41. Synthesis of (−)-Conduritol C (1L-Cyclohex-5-ene-1,2,3/4-tetrol)[1])

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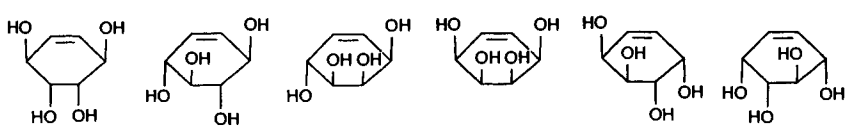
(1*R*,2*R*,4*R*)-2-*endo*-Cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl acetate ((−)-**7**) has been transformed into the all-*cis*-configurated 4L-4,5,6/0-trihydroxycyclohex-2-en-1-one derivatives (−)-**12** and (−)-**19**. (−)-Conduritol C ((−)-**3**) was derived in a stereospecific manner from (−)-**12**.

Introduction. – Among the six possible structures of the conduritols (cyclohexenetetrols), conduritols A (**1**) and D (**4**) are *meso* and conduritols B (**2**), C (**3**), E (**5**), and F (**6**) exist as pairs of enantiomers [3]. From the bark of *Marsdenia Condurango*, **1** was isolated already in 1908 by *Kubler* [4]. In 1962, *Plouvier* [5] isolated 'leucanthemitol' (= (+)-conduritol F) from *Chrysanthenum leucanthemitum*. This compound was then discovered in many other plants [6] [7]. The syntheses of *meso* **1** and **4** and of racemic **2**, **3**, **5**, and **6** have been reported [3] [8–13][3]). In 1958, *Angyal et al.* [14] presented a synthesis of (+)-conduritol E (= 1D-cyclohex-5-ene-1,2/3,4-tetrol; (+)-**5**). In 1981, *Paulsen et al.* [15] reported the syntheses of (−)-conduritol B (= 1L-cyclohex-5-ene-1,3/2,4-tetrol; (−)-**2**) and (−)-conduritol F (= 1L-cyclohex-5-ene-1,2,4/3-tetrol; (−)-**6**)[4]).



1 (−)-**2** (−)-**3** **4** (+)-**5** (−)-**6**

The biosynthesis of natural conduritols has been studied [6]. Interestingly, their derivatives (*e.g.* epoxycyclohexanetetrols [8] [18], epoxycyclohexenediols [19] [20], aminoconduritols [21], and bromoconduritols [19] [22]) have biological activities (*e.g.* glycosidase inhibitors). This should stimulate the development of new syntheses of optically pure conduritols. Whereas racemic conduritol C ((±)-**3**) has been derived from *epi*-inositol [23] and from cyclohexa-3,5-diene-1,2-diol [24], we report here the first total synthesis of optically pure (−)-conduritol C ((−)-**3**).

[1]) Enantiomerically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives ('naked sugars' [1]) as synthetic intermediates, Part VI; Part V: [2].

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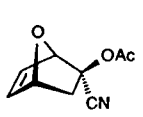
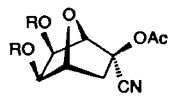
[3]) For recent syntheses, see conduritol A [8], (±)-conduritol B [9] [10], (±)-tetra-*O*-benzylconduritol B [11], (±)-1,2-di-*O*-benzoyl-4-*O*-methylconduritol F [12], and (±)-anhydroconduritols [13].

[4]) For the determination of the absolute configuration of the cyclohexanetetrols, see [16] [17].

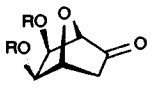
Results and Discussion. – Our starting material is the 'naked sugar' (−)-**7** ((−)-(1*R*,2*R*,4*R*)-2-*endo*-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl acetate, ee > 99%) [25]. Stereospecific *cis*-bis-hydroxylation of (−)-**7** with H_2O_2 in *t*-BuOH and a catalytical amount of OsO_4 gave diol (−)-**8** which was silylated with (*t*-Bu)Me_2SiCl and imidazole in DMF [26] to (−)-**9** (74% based on (−)-**7**). Saponification of (−)-**9** in the presence of formaline yielded ketone (+)-**10** (80%)



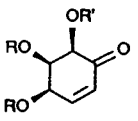
(−)-**7**



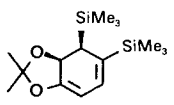
(−)-**8** R = H
(−)-**9** R = (*t*-Bu)Me_2Si



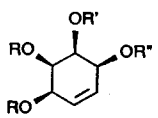
(+)-**10** R = (*t*-Bu)Me_2Si
(±)-**13** R, R = Me_2C[a])



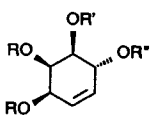
11 R = (*t*-Bu)Me_2Si, R' = Me_3Si
(−)-**12** R = (*t*-Bu)Me_2Si, R' = H
(±)-**14** R, R = Me_2C, R' = Me_3Si[a])
(±)-**16** R, R = Me_2C, R' = H[a])
(−)-**19** R = (*t*-Bu)Me_2Si, R' = Ac
(±)-**26** R = R' = Ac[a])
(±)-**27** R = R' = H[a])



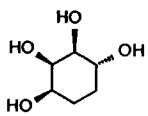
(±)-**15**[a])



(±)-**17** R, R = Me_2C, R' = R'' = H[a])
(±)-**18** R = (*t*-Bu)Me_2Si, R' = Me_3Si, R'' = H[a])
(−)-**20** R = (*t*-Bu)Me_2Si, R' = Ac, R'' = H
28 R = R' = R'' = Ac



(−)-**21** R = (*t*-Bu)Me_2Si, R' = Ac, R'' = PhCO
(−)-**22** R = R' = R'' = Ac



(−)-**23**

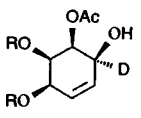
[a]) Only one enantiomer is represented.

Strong bases such as NaOMe or $LiN(SiMe_3)_2$ which are used to isomerize 7-oxabicyclo[2.2.1]heptane-2-carboxylates or 7-oxabicyclo[2.2.1]hept-2-yl alkyl ketones into the corresponding 1-substituted 5-hydroxycyclohex-1-enes [27] induced quick decomposition of (+)-**10**. With Et_3N, the ring opening of the O-bridge occurred, only if trimethylsilyl triflate ($TfOSiMe_3$) was added to the reaction mixture and led to the formation of **11**. The latter was readily hydrolyzed with $MeOH/H_2O/HF$ to afford crystalline (−)-**12** (87% based on (+)-**10**). Treatment of the acetonide (±)-**13** [28] with $Et_3N/TfOSiMe_3$ in PhH (0°) for 105 min gave a 1:1.4:1 mixture (±)-**13**/(±)-**14**/(±)-**15**. After prolonged reaction time or using a large excess of $Et_3N/TfOSiMe_3$, the unstable cyclohexadiene derivative (±)-**15** was the major product. Acidic hydrolysis ($MeOH/H_2O/HCl$, 20°) of (±)-**14** gave hydroxyketone (±)-**16** (71%).

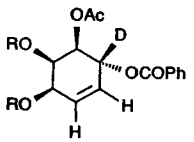
Reduction of (±)-**16** with $NaBH_4/CeCl_3$ in MeOH [29] afforded the partially protected conduritol D derivative (±)-**17** (73%) which, on acidic hydrolysis, gave conduritol D (**4**) quantitatively. Reduction of (±)-**11** with diisobutylaluminium hydride (DIBAH) in THF afforded (±)-**18** in excellent yield. All our attempts to displace the unprotected alcohol in (±)-**18** using the *Mitsunobu* method [30] failed.

The acetate (−)-**19** (95%) was, thus, prepared by treating (−)-**12** with Ac_2O/pyridine and 4-(dimethylamino)pyridine. Reduction of (−)-**19** with $NaBH_4$ and $CeCl_3$ in MeOH

afforded (−)-**20** (92%) which was converted readily into the benzoate (−)-**21** (87%) on treatment with diethyl azodicarboxylate, Ph_3P, and benzoic acid in THF. (−)-Conduritol C ((−)-**3**) was obtained in 71% yield, after removal of the protective groups in (−)-**21**. Acetylation (Ac_2O/pyridine) of (−)-**3** gave tetraacetate (−)-**22** and hydrogenation of (−)-**3** (H_2, Pd/C, MeOH) the (−)-1L-cyclohexane-1,2,3/4-tetrol ((−)-**23**) whose characteristics (see *Exper. Part*) were similar to those reported by *Posternak et al.* [31] [32] for this compound. Thus, our total synthesis confirms the absolute configuration (1L) attributed in 1955 [16] to (−)-**23**.



(±)-**24** R = (*t*-Bu)Me_2Si[a])



(±)-**25** R = (*t*-Bu)Me_2Si[a])

[a]) Only one enantiomer is represented.

The *Mitsunobu* displacement reaction has been shown to be a S_N2 process which does not involve allylic rearrangement with allylic alcohols [33]. We have demonstrated that this applies also to reaction (−)-**20**→(−)-**21** in the following manner. Reduction of (±)-**19** with $NaBD_4/CeCl_3$ in MeOH gave the deuterated conduritol-D derivative (±)-**24** which, on treatment with Ph_3P, diethyl azodicarboxylate, and benzoic acid gave exclusively (±)-**25**, with no deuterium incorporation in the olefinic moiety.

Another, lower-yield and less selective synthesis of conduritol C was realized in the following way. Deprotection (Bu_4NF/THF) of (±)-**12** followed by acetylation (Ac_2O/pyridine) gave the triacetate (±)-**26**. Its reduction[5]) with $NaBH_4/CeCl_3$ in MeOH/H_2O at 0° led, after acetylation, to a mixture of **28** and (±)-**22**, isolated in 51 and 35% yield, respectively[6]).

Conclusion. – The 'naked sugar' (−)-**7** has been converted into (−)-conduritol C ((−)-**3**) in 28% overall yield. Chiral derivatives of conduritol D (**4**) were also obtained readily. A very smooth technique for the isomerization of 7-oxabicyclo[2.2.1]heptan-2-ones into the corresponding 6-hydroxycyclohex-2-en-1-ones[7]) has been developed.

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[5]) Reduction of (±)-**12**, (±)-**14**, (±)-**16**, and (±)-**19** by several reducing agents ($NaBH_4$, $NaBH_4/CeCl_3$, $LiAlH_4$, DIBAH) gave only all-*cis*-conduritol-D derivatives, with no significant amount of conduritol-C derivatives. Reduction of the trihydroxyketone (±)-**27** by $NaBH_4$ yielded a *ca.* 1:1 mixture of conduritols C and D.

[6]) Protected 4L-4,5,6/0-trihydroxycyclohex-2-en-1-ones such as **11** are intermediates [34] in the synthesis of COTC ((4*R*,5*R*,6*R*)-2-[(crotonyloxy)methyl]-4,5,6-trihydroxycyclohex-2-en-1-one) [35], a glyoxalase inhibitor with potential cytotoxic and anticancer activity [36].

[7]) Enone (−)-**12** has been transformed [37] into the aglycone of a 'cyanoglucoside' ([(1*Z*,4*R*,5*R*,6*S*)-6-(β-D-glucosyloxy)-4,5-dihydroxycyclohex-2-ene-1-ylidene]acetonitrile) isolated from *Ilex Warburgii* [38].

Experimental Part

General. See [28].

*(−)-(1R,2R,4R,5S,6R)-2-*endo*-Cyano-5-*exo*,6-*exo*-dihydroxy-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Acetate* ((−)-**8**). To a soln. of (−)-**7** [25] (5.1 g, 28.5 mmol; $[\alpha]_{589}^{25} = +57.7$, ee > 99%) in 50 ml of *t*-BuOH, OsO_4 (4% soln. in CCl_4; 1 ml, 0.2 mmol) and H_2O_2 (30% soln. in H_2O; 15 ml, 0.15 mol) were successively added. This black mixture was left at 25° until it was decolorized (3 weeks). Sufficient $NaHSO_3$ (40% soln. in H_2O; *ca.* 30 ml, *ca.* 0.15 mol) was then added under vigourous stirring at 0° to reduce peroxides. The mixture was then poured into sat. aq. NaCl soln. (100 ml) and extracted with AcOEt (200 ml, 7 times). The combined org. phases were washed with sat. aq. NaCl soln. (20 ml), dried ($MgSO_4$), and evaporated. The residue was dissolved in hot $CHCl_3$ (100 ml), dried ($MgSO_4$), and left overnight at −30°. Pure (−)-**8** crystallized out (3.55 g, 58.4%; m.p. 117–119°); the residue (2.3 g) left by evaporation of the mother-liquors was dissolved in DMF (12 ml) and treated successively by imidazole (2 g, 29 mmol) and (*t*-Bu)Me_2SiCl (4.3 g, 28 mmol). After 8 h at 25°, imidazole (1 g, 14 mmol) and (*t*-Bu)Me_2SiCl (2.1 g, 14 mmol) were added and the mixture left for 15 h. Extraction and chromatography *(vide infra)* yielded 2.7 g (21.5% from (−)-**7**) of (−)-**9** as a clear oil. Data of (−)-**8**: Recrystallization from $CHCl_3$ gave an anal. sample. M.p. 119–121°. $[\alpha]_{589}^{25} = -42$, $[\alpha]_{578}^{25} = -44$, $[\alpha]_{546}^{25} = -50$, $[\alpha]_{436}^{25} = -86$, $[\alpha]_{365}^{25} = -136$ ($c = 1$, $CHCl_3$). IR (KBr): 3430, 3350, 2970, 2240, 1745, 1445, 1370, 1225, 1195, 1110, 1045, 1010, 920, 875. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.68 (br. *d*, $^4J = 1.5$, H–C(1)); 4.54 (*m*, H–C(4)); 4.50, 4.03 (2*d*, $^3J = 6$, H–C(5), H–C(6)); 2.26 (*m*, 2 H–C(3)); 2.15 (*s*, CH_3COO). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 169.1 (*s*, CO); 116.2 (*s*, CN); 86.9 (*dm*, ^1J(C,H) = 172); 81.7 (*dm*, ^1J(C,H) = 169); 73.0 (*dm*, ^1J(C,H) = 165); 72.2 (*s*, C(2)); 69.9 (*d*, ^1J(C,H) = 153); 41.4 (*t*, ^1J(C,H) = 138, C(3)); 20.8 (*q*, ^1J(C,H) = 129, CH_3CO). MS (70 eV): 142 (6, $M^{+\cdot} - 31$), 171 (10), 154 (11), 128 (17), 125 (19), 124 (95), 60 (100). Anal. calc. for $C_9H_{11}NO_5$ (213.188): C 50.71, H 5.20; found: C 50.80, H 5.27.

*(−)-(1R,2R,4R,5R,6S)-5-*exo*,6-*exo*-Bis{[(*tert*-butyl)dimethylsilyl]oxy}-2-*endo*-cyano-7-oxabicyclo-[2.2.1]hept-2-*exo*-yl Acetate* ((−)-**9**). To a soln. of (−)-**8** (3.3 g, 15.5 mmol) in dry DMF (18 ml), imidazole (3 g, 44 mmol) and (*t*-Bu)Me_2SiCl (6.5 g, 43 mmol) were successively added. After stirring at 25° for 8 h, imidazole (1.5 g, 22 mmol) and (*t*-Bu)Me_2SiCl (3.2 g, 21 mmol) were added. After 15 h at 25°, the mixture was poured in Et_2O (250 ml) and washed successively with sat. aq. NaCl soln. (30 ml), 2M aq. HCl (50 ml), 10% aq. K_2CO_3 soln. (50 ml), and sat. aq. NaCl soln. (20 ml). The aq. layers were extracted successively with Et_2O (120 ml). The combined org. phases were dried ($MgSO_4$), evaporated, vacuum-dried (40°/0.03 Torr), and purified by column chromatography on silica gel (*Lobar*, size *C*, Et_2O/petroleum ether 1:6) yielding 6.15 g (90%) of a clear oil. All recrystallization attempts were unsuccessful. $[\alpha]_{589}^{25} = -20.6$, $[\alpha]_{578}^{25} = -21.4$, $[\alpha]_{546}^{25} = -24.4$, $[\alpha]_{436}^{25} = -41.5$, $[\alpha]_{365}^{25} = -65$ ($c = 11$, $CHCl_3$). IR (film): 2950, 2920, 2880, 2850, 2240, 1750, 1465, 1365, 1245, 1210, 1145, 1050, 1020, 930, 900, 880, 830, 770, 665. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.60 (br. *s*, H–C(1)); 4.45 (*m*, H–C(4)); 4.44, 3.95 (2*d*, $^3J = 6$, H–C(5), H–C(6)); 2.20 (*m*, 2 H–C(3)); 2.14 (*s*, CH_3CO); 0.96, 0.93 (2*s*, 2 (*t*-Bu)Si); 0.20, 0.17, 0.13, 0.12 (4*s*, 2 Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 169.2 (*s*, COO); 116.6 (*s*, CN); 87.4 (*dm*, ^1J(C,H) = 172), 82.2 (*dm*, ^1J(C,H) = 162)(C(1), C(4)); 75.6 (*dm*, ^1J(C,H) = 142), 72.3 (*d*, ^1J(C,H) = 145)(C(5), C(6)); 72.4 (*s*, C(2)); 41.4 (*t*, ^1J(C,H) = 139, C(3)); 26.0 (*qm*, ^1J(C,H) = 126, 2 (CH_3)$_3$CSi); 20.9 (*q*, ^1J(C,H) = 130, CH_3CO); 18.6, 18.4 (2*s*, 2 (CH_3)$_3C$Si); −4.3, −4.5, −4.8 (3*q*, ^1J(C,H) = 119, 2 (CH_3)$_2$Si). MS (70 eV): 384 (9, $M^{+\cdot} - 57$), 324 (9), 210 (9), 147 (17), 142 (13), 133 (5), 117 (23), 75 (38), 74 (9), 73 (100). Anal. calc. for $C_{21}H_{39}NO_5Si_2$ (441.715): C 57.10, H 8.90; found: C 57.22, H 8.82.

*(+)-(1R,4R,5R,6S)-5-*exo*,6-*exo*-Bis{[(*tert*-butyl)dimethylsilyl]oxy}-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**10**). Formaline (38% aq. CH_2O soln.; 4.5 ml, 62 mmol) and K_2CO_3 (0.33 g, 2.4 mmol) were added successively to a soln. of (−)-**9** (5 g, 11.3 mmol) in MeOH (60 ml). After stirring at 25° for 45 min, the mixture was poured into Et_2O (350 ml) and washed successively with 1N HCl (20 ml), sat. aq. $NaHCO_3$ soln. (25 ml), and sat. aq. NaCl soln. (25 ml). The aq. layers were extracted with Et_2O (100 ml), the combined org. extracts dried ($MgSO_4$) and evaporated, and the residue was purified by column chromatography on silica gel (*Lobar*, size *C*, Et_2O/petroleum ether 1:4) yielding 3.36 g (80%) of a light yellow oil (all recrystallization attempts were unsuccessful, but (±)-**10** was obtained as white crystals, m.p. 41–42°). $[\alpha]_{589}^{25} = +35$, $[\alpha]_{578}^{25} = +37$, $[\alpha]_{546}^{25} = +44.5$, $[\alpha]_{436}^{25} = +99$, $[\alpha]_{365}^{25} = +272$ ($c = 3$, $CHCl_3$). UV (isooctane): 330 (37), 317 (60), 306 (56), 294 (sh, 40). IR (film): 2950, 2930, 2890, 2860, 1770, 1460, 1255, 1195, 1155, 1130, 1110, 990, 965, 905, 835, 780. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.76 (*dd*, $^3J = 6.5$, $^4J = 1.8$, H–C(4)); 4.17 (*t*, $^4J = 1.8$, H–C(1)); 4.08 (*s*, H–C(5), H–C(6)); 2.33 (*ddd*, $^2J = 18$, $^3J = 6.5$, 1.8, H_{exo}–C(3)); 1.89 (*d*, $^2J = 18$, H_{endo}–C(3)); 0.91, 0.90 (2*s*, 2 *t*-BuSi); 0.10, 0.08 (2*s*, 2 Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$); 210.2 (*s*, C(2)); 87.3 (*dm*, ^1J(C,H) = 168), 83.4 (*dm*, ^1J(C,H) = 164)(C(1), C(4)); 76.1 (*dm*, ^1J(C,H) = 146), 72.4 (*dm*, ^1J(C,H) = 148)(C(5), C(6)); 40.3 (*t*, ^1J(C,H) = 135, C(3)); 26.0 (*qm*, ^1J(C,H) = 125, 2 (CH_3)$_3$CSi); 18.5 (*s*, 2 (CH_3)$_3C$Si); −4.4, −5.0 (2*q*, ^1J(C,H) = 118, 2 (CH_3)$_2$Si). MS (70 eV): 315 (14, $M^{+\cdot} - 57$), 299 (7), 231 (17), 199 (7), 185 (5), 183 (7), 171 (12), 147 (23), 133 (8), 115 (9), 81 (21), 75 (17), 74 (8), 73 (100). Anal. calc. for $C_{18}H_{36}O_4Si_2$ (372.65): C 58.02, H 9.74; found: C 58.04, H 9.75.

(–)-(4R,5S,6R)-4,5-Bis{[(tert-butyl)dimethylsilyl]oxy}-6-hydroxycyclohex-2-en-1-one ((–)-**12**). A soln. of $TfOSiMe_3$ (2.6 ml, 14.3 mmol) in PhH (15 ml) was added dropwise to a stirred soln. of (+)-**10** (2.6 g, 7 mmol) and Et_3N (2.3 ml, 16.5 mmol) in PhH (20 ml). After 2 h at 25°, the mixture was poured in Et_2O (250 ml) and washed successively with H_2O (40 ml), 1N HCl (20 ml), sat. aq. $NaHCO_3$ soln. (20 ml), and sat. aq. NaCl soln. (15 ml). After solvent evaporation, the crude oil obtained was dissolved in $MeOH/H_2O$ 10:1 (30 ml) and HF (40% aq. soln.; 0.6 ml, 13 mmol) was added. After stirring at 25° for 90 min, the mixture was poured into Et_2O (250 ml) and washed successively with sat. aq. $NaHCO_3$ soln. (20 ml) and sat. aq. NaCl soln. (15 ml). After drying ($MgSO_4$), solvent evaporation, and column chromatography on silica gel (*Lobar*, Et_2O/petroleum ether 1:6), a slowly crystallizing oil (2.28 g, 87%) was obtained. This white solid (m.p. 51–54°) was recrystallized from $MeOH/H_2O$ to give an anal. sample. M.p. 54–56° ((±)-**12** obtained from (±)-**10**, m.p. 46–48°). $[\alpha]_{589}^{25} = -157$, $[\alpha]_{578}^{25} = -165$, $[\alpha]_{546}^{25} = -193$, $[\alpha]_{436}^{25} = -388$, $[\alpha]_{365}^{25} = -855$ ($c = 4$, $CHCl_3$). IR (KBr): 3500, 2960, 2930, 2900, 1695, 1470, 1380, 1250, 1165, 1075, 940, 865, 835, 775. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.66 (*ddd*, ^3J = 10,5, 2, ^4J = 2.5, H–C(3)); 6.09 (*dd*, ^3J = 10.5, ^4J = 2.7, H–C(2)); 4.65 (*ddd*, ^3J = 2.5, 2, ^4J = 2.7, H–C(4)); 4.42 (*ddd*, ^3J = 2.5, 1.8, ^4J = 2.5, H–C(5)); 4.17 (*d*, ^3J = 1.8, H–C(6)); 3.5 (br. *s*, OH); 0.96, 0.81 (2*s*, 2 *t*-BuSi); 0.16, 0.06 (2*s*, 2 Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 198.3 (*s*, C(1)); 151.7 (*dt*, ^1J(C,H) = 164, ^nJ(C,H) = 6, C(3)); 125.6 (*dd*, ^1J(C,H) = 165, ^nJ(C,H) = 4, C(2)); 79.2 (*d*, ^1J(C,H) = 150); 76.7 (*dt*, ^1J(C,H) = 139, ^nJ(C,H) = 5); 71.3 (*ddd*, ^1J(C,H) = 135, ^nJ(C,H) = 10, 4); 26.0, 25.7 (2*qm*, ^1J(C,H) = 122, 2 (CH_3)$_3$CSi); 18.4, 18.3 (2*s*, 2 (CH_3)$_3C$Si); –4.4, –4.5, –4.6, –4.9 (4*q*, ^1J(C,H) = 120, 2 (CH_3)$_2$Si). MS (70 eV): 372 (1, M^+), 357 (1), 316 (9), 315 (34), 299 (10), 287 (4), 227 (4), 225 (6), 199 (6), 198 (35), 183 (58), 155 (32), 147 (28), 73 (100). Anal. calc. for $C_{18}H_{36}O_4Si_2$ (372.65): C 58.02, H 9.74; found: C 57.99, H 9.78.

(4RS,5RS,6RS)-4,5-(Isopropylidenedioxy)-6-[(trimethylsilyl)oxy]cyclohex-2-en-1-one ((±)-**14**). To a stirred soln. of (±)-**13** [28a] (7.36 g, 40 mmol) and Et_3N (12.4 ml, 9 g, 88 mmol) in anh. PhH (100 ml) at 0°, a soln. of $TfOSiMe_3$ (14.5 ml, 17.8 g, 80 mmol) in anh. PhH (80 ml) was added dropwise within *ca.* 15 min. After stirring at 0° for 135 min, the mixture was poured portionwise into a vigourously stirred mixture of sat. aq. $NaHCO_3$ soln. (100 ml), sat. aq. NaCl soln. (50 ml), ice (200 g), and CH_2Cl_2 (200 ml). The aq. layer was extracted with CH_2Cl_2 (100 ml, twice). The org. phases were dried ($MgSO_4$) and evaporated giving (±)-**13**/(±)-**14**/(±)-**15** 1:1.4:1 (^{1}H-NMR (360 MHz, $CDCl_3$)). Chromatography on a column of silica gel at –20° (AcOEt/$CHCl_3$ 1:9) afforded first 2.8 g (21%) of impure (±)-**15**, then 3.9 g of crude (±)-**14**, and finally 2.2 g (30%) of (±)-**13**. The 2nd fraction was recrystallized from hexane yielding 3.65 g (36%) of (±)-**14** as white crystals. M.p. 115–117°. UV (dioxane): 331 (34), 214 (7100). IR (CCl_4): 3000, 2960, 2940, 2900, 1717, 1385, 1375, 1250, 1170, 1095, 1050. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.59 (*dt*, ^3J = 10, 2, ^4J = 2, H–C(3)); 6.05 (*dd*, ^3J = 10, ^4J = 1, H–C(2)); 4.95–4.65 (*m*, H–C(4), H–C(5)); 4.48 (*d*, ^3J = 3, H–C(6)); 1.40, 1.35 (2*s*, Me_2C); 0.20 (*s*, Me_3Si). ^{13}C-NMR (15.08 MHz, $CDCl_3$): 194.8 (*s*, C(1)); 143.7 (*d*, ^1J(C,H) = 166, C(3)); 127.1 (*d*, ^1J(C,H) = 168, C(2)); 111.3 (*s*, Me_2C); 79.4 (*d*, ^1J(C,H) = 154); 73.8, 73.3 (2*d*, ^1J(C,H) = 140); 27.5, 26.6 (2*q*, ^1J(C,H) = 126, (CH_3)$_2$C); 0.2 (*q*, ^1J(C,H) = 120, (CH_3)$_3$Si). CI-MS (CH_4): 257 (5, $[M + 1]^+$), 242 (10, $[M - 14]^+$). Anal. calc. for $C_{12}H_{20}O_4Si$ (256.37): C 56.22, H 7.86; found: C 56.34, H 7.79.

(5RS,6SR)-1,6-(Isopropylidenedioxy)-4,5-bis[(trimethylsilyl)oxy]cyclohexa-1,3-diene ((±)-**15**). A soln. of $TfOSiMe_3$ (3.6 ml, 20 mmol) and Et_3N (3.1 ml, 22 mmol) in anh. PhH (20 ml) was added dropwise to a stirred soln. of (±)-**13** [28a] (921 mg, 5 mmol) and 1,4-diazabicyclo[2.2.2]octane (5.6 g, 50 mmol) in anh. PhH (30 ml). After heating to 80° for 24 h, the mixture was poured into a vigourously stirred mixture of sat. aq. $NaHCO_3$ soln. (50 ml), ice (100 g), and CH_2Cl_2 (100 ml). The aq. layer was extracted with CH_2Cl_2 (100 ml, twice). The org. extracts were combined, washed with sat. aq. NaCl soln. (50 ml, 3 times), and dried ($MgSO_4$). After solvent evaporation, the residue was purified by column chromatography on silica gel (AcOEt/hexane 1:9), yielding 1.33 g (81%) of a colourless oil, b.p. 120°/10^{-2} Torr. This unstable product was contaminated with aromatic impurities. IR (film): 3000, 2970, 2910, 1685, 1610, 1500, 1470, 1380, 1250, 1045, 925, 910, 840. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.55 (*d*, ^3J = 10), 5.33 (*dd*, ^3J = 10, ^4J = 3, H–C(2), H–C(3)); 4.63 (*dd*, ^3J = 10, ^4J = 3), 4.34 (*d*, ^3J = 10, H–C(5), H–C(6)); 1.21, 1.18 (2*s*, Me_2C); 0.2 (*s*, 2 Me_3Si).

(4RS,5SR,6RS)-6-Hydroxy-4,5-(isopropylidenedioxy)cyclohex-2-en-1-one ((±)-**16**). One drop of 1N HCl was added to a soln. of (±)-**14** (1.28 g, 5 mmol) in MeOH (50 ml). After 5 min at 20°, the mixture was poured into a vigourously stirred mixture of H_2O (100 ml), sat. aq. $NaHCO_3$ soln. (1 ml), and CH_2Cl_2 (100 ml). The org. phase was washed with sat. aq. NaCl soln. (50 ml, twice) and dried ($MgSO_4$). After solvent evaporation, the residue was recrystallized from hexane/AcOEt yielding 0.65 g (71%) of colourless crystals. M.p. 152–153°. UV (dioxane): 322 (40), 214 (7500). UV (95% aq. EtOH): 321 (38), 211 (9800). IR ($CHCl_3$): 3520, 3035, 3000, 2945, 2910, 1705, 1620, 1455, 1410, 1385, 1375, 1240, 1160, 1140, 1125, 1085, 1045, 990. ^{1}H-NMR (80 MHz, $CDCl_3$): 6.68 (*dt*, ^3J = 10, 2, ^4J = 2, H–C(3)); 6.16 (*dd*, ^3J = 10, ^4J = 1, H–C(2)); 5.0–4.8 (*m*, 2 H); 4.44 (*t*, ^3J = 2, H–C(4), H–C(5), OH); 3.68 (*d*, ^3J = 2, H–C(6)); 1.38, 1.33 (2*s*, Me_2C). ^{13}C-NMR (15.08 MHz, $CDCl_3$): 196.4 (*s*, C(1)); 145.9 (*d*, ^1J(C,H) = 166, C(3)); 125.8 (*d*, ^1J(C,H) = 128, C(2)); 111.5 (*s*, Me_2C); 77.6 (*d*, ^1J(C,H) = 156); 72.5, 72.4 (2*d*,

^1J(C,H) = 148); 27.4, 26.6 (2*q*, ^1J(C,H) = 127, (CH_3)$_2$C). MS (70 eV): 169 (76, $M^+ - 15$), 109 (58), 97 (100). Anal. calc. for $C_9H_{12}O_4$ (184.19): C 58.69, H 6.52; found: C 58.79, H 6.58.

1,2-O-(Isopropylidene)cyclohex-5-ene-1,2,3,4/0-tetrol (= *(±)-1,2-O-(Isopropylidene)conduritol D*; (±)-**17**). $NaBH_4$ (98 mg, 2.6 mmol) was added portionwise to a stirred soln. of (±)-**16** (323 mg, 1.73 mmol) in 0.4M methanolic $CeCl_3 \cdot 7\,H_2O$ (5 ml, 2 mmol) at 0°. After 10 min at 0°, H_2O (15 ml) was added and the mixture extracted with AcOEt (100 ml, 3 times). The combined org. phases were washed with sat. aq. NaCl soln. (15 ml), dried ($MgSO_4$), and evaporated. The residue was filtered through a short column of silica gel (AcOEt/acetone 9:1) and recrystallized from Et_2O/hexane, yielding 239 mg (73%) of colourless crystals. M.p. 86–87°. IR ($CHCl_3$): 3570, 3040, 3000, 2940, 1385, 1230, 1085, 1035. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.95 (br. *ddd*, ^3J = 9.6, 4.5, ^4J = 1, H–C(5)); 5.74 (*ddt*, ^3J = 9.6, 2.7, ^4J = ^5J = 1, H–C(6)); 4.4–4.65 (*m*, H–C(1), H–C(2)); 4.08 (*dddt*, ^3J = 10.8, 4.5, 3.6, ^4J = ^5J = 1, H–C(4)); 3.80 (*dddd*, ^3J = 8.1, 3.6, 2, ^5J = 1, H–C(3)); 3.37 (*d*, ^3J = 8.1, OH–C(3)); 2.84 (*d*, ^3J = 10.8, OH–C(4)); 1.43, 1.34 (2*s*, Me_2C). ^{13}C-NMR (15.08 MHz, $CDCl_3$): 129.1, 127.5 (2*d*, ^1J(C,H) = 164); 110.5 (*s*), 76.7 (*d*, ^1J(C,H) = 148); 72.8 (*d*, ^1J(C,H) = 152); 66.8, 66.4 (2*d*, ^1J(C,H) = 144); 27.6, 25.9 (2*q*, ^1J(C,H) = 126). CI-MS (CH_4): 187 (5, $[M + 1]^+$), 171 (11, $[M - 15]^+$), 111 (100). Anal. calc. for $C_9H_{14}O_4$ (186.21): C 58.05, H 7.58; found: C 58.08, H 7.55.

Cyclohex-5-ene-1,2,3,4/0-tetrol (= *Conduritol D*; **4**). A soln. of (±)-**17** (186 mg, 1 mmol) in MeOH (3 ml) was added to 2N aq. HCl (3 ml). After stirring at 20° for 2 days, AcOEt (50 ml) was added and the mixture evaporated; this addition/evaporation was repeated twice, yielding 146 mg (100%) of **4** as a colourless oil. IR (film): 3340, 2900, 1635, 1560, 1400, 1250, 1155, 1095, 1045, 1015, 930, 905. ^{1}H-NMR (360 MHz, CD_3COCD_3): 5.87 (*s*, H–C(5), H–C(6)); 4.7, 4.3 (2*m*, 4 OH); 4.22 (br. *s*, H–C(1), H–C(4)); 3.94 (br. *s*, H–C(2), H–C(3)). Anal. calc. for $C_6H_{10}O_4$ (146.14): C 49.31, H 6.90; found: C 49.46, H 7.03.

Tetra-O-acetylcyclohex-5-ene-1,2,3,4/0-tetrol (= *Tetraacetylconduritol D*; **28**). A mixture of conduritol D (**4**; 146 mg, 1 mmol), pyridine (0.32 ml, 4 mmol), and Ac_2O (4 ml, 42 mmol) was allowed to stand at 20° for 2 h. After solvent evaporation, toluene (20 ml) was added and the mixture evaporated to dryness. This operation was repeated 3 times. The residue was filtered through a short column of silica gel (AcOEt/hexane 1:1) and recrystallized from Et_2O/hexane, yielding 298 mg (95%) of colourless crystals. M.p. 103–105° ([3]: 102–104°). IR (KBr): 2960, 1755, 1370, 1235, 1215, 1080. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.91 (br. *s*, H–C(5), H–C(6)); 5.56 (br. *d*, ^3J = 4, H–C(1), H–C(4)); 5.39 (br. *d*, ^3J = 4, H–C(2), H–C(3)); 2.05 (*s*, 4 AcO). Anal. calc. for $C_{14}H_{18}O_8$ (314.29): C 53.50, H 5.77; found: C 53.58, H 5.79.

*1,2-Bis-O-[(*tert*-butyl)dimethylsilyl]-3-O-(trimethylsilyl)cyclohex-5-ene-1,2,3,4/0-tetrol* ((±)-**18**). DIBAH (1.2M soln. in toluene; 1.7 ml, 2 mmol) was added dropwise to a stirred soln. of (±)-**11** (prepared from (±)-**10**; 445 mg, 1 mmol) in anh. toluene (40 ml) cooled to −90°. After stirring at −80° for 6 h, MeOH (1 ml) was added dropwise and the mixture poured into a vigourously stirred mixture of CH_2Cl_2 (100 ml) and 10% aq. NH_4Cl soln. (100 ml) at 0°. The aq. phase was extracted with CH_2Cl_2 (100 ml, twice). The org. extracts were combined, washed with sat. aq. NaCl soln. (100 ml, 3 times), and dried ($MgSO_4$). After solvent evaporation, the residue was filtered through a short column of silica gel (Et_2O/hexane 1:2) yielding 433 mg (97%) of a colourless oil. IR (film): 3550, 3050, 2965, 2940, 2910, 2870, 1710, 1465, 1410, 1390, 1360, 1250, 1180, 1085, 1045, 1005. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.93 (*dm*, ^3J = 5, H–C(5)); 5.53 (br. *d*, ^3J = 5, H–C(6)); 4.21, 4.01 (2*m*), 3.58 (br. *d*, ^3J = 2.5, H–C(1), H–C(2), H–C(3)); 3.92 (*m*, H–C(4)); 3.38 (*d*, ^3J = 5.2, OH–C(4)); 0.94, 0.90 (2*s*, 2 *t*-BuSi); 0.18, 0.15, 0.11 (3*s*, 2 Me_2Si, Me_3Si). MS (70 eV): 429 (5, $M^+ - 17$), 389 (14), 388 (15), 387 (35), 309 (18), 307 (13), 299 (24), 257 (13), 167 (13), 147 (40), 133 (10), 81 (10), 75 (100). Anal. calc. for $C_{21}H_{46}O_4Si_3$ (446.53): C 56.49, H 10.38; found: C 56.50; H 10.23.

*(−)-(1R,5R,6S)-5,6-Bis{[(*tert*-butyl)dimethylsilyl]oxy}-2-oxocyclohex-3-en-1-yl Acetate* ((−)-**19**). At 0°, 4-(dimethylamino)pyridine (85 mg, 0.7 mmol) was added to a soln. of (−)-**12** (1.96 g, 5.27 mmol) in Ac_2O/pyridine 1:1 (10 ml). After stirring at 0° for 1 h, the mixture was poured in Et_2O (250 ml) and washed successively with 3N HCl (40 ml), 10% aq. K_2CO_3 soln. (80 ml), and sat. aq. NaCl soln. (50 ml). The aq. layers were extracted successively with Et_2O (100 ml). The combined org. phases were dried ($MgSO_4$) and evaporated. The solid obtained was recrystallized from MeOH/H_2O to yield 1.8 g of white crystals, m.p. 104–106.5°. An other recrystallization (MeOH/H_2O) gave 1.69 g (77.5%) of white crystals, m.p. 107.5–109°. The combined mother-liquors were purified by column chromatography on silica gel (*Lobar*, Et_2O/petroleum ether 1:9) to give 380 mg (17.5%) of (−)-**19** as white crystals, m.p. 105–107° ((±)-**19** obtained from (±)-**12**, m.p. 107–109°). $[\alpha]_{589}^{25} = -150$, $[\alpha]_{578}^{25} = -157$, $[\alpha]_{546}^{25} = -183$, $[\alpha]_{436}^{25} = -364$, $[\alpha]_{365}^{25} = -840$ (*c* = 2.5, $CHCl_3$). IR (KBr): 2960, 2930, 2860, 1745, 1695, 1470, 1385, 1375, 1360, 1250, 1235, 1215, 1175, 1100, 1060, 1020, 950, 870, 775. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.61 (*dt*, ^3J = 10, 2, ^4J = 2, H–C(4)); 6.04 (*dd*, ^3J = 10, ^4J = 2.5, H–C(3)); 5.32 (*d*, ^3J = 1.7, H–C(1)); 4.72 (br. *q*, ^3J = 2.5, 2, ^4J = 2.5, H–C(5)); 4.38 (br. *q*, ^3J = 2.5, 1.7, ^4J = 2, H–C(6)); 2.22 (*s*, CH_3CO); 0.95, 0.84 (2*s*, 2 *t*-BuSi); 0.17, 0.16, 0.08, 0.07 (4*s*, 2 Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 191.5 (*s*, C(2)); 170 (*s*, COO); 149.8 (*dt*, ^1J(C,H) = 163, ^nJ(C,H) = 6, C(4)); 127.1 (*dd*, ^1J(C,H) = 167, ^nJ(C,H) = 4, C(3)); 77.15 (*dm*, ^1J(C,H) = 150); 77.05 (*dm*,

^1J(C,H) = 135); 71.3 (*ddd*, ^1J(C,H) = 140, ^nJ(C,H) = 11, 4); 26.0, 25.6 (2*qm*, ^1J(C,H) = 125, 2 (CH_3)$_3$CSi); 20.7 (*q*, ^1J(C,H) = 130, CH_3CO); 18.4, 18.3 (2*s*, 2 (CH_3)$_3C$Si); −4.35, −4.4, −4.75, −4.85 (4*q*, ^1J(C,H) = 119, 2 (CH_3)$_2$Si). MS (70 eV): 357 (4, M^{+} − 57), 315 (8), 225 (18), 198 (32), 183 (54), 155 (13), 147 (31), 133 (13), 117 (9), 81 (15), 75 (35), 73 (100). Anal. calc. for $C_{20}H_{38}O_5Si_2$ (414.69): C 57.93, H 9.24; found: C 57.93, H 9.24.

*(−)-1*L*-3-*O*-Acetyl-1,2-bis-*O*-[(*tert*-butyl)dimethylsilyl]cyclohex-5-ene-1,2,3,4/0-tetrol* ((−)-**20**). $CeCl_3 \cdot 7H_2O$ (1.87 g, 5 mmol) and (−)-**19** (1.98 g, 4.77 mmol) were dissolved in MeOH (35 ml) at 40°. To this soln. cooled to 10°, $NaBH_4$ (300 mg, 7.8 mmol) was added portionwise within 15 min. The mixture was then stirred for 10 min at 10°, poured in H_2O (85 ml) and extracted with Et_2O (150 ml, 4 times). The combined org. phases were washed with sat. aq. NaCl soln. (30 ml), dried ($MgSO_4$), and evaporated. Usually, the solid obtained was shown (^{1}H-NMR) to be a *ca.* 7:1 mixture of (−)-**20** and (−)-**19**; as the separation turned out to be difficult, this solid was again reduced by $NaBH_4$ (200 mg, 5 mmol)/$CeCl_3 \cdot 7H_2O$ (1.87 g, 5 mmol) in MeOH (20 ml), according to the same procedure (*vide supra*). Then the solid obtained was recrystallized twice from MeOH/H_2O to afford 1.39 g (70%) of (−)-**20** as colourless crystals, m.p. 92–93°. The combined mother-liquors were evaporated and purified by column chromatography on silica gel (*Lobar*, Et_2O/petroleum ether 1:5) to yield 430 mg (22%) of (−)-**20** as white crystals, m.p. 90–92° ((±)-**20** obtained from (±)-**19**, m.p. 87–89°). $[\alpha]_{589}^{25} = -29$, $[\alpha]_{578}^{25} = -30$, $[\alpha]_{546}^{25} = -34.5$, $[\alpha]_{436}^{25} = -65$, $[\alpha]_{365}^{25} = -113$ (*c* = 3, $CHCl_3$). IR (KBr): 3520, 2960, 2930, 2900, 2860, 1720, 1460, 1420, 1390, 1360, 1245, 1100, 1085, 1050, 1035, 970, 890, 875, 835, 775. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.92 (*ddd*, ^3J = 10.5, 4.5, ^4J = 2.5, H–C(5)); 5.57 (*dt*, ^3J = 10.5, 1.8, ^4J = 1.8, H–C(6)); 4.71 (*dd*, ^3J = 6, 1.5, H–C(3)); 4.29 (*ddd*, ^3J = 3.5, 1.8, ^4J = 2.5, H–C(1)); 4.17 (*m*, H–C(2), H–C(4)); 3.3 (*m*, OH); 2.17 (*s*, CH_3CO); 0.94, 0.92 (2*s*, 2 *t*-BuSi); 0.16, 0.13, 0.12 (3*s*, 2 Me_2Si). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 170.5 (*s*, COO); 130.2 (*dq*, ^1J(C,H) = 161, ^nJ(C,H) = 5), 128.0 (*dt*, ^1J(C,H) = 164, ^nJ(C,H) = 4)(C(5), C(6)); 74.1 (*d*, ^1J(C,H) = 148); 71.1 (*dm*, ^1J(C,H) = 144); 70.8 (*ddd*, ^1J(C,H) = 138, ^nJ(C,H) = 11, 4); 65.3 (*dd*, ^1J(C,H) = 150, ^nJ(C,H) = 9); 26.2, 25.8 (2*qm*, ^1J(C,H) = 126, 2 (CH_3)$_3$CSi); 21.1 (*q*, ^1J(C,H) = 130, CH_3CO); 18.5, 18.4 (2*s*, 2 (CH_3)$_3C$Si); −4.25, −4.3, −4.76, −4.85 (4*q*, ^1J(C,H) = 119, 2 (CH_3)$_2$Si). MS (70 eV): 359 (0.3, M^{+} − 57), 327 (1), 300 (2), 299 (9), 225 (7), 209 (14), 200 (27), 167 (31), 149 (11), 147 (31), 133 (14), 117 (13), 111 (9), 75 (69), 73 (100). Anal. calc. for $C_{20}H_{40}O_5Si_2$ (416.71): C 57.65, H 9.68; found: C 57.80, H 9.72.

*(−)-1*L*-3-*O*-Acetyl-4-*O*-benzoyl-1,2-bis-*O*-[(*tert*-butyl)dimethylsilyl]cyclohex-5-ene-1,2,3/4-tetrol* ((−)-**21**). Diethyl azodicarboxylate (1.05 ml, 6.7 mmol) was added dropwise to a soln. of (−)-**20** (1.58 g, 3.8 mmol), Ph_3P (1.83 g, 7 mmol), and benzoic acid (0.86 g, 7 mmol) in THF (20 ml). After 1 h at 20–25° (occasional cooling with a cold-water bath was necessary), Ph_3P (393 mg, 1.5 mmol), benzoic acid (183 mg, 1.5 mmol), and diethyl azodicarboxylate (0.22 ml, 1.4 mmol) were successively added. After 2 h at 20–25°, silica gel (10 g) was added, the mixture evaporated, and the resulting powder poured on the top of a small silica-gel column. Elution with Et_2O/petroleum ether 1:5 gave, after evaporation, an oil which was purified by column chromatography on silica gel (*Lobar*, Et_2O/petrolcum ether 1:30) to yield (−)-**21** as a colourless oil (1.71 g, 87%; (±)-**21** obtained from (±)-**20**, m.p. 67–69°). $[\alpha]_{589}^{25} = -177$, $[\alpha]_{578}^{25} = -185$, $[\alpha]_{546}^{25} = -212$, $[\alpha]_{436}^{25} = -378$, $[\alpha]_{365}^{25} = -633$ (*c* = 6.5, $CHCl_3$). IR (KBr): 3070, 2960, 2930, 2900, 2860, 1740, 1710, 1600, 1580, 1470, 1385, 1270, 1250, 1180, 1110, 1090, 1035, 1020, 995, 900, 870, 830, 775, 710. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.03 (br. *d*, ^3J = 8), 7.56 (br. *t*, ^3J = 8), 7.44 (br. *t*, ^3J = 8) (arom. CH); 5.93 (*dq*, ^3J = 8.5, ^3J = ^4J = ^5J = 2, H–C(4)); 5.69 (*dt*, ^3J = 10.5, ^3J = ^4J = 2, H–C(5)); 5.62 (br. *dtd*, ^3J = 10.5, 2, ^4J = 2, 1.5, H–C(6)); 5.24 (*dd*, ^3J = 8.5, 1.5, H–C(3)); 4.51 (*dq*, ^3J = 3, ^3J = ^4J = ^5J = 2, H–C(1)); 4.21 (*dt*, ^3J = 3, ^3J = ^4J = 1.5, H–C(2)); 2.04 (*s*, CH_3CO); 0.94, 0.93 (2*s*, 2 *t*-BuSi); 0.13 (*s*, 6 H); 0.11 (*s*, 3 H); 0.10 (*s*, 3 H, 2 Me_2Si). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 169.5, 166.2 (2*s*, 2 COO); 133.1 (*dm*, ^1J(C,H) = 162), 132.3 (*dm*, ^1J(C,H) = 165), 129.7, 128.4 (2*dm*, ^1J(C,H) = 162), 124.3 (*dm*, ^1J(C,H) = 165) (arom. C, C(5), C(6)); 74.3, 74.2, 72.1 (3*dm*, ^1J(C,H) = 150), 70.3 (*dm*, ^1J(C,H) = 138, C(1), C(2), C(3), C(4)); 26.2, 25.8 (2*qm*, ^1J(C,H) = 123, 2 (CH_3)$_3$CSi); 21.1 (*q*, ^1J(C,H) = 130, CH_3CO); 18.5, 18.3 (2*s*, 2 (CH_3)$_3C$Si); −4.26, −4.30, −4.75, −4.81 (4*q*, ^1J(C,H) = 120, 2 (CH_3)$_2$Si). MS (70 eV): 463 (1, M^{+} − 57), 299 (4), 255 (11), 225 (7), 213 (12), 209 (10), 167 (14), 147 (9), 133 (5), 106 (8), 105 (100), 77 (14), 75 (13), 73 (35). Anal. calc. for $C_{27}H_{44}O_6Si_2$ (520.81): C 62.27, H 8.52; found: C 62.35 H 8.43.

*(−)-1*L*-Cyclohex-5-ene-1,2,3/4-tetrol* (= *(−)-Conduritol C*; (−)-**3**). Bu_4NF (1M soln. in THF; 8 ml, 8 mmol) was added to a soln. of (−)-**21** (1.5 g, 2.9 mmol) in THF (40 ml) cooled to 0°. After stirring for 45 min at 0°, sat. aq. NaCl soln. (25 ml) was added and the mixture extracted with AcOEt (120 ml, 4 times). The org. extract was dried ($MgSO_4$), evaporated, and filtered through a 25-cm column of silica gel (AcOEt/petroleum ether 3:2). After evaporation, the eluate (820 mg) was dissolved in MeOH (20 ml), MeONa (30% soln. in MeOH; 0.3 ml, 1.6 mmol) added, and the mixture stirred for 15 min. Then, *Amberlite IR-120* (H^+-form, 1.2 g) was added. After stirring for 5 min, the mixture was filtered and the *Amberlite* resin extracted with MeOH (15 ml, twice). The combined filtrate was evaporated and dried at 50°/0.03 Torr and the sirup obtained dissolved in warm MeOH (4 ml). Addition of

Et_2O (10 ml) caused the precipitation of colored impurities which were removed by filtration on *Celite*. The filtrate was left overnight at −35° to yield 195 mg of crystals, m.p. 121–123°. Recrystallization from MeOH/Et_2O gave 178 mg of white crystals, m.p. 129–130°. The combined mother-liquors were evaporated and the sirupy residue purified by 2 successive recrystallizations (MeOH/Et_2O) yielding 80 mg of colourless crystals, m.p. 129.5–131° (total yield 61%). The *Celite* was extracted with hot MeOH (10 ml) and the filtrate combined with the mother liquors and evaporated. The sirupy residue obtained (150 mg, impure (−)-**3**) was acetylated yielding an additional 10% of the corresponding acetate (−)-**22** (*vide infra*). Data of (−)-**3**: ((±)-**3** obtained from (±)-**21**, m.p. 146–148°; [23]: 151.5–152°; [24]: 148–149°). $[\alpha]_{589}^{25} = -209$, $[\alpha]_{578}^{25} = -218$, $[\alpha]_{546}^{25} = -249$, $[\alpha]_{436}^{25} = -432$, $[\alpha]_{365}^{25} = -665$ ($c = 2$, H_2O). IR (KBr): 3400, 2900, 1430, 1140, 1050, 1020, 840. ^{1}H-NMR (360 MHz, CD_3OD): 5.64 (*dt*, $^3J = 10.5$, $^3J = {}^4J = 2$, H–C(5)); 5.55 (*dtd*, $^3J = 10.5$, 2, $^4J = 2$, 1, H–C(6)); 4.24 (*m*, H–C(4), H–C(1)); 4.01 (*ddd*, $^3J = 2$, 1.5, $^4J = 1$, H–C(2)); 3.51 (br. *dd*, $^3J = 8$, 1.5, H–C(3)). ^{13}C-NMR (90.55 MHz, CD_3OD): 130.8 (*dd*, ^1J(C,H) = 160, $^n J$(C,H) = 5), 130.1 (*dm*, ^1J(C,H) = 162, C(5), C(6)); 76.2 (*dm*, ^1J(C,H) = 143); 73.9 (*dm*, ^1J(C,H) = 146); 70.7 (*dm*, ^1J(C,H) = 146); 69.5 (br. *dd*, ^1J(C,H) = 140, $^n J$(C,H) = 10). MS (70 eV): 128 (0.3, $M^{+\cdot} - 18$), 111 (1), 110 (5), 99 (15), 94 (6), 87 (5), 86 (100), 82 (20), 81 (13), 57 (78), 55 (19), 53 (19). Anal. calc. for $C_6H_{10}O_4$ (146.143): C 49.31, H 6.90; found: C 49.46, H 6.99.

*(−)-1*L*-1,2,3,4-Tetra-*O*-acetylcyclohex-5-ene-1,2,3/4-tetrol* (= *(−)-Tetraacetylconduritol C*; (−)-**22**). A soln. of (−)-**3** (150 mg; impure syrup, *vide supra*) in Ac_2O (2 ml, 21 mmol) and pyridine (2 ml, 25 mmol) was left overnight and then poured in H_2O (15 ml) and extracted with AcOEt (60 ml, twice). The extract was washed successively with 2N HCl (15 ml), 10% aq. K_2CO_3 soln. (20 ml), and sat. aq. NaCl soln. (10 ml). The aq. layers were extracted successively with AcOEt (50 ml). The combined org. phases were dried ($MgSO_4$), evaporated, and purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 1:2), giving 94 mg of colourless crystals, m.p. 95–97°. Recrystallization from Et_2O/petroleum ether gave 89 mg of crystals, m.p. 96–97.5° ((±)-**22** obtained from (±)-**3**, m.p. 90–91°; [23]: 90–92°). $[\alpha]_{589}^{25} = -186$, $[\alpha]_{578}^{25} = -193$, $[\alpha]_{546}^{25} = -221$, $[\alpha]_{436}^{25} = -388$, $[\alpha]_{365}^{25} = -635$ ($c = 2$, $CHCl_3$). IR (KBr): 3020, 2980, 2940, 1750, 1430, 1230, 1150, 1090, 1050, 1020, 950, 930. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.55–5.85 (*m*, 5 H); 5.20 (br. *d*, $^3J = 8$); 2.13, 2.07, 2.02, 2.01 (4*s*, 4 CH_3CO). Anal. calc. for $C_{14}H_{18}O_8$ (314.29): C 53.50, H 5.77; found: C 53.44, H 5.76.

*(−)-1*L*-Cyclohexane-1,2,3/4-tetrol* ((−)-**23**). A mixture of (−)-**3** (42 mg, 0.3 mmol) and 10% Pd/C (10 mg) in MeOH (4 ml) was pressurized (1 atm) with H_2. After stirring at 25° for 2 h, H_2 was evacuated, replaced by N_2, and the mixture filtered through *Celite*. The *Celite* was extracted with MeOH (5 ml, 3 times), the combined filtrate evaporated, and the white solid recrystallized from MeOH/Et_2O yielding 38 mg (89%) of crystals. M.p. 157–158° ([32]: 158–159°). $[\alpha]_{589}^{25} = -39$, $[\alpha]_{578}^{25} = -40$, $[\alpha]_{546}^{25} = -45$, $[\alpha]_{436}^{25} = -73.5$, $[\alpha]_{365}^{25} = -108$ ($c = 1$, H_2O; [31]: $[\alpha]_{589}^{20} = -35.8 \pm 2$ ($c = 4.7$, H_2O); [32]: $[\alpha]_{589}^{20} = +37.5 \pm 1.9$ ($c = 1$, H_2O) for (+)-**23**). ^{1}H-NMR (360 MHz, CD_3OD): 3.9 (*td*, $^3J = 3$, 3, $^4J = 1$, H–C(2)); 3.67 (*ddd*, $^3J = 10$, 9, 4.5, H–C(4)); 3.58 (*ddd*, $^3J = 10$, 4.5, 3, H–C(1)); 3.23 (*dd*, $^3J = 9$, 3, H–C(3)); 1.83 (*dq*, $^2J = 13$, $^3J = 4.5$, H_{eq}–C(5)); 1.70 (*tdd*, $^2J = 13$, $^3J = 13$, 10, 4.5, H_{ax}–C(6)); 1.59 (*dqd*, $^2J = 13$, $^3J = 4.5$, $^4J = 1$, H_{eq}–C(6)); 1.19 (*tdd*, $^2J = 13$, $^3J = 13$, 10, 4.5, H_{ax}–C(5)). Anal. calc. for $C_6H_{12}O_4$ (148.157): C 48.64, H 8.16; found: C 48.64, H 8.20.

*(1*RS,*2*RS,*3*RS*)-6-Oxocyclohex-4-ene-1,2,3-triyl Triacetate* ((±)-**26**). A soln. of (±)-**12** (373 mg, 1 mmol), and Bu_4NF (1M soln. in THF, 2.2 ml, 2.2 mmol) in THF (5 ml) was stirred at 0° for 10 min. Pyridine (1.2 ml, 15 mmol) and Ac_2O (1.4 ml, 15 mmol) were added. After stirring at 0° for 1 h, then at 20° overnight, the mixture was poured in ice-water (30 ml) and extracted with CH_2Cl_2 (50 ml, 3 times). The org. extract was washed successively with 2N HCl (10 ml), 10% aq. K_2CO_3 soln. (15 ml), and sat. aq. NaCl soln. (15 ml). The aq. layers were extracted successively with CH_2Cl_2 (70 ml). The combined org. phases were dried ($MgSO_4$), evaporated, and purified by column chromatography on silica gel (AcOEt/hexane 1:1), yielding 235 mg (87%) of colourless crystals. M.p. 124–126°. IR (KBr): 3005, 2940, 1755, 1715, 1435, 1375, 1225, 1160, 1115, 1090, 1040, 1025, 960. ^{1}H-NMR (80 MHz, $CDCl_3$): 6.65 (*dt*, $^3J = 10.5$, 2, $^4J = 2$, H–C(4)); 6.23 (*dd*, $^3J = 10.5$, $^4J = 2.5$, H–C(5)); 5.90 (*m*, H–C(2), H–C(3)); 5.61 (*d*, $^3J = 2.5$, H–C(1)); 2.17 (*s*, AcO); 2.07 (*s*, 2 AcO). ^{13}C-NMR (15.08 MHz, $CDCl_3$): 189.8 (*s*, C(6)); 170.0, 169.5, 169.4, (3*s*, 3 COO); 144.2 (*d*, ^1J(C,H) = 168, C(4)); 128.8 (*d*, ^1J(C,H) = 172, C(5)); 72.4, 72.3 (2*d*, ^1J(C,H) = 150); 68.0 (*d*, ^1J(C,H) = 148); 20.3, 20.2, 20.1 (3*q*, ^1J(C,H) = 130, CH_3CO). MS (70 eV): 270 (6, $M^{+\cdot}$), 228 (4), 210 (3), 168 (25), 145 (7), 139 (22), 127 (9), 126 (100), 125 (15), 109 (7). Anal. calc. for $C_{12}H_{14}O_7$ (270.24): C 53.34, H 5.22; found: C 53.43, H 5.18.

*Reduction of (±)-***26** *by $NaBH_4/CeCl_3$.* $NaBH_4$ (115 mg, 3 mmol) was added portionwise within 10 min to a stirred soln. of (±)-**26** (338 mg, 1.25 mmol) in 0.4M methanolic $CeCl_3 \cdot 7H_2O$ (5 ml, 2 mmol) at 0°. After 15 min at 0°, the mixture was poured in ice-water (10 ml) and extracted with AcOEt (60 ml, 3 times). The combined org. phases were washed with sat. aq. NaCl soln. (15 ml), evaporated, and vacuum-dried (25°/0.1 Torr). The residue was dissolved in CH_2Cl_2 (5 ml) and the soln. dried ($MgSO_4$); then pyridine (1 ml, 12 mmol) and Ac_2O (1 ml, 11 mmol) were added. After 2 h at 20°, the mixture was poured in ice-water (20 ml) and extracted with AcOEt (70 ml, 3 times).

The org. extract was washed successively with 2N HCl (10 ml), 10% aq. K_2CO_3 soln. (15 ml), and sat. aq. NaCl soln. (15 ml). The aq. layers were extracted successively with AcOEt (70 ml). The combined org. phase was dried ($MgSO_4$) and evaporated and the residue purified by column chromatography on silica gel (AcOEt/hexane 1:1). A first fraction yielded 201 mg (51%) of *tetraacetylconduritol D* (**28**) as white crystals, m.p. 103–105°. The second fraction yielded 138 mg (35%) of *(±)-tetraacetylconduritol C* ((±)-**22**) as white crystals, m.p. 90–91°.

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