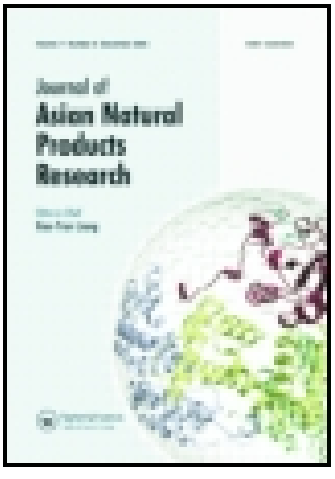

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Concise stereoselective total synthesis of (+)-muricatacin and (+)-epi-muricatacin

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Concise stereoselective total synthesis of (+)-muricatacin and (+)-*epi*-muricatacin

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Efficient stereoselective total synthesis of (+)-muricatacin (**1**) and (+)-*epi*-muricatacin (**8**) was accomplished from commercially available chemical pent-4-ynoic acid via Shi's asymmetric epoxidation and Mitsunobu reaction as the key steps in 17.8% and 26.9% overall yields, respectively.

Keywords: (+)-muricatacin; (+)-*epi*-muricatacin; total synthesis; asymmetric epoxidation

1. Introduction

Muricatacin is a natural product which was first isolated in 1991 from the seeds of *Annona muricata* and identified as a scalemic mixture of (4*S*, 5*S*) (**1**) and (4*R*, 5*R*) isomers [1]. Structurally, it belongs to γ-lactones family which were found to display a wide range of biological properties such as immunosuppressant, antimalarial, insecticidal activities [2], as well as cytotoxicities against various types of human cancer cells [3,4]. Some of these biologically active natural γ-lactones are depicted in Figure 1. Because of its simple structure and potent biological activity, muricatacin has garnered much attention from the synthetic community. Several groups have reported the total synthesis of the natural (+)/(−)-muricatacin and also their unnatural epimers (+)/(−)-*epi*-muricatacin, respectively [5–7]. Most of them introduced the chiral center to the molecule from the chiral pools such as tri-*O*-acetyl-D-glucal [8], D-(−)-lyxose [9], L-(+)-tartaric acid [10], D-mannitol [11], and D-ribose [12]. However, the short and more efficient synthetic approaches with high overall yields are still required.

Shi's asymmetric epoxidation is an efficient way to introduce two chiral centers at the same time, which have provided a new protocol for obtaining chiral compounds in an environmentally benign manner [13]. To the best of our knowledge, the application of Shi's asymmetric epoxidation in the synthesis of natural and unnatural muricatacin isomers and the other analogs have not been reported. So herein, we report an asymmetric total synthesis of (+)-muricatacin as well as (+)-*epi*-muricatacin via Shi's asymmetric epoxidation and Mitsunobu reaction as the key steps in very efficient synthetic routes and high overall yields. The synthetic sequence was simple, cheap, and was amenable for the synthesis of a number of lactones.

2. Results and discussion

The synthesis of (+)-muricatacin **1** first involved the preparation of the fatty acid **3**. Heptadec-4-ynoic acid **3** can be prepared in four steps (including THP protection, coupling to 1-iodotridecane, methanolysis of the THP ether, and Jones's oxidation)

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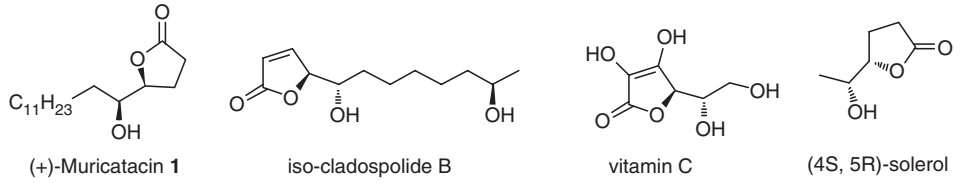
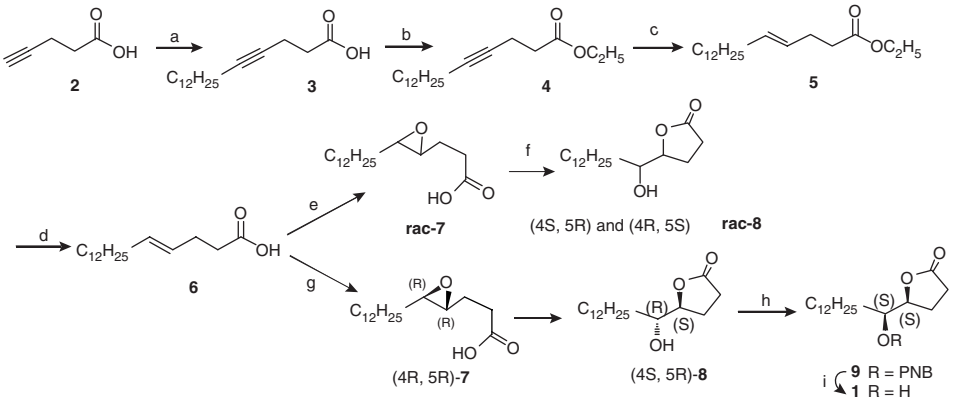


Figure 1. Some natural products containing γ-lactones.

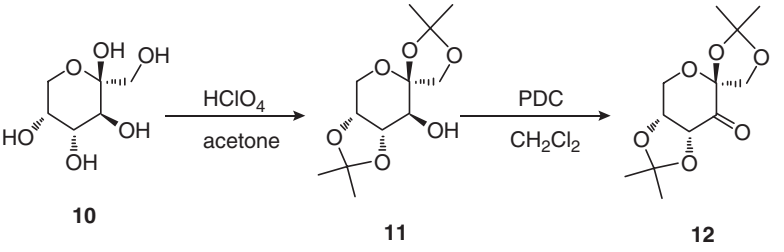
from pent-4-yn-1-ol according to the procedure in the literature [14]. In an effort to obtain fatty acid **3** in minimum steps and higher yield, we deprotoned the terminal alkyne of commercial available acid **2** with *n*-BuLi in the solvents of tetrahydrogenfuran/hexamethylphosphoramide (THF/HMPA), then it was subsequently coupled to bromododecane to generate the internal alkyne acid **3** in a satisfactory yield (77%) (Scheme 1). Ethyl ester **4**, which was obtained in 96% yield by esterification of alkyne acid **3** in the presence of sulfuric acid, was luckily reduced by the solution of red-Al at −40°C to afford *E*-olefin **5** without ester reduction in a moderate yield (63%) [15].

Then, compound **5** was hydrolyzed by NaOH to afford acid **6**. With the key intermediate **6** in hand, as a part of our continuing efforts to synthesize lactones with our own methodology [16,17], reaction of acid **6** with peroxyacetic acid in the presence of Na_2CO_3 gave epoxy acid ***rac*-7**, which could automatically cyclize to afford *erythro*-isomer of muricatacin in the presence of catalytic quantity of (+)-camphorsulfonic acid. In an effort to extend the application of the above procedure, we chose the Shi's asymmetric epoxidation procedure for the enantioselective conversion of trans-alkenoic acid **6** to (+)-*epi*-muricatacin (4*S*, 5*R*)-**8** via epoxide (4*R*, 5*R*)-**7** [18].

The catalyst ketone **12** was readily prepared following the original route from D-fructose **10** which is shown in Scheme 2 [19]. Then applying the model offered by Shi to our system (Figure 2), we anticipated to approach the site of the



Scheme 1. Synthetic route of (+)-muricatacin (**1**) and (+)-*epi*-muricatacin (**8**). Reagents and conditions: (a) (i) *n*-BuLi, THF/HMPA, −78°C to 0°C, 2 h; (ii) bromododecane, −78°C to r.t., 15 h, 77%. (b) CH_3CH_2OH, H_2SO_4, reflux, 5 h, 96%. (c) red-Al, −40°C, THF, 63%. (d) NaOH, C_2H_5OH/H_2O, 60°C, 2.5 h, 74%. (e) Peracetic acid, r.t., 1.5 h. (f) CSA, r.t., 4 h, 68% for two steps. (g) $Na_2B_4O_7$, Na_2(EDTA), Bu_4NHSO_4, ketone **12**, CH_3CN, r.t., 12 h, 78% for two steps. (h) Ph_3P, DEAD, PNBA, THF, r.t., 4 h, 78%. (i) K_2CO_3, CH_3OH, r.t., 30 min, 85%.



Scheme 2. Synthesis of catalyst **12**. Reagents and conditions: (a) perchloric acid, acetone, 0°C, 53%. (b) PCC, CH_2Cl_2, r.t., 93%.

dioxirane catalyst from the bottom face of compound **6**. Following olefin epoxidation, cyclization of the corresponding carboxylate onto the resulting epoxide from the other side (S_N2 displacement) was thought likely to occur *in situ* under that basic conditions, to yield *(+)-epi*-muricatacin (4*S*, 5*R*)-**8** [20,21].

The application of common Shi epoxidation conditions, which involved 0.3 equiv. of catalyst **12** and 0.04 equiv. of Bu_4NHSO_4 in $CH_3CN–H_2O$ system, then warmed to room temperature, and it could only provide compound (4*S*, 5*R*)-**8** with low enantioselectivity [e.e. 57.7%, the e.e. value was determined by chiral HPLC (Chiralpak AD column) of the *p*-nitrobenzoate derivative]. We proposed that the low enantioselectivity was due to significant water solubility of the carboxylic acid substrate **6** at the high pH (pH 10) required for efficient oxidation of **12** by Oxone, resulting in direct epoxidation by Oxone representing the major oxidation pathway.

In an effort to improve the enantioselectivity of the above procedure, we increased the amount of Shi catalyst **12** and phase-transfer catalyst (Bu_4NHSO_4) (Table 1). Gratifyingly, Shi epoxidation of **6** using improved conditions, followed by warming the system to room temperature and stirred overnight, afforded (+)-*epi*-muricatacin (4*S*, 5*R*)-**8** in 78% yield and 96.2% enantioselectivity.

The C-5 configuration of compound (4*S*, 5*R*)-**8** was inversed in the typical Mitsunobu reaction condition to afford the (4*S*, 5*S*)-lactone *p*-nitrobenzoate **9** in 90% yield, then hydrolysis of the esters (4*S*, 5*S*)-lactone *p*-nitrobenzoates **9** with K_2CO_3 in MeOH produced the (4*S*, 5*S*)-lactone **1** in 85% yield with high optical purity [22]. All of these compounds were characterized by ^{1}H NMR, ^{13}C NMR, and HR-MS data.

It had been reported that the biological activity of this natural product was affected by the side chain [23]. Therefore, various analogs of muricatacin might be synthesized through this approach by using different intermediate olefin. Further application of this strategy for the synthesis of a number of bio-active lactones is in progress in our laboratory.

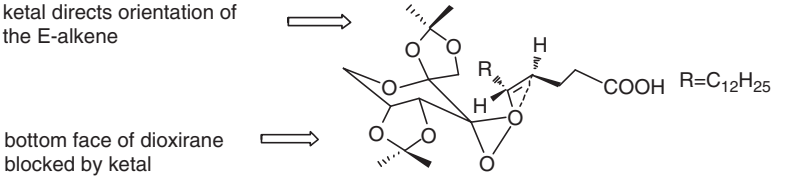


Figure 2. Shi's model.

Table 1. Optimization of preparation (4*S*, 5*R*)-**8** through (4*R*, 5*R*)-**7** via Shi's asymmetric epoxidation of **6**.

Entry	The molar ratio of **6**:**12**:Bu_4NHSO_4	Yield %	$[\alpha]_D^{25}$	e.e.% of **8**
1	1:0.3:0.04	70	+9.6°	57.7
2	1:1:0.1	78	+15.1°	96.2

3. Experimental

3.1 General experimental procedures

Melting points were measured on a Yanagimoto apparatus (Yanagimoto MFG Co., Kyoto, Japan) and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brüker DPX 300 NMR Spectrometer (Brüker Biospin Co., Stuttgart, Germany) with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. HR-MS were obtained on a Brüker Apex II mass spectrometer (Brüker Co., Bremen, Germany) using nitrobenzoyl alcohol and sodium chloride as matrices. The solvents were analytical grade and newly distilled before usage.

3.2 General procedures for the synthetic compounds

3.2.1 Heptadec-4-ynoic acid 3

n-BuLi (36 ml of 2.5 M solution in hexanes, 90 mmol) was added dropwise with stirring to a −78°C solution of pent-4-ynoic acid **2** (3.0 g, 30 mmol) in (THF/HMPA 2:1, 150 ml) under an argon atmosphere. After 30 min, the reaction mixture was warmed to 0°C and maintained at this temperature for 2 h. After cooling to −78°C, a solution of 1-bromododecane (9.4 ml, 39 mmol) in THF (10 ml) was added and the reaction temperature was slowly raised to 25°C over 3 h. After 12 h, the reaction mixture was quenched with saturated NH_4Cl solution (5 ml) and the pH was adjusted to 3 using 3 M HCl. The mixture was extracted with EtOAc, and the combined extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (petroleum ether–EtOAc; 5:1; v/v) to give a white solid **3**, m.p. 61–63°C (6.1 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.58–2.47 (m, 4H), 2.12 (t, $J = 6.3$ Hz, 2H), 1.48–1.26 (m, 20H), 0.88 (t, $J = 6.2$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 178.4, 81.4, 76.6, 34.0, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 28.9, 28.8, 22.7, 18.6, 14.5, 14.1. HR-ESI-MS: m/z 289.2145 $[M + Na]^+$ (calcd for $C_{17}H_{30}O_2Na$, 289.2138).

3.2.2 Ethyl heptadec-4-ynoate 4

Heptadec-4-ynoic acid **3** (3.3 g, 12.4 mmol) was dissolved in methanol (60 ml), and 0.5 ml of concentrated H_2SO_4 was added. After 5 h at reflux temperature, the solvent was evaporated, and the residue was purified by silica gel column chromatography (petroleum ether–EtOAc; 100:1; v/v) to give **4** (3.5 g, 96%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.15 (q, $J = 7.1$ Hz, 2H), 2.49–2.46 (m, 4H), 2.13–2.09 (m, 2H), 1.48–1.23 (m, 25H), 0.88 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 172.1, 81.1, 76.6, 60.4, 34.2, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 28.9, 28.8, 22.6, 16.6, 14.8, 14.2, 14.0. HR-ESI-MS: m/z 317.2451 $[M + Na]^+$ (calcd for $C_{19}H_{34}O_2Na$, 317.2451).

3.2.3 (E)-Ethyl heptadec-4-enoate 5

To a solution of ethyl heptadec-4-ynoate **4** (1.47 g, 5 mmol) in dry diethyl ether was carefully added the solution of Red-Al (1.5 ml, 5 mmol, 3.33 mol/l in toluene) at −40°C. The solution was stirred for 30 min at −40°C and then slowly warmed to −20°C over 3 h. Then, 2 M HCl was

added. The resulting mixture was diluted with diethyl ether and then washed with $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4. After filtration and concentration, the residue was purified by silica gel chromatography (petroleum ether–EtOAc; 100:1; v/v) to give **5** (0.93 g, 63%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 5.49–5.38 (m, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 2.37–2.27 (m, 4H), 1.99–1.92 (m, 2H), 1.30–1.22 (m, 23H), 0.88 (t, $J = 6.7$ Hz, 3H), which was identical to that in the literature [24].

3.2.4 *(E)-Heptadec-4-enoic acid* ***6***

To a solution of compound **5** (0.889 g, 3 mmol) in 10 ml CH_3CH_2OH was added 3 M NaOH (10 ml). After being stirred for 2.5 h at 60°C, the reaction mixture was diluted with water and extracted with ether. The aqueous layer was acidified with concentrated HCl to pH 2 and extracted with ethyl acetate. The organic phase was combined, dried with Na_2SO_4, filtered, and concentrated to give the pure acid **6** (0.59 g, 74%) as a white solid, m.p. 56.4–57.2°C. ^{1}H NMR ($CDCl_3$) δ: 3.51–5.36 (m, 2H), 5.43–2.28 (m, 4H), 1.96 (t, $J = 6.4$ Hz, 2H), 1.25 (br, 20H), 0.88 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 179.5, 132.2, 127.5, 34.2, 32.5, 31.9, 29.7, 29.6 (3 × C), 29.5, 29.4 (2 × C), 29.1, 27.6, 22.7, 14.1. HR-ESI-MS: *m/z* 291.2295 $[M + Na]^+$ (calcd for $C_{17}H_{32}O_2Na$, 291.2295).

3.2.5 *The mixture of (4*S*, 5*R*) and (4*R*, 5*S*)-lactone* **rac-*8***

To a solution of the acid **6** (0.59 g, 2.1 mmol) in CH_2Cl_2 (15 ml) was added the peracetic acid solution (6.3 ml; 3 × 2.1 ml) and anhydrous Na_2CO_3 (2.1 g; 3 × 0.7 g). The reaction mixture was stirred for 1.5 h at room temperature. After the reaction was finished as detected by TLC, the mixture was diluted with saturated $Na_2S_2O_3$ (10 ml) and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo* to give a white solid ***rac*-7**. Then the product ***rac*-7** was dissolved in CH_2Cl_2 (20 ml), and 0.03 g of camphorsulfonic acid was added. The mixture was stirred for 4 h at room temperature. After the reaction was finished, the organic phase was washed with 5% Na_2CO_3 solution and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether–EtOAc; 3:1; v/v) to afford the mixture of (4*S*, 5*R*) and (4*R*, 5*S*)-lactone *rac*-**8** as a white solid, m.p. 70.4–71.4°C. ^{1}H NMR ($CDCl_3$) δ: 4.46–4.40 (m, 1H), 3.93 (br, 1H), 2.64–2.45 (m, 2H), 2.30–2.12 (m, 2H), 1.97 (d, $J = 3.3$ Hz, 1H), 1.52–1.26 (m, 22H), 0.88 (t, $J = 6.7$ Hz, 3H), which was identical to that in the literature [25].

3.2.6 *(+)-epi-Muricatacin* ***8*** *[(4*S*, 5*R*)-lactone]*

To a 100-ml three-neck round-bottom flask were added buffer (0.05 M $Na_2B_4O_7 \cdot 10H_2O$ in 4×10^{-4} M aqueous Na_2(EDTA) (20 ml), acetonitrile (30 ml), (*E*)-heptadec-4-enoic acid **6** (0.54 g, 2 mmol), tetrabutylammonium hydrogen sulfate (0.075 g, 0.2 mmol), and ketone **12** (0.5 g, 2 mmol). The reaction mixture was cooled with an ice bath. A solution of Oxone (1.7 g, 2.76 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M 13 ml) and a solution of K_2CO_3 (1.6 g, 11.6 mmol) in water (13 ml) were added dropwise through two separate addition funnels over a period of 3 h. Then the epoxidation reaction mixture was allowed to warm to room temperature and stirred over 12 h. Then, the mixture was extracted with EtOAc (3 ml × 30 ml), washed with 5% Na_2CO_3 and brine, dried over Na_2SO_4. The organic phase was concentrated and purified by flash chromatography eluting with petroleum ether–EtOAc (6:1) to give a white solid, which was recrystallized from hexane to get (+)-

epi-muricatacin (4*S*, 5*R*)-**8** as a colorless needle crystal (0.44 g, 78%), m.p. 70.0–70.8°C, $[\alpha]_D^{25}$ + 15.1 (c = 1.2, $CHCl_3$). {lit.[12] m.p. 71–73°C, $[\alpha]_D^{25}$ + 16.6 (c = 0.78, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$) δ: 4.46–4.41 (m, 1H), 3.93 (br, 1H), 2.61–2.51 (m, 2H), 2.30–2.12 (m, 2H), 1.96 (d, J = 3.4 Hz, 1H), 1.55–1.26 (m, 22H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 177.5, 82.8, 71.4, 31.9 (2 × C), 29.6 (2 × C), 29.5 (3 × C), 29.3, 28.7, 25.6, 22.6, 21.1, 14.1. HR-ESI-MS: *m/z* 307.2245 $[M + Na]^+$ (calcd for $C_{17}H_{32}O_3Na$, 307.2244).

3.2.7 (4S, 5S)-Lactone 4-nitrobenzoate **9**

Under the atmosphere of nitrogen, 25 ml of dry THF was added into a 50-ml round-bottom flask. It was cooled to 0°C, and then triphenylphosphine (1.05 g, 4 mmol) and diethyl azodicarboxylate (DEAD, 0.59 g, 4 mmol) were added, followed by (4*S*, 5*R*)-**8** (0.28 g, 1 mmol) and *p*-nitrobenzoic acid (0.20 g, 1.2 mmol). The mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (10:1 to 5:1 (v/v) petroleum ether–EtOAc) to afford 0.35 g (81% yield) of (4*S*, 5*S*)-lactone 4-nitrobenzoate compound **9** as a light yellow oil. ^{1}H NMR ($CDCl_3$) δ: 8.33–8.28 (m, 2H), 8.24–8.19 (m, 2H), 5.35–5.29 (m, 1H), 4.80–4.74 (m, 1H), 2.59–2.40 (m, 3H), 2.10–2.05 (m, 1H), 1.87–1.80 (m, 2H), 1.43–1.23 (m, 20H), 0.86 (t, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 176.2, 163.9, 150.5, 134.8, 130.7, 123.4, 79.7, 76.0, 31.6, 30.4, 29.4 (2 × C), 29.3, 29.2, 29.1 (2 × C), 27.9, 24.9, 23.9, 22.4, 13.8. HR-ESI-MS: *m/z* 456.2360 $[M + Na]^+$ (calcd for $C_{24}H_{35}NO_6Na$, 456.2362).

3.2.8 (+)-Muricatacin **1**

Here, 15 ml of CH_3OH, K_2CO_3 (0.35 g, 2.5 mmol) and compound **9** (0.22 g, 0.5 mmol) were added into a 50-ml round-bottom flask. The mixture was stirred for 30 min at room temperature and then filtered. The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel (4:1 (v/v) hexanes/EtOAc) to afford 0.24 g of (+)-muricatacin **1** in 85% yield as a white solid, m.p. 67.8–68.8°C, $[\alpha]_D^{25}$ + 23.2 (c = 0.24, $CHCl_3$). {lit.[12] m.p. 68–70°C, $[\alpha]_D^{25}$ + 22.4 (c = 0.42, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$) δ: 4.44–4.38 (m, 1H), 3.59–3.55 (m, 1H), 2.63–2.47 (m, 2H), 2.26–2.09 (m, 2H), 1.84 (d, J = 6.0 Hz, 1H), 1.56–1.26 (m, 22H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 177.1, 82.9, 73.6, 33.0, 31.9, 29.6 (2 × C), 29.5 (2 × C), 29.3, 28.7, 25.4, 24.7, 22.7, 14.1. HR-ESI-MS: *m/z* 307.2246 $[M + Na]^+$ (calcd for $C_{17}H_{32}O_3Na$, 307.2244).

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