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Note

Carbon–carbon bond formation in carbohydrates by a photoreductive cyclization reaction

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Intensive work has been devoted to the synthesis of branched-chain sugars [1–3]. A strategy based on a radical cyclization reaction for the stereoselective C–C bond formation at the anomeric center has led to the formation of α- and β-*C*-glycosyl compounds [4]. In these syntheses, the initial radical is centered on the pyranosidic ring and the radical acceptor is located on a glycosyl side-chain [4]. Alternatively, the radical acceptor can be part of the pyranosidic ring and the radical is generated on a glycosyl side-chain [5]. Stereoselective synthesis of 2-*C*-branched pyranosides has also been accomplished by using radical cyclization [6].

We now report the synthesis of 2-oxabicyclo[4.3.0]nonan-7-ols, which involves a photoreductive radical cyclization [7] in which the radical is generated on the alkyl side-chain and the radical acceptor is part of the pyranosidic ring. Our starting materials are δ,ε-unsaturated *C*-glycosyl ketones and aldehydes of type **A**, the synthesis of which has been achieved by condensation of unsaturated *tert*-butyldimethylsilyl ethers on peracetylated glycals in the presence of a Lewis acid such as zinc bromide [8].

The photoreductive cyclization of systems of type **A** into the corresponding cyclopentanols of type **B** was carried out by irradiation at 254 nm in the presence of triethylamine (Scheme 1). The results are summarized in Scheme 2.

The *C*-glycosyl derivatives **1a**/**1b**, which were obtained as a mixture of two isomers in a ratio 4:1 led, after irradiation, to a mixture from which **7a** and **7b** were isolated in 58% and 15% yield, respectively. Similarly, the irradiation of **2** led to a 7:3 mixture of

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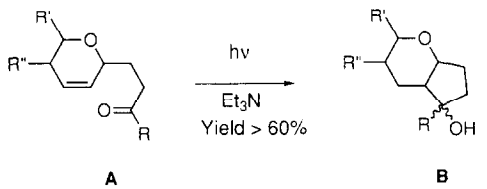
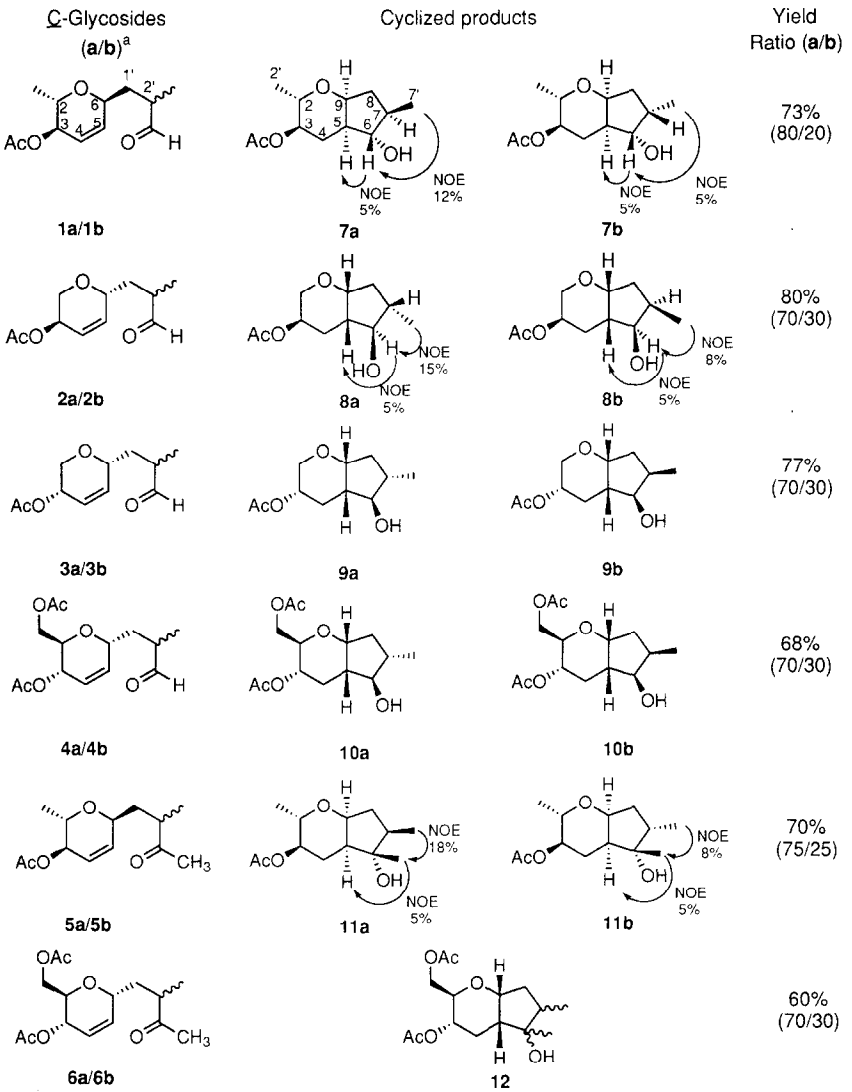


Scheme 1. Photoreductive cyclization of δ,ε-unsaturated *C*-glycosyl ketones and aldehydes.



Scheme 2. Irradiation of *C*-glycosyl derivatives in the presence of triethylamine. [a]The ratio **a**/**b** for compounds **1**–**4** is probably the thermodynamic ratio as it does not change in the presence of triethylamine. On the contrary, a 1:1 mixture of **5a**/**5b** was converted into a 3:1 mixture when treated by triethylamine. The same phenomenon was observed for compounds **6a**/**6b**. This is probably due to the fact that these compounds undergo epimerization at C-2′ in the presence of a base.

8a/8b (yield 80%). The ^{1}H NMR signal assignments were achieved by analysis of the COSY $^{1}H-^{1}H$ and COSY $^{13}C-^{1}H$ 2D-NMR spectra. The coupling constants of cyclopentanes are notoriously known for not being diagnostic of the *cis* or *trans* relative configurations of vicinal protons. This is also the case for these fused bicyclic systems. The coupling constants H-6–H-5 and H-6–H-7 vary between 5 Hz and 8 Hz (Table 1).

Irradiation of the protons of the methyl group at 0.90 ppm in **7a** led to a 12% increase in the integration of the signal assigned to H-6 (NOE). In compound **7b**, irradiation of the same group of protons at 1.10 ppm led to a 5% increase of the intensity of the signal assigned to H-6. NOE experiments have also been carried out with **8a** and **8b**. For instance, irradiation of the C-7′ methyl signal (0.90 ppm) in **8a** led to a 15% increase of the intensity of the signal assigned to H-6. Similarly, irradiation of the C-7′ methyl signal (1.05 ppm) in **8b** led to a 8% increase of the signal assigned to H-6. It appears that, for these 2-oxabicyclo[4.3.0]nonan-7-ols, a coupling constant of ~ 8.0 Hz implies a *trans* relationship between the vicinal protons H-6–H-5 and H-6–H-7 and that a coupling constant of ~ 5.3 Hz is typical of vicinal protons having a *cis* relationship. We tentatively assign the *trans* relationship between protons H-5–H-6 based on the small NOE effect (5%) detected between them.

Irradiation (254 nm) of **3** and **4** led to **9a/9b** (yield 78%) and **10a/10b** (yield 68%), respectively. Since **9a** and **9b**, **10a** and **10b** showed similar ^{1}H NMR characteristics compared to **8a** and **8b**, we deduce that for the major isomers, H-6 and H-7 have a *trans* relationship, while for the minor isomers, H-6 and H-7 adopt a *cis* relationship.

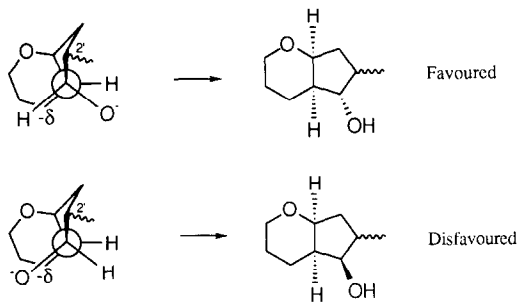
Irradiation of **5**, under photoreductive conditions, produced a 3:1 mixture of two isomers **11a** and **11b** in a 70% yield. NOE Experiments confirmed the proximity of the methyl groups at C-6 and at C-7 in **11a** (18% increase) and in **11b** (8% intensity increase). This result is in agreement with a *cis* relationship between the methyl groups at C-6 and C-7 in **11a** and a *trans* relationship between the methyl groups at C-6 and C-7 in **11b**.

Irradiation of **6** in the presence of triethylamine produced **12** (60% yield), which was a 7:3 mixture of two isomers that could not be separated by flash chromatography.

The relative configuration of the hydroxyl and pyranosyl ring deserves further comments. In the special case of a ketyl radical anion intermediate, the stereoselectivity can be rationalized considering repulsive electrostatic interaction between the negatively charged oxygen atom and the partially negatively charged terminal sp^2 carbon atom in the C_5 cyclic transition state (Scheme 3). This is in agreement with the accepted hypothesis of control, in the transition state, of the radical-anion addition to the alkene

Table 1
Coupling constants in Hz for vicinal protons H-5–H-6 and H-6–H-7 in compounds **7** and **8**

Compounds	Protons	
	H-5–H-6	H-6–H-7
7a	8.1	8.1
7b	8.1	5.5
8a	8.1	8.1
8b	8.0	5.2



Scheme 3. Possible transition states for the intramolecular ketyl radical-anion addition at the unsaturation.

[9]. We therefore suppose that the relative configuration can be controlled by the dihedral angle between the C–O bond and the olefinic bond. The transition state with the greatest dihedral angle between these bonds will be favored. The methyl group at C-2′ did not seem to have any influence on the cyclization.

The proposed strategy should prove useful for generating C–C bonds at C-2 of pyranosides in high yield and stereoselectivity.

1. Experimental

General methods.—All experiments were run under an Ar atmosphere. ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker AC 300 instrument at 300 MHz and 75 MHz respectively, in $CDCl_3$ (Me_4Si as internal standard). Homonuclear $^{1}H\{^{1}H\}$ NOEs were determined by means of the NOE difference technique, using 8 s low-power (5 mW) presaturation. 512 Transients were acquired using 32 K data points and a sweep width of 3000 Hz, in alternate groups of eight, irradiating on/off resonance. A 90° pulse was used during acquisition. IR spectra were recorded on a Perkin–Elmer Infracord 137 spectrometer. Mass spectra were run on a Hewlett–Packard (EI mode at 70 eV). Flash chromatography was performed with E. Merck Silicagel 0.043–0.063 nm.

Products **1–6** were synthesized according to [8]. Preparative irradiations were conducted in a carrousel type system equipped with 12 low pressure mercury Philips TUV 15 lamps (254 nm), using 10 mm o.d. quartz tubes. Acetonitrile and triethylamine were distilled from CaH_2. In a typical experiment, a solution of *C*-glycoside (0.5 g, 1 equiv) in dry MeCN (5×10^{-2} M) was deoxygenated by bubbling Ar for 15 min. Triethylamine (5 equiv) was added and the solution was irradiated at 254 nm for 2 h. Triethylamine and MeCN were evaporated and the crude mixture was purified by flash chromatography.

The numbering of compounds **7–12** used for the interpretation of NMR spectra is indicated in Scheme 2.

(1S,3S,4R,6R,7S,8R) [(1S,3S,4R,6R,7S,8S)]-4-Acetoxy-3,8-dimethyl-2-oxabicyclo[4.3.0]nonan-7-ol (**7a,7b**).—The two isomers were separated by flash chromatography with 7:3 petroleum ether–EtOAc as the eluent. Isomer **7a** was obtained as a syrup

(0.292 g, 58%); $[\alpha]_D$ −117° (*c* 2, $CHCl_3$); IR ($CHCl_3$): 3550, 1730 cm^{-1}; NMR, ^1H: δ 0.90 (d, 3 H, $J_{CH,CH_3\text{-}7,7'}$ 7.1 Hz, CH_3-7′), 1.25 (d, 3 H, $J_{CH,CH_3\text{-}2,2'}$ 7.0 Hz, CH_3-2′), 1.34 (ddd, 1 H, $J_{8,7}$ 9.7, $J_{8,8'}$ 14.1, $J_{8,9}$ 4.4 Hz, H-8), 1.56 (m, 1 H, H-4), 1.69 (m, 1 H, H-7), 1.73 (dd, 1 H, $J_{5,6}$ 8.1, $J_{5,9}$ 5.6 Hz, H-5), 2.08 (m, 1 H, H-4), 2.10 (s, 3 H, *Me*COO), 2.23 (ddd, 1 H, $J_{8',7}$ 8.7, $J_{8',8}$ 14.1, $J_{8',9}$ 7.2 Hz, H-8′), 3.73 (dd, 1 H, $J_{6,5}$ 8.1, $J_{6,7}$ 8.1 Hz, H-6), 3.90 (m, 2 H, H-2, OH), 4.18 (ddd, 1 H, $J_{9,8}$ 7.2, $J_{9,8'}$ 4.4, $J_{9,5}$ 5.6 Hz, H-9), 4.59 (m, 1 H, H-3); ^{13}C ($CDCl_3$): δ 16.1 (q, C-2′), 18.2 (q, CH_3-7′), 21.3 (q, *Me*COO), 24.3 (t, C-4), 36.7 (t, C-8), 40.0 (d, C-7), 44.2 (d, C-5), 69.1 (d, C-9), 70.5 (d, C-2), 71.3 (d, C-3), 82.1 (d, C-6), 170.4 (s, Me*C*OO). MS *m*/*z* 228 ($M^{+\cdot}$, 18), 188 (100), 128 (71). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.25; H, 8.80.

Isomer **7b** was obtained as a syrup (0.075 g, 15%); $[\alpha]_D$ +139° (*c* 2, $CHCl_3$); IR ($CHCl_3$): 3550, 1730 cm^{-1}; NMR, ^1H: δ 1.10 (d, 3 H $J_{CH,CH_3\text{-}7,7'}$ 7.0 Hz, CH_3-7′), 1.20 (d, 3 H, $J_{CH,CH_3\text{-}2,2'}$ 6.9 Hz, CH_3-2′), 1.54 (m, 1 H, H-4), 1.62 (m, 1 H, H-8), 1.87 (m, 1 H, H-8), 2.00 (m, 1 H, H-5); 2.05 (m, 1 H, H-4), 2.20 (s, 3 H, *Me*COO), 2.37 (ddd, 1 H, $J_{7,6}$ 5.5, $J_{7,8}$ 8.1, $J_{7,8'}$ 5.6 Hz, H-7), 3.70 (sl, 2 H, H-2, OH), 4.00 (dd, 1 H, $J_{6,7}$ 5.5, $J_{6,5}$ 8.1 Hz, H-6), 4.20 (m, 1 H, H-9), 4.10 (m, 1 H, H-3); ^{13}C ($CDCl_3$): δ 14.0 (q, CH_3-7′), 16.5 (q, CH_3-2′), 21.1 (q, *Me*COO), 25.9 (t, C-4), 34.7 (d, C-7), 36.8 (t, C-8), 44.9 (d, C-5), 70.0 (d, C-2), 71.2 (d, C-9), 72.0 (d, C-3), 78.8 (C-6), 170.3 (s, Me*C*OO). MS: *m*/*z* 228 ($M^{+\cdot}$, 18), 188 (100), 128 (78). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.05; H, 8.51.

(1R,4R,6S,7R,8S) [(1R,4R,6S,7R,8R)]-4-Acetoxy-8-methyl-2-oxabicyclo[4.3.0]nonan-7-ol (**8a**,**8b**).—The two isomers were separated by flash chromatography with 6:4 petroleum ether–EtOAc as the eluent. Isomer **8a** was obtained as a syrup (0.282 g, 56%); $[\alpha]_D$ −128° (*c* 1.5, $CHCl_3$); IR ($CHCl_3$): 3500, 1700 cm^{-1}; NMR, ^1H: δ 0.90 (d, 3 H, $J_{CH,CH_3\text{-}7,7'}$ 7.0 Hz, CH_3-7′), 1.25–1.75 (m, 3 H, 2 × H-4, H-7), 1.83 (m, 1 H, H-5), 2.05 (s, 3 H, *Me*COO), 2.10–2.40 (m, 3 H, 2 × H-8, OH), 3.20 (dt, 1 H, $J_{9,8}$ 7.5, $J_{9,5}$ 1.2 Hz, H-9), 3.75 (dd, 1 H, $J_{6,5}$ 8.1, $J_{6,7}$ 8.1 Hz, H-6), 3.90–4.10 (m, 2 × H-2) 4.80–5.20 (m, 1 H, H-3); ^{13}C ($CDCl_3$): δ 18.2 (q, CH_3-7′), 20.9 (q, *Me*COO), 25.8 (t, C-4), 34.4 (d, C-7), 38.0 (t, C-8), 38.8 (d, C-5), 65.2 (d, C-9), 66.5 (d, C-3), 68.7 (t, C-2), 78.9 (d, C-6), 170.4 (s, Me*C*OO). MS: *m*/*z* 214 ($M^{+\cdot}$, 12), 202 (100), 184 (73). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.46. Found: C, 61.70; H, 8.52.

Isomer **8b** was obtained as a syrup (0.120 g, 24%); $[\alpha]_D$ +110° (*c* 2, $CHCl_3$); IR ($CHCl_3$): 3500, 1705 cm^{-1}; NMR, ^1H: δ 1.05 (d, 3 H, $J_{CH,CH_3\text{-}7,7'}$ 6.9 Hz, CH_3-7′), 1.35–1.80 (m, 3 H, 2 × H-4, H-7), 1.90 (m, 1 H, H-5), 2.10 (s, 3 H, *Me*COO), 2.12–2.40 (m, 3 H, 2 × H-8, OH), 3.20 (dt, 1 H, $J_{9,8}$ 7.5, $J_{9,5}$ 1.2 Hz, H-9), 3.55–4.00 (m, 2 H, 2 × H-2), 4.05 (dd, 1 H, $J_{6,5}$ 8.0, $J_{6,7}$ 5.2 Hz, H-6), 4.84–5.20 (m, 1 H, H-3); ^{13}C ($CDCl_3$): δ 18.9 (q, CH_3-7′), 20.9 (q, *Me*COO), 25.8 (t, C-4), 37.0 (d, C-7), 38.4 (t, C-8), 38.8 (d, C-5), 65.5 (d, C-9), 67.0 (d, C-3), 68.7 (t, C-2), 78.4 (d, C-6), 170.4 (s, Me*C*OO). MS: *m*/*z* 214 ($M^{+\cdot}$, 9), 202 (100), 184 (70). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.46. Found: C, 61.63; H, 8.49.

(1R,4S,6S,7R,8S) [(1R,4S,6S,7R,8R)]-4-Acetoxy-8-methyl-2-oxabicyclo[4.3.0]nonan-7-ol (**9a**,**9b**).—The two isomers were purified by flash chromatography with 6:4 petroleum ether–EtOAc as the eluent. Isomer **9a** was obtained as a

syrup (0.272 g, 54%); $[\alpha]_D$ +136° (*c* 1.5, $CHCl_3$); IR ($CHCl_3$): 3500, 1700 cm^{-1}; NMR, ^1H: δ 0.92 (d, 3 H, $J_{CH,CH_3\text{-}7,7'}$ 7.0 Hz, CH_3-7'), 2.15 (s, 3 H, *Me*COO), 1.24–1.75 (m, 3 H, 2 × H-4, H-7), 1.85 (m, 1 H, H-5), 2.12–2.40 (m, 3 H, 2 × H-8, OH), 3.20 (dt, 1 H, $J_{9,8}$ 7.5, $J_{9,5}$ 1.2 Hz, H-9), 3.55–400 (m, 2 H, 2 × H-2), 4.10 (m, 1 H, H-6), 4.84–5.20 (m, 1 H, H-3); ^{13}C ($CDCl_3$): δ 20.2 (q, CH_3-7'), 21.2 (q, *Me*COO), 24.8 (t, C-4), 34.8 (d, C-7), 39.1 (t, C-8), 40.8 (d, C-5), 64.2 (d, C-9), 65.5 (d, C-3), 67.9 (t, C-2), 79.9 (d, C-6), 170.2 (s, Me*C*OO). MS: *m*/*z* 214 (M^+, 12), 202 (100), 184 (73). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.46. Found: C, 61.60; H, 8.25.

Isomer **9b** was obtained as a syrup (0.116 g, 23%); $[\alpha]_D$ −130° (*c* 2, $CHCl_3$). IR ($CHCl_3$): 3500, 1700 cm^{-1}; NMR, ^1H: δ 1.01 (d, 3 H, $J_{CH,CH_3\text{-}7,7'}$ 7.0 Hz, CH_3-7'), 1.24–1.60 (m, 3 H, 2 × H-4, H-7), 1.90 (m, 1 H, H-5), 2.12 (s, 3H, *Me*COO), 2.12–2.40 (m, 3 H, 2 × H-8, OH), 3.20 (dt, 1 H, $J_{9,8}$ 7.5, $J_{9,5}$ 1.2 Hz, H-9), 3.59–3.90 (m, 2 H, 2 × H-2), 4.05 (m, 1 H, H-6), 4.84–5.20 (m, 1 H, H-3); ^{13}C ($CDCl_3$): δ 17.2 (q, CH_3-7'), 24.8 (q, *Me*COO), 26.9 (t, C-4), 36.8 (d, C-7), 37.9 (t, C-8), 39.0 (d, C-5), 64.9 (d, C-9), 66.2 (d, C-3), 69.0 (t, C-2), 77.4 (d, C-6), 170.4 (s). MS: *m*/*z* 214 (M^+, 6), 202 (100), 184 (70). Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.46. Found: C, 61.82; H, 8.53.

(1R,3R,4S,6S,7R,8S) [(1R,3R,4S,6S,7R,8R)]-4-Acetoxy-3-(acetoxymethyl)-8-methyl-2-oxabicyclo[4.3.0]nonan-7-ol (**10a,10b**).—The two isomers were separated by flash chromatography with 7:3 petroleum ether–EtOAc as the eluent. Isomer **10a** was obtained as a syrup (0.242 g, 48%); $[\alpha]_D$ +198° (*c* 0.1, $CHCl_3$); IR ($CHCl_3$): 3550, 1730 cm^{-1}; NMR, ^1H: δ 1.00 (d, 3 H, $J_{CH,CH_3\text{-}7,7'}$ 7.0 Hz, CH_3-7'), 1.20–1.65 (m, 4 H, 2 × H-8, 2 × H-4), 1.70 (ddd, 1 H, $J_{7,6}$ 8.1, $J_{7,8}$ 8.7, $J_{7,8'}$ 9.7 Hz, H-7), 1.75 (m, 1 H, H-5), 2.15 (s, 6 H, *Me*COO), 3.60 (dd, 1 H, $J_{6,5}$ 8.1, $J_{6,7}$ 8.1 Hz, H-6), 3.85–4.70 (m, 6 H, H-9, 2 × H-2', H-2, H-3, OH); ^{13}C ($CDCl_3$): δ 13.8 (q, CH_3-7'), 18.3 (q, *Me*COO), 20.8 (q, *Me*COO), 27.2 (t, C-4), 36.6 (t, C-8), 38.2 (d, C-7), 45.6 (d, C-5), 62.5 (t, C-2'), 68.0 (d, C-9), 71.0 (d, C-2), 72.7 (d, C-3), 79.6 (d, C-6), 170.2 (s, Me*C*OO), 170.8 (s, Me*C*OO). MS: *m*/*z* 286 (M^+, 12), 268 (35), 222 (100). Anal. Calcd. for $C_{14}H_{22}O_6$: C, 58.72; H, 7.74. Found: C, 58.60; H, 7.70.

Isomer **10b** (0.100 g, 20%); $[\alpha]_D$ −10° (*c* 0.5, $CHCl_3$); IR ($CHCl_3$): 3470, 1720 cm^{-1}; NMR, ^1H: δ 1.12 (d, 3 H, $J_{CH,CH_3\text{-}7,7'}$ 7.1 Hz, CH_3-7'), 1.20–1.80 (m, 5 H, 2 × H-8, 2 × H-4, H-5), 1.85 (m, 1 H, H-7), 1.95 (s, 6 H, 2 × *Me*COO), 2.35 (s, 1 H, OH), 3.60 (dd, 1 H, $J_{6,5}$ 8.1, $J_{6,7}$ 5.6 Hz, H-6), 3.75–450 (m, 5 H, H-2, H-9, H-3, 2 × H-2'); ^{13}C ($CDCl_3$): δ 13.6 (q, CH_3-7'), 18.3 (q, *Me*COO), 21.1 (q, *Me*COO), 24.3 (t, C-4), 35.0 (t, C-8), 38.0 (d, C-7), 45.6 (d, C-5), 62.7 (t, C-2'), 68.8 (d, C-9), 71.9 (d, C-2), 72.4 (d, C-3), 79.4 (d, C-6), 170.0 (s, Me*C*OO), 170.8 (s, Me*C*OO). MS: *m*/*z* 286 (M^+, 5), 268 (30), 222 (100). Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.72; H, 7.74. Found: C, 58.87; H, 7.65.

(1S,3S,4R,6R,7S,8R) [(1S,3S,4R,6R,7S,8S)]-4-Acetoxy-3,7,8-trimethyl-2-oxabicyclo[4.3.0]nonan-7-ol (**11a,11b**) .—The two isomers were purified by flash chromatography with 7:3 petroleum ether–EtOAc as the eluent. Isomer **11a** was obtained as a syrup (0.262 g, 52%); $[\alpha]_D$ +237° (*c* 0.1, $CHCl_3$); IR ($CHCl_3$): 3500, 1720 cm^{-1}; NMR, ^1H: δ 0.90 (d, 3 H, $J_{CH,CH_3\text{-}7,7'}$ 7.0 Hz, CH_3-7'), 1.15 (s, 3H, CH_3-6'), 1.25 (d, 3 H, $J_{CH,CH_3\text{-}2,2'}$ 7.1 Hz, CH_3-2'), 1.30–2.00 (m, 5 H, 2 × H-4, H-5, OH, H-7), 2.12 (s, 3 H, *Me*COO), 2.20–2.40 (m, 2 H, 2 × H-8), 3.70 (dt, 1 H, $J_{9,5}$ 1.6,

$J_{9,8}$ 6.3 Hz, H-9), 4.30 (m, 1 H, H-2), 4.60 (m, 1 H, H-3); ^{13}C ($CDCl_3$): δ 16.3 (q, CH_3-2′), 17.5 (q, CH_3-7′), 20.2 (q, *Me*COO), 21.2 (t, C-4), 29.0 (t, C-8), 39.1 (d, C-7), 49.1 (d, C-5), 69.7 (q, *C*H_3-6′), 71.5 (d, C-2), 73.9 (d, C-3), 81.2 (s, C-6) 170.2 (s, Me*C*OO). MS: *m*/*z* 242 ($M^{+\cdot}$, 18), 232 (35), 192 (100), 121 (45). Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.44; H 9.15. Found: C, 64.57; H, 9.30.

Isomer **11b** was obtained as a syrup (0.090 g, 18%); $[\alpha]_D$ −53° (*c* 0.5, $CHCl_3$); IR ($CHCl_3$): 3500, 1720 cm^{-1}; NMR, ^1H: δ 0.95 (d, 3 H, $J_{CH.CH_3\text{-}7,7'}$ 7.0 Hz, CH_3-7′), 1.20 (s, 3 H, C*H*$_3$-6′), 1.30 (d, 3 H, $J_{CH.CH_3\text{-}2,2'}$ 7.0 Hz, CH_3-2′), 1.35–2.15 (m, 5 H, 2 × H-4, H-5, OH, H-7), 2.20 (s, 3 H, *Me*COO), 2.30–2.40 (m, 2 H, 2 × H-8), 3.60 (dt, 1 H, $J_{9,8}$ 6.4, $J_{9,5}$ 1.7 Hz, H-9), 4.30–4.65 (m, 1 H, H-2), 4.60 (m, 1H, H-3); ^{13}C ($CDCl_3$): δ 15.9 (q, CH_3-2′), 16.7 (q, *C*H_3-7′), 17.7 (q, *Me*COO), 21.0 (t, C-4), 28.6 (t, C-8), 38.7 (d, C-7), 49.0 (d, C-5), 68.3 (d, C-2), 71.0 (q, *C*H_3-6′), 72.4 (d, C-3), 81.8 (s, C-6), 170.0 (s, Me*C*OO). MS: *m*/*z* 242 ($M^{+\cdot}$, 20), 232 (25), 192 (100), 121 (35). Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.44; H 9.15. Found: C, 64.51; H, 9.24.

(1R,3R,4S,6S)-4-Acetoxy-3-(acetoxymethyl)-7,8-dimethyl-2-oxabicyclo[4.3.0]nonan-7-ol (**12**).—The purification was achieved by flash chromatography with petroleum ether–EtOAc as the eluent. Compound **12** was obtained as a syrup (0.302 g, 60%); $[\alpha]_D$ +188° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 3470, 1720 cm^{-1}; NMR, ^1H: δ for the major isomer 0.95 (d, 3 H, $J_{CH.CH_3\text{-}7,7'}$ 7.2 Hz, C*H*$_3$-7′), 2.10 (s, 6 H, 2 × *Me*COO); for the minor isomer 1.15 (d, 3 H, $J_{CH.CH_3\text{-}7,7'}$ 7.0 Hz, C*H*$_3$-7′), 1.90 (s, 6 H, 2 × *Me*COO); for both isomers 1.00 (s, 3 H, CH_3-6′), 1.30–1.60 (m, 4 H, 2 × H-4, H-7), 2.10–2.40 (m, 3 H, 2 × H-8), 4.00–4.50 (m, 5 H, H-9, H-3, H-2, 2 × H-2′); ^{13}C ($CDCl_3$): δ for the major isomer 12.3 (q, CH_3-7′), 20.7 (q, *Me*COO), 20.9 (q, *Me*COO), 28.1 (t, C-4), 34.7 (t, C-8), 38.1 (d, C-7), 48.9 (d, C-5), 62.6 (t, C-2′), 67.2 (q, CH_3-6′), 68.4 (d, C-2), 69.0 (d, C-9), 70.6 (d, C-3), 81.3 (s, C-6), 170.8 (s, Me*C*OO), 170.9 (s, Me*C*OO); for the minor isomer 18.9 (q, CH_3-7′), 20.5 (q, *Me*COO), 20.8 (q, *Me*COO), 28.1 (t, C-4), 34.3 (t, C-8), 38.2 (d, C-7), 48.9 (d, C-5), 62.1 (t, C-2′), 67.0 (q, CH_3-6′), 68.4 (d, C-2), 70.0 (d, C-9), 70.5 (d, C-3), 80.9 (s, C-6), 170.8 (s, Me*C*OO), 170.9 (s, Me*C*OO). MS: *m*/*z* 300 ($M^{+\cdot}$, 6), 282 (100), 202 (73). Anal. Calcd. for $C_{15}H_{24}O_6$: C, 59.98; H 8.05. Found: C, 59.75; H, 8.12.

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