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Fragmentation of Carbohydrate Anomeric Alkoxy Radicals. A New Synthesis of Chiral 1-Halo-1-iodo Compounds

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General Methods. Melting points were determined with a hot-stage apparatus and are uncorrected. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were recorded in $CHCl_3$ solutions unless otherwise stated. NMR spectra were determined at 500 MHz for ^1H and 125.7 MHz for ^{13}C in $CDCl_3$ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF (0.063–0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5% vanillin in H_2SO_4–EtOH (4:1) and further heating until development of color.

General procedure for the synthesis of chlorohydrins (2, 9, 15, and 21). A solution of the corresponding 2-deoxy-hex-1-enitol (1 mmol) in THF (45 mL) and H_2O (5 mL), containing *N*-chlorosuccinimide (2 mmol) was refluxed for 8 h. The reaction mixture

was then poured into water and extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo. Column chromatography of the residue (*n*-hexane–EtOAc mixtures) afforded the required chlorohydrin compounds.

General procedure for the synthesis of bromohydrins (3, 10, 16, 22, and 27). A solution of the corresponding 2-deoxy-hex-1-enitol (1 mmol) in THF (35 mL) and H_2O (4 mL), containing recently crystallized *N*-bromoacetamide (1.5 mmol) was stirred at room temperature for 4 h. The reaction mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was dried and concentrated in vacuo. Column chromatography of the residue (*n*-hexane–EtOAc mixtures) afforded the required bromohydrin compounds.

General procedure for the synthesis of iodohydrins (4, 11, 17, 23, and 30). A solution of the corresponding 2-deoxy-hex-1-enitol (1 mmol) in THF (10 mL) and H_2O (10 mL), containing *N*-iodosuccinimide (1.2 mmol) was stirred at room temperature for 20 min. The reaction mixture was diluted with EtOAc, poured into water and extracted with EtOAc. The organic layer was washed with 10% aqueous sodium thiosulfate, dried and concentrated in vacuo. Chromatotron chromatography of the residue (*n*-hexane–EtOAc mixtures) afforded the required iodohydrin compounds.

General procedure for the synthesis of 1-halo-1-iodo compounds. A solution of the halohydrin (1 mmol) in CH_2Cl_2 (50 mL) containing (diacetoxyiodo)benzene (1.5 mmol) and iodine (1.5 mmol) was irradiated with two 80 W tungsten-filament lamps at reflux temperature. The reaction mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was washed with 10% aqueous sodium thiosulfate, dried and concentrated in vacuo. Chromatotron chromatography of the residue (*n*-hexane–EtOAc mixtures) afforded the required halo-iodine compounds.

2,3,5-tri-*O*-Acetyl-1-deoxy-1-fluoro-4-*O*-formyl-1-iodo-D-arabinitol (5). Crystalline solid (96%): diastereoisomeric mixture (1:1); ^{1}H NMR (C_6D_6) 1.57 (3H, s), 1.59 (3H, s), 1.65 (3H, s), 1.67 (6H, s), 1.72 (3H, s), 4.01 (2H, dd, J = 12.5, 5.1 Hz), 4.15 (1H, dd, J = 12.6, 2.9 Hz), 4.16 (1H, dd, J = 12.6, 3.4 Hz), 5.27 (2H, m), 5.54 (1H, ddd, $^{2}J_{FH}$ = 12.8 Hz, J = 5.7, 2.0 Hz), 5.60 (1H, ddd, $^{2}J_{FH}$ = 17.9, J = 4.6, 2.5 Hz) 5.66 (1H, dd, J = 8.6, 2.6 Hz), 5.83 (1H, ddd, $^{3}J_{FH}$ = 1.6 Hz, J = 8.7, 1.6 Hz), 6.46 (1H, dd, $^{1}J_{FH}$ = 49.1 Hz, J = 4.6 Hz), 6.51 (1H, dd, $^{1}J_{FH}$ = 48.8 Hz, J = 5.7 Hz), 7.35 (1H, s), 7.40 (1H, s); ^{13}C NMR (C_6D_6) 19.9 (CH_3), 20.0 (CH_3), 20.1 (CH_3), 61.4 (CH_2), 67.3 (CH), 68.1 (CH), 68.2 (CH), 68.5 (CH), 69.6 (CH, $^{1}J_{FC}$ = 258.3 Hz), 70.5 (CH, $^{1}J_{FC}$ = 256.2 Hz), 72.7 (CH, $^{2}J_{FC}$ = 24.4 Hz), 73.2 (CH, $^{2}J_{FC}$ = 18.3 Hz), 168.9 (C), 169.0 (C), 169.1 (C), 169.2 (C), 169.78 (C), 169.8 (C); MS (rel intensity) 307 (M^+ – I, 100), 205 (8), 159 (12), 157 (11), 139 (28); HRMS calcd for $C_{12}H_{16}FO_8$ 307.082921, found 307.085159. Anal. Calcd for $C_{12}H_{16}FIO_8$: C, 33.20; H, 3.71. Found: C, 33.49; H, 3.48.

2,3,5-tri-*O*-Acetyl-1-chloro-1-deoxy-4-*O*-formyl-1-iodo-D-arabinitol (6). Crystalline solid (95%): diastereoisomeric mixture (1:1); ^{1}H NMR (C_6D_6) 1.59 (3H, s), 1.60 (3H, s), 1.66 (6H, s), 1.73 (6H, s), 4.97 (1H, dd, J = 12.4, 5.8 Hz), 4.99 (1H, dd, J = 12.5, 5.6 Hz), 4.20 (2H, dd, J = 12.5, 3.2 Hz), 5.26 (1H, m), 5.29 (1H, m), 5.53 (1H, d, J = 7.7 Hz), 5.55 (1H, dd, J = 2.1, 7.8 Hz), 5.58 (1H, d, J = 6.7 Hz), 5.66 (1H, dd, J = 3.1, 6.7 Hz), 7.42 (1H, s), 7.44 (1H, s); ^{13}C NMR (C_6D_6) 20.0 (CH_3), 20.1 (CH_3), 20.2 (CH_3), 20.4 (CH_3), 24.6 (CH), 25.3 (CH), 61.6 (CH_2), 67.8 (CH), 68.4 (CH), 68.5 (CH), 69.3 (CH), 74.1 (CH), 159.3 (CH), 159.4 (CH), 168.9 (C), 168.95 (C), 168.98 (C), 169.9 (C); MS (rel intensity) 325/323 (M^+ – I, 32/100), 223/221 (85), 175 (38), 157 (27), 139 (79); HRMS calcd for $C_{12}H_{16}{}^{35}ClO_8$ 323.053370, found 323.052559. Anal. Calcd for $C_{12}H_{16}ClIO_8$: C, 31.99; H, 3.58. Found: C, 31.95; H, 3.28.

2,3,5-tri-*O*-Acetyl-1-bromo-1-deoxy-4-*O*-formyl-1-iodo-D-arabinitol (7). Crystalline solid (99%): diastereoisomeric mixture (1:1); ^{1}H NMR (C_6D_6) 1.57 (3H, s), 1.59 (3H, s), 1.65 (6H, s), 1.73 (6H, s), 3.96 (1H, dd, *J* = 12.9, 6.5 Hz), 3.97 (1H, dd, *J* = 13.0, 6.3 Hz), 4.20 (2H, dd, *J* = 3.3, 12.4 Hz), 5.26 (1H, m), 5.28 (1H, m), 5.30 (2H, d, *J* = 7.5 Hz), 5.34 (2H, d, *J* = 6.9 Hz), 5.57 (1H, dd, *J* = 2.6, 7.5 Hz), 5.64 (1H, dd, *J* = 3.1, 6.9 Hz), 5.90 (2H, dd, *J* = 2.7, 7.8 Hz), 7.38 (1H, s), 7.39 (1H, s); ^{13}C NMR (C_6D_6) 6.2 (CH), 6.6 (CH), 20.0 (CH_3), 20.1 (CH_3), 20.2 (CH_3), 20.3 (CH_3), 61.6 (CH_2), 68.48 (CH), 68.5 (CH), 68.6 (CH), 69.5 (CH), 73.77 (CH), 73.8 (CH), 159.0 (CH), 159.1(CH), 169.0 (C), 169.1 (C), 169.8 (C); MS (rel intensity) 436/434 (M^+ – AcOH, 2), 369/367 (18), 281/279 (30), 267/265 (100); HRMS calcd for $C_{10}H_{12}{}^{81}BrIO_6$ 435.884155, found 435.887161. Anal. Calcd for $C_{12}H_{16}BrIO_8$: C, 29.11; H, 3.26. Found: C, 29.39; H, 3.03.

2,3,5-tri-*O*-Acetyl-1-deoxy-4-*O*-formyl-1,1-diiodo-D-arabinitol (8). Crystalline solid (92%): mp 109–110 ^{o}C (from *n*-hexane–EtOAc); $[\alpha]_D$ = +45 (*c* = 1.42); IR 3013, 1754 cm^{-1}; ^{1}H NMR 2.04 (3H, s), 2.12 (3H, s), 2.14 (3H, s), 4.08 (1H, dd, *J* = 12.4, 5.9 Hz), 4.27 (1H, dd, *J* = 12.4, 3.3 Hz), 5.06 (1H, d, *J* = 7.5 Hz), 5.18 (1H, m), 5.25 (1H, dd, *J* = 7.5, 3.0 Hz), 5.76 (1H, dd, *J* = 7.3, 3.0 Hz), 7.98 (1H, s); ^{13}C NMR –33.9 (CH), 20.6 (3 × CH_3), 61.5 (CH_2), 68.6 (CH), 68.9 (CH), 73.4 (CH), 159.4(CH), 169.3 (2 × C), 170.4 (C); MS (rel intensity) 542 (M^+, <1), 482 (3), 207 (100); HRMS calcd for $C_{12}H_{16}I_2O_8$ 541.8935, found 541.8989. Anal. Calcd for $C_{12}H_{16}I_2O_8$: C, 26.59; H, 2.98. Found: C, 26.72; H, 2.82.

1,3,4-tri-*O*-Acetyl-5-chloro-5-deoxy-2-*O*-formyl-5-iodo-D-arabinitol (12). Crystalline solid (96%): diastereoisomeric mixture (3:2); ^{1}H NMR (C_6D_6) (major) 1.59 (3H, s), 1.64 (3H, s), 1.73 (3H, s), 3.81 (1H, dd, *J* = 7.3, 11.8 Hz), 4.24 (1H, dd, *J* = 4.9, 11.8 Hz), 5.14 (1H, dd, *J* = 2.7, 8.7 Hz), 5.39 (1H, ddd, *J* = 0.7, 2.0, 8.9 Hz), 5.49 (1H,

m), 5.65 (1H, d, *J* = 2.7 Hz), 7.54 (1H, s); (minor) 1.56 (3H, s), 1.65 (3H, s), 1.78 (3H, s), 3.80 (1H, dd, *J* = 7.0, 11.8 Hz), 3.79 (1H, dd, *J* = 7.0, 7.0 Hz), 4.26 (1H, dd, *J* = 5.1, 11.8 Hz), 5.45 (1H, m), 5.54 (1H, ddd, *J* = 0.7, 2.0, 9.1 Hz), 5.63 (1H, dd, *J* = 2.2, 9.0 Hz), 5.72 (1H, d, *J* = 2.2 Hz), 7.58 (1H, s); ^{13}C NMR (C_6D_6) 19.9 (CH_3), 20.0 (CH_3), 20.1 (CH_3), 20.2 (CH_3), 20.3 (CH_3), 25.1 (CH), 27.6 (CH), 62.1 (CH_2), 67.5 (CH), 67.7 (CH), 69.6 (CH), 71.6 (CH), 73.0 (CH), 73.7 (CH), 159.7 (CH), 159.74 (CH), 168.8 (C), 168.9 (C), 169.0 (C), 169.7 (C); MS (rel intensity) 392/390 (M^+ – AcOH, 1.5/5), 325/323 (34/100), 223/221 (25/80); HRMS calcd for $C_{10}H_{12}{}^{37}ClIO_6$ 391.933768, found 391.940445. Anal. Calcd for $C_{12}H_{16}ClIO_8$: C, 31.99; H, 3.58. Found: C, 32.18; H, 3.33.

1,3,4-tri-*O*-Acetyl-5-bromo-5-deoxy-2-*O*-formyl-5-iodo-D-arabinitol (13). Crystalline solid (98%): diastereoisomeric mixture (3:2); ^{1}H NMR (C_6D_6) 1.56 (3H, s), 1.57 (3H, s), 1.64 (3H, s), 1.65 (3H, s), 1.75 (3H, s), 1.77 (3H, s), 3.803 (1H, dd, *J* = 11.7, 7.4 Hz), 3.805 (1H, dd, *J* = 11.7, 7.5 Hz), 4.26 (1H, dd, *J* = 4.9, 10.9 Hz), 4.28 (1H, dd, *J* = 4.9, 10.7 Hz), 5.23 (1H, dd, *J* = 2.6, 8.7 Hz), 5.38 (1H, ddd, *J* = 0.7, 2.0, 8.8 Hz), 5.46 (1H, d, *J* = 2.6 Hz), 5.46–5.52 (3H, m), 5.50 (1H, d, *J* = 1.7 Hz), 5.59 (1H, dd, *J* = 2.2, 8.8 Hz), 7.53 (1H, s), 7.55 (1H, s); ^{13}C NMR (C_6D_6) 7.1 (CH), 8.8 (CH), 19.9 (CH_3), 20.0 (CH_3), 20.1 (CH_3), 20.2 (CH_3), 20.3 (CH_3), 62.1 (CH_2), 62.13 (CH_2), 67.5 (CH), 67.7 (CH), 70.9 (CH), 72.1 (CH), 73.0 (CH), 73.5 (CH), 160.0 (CH), 168.7 (C), 168.9 (C), 169.0 (C), 169.7 (C); MS (rel intensity) 436/434 (M^+ – AcOH, 16), 267/265 (84), 115 (91); HRMS calcd for $C_{10}H_{12}{}^{81}BrIO_6$ 435.884199, found 435.883102. Anal. Calcd for $C_{12}H_{16}BrIO_8$: C, 29.11; H, 3.26. Found: C, 29.01; H, 3.17.

1,3,4-tri-*O*-Acetyl-5-deoxy-2-*O*-formyl-5,5-diiodo-D-arabinitol (14). Crystalline solid (84%): mp 122–123 ^{o}C (from *n*-hexane–EtOAc); $[\alpha]_D$ = +11 (*c* = 0.32); IR 3027, 2953, 1753 cm^{-1}; ^{1}H NMR 1.99 (3H, s), 2.14 (3H, s), 2.15 (3H, s), 3.85 (1H, dd, *J* = 11.8, 7.6 Hz), 4.29 (1H, dd, *J* = 11.8, 4.7 Hz), 5.02 (1H, dd, *J* = 8.4, 2.7 Hz), 5.21 (1H, dd, *J* =

8.4, 1.2 Hz), 5.24 (1H, d, *J* = 2.7 Hz), 5.38 (1H, ddd, *J* = 7.6, 4.7, 1.2 Hz), 7.97 (1H, s); ^{13}C NMR –32.3 (CH), 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 62.0 (CH_2), 67.2 (CH), 72.1 (CH), 73.4 (CH), 159.7(CH), 169.1 (2 × C), 170.3 (C); MS (rel intensity) 482 (M^+ – AcOH, 19), 415 (10), 327 (59), 313 (100); HRMS calcd for $C_{10}H_{12}I_2O_6$ 481.8723, found 481.8750. Anal. Calcd for $C_{12}H_{16}I_2O_8$: C, 26.59; H, 2.98. Found: C, 26.82; H, 2.64.

(5*R*)-1-*O*-Benzyl-5-chloro-5-deoxy-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (18*R*). Oil (52%): $[\alpha]_D$ = +43 (*c* = 1.33); IR 1728 cm^{-1}; ^{1}H NMR 1.40 (3H, s), 1.52 (3H, s), 3.63 (1H, dd, *J* = 6.9, 9.6 Hz), 3.67 (1H, dd, *J* = 6.1, 9.7 Hz), 4.45 (1H, dd, *J* = 5.9, 9.7 Hz), 4.50 (1H, dd, *J* = 2.2, 5.8 Hz), 4.54 (2H, s), 5.45 (1H, m), 5.69 (1H, d, *J* = 9.3 Hz), 7.29–7.36 (5H, m) 8.10 (1H, s); ^{13}C NMR (50.3 MHz) 25.3 (CH_3), 25.8 (CH), 26.8 (CH_3), 68.2 (CH_2), 68.5 (CH), 73.3 (CH_2), 74.2 (CH), 82.2 (CH), 109.3 (C), 127.7 (2 × CH), 127.9 (CH), 128.4 (2 × CH), 137.4 (C), 160.2 (CH); MS (rel intensity) 441/439 (M^+ – Me, 2/5), 398/396 (0.3/1), 277/275 (2/6), 185 (12); HRMS calcd for $C_{15}H_{17}{}^{37}ClIO_5$ 440.977979, found 440.973724. Anal. Calcd for $C_{16}H_{20}ClIO_5$: C, 42.27; H, 4.43. Found: C, 42.47; H, 4.17.

(5*S*)-1-*O*-Benzyl-5-chloro-5-deoxy-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (18*S*). Oil (40%): $[\alpha]_D$ = –25 (*c* = 0.5); IR 1725 cm^{-1}; ^{1}H NMR 1.42 (3H, s), 1.58 (3H, s), 3.59 (1H, dd, *J* = 6.8, 9.8 Hz), 3.68 (1H, dd, *J* = 5.9, 9.9 Hz), 4.42 (1H, dd, *J* = 4.7, 5.9 Hz), 4.54 (1H, d, *J* = 11.8 Hz), 4.55 (1H, d, *J* = 11.8 Hz), 4.71 (1H, dd, *J* = 6.5, 6.5 Hz), 5.53 (1H, ddd, *J* = 6.1, 6.1, 6.1 Hz), 5.75 (1H, d, *J* = 6.8 Hz), 7.30–7.38 (5H, m), 8.10 (1H, s); ^{13}C NMR 25.4 (CH), 25.6 (CH_3), 26.3 (CH_3), 68.6 (CH_2), 68.6 (CH), 73.6 (CH_2), 76.7 (CH), 82.9 (CH), 110.4 (C), 127.8 (2 × CH), 128.0 (CH), 128.6 (2 × CH), 137.1 (C), 160.1 (CH); MS (rel intensity) 456/454 (M^+, 0.2/0.6), 441/439 (1/3), 277/275 (1/3), 185 (9); HRMS calcd for $C_{16}H_{20}{}^{35}ClIO_5$ 454.004404, found 454.001106. Anal. Calcd for $C_{16}H_{20}ClIO_5$: C, 42.27; H, 4.43. Found: C, 42.35; H, 4.27.

(5*R*)-1-*O*-Benzyl-5-bromo-5-deoxy-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (19*R*). Oil: $[\alpha]_D$ = +38 (*c* = 0.64); IR 1725 cm^{-1}; ^1H NMR 1.41 (3H, s), 1.54 (3H, s), 3.62 (1H, dd, *J* = 6.8, 9.8 Hz), 3.66 (1H, dd, *J* = 6.3, 9.8 Hz), 4.50 (1H, dd, *J* = 1.5, 5.9 Hz), 4.54 (2H, s), 4.58 (1H, dd, *J* = 6.0, 10.0 Hz), 5.41 (1H, d, *J* = 10.0 Hz), 5.50 (1H, ddd, *J* = 1.3, 6.6, 6.6 Hz), 7.28–7.34 (5H, m), 8.11 (1H, s); ^{13}C NMR 6.3 (CH), 25.4 (CH_3), 26.7 (CH_3), 68.3 (CH_2), 68.5 (CH), 73.4 (CH_2), 74.6 (CH), 82.1 (CH), 109.4 (C), 127.8 (2 × CH), 127.9 (CH), 128.4 (2 × CH), 137.5 (C), 160.2 (CH); MS (rel intensity) 500/498 (M^+, <1), 485/483 (3), 321/319 (3), 209/207 (15); HRMS calcd for $C_{16}H_{20}{}^{81}BrIO_5$ 499.951841, found 499.956512. Anal. Calcd for $C_{16}H_{20}BrIO_5$: C, 38.50; H, 4.04. Found: C, 38.72; H, 3.98.

(5*S*)-1-*O*-Benzyl-5-bromo-5-deoxy-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (19*S*). Oil: $[\alpha]_D$ = –12 (*c* = 0.73); IR 1725 cm^{-1}; ^1H NMR 1.42 (3H, s), 1.58 (3H, s), 3.61 (1H, dd, *J* = 6.8, 9.9 Hz), 3.66 (1H, dd, *J* = 6.2, 9.9 Hz), 4.46 (1H, dd, *J* = 3.3, 6.1 Hz), 4.54 (1H, d, *J* = 11.9 Hz), 4.55 (1H, d, *J* = 11.9 Hz), 4.74 (1H, dd, *J* = 8.4, 6.1 Hz), 5.44 (1H, d, *J* = 8.4 Hz), 5.54 (1H, ddd, *J* = 3.5, 6.8, 6.8 Hz), 7.30–7.37 (5H, m), 8.11 (1H, s); ^{13}C NMR 6.1 (CH), 25.5 (CH_3), 26.5 (CH_3), 68.4 (CH_2), 68.5 (CH), 73.5 (CH_2), 76.4 (CH), 82.7 (CH), 110.2 (C), 127.8 (2 × CH), 128.0 (CH), 128.6 (2 × CH), 137.3 (C), 160.2 (CH); MS (rel intensity) 500/498 (M^+, <1), 485/483 (1), 321/319 (2), 209/207 (9); HRMS calcd for $C_{16}H_{20}{}^{81}BrIO_5$ 499.951841, found 499.948303. Anal. Calcd for $C_{16}H_{20}BrIO_5$: C, 38.50; H, 4.04. Found: C, 38.67; H, 3.93.

1-*O*-Benzyl-5-deoxy-2-*O*-formyl-5,5-diiodo-3,4-*O*-isopropylidene-D-arabinitol (20). Oil (90%): $[\alpha]_D$ = +29 (*c* = 1.88); IR 3010, 2938, 1724 cm^{-1}; ^1H NMR 1.40 (3H, s), 1.54 (3H, s), 3.60 (1H, dd, *J* = 9.9, 6.6 Hz), 3.63 (1H, dd, *J* = 9.9, 6.4 Hz), 4.50 (1H, dd, *J* = 5.9, 1.8 Hz), 4.53 (1H, s), 4.54 (1H, s), 4.62 (1H, dd, *J* = 10.1, 5.9 Hz), 4.91 (1H, d, *J* = 10.1 Hz), 5.50 (1H, ddd, *J* = 6.6, 6.4, 1.8 Hz), 7.97–7.27 (5H, m), 8.10 (1H, s); ^{13}C

NMR –34.2 (CH), 25.5 (CH_3), 26.7 (CH_3), 68.2 (CH), 68.5 (CH_2), 73.3 (CH_2), 75.0 (CH), 82.6 (CH), 109.6 (C), 127.8 (2 × CH), 127.8 (CH), 128.5 (2 × CH), 137.4 (C), 160.3 (CH); MS (rel intensity) 546 (M^+, < 1), 531 (2), 91 (100); HRMS calcd for $C_{16}H_{20}I_2O_5$ 545.9400, found 545.9393. Anal. Calcd for $C_{16}H_{20}I_2O_5$: C, 35.17; H, 3.69. Found: C, 35.41; H, 3.60.

1-Chloro-1-deoxy-3-*O*-formyl-1-iodo-2-*O*-methyl-4,5-*O*-(1-methylethylidene)-D-arabinitol (24). Oil (83%): diastereoisomeric mixture (3:2); IR 2991, 2938, 1732 cm^{-1}; ^1H NMR (major) 1.34 (3H, s), 1.43 (3H, s), 3.70 (3H, s), 3.82 (1H, m), 3.83–3.86 (1H, m), 3.99–4.02 (1H, m), 4.18–4.22 (1H, m), 5.47 (1H, dd, *J* = 7.9, 2.8 Hz), 5.73 (1H, d, *J* = 7.2), 8.06 (1H, s); (minor) 1.34 (3H, s), 1.43 (3H, s), 3.70 (3H, s), 3.71 (1H, dd, *J* = 2.3, 7.6 Hz), 3.83–3.86 (1H, m), 3.99–4.02 (1H, m), 4.18–4.22 (1H, m), 5.42 (1H, dd, *J* = 8.4, 2.3 Hz), 5.68 (1H, d, *J* = 7.6 Hz), 8.06 (1H, s); ^{13}C NMR (major) 25.4 (CH_3), 26.7 (CH_3), 28.1 (CH) 62.3 (CH_3), 66.6 (CH_2), 72.7 (CH), 74.2 (CH), 84.7 (CH), 110.1 (C), 159.8 (CH); (minor) 25.4 (CH_3), 26.7 (CH_3), 27.6 (CH), 61.8 (CH_3), 67.0 (CH_2), 71.7 (CH), 73.9 (CH), 84.9 (CH), 110.0 (C), 159.7 (CH); MS (rel intensity) 365/363 (M^+ – Me, 18/55), 221/219 (7/23), 101 (100); HRMS calcd for $C_9H_{13}{}^{37}ClIO_5$ 364.9467, found 364.9486. Anal. Calcd for $C_{10}H_{16}ClIO_5$: C, 47.53; H, 6.78. Found: C, 47.22; H, 7.12.

1-Bromo-1-deoxy-3-*O*-formyl-1-iodo-2-*O*-methyl-4,5-*O*-isopropylidene-D-arabinitol (25). Oil (92%): diastereoisomeric mixture (3:2); IR 2991, 2938, 2890, 1732 cm^{-1}; ^1H NMR (major) 1.26 (3H, s), 1.40 (3H, s), 3.44 (3H, s), 3.71 (1H, dd, *J* = 7.3, 3.1 Hz), 3.77 (1H, dd, *J* = 8.8, 6.1 Hz), 3.84–3.88 (1H. m), 3.97–4.03 (1H, m), 5.41 (1H, d, *J* = 7.3 Hz), 5.63 (1H, dd, *J* = 7.9, 3.1 Hz), 7.49 (1H, s); (minor) 1.25 (3H, s), 1.38 (3H, s), 3.47 (3H, s), 3.63 (1H, dd, *J* = 7.5, 3.0 Hz), 3.77 (1H, dd, *J* = 8.8, 6.1 Hz), 3.84–3.88 (1H, m), 3.97–4.03 (1H, m), 5.42 (1H, d, *J* = 7.5 Hz), 5.57 (1H, dd, *J* = 8.2, 3.0 Hz), 7.48 (1H, s); ^{13}C NMR (major) 10.0 (CH), 25.4 (CH_3), 26.7 (CH_3), 62.1 (CH_3), 66.7

(CH_2), 72.8 (CH), 74.3 (CH), 84.4 (CH), 110.1 (C), 159.9 (CH); (minor) 9.9 (CH), 25.4 (CH_3), 26.7 (CH_3), 62.0 (CH_3), 66.9 (CH_2), 72.2 (CH), 74.1 (CH), 84.5 (CH), 110.1 (C), 159.8 (CH); MS (rel intensity) 409/407 (M^+ – Me, 2), 265/263 (43), 184 (51), 101 (100); HRMS calcd for $C_9H_{13}{}^{81}BrIO_5$ 408.8971, found 408.8984. Anal. Calcd for $C_{10}H_{16}BrIO_5$: C, 28.39; H, 3.81. Found: C, 28.51; H, 3.58.

1-Deoxy-3-*O*-formyl-1,1-diiodo-2-*O*-methyl-4,5-*O*-isopropylidene-D-arabinitol (26). Oil (69%): $[\alpha]_D$ = +12 (*c* = 1.04); IR 2992, 2938, 1732 cm^{-1}; ^1H NMR 1.35 (3H, s), 1.46 (3H, s), 3.60 (1H, dd, *J* = 7.0, 3.0 Hz), 3.72 (3H, s), 3.85 (1H, dd, *J* = 8.9, 5.3 Hz), 4.02 (1H, dd, *J* = 8.9, 6.1 Hz), 4.18 (1H, ddd, *J* = 8.1, 6.1, 5.3 Hz), 5.14 (1H, d, *J* = 7.0 Hz), 5.49 (1H, dd, *J* = 8.1, 3.0 Hz), 8.09 (1H, s); ^{13}C NMR –27.8 (CH), 25.4 (CH_3), 26.7 (CH_3), 62.0 (CH_3), 66.8 (CH_2), 72.6 (CH), 74.4 (CH), 84.3 (CH), 110.1 (C), 160.0 (CH); MS (rel intensity) 470 (M^+ , 1), 455 (22), 438 (6), 343 (8), 101 (100); HRMS calcd for $C_{10}H_{16}I_2O_5$ 469.9087, found 469.9064. Anal. Calcd for $C_{10}H_{16}I_2O_5$: C, 25.54; H, 3.43. Found: C, 25.66; H, 3.26.

(5*R*)-5-Bromo-5-deoxy-1-*O*-(3,5-dinitrobenzoyl)-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (28). Crystalline solid (66%): mp 99–100 °C (from *n*-hexane–EtOAc); $[\alpha]_D$ = +23 (*c* = 0.45); IR 3100, 1731, 1549 cm^{-1}; ^1H NMR 1.46 (3H, s), 1.58 (3H, s), 4.52 (1H, d, *J* = 5.8 Hz), 4.58 (1H, dd, *J* = 11.7, 7.6 Hz), 4.72 (1H, dd, *J* = 10.5, 6.1 Hz), 4.73 (1H, dd, *J* = 11.0, 4.7 Hz), 5.32 (1H, d, *J* = 10.8 Hz), 5.78 (1H, dd, *J* = 7.2, 3.6 Hz), 8.20 (1H, s), 9.13 (2H, d, *J* = 1.8 Hz), 9.24 (1H, dd, *J* = 2.0, 2.0 Hz); ^{13}C NMR (125.7 MHz) 3.6 (CH), 25.4 (CH_3), 26.6 (CH_3), 65.9 (CH_2), 67.6 (CH), 74.8 (CH), 82.4 (CH), 110.2 (C), 122.6 (CH), 129.5 (2 × CH), 133.2 (C), 148.7 (2 × C), 160.1 (CH), 162.2 (C); MS (rel intensity) 589/587 (M^+ – Me, 90), 477/475 (9), 321/319 (28), 195 (100); HRMS calcd for $C_{15}H_{13}{}^{81}BrIN_2O_{10}$ 588.877787, found 588.874176. Anal. Calcd for $C_{16}H_{16}BrIN_2O_{10}$: C, 31.86; H, 2.67; N, 4.64. Found: C, 31.95; H, 2.51;

N, 4.51. Crystal data for **28**: $C_{16}H_{16}BrIN_2O_{10}$, M_τ = 603.12, monoclinic, space group $P2_1$, a = 8.0662 (2), b = 9.0388 (3), c = 14.8243 (6) Å, β = 105.710 (2)°, V = 1040.45 (6) Å^3, Z = 2, ρ_{calcd} = 1.925 g cm^{-3}. μ(Mo$_{K\alpha}$) = 0.71073 Å, F(000) = 588, T = 150 (2) K; colorless crystal, 0.55×0.40×0.25 mm, Rigaku AFC7-S diffractometer, collected reflections 6834. The structure was solved by direct methods, all non-hydrogen atoms were refined anisotropically using full-matrix lest-squared based on F^2 to give R_1 = 0.0247, wR_2 = 0.0631 for 3585 independently observed reflections ($|F_o| > 2\sigma(|F_o|)$) and 274 parameters.

(5*S*)-5-Bromo-5-deoxy-1-*O*-(3,5-dinitrobenzoyl)-2-*O*-formyl-5-iodo-3,4-*O*-isopropylidene-D-arabinitol (29). Crystalline solid (34%): mp 129–129.5 °C (from *n*-hexane–EtOAc); $[\alpha]_D$ = –10 (c = 0.88); IR 3101, 1728, 1549 cm^{-1}; ^{1}H NMR 1.47 (3H, s), 1.60 (3H, s), 4.53 (1H, d, J = 5.8 Hz), 4.55 (1H, dd, J = 11.7, 7.2 Hz), 4.71 (1H, dd, J = 11.7, 4.0 Hz), 4.83 (1H, dd, J = 10.5, 6.1 Hz), 5.25 (1H, d, J = 10.8 Hz), 5.76 (1H, dd, J = 7.6, 4.0 Hz), 8.20 (1H, s), 9.13 (2H, d, J = 1.8 Hz), 9.24 (1H, dd, J = 2.0, 2.0 Hz); ^{13}C NMR (125.7 MHz) 3.3 (CH), 25.6 (CH_3), 26.6 (CH_3), 65.7 (CH_2), 67.5 (CH), 76.1 (CH), 82.7 (CH), 111.2 (C), 122.7 (CH), 129.5 (2 × CH), 133.2 (C), 148.7 (2 × C), 160.1 (CH), 162.1 (C); MS (rel intensity) 589/587 (M^+ – Me, 20), 393/395 (14), 321/319 (35), 195 (57); HRMS calcd for $C_{15}H_{13}{}^{81}BrIN_2O_{10}$ 588.877787, found 588.874725. Anal. Calcd for $C_{16}H_{16}BrIN_2O_{10}$: C, 31.86; H, 2.67; N, 4.64. Found: C, 31.97; H, 2.64; N, 4.39.

3,5-di-*O*-Acetyl-1,2-dideoxy-4-*O*-formyl-1,1-diiodo-D-*erythro*-pentitol (31). Oil (94%): $[\alpha]_D$ = +5 (c = 0.442); IR 3025, 2945, 1738 cm^{-1}; ^{1}H NMR 2.05 (3H, s), 2.06 (3H, s), 2.65 (1H, ddd, J = 15.2, 10.7, 9.9 Hz), 2.86 (1H, ddd, J = 15.2, 3.6, 2.6 Hz), 4.14 (1H, dd, J = 12.1, 7.0 Hz), 4.23 (1H, dd, J = 12.1, 4.0 Hz), 4.93 (1H, dd, J = 10.7, 3.6 Hz), 5.03 (1H, ddd, J = 9.9, 2.6, 3.5 Hz), 5.39 (1H, ddd, J = 7.0, 4.0, 3.5 Hz), 8.06

(1H, s); ^{13}C NMR –36.7 (CH), 20.6 (CH_3), 20.7 (CH_3), 47.7 (CH_2), 61.6 (CH_2), 70.0 (CH), 73.0 (CH), 159.6 (CH), 169.8(C), 170.3 (C); MS (rel intensity) 484 (M^+, <1), 357 (23), 209 (100); HRMS calcd for $C_{10}H_{14}I_2O_6$ 483.8880, found 483.8832. Anal. Calcd for $C_{10}H_{14}I_2O_6$: C, 24.81; H, 2.92. Found: C, 25.05; H, 2.90.

(2*R*,3*S*,5*E*)-1,3-Diacetoxy-2-formyloxy-8-phenyl-5-octene (32). Oil (70%): $[\alpha]_D$ = +26 (*c* = 1.71); IR 2938, 1732 cm^{-1}; ^{1}H NMR 2.04 (3H, s), 2.06 (3H, s), 2.34 (4H, m), 2.66 (2H, t, *J* = 7.9 Hz), 4.18 (1H, dd, J = 12.4, 7.2 Hz), 4.32 (1H, dd, *J* = 12.3, 3.1 Hz), 5.11 (1H, ddd, *J* = 7.5, 3.7, 3.7 Hz), 5.29 (1H, ddd, *J* = 7.5, 3.7, 3,7 Hz), 5.36 (1H, ddd, *J* = 14.9, 7.3, 7.3 Hz), 5.57 (1H, ddd, *J* = 14.8, 7.2, 7.2 Hz), 7.18 (3H, m), 7,28 (2H, m), 8,06 (1H, s); ^{13}C NMR 20.7 (CH_3), 20.8 (CH_3), 33.5 (CH_2), 34.2 (CH_2), 35.6 (CH_2), 61.7 (CH_2), 71.0 (2 × CH), 124.0 (CH), 125.8 (CH), 128.3 (2 × CH), 128.5 (2 × CH), 134.2 (CH), 141.6 (C), 159.9 (CH), 170.0 (C), 170.6 (C); MS (rel intensity) 288 (M^+ – AcOH, <1), 242 (<1), 228 (18), 182 (16), 109 (35), 91 (100); HRMS calcd for $C_{19}H_{24}O_6$ 348.1573, found 348.1499. Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.83; H, 6.57.