17. Total Syntheses of (−)-Conduritol B ((−)-1L-Cyclohex-5-ene-1,3/2,4-tetrol) and of (+)-Conduritol F ((+)-1D-Cyclohex-5-ene-1,2,4/3-tetrol). Determination of the Absolute Configuration of (+)-Leucanthemitol[1])

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(25.X.89)

The 'naked sugar' (+)-(1*R*,2*R*,4*R*)-2-*endo*-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl acetate ((+)-**4**) was converted (7 steps, 45% overall) with high stereoselectivity into (−)-(4*R*,5*S*,6*R*)-4,5,6-tris{[(*tert*-butyl)dimethylsilyl]oxy}cyclohex-2-en-1-one ((−)-**11**). Reduction of (−)-**11** with $NaBH_4 \cdot CeCl_3 \cdot 7\,H_2O$, followed by deprotection of the silyl ether moieties gave (+)-conduritol F ((+)-**1**; 47%) whose characteristics were identical to those of natural (+)-leucanthemitol. Reduction of (−)-**11** with DIBAH, followed by deprotection of the silyl ether moiety led to (−)-conduritol B ((−)-**3**; 51%).

Introduction. – There is currently considerable interest in the synthesis of conduritols (= cyclohex-5-ene-1,2,3,4-tetrols) [4] as these compounds are useful precursors in the preparation of cyclitols and pseudo-sugars [4] [5], and also because their derivatives present interesting biological activities [6]. From the bark of *Marsdenia Condurango*, conduritol A (= cyclohex-5-ene-1,4/2,3-tetrol) was isolated already in 1908 by *Kubler* [7]. In 1962, *Plouvier* [8] isolated from *Chrysanthemum leucanthemitum* a second natural conduritol called leucanthemicol (m.p. 131.5°, $[\alpha]_D = +101.5$ (H_2O)); the structure of 1L-cyclohex-5-ene-1,2,4/3-tetrol ((−)-**1**) was retained on the basis of the characteristics (m.p. 161°, $[\alpha]_D = -40$) obtained for its product of hydrogenation that were similar to those reported by *Posternak* and *Reymond* [9] for 1L-cyclohexane-1,2,4/3-tetrol ((−)-**2**) (m.p. 161°, $[\alpha]_D = -38.5$). *Kindl et al.* [10] also reported the catalytical hydrogenation of natural (+)-leucanthemitol to a product of the same melting point as (−)-**2**. More recently, *Plouvier* and *Martin* established the relative configuration of tetra-*O*-acetylleucanthemitol to be that of conduritol F by 2D-NMR studies [11]. In 1959, racemic (±)-conduritol F was prepared by *Nakajima et al.* [12]. In 1981, *Paulsen et al.* [13] obtained (−)-conduritol F (1L-cyclohex-5-ene-1,2,4/3-tetrol; (−)-**1**) from (−)-quebrachitol and described this compound to be an oil ($[\alpha]_D = -70.5$ (MeOH)) rather than a solid. The discrepancies between the data reported for the natural (+)-leucanthemitol by *Plouvier* [8] and those for (−)-conduritol F by *Paulsen et al.* [13] convinced us that a total synthesis of these compounds could solve the ambiguities mentioned above and ascertain the absolute configuration of natural (+)-leucanthemitol. Recently, we presented the first total synthesis

[1]) Enantiomerically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives ('naked sugars' [1]) as synthetic intermediates, Part XI. Part X, see [2]; Part IX, see [3].

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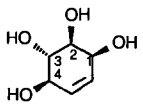
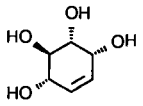
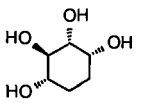


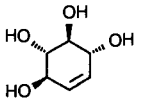
(+)-**1**



(-)-**1**



(-)-**2**

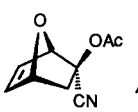


(-)-**3**

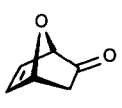
of (−)-conduritol C (1L-cyclohex-5-ene-1,2,3/4-tetrol) based on the ethereal-ring opening of a 7-oxabicyclo[2.2.1]heptan-2-one derivative [14]. The same approach has been applied now to the stereoselective total syntheses of (−)-conduritol B ((−)-**3**) which was prepared for the first time by *Paulsen et al.* [13] and of (+)-conduritol F ((+)-**1**) whose characteristics were found to be identical with those of natural (+)-leucanthemitol.

Results and Discussion. – Our starting material is the 'naked sugar' (+)-**4** ((+)-(1*R*,2*R*,4*R*)-2-*endo*-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl acetate; *e.e.* > 99%) [15]. Saponification with MeONa/MeOH followed by treatment with formaline gave (+)-**5** (93%). The corresponding dibenzyl acetal (+)-**6** (86%) [16] was obtained using *Noyori*'s method [17]. Epoxidation with 3-chloroperbenzoic acid afforded (+)-**7** (93%); treatment with HSO_3F in benzylic alcohol led to the partially protected *trans*-diol (−)-**8** (87%) [16]. Pd-catalyzed hydrogenolysis of (−)-**8** gave (+)-**9** (83%) which was converted into (−)-**10** (94%) with *t*-$BuMe_2SiCl$/imidazole. Treatment of ketone (−)-**10** with *t*-$BuMe_2SiOTf$ ((*tert*-butyl)dimethylsilyl trifluoromethanesulfonate) in the presence of Et_3N afforded the cyclohex-2-enone derivative (−)-**11** (89%).

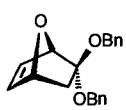
Dreiding models of (−)-**11** suggested that both faces of its carbonyl moiety should be equally available for nucleophilic attack and thus, the chances to find different reduction



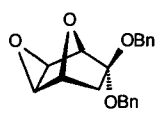
(+)-**4**



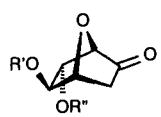
(+)-**5**



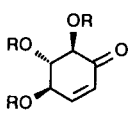
(+)-**6**



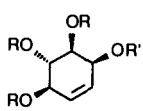
(+)-**7**



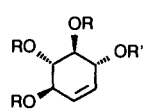
(-)-**8** R'=H, R''=Bn
(+)-**9** R'=R''=H
(-)-**10** R'=R''=*t*-$BuMe_2Si$



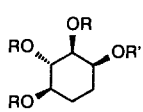
(-)-**11** R=*t*-$BuMe_2Si$



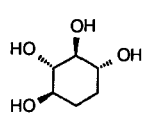
(-)-**12** R=*t*-$BuMe_2Si$, R'=H
(-)-**1** R=R'=H
(+)-**14** R=R'=Ac



(-)-**13** R=*t*-$BuMe_2Si$, R'=H
(-)-**3** R=R'=H
(-)-**15** R=R'=Ac



(+)-**16** R=R'=Ac
(+)-**2** R=R'=H



(-)-**17**

conditions under which either conduritol B or conduritol F derivatives could be obtained selectively were good, *a priori*. With *L-Selectride* (−78°, 2 h), $NaBH_4$ (10°, 2 h), and $LiAlH_4$ (−78°, 1 h) in THF, we found that the reduction of the C=C bond of (−)-**11** was competitive with that of the ketone function. With DIBAH (diisobutylaluminium hydride; 1.3 equiv., THF, −78°, 3 h), a 1:5.3 mixture (−)-**12**/(−)-**13** was obtained in good yield. Interestingly, reversal of the stereoselectivity was observed with $NaBH_4 \cdot CeCl_3$ (6 equiv.), $NaBH_4 \cdot EuCl_3$ (5.5 equiv.) and $NaBH_4 \cdot SmCl_3$ (8 equiv.) in MeOH (0–10°) which led to 2.5:1, 2:1, and 2:1 mixtures (−)-**12**/(−)-**13**, respectively. Column chromatography allowed one to isolate (−)-**12** and (−)-**13** as pure substances (see *Exper. Part*). Cleavage of the silyl ethers of (−)-**12** with HF/MeCN [18] gave (+)-**1**. Purification of (+)-**1** was achieved by preparation of its tetra-*O*-acetyl derivative (+)-**14** (84% based on (−)-**12**) whose data were identical to those reported for (+)-1D-tetra-*O*-acetylleucanthemitol [11]. Ammonolysis of (+)-**14** (NH_3/MeOH) afforded pure (+)-conduritol F ((+)-**1**; 93%) with characteristics almost identical to those published for natural (+)-leucanthemitol [8]. Similarly, treatment of (−)-**13** with HF/MeCN gave crude (−)-**3** whose tetraacetate (−)-**15** (79% based on (−)-**13**) could be purified by column chromatography. Ammonolysis (NH_3/MeOH) of (−)-**15** (93%) afforded pure (−)-conduritol B ((−)-**3**). Characteristics of (−)-**15** and (−)-**3** were comparable to those reported by *Paulsen et al.* for these compounds [13].

Catalytical hydrogenation of (+)-**14** (H_2, Pd/C, EtOH) gave tetraacetate (+)-**16** (94%) which afforded (+)-**2** (87%) by ammonolysis in MeOH. Our sample of (+)-**16** was contaminated by 3–5% of unknown impurities that could not be removed by a combination of chromatography and recrystallization. Nevertheless, the characteristics observed for (+)-**16** were comparable to those reported by *Posternak* and *Reymond* [9a] for this compound. Similarly, catalytical hydrogenation (H_2, Pd/C, EtOH) of (−)-**3** afforded (−)-1L-cyclohexane-1,3/2,4-tetrol ((−)-**17**; 87%) whose characteristics were identical to those reported for this compound [9].

Conclusion. – The 'naked sugar' (+)-**4** has been converted into (+)-conduritol F ((+)-**1**) in 9 steps and 20% overall yield. The characteristics of (+)-**1** were identical to those of natural (+)-leucanthemitol, thus confirming the proposal of *Paulsen et al.* for the structure of this compound. (−)-Conduritol B ((−)-**3**) has also been obtained from (+)-**4** (9 steps, 26% overall yield). Our results confirm also the absolute configurations proposed by *Posternak* and *Reymond* in 1955 [9a] for (+)-1D-cyclohexane-1,2,4/3-tetrol ((+)-**2**) and for (−)-1L-cyclohexane-1,3/2,4-tetrol ((−)-**17**). Since 'naked sugar' (−)-**5** ((1*S*,4*S*)-7-oxabicyclo[2.2.1]hept-5-en-2-one) is as readily available as (+)-**5** [1b] [15b] [19], (−)-conduritol F ((−)-**1**) and (+)-conduritol B ((+)-**3**) can be prepared in the same way as (+)-**1** and (−)-**3**, respectively.

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Experimental Part

General. See [20].

(+)-(1R,4R)-5,5-Bis(benzyloxy)-7-oxabicyclo[2.2.1]hept-2-ene ((+)-**6**). Same procedure as for (±)-**6** [16] starting with (+)-**5** (3.9 g, 35.2 mmol), (benzyloxy)trimethylsilane (16.3 g, 90 mmol), and $CF_3SO_3SiMe_3$ (190 µl, 1 mmol). Yield: 9.3 g (86%), colourless crystals. M.p. 83–84°. $[\alpha]_D^{25} = +102.6$, $[\alpha]_{578}^{25} = +107.3$, $[\alpha]_{546}^{25} = +123.7$, $[\alpha]_{436}^{25} = +225.8$, $[\alpha]_{365}^{25} = +390$ ($c = 2.3$, $CHCl_3$). For (±)-**6**, see [16].

*(+)-(1R,4R,5R,6R)-2,2-Bis(benzyloxy)-5,6-*exo*-epoxy-7-oxabicyclo[2.2.1]heptane* ((+)-**7**). A mixture of (+)-**6** (9.2 g, 30 mmol) and 3-$ClC_6H_4CO_3H$ (55%; 11 g, 32 mmol) in anh. $CHCl_3$ (70 ml) was stirred at 20° for 3 h. AcOEt (250 ml) was added and the mixture washed successively with 10% aq. K_2CO_3 soln. (70 ml, twice) and sat. aq. NaCl soln. (30 ml). After drying ($MgSO_4$) and evaporation, the crude (+)-**7** was purified by column chromatography on silica gel (AcOEt/hexane 1:3): 9 g (93%), colourless crystals. M.p. 98–100°. $[\alpha]_D^{25} = +30.7$, $[\alpha]_{578}^{25} = +32$, $[\alpha]_{546}^{25} = +36.5$, $[\alpha]_{436}^{25} = +62.7$, $[\alpha]_{365}^{25} = +100$ ($c = 2.3$, $CHCl_3$). For (±)-**7**, see [16].

*(−)-(1R,4R,5R,6S)-6-*endo-*(Benzyloxy)-5-*exo*-hydroxy-7-oxabicyclo[2.2.1]heptan-2-one* ((−)-**8**). Same procedure as for (±)-**8** [16] starting with (+)-**7** (89 g, 27.5 mmol), benzylic alcohol (24.8 ml, 26 g, 240 mmol), HSO_3F (0.94 ml, 16.5 mmol), and anh. CH_2Cl_2 (200 ml). Yield: 5.6 g (87%), colourless crystals. M.p. 89–90°. $[\alpha]_D^{25} = -48$, $[\alpha]_{578}^{25} = -50$, $[\alpha]_{546}^{25} = -57$, $[\alpha]_{436}^{25} = -94.6$, $[\alpha]_{365}^{25} = -146.6$ ($c = 2.3$, $CHCl_3$). For (±)-**8**, see [16].

*(+)-(1R,4R,5S,6S)-5-*exo*,6-*endo*-Dihydroxy-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**9**). A soln. of (−)-**8** (3.9 g, 16.7 mmol) in EtOH/H_2O 9:1 (150 ml) was degassed *in vacuo*. Under N_2 5% Pd/C (200 mg) was added. After evacuation of N_2 *(in vacuo)*, the soln. was pressurized (1 atm) with H_2 and stirred for 4 d at 25°. After degassing and filtration, the solvent was evaporated and the residue recrystallized from AcOEt/petroleum ether: 2 g (83%), colourless crystals. M.p. 89–90°. $[\alpha]_D^{25} = +0.1$, $[\alpha]_{578}^{25} = +0.3$, $[\alpha]_{546}^{25} = +1.8$, $[\alpha]_{436}^{25} = +21$, $[\alpha]_{365}^{25} = +94.6$ ($c = 2$, MeOH). IR (KBr): 3300, 3060, 3010, 2950, 1770, 1420, 1380, 1340, 1320, 1260, 1210, 1140, 1110, 1060, 1005, 990, 960, 930, 890, 830, 780. ^{1}H-NMR (360 MHz, CD_3OD): 4.66 (*ddd*, $^3J = 6.8$, $^4J = 1.7$, 1.0, H–C(4)); 4.29 (*ddd*, $^3J = 5.7$, $^4J = 1.3$, 1.0, H–C(1)); 4.16 (*ddd*, $^3J = 5.7$, 0.8, $^4J = 1.7$, H–C(6)); 3.94 (*d*, $^3J = 0.8$, H–C(5)); 2.5 (*ddd*, $^2J = 17.7$, $^3J = 6.8$, $^4J = 1.3$, H_{exo}–C(3)); 2.16 (*d*, $^2J = 17.7$, H_{endo}–C(3)). ^{13}C-NMR (90.55 MHz, CD_3OD): 210.6 (*s*, C(2)); 84.3 (*dd*, ^1J(C,H) = 168, ^nJ(C,H) = 4); 83.1 (*d*, ^1J(C,H) = 170); 81.1 (*d*, ^1J(C,H) = 148); 79.1 (*d*, ^1J(C,H) = 154); 39.9 (*t*, ^1J(C,H) = 135, C(3)). MS (70 eV): 144 (0.7, $M^{+\cdot}$), 126 (5), 97 (8), 85 (36), 84 (100), 57 (96). Anal. calc. for $C_6H_8O_4$ (144.12): C 50.00, H 5.59; found: C 49.92, H 5.65.

(±)-**9**: Same procedure as for (+)-**9**, starting with (±)-**8**: Colourless crystals. M.p. 112–114°.

*(−)-(1R,4R,5R,6R)-5-*exo*,6-*endo*-Bis{[(*tert*-butyl)dimethylsilyl]oxy}-7-oxabicyclo[2.2.1]heptan-2-one* ((−)-**10**). A mixture of (+)-**9** (2 g, 13.9 mmol), *t*-$BuMe_2SiCl$ (5.4 g, 36 mmol), and imidazole (2.8 g, 41.6 mmol) in anh. DMF (30 ml) was stirred at 20° for 4 h. After the addition of AcOEt (100 ml), the soln. was washed successively with 1N HCl (20 ml), sat. aq. $NaHCO_3$ soln. (20 ml), and sat. aq. NaCl soln. (20 ml). The aq. phases were extracted with AcOEt (50 ml). The org. phases were combined, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 3:7) yielding a colourless oil which crystallized slowly form cold MeOH/H_2O: 4.87 g (94%), colourless crystals. M.p. 25°. $[\alpha]_D^{25} = -15.2$, $[\alpha]_{578}^{25} = -15.8$, $[\alpha]_{546}^{25} = -17.5$, $[\alpha]_{436}^{25} = -27.2$, $[\alpha]_{365}^{25} = -31.9$ ($c = 2.4$, $CHCl_3$). IR (KBr): 3000, 2960, 2930, 2890, 2860, 1770, 1470, 1410, 1390, 1360, 1250, 1100, 1010, 990, 970, 940, 890, 860, 830, 780. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.52 (*ddd*, $^3J = 6.5$, $^4J = 1.7$, 1.0, H–C(4)); 4.19 (*ddd*, $^3J = 6$, $^4J = 1.5$, 1.0, H–C(1)); 4.1 (*ddd*, $^3J = 6$, 0.7, $^4J = 1.7$, H–C(6)); 3.86 (*d*, $^3J = 0.7$, H–C(5)); 2.42 (*ddd*, $^2J = 17.7$, $^3J = 6.5$, $^4J = 1.5$, H_{exo}–C(3)); 2.03 (*d*, $^2J = 17.7$, H_{endo}–C(3)); 0.92, 0.86 (2*s*, 2 *t*-BuSi); 0.12, 0.09 (2*s*, 2 Me_2Si). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 207.2 (*s*, C(2)); 83.9 (*dd*, ^1J(C,H) = 160, ^nJ(C,H) = 3); 82.3 (*d*, ^1J(C,H) = 148); 81.6 (*dm*, ^1J(C,H) = 165); 79.8 (*d*, ^1J(C,H) = 152); 38.9 (*t*, ^1J(C,H) = 195, C(3)); 25.7, 25.6 (2*qm*, ^1J(C,H) = 126, 2 *t*-BuSi); 18.0, 17.8 (2*s*, 2 *t*-BuSi); –4.5, –4.7, –5.1 (3*q*, 2 Me_2Si). MS (70 eV): 316 (4), 315 (17, $[M - 57]^+$), 233 (6), 232 (14), 231 (68), 183 (14), 171 (10), 133 (10), 115 (13), 75 (17), 73 (100), 59 (16). Anal. calc. for $C_{18}H_{36}O_4Si_2$ (372.64): C 58.08, H 9.73, Si 15.07; found: C 58.05, H 9.61, Si 15.09.

(±)-**10**: Same procedure as for (−)-**10**, starting with (±)-**9**. Colourless crystals. M.p. 47.5–49.5°.

*(−)-(4R,5S,6R)-4,5,6-Tris-{[(*tert*-butyl)dimethylsilyl]oxy}cyclohex-2-en-1-one* ((−)-**11**). A soln. of $CF_3SO_3Si(t\text{-Bu})Me_2$ (5.9 ml, 6.8 g, 26 mmol) in anh. benzene (20 ml) was added slowly to a stirred soln. of (−)-**10** (4.9 g, 13.1 mmol) and Et_3N (4.8 ml, 3.5 g, 34 mmol) in anh. benzene (25 ml). After stirring at 20° for 4 h, $CF_3SO_3Si(t\text{-Bu})Me_2$ (3 ml, 3.5 g, 13 mmol) and Et_3N (2.4 ml, 1.7 g, 17 mmol) were added. After stirring at 20° for 1 h, the mixture was poured into Et_2O (300 ml) and the soln. washed successively with H_2O (20 ml), 1N HCl (20 ml), sat. aq. $NaHCO_3$ soln. (20 ml) and sat. aq. NaCl soln. (20 ml). The aq. phases were extracted with Et_2O (50 ml). The org. phases were combined, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (*Lobar*, Et_2O/petroleum ether 1:9): 5.67 g (89%), colourless oil which crystallized slowly. M.p. 44–48°. $[\alpha]_D^{25} = -65$, $[\alpha]_{578}^{25} = -67.6$, $[\alpha]_{546}^{25} = -80$, $[\alpha]_{436}^{25} = -168$ ($c = 2.5$, $CHCl_3$). IR (film): 3260, 3060, 2960, 2930, 2890,

2860, 1705, 1420, 1390, 1360, 1250, 1155, 1090, 1060, 1000, 990, 960, 935, 910, 880, 830, 770. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.68 (*dd*, ^3J = 10.5, 2.5, H–C(3)); 5.98 (*dd*, ^3J = 10.5, ^4J = 2, H–C(2)); 4.33 (*ddd*, ^3J = 6, 2.5, ^4J = 2, H–C(4)); 3.9 (*d*, ^3J = 8.5, H–C(6)); 3.8 (*dd*, ^3J = 8.5, 6, H–C(5)); 0.95, 0.94, 0.91 (3*s*, 3 *t*-BuSi); 0.16, 0.10. 0.06, 0.02 (4*s*, 3 Me_2Si). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 197.4 (*s*, C(1)); 148.8 (*d*, ^1J(C,H) = 162, C(3)); 126.8 (*d*, ^1J(C,H) = 165, C(2)); 77.6 (*d*, ^1J(C,H) = 140); 77.5 (*d*, ^1J(C,H) = 145); 72.9 (*d*, ^1J(C,H) = 140); 26.3, 26.2, 26.0 (3*qm*, ^1J(C,H) = 125, 3 *t*-BuSi); 18.6, 18.2, 17.9 (3*s*, 3 *t*-BuSi); –3.7, –3.9, –4.6, –4.7 (4*q*, ^1J(C,H) = 120, 3 Me_2Si). MS (70 eV): 430 (12), 429 (29, $[M-57]^+$), 401 (7), 147 (9), 133 (6), 75 (20), 74 (9), 73 (100), 57 (28). Anal. calc. for $C_{24}H_{50}O_4Si_3$ (486.91): C 59.20, H 10.35, Si 17.3; found: C 59.24, H 10.44, Si 17.25.

(±)-**11**: Same procedure as for (–)-**10**, starting with (±)-**10**. Colourless oil.

*(–)-1-*D*-2,3,4-Tris-*O*-[(*tert*-butyl)dimethylsilyl]cyclohex-2-ene-1,2,4/3-tetrol* ((–)-**12**). $NaBH_4$ (653 mg, 17.3 mmol) was added portionwise to a stirred soln. of (–)-**11** (5.6 g, 11.5 mmol) and $CeCl_3 \cdot 7\,H_2O$ (6.44 g, 17.3 mmol) in MeOH (180 ml) cooled to 0°. After stirring at 0° for 2 h, H_2O (40 ml) was added, and the two phases were separated. The aq. layer was extracted with AcOEt (100 ml, 3 times). The org. phases were combined, washed with sat. aq. NaCl soln. (20 ml), dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (*Lobar*, Et_2O/petroleum ether 1:9) yielding 4.77 g of colourless oil containing 3.41 g (60%) of (–)-**12** and 1.36 g (24%) of (–)-**13** (by ^{1}H-NMR). Pure (–)-**12** was obtained by prep. HPLC (*Zorbax-sil*, 250 × 21 mm, 8 ml/min, Et_2O/petroleum ether 1:20) yielding 2.6 g (46%; t_R 20 min). A 2nd fraction (t_R 22 min) yielded 0.55 g of (–)-**13** (see below). (–)-**12**: colourless oil that crystallized as white needles. M.p. 39–42°. $[\alpha]_D^{25} = -24$, $[\alpha]_{578}^{25} = -25$, $[\alpha]_{546}^{25} = -28.6$, $[\alpha]_{436}^{25} = -50$, $[\alpha]_{365}^{25} = -82.4$ (*c* = 2.5, $CHCl_3$). IR (film): 3260, 2960, 2940, 2890, 2860, 1470, 1360, 1250, 1170, 1120, 1080, 1000, 970, 940, 890, 870, 830, 780. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.62 (*s*, H–C(5), H–C(6)); 4.23 (br. *dd*, ^3J = 10, 4.5, H–C(1)); 3.94 (br. *s*, H–C(4)); 3.90 (*m*, ^3J = 5, 2, H–C(3)); 3.81 (*dd*, ^3J = 5, 4.5, H–C(2)); 2.30 (*d*, ^3J = 10, OH); 0.92, 0.91, 0.89 (3*s*, 3 *t*-BuSi); 0.14, 0.10, 0.09 (3*s*, 3 Me_2Si). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 129.1, 128.4 (2*d*, ^1J(C,H) = 160, C(5), C(6)); 73.9 (*d*, ^1J(C,H) = 145); 71.2 (*dm*, ^1J(C,H) = 143); 71.0 (*d*, ^1J(C,H) = 147); 66.0 (*d*, ^1J(C,H) = 148); 26.1, 26.05, 25.9 (3*qm*, ^1J(C,H) = 126, 3 *t*-BuSi); 18.3, 17.9 (2*s*, 3 *t*-BuSi); –3.8, –4.2, –4.3, –4.4, –4.9 (5*q*, ^1J(C,H) = 118, 3 Me_2Si). MS (70 eV): 431 (1.6, $[M-57]^+$), 299 (18), 288 (16), 225 (9), 200 (17), 197 (7), 147 (20), 133 (8), 75 (35), 73 (100). Anal. calc. for $C_{24}H_{52}O_4Si_3$ (488.93): C 58.96, H 10.72, Si 17.23; found: C 59.03, H 10.66, Si 17.20.

(±)-**12**: From (±)-**11** following the same procedure as for (–)-**12**. Colourless oil.

*(–)-1-*L*-2,3,4-Tris-*O*-[(*tert*-butyl)dimethylsilyl]cyclohex-2-ene-1,3/2,4-tetrol* ((–)-**13**). A 1.2M soln. of DIBAH in anh. toluene (6.7 ml, 8 mmol) was added dropwise to a stirred soln. of (–)-**11** (3 g, 6.17 mmol) in anh. THF (50 ml) cooled to –78° and under Ar. After stirring at –78° for 3 h, acetone (10 ml) was added and the mixture poured into 1N HCl (20 ml). The aq. layer was extracted with Et_2O (100 ml, 3 times). The org. phases were combined, washed successively with sat. aq. $NaHCO_3$ soln. (15 ml) and sat. aq. NaCl soln. (15 ml), dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (*Lobar*, Et_2O/petroleum ether 1:9) yielding 2.5 g of a colourless oil containing 2.1 g (70%) of (–)-**13** and 0.4 g (13%) of (–)-**12**. Pure (–)-**13** was obtained by prep. HPLC (*Zorbax-sil*, 250 × 21 mm, 8 ml/min, Et_2O/petroleum ether 1:20): 1.75 g (58%), colourless oil. $[\alpha]_D^{25} = -8.3$, $[\alpha]_{578}^{25} = -8.7$, $[\alpha]_{546}^{25} = -10.5$, $[\alpha]_{436}^{25} = -17.5$, $[\alpha]_{365}^{25} = -28.3$ (*c* = 2.9, $CHCl_3$). IR (film): 3260, 2950, 2930, 2900, 2860, 1470, 1250, 1170, 1120, 1080, 900, 870, 830, 770. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.98 (*dd*, ^3J = 10.3, 5, H–C(5)); 5.79 (br. *dd*, ^3J = 10.3, 4, H–C(6)); 3.98 (br. *t*, ^3J = 3.5, 3, H–C(3)); 3.93–3.96 (*m*, H–C(1), H–C(2)); 3.81 (br. *ddd*, ^3J = 11, 5, 3, H–C(4)); 2.76 (*d*, ^3J = 11, OH); 0.90, 0.89 (2*s*, 3 *t*-BuSi); 0.15, 0.14, 0.10, 0.09 (4*s*, 3 Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 129.0 (*d*, ^1J(C,H) = 162); 128.4 (*d*, ^1J(C,H) = 164); 73.8 (*d*, ^1J(C,H) = 147); 71.2 (*dm*, ^1J(C,H) = 145); 71.0, 66.0 (2*d*, ^1J(C,H) = 145); 26.1, 26.0, 25.8 (3*qm*, ^1J(C,H) = 125, 3 *t*-BuSi); 18.3, 18.2, 17.9 (3*s*, 3 *t*-BuSi); –3.8, –4.26, –4.32, –4.35, –4.4, –4.9 (6*q*, ^1J(C,H) = 119, 3 Me_2Si). MS (70 eV): 432 (1), 431 (3, $[M-57]^+$), 299 (14), 288 (7), 225 (22), 200 (9), 197 (15), 167 (8), 149 (14), 147 (27), 133 (12), 115 (6), 75 (46), 73 (100), 57 (51). Anal. calc. for $C_{24}H_{52}O_4Si_3$ (488.93): C 58.96, H 10.72, Si 17.23; found: C 59.06, H 10.75, Si 17.18.

(±)-**13**: From (±)-**11** following the same procedure as for (–)-**13**. Colourless oil.

*(+)-1-*D*-Tetra-*O*-acetylcyclohex-5-ene-1,2,4/3-tetrol* (= *(+)-Tetra-*O*-acetylconduritol F*; (+)-**14**). A mixture of (–)-**12** (776 mg, 1.6 mmol) and 40% aq. HF soln. (1 ml, 1.13 g, 22.6 mmol) in MeCN (12 ml) was stirred at 25° for 4 h. After evaporation, the residue was dissolved in Ac_2O (8 ml, 168 mmol) and pyridine (4 ml, 50 mmol). The soln. was allowed to stand at 25° for 6 h, then H_2O (50 ml) was added. The aq. layer was extracted with AcOEt (100 ml, 3 times) and the combined org. phase washed successively with 2N HCl (25 ml), 20% aq. K_2CO_3 soln. (60 ml), and sat. aq. NaCl soln. The aq. phases were extracted with AcOEt (50 ml). The org. extracts were combined, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 1:2): 423 mg (84%), colourless oil [8]. $[\alpha]_D^{25} = +45.6$, $[\alpha]_{578}^{25} = +47.2$, $[\alpha]_{546}^{25} = +54.6$, $[\alpha]_{436}^{25} = +100.6$, $[\alpha]_{365}^{25} = +160.5$ (*c* = 1.12, $CHCl_3$). IR (film): 3250, 3060, 2980, 2940, 2860, 1750, 1460, 1370, 1220,

1050, 970, 930, 790. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.91 (*ddd*, ^3J = 10, 5, ^4J = 1, H–C(6)); 5.84 (*dd*, ^3J = 10, 2, H–C(5)); 5.62 (*dd*, ^3J = 5, 4, H–C(1)); 5.56 (*dd*, ^3J = 10, 7.5, H–C(3)); 5.52 (*ddd*, ^3J = 7.5, 2, ^4J = 1, H–C(4)); 5.14 (*dd*, ^3J = 10, 4, H–C(2)); 2.11, 2.08, 2.05, 2.02 (4*s*, 4 CH_3CO); spectrum identical to that of the tetraacetate obtained from natural (+)-leucanthemitol [11]. ^{13}C-NMR (62.9 MHz, $CDCl_3$): 170.3, 170.1, 169.8 (3*s*, 3 CO); 130.7, 125.2 (2*dm*, ^1J(C,H) = 169); 71.7 (*dm*, ^1J(C,H) = 150); 69.0 (*dm*, ^1J(C,H) = 152); 68.4 (*dm*, ^1J(C,H) = 148); 65.7 (*dm*, ^1J(C,H) = 158); 20.85, 20.8, 20.7, 20.5 (4*q*, ^1J(C,H) = 130). MS (70 eV): 255 (1, $[M - 59]^+$), 212 (7), 183 (5), 170 (5), 153 (6), 152 (32), 141 (19), 128 (13), 111 (22), 110 (100), 99 (15), 82 (11), 81 (12). Anal. calc. for $C_{14}H_{18}O_8$ (314.29): C 53.50, H 5.77; found: C 53.54, H 5.74.

(±)-**14**: From (±)-**11** following the same procedure as for (+)-**14**. Colourless crystals. M.p. 88–89° (Et_2O/petroleum ether; [12]: 92°).

*(+)-1*D-*Cyclohex-5-ene-1,2,4/3-tetrol* (= *(+)-Conduritol F;* (+)-**1**). A soln. of (+)-**14** (400 mg, 1.27 mmol) in MeOH (20 ml) sat. with gaseous NH_3 was allowed to stand at 25° overnight. After evaporation, the acetamide was eliminated by sublimation (35°/10^{-1} Torr). The residue (180 mg, 97%; colourless prims) was recrystallized from MeOH/Et_2O: 172 mg (93%), colourless crystals. M.p. 129–130° [8]: 131.5°; [10]: 132°. $[\alpha]_D^{25}$ = +97.4, $[\alpha]_{578}^{25}$ = +100.4, $[\alpha]_{546}^{25}$ = +114.2, $[\alpha]_{436}^{25}$ = +194.9, $[\alpha]_{365}^{25}$ = +307.1 (*c* = 0.7, H_2O; [8]: $[\alpha]_D$ = +101.5 (*c* = 1.5, H_2O)). IR (KBr): 3400, 2920, 1640, 1400, 1100, 1060, 1010, 950, 870, 800. ^{1}H-NMR (250 MHz, CD_3OD): 5.85 (*ddd*, ^2J = 10, ^3J = 4.7, 2, H–C(5)); 5.76 (*dd*, ^2J = 10, ^3J = 2, H–C(6)); 4.21 (*ddd*, ^3J = 4.7, 4.2, ^5J = 1, H–C(4)); 3.98 (*dtd*, ^3J = 7.6, 2, ^4J = 2, ^5J = 1, H–C(1)); 3.67 (*dd*, ^3J = 10.4, 7.6, H–C(2)); 3.46 (*dd*, ^3J = 10.4, 4.2, H–C(3)); spectrum similar with that reported in [22]. ^{13}C-NMR (62.9 MHz, CD_3OD): 133.9 (*dt*, ^1J(C,H) = 161, ^nJ(C,H) = 6); 128.1 (*dt*, ^1J(C,H) = 162, ^nJ(C,H) = 4); 74.0, 73.9 (2*dm*, ^1J(C,H) = 140); 72.7 (*dm*, ^1J(C,H) = 142); 68.1 (*dd*, ^1J(C,H) = 145, ^nJ(C,H) = 10). MS (70 eV): 110 (2.5, $[M - 36]^+$), 99 (17), 86 (100), 82 (8), 81 (9), 71 (8), 60 (10), 57 (76). Anal. calc. for $C_6H_{10}O_4$ (146.143): C 49.31, H 6.89; found: C 49.28, H 6.95.

(±)-**1**: From (±)-**14** following the same procedure as for (+)-**1**. Colourless crystals. M.p. 106–107° ([12]: 103–104°).

*(−)-1*L-*Tetra*-O-*acetylcyclohex-5-en-1,3/2,4-tetrol* (= *(−)-Tetra*-O-*acetylconduritol B;* (−)-**15**). A soln. of (−)-**13** (430 mg, 0.88 mmol) and 40% aq. HF soln. (1 ml, 1.13 g, 22.6 mmol) in MeCN (6 ml) was stirred at 25° for 4 h. After evaporation, the residue was dissolved in Ac_2O (6 ml, 64 mmol) and pyridine (2 ml, 25 mmol). After stirring at 25° for 6 h, H_2O (20 ml) was added. The aq. layer was extracted with AcOEt (100 ml, 3 times). The org. phases were combined and washed successively with 2N HCl (25 ml), 20% aq. K_2CO_3 soln. (40 ml) and sat. aq. NaCl soln. (20 ml). The aq. phases were extracted with AcOEt (50 ml). The org. phases were combined, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 1:2) yielding 240 mg (86%) of colourless oil that crystallized from Et_2O/petroleum ether: 220 mg (79%), colourless needles. M.p. 120–121° ([13]: 119°). $[\alpha]_D^{25}$ = −172.4, $[\alpha]_{578}^{25}$ = −180, $[\alpha]_{546}^{25}$ = −206.2, $[\alpha]_{436}^{25}$ = −364.3, $[\alpha]_{365}^{25}$ = −600 (*c* = 1.1, $CHCl_3$; [13]: $[\alpha]_D^{20}$ = −176.8 (*c* = 1.2, $CHCl_3$)). IR (KBr): 3250, 3080, 2960, 1760, 1440, 1380, 1220, 1140, 1070, 1050, 1030, 970, 930, 800. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.70 (*s*, H–C(5), H–C(6)); 5.59, 5.33 (*AA'XX'*, 4 H, J(H–C(1), H–C(2)) = 8, J(H–C(1), H–C(4)) = 2.5, J(H–C(2), H–C(3)) = 11, J(H–C(1), H–C(3)) = 0); 2.06, 2.04 (2*s*, 2 Ac). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 170.3 (*s*, CO); 127.4 (*d*, ^1J(C,H) = 168); 71.4, 71.2 (2*d*, ^1J(C,H) = 155); 20.8, 20.6 (2*q*, ^1J(C,H) = 130). MS (70 eV): 212 (3), 194 (1), 183 (2), 170 (3), 153 (5), 152 (35), 141 (10), 128 (8), 111 (17), 110 (100), 99 (10), 82 (8), 81 (6). Anal. calc. for $C_{14}H_{18}O_8$ (314.29): C 53.50, H 5.77; found: C 53.47, H 5.73.

(±)-**15**: From (±)-**13** following the same procedure as for (−)-**15**. M.p. 86–88° ([12] [23]: 92–93°).

*(−)-1*L-*Cyclohex-5-ene-1,3/2,4-tetrol* (= *(−)-Conduritol B;* (−)-**3**). Same procedure as for (+)-**1**, starting with (−)-**15** (130 mg, 0.41 mmol): 56 mg (93%), colourless needles. M.p. 174–175° ([13]: 179°). $[\alpha]_D^{20}$ = −179, $[\alpha]_{578}^{20}$ = −185.7, $[\alpha]_{546}^{20}$ = −212.7, $[\alpha]_{436}^{20}$ = −371.6, $[\alpha]_{365}^{20}$ = −604 (*c* = 1.2, MeOH; [13]: $[\alpha]_D^{20}$ = −156 (*c* = 1.2, MeOH)). IR (KBr): 3260, 2900, 2440, 1420, 1380, 1270, 1200, 1130, 1080, 1030, 1000, 950, 790. ^{1}H-NMR (250 MHz, CD_3OD): 5.62 (*s*, H–C(5), H–C(6)); 4.12, 3.42 (*AA'XX'*, 4 H, J(H–C(1), H–C(2)) = 7.5, J(H–C(1), H–C(4)) = 3, J(H–C(2), H–C(3)) = 10, J(H–C(1), H–C(3)) = 0); spectrum similar with that reported in [22]. ^{13}C-NMR (62.9 MHz, CD_3OD): 130.7 (*d*, ^1J(C,H) = 161); 77.5 (*d*, ^1J(C,H) = 142); 73.6 (*dm*, ^1J(C,H) = 141). MS (70 eV): 128 (0.3, $[M - 18]^{+\cdot}$), 110 (3), 99 (24), 86 (100), 82 (11), 81 (9), 71 (12), 60 (11), 58 (8), 57 (77). Anal. calc. for $C_6H_{10}O_4$ (146.143): C 49.31, H 6.89; found: C 49.47, H 6.93.

(±)-**3**: From (±)-**15** following the same procedure as for (−)-**3**. M.p. 201–202° ([23]: 205°).

*(+)-1*D-*Tetra*-O-*acetylcyclohexane-1,2,4/3-tetrol* ((+)-**16**). To a degassed soln. of (+)-**14** (67 mg, 0.21 mmol) in EtOH (5 ml), 10% Pd/C (40 mg) was added. The soln. was pressurized (1 atm) with H_2 and stirred at 25° for 10 min. The mixture was filtered through *Celite* and the filtrate evaporated. The residue was purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 1:2) yielding 63 mg (94%), colourless oil. $[\alpha]_D^{25}$ = +33.5, $[\alpha]_{578}^{25}$ = +34.1, $[\alpha]_{546}^{25}$ = +38.1, $[\alpha]_{436}^{25}$ = +61.5, $[\alpha]_{365}^{25}$ = +92.8 (*c* = 1.05, $CHCl_3$). IR (KBr): 2980,

2940, 1750, 1440, 1370, 1240, 1100, 1050, 1040, 940, 920, 830. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.4 (*m*, 2 H); 2.14, 2.04, 2.03, 2.00 (4*s*, CH_3CO); 1.6–2.1 (*m*, 4 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 169.9 (*s*, $COCH_3$); 72.1, 71.9, 70.9 (3*d*, ^1J(C,H) = 150); 68.4 (*d*, ^1J(C,H) = 145); 24.5 (*t*, ^1J(C,H) = 130); 24.0 (*t*, ^1J(C,H) = 135); 20.9, 20.8, 20.6, 20.5 (4*q*, ^1J(C,H) = 130, CH_3CO). MS (70 eV): 214 (2.5), 196 (14), 172 (3), 171 (16), 170 (6), 155 (13), 154 (83), 136 (18), 129 (14), 128 (16), 113 (14), 112 (100), 111 (19), 103 (19), 95 (13), 94 (42), 84 (13), 83 (22). Anal. calc. for $C_{14}H_{20}O_8$ (316.308): C 53.16, H 6.37; found: C 53.15, H 6.35.

(±)-**16**: From (±)-**14** following the same procedure as for (+)-**16**. After recrystallization from Et_2O/petroleum ether, white crystals. M.p. 80–81°.

*(+)-1*D-*Cyclohexane-1,2,4/3-tetrol* ((+)-**2**). Same procedure as for (+)-**1**, starting with (+)-**16** (61 mg, 0.193 mmol) and MeOH (5 ml): 25 mg (87%), colourless crystals. M.p. 135–136° ([9a]: 138–139°; [9b]: 158–160°). $[\alpha]_D^{20}$ = +31, $[\alpha]_{578}^{20}$ = +31.5, $[\alpha]_{546}^{20}$ = +35.5, $[\alpha]_{436}^{20}$ = +56.1, $[\alpha]_{365}^{20}$ = +95.3 (*c* = 0.7, H_2O; [9a]: $[\alpha]_D^{18}$ = +38 ± 2.2 (*c* = 0.46, H_2O)). IR (KBr): 3400, 3300, 2960, 2940, 2860, 1580, 1440, 1350, 1300, 1250, 1210, 1180, 1130, 1110, 1050, 1030, 990, 930, 880, 850. ^{1}H-NMR (250 MHz, CD_3OD): 3.98 (*q*, ^3J = 3, H–C(1)); 3.58 (*t*, ^3J = 9, H–C(3)); 3.41 (*td*, ^3J = 9, 9, 5.5, H–C(4)); 3.35 (*dd*, ^3J = 9, 3, H–C(2)); 1.85 (*dq*, ^2J = 14, ^3J = 3.5, H_{eq}–C(6)); 1.85–1.71 (*m*, H_{ax}–C(5), H_{eq}–C(5)); 1.54 (*dddd*, ^2J = 14, ^3J = 12, 3, 2.5, H_{ax}–C(6)). ^{13}C-NMR (62.9 MHz, CD_3OD): 76.5, 76.1 (2*d*, ^1J(C,H) = 145); 74.2 (*d*, ^1J(C,H) = 140); 70.6 (*d*, ^1J(C,H) = 145); 28.1 (*t*, ^1J(C,H) = 125); 27.7 (*t*, ^1J(C,H) = 130). MS (70 eV): 112 (13, $[M - 36]^+$), 86 (100), 83 (17), 73 (88), 71 (26), 70 (20), 60 (41), 57 (52). Anal. calc. for $C_6H_{12}O_4$ (148.158): C 48.64, H 8.18; found: C 48.57, H 8.20.

(±)-**2**: From (±)-**16** following the same procedure as for (+)-**2** colourless crystals. M.p. 138–139° ([9b]: 142°).

*(−)-1*L-*Cyclohexane-1,3/2,4-tetrol* ((−)-**17**). To a degassed soln. of (−)-**3** (17 mg, 0.2 mmol) in EtOH (3 ml), 10% Pd/C (20 mg) was added. The soln. was pressurized (1 atm) with H_2 and stirred at 25° for 10 min. After filtration through *Celite*, the soln. was evaporated and the white solid recrystallized from MeOH/Et_2O: 15 mg (87%), white crystals. M.p. 144–145° ([9a]: 146–148°). $[\alpha]_D^{17}$ = −27.2, $[\alpha]_{578}^{17}$ = −27.6, $[\alpha]_{546}^{17}$ = −29.2, $[\alpha]_{436}^{17}$ = −51, $[\alpha]_{365}^{17}$ = −88.2 (*c* = 0.5, H_2O; [9a]: $[\alpha]_D^{17}$ = −28.8 (*c* = 1.1, H_2O)). IR (KBr): 3400, 3280, 3060, 3020, 2960, 1680, 1500, 1440, 1330, 1270, 1200, 1140, 1090, 1060, 1020, 990, 900. ^{1}H-NMR (250 MHz, CD_3OD): 3.42 (*m*, H–C(1), H–C(4)); 3.15 (part of *AA'XX'*, ^3J(H–C(1),H–C(2)) = ^3J(H–C(2),H–C(3)) = 9, ^4J(H–C(1), H–C(3)) = ^5J(H–C(1),H–C(4)) = 0, H–C(2), H–C(3)); 1.92 (*m*, 2H, H_{eq}–C(5), H_{eq}–C(6)); 1.38 (*m*, 2H, H_{ax}–C(5), H_{ax}–C(6)). ^{13}C-NMR (62.9 MHz, CD_3OD); 79.1, 73.9 (2*d*, ^1J(C,H) = 140); 30.0 (*t*, ^1J(C,H) = 129). MS (70 eV): 112 (19, $[M - 36]^+$), 86 (94), 83 (19), 73 (100), 71 (32), 70 (21), 60 (56), 57 (61). Anal. calc. for $C_6H_{12}O_4$ (148.158): C 48.64, H 8.18; found: C 48.59, H 8.27.

(±)-**17**: Same procedure as for (−)-**17**, starting with (±)-**3**. M.p. 182–184°. [9b] [24]: 187°.

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