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Iridoids from *Crescentia alata*[§]

María Guadalupe Valladares and María Yolanda Rios*

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Chamilpa 62209, Cuernavaca, Morelos, México

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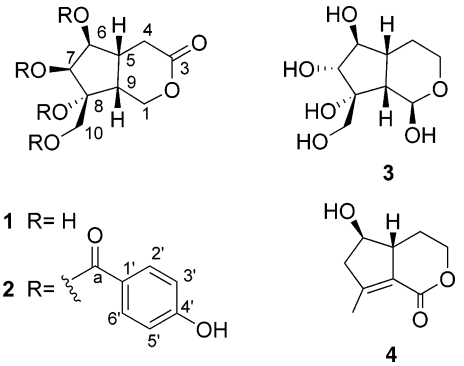
Four new 11-nor-iridoids, 6β,7β,8α,10-tetrahydroxy-*cis*-2-oxabicyclo[4.3.0]nonan-3-one (**1**), 6β,7β,8α,10-tetra-*p*-hydroxybenzoyl-*cis*-2-oxabicyclo[4.3.0]nonan-3-one (**2**), 1β,6β,7α,8α,10-pentahydroxy-*cis*-2-oxabicyclo[4.3.0]nonane (**3**), and 6β-hydroxy-2-oxabicyclo[4.3.0]Δ^{8-9}-nonen-1-one (**4**), were isolated from the pulp of the fruits of *Crescentia alata*. Although a limited number of *Crescentia* species have been studied chemically, iridoids lacking C-11 have been isolated from the fruits of these species, and the isolation of compounds **1**−**4** from *C. alata* is in accordance with the constituents of the species previously analyzed. The structures of these compounds were established on the basis of IR, UV, ^{1}H and ^{13}C NMR, DEPT, COSY, HSQC, HMBC, MS, and X-ray data.

Crescentia alata Kunth (Bignoniaceae) [common names: cuatecomatl, kuhteconatl (náhuatl), cuastecomate, and cirian] is a tree growing in mild and hot, dry arid zones of Mexico. The black mature pulp of the fruits from this plant has been employed since the eighteenth century to prepare a tonic used to relieve different respiratory infections, cough, asthma, bronchitis, tuberculosis, and breast pain.[1] A previous report to validate the use of *C. alata* in the traditional medicine of Guatemala as an anti-inflammatory remedy showed that a methanol extract of the leaves from this plant exerted significant activity *in vivo* and that this extract contained rutin, kaempferol, and kaempferol 3-*O*-rutinoside.[2] There have been no previous literature reports on the chemical composition of the fruits of this species.

C. alata is a 10 to 14 m tree with spherical fruits of approximately 15 cm diameter. The mature fruits included a black pulp, and the methanol extract yielded compounds **1**−**4**, triacylglycerides, 3β-sitosterol palmitate,[3] stigmast-4-en-3-one,[4] stigmast-4,22-dien-3-one,[5] ningpogenine,[6] sucrose, and glycerol. The structure elucidation of compounds **1**−**4** is described herein.



3 **4**

Compound **1** was isolated as white needles and had, on the basis of HRCIMS [(M + H)$^+$, *m*/*z* 219.0865], a molecular formula of $C_9H_{14}O_6$, indicating three unsaturation degrees. One of these was due to the presence of a carbonyl group (1713 cm^{-1} in the IR and δ_C 176.3 in ^{13}C NMR spectrum). A bicyclic nor-iridoid skeleton was evidenced from the nine carbon resonances in the ^{13}C NMR and DEPT spectra of **1**, corresponding to three CH_2, four CH, and two quaternary carbons. Of these, in addition to the carbonyl group (*vide supra*), five signals were assigned to oxygenated carbons at δ 82.6 (C), 79.9 (CH), 79.4 (CH), 68.2 (CH_2), and 66.2 (CH_2), and three signals at δ 41.2 (CH), 41.0 (CH), and 33.8 (CH_2) were due to sp^3 carbons. In accordance with the COSY spectrum, three *gem* correlations were observed: the signal at δ_H 4.48 showed a cross-peak with the signal at δ_H 4.33 (H-1), the signal at δ_H 3.73 with those at δ_H 3.63 (H-10), and the signal at δ_H 2.73 with those at δ_H 2.58 (H-4). On the basis of the HMBC and HSQC spectra, the signals at δ_H 4.48 and 4.33 (δ_C 68.2, H-1) showed cross-peaks with the signals at δ_C 176.3 (C-3), 41.0 (C-5), 82.6 (C-8), and 41.2 (C-9), establishing that C-3 corresponded to the carbonyl group and that C-8 was an oxygenated quaternary carbon; the signals at δ_H 2.73 and 2.58 (δ_C 33.8, H-4) showed cross-peaks with C-3, C-5, C-9, and the signal at δ_C 79.4 (C-6), establishing that C-6 was an oxygenated tertiary carbon; the signal at δ_H 3.76 (δ_C 79.9) showed cross-peaks with C-5, C-8, and C-9, establishing that it corresponds to C-7 and identifies this as an oxygenated tertiary carbon; finally, the signals at δ_H 3.73 and 3.63 (δ_C 66.2, H-10) showed cross-peaks with C-7, C-8, and C-9. As a consequence, the four hydroxyl groups deduced from the molecular formula were located at C-6, C-7, C-8, and C-10, and this compound corresponded to 6,7,8,10-tetrahydroxy-2-oxabicyclo[4.3.0]nonan-3-one. The structure **1** was confirmed by X-ray diffraction measurements (Figure 1), showing a *cis* A/B ring junction and a *syn* orientation among H-5, OH-6, OH-7, CH_2-10, and H-9. In accordance with the biosynthetic origin of the iridoids,[7] the *cis* A/B ring junction is β, and **1** corresponds to 6β,7β,8α,10-tetrahydroxy-*cis*-2-oxabicyclo[4.3.0]nonan-3-one. On the basis of X-ray diffraction measurements and the ^{1}H NMR analysis, a value of J_{H5-H9} = 8.8 Hz corresponds to the β *cis* relationship between these hydrogens, a value of J_{H5-H6} = 8.0 Hz justified its *anti* relationship, and a value of J_{H6-H7} = 3.6 Hz justified a H_6-H_7 *syn* relationship.

The presence of aromatic rings in compound **2** was evident from the absorptions at 1606 and 1464 cm^{-1} in the IR spectrum and the absorption maximum at 251 nm in the UV spectrum. The presence of four *para*-substituted benzoyl residues was deduced from the observation of four signals for carbonyl groups at δ_C 165.0, 164.9, 164.4, and 164.0; eight singlet signals at δ_C 129.6, 129.4, 129.1,

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* Corresponding author. Tel and Fax: +52 (777) 329 79 97. E-mail: myolanda@uaem.mx.

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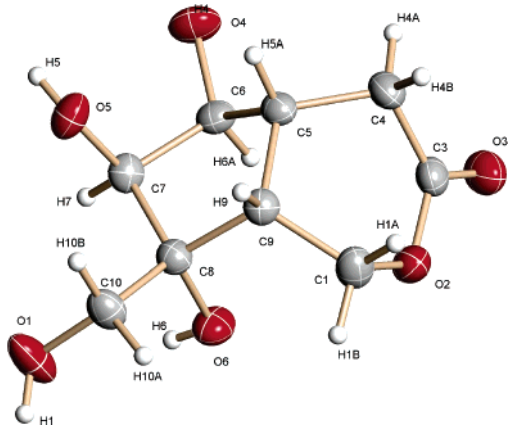

Figure 1. ORTEP view of 6β,7β,8α,10-tetrahydroxy-*cis*-2-oxabicyclo[4.3.0]nonan-3-one (**1**).

129.0, 128.0, 127.8, 127.7, and 127.6; and four AB systems at δ_H 7.95 d (8.4 Hz, δ_C 131.25), 7.77 d (8.8 Hz, δ_C 131.22), 7.73 d (8.4 Hz, δ_C 131.5), 7.66 d (8.4 Hz, δ_C 132.4), 7.61 d (8.4 Hz, δ_C 131.0), 7.54 d (8.4 Hz, δ_C 132.2), 7.53 d (8.8 Hz, δ_C 132.1), and 7.46 d (8.4 Hz, δ_C 132.1) in the ^{1}H, ^{13}C NMR and HSQC spectra. The bicyclic nor-iridoid nature of **2** was deduced from analysis of the nine additional signals in the ^{13}C NMR spectrum and from their corresponding signals in the ^{1}H NMR spectrum. The downfield shift observed for H-6 ($\Delta\delta$ 5.50−4.06 = 1.44), H-7 ($\Delta\delta$ 6.40 − 3.76 = 2.64), H-10a ($\Delta\delta$ 5.36 − 3.73 = 1.63), H-10b ($\Delta\delta$ 5.10 − 3.63 = 1.47), and C-8 ($\Delta\delta$ 88.1 − 82.6 = 5.5) with respect to **1** established that the four *para*-substituted benzoyl residues were located on the oxygens at C-6 to C-10 and that this natural product corresponded to the tetra-*p*-hydroxybenzoyl derivative of **1**. On the basis of ^{1}H NMR analysis, the β *cis* A/B ring junction was established in accordance with a value of J = 11.6 Hz for H_5−H_9, an *anti* relationship between H_5−H_6 was deduced from the value of J_{H5-H6} = 7.2 Hz, and a *syn* relationship between H_6−H_7 was established from J_{H6-H7} = 4.4 Hz. Thus, this natural product corresponds to 6β,7β,8α,10-tetra-*p*-hydroxybenzoyl-*cis*-2-oxabicyclo-[4.3.0]nonan-3-one (**2**). Compound **2** gave the HRFABMS peak at *m*/*z* 458.1262, corresponding to $[M - 2C_7H_4O_2]^+$, which justified the molecular formula $C_{37}H_{30}O_{14}$ and 23 unsaturation degrees.

Compound **3** was isolated as a white, amorphous powder with a positive ion HRCIMS $(M + H)^+$ at *m*/*z* 221.0616 ($C_9H_{16}O_6$) and two unsaturation degrees, in accordance with a bicyclic nor-iridoid skeleton. Nine carbon resonances were observed from the ^{13}C NMR and DEPT spectra: three CH_2, five CH, and one quaternary carbon. Of these, six signals were assigned to oxygenated carbons (one of a hemiacetal function), and three signals were due to sp^3 carbons. These data were in agreement with a dihydroisomer of **1**. The hemiacetal function was at C-1 on the basis of the HMBC and HSQC spectra. Compound **3** had a β *cis* A/B ring junction in accordance with a J = 10.0 Hz for H_5−H_9, an *anti* relationship between H_5−H_6 (J = 10.0 Hz), and an *anti* relationship between H_6−H_7 (J = 10.0 Hz); a value of J_{H9-H1} = 5.2 Hz justified an *anti* relationship between those hydrogens[8] and the β orientation of OH-1. As a consequence, compound **3** corresponds to 1β,6β,7α,8α,10-pentahydroxy-*cis*-2-oxabicyclo[4.3.0]nonane.

Compound **4** was a bicyclic nor-iridoid isolated as a yellow oil, which showed a positive ion in HREIMS [$(M)^+$] at *m*/*z* 168.0739 ($C_9H_{12}O_3$) and four unsaturation degrees. Two of these were due to the bicyclic skeleton, and two were due to a tetrasubstituted α,β-unsaturated carbonyl ester. The α,β-unsaturated carbonyl ester was located at C-1, C-9, and C-8 in accordance with cross-peaks between δ_H 2.65 and 2.54 (δ_C 46.9, H-7) and δ_H 2.20 (δ_C 17.0, H-10) and signals at δ_C 157.0 (C-8) and 122.6 (C-9) in the HMBC spectrum. Both hydrogens H-7 and δ_H 2.20 (δ_C 28.3, H-4b) showed cross-peaks with C-6 (δ_C 78.6), while δ_H 4.20 (H-6) showed cross-peaks with C-4 and C-5 (δ_C 50.1), establishing that a hydroxyl group was on C-6. In accordance with a J_{H5-H6} = 7.6 Hz, the OH-6 is β. Compound **4** was thus identified as 6β-hydroxy-2-oxabicyclo-[4.3.0]Δ^{8-9}-nonen-1-one.

Although a limited number of species from the genus *Crescentia* have been studied chemically, iridoids lacking C-11 have been isolated from the fruits of these species,[9,10] and the isolation of compounds **1**−**4** from *C. alata* is totally in accordance with the chemical constituents of the species previously analyzed.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer 341 MC polarimeter, and UV spectra were recorded on a Hewlett-Packard 8453 spectrometer using $CHCl_3$ as solvent. IR spectra were obtained in KBr or as films ($CHCl_3$) on a Bruker Vector 22 IR spectrometer. All NMR spectra were recorded on a Varian Unity 400 spectrometer at 400 MHz for ^{1}H NMR, ^{1}H−^{1}H COSY, HSQC, and HMBC and 100 MHz for ^{13}C NMR and ^{13}C DEPT, using $CDCl_3$ or CD_3OD as solvent as indicated. Chemical shifts are reported in ppm (δ) relative to the TMS signal. CIMS, EIMS, HRCIMS, and HREIMS were recorded on a JEOL JMStation-JM 700 mass spectrometer in a matrix of glycerol. X-ray diffraction measurements were obtained on a monocrystal Bruker Smart Apex (low temperature). GC-MS analyses were obtained using a Agilent 6890 GC System/5973 MSD chromatograph equipped with a HP-1 capillary column (length 30 m, i.d. 0.25 mm, 0.25 μm). The carrier gas was helium, and the linear gas velocity was 36 cm/s. The injector temperature was 250 °C, and the column temperature, initially at 45 °C, was gradually increased at a rate of 10 °C/min to 250 °C. For detection, a flame ionization detector at 280 °C, IE (scan 30−550 u), was used. The identification of each component was based on a comparison of its mass spectrum with those contained in the N-15598 Mass Spectral Library.

Plant Material. The mature fruits of *C. alata* were collected at Sierra de Huahutla, Morelos, México, in March 2003. The botanical specimen (voucher 17197) was identified by Biol. Juan Carlos Juárez Delgado from Centro de Educación AMbiental e Investigación de la Sierra de Huautla (CEAMISH) and deposited at the Herbarium of the Universidad Autónoma del Estado de Morelos (HUMO), Cuernavaca, Morelos, México.

Extraction and Isolation. The air-dried pulp of the mature fruits from *C. alata* (4 kg) was extracted with MeOH (20 L × 3) at room temperature. The extraction solvent was concentrated to dryness *in vacuo* to obtain 210 g of residue. Fractionation of this extract by open column chromatography was performed with a *n*-hexane−acetone gradient, collecting fractions of 500 mL each. The composition of the fractions was monitored by TLC, and the compounds were visualized using a UV lamp or by spraying with a 1% solution of $(NH_4)_4Ce(SO_4)_4{\cdot}H_2O$ in 2 N H_2SO_4. On the basis of TLC, the fractions were pooled into seven groups: F-1 (10.2 g, *n*-hexane, 100%), F-2 (7.7 g, *n*-hexane−acetone, 95:5), F-3 (3.9 g, *n*-hexane−acetone, 9:1), F-4 (4.7 g, *n*-hexane−acetone, 8:2), F-5 (9.0 g, *n*-hexane−acetone, 7:3), F-6 (6.6 g, *n*-hexane−acetone, 6:4), and F-7 (2.4 g, *n*-hexane−acetone, 5:5). Each fraction was further separated using column chromatography over silica gel 60 and a gradient of *n*-hexane−acetone−methanol as eluent. Fraction F-1 yielded a mixture of palmitic, palmitoleic, stearic, oleic, and linolenic acids (4.6 g, 2.19%, GC-MS retention times 18.50, 18.73, 20.21, 20.55, and 20.90 min, respectively); fraction F-2 yielded β-sitosteryl palmitate (236 mg, 0.11%) and an equal proportion mixture of estigmastan-4-en-3-one and estigmastan-4,22-dien-3-one (477 mg, 0.22%); fraction F-3 yielded a mixture of estigmastan-4-en-3-one and estigmastan-4,22-dien-3-one (89 mg, 0.04%), 6β,7β,8α,10-tetra-*p*-hydroxybenzoyl-*cis*-2-oxabicyclo[4.3.0]nonan-3-one (**2**, 79 mg, 0.037%), and 6β-hydroxy-2-oxabicyclo[4.3.0]Δ^{8-9}-nonen-1-one (**4**, 39 mg, 0.018%); fraction F-4 yielded ningpogenine (1.3 g, 0.62%); fraction F-5 yielded ningpogenine (286 mg, 0.14%) and 1β,6β,7α,8α,10-pentahydroxy-*cis*-2-oxabicyclo[4.3.0]nonane (**3**, 70 mg, 0.03%); fraction F-6 yielded **3** (43 mg, 0.02%) and sucrose (882 mg, 0.42%); and fraction F-7 yielded 6β,7β,8α,10-tetrahydroxy-*cis*-2-oxabicyclo[4.3.0]nonan-3-one (**1**, 384 mg, 0.18%) and glycerol (167 mg, 0.08%).

6β,7β,8α,10-Tetrahydroxy-*cis*-2-oxabicyclo[4.3.0]nonan-3-one (1): white needles; mp 164−165 °C; $[\alpha]_D^{25}$ +0.131 (*c* 0.45, $CHCl_3$); IR (KBr) ν_{max} 3381, 2927, 2855, 1713, 1466, 1380, 1095 cm^{-1}; ^{1}H NMR

(CD_3OD, 400 MHz) δ 4.48 (1H, dd, J = 12.0, 8.0 Hz, H-1a), 4.33 dd (1H, dd, J = 12.0, 6.8 Hz, H-1b), 4.06 (1H, dd, J = 8.0, 3.6 Hz, H-6), 3.76 (1H, d, J = 3.6 Hz, H-7), 3.73 (1H, d, J = 11.2 Hz, H-10a), 3.63 (1H, d, J = 11.2 Hz, H-10b), 2.73 (1H, dd, J = 14.4, 5.6 Hz, H-4a), 2.58 (1H, dd, J = 14.4, 8.0 Hz, H-4b), 2.53 (1H, dddd, J = 8.0, 8.8, 8.0, 5.6 Hz, H-5), 2.47 (1H, ddd, J = 8.0, 8.8, 6.8 Hz, H-9); ^{13}C NMR (CD_3OD, 100 MHz) δ 176.3 (C, C-3), 82.6 (C, C-8), 79.9 (CH, C-7a), 79.4 (CH, C-6), 68.2 (CH_2, C-1), 66.2 (CH_2, C-10), 41.2 (CH, C-9), 41.0 (CH, C-5), 33.8 (CH_2, C-4); CIMS m/z 219 $[M + H]^+$ (76), 201 $[M + H - H_2O]^+$ (35), 183 $[M + H - 2H_2O]^+$ (100), 165 $[M + H - 3H_2O]^+$ (79), 153 (53), 137 $[M + H - 3H_2O - CO]^+$ (67), 123 (23); HRCIMS m/z 219.0865 $[M + H]^+$ (calcd for $C_9H_{15}O_6$, 219.0868).

X-ray crystallographic analysis data of 1: crystal size 0.23 × 0.09 × 0.04 mm; molecular formula $C_9H_{14}O_6$; crystal system monoclinic; space group $P2(1)$; unit cell dimensions (a, b, c) 8.7505(9) Å, 5.1734(5) Å, 10.6057(11) Å; $\alpha = 90°$, $\beta = 98.6820(10)°$, $\gamma = 90°$, volume 474.62(8) Å^3; Z = 2; density 1.527 mg m^{-3}; absorption coefficient 0.129 mm^{-1}; $F(000)$ = 232; diffractometer used, Bruker APEX; radiation (λ) Cu Kα (0.71073 Å); 2θ range 1.94−25.00°; reflections collected, 4588; independent reflections, 1673; observed reflections, 1673 [R(int) = 0.0200]; final R indices (obsd data), R = 0.0284, R_w = 0.0746; goodness of fit, 1.080; T = 273(2) K. The structure was solved by direct methods and refined by full matrix least-squares on F^2.[11]

6β,7β,8α,10-Tetra-*p*-hydroxybenzoyl-*cis*-2-oxabicyclo[4.3.0]nonan-3-one (2): white, amorphous powder; $[\alpha]_D^{25}$ +56.2 (c 0.83, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 251 (2.70), 272 (0.96), 385 (0.35) nm; IR ($CHCl_3$) ν_{max} 3390, 2925, 2854, 1714, 1606, 1464, 1089 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (2H, d, J = 8.4 Hz, H-2‴,6‴), 7.77 (2H, d, J = 8.8 Hz, H-2″,6″), 7.73 (2H, d, J = 8.4 Hz, H-2⁗,5⁗), 7.66 (2H, d, J = 8.4 Hz, H-3‴,5‴), 7.61 (2H, d, J = 8.4 Hz, H-2′,6′), 7.54 (2H, d, J = 8.4 Hz, H-3⁗,5⁗), 7.53 (2H, d, J = 8.8 Hz, H-3″,5″), 7.46 (2H, d, J = 8.4 Hz, H-3′,5′), 6.40 (1H, d, J = 4.4 Hz, H-7), 5.50 (1H, dd, J = 7.2, 4.4 Hz, H-6), 5.36 (1H, d, J = 12.4 Hz, H-10a), 5.10 (1H, d, J = 12.4 Hz, H-10b), 4.70 (1H, dd, J = 12.4, 6.4 Hz, H-1a), 4.55 dd (1H, dd, J = 12.4, 5.6 Hz, H-1b), 3.33 (1H, ddd, J = 11.6, 6.4, 5.6 Hz, H-9), 3.16 (1H, dddd, J = 11.6, 7.2, 6.8, 7.2 Hz, H-5), 2.91 (1H, dd, J = 15.6, 6.8 Hz, H-4a), 2.79 (1H, dd, J = 15.6, 7.2 Hz, H-4b); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 65.7 (CH_2, C-1), 170.6 (C, C-3), 32.2 (CH_2, C-4), 38.2 (CH, C-5), 77.0 (CH, C-6), 75.9 (CH, C-7), 88.1 (C, C-8), 42.0 (CH, C-9), 63.5 (CH_2, C-10), 164.92 (C, C-a′), 128.0 (C, C-1′), 131.0 (CH, C-2′, C-6′), 132.07 (CH, C-3′, C-5′), 129.1 (C, C-4′), 164.0 (C, C-a″), 127.7 (C, C-1″), 131.22 (CH, C-2″, C-6″), 132.09 (CH, C-3″, C-5″), 129.4 (C, C-4″), 164.4 (C, C-a‴), 127.8 (C, C-1‴), 131.25 (CH, C-2‴, C-6‴), 132.4 (CH, C-3‴, C-5‴), 129.6 (C, C-4‴), 164.96 (C, C-a⁗), 127.6 (C, C-1⁗), 131.5 (CH, C-2⁗, C-6⁗), 132.2 (CH, C-3⁗, C-5⁗), 129.0 (C, C-4⁗); CIMS m/z 458 $[C_{23}H_{22}O_{10}, M - 2C_7H_4O_2]^+$ (20), 430 $[C_{22}H_{22}O_9, M - 2C_7H_4O_2 - CO]^+$ (100), 412 $[C_{22}H_{20}O_8, M - 2C_7H_4O_2 - CO - H_2O]^+$ (30), 293 $[C_{15}H_{17}O_6, M - 3C_7H_4O_2 - CO_2 - H]^+$ (97), 277 (43), 201 $[C_9H_{13}O_5, M - 4C_7H_4O_2 + H - H_2O]^+$ (24), 155 (29); (+)-FABMS m/z 430 $[C_{22}H_{22}O_9, M - 2C_7H_4O_2 - CO]^+$ (100), 412 $[C_{22}H_{20}O_8, M - 2C_7H_4O_2 - CO - H_2O]^+$ (57), 377 $[C_{22}H_{17}O_6, M - 2C_7H_4O_2 - CO - 3H_2O]^+$ (43), 339 $[C_{16}H_{19}O_8, M - 3C_7H_4O_2 + H]^+$ (22), 293 $[C_{15}H_{17}O_6, M - 3C_7H_4O_2 - CO_2 - H]^+$ (52), 279 (33); HRFABMS m/z 458.1262 $[M - 2C_7H_4O_2]^+$ (calcd for $C_{23}H_{22}O_{10}$, 458.1213).

1β,6β,7α,8α,10-Pentahydroxy-*cis*-2-oxabicyclo[4.3.0]nonane (3): white, amorphous powder; $[\alpha]_D^{25}$ +78.2 (c 0.11, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3382, 2918, 2851, 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.40 (1H, d, J = 5.2 Hz, H-1), 4.49 (1H, d, J = 10.4 Hz, H-10a), 4.14 (1H, dd, J = 10.0, 2.0 Hz, H-7), 3.99 (1H, dd, J = 10.0, 10.0 Hz, H-6), 3.90 (1H, ddd, J = 12.0, 12.0, 2.8 Hz, H-3a), 3.63 (1H, ddd, J = 12.0, 5.2, 2.0 Hz, H-3b), 3.51 (1H, dd, J = 10.4, 2.0 Hz, H-10b), 2.42 (1H, dd, J = 10.0, 5.2 Hz, H-9), 2.28 (1H, dddd, J = 10.0, 10.0, 6.0, 2.0 Hz, H-5), 1.84 (1H, dddd, J = 14.8, 12.0, 6.0, 1.2 Hz, H-4a), 1.71 (1H, dd, J = 14.8, 2.8 Hz, H-4b); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 100.1 (CH, C-1), 85.0 (C, C-8), 75.6 (CH, C-6), 73.6 (CH, C-7), 72.4 (CH_2, C-10), 55.8 (CH_2, C-3), 44.3 (CH, C-9), 35.2 (CH, C-5), 21.1 (CH_2, C-4); CIMS m/z 221 $[M + H]^+$ (43), 203 $[M + H - H_2O]^+$ (100), 185 $[M + H - 2H_2O]^+$ (34), 167 $[M + H - 3H_2O]^+$ (56), 155 (26), 149 $[M + H - 4H_2O]^+$ (19), 121 (17), 113 (33), 84 (21); HRCIMS m/z 221.0616 $[M + H]^+$ (calcd for $C_9H_{16}O_6$, 221.1225).

6β-Hydroxy-2-oxabicyclo[4.3.0]Δ$^{8-9}$-nonen-1-one (4): yellow oil; $[\alpha]_D^{25}$ +0.68 (c 0.06, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 246 (1.84) nm; IR ($CHCl_3$) ν_{max} 3365, 1727, 1652, 1603, 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.43 (1H, ddd, J = 11.2, 4.8, 2.8 Hz, H-3a), 4.27 (1H, ddd, J = 11.2, 12.0, 2.8 Hz, H-3b), 4.20 (1H, dt, J = 7.6, 8.8 Hz, H-6), 2.87 (1H, m, H-5), 2.65 (1H, ddd, J = 16.8, 8.0, 1.2 Hz, H-7a), 2.54 (1H, ddc, J = 16.8, 8.8, 1.6 Hz, H-7b), 2.20 (3H, s, H-10), 2.20 (1H, m, H-4b), 1.67 (1H, dddd, J = 13.6, 12.0, 12.0, 4.8 Hz, H-4a); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.1 (C, C-1), 69.4 (CH_2, C-3), 28.3 (CH_2, C-4), 50.1 (CH, C-5), 78.6 (CH, C-6), 46.9 (CH_2, C-7), 157.0 (C, C-8), 122.6 (C, C-9), 17.0 (CH_3, C-10); EIMS m/z 168 $[M]^+$ (75), 154 $[M + CH_2]^+$ (58), 149 $[M + H_2O - H]^+$ (40), 137 (35), 125 (24), 111 (38), 97 (53), 84 (100), 71 (57), 57 (57), 55 (44), 43 (38); HREIMS m/z 168.0739 $[M]^+$ (calcd for $C_9H_{12}O_3$, 168.0786).

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Supporting Information Available: Crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(11) CCDC 629925 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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