** (**3b**). Yield: 89 %. R_f =0.50 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 5.40–5.31 (m, 2H), 3.59 (t, J = 6.7 Hz, 2H), 2.12–2.00 (m, 4H), 1.63–1.56 (m, 6H), 1.34-1.25 (d, J = 18.3 Hz, 10H), 0.87 (t, J = 6.6 Hz, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 130.61, 128.81, 62.23, 32.59, 31.90, 29.72, 29.60, 29.58, 29.33, 27.19, 23.55, 22.66, 14.03. MS (MALDI TOF) m/z 212.37 $[M]^+$. Calcd for $C_{14}H_{28}O$: C 79.18; H 13.29. Found: C 79.16; H 13.25. **(Z)-5-phenylpent-4-en-1-ol (3c).** Yield: 90 %. R_f =0.52 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 7.38–7.23 (m, 5H), 6.50–6.46 (m, 1H), 5.73–5.67 (m, 1H), 3.67 (t, J = 6.7 Hz, 2H), 2.48–2.42 (m, 2H), 1.78-1.71 (m, 2H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 137.54, 132.09, 129.47, 128.75, 128.20, 126.61, 62.34, 32.84, 24.91. MS (MALDI TOF) m/z 162.23 $[M]^+$. Calcd for $C_{11}H_{14}O$: C 81.44; H 8.70. Found: C 81.45; H 8.73. **(Z)-henicos-4-en-1-ol** (**3d**). Yield: 91 %. R_f =0.50 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 5.44–5.34 (m, 2H), 3.66 (t, J = 6.7 Hz, 2H), 2.16–2.03 (m, 4H), 1.88–1.62 (m, 8H), 1.50-1.20 (m, 22H), 0.89 (t, J = 6.6 Hz, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 130.80, 62.59, 32.64, 31.93, 29.70, 29.66, 29.56, 29.36, 29.17, 29.09, 28.90, 27.21, 23.59, 22.69, 14.10. MS (MALDI TOF) m/z 310.56 $[M]^+$. Calcd for $C_{21}H_{42}O$: C 81.24; H 13.61. Found: C 81.22; H 13.63.

Synthesis of tetrahydropyran ethers (4a-d). Concentrated HCl (0.012 mL) was added to a mixture of alcohol **(3a-d)** (12.0 mmol) and dihydropyran (1.048 g, 10.0 mmol) at 0 °C. The mixture was stirred for 18 h at room temperature, followed by the addition of solid KOH (0.022 g) and stirring for 15 min at room temperature. After filtration, the product was isolated by column chromatography (hexane—ethyl acetate, 5 : 1) as a yellow oily liquid. **(Z)-2-(non-4-en-1-yloxy)tetrahydro-2H-pyran (4a).** R_f =0.70 (5:1 petroleum ether/ethyl acetate). NMR ^{1}H (400 MHz, $CDCl_3$) δ 5.34–5.31 (m, 2H), 4.53 (t, J = 6.7 Hz, 1H), 3.85–3.32 (m, 4H), 2.16–2.11 (m, 4H), 2.13–1.97 (m, 4H), 1.83–1.45 (m, 4H), 1.36–1.32 (d, J = 18.3 Hz, 4H), 0.86 (t, J = 6.6 Hz, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 130.35, 128.91, 98.69, 66.84, 62.07, 31.86, 30.70, 29.74, 26.83, 25.49, 23.79, 22.28, 19.55, 13.88. MS (MALDI TOF) m/z 226.36 $[M]^+$. Calcd for $C_{14}H_{26}O_2$: C 74.29; H 11.58. Found: C 74.22; H 11.53**. (Z)-2-(tetradec-4-en-1-yloxy)tetrahydro-2H-pyran (4b).** R_f =0.71 (5:1 petroleum ether/ethyl acetate). NMR ^{1}H (400 MHz, $CDCl_3$) δ 5.35–5.23 (m, 2H), 4.51 (t, J = 6.7 Hz, 1H), 3.83–3.29 (m, 4H), 2.14–1.94 (m, 4H), 1.83–1.73 (m, 6H), 1.67–1.42 (m, 6H), 1.30–1.22 (d, J = 18.3 Hz, 10H), 0.83 (t, J = 6.6 Hz, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 130.34, 128.85, 98.58, 98.51, 66.74, 61.90, 31.86, 30.67, 29.73, 29.68, 29.57, 29.52, 29.30, 29.27, 27.12, 25.50, 23.79, 22.61, 19.49, 13.96. MS (MALDI TOF) m/z 296.49 $[M]^+$. Calcd for $C_{19}H_{36}O_2$: C 76.97; H 12.24. Found: C 76.99; H 12.26. **(Z)-2-((5-phenylpent-4-en-1-yl)oxy)tetrahydro-2H-pyran (4c).** R_f =0.72 (5:1 petroleum ether/ethyl acetate). NMR ^{1}H (400 MHz, $CDCl_3$) δ 7.39–7.23 (m, 5H), 6.52–6.48 (m, 1H), 5.77–5.70 (m, 1H), 4.60 (t, J = 6.7 Hz, 1H), 3.90–3.43 (m, 4H), 2.55–2.48 (m, 2H), 1.87–1.49 (m, 8H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 137.67, 132.30, 129.41, 128.81, 128.13, 126.53, 98.75, 66.75, 62.07, 30.76, 30.07, 25.59, 25.35, 19.57. MS (MALDI TOF) m/z 246.34 $[M]^+$. Calcd for $C_{16}H_{22}O_2$: C 78.01; H 9.00. Found: C 78.05; H 9.03.

(Z)-2-(henicos-4-en-1-yloxy)tetrahydro-2H-pyran (4d). R_f =0.71 (5:1 petroleum ether/ethyl acetate). NMR ^{1}H (400 MHz, $CDCl_3$) δ 5.40–5.33 (m, 2H), 4.58 (t, J = 6.7 Hz, 1H), 3.90–3.37 (m, 4H), 2.16–2.00 (m, 4H), 1.67–1.51 (m, 6H), 1.35–1.25 (m, 30H), 0.88 (t, J = 6.6 Hz, 3H). NMR ^{13}C (101 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.49, 128.93, 128.90, 98.76, 66.93, 62.17, 31.94, 30.76, 29.79, 29.71, 29.67, 29.58, 29.38, 29.35, 27.21, 25.53, 23.85, 22.69, 19.62, 14.08. MS (MALDI TOF) m/z 394.67 $[M]^+$. Calcd for $C_{26}H_{50}O_2$: C 79.10; H 12.78. Found: C 79.12; H 12.77.

Synthesis of cyclopropane-containing alcohols (5a-d). The reagent Et3Al (0.9 mL, 6 mmol) was added to a solution of **4a-d** (2 mmol) and CH_2I_2 (0.48 mL, 6 mmol) in CH_2Cl_2 (5 mL) at 0 °C under argon. The mixture was stirred at room temperature (~20 °C) for 6 h and diluted with CH_2Cl_2 (5 mL), then water (3 mL) was added dropwise with cooling in an ice—water bath. The mixture was extracted with diethyl ether (3×5 mL). The combined organic layers were dried with anhydrous $MgSO_4$ and concentrated on a rotary evaporator. The product was isolated by column chromatography (hexane—ethyl acetate, 20 : 1**). 3-(2-butylcyclopropyl)propan-1-ol (5a)**. R_f =0.42 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 3.60 (t, J = 6.6 Hz, 1H), 1.66–1.59 (m, 4H), 1.49–1.10 (m, 8H), 0.85 (t, J = 6.6 Hz, 3H), 0.64–0.60 (d, 2H), 0.57–0.53 (m, 1H), -0.35 (qw, J = 9.3 Hz, J = 4.9 Hz, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 62.52, 33.14, 32.36, 28.28, 24.91, 22.59, 15.74, 15.41, 14.03, 10.86. MS (MALDI TOF) m/z 156.27 $[M]^+$. Calcd for $C_{10}H_{20}O$: C 76.86; H 12.86. Found: C 76.81; H 12.88. **3-(2-nonylcyclopropyl)propan-1-ol (5b)**. R_f =0.41 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 3.74 (t, J = 6.6 Hz, 1H), 1.76–1.68 (m, 8H), 1.45–1.17 (m, 14H), 0.90 (t, J = 6.6 Hz, 3H), 0.76–0.71 (d, 2H), 0.67–0.63 (m, 1H), -0.22 (qw, *J* = 9.3 Hz, *J* = 4.9 Hz, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 63.55, 31.92, 31.77, 30.03, 29.30, 28.86, 22.68, 15.16, 14.10, 12.13, 10.57. MS (MALDI TOF) m/z 226.40 $[M]^+$. Calcd for $C_{15}H_{30}O$: C 79.58; H 13.36. Found: C 79.56; H 13.38. **3-(2-phenylcyclopropyl)propan-1-ol (5c).** R_f =0.40 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 7.39–7.19 (m, 5H), 3.51 (t, J = 6.6 Hz, 2H), 1.64–1.49 (m, 2H), 1.26–1.19 (m, 1H), 1.14–1.00 (m, 2H), 0.78–0.71 (d, 1H), 0.72 (qw, *J* = 9.3 Hz, *J* = 4.9 Hz, 2H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 139.41, 128.77, 127.92, 125.69, 62.49, 32.86, 24.95, 21.11, 18.85, 9.66. MS (MALDI TOF) m/z 176.25 $[M]^+$. Calcd for $C_{12}H_{16}O$: C 81.77; H 9.15. Found: C 81.78; H 9.14. **3-(2-hexadecylcyclopropyl)propan-1-ol (5d)**. R_f =0.41 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 3.66 (t, J = 6.6 Hz, 1H), 1.71–1.62 (m, 12H), 1.47–1.12 (m, 14H), 0.88 (t, J = 6.6 Hz, 3H), 0.71–0.69 (d, 2H), 0.65–0.57 (m, 1H), -0.29 (qw, J = 9.3 Hz, J = 4.9 Hz, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 62.70, 33.21, 31.94, 30.21, 29.76, 29.73, 29.68, 29.38, 28.68, 24.96, 22.68, 15.85, 15.46, 14.06, 10.95. MS (MALDI TOF) m/z 324.58 $[M]^+$. Calcd for $C_{22}H_{44}O$: C 79.58; H 13.36. Found: C 81.41; H 13.66.

Synthesis of cyclopropan-containing acid (6a-d). Cyclopropane-containing alcohols **(5a-d)** (1.76 mmol) was added to a solution of pyridinium dichromate (1.698 g, 4.48 mmol) in DMF (6.8 mL) at room temperature. The mixture was stirred for 6 h, followed by the addition of water (55 mL) and extraction with ethyl acetate (3×15 mL). The combined organic layers were dried with anhydrous $MgSO_4$ and concentrated on a rotary

evaporator. The product was isolated by column chromatography (hexane—ethyl acetate, 10 : 1) to obtain compound **6a-d** as a white oily liquid. **3-(2-butylcyclopropyl)propanoic acid (6a).** R_f =0.42 (**5**:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 2.48 (t, J = 7.6 Hz, 1H), 1.80–1.50 (m, 4H), 1.41–1.19 (m, 6H), 0.92 (t, J = 6.6 Hz, 3H), 0.75–0.62 (d, 2H), -0.22 (qw, *J* = 10.0 Hz, *J* = 5.2 Hz, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 179.95, 34.57, 32.36, 28.25, 24.13, 22.63, 15.97, 15.13, 14.12, 10.78. MS (MALDI TOF) m/z 170.25 $[M]^+$. Calcd for $C_{10}H_{18}O_2$: C 70.55; H 10.66. Found: C 70.57; H 10.68. **3-(2-nonylcyclopropyl)propanoic acid (6b).** R_f =0.41 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 2.48 (t, J = 7.6 Hz, 1H), 1.83–1.50 (m, 10H), 1.41–1.17 (m, 10H), 0.91 (t, J = 6.6 Hz, 3H), 0.76–0.61 (d, 2H), -0.23 (qw, *J* = 10.0 Hz, *J* = 5.2 Hz, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 180.02, 34.57, 31.93, 30.15, 29.71, 29.65, 29.36, 28.58, 24.12, 22.70, 16.00, 15.13, 14.12, 10.79. MS (MALDI TOF) m/z 240.38 $[M]^+$. Calcd for $C_{15}H_{28}O_2$: C 74.95; H 11.74. Found: C 74.92; H 11.73. **3-(2-phenylcyclopropyl)propanoic acid (6c).** R_f =0.40 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 7.32–7.20 (m, 5H), 2.32 (t, J = 7.6 Hz, 1H), 1.51–1.46 (m, 1H), 1.38–1.26 (m, 2H), 1.21–1.17 (m, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 179.79, 138.73, 128.97, 128.02, 125.88, 33.63, 23.94, 21.05, 18.12, 9.38. MS (MALDI TOF) m/z 190.24 $[M]^+$. Calcd for $C_{12}H_{14}O_2$: C 75.76; H 7.42. Found: C 75.78; H 7.40. **3-(2-hexadecylcyclopropyl)propanoic acid (6d).** R_f =0.41 (5:1 petroleum ether/ethyl acetate NMR ^{1}H (400 MHz, $CDCl_3$) δ 2.48 (t, J = 7.6 Hz, 1H), 1.87–1.74 (m, 12H), 1.42–1.18 (m, 20H), 0.91 (t, J = 6.6 Hz, 3H), 0.77–0.64 (d, 2H), -0.23 (qw, J = 10.0 Hz, J = 5.2 Hz, 1H). NMR ^{13}C (101 MHz, $CDCl_3$) δ 180.59, 31.96, 30.18, 29.74, 29.70, 29.66, 29.40, 28.60, 24.12, 22.72, 16.01, 15.14, 14.11, 10.79. MS (MALDI TOF) m/z 338.57 $[M]^+$. Calcd for $C_{22}H_{42}O_2$: C 74.95; H 11.74. Found: C 78.05; H 12.50.

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