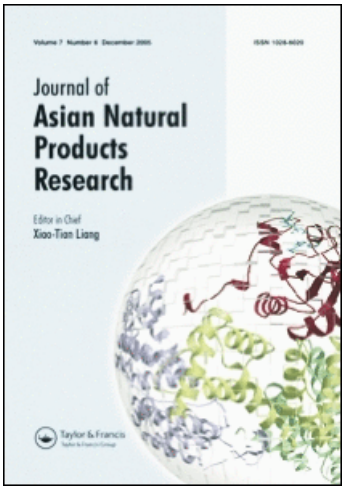

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Total synthesis of (+)-conagenin

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A new approach for the synthesis of the (+)-conagenin has been achieved based on Evans asymmetry *syn*-aldol reaction and the self-regeneration of stereocenters strategy.

Keywords: conagenin; low-molecular-weight immunomodulator; Evans *syn*-aldol reaction

1. Introduction

(+)-Conagenin (**1**), isolated from the fermentation broth of *Streptomyces roseosporus* MI696-AF3 in 1991, exhibits specific action on T cells without activation of macrophages [1]. Conagenin can improve the antitumor efficacy of adriamycin and mitomycin C against murine leukemias and reduce their toxicity [2]. These suggest its potential utility for cancer chemotherapy. Although (+)-conagenin has been obtained by total synthesis [3], the known synthesis is too complex or costly to provide an inexpensive supply. We have, therefore, embanked on research to develop a new facile synthetic route to it. Reported herein is a practical synthesis of (+)-conagenin based on Evans asymmetry *syn*-aldol reaction and the self-regeneration of stereocenters (SRS) strategy.

2. Results and discussion

Disconnection of the amide bond in (+)-conagenin (**1**) reveals the (2*R*,3*S*,4*R*)-2,4-dihydroxy-3-methylpentanoic acid and (*S*)-methylserine, as outlined in Scheme 1, where the use of Evans asymmetry *syn*-aldol reaction and asymmetry reduction would enable installation of the C2–C4 stereotetrad. The (*S*)-methylserine moiety present in **1** might then be prepared by using the Seebach's 'SRS' protocol.

We prepared the (2*R*,3*S*,4*R*)-2,4-dihydroxy-3-methylpentanoic acid via aldol reaction using an oxazolidinethione auxiliary, the reaction was carried out with Crimmins condition [6]. Condensation of (4*S*)-4-benzyl-1,3-oxazolidine-2-thione and propionyl chloride [4] gave thione **2** in 80% yield. Treatment of **2** with benzaldehyde in the presence of $TiCl_4$/diisopropylethylamine [5] produced compound **3** in 50% yield, and then transamination to the Weinreb's amide **4** occurred by exposure of **3** to N,O-dimethylhydroxylamine hydrochloride and imidazole in dry CH_2Cl_2 [6] in 75% yield, Weinreb's amide **4** was reacted with CH_3MgCl in dry THF [7] to give compound **5** in 79.4% yield. Diol **6** was obtained by reduction of **5** with $NaBH_4$ in the presence of Et_3B in dry THF and methanol [8] in 75% yield. After acylation of diol **6** [3c], then oxidation of the product **7** with periodic acid catalyzed

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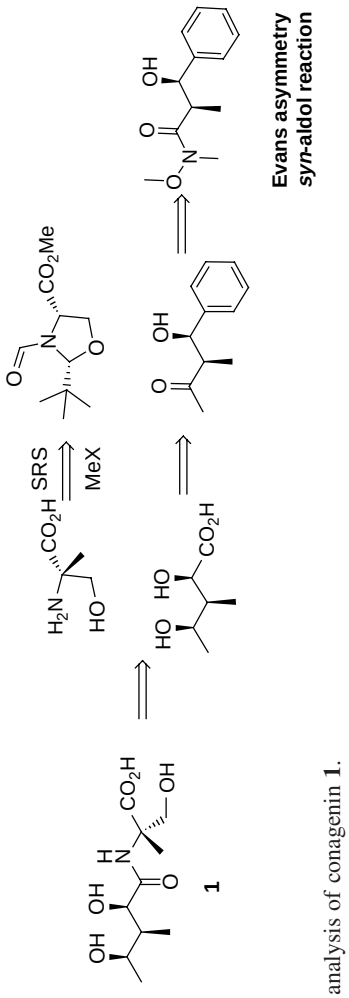


Scheme 1. Retrosynthetic analysis of conagenin **1**.

by $RuCl_3{\cdot}nH_2O$ [3c], acid **8** was provided in 60% yield (two steps) (Scheme 2).

The (*S*)-methylserine moiety was synthesized according to the literature with slight modification; the reaction of (*S*)-serine methyl ester hydrochloride with pivaldehyde gave oxazolidine **9** [10], and subsequent *N*-formylation of **9** using sodium formate and formic acid provided compound **10** [11]. To a mixture of **10** in THF/hexane/DMPU (6:1:1), dropwise addition of NaHMDS at -78°C led to compound **11**. Formyl group was removed using a saturated HCl methanol solution, and then treatment with aqueous 3 M HCl in THF produced (*S*)-α-methylserine methyl ester **12** ([9]; Scheme 3).

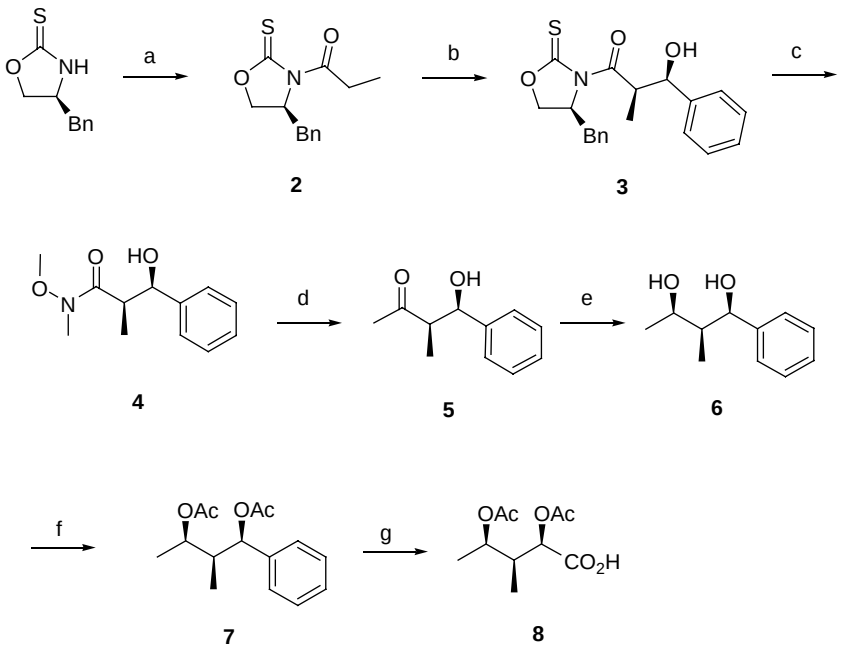
Finally, condensation of acid **8** and (*S*)-α-methylserine methyl ester **12** with DCC, HOBt, and DMAP in DMF gave amide **13**. De-protection of **13** with 1 M K_2CO_3 in methanol afforded (+)-conagenin (**1**) ([3g]; Scheme 4). The synthetic compound was spectroscopically in good agreement with the natural and synthetic (+)-conagenin.

In conclusion, we have developed an efficient method for the synthesis of the (+)-conagenin. The key features in this strategy were based on Evans asymmetry *syn*-aldol reaction.

3. Experimental

3.1 General experimental procedures

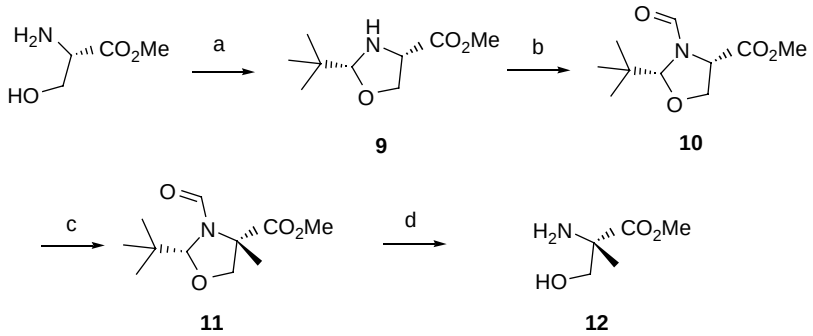
Melting points were determined with a Yanaco micrometer and are uncorrected. The NMR spectra were taken on a Mercury-300 spectrometer with TMS as the internal reference. ESI-MS were obtained on Agilent LC/MSD TOF. The optical rotations were recorded on a Perkin-Elmer 241 polarimeter. Column chromatography was performed on silica gel (160–200 mesh; Qingdao Haiyang Chemical Co., Ltd, Qingdao, China). CH_2Cl_2 was distilled from P_2O_5; THF was distilled from sodium benzophenone ketyl.



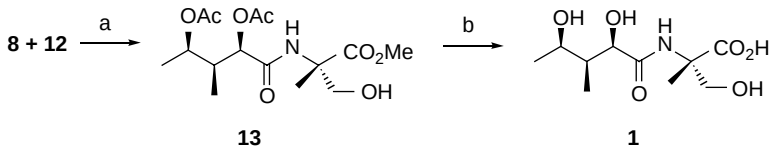
Scheme 2. Synthesis of compound **8**. Reagents and conditions: (a) propionyl chloride, Et_3N, dry CH_2Cl_2, 0°C; (b) benzaldehyde, titanium tetrachloride, diisopropylethylamine, dry CH_2Cl_2, −78°C; (c) N,O-dimethylhydroxylamine hydrochloride, imidazole, dry CH_2Cl_2; (d) CH_3MgCl, dry THF; (e) Et_3B, $NaBH_4$, THF, CH_3OH, −78°C; (f) pyridine, Ac_2O, DMAP; and (g) H_5IO_6, $RuCl_3{\cdot}nH_2O$, $CCl_4/CH_3CN/H_2O$.

3.2 (S)-3-(1-Oxopropyl)-4-benzyl-1,3-oxazolidine-2-thione (2)

To a cooled (0°C) solution of (4*S*)-benzyl-1,3-oxazolidine-2-thione (6.0 g, 31 mmol) and triethylamine (21.6 ml, 155 mmol) in dry CH_2Cl_2 (60 ml) was added propionyl-chloride (5.43 ml, 62 mmol), and then stirred at room temperature for 2 h; the reaction solution was filtered and the solution was washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of solvent and purification



Scheme 3. Synthesis of (*S*)-α-methylserine methyl ester **12**. Reagents and conditions: (a) pivaldehyde, Et_3N, *n*-pentane, reflux; (b) sodium formate, formic acid, Ac_2O, rt; (c) NaHMDS, CH_3I, THF/hexane/DMPU (6:1:1), −78°C; and (d) saturated HCl methanol, rt, then 3 M HCl, THF.



Scheme 4. Synthesis of (+)-conagenin **1**. Reagents and conditions: (a) DCC, HOBt, DMAP, DMF, rt and (b) 1 M K_2CO_3, methanol, rt.

by column chromatography (silica gel; PE/EtOAc, 8/1), thione **2** was obtained as a white solid (6.2 g, 80%); mp 85–86°C; $[\alpha]_D^{18}$ + 125.9 (c = 0.72, $CHCl_3$) (lit. [12], $[\alpha]_D^{20}$ + 122 (c = 1.0, $CHCl_3$)); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.23–7.39 (m, 5H, ArH), 4.96 (m, 1H, 4-H), 4.33 (m, 2H, 5-H), 3.44 (m, 1H, —C*H*HPh), 3.27 (m, 2H, CH_2CO), 2.79 (dd, J = 10.2, 13.2 Hz, 1H, —CH*H*Ph), 1.25 (t, J = 7.2 Hz, 3H, CH_3); ESI-MS: m/z 272 $[M+Na]^+$, 194, 178, 117, 91, 69; HR-ESI-MS: m/z 272.0721 $[M+Na]^+$ (calcd for $C_{13}H_{15}NO_2SNa$, 272.0716).

3.3 (4S)-3-[(2R,3R)-3-Hydroxy-2-methyl-1-oxo-3-phenylpropyl]-4-benzyl-1,3-oxazolidine-2-thione (3)

A solution of thione **2** (3.5 g, 14 mmol) in dry CH_2Cl_2 (84 ml) was cooled to 0°C under nitrogen. Then titanium tetrachloride (3.08 ml, 28 mmol) was added dropwise to the above solution. After the mixture was stirred for 5 min, diisopropylethylamine (2.7 ml, 15.4 mmol) was added and the resulted dark red solution was stirred for 20 min at 0°C, then cooled to −78°C, the fresh distilled benzaldehyde (1.57 ml, 15.5 mmol) was added. The solution was stirred for 1 h at −78°C and 3 h at 0°C and the reaction mixture was quenched with NH_4Cl solution. The organic layers were separated and washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel; PE/EtOAc, 10/1) to afford thione **3** as a white solid (2.5 g, 50%); mp 137–138°C; $[\alpha]_D^{18}$ + 136.4 (c = 1.0, CH_2Cl_2) (lit. [4], $[\alpha]_D^{24}$ + 137.4 (c = 1.0, CH_2Cl_2)); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.17–7.48 (m, 10H, ArH), 5.35 (m, 1H, PhCH), 4.97 (m, 1H, 4-H), 4.85 (d, J = 8.1 Hz, 1H, OH), 4.30 (m, 2H, 5-H), 3.60 (br, 1H, CHCO), 3.18 (dd, J = 3.0, 13.2 Hz, 1H, —C*H*HPh), 2.69 (dd, J = 9.6, 13.2 Hz, 1H, —CH*H*Ph), 1.12 (d, J = 6.6 Hz, 3H, CH_3); ESI-MS: m/z 378 $[M+Na]^+$, 338, 194, 145, 117, 91; HR-ESI-MS: m/z 378.1149 $[M+Na]^+$ (calcd for $C_{20}H_{21}NO_3SNa$, 378.1140).

3.4 (2R,3R)-3-Hydroxy-N-methoxy-2,N-dimethyl-3-phenyl-propionamide (4)

To a solution of thione **3** (1.5 g, 4.2 mmol) in dry CH_2Cl_2 (20 ml) were added N,O-dimethylhydroxylamine hydrochloride (474 mg, 4.86 mmol) and imidazole (639 mg, 9.40 mmol). After refluxing for 10 h, the reaction mixture was diluted with CH_2Cl_2 (50 ml). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel; PE/EtOAc, 8/1) to afford Weinreb's amide **4** as a white solid (705 mg, 75%); mp 46–47°C; $[\alpha]_D^{18}$ − 9.4 (c = 0.93, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.15–7.24 (m, 5H, ArH), 5.99 (d, J = 2.4 Hz, 1H, PhCH), 3.57 (s, 3H, OCH_3), 3.10 (s, 3H, NCH_3), 3.03 (br, 1H, CHCO), 0.97 (d, J = 7.2 Hz, 3H, CH_3); ESI-MS: m/z 246 $[M+Na]^+$, 206, 194, 150; HR-ESI-MS: m/z 246.1097 $[M+Na]^+$ (calcd for $C_{12}H_{17}NO_3Na$, 246.1106).

3.5 [3R,4R]-(+)-4-Hydroxy-3-methyl-4-phenyl-2-butanone (5)

A solution of Weinreb's amide **4** (990 mg, 4.44 mmol) in dry THF (12 ml) was cooled to 0°C under nitrogen. Then 22% wt CH_3MgCl in dry THF (6.8 ml, 20.4 mmol) was added dropwise. The mixture was stirred for 10 h, then quenched with half saturated aqueous NH_4Cl solution. The organic layers were separated, and the aqueous layer was extracted with EtOAc (2×25 ml). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel; PE/EtOAc, 10/1) to afford compound butanone **5** as a colorless oil (627 mg, 79.4%). $[\alpha]_D^{20} + 51.9$ ($c = 0.75$, $CHCl_3$) (lit. [3f], $[\alpha]_D^{27} + 51$ ($c = 0.95$, $CHCl_3$)); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.29–7.38 (m, 5H, ArH), 5.12 (s, 1H, PhCH), 2.99 (s, 1H, OH), 2.84 (m, 1H, CHCO), 2.16 (s, 3H, CH_3CO), 1.09 (d, $J = 7.2$ Hz, 3H, CH_3); HR-ESI-MS: *m/z* 201.0889 $[M+Na]^+$ (calcd for $C_{11}H_{14}O_2Na$, 201.0891).

3.6 (1R,2S,3R)-(−)-2-Methyl-1-phenyl-1,3-butanediol (6)

To a solution of butanone **5** (200 mg, 1.12 mmol) in dry THF (3 ml) and dry methanol (1.5 ml) under nitrogen was added 1 M Et_3B (1.23 ml, 1.23 mmol) at −78°C. After stirring for 1.5 h, $NaBH_4$ (64 mg, 1.68 mmol) was added and stirred for 3 h at −78°C, then quenched with HOAc (0.3 ml) at −10°C, then stirred for 10 min at room temperature. The reaction mixture was concentrated *in vacuo*. The resulted residue was dissolved with EtOAc, and washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel; PE/EtOAc, 10/1) to afford diol **6** as a colorless oil (705 mg, 75%). $[\alpha]_D^{20} + 38.3$ ($c = 1.43$, $CHCl_3$) (lit. [3c], $[\alpha]_D^{18} + 41$ ($c = 1.05$, $CHCl_3$)); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.14–7.28 (m, 5H, ArH), 4.92 (d, $J = 2.7$ Hz, 1H, PhCH), 4.14 (m, 1H, CHOH), 3.00 (s, 1H, OH), 1.60 (m, 1H, $CHCH_3$), 1.12 (d, $J = 6.3$ Hz, 3H, CH_3), 0.72 (d, $J = 7.2$ Hz, 3H, CH_3); ESI-MS: *m/z* 246 $[M+Na]^+$, 203, 119, 91; HR-ESI-MS: *m/z* 203.1039 $[M+Na]^+$ (calcd for $C_{11}H_{16}O_2Na$, 203.1048).

3.7 (2R,3S,4R)-2,4-Di(acetyloxy)-3-methylpentanoic acid (8)

To a solution of diol **6** (180 mg, 1.0 mmol) in pyridine (1.7 ml) and Ac_2O (1.7 ml) was added DMAP (3.4 mg, 0.27 mmol). After stirring for 2 h at room temperature, the mixture was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel; PE/EtOAc, 10/1) to afford acetate **7** as a colorless oil (210 mg). To a solution of acetate **7** (210 mg, 0.8 mmol) and $RuCl_3 \cdot nH_2O$ in $CCl_4/CH_3CN/H_2O$ (2 ml/2 ml/3 ml), periodic acid (3.3 g, 14.5 mmol) was added. After stirring for 24 h at room temperature, 2-propanol (1.8 ml) was added and stirred for 30 min. CH_2Cl_2 (37 ml) and H_2O (18 ml) were added. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3× 20 ml). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel; $CHCl_3/CH_3OH$, 20/1) to afford acid **8** as a colorless oil (140 mg, 60% two steps). $[\alpha]_D^{18} + 3.1$ ($c = 0.48$, $CHCl_3$) (lit. [3g], $[\alpha]_D^{15} + 1.5$ ($c = 0.5$, $CHCl_3$)); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 5.15 (d, $J = 3.3$ Hz, 1H, $CHCO_2H$), 4.96 (m, 1H, CHOH), 2.30 (m, 1H, CH), 2.15 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 1.24 (d, $J = 6.0$ Hz, 3H, CH_3), 1.07 (d, $J = 6.6$ Hz, 3H, CH_3); ESI-MS: *m/z* 255 $[M+Na]^+$, 195, 173, 145, 131, 113, 98, 74, 61; HR-ESI-MS: *m/z* 255.0856 $[M+Na]^+$ (calcd for $C_{10}H_{16}O_6Na$, 255.0845).

3.8 The synthesis of compound 12 from (S)-serine methyl ester hydrochloride has been reported in the literature [9]

3.9 Methyl (S)-2-((2R,3S,4R)-2,4-diacetoxy-3-methylpentanoylamino)-3-hydroxy-3-methylpropanoate (13)

DCC (144 mg, 0.7 mmol) was added to a mixed solution of (*S*)-methylserinate **12** (49.4 mg, 0.4 mmol), acid **8** (70 mg, 0.3 mmol), and HOBt (82.4 mg, 0.58 mmol) in DMF (3 ml) at 0°C. After stirring for 30 min at 0°C, DMAP (37 mg, 0.3 mmol) was added. After stirring overnight at room temperature, the reaction solution was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel; PE/EtOAc, 5/1 to 3/1) to afford acid **13** as a colorless oil (70 mg, 66.9%). $[\alpha]_D^{16} +$ 33.1 ($c = 0.5$, $CHCl_3$) (lit. [3g], $[\alpha]_D^{15} + 34$ ($c = 0.48$, $CHCl_3$)); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.13 (s, 1H, NH), 5.01 (m, 2H, 2× CHOAc), 4.15 (d, 1H, $J = 11.4$ Hz, NCHHOH), 3.81 (d, 1H, $J = 11.4$ Hz, NCHHOH), 3.80 (s, 3H, OCH_3), 2.28 (m, 1H, $CHCH_3$), 2.18 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 1.55 (s, 3H, CH_3), 1.26 (d, $J = 6.6$ Hz, 3H, CH_3), 1.02 (d, $J = 6.6$ Hz, 3H, CH_3); ESI-MS: *m/z* 348 $[M+H]^+$, 288, 228; HR-ESI-MS: *m/z* 348.1664 $[M+H]^+$ (calcd for $C_{15}H_{26}NO_8$, 348.1652).

3.10 Conagenin (1)

A solution of amide **13** (45 mg, 0.13 mmol) in methanol (1.5 ml) was cooled to 0°C. Then 1 M K_2CO_3 (0.5 ml, 0.5 mmol) was added dropwise at 0°C. The mixture was stirred for 2 h at room temperature, then neutralized with 1 M $KHSO_4$ (1.25 ml, 1.25 mmol) solution. After concentrated *in vacuo*, the residue was purified by column chromatography (silica gel; $CHCl_3/CH_3OH$, 8/1) to afford conagenin **1** as a colorless solid (28 mg, 86.7%); mp 152–154°C; $[\alpha]_D^{18} + 50.2$ ($c = 0.55$, CH_3OH) (lit. [1a], $[\alpha]_D^{23} + 55.4$); ^{1}H NMR (600 MHz, CD_3OD) δ (ppm) 4.10 (d, 1H, $J = 2.4$ Hz, COCHOH), 3.96 (d, 1H, $J = 10.8$ Hz, NCCHOH), 3.80 (m, 1H, MeCHOH), 3.77 (d, 1H, $J = 10.8$ Hz, NCCHOH), 1.84 (m, 1H, CHMe), 1.46 (s, 3H, $NCCH_3$), 1.16 (d, 3H, $J = 6.0$ Hz, CH_3), 1.55 (d, 3H, $J = 7.2$ Hz, CH_3); ^{13}C NMR (150 MHz, CD_3OD) δ (ppm) 175.8, 175.8, 75.2, 71.2, 66.0, 62.5, 43.7, 21.2, 19.9, 8.2; ESI-MS: *m/z* 250 $[M+H]^+$, 232; HR-ESI-MS: *m/z* 250.1286 $[M+H]^+$ (calcd for $C_{15}H_{26}NO_8$, 250.1285).

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