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Reactivity of Chiral Sesquiterpene Synthons Obtained by the Degradation of Maslinic Acid from Olive-Pressing Residues
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Reactivity of Chiral Sesquiterpene Synthons Obtained by the Degradation of Maslinic Acid from Olive-Pressing Residues

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Abstract: Maslinic acid, a naturally occurring compound isolated from the solid wastes of olive-oil pressing, was fragmented through the C-ring via oxidative procedures to obtain two structural fragments. The chemical behaviors of cis-decalin, from the D and E rings, and of trans-decalin fragments, from the A and B rings, were investigated in depth using several chemical and enzymatic reactions. These decalin chiral synthons are interesting intermediates to semisynthesize phenanthrene- and drimane-type compounds and natural tricyclic triterpenes.

Keywords: Maslinic acid, oleanene, olive oil, oxidative cleavage, sesquiterpene synthons, triterpene

INTRODUCTION

The degradation of high-molecular-weight terpene compounds has frequently been regarded as an efficient way of accessing suitable molecular fragments for the synthesis of sesquiterpene compounds. Maslinic acid (2α,3β-dihydroxy-12-oleanen-28-oic acid) (1a) (Fig. 1) belongs to the pentacyclic triterpene family. It is a natural product widely found in nature and is obtained in large quantities from olive-pressing residues. This acid and some other closely related products that possess interesting pharmacological
activities\textsuperscript{[7–9]} constituted the starting material for the semisynthesis of several triterpene derivatives with a functionalized, contracted, or deoxygenated A-ring.\textsuperscript{[10]} We have recently reported the formation of several triene systems via chemical and photochemical isomerization processes of maslinic acid.\textsuperscript{[11]} The oxidative cleavage of these triene systems afforded the \textit{cis}- and \textit{trans}-decalin-type chiral synthons \textsuperscript{2–6}\textsuperscript{[12]} (Fig. 1). These kinds of substrates are appropriate synthons for semisynthesizing phenanthrenes and hydrophenanthrenes,\textsuperscript{[13–15]} naturally occurring tricyclic triterpenes such as achilleol B\textsuperscript{[16]} and camelliol A and C\textsuperscript{[17]} and drimane compounds.\textsuperscript{[18,19]}

Here we report on the reactivity of the previously mentioned \textit{cis}- and \textit{trans}-decalin fragments. We initially studied the chemical behavior of \textit{cis}-sesquiterpene fragments from the D and E rings of the triterpene skeleton (compounds \textsuperscript{2}, \textsuperscript{3}, and \textsuperscript{4}) by carrying out different reduction, condensation, and acetylation reactions. Similarly, we describe the reactivity of the \textit{trans}-decalin fragments (products \textsuperscript{5} and \textsuperscript{6}) from the A and B rings of maslinic acid by performing several epoxide-opening, dehydration, acetylation, and ring-cleavage reactions.

**RESULTS AND DISCUSSION**

Maslinic acid (\textsuperscript{1a}) was obtained from the solid wastes of olive-oil pressing by successive extractions with hexane and ethyl acetate in Soxhlet.\textsuperscript{[6]} After flash chromatography on a silica-gel column, a large quantity of maslinic acid was obtained, and its carboxylic group was protected as methyl ester (\textsuperscript{1b}). This ester was converted into a diene derivative by a key
bromination–dehydrobromination process and into several triene derivatives by photochemical reaction with a high-pressure Hg street lamp in a borosilicate flask and/or photochemical isomerization in a quartz flask. Some of the double bonds were epoxidized and the ozonolysis of these epoxydienes led to compounds 2–6 (Fig. 1). This cleavage implied the breakup via the C ring into two carbonyl fragments, one of which included the D and E rings (compounds 2, 3, and 4) and the other the A and B rings of the original triterpene molecule. In the A- and B-ring fragments, the C8/C26 exocyclic double bond of the substrate was also affected during the ozonolysis process, giving the stereoisomeric epoxides 5 and 6.

Compounds 2 and 3 are unstable epoxyaldehydes, which spontaneously gave the α,β-unsaturated aldehydes 7 and 8, respectively (Scheme 1). This rearrangement occurred by the opening of the epoxy group and a proton loss at C-12. The structures of 7 and 8 were confirmed by two-dimensional (2D) NMR and NOE experiments. Positive NOE effects between H-12 and the C-7 methyl group and between the aldehydic proton and H-5 corroborated the structures of compounds 7 and 8. Treatment of aldehyde 2 with Tebbe reagent gave compounds 9 and 10 (Scheme 1). The spectroscopic data showed that compound 10 had an exocyclic double bond at C-6 with 9 possessing an allylic group at the same carbon. Treatment of compound 2 with a Wittig reagent gave products 11 and 12. Compound 11 was the expected carboxethyl derivative, and product 12 had an allylic carboxethyl group and a conjugated double bond between C-6 and C-12.

To study the chemical behavior of cis-decalin 4, several reductions and chemical or enzymatic acetylations were performed (Scheme 2). Reduction

```
7 R1=OH; R2=CH3
8 R1=CH3; R2=OH
9 (45%)

10 (15%)

11 (40%)

12 (20%)
```

Scheme 1. Reactions of epoxyaldehyde 2: (a) Tebbe reagent/THF/0°C; (b) BrPh3PCH2COOEt/NaH/THF/rt. All reactions from 2.
of 4 with LiAlH₄ gave compound 13a. To decrease the polarity of 13a, the hydroxyl groups were acetylated via different methods. Treatment of 13a with Ac₂O and pyridine at 0°C led to 13b, in which both primary hydroxyl groups were acetylated. To achieve a selective acetylation of these primary hydroxyls, their biocatalytic acetylation with the lipases, *Candida antarctica* (CAL), *Mucor miehei* (MML) (Novo-Nordisk), *Candida cylindracea* (CCL), and *Porcine pancreas* (PPL) (Aldrich) was studied. Vinyl acetate was used as solvent and acetylating agent, and the enzyme–substrate ratio was fixed at 6:1. The results of these enzymatic reactions at different times are summarized in Table 1. It is evident that CAL acetylated the C-13 hydroxyl group with high selectivity, affording compound 13c. Furthermore, PPL and MML also gave only 13c, but with a longer reaction time and lower yield. With CCL, however, the hydroxyl group at C-16 was acetylated, giving a high yield of product 13d after a short reaction time. One of the most notable results from these assays was that CAL and CCL gave excellent yields of two different monoacetates, 13c and 13d, with opposite regioselectivity.

The reactivity of the trans-decalin oxiranes 5 and 6 also was studied (Scheme 3). Thus, cleavage of these epoxides 5 and 6 with KOAc/HOAc afforded compounds 14 and 15. Several NOE experiments were performed to check the stereochemistry of these products, thus detecting positive NOE

### Table 1. Products and yields for enzymatic acetylation of 13a

<table>
<thead>
<tr>
<th>Product</th>
<th>CAL (24 h)</th>
<th>PPL (48 h)</th>
<th>MML (48 h)</th>
<th>CCL (3 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13c</td>
<td>95%</td>
<td>25%</td>
<td>65%</td>
<td>0%</td>
</tr>
<tr>
<td>13d</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>89%</td>
</tr>
</tbody>
</table>
effects between H-11 and the methyl group at C-14 for compound 18. Treatment of compound 14 with POCl3 afforded compounds 16, 17, and 18. The major product 16 was formed via dehydration of the C-8 hydroxyl group of compound 14 and had a nor-drimene skeleton with a 2α,3β-dihydroxydrimenal structure. Products 17 and 18, however, were chlorinated derivatives on C-8.

Several reactions to open epoxide 5 were carried out (Scheme 4). The reaction with titanocene gave product 19 in acceptable yield. The structure of this product was established from its spectroscopic characteristics and the positive NOE effect between 3H-14 and H-8, permitting determination of the configuration at C-8. This configuration can be explained by postulating that during the radical process the titanocene intermediate facilitates the entry of the hydrogen via the β face. Epoxide 5 was reduced with NaBH₄ to obtain the α-hydroxyepoxy derivative 20, which was treated with HCl to give 21. Compound 5 was also treated with LiAlH₄, affording the tetrol 22a. This compound was acetylated with Ac₂O in pyridine at rt, and thus the main triacetoxy derivative 22b (89%) and the minor diacetoxy compound 22c were isolated. Product 22d was obtained by an enzymatic reaction of tetrol 22a with vinyl acetate and the lipase CCL. In this case, the four previously mentioned lipases were also tested but only CCL induced acetylation of any hydroxyl groups. Once more CCL caused a regioselective acetylation affording 22d. To selectively protect the hydroxyl groups of the A ring, tetrol 22a was treated with dimethoxypropane and PTSP to give compound 23 in good yield. Finally, to cleave the bond between C-8 and C-9, compound 23 was oxidized with
sodium periodate to afford derivative 24, which could be used as the starting material to semisynthesize the naturally occurring compound camelliol C.

CONCLUSIONS

Maslinic acid was fragmented via oxidative procedures to obtain two structural fragments, the reactivities of which were investigated in detail. The cis- and trans-decalin chiral synthons permitted access to phenanthrene- and drimane-type compounds and to natural tricyclic triterpenes. The cis-decalin synthons, derived from the D and E rings of the original maslinic acid, are unstable epoxyaldehydes that tend to form α,β-unsaturated compounds and intramolecular acetals. Trans-decalin synthons, including the A and B rings of the maslinic acid, are nor-sesquiterpene epoxyketones, the reactivities of which were also investigated in depth. The epoxy group of these compounds was opened by different methods, and the subsequent reduction, dehydration, and B-ring oxidative-cleavage reactions afforded chiral synthons that are of interest in the synthesis of sesquiterpenes.

EXPERIMENTAL

General

Melting points were determined on a Kofler apparatus and are uncorrected. Optical rotations were measured on a Perkin Elmer 341 polarimeter at
25°C. IR spectra were recorded on a Mattson Satellite FT-IR spectrometer. High-resolution mass spectra were obtained on a Micromass Autospec-Q spectrometer (EBE geometry). Measurements of NMR spectra (300.13 MHz 1H and 75.47 MHz 13C) were recorded in CDCl3 on a Bruker AM-300 spectrometer. The assignments of 13C chemical shifts were done by DEPT using a flip angle of 135°. NOE experiments were done by irradiation for 4 s in series of eight scans. Silica gel (40–60 μm) was used for flash chromatography. CH2Cl2 or CHCl3 containing increasing amounts of Me2CO (from 100:1 to 1:1) and also mixtures of hexane–EtOAc (from 40:1 to 1:1) were used as eluents. Analytical plates (silica gel) were rendered visible by spraying with H2SO4-HOAc followed by heating to 120°C

Isolation of Starting Material

Maslinic acid (1a) was isolated from the solid waste of olive-oil pressing,[6] which was extracted in a Soxhlet with EtOAc. It was purified from these mixtures by column chromatography over silica gel and transformed into the corresponding methyl ester, 1b[10] with ethereal CH2N2 or NaOH-MeI. Treatment of 1b with NBS/AIBN, irradiation using a 125-W high-pressure Hg street lamp, and treatment with ozone afforded compounds 2–6.[11,12]

Spontaneous Rearrangement of 2

Product 2 underwent spontaneous rearrangement in 1 week to give compound 7 (45%): viscous oil; [α]D20 −18 (CHCl3; c 1); νmax(CHCl3) cm⁻¹: 3448, 2949, 2863, 1728, 1673, 1457, 1259, 1040; 1H NMR (CDCl3) δ 10.19 (1H, d, J = 7.6 Hz, H-13), 5.98 (1H, d, J = 7.6 Hz, H-12), 4.18 (1H, dd, J1 = 7.6 Hz, J2 = 13.6 Hz, H-5β), 3.60 (3H, s, COOCH3), 1.33 (3H, s, CH3), 0.96 (3H, s, CH3) and 0.92 (3H, s, CH3); 13C NMR (CDCl3) δ 192.0 (CH, C-13),177.4 (C, C-16), 167.2 (C, C-6), 125.5 (CH, C-12), 71.2 (C, C-7), 52.1 (CH3, COOCH3), 48.5 (C, C-10), 43.0 (CH2, C-4), 38.0 (CH2, C-2), 36.0 (CH, C-5), 33.8 (CH2, C-1), 32.9 (CH3, C-15), 31.7 (CH2, C-8), 30.8 (C, C-3), 29.0 (CH3, C-11), 23.5 (CH3, C-14), 22.2 (CH2, C-9); HRLSIMS m/z 317.1725 [M + Na]+ (calcd. for C17H26O4Na, 317.1729).

Spontaneous Rearrangement of 3

Product 3 underwent spontaneous rearrangement in 1 week to form compound 8 (43%): viscous oil; [α]D20 −78 (CHCl3; c 1); νmax(CHCl3) cm⁻¹: 3440, 2928, 2863, 1728, 1700, 1463, 1253; 1H NMR (CDCl3) δ 10.15 (1H, d, J = 8.0 Hz, H-13), 6.37 (1H, d, J = 8.0 Hz, H-12), 4.25 (1H, dd, J1 = 4.5 Hz, J2 = 14.1 Hz, H-5 β), 3.64 (3H, s, COOCH3), 1.43 (3H, s,
CH3), 0.98 (3H, s, CH3) and 0.93 (3H, s, CH3); 13C NMR (CDCl3) δ 191.4 (CH, C-13), 177.2 (C, C-16), 172.3 (C, C-6), 124.8 (CH, C-12), 71.6 (C, C-7), 52.3 (CH3, COOCH3), 47.7 (C, C-10), 43.3 (CH2, C-4), 39.6 (CH2, C-2), 35.9 (CH, C-5), 33.8 (CH2, C-1), 32.8 (CH3, C-15), 31.2 (CH3, C-11), 31.0 (C, C-3), 29.7 (CH2, C-8), 24.6 (CH2, C-9), 23.3 (CH3, C-14); HRLSIMS m/z 317.1732 [M + Na]+ (calcd. for C17H26O4Na, 317.1729).

Treatment of 2 with Tebbe Reagent

Product 2 (50 mg, 0.2 mmol) was dissolved in 2 mL of dry THF and cooled to 0°C, and 0.35 mL of Tebbe reagent (0.5 M in toluene) was added dropwise. When the starting material was consumed (20 min), MeOH was added to destroy excess reagent, and the mixture was diluted with H2O and extracted with CH2Cl2. The organic phase was dried with anhydrous Na2SO4 and evaporated under reduced pressure. Chromatography over silica gel afforded 24 mg of 9 (45%): viscous oil; [α]20D + 32 (CHCl3; c 1); νmax(CHCl3) cm⁻¹: 2949, 2863, 1730, 1462, 1251, 1179; 1H NMR (CDCl3) δ 5.96 (1H, m, H-13), 5.15–4.95 (2H, m, H-14a and H-14b), 3.66 (3H, s, COOCH3), 2.50–2.20 (3H, m, H-5, H-12a and H-12b), 1.24 (3H, s, CH3), 0.91 (3H, s, CH3) and 0.87 (3H, s, CH3); 13C NMR (CDCl3) δ 178.0 (C, C-17), 134.5 (CH, C-13), 116.9 (CH2, C-14), 66.9 (C, C-6), 62.4 (C, C-7), 51.6 (CH3, COOCH3), 45.3 (C, C-10), 39.8 (CH2, C-12), 35.9 (CH2, C-4), 34.1 (CH2, C-2), 33.6 (CH, C-5), 32.8 (CH3, C-16), 31.5 and 30.2 (CH2, C-1 and C-8), 29.9 (C, C-3), 24.1 (CH3, C-15), 23.0 (CH2, C-9), 19.8 (CH3, C-11); HRLSIMS m/z 293.2113 [M + Na]+ (calcd. for C18H29O3Na, 293.2117); and 8 mg of 10 (15%): viscous oil, [α]20D + 21 (CHCl3; c 1); νmax(CHCl3) cm⁻¹: 3462, 2948, 2862, 1728, 1464, 1366, 1250, 1166, 1041; 1H NMR (CDCl3) δ 5.04 (1H, d, J = 1.3 Hz, H-12a), 4.92 (1H, d, J = 1.3 Hz, H-12b), 3.63 (3H, s, COOCH3), 3.06 (1H, m, H-5β), 1.33 (3H, s, CH3), 0.94 (3H, s, CH3) and 0.91 (3H, s, CH3); 13C NMR (CDCl3) δ 178.1 (C, C-15), 153.4 (C, C-6), 112.0 (CH2, C-12), 70.9 (C, C-7), 51.7 (CH3, COOCH3), 48.6 (C, C-10), 43.3 (CH, C-5), 43.1 (CH2, C-4), 37.9 (CH2, C-8), 34.0 (CH2, C-2), 33.1 (CH3, C-14), 32.0 (CH2, C-1), 30.6 (C, C-3), 29.4 (CH3, C-13), 23.7 (CH3, C-11), 22.7 (CH2, C-9); HRLSIMS m/z 289.1778 [M + Na]+ (calcd. for C18H29O3Na, 289.1780).

Wittig Reaction of 2

Br(Ph)3P(CH2)2COOEt (150 mg, 0.4 mmol) was dissolved in 5 mL of dry THF, and 25 mg of dry NaH (95%) was added. The mixture was stirred for 1 h at rt, 100 mg of 2 (0.3 mmol) in 2 mL of THF was added, and stirring continued for 10 h. The mixture was diluted with H2O and extracted with CH2Cl2. The organic phase was dried with anhydrous Na2SO4 and evaporated under
reduced pressure. Chromatography over silica gel yielded 49 mg of 11 (40%): viscous oil; \([\alpha]_D^{20} + 8\) (CHCl\_3; c 1); \(v_{\text{max}}^{\text{CHCl}_3}\) \(\text{cm}^{-1}\): 2949, 2863, 1723, 1456, 1267; \(^1\)H NMR (CDCl\_3) \(\delta\) 7.10 (1H, ddd, \(J_1 = 7.7\) Hz, \(J_2 = 7.7\) Hz, \(J_3 = 15.5\) Hz, H-13), 5.88 (1H, ddd, \(J_1 = 1.5\) Hz, \(J_2 = 1.5\) Hz, \(J_3 = 15.5\) Hz, H-14), 4.20 (2H, q, \(J = 7.1\) Hz, COOC\_H\_2CH\_3), 3.68 (3H, s, COOCH\_3), 2.59 (1H, ddd, \(J_1 = 1.5\) Hz, \(J_2 = 7.7\) Hz, \(J_3 = 14.8\) Hz, H-12a), 2.48–2.32 (2H, m, H-12b and H-5b), 1.29 (3H, t, \(J = 7.1\) Hz, COOCH\_2C\_H\_3), 1.25 (3H, s, CH\_3), 0.91 (3H, s, CH\_3) and 0.86 (3H, s, CH\_3); \(^{13}\)C NMR (CDCl\_3) \(\delta\) 177.8 (C, C-18), 166.4 (C, C-15), 144.8 (CH, C-14), 123.4 (CH, C-13), 66.4 (C, C-6), 62.4 (C, C-7), 60.3 (CH\_2, COOCH\_2CH\_3), 51.8 (CH\_3, COOCH\_3), 45.2 (C, C-10), 38.2 (CH\_2, C-12), 35.9 (CH, C-4), 34.0 (CH, C-5), 34.0 (CH\_2, C-2), 32.8 (CH\_3, C-17), 31.3 (CH\_2, C-1), 29.9 (C, C-3), 29.8 (CH\_2, C-8), 24.0 (CH\_3, C-16), 23.0 (CH\_2, C-9), 19.8 (CH\_3, C-11), 14.4 (CH\_2, COOCH\_2CH\_3); HRLSIMS \(m/z\) 387.2139 \([M + Na]^+\) (calcd. for C\(_{21}\)H\(_{32}\)O\(_5\)Na, 387.2147); and 25 mg of 12 (20%): viscous oil; \([\alpha]_D^{20} + 4\) (CHCl\_3; c 1); \(v_{\text{max}}^{\text{CHCl}_3}\) \(\text{cm}^{-1}\): 3449, 2929, 2857, 1718, 1629, 1458, 1260; \(^1\)H NMR (CDCl\_3) \(\delta\) 7.72 (1H, dd, \(J_1 = 11.4\) Hz, \(J_2 = 15.1\) Hz, H-13), 6.25 (1H, d, \(J = 11.4\) Hz, H-12), 5.93 (1H, d, \(J = 15.1\) Hz, H-14), 4.20 (2H, q, \(J = 7.2\) Hz, COOC\_H\_2CH\_3), 3.70 (1H, dd, \(J = 7.2\) Hz, \(J = 10.3\) Hz, \(J = 15.1\) Hz, H-11), 3.60 (3H, s, COOCH\_3), 1.38 (3H, s, CH\_3), 1.29 (3H, t, \(J = 7.2\) Hz, COOCH\_2CH\_3), 1.02 (3H, s, CH\_3) and 0.92 (3H, s, CH\_3); \(^{13}\)C NMR (CDCl\_3) \(\delta\) 177.8 (C, C-18), 167.2 (C, C-15), 154.7 (C, C-6), 139.2 (CH, C-14), 123.1 and 122.5 (CH, C-12 and C-13), 71.5 (C, C-7), 60.4 (CH\_2, COOCH\_2CH\_3), 51.9 (CH\_3, COOCH\_3), 48.3 (C, C-10), 42.5 (CH\_2, C-4), 37.9 (CH\_2, C-8), 36.1 (CH, C-5), 33.9 (CH\_2, C-2), 32.9 (CH\_3, C-17), 31.9 (CH\_2, C-1), 30.8 (C, C-3), 29.4 (CH\_3, C-1), 23.4 (CH\_3, C-11), 22.3 (CH\_2, C-9), 14.4 (CH\_3, COOCH\_2CH\_3); HRLSIMS \(m/z\) 387.2143 \([M + Na]^+\) (calcd. for C\(_{21}\)H\(_{32}\)O\(_5\)Na, 387.2147).

**Reduction of 4 with LiAlH\(_4\)**

Product 4 (200 mg, 0.6 mmol) was dissolved in 10 mL of dry THF, 1 mL of a 0.1 M solution of LiAlH\(_4\) in THF was added, and the mixture was kept at reflux for 2 h. The mixture was diluted with H\(_2\)O and extracted with CH\(_2\)Cl\(_2\). The organic layer was dried with anhydrous Na\(_2\)SO\(_4\) and evaporated under reduced pressure. Chromatography over silica gel gave 178 mg of 13a (96%), a very polar compound, characterized as the different mono and diacetyl derivatives (compounds 13b, 13c, and 13d), described later.

**Acetylation of 13a**

Compound 13a (100 mg, 0.3 mmol) was dissolved in 4 mL of pyridine, and cooled to 0°C, and 2 mL of Ac\(_2\)O was added with stirring for 2 h. The
mixture was diluted with cold H₂O, acidified with 0.1 N HCl solution, and extracted with CH₂Cl₂. The organic layer was neutralized with saturated aqueous NaHCO₃, dried with anhydrous Na₂SO₄, and evaporated under reduced pressure. Chromatography over silica gel afforded 119 mg of 13b (92%): viscous oil; [α]D²⁰ + 2 (CHCl₃; c 1); ν(CHCl₃) cm⁻¹: 3513, 1948, 1864, 1721, 1252; ¹H NMR (CDCl₃) δ 4.31 (1H, d, J = 10.9 Hz, H-16a), 4.24 (2H, m, H-13), 4.23 (1H, d, J = 10.9 Hz, H-16b), 2.05 (3H, s, COCH₃), 2.05 (3H, s, COCH₃), 1.20 (3H, s, CH₃), 0.89 (3H, s, CH₃) and 0.85 (3H, s, CH₃); ¹³C NMR (CDCl₃) δ 171.5 (C, COCH₃), 77.5 (C, C-6), 74.4 (C, C-7), 72.3 (CH₂, C-16), 61.1 (CH₂, C-13), 40.2 (CH, C-5), 38.4 (CH₂, C-4), 36.5 (C, C-10), 34.0, 33.5, 32.4 and 31.9 (CH₂, C-1, C-2, C-8 and C-12), 33.2 (CH₃, C-15), 30.7 (C, C-3), 26.2 (CH₃, C-14), 23.2 (CH₃, C-11), 22.6 (CH, C-9), 21.2 (CH₃, COCH₃), 21.1 (CH₃, COCH₃); HRLSIMS m/z 393.2245 [M + Na]⁺ (calcd. for C₂₀H₃₄O₆Na, 393.2253).

Enzymatic Acetylation of 13a

Four samples of 100 mg each of 13a were dissolved in 30 mL of vinyl acetate, and 600 mg of the four lipases indicated in Table 1 were added. The different suspensions were shaken on an orbital shaker at 45°C for the times indicated in Table 1. When the enzymatic reaction was stopped, the mixture was filtered and the solvent evaporated under reduced pressure. Chromatography over silica gel afforded compounds 13c and 13d in yields given in Table 1: 13c: viscous oil; [α]D²⁰ + 8 (CHCl₃; c 1); ν(CHCl₃) cm⁻¹: 3422, 2948, 2863, 1725, 1257; ¹H NMR (CDCl₃) δ 4.24 (2H, m, H-13), 4.00 (1H, d, J = 10.7 Hz, H-16a), 3.08 (1H, d, J = 10.7 Hz, H-16b), 2.04 (3H, s, COCH₃), 1.18 (3H, s, CH₃), 0.88 (3H, s, CH₃) and 0.85 (3H, s, CH₃); ¹³C NMR (CDCl₃) δ 171.4 (C, COCH₃), 77.4 (C, C-6), 74.3 (C, C-7), 71.0 (C, C-16), 60.1 (C, C-13), 38.5 (CH₂, C-4), 38.2 (CH, C-5), 37.1 (C, C-10), 34.4, 33.8 and 33.8 (CH₂, C-1, C-2 and C-12), 33.3 (CH₃, C-15), 31.9 (CH₂, C-8), 30.7 (C, C-3), 26.0 (CH₃, C-14), 23.1 (CH₃, C-11), 23.1 (CH₂, C-9), 21.2 (CH₃, COCH₃); HRLSIMS m/z 351.2148 [M + Na]⁺ (calcd. for C₁₈H₃₂O₅Na, 351.2147); and 13d: viscous oil; [α]D²⁰ + 5 (CHCl₃; c 1); ν(CHCl₃) cm⁻¹: 3441, 1939, 1864, 1714, 1273; ¹H NMR (CDCl₃) δ 4.42 (1H, d, J = 10.8 Hz, H-16a), 4.25 (1H, d, J = 10.8 Hz, H-16b), 3.95 (2H, m, H-13), 2.04 (3H, s, COCH₃), 1.23 (3H, s, CH₃), 0.88 (3H, s, CH₃) and 0.87 (3H, s, CH₃); ¹³C NMR (CDCl₃) δ 171.5 (C, COCH₃), 78.2 (C, C-6), 74.5 (C, C-7), 72.5 (CH₂, C-16), 59.9 (CH₂, C-13), 40.4 (CH, C-5), 38.5 (CH₂, C-4), 36.6 (C, C-10), 34.2, 33.4, 33.2 and 32.4 (CH₂, C-1, C-2, C-8 and C-12), 33.3 (CH₃, C-15), 30.7 (C, C-3), 26.4 (CH₃, C-14), 23.3 (CH₃, C-11), 22.4 (CH₂, C-9), 21.1 (CH₃, COCH₃); HRLSIMS m/z 351.2138 [M + Na]⁺ (calcd. for C₁₈H₃₂O₅Na, 351.2147).
Acetolysis of 5

Product 5 (60 mg, 0.2 mmol) was dissolved in 8 mL of a solution of KOAc/ HOAc (0.5 N), and the mixture was stirred at reflux for 7 h. The mixture was diluted with H2O, neutralized with saturated aqueous NaHCO3 and extracted with CH2Cl2. The organic phase was dried with anhydrous Na2SO4 and evaporated under reduced pressure. The mixture was chromatographed on a silica-gel column to yield 62 mg of 14 (89%): viscous oil; [α]D20 19 (CHCl3; c 1); νCHCl3 cm⁻¹: 3454, 2954, 1741, 1371, 1249, 1043; 1H NMR (CDCl3) δ 5.13 (1H, ddd, J1 = 4.6 Hz, J2 = 10.3 Hz, J3 = 12.0 Hz, H-2b), 4.71 (1H, d, J = 10.3 Hz, H-3a), 4.40 (1H, d, J = 11.6 Hz, H-11a), 3.96 (1H, d, J = 11.6 Hz, H-11b), 2.07 (3H, s, COCH3), 2.05 (3H, s, COCH3), 1.99 (3H, s, COCH3), 1.43 (3H, s, CH3), 1.02 (3H, s, CH3) and 0.92 (3H, s, CH3); 13C NMR (CDCl3) δ 210.8 (C, C-9), 171.1 (C, COCH3), 170.6 (C, COCH3), 170.5 (C, COCH3), 79.7 (CH, C-3), 75.6 (C, C-8), 69.5 (CH, C-2), 68.4 (CH2, C-11), 50.3 (CH, C-5), 49.1 (C, C-10), 40.1 (C, C-4), 37.8 (CH2, C-1), 34.5 (CH2, C-7), 28.2 (CH3, C-12), 21.1 (CH3, COCH3), 20.8 (CH3, COCH3), 20.8 (CH3, COCH3), 20.0 (CH3, C-14), 17.8 (CH3, C-13), 16.6 (CH2, C-6); HRLSIMS m/z 421.1832 [M + Na]⁺ (calcd. for C20H30O8Na, 421.1838).

Acetolysis of 6

Product 6 (30 mg, 0.1 mmol) was dissolved in 8 mL of a solution of KOAc/ HOAc (0.5 N), and the mixture was stirred at reflux for 7 h. The reaction was diluted with H2O, neutralized with saturated aqueous NaHCO3, extracted with CH2Cl2. The organic layer was dried with anhydrous Na2SO4 and evaporated under reduced pressure. The mixture was chromatographed on a silica-gel column to give 31 mg of 15 (90%): white powder; [α]D20 2 (CHCl3; c 1); νCHCl3 cm⁻¹: 3475, 2952, 1743, 1370, 1245, 1045; 1H NMR (CDCl3) δ 5.12 (1H, ddd, J1 = 4.5 Hz, J2 = 10.3 Hz, J3 = 12.0 Hz, H-2b), 4.72 (1H, d, J = 10.3 Hz, H-3a), 4.33 (1H, d, J = 11.8 Hz, H-11a), 4.19 (1H, d, J = 11.8 Hz, H-11b), 2.05 (3H, s, COCH3), 2.02 (3H, s, COCH3), 2.00 (3H, s, COCH3), 1.25 (3H, s, CH3), 0.99 (3H, s, CH3) and 0.92 (3H, s, CH3); 13C NMR (CDCl3) δ 210.9 (C, C-9), 170.6 (C, COCH3), 170.5 (C, COCH3), 170.5 (C, COCH3), 79.3 (CH, C-3), 77.3 (C, C-8), 69.4 (CH, C-2), 69.1 (CH2, C-11), 52.6 (CH, C-5), 48.4 (C, C-10), 40.2 (C, C-4), 38.0 (CH2, C-1), 36.9 (CH2, C-7), 28.2 (CH3, C-12), 21.1 (CH3, COCH3), 20.8 (CH3, COCH3), 20.8 (CH3, COCH3), 18.9 (CH3, C-6), 17.9 (CH3, C-14), 17.6 (CH3, C-13); HRLSIMS m/z 421.1840 [M + Na]⁺ (calcd. for C20H30O8Na, 421.1839).

Treatment of 14 with POCl3

Product 14 (100 mg, 0.3 mmol) was dissolved in 8 mL of pyridine, and 1 mL of POCl3 was added. The mixture was stirred at reflux for 15 min, diluted with cold
H2O, neutralized with saturated aqueous NaHCO3, and extracted with CH2Cl2.
The organic phase was dried with anhydrous Na2SO4 and evaporated under reduced pressure. Chromatography over silica gel gave 49 mg of 16 (52%): white powder; [α]D20 + 20 (CHCl3; c 1); vCHCl3 cm⁻¹: 2971, 2939, 1742, 1677, 1370, 1247, 1048; ¹H NMR (CDCl3) δ 6.94 (1H, dd, J1 = 3.7 Hz, J2 = 4.5 Hz, H-7), 5.15 (1H,ddd, J1 = 4.6 Hz, J2 = 10.3 Hz, J3 = 12.1 Hz, H-2β), 4.74 (1H, d, J = 10.3 Hz, H-3α), 4.70 (1H, d, J = 3.9 Hz, H-1α), 4.70 (1H, dd, J = 3.9 Hz, H-11b), 2.06 (3H, s, COCH3), 1.17 (3H, s, CH3), 1.07 (3H, s, CH3) and 0.92 (3H, s, CH3); ¹³C NMR (CDCl3) δ 201.1 (C, C-9), 170.7 (C, COCH3), 170.4 (C, COCH3), 169.8 (C, COCH3), 79.6 (CH, C-3), 69.2 (CH, C-2), 67.0 (CH2, C-11), 64.8 (C, C-8), 47.0 (C, C-10), 42.5 (CH, C-5), 40.0 (C, C-4), 38.8 (CH2, C-1), 29.3 (CH2, C-7), 27.3 (CH3, C-14), 21.1 (CH3, COCH3), 20.9 (CH3, COCH3), 20.7 (CH3, COCH3), 19.4 (CH3, C-12), 17.2 (CH3, C-13), 15.9 (CH3, C-6); HRLSIMS m/z 439.1492 [M + Na]⁺ (calcd. for C20H29ClO7Na, 439.1500).

Opening of Epoxide 5 with Blue Titanocene

Cp₂TiCl₂ (700 mg, 3 eq) was dissolved in 30 mL of dry THF, 1 g of Mn (8 eq) was added, and the mixture was stirred for 30 min. Then 338 mg of 5 (1 eq) in
THF with 20 eq of H₂O were added, and the mixture was stirred at rt for 3 h. The mixture was acidified with 0.1N HCl solution, neutralized with saturated aqueous NaHCO₃, and extracted with CH₂Cl₂. The organic layer was dried with anhydrous Na₂SO₄ and evaporated under reduced pressure. Chromatography over silica gel yielded 221 mg of 19 (65%): viscous oil; [α]D20 -30 (CHCl₃; c 1); νmax(CHCl₃) cm⁻¹: 3449, 2940, 1741, 1247; ¹H NMR (CDCl₃) δ 5.12 (1H, ddd, J1 = 4.6 Hz, J2 = 10.3, J3 = 12.1 Hz, H-2), 2.78 (1H, m, H-8), 1.27 (3H, s, CH₃), 1.00 (3H, s, CH₃) and 0.90 (3H, s, CH₃); ¹³C NMR (CDCl₃) δ 215.0 (C, C-9), 170.6 (C, COCH₃), 170.5 (C, COCH₃), 79.5 (CH, C-3), 69.6 (CH, C-2), 62.7 (CH₂, C-11), 52.6 (CH, C-5), 49.2 (C, C-10), 46.8 (CH, C-8), 40.3 (C, C-4), 36.8 (CH₂, C-1), 28.9 (CH₂, C-7), 20.9 (CH₃, COCH₃), 21.1 (CH₄, COCH₃), 20.3 (CH₂, C-6), 19.4 (CH₃, COCH₃), 17.9 (CH₃, C-13); HRLSIMS m/z 363.1536 [M +Na]+ (calcd. for C₁₈H₂₈O₆Na 363.1540).

Reduction of 5 with NaBH₄

Product 5 (75 mg, 0.2 mmol) was dissolved in 10 mL of i-PrOH/EtOH 5:2, and 10 mg (0.3 mmol) of NaBH₄ were added. The mixture was kept at rt for 2 h, diluted with H₂O, and extracted with CH₂Cl₂. The organic layer was dried with anhydrous Na₂SO₄ and evaporated under reduced pressure. Chromatography over silica gel afforded 54 mg of 20 (72%): white powder; [α]D20 -3 (CHCl₃; c 1); νmax(CHCl₃) cm⁻¹: 3475, 2951, 1740, 1249, 1035; ¹H NMR (CDCl₃) δ 5.07 (1H, ddd, J1 = 4.4 Hz, J2 = 10.4 Hz, J3 = 11.8 Hz, H-2), 2.86 (1H, d, J = 4.7 Hz, H-11a), 2.35 (1H, d, J = 4.7 Hz, H-11b), 2.06 (3H, s, COCH₃), 1.99 (3H, s, COCH₃), 1.04 (3H, s, CH₃), 0.97 (3H, s, CH₃) and 0.95 (3H, s, CH₃); ¹³C NMR (CDCl₃) δ 170.8 (C, COCH₃), 170.5 (C, COCH₃), 80.3 (CH, C-3), 76.6 (CH, C-9), 69.2 (CH, C-2), 57.9 (C, C-8), 51.0 (CH, C-5), 47.0 (CH₂, C-11), 41.8 (CH₂, C-1), 41.6 and 39.5 (C, C-4 and C-10), 32.2 (CH₂, C-7), 28.6 (CH₃, C-12), 21.1 (CH₄, COCH₃), 21.0 (CH₃, COCH₃), 19.0 (CH₂, C-6), 17.9 and 17.8 (CH₃, C-13 and C-14); HRLSIMS m/z 363.1789 [M + Na]+ (calcd. for C₁₈H₂₈O₆Na 363.1784).

Opening of Epoxide 20 with HCl

Compound 20 (20 mg, 0.1 mmol) was dissolved in 5 mL of THF, and a catalytic amount of 0.1N HCl solution was added. The mixture was stirred at rt for 3 h, diluted with H₂O, neutralized with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The organic layer was dried with anhydrous
Na$_2$SO$_4$ and evaporated under reduced pressure. Chromatography over silica gel gave 19 mg of 21 (86%): white powder; [$\alpha$]$_{D}^{20} = -10$ (CHCl$_3$; c 1); $\nu_{\text{max}}^{\text{CHCl}_3}$ cm$^{-1}$: 3480, 2970, 1742, 1370, 1038; $^1$H NMR (CDCl$_3$) $\delta$ 5.12 (1H, ddd, $J_1 = 4.5$ Hz, $J_2 = 10.4$ Hz, $J_3 = 11.5$ Hz, H-2$\beta$), 4.76 (1H, d, $J = 10.4$ Hz, H-3$\alpha$), 3.56 (1H, d, $J = 10.9$ Hz, H-11$\beta$), 3.17 (1H, s, H-9$\alpha$), 2.05 (3H, s, COCH$_3$), 1.98 (3H, s, COCH$_3$), 1.16 (3H, s, CH$_3$), 0.95 (3H, s, CH$_3$) and 0.91 (3H, s, CH$_3$); $^{13}$C NMR (CDCl$_3$) $\delta$ 170.8 (C, COCH$_3$), 170.5 (C, COCH$_3$), 80.3 (CH, C-3), 79.0 (CH, C-9), 74.0 (C, C-8), 69.4 (CH, C-2), 52.0 (CH$_2$, C-11), 51.5 (CH, C-5), 42.4 (CH$_2$, C-1), 40.6 (C, C-10), 39.4 (C, C-4), 34.1 (CH$_2$, C-7), 28.5 (CH$_3$, C-12), 21.1 (CH$_3$, COCH$_3$), 20.9 (CH$_3$, COCH$_3$), 17.8 (CH$_3$, C-14), 17.0 (CH$_2$, C-6), 14.6 (CH$_3$, C-13); HRLSIMS $m/z$ 399.1236 [M + Na]$^+$ (calcd. for C$_{18}$H$_{29}$ClO$_6$Na, 399.1243).

Reduction of 5 with LiAlH$_4$

Product 5 (250 mg, 0.7 mmol) was dissolved in 15 mL of dry THF, 1 mL of a 0.1 M solution of LiAlH$_4$ in THF was added, and the mixture was kept at reflux for 2 h. The mixture was diluted with H$_2$O and extracted with CH$_2$Cl$_2$. The organic phase was dried with anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. Chromatography over silica gel afforded 171 mg of 22a (90%), a very polar compound, characterized as the different mono-, di-, and triacetyl derivatives (22b, 22c, and 22d), described later.

Acetylation of 22a

Compound 22a (50 mg, 0.2 mmol) was dissolved in 10 mL of pyridine, and 5 mL of Ac$_2$O was added. The mixture was stirred at rt for 24 h. The mixture was diluted with cold H$_2$O, acidified with 0.1 N HCl solution, and extracted with CH$_2$Cl$_2$. The organic layer was neutralized with saturated aqueous NaHCO$_3$, dried with anhydrous Na$_2$SO$_4$, and evaporated under reduced pressure. Chromatography over silica gel gave products 22b (89%) and 22c (10%): 22b: white powder; [$\alpha$]$_{D}^{20} = -6$ (CHCl$_3$; c 1); $\nu_{\text{max}}^{\text{CHCl}_3}$ cm$^{-1}$: 2971, 2940, 1791, 1370, 1037; $^1$H NMR (CDCl$_3$) $\delta$ 5.08 (1H, ddd, $J_1 = 4.8$ Hz, $J_2 = 10.3$ Hz, $J_3 = 11.8$ Hz, H-2$\beta$), 4.73 (1H, d, $J = 10.3$ Hz, H-3$\alpha$), 4.49 (1H, s, H-9$\alpha$), 2.14 (3H, s, COCH$_3$), 2.04 (3H, s, COCH$_3$), 1.97 (3H, s, COCH$_3$), 1.24 (3H, s, CH$_3$), 1.06 (3H, s, CH$_3$), 0.94 (3H, s, CH$_3$) and 0.91 (3H, s, CH$_3$); $^{13}$C NMR (CDCl$_3$) $\delta$ 170.6 (C, COCH$_3$), 170.4 (C, COCH$_3$), 83.6 (CH, C-3), 80.2 (CH, C-9), 72.2 (C, C-8), 69.2 (CH, C-2), 52.1 (CH$_2$, C-1), 41.6 (CH$_2$, C-1), 40.6 and 38.5 (C, C-4 and C-10), 39.4 (CH$_2$, C-7), 29.0 (CH$_3$, C-11), 28.6 (CH$_3$, C-12), 21.2 (CH$_3$, COCH$_3$), 20.9 (CH$_3$, COCH$_3$), 17.7 (CH$_3$, C-13), 17.6 (CH$_2$, C-6), 16.0 (CH$_3$, C-14); HRLSIMS $m/z$ 407.2041
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\[ \text{[M + Na]}^+ \] (calcld. for \( \text{C}_{20}\text{H}_{32}\text{O}_7\text{Na} \ 407.2045 \)); **22c**: white powder; \([\alpha]_D^{20} - 10 \) (CHCl\(_3\); c 1); \( v_{\text{max}}^{\text{CHCl}_3} \) cm\(^{-1}\): 3449, 2925, 1742, 1719, 1459, 1253, 1023; \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 4.92 (1H, ddd, \( J_1 = 4.5 \) Hz, \( J_2 = 10.1 \) Hz, \( J_3 = 11.6 \) Hz, H-2\( \beta \)), 4.48 (1H, d, \( J = 10.1 \) Hz, H-3\( \alpha \)), 3.18 (1H, d, \( J = 10.1 \) Hz, H-9\( \alpha \)), 2.15 (3H, s, COCH\(_3\)), 2.06 (3H, s, COCH\(_3\)), 1.22 (3H, s, CH\(_3\)), 1.07 (3H, s, CH\(_3\)), 1.06 (3H, s, CH\(_3\)) and 0.90 (3H, s, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 171.7 (C, COCH\(_3\)), 170.6 (C, 1 COCH\(_3\)), 83.8 (CH, C-3), 80.5 (CH, C-9), 72.4 (CH, C-2), 72.2 (C, C-8), 52.2 (CH, C-5), 41.3 (CH\(_2\), C-1), 40.7 and 39.8 (C, C-4 and C-10), 38.6 (CH\(_2\), C-7), 29.1 (CH\(_3\), C-11), 28.7 (CH\(_3\), C-12), 21.5 (CH\(_3\), COCH\(_3\)), 21.0 (CH\(_3\), COCH\(_3\)), 17.6 (CH\(_2\), C-6), 16.6 (CH\(_3\), C-13), 15.9 (CH\(_3\), C-14); HRLSIMS \( m/z \) 365.1941 [M + Na\(^+\)] (calcld. for \( \text{C}_{18}\text{H}_{30}\text{O}_6\text{Na} \ 365.1940 \)).

**Enzymatic Acetylation of 22a with CCL**

Compound **22a** (50 mg, 0.2 mmol) was dissolved in 15 mL of vinyl acetate, and 300 mg of lipase CCL was added. The mixture was shaken on an orbital shaker at 40°C for 20 h. The reaction was filtered and the solvent evaporated under reduced pressure. Chromatography over silica gel yielded 38 mg of monoacetate **22d** (65%): white powder; \([\alpha]_D^{20} - 2 \) (CHCl\(_3\); c 1); \( v_{\text{max}}^{\text{CHCl}_3} \) cm\(^{-1}\): 3431, 2965, 1726, 1367, 1254, 1050; \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 4.97 (1H, ddd, \( J_1 = 4.4 \) Hz, \( J_2 = 10.1 \) Hz, \( J_3 = 11.5 \) Hz, H-2\( \beta \)), 3.17 (1H, d, \( J = 10.1 \) Hz, H-3\( \alpha \)), 2.86 (1H, s, H-9\( \alpha \)), 2.07 (3H, s, COCH\(_3\)), 1.22 (3H, s, CH\(_3\)), 1.12 (3H, s, CH\(_3\)), 1.06 (3H, s, CH\(_3\)) and 0.90 (3H, s, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 171.8 (C, COCH\(_3\)), 83.6 (CH, C-3), 81.0 (CH, C-9), 72.7 (CH, C-2), 72.4 (C, C-8), 52.2 (CH, C-5), 42.3 (CH\(_2\), C-1), 40.8 and 39.9 (C, C-4 and C-10), 39.2 (CH\(_2\), C-7), 29.5 (CH\(_3\), C-11), 28.7 (CH\(_3\), C-12), 21.4 (CH\(_3\), COCH\(_3\)), 17.6 (CH\(_2\), C-6), 16.8 (CH\(_3\), C-13), 14.6 (CH\(_3\), C-14); HRLSIMS \( m/z \) 323.1152 [M + Na\(^+\)] (calcld. for \( \text{C}_{16}\text{H}_{28}\text{O}_5\text{Na} \ 323.1160 \)).

**Treatment of 22a with 2,2-Dimethoxypropane**

Compound **22a** (100 mg, 0.4 mmol) was dissolved in 5 mL of 2,2-dimethoxy-propane, a catalytic amount of PTSP was added, and the mixture was stirred at rt for 5 h. The mixture was diluted with H\(_2\)O and extracted with CH\(_2\)Cl\(_2\). The organic phase was dried with anhydrous Na\(_2\)SO\(_4\) and evaporated under reduced pressure. Chromatography over silica gel yielded 88 mg of **23** (76%): white powder; \([\alpha]_D^{20} + 4 \) (CHCl\(_3\); c 1); \( v_{\text{max}}^{\text{CHCl}_3} \) cm\(^{-1}\): 3263, 2926, 1642, 1369; \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 3.72 (1H, ddd, \( J_1 = 3.9 \) Hz, \( J_2 = 9.4 \) Hz, \( J_3 = 11.8 \) Hz, H-2\( \beta \)), 3.00 (1H, d, \( J = 9.4 \) Hz, H-3\( \alpha \)), 2.94 (1H, s, H-9\( \alpha \)), 1.46 (3H, s, CH\(_3\) acetonide), 1.42 (3H, s, CH\(_3\) acetonide), 1.22 (3H, s, 3H-11), 1.11 (3H, s, 3H-14), 1.05 (3H, s, 3H-12) and 0.91 (3H, s, 3H-13); \(^{13}\)C NMR
Oxidation of 23 with NaIO₄

Compound 23 (45 mg, 0.1 mmol) was dissolved in 5 ml of acetone, and 50 mg of NaIO₄ (0.2 mmol) in 2 mL of H₂O was added. The mixture was stirred for 12 h at rt, diluted with H₂O, and extracted with CH₂Cl₂. The organic layer was dried with anhydrous Na₂SO₄ and evaporated under reduced pressure. Chromatography over silica gel yielded 31 mg of 24 (70%): viscous oil; [α]D 20 + 3 (CHCl₃; c 1); νmaxCHCl₃ cm⁻¹: 2925, 2854, 1723, 1648, 1460, 1377; ¹H NMR (CDCl₃) δ 9.31 (1H, s, H-9), 3.72 (1H, ddd, J₁ = 4.0 Hz, J₂ = 9.4 Hz, J₃ = 11.7 Hz, H-2b), 3.08 (1H, d, J = 9.4 Hz, H-3a), 2.08 (3H, s, CH₃), 1.43 (3H, s, CH₃ acetone), 1.40 (3H, s, CH₃ acetone), 1.13 (3H, s, 3H-14), 0.98 (3H, s, 3H-12) and 0.87 (3H, s, 3H-13); ¹³C NMR (CDCl₃) δ 207.6 (C, C-8), 204.4 (CH, C-9), 109.5 (C, COO acetone), 88.2 (CH, C-3), 71.0 (CH, C-2), 51.9 (C, C-10), 47.1 (CH, C-5), 43.6 (CH₂, C-7), 38.9 (C, C-4), 35.8 (CH₂, C-1), 30.0 (CH₃, C-11), 28.6 (CH₃, C-12), 27.2 (CH₃ acetone), 26.9 (CH₃ acetone), 20.0 (CH₂, C-6), 16.3 and 16.2 (CH₃, C-13 and C-14); HRALSIMS m/z 319.1888 [M + Na]⁺ (calcd. for C₁₇H₂₈O₄Na 319.1888).

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