1. Enantioselective Synthesis of (−)-Conduramine C_1 and Aminobromocyclitol Derivatives[1])

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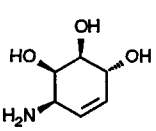
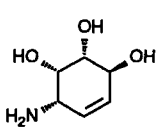
(7.X.93)

(1*S*,2*R*,6*R*,7*R*)-4-Phenyl-3,10-dioxa-5-azatricyclo[5.2.1.$0^{2,6}$]dec-4-en-9-one ((+)-**5**) obtained in 6 steps from the *Diels-Alder* adduct of furan to 1-cyanovinyl (1*S*)-camphanate ((+)-**3**) was reduced to the corresponding *endo*-alcohol (−)-**6** the treatment of which with HBr/AcOH provided (−)-(3a*S*,4*S*,6*R*,7*S*,7a*R*)-4β-bromo-3aβ,4,5,6,7,7aβ-hexahydro-2-phenyl-1,3-benzoxazole-6β,7α-diyl diacetate ((−)-**17**). Elimination of HBr with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and acidic hydrolysis furnished (−)-(1*R*,2*S*,3*R*,4*R*)-4-aminocyclohex-5-ene-1,2,3-triol (= (−)-conduramine C_1; (−)-**1**).

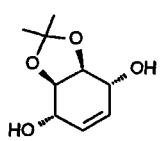
Introduction. – Conduritols (cyclohex-5-ene-1,2,3,4-tetrols) [2] [3] and conduramines (conduritols in which one of the OH groups is exchanged with an amino moiety) [2] [4–14] have become prominent compounds, because they are useful intermediates in the synthesis of amino- and diaminocyclitols [4] [8a–c, e–h] [9] [11–13] [15] [16], the aglycon parts of numerous aminoglycoside antibiotics. Moreover, some derivatives inhibit certain glycosidases [2b] [17]. The first examples of synthesis of optically pure conduramines were presented in 1981 by *Paulsen* and coworkers who derived conduramine F_1 and conduramine F_4 from natural quebrachitol [5]. More recently, *Ogawa* and coworkers [13], as well as *Knapp* and coworkers [14], applied the *Ferrier* cyclization to transform D-glucose into conduramine C_2, C_4, and F_1. Asymmetric total syntheses of conduritols and conduramines were reported in the last few years based on the *Diels-Alder* addition of nitroso derivatives onto cyclohexa-3,5-diene-1,2-diol systems [8d–f], or on the microbial oxidation of bromo- or chlorobenzene [9]. In 1992, *Johnson* and coworkers [10] reported the first synthesis of (−)-conduramine C_1 ((−)-**1**) and of (+)-conduramine C_1 ((+)-**1**) following a process that implies the microbial oxidation of benzene into cyclohexa-3,5-diene-1,2-diol, its conversion into *meso*-2,3-*O*-isopropylideneconduritol A (**2**), and the desym-



(-)-**1**



(+)-**1**



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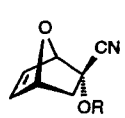
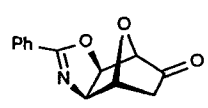


(+)-**3** R=(1*S*)-camphanoyl
(±)-**4** R=Ac



(+)-**5**

[1]) 'Naked Sugars' as Synthetic Intermediates, Part XXV. Part XXIV, see [1a]; Part XXIII, see [1b].

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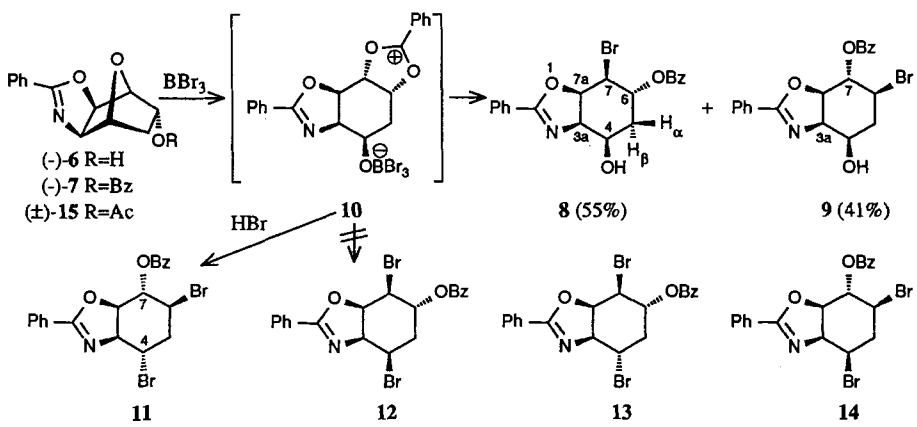
metrization of the latter by monoacetylation with isopropenyl acetate catalyzed by *Pseudomonas cepacia* lipase (Amano P-30). We wish to report here an alternative approach to the asymmetric total synthesis of these conduramines based on the 'naked sugar' technology [18].

Results and Discussion. – The stereoselective aminohydroxylation of the olefinic moiety of the 'naked sugar' (+)-**3** (*Diels-Alder* adduct of furan to 1-cyanovinyl (1*S*)-camphanate [18]) followed a method we had described earlier in the racemic series [19]. The tricyclic ketone (+)-**5** was obtained from (+)-**3** in 6 steps with an overall yield of 46% with recovery of the chiral auxiliary ((1*S*)-camphanic acid). Reduction of ketone (+)-**5** with $Na(CN)BH_3$ in MeOH gave the *endo*-alcohol (−)-**6** (97%) with high stereoselectivity, the *exo*-face being less sterically hindered than the *endo*-face of the ketone. Attempts to open the oxa-bridge of racemic (±)-**7** (obtained by benzoylation of (±)-**6** derived from (±)-**4** [19]) applying the method of *Koreeda* [20] and *Jones* [21] led to a near 1:1 mixture of bromides **8** and **9** (*Scheme 1*). Under these conditions (BBr_3/CH_2Cl_2), the oxa-ring

Scheme 1

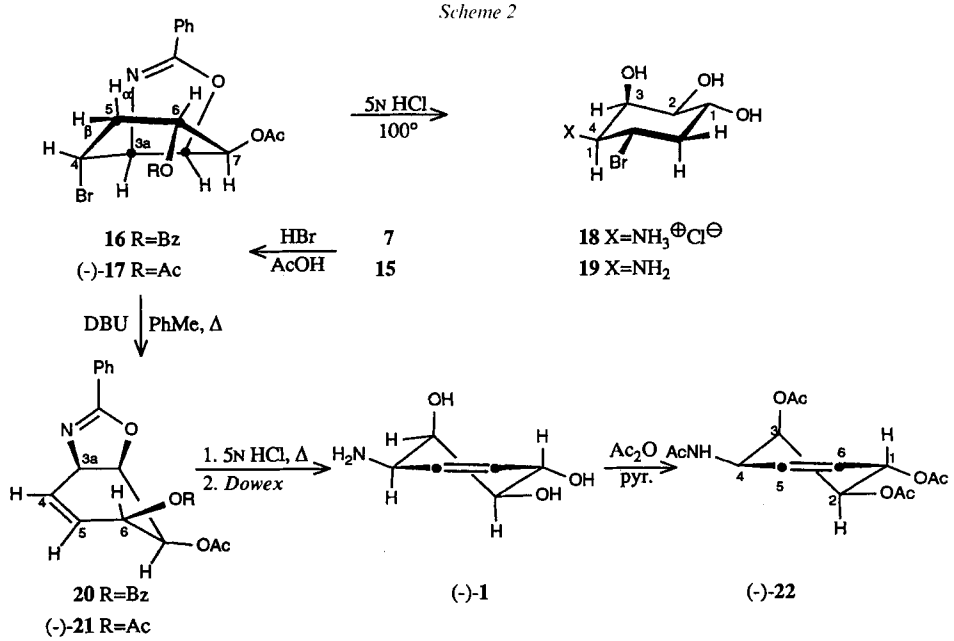


opening is assisted by the *endo*-benzoyloxy group leading to the hypothetical cationic intermediate **10** which can be attacked by the nucleophile (Br^-) either at position C(6) or C(7). When a trace of H_2O was present, a third compound **11** was formed together with **8**/**9** that resulted probably from the acid-promoted S_N2 displacement of the tribromoborate moiety of **10** by the Br^- ion (*Scheme 1*). The dibromide **11** was the major product of the reaction of (±)-**7** with BBr_3 in wet CH_2Cl_2. No other isomeric dibromides such as **12**–**14** were observed in the crude reaction mixtures. When pure **8** or **9** were treated with BBr_3/CH_2Cl_2, only decomposition was observed.

The structures of **8**, **9**, and **11** were deduced from their spectral data and elemental analyses (see *Exper. Part*). The ^{1}H-NMR spectral assignments were confirmed by NOE measurements and by double irradiations. These compounds exist probably as rapidly equilibrating mixtures of conformers. The *cis*-relationship between protons at C(4) and C(7) of **11** was confirmed by the observation of a strong NOE between these protons.

Regio- and stereoselective oxa-ring openings of (±)-**7** and of the corresponding acetate (±)-**15** (derived from (±)-**6** by treatment with Ac_2O/pyridine) were observed on treating these compounds with HBr in AcOH [22] [23]. The corresponding monobromides **16** and (±)-**17** were isolated in 56% yield (*Scheme 2*). They result from a S_N2-type displacement of the ethereal bridge, the nucleophile (Br^-) attacking preferentially the least hindered bridgehead center C(7) rather than C(1) of the oxonium-ion intermediate. The structures of **16** and (±)-**17** were deduced from their spectral data and their elemental analyses and were further confirmed by their transformations described in *Scheme 2*.

Scheme 2



The *cis*-relationship between H–C(3a) and H–C(7) and between H–C(4) and H–C(6) of **16** and (±)-**17** were ascertained by the observation of NOE's between these proton pairs. The distinction between H_α and H_β at C(5) was confirmed also by NOE's measured between these protons and H–C(6) and H–C(7), respectively. A typical *W*-type $^4J \approx 1$ Hz was measured between H–C(3a) and H_β–C(5). Considering the coupling constants between vicinal protons, one can propose the 'average' conformation shown in *Scheme 2* for **16** and (±)-**17**.

Acidic hydrolysis (5N HCl, 100°, 2 h) of **16** and (±)-**17** afforded the chlorohydrate of the aminobromocyclitol **18** which liberated the free base **19** after chromatography on ion-exchange resin. The ^{1}H-NMR spectra of **18** and **19** were consistent with a single chair conformation (*Scheme 2*) in which four of the five substituents of the cyclohexane ring occupy equatorial positions (see *Exper. Part*). Treatment of **16** and (±)-**17** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in boiling toluene gave the protected (±)-conduramine-C_1 derivatives **20** (94%) and (±)-**21** (95%), respectively. Their ^{1}H-NMR spectra suggested an envelope or near-envelope conformation (*Scheme 2*) in which H–C(6) and H–C(7) approach a nearly antiperiplanar relationship (^3J(H–C(6),H–C(7)) = 8.5 Hz). A typical homoallylic coupling constant ^5J(H–C(3a),H–C(6)) = 2.0 Hz was observed for these compounds [24]. Hydrolysis (5N HCl, 100°, 2 h) of **20** and (±)-**21** led to (±)-**1**·HCl

(100%) and then to (±)-**1** (74%) after *Dowex* chromatography. The ^{1}H-NMR spectra of (±)-**1**·HCl, (±)-**1**, and of the corresponding peracetylated derivative (±)-**22** were consistent with half-chair conformations in which three of the four substituents of the cyclohexane ring are in pseudoequatorial positions.

Optically pure (−)-conduramine C_1 ((−)-**1**) was obtained by treating the optically pure alcohol (−)-**6** with boiling HBr/AcOH. This gave (−)-**17** (56%) which eliminated HBr to provide (−)-**21** (95%). Acidic hydrolysis furnished (−)-**1** (95%).

Conclusion. – The 'naked sugar' (+)-**3** was converted into (−)-conduramine C_1 ((−)-**1**) in 10 steps and 23.3% overall yield. This approach is less efficient than that of *Johnson* and coworkers [10] who derived (−)-**1** from cyclohexa-3,5-diene-1,2-diol in 6 steps and 23.5% overall yield using an enzymatic esterification for the desymmetrization. Our method can also be applied with the same ease to the preparation of (+)-conduramine C_1 starting with the readily available *Diels-Alder* adduct of furan to 1-cyanovinyl (1*R*)-camphanate [18] instead of (+)-**3**. Furthermore, it allows one to obtain various aminobromocyclitol derivatives in both their enantiomeric forms, compounds that can be intermediates in the total synthesis of antibiotics and analogues or be potentially bioactive themselves.

We are grateful to the *Swiss National Science Foundation*, Bern, the *Fonds Herbette*, Lausanne, and to the *Ciba-Geigy-Jubiläums-Stiftung*, Basel, for generous financial support. We thank also Prof. *C. R. Johnson* for exchange of informations and copies of spectra of (−)-**1**.

Experimental Part

General. See [25].

*(1S,2R,6R,7R,9R)-4-Phenyl-3,10-dioxa-5-azatricyclo[5.2.1.0^{2,6}]dec-4-en-9-*endo*-ol* ((−)-**6**). $Na(CN)BH_3$ (413 mg, 6.56 mmol) was added to a soln. of (+)-**5** [26] (0.5 g, 2.18 mmol) in abs. MeOH (10 ml) stirred at 0°. After stirring at 20° for 90 min, $Na(CN)BH_3$ (413 mg) was added and the mixture stirred at 20° for 4 h. Aq. 1N HCl was added until neutralization and the solvent evaporated. The residue was purified by flash chromatography (FC; silica gel (20 g), AcOEt/Et_2O 1:1). A 1st fraction (R_f 0.33 (UV)) afforded 80 mg of (+)-**5** and a second (R_f 0.14 (UV)) 409 mg (81%; 97% based on converted (+)-**5**) of (−)-**6**. Colorless crystals. M.p. 195–198° (from Et_2O). $[\alpha]_{589}^{25} = -135$, $[\alpha]_{577}^{25} = -142$, $[\alpha]_{546}^{25} = -161$, $[\alpha]_{435}^{25} = -306$, $[\alpha]_{405}^{25} = -396$ (c = 1.0, MeOH). UV (MeCN): 241 (2050), 229 (1980), 200 (4350). IR (KBr): 3300, 1640, 1580, 1450, 1355, 1270, 1155, 1085, 1070, 1030, 930, 910, 860, 840, 795, 780, 695. ^{1}H-NMR (250 MHz, MeOD): 7.96–7.91 (*m*, 2 arom. H); 7.61–7.45 (*m*, 3 arom. H); 5.46 (*d*, ^3J(H–C(2),H–C(6)) = 7.0, H–C(2)); 4.57 (*d*, ^3J = 7.0, H–C(6)); 4.55 (*dd*, ^3J(H–C(1),H–C(9)) = 5.0, H–C(1)); 4.45 (*dd*, ^3J(H–C(7),H_{exo}–C(8)) = 6.0, H–C(7)); 4.32 (*ddd*, ^3J(H–C(1),H–C(9)) = 5.0, ^3J(H_{exo}–C(8),H–C(9)) = 10.0, ^3J(H_{endo}–C(8),H–C(9)) = 3.0, H–C(9)); 2.25 (*ddd*, ^2J = 13.0, ^3J = 10.0, 6.0, H_{exo}–C(8)); 1.37 (*dd*, ^2J = 13.0, ^3J = 3.0, H_{endo}–C(8)). ^{13}C-NMR (90.55 MHz, MeOD): 168.3 (*s*, C(4)); 133.1, 129.6, 129.4 (3*d*, ^1J(C,H) = 160, arom. CH); 128.2 (*s*, arom. C); 83.8 (*d*, ^1J(C,H) = 165, C(2)); 83.2 (*d*, ^1J(C,H) = 160, C(6)); 82.8 (*d*, ^1J(C,H) = 165, C(1)); 76.1 (*d*, ^1J(C,H) = 155, C(7)); 70.3 (*d*, ^1J(C,H) = 155, C(9)); 37.2 (*t*, ^1J(C,H) = 130, C(8)). CI-MS (NH_3): 232 (6, $[M+1]^+$), 231 (4, M^+), 158 (17), 105 (100), 104 (14), 77 (34). Anal. calc. for $C_{13}H_{15}NO_3$ (231.25): C 67.52, H 5.67, N 6.06; found: C 67.55, H 5.73, N 5.99.

*(1RS,2SR,6SR,7SR,9SR)-4-Phenyl-3,10-dioxa-5-azatricyclo[5.2.1.0^{2,6}]dec-4-en-9-*endo*-ol* ((±)-**6**). Prepared from (±)-**5** [19] as described above. M.p. 180–240° (dec.).

*(1RS,2SR,6SR,7SR,9SR)-4-Phenyl-3,10-dioxa-5-azatricyclo[5.2.1.0^{2,6}]dec-4-en-9-*endo*-yl Benzoate* ((±)-**7**). A mixture of (±)-**5** [19] (115 mg, 0.502 mmol), MeOH (2 ml), and $NaBH_4$ (19 mg, 1 mmol) was stirred at 20° for 1 h. NH_4Cl (100 mg) was added and the mixture stirred at 20° for 15 min. The solvent was evaporated and the residue purified by FC (silica gel, AcOEt/Et_2O 1:1) giving a fraction (R_f 0.14) that was mixed with pyridine (2 ml) and then benzoyl chloride (175 µl, 1.5 mmol). After stirring at 20° for 15 h, the solvent was evaporated, toluene (2 ml) added, and the solvent evaporated. The same operation was repeated twice. The residue was purified by FC (silica gel, AcOEt/Et_2O 1:1; R_f 0.50 (UV)): 101 mg (60%) of (±)-**7**. Colorless crystals. M.p. 152–153.5°. UV (MeCN): 230 (19810). IR (KBr): 3060, 3000, 2960, 1720, 1645, 1600, 1580, 1495, 1435, 1355, 1270, 1225, 1155,

1110, 1065, 1030, 1010, 930, 865, 840, 795, 715, 690. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.07–7.92 (*m*, 4 H); 7.66–7.38 (*m*, 6 arom. H); 5.29 (*d*, ^3J = 7.0, H–C(2)); 5.28 (*ddd*, ^3J = 10.0, 5.2, 3.2, H–C(9)); 4.94 (*dd*, ^3J = 5.2, H–C(1)); 4.65 (*dd*, ^3J = 6.0, H–C(7)); 4.62 (*d*, ^3J = 7.0, H–C(6)); 2.53 (*ddd*, ^2J = 13.5, ^3J = 10.0, 6.0, H_{exo}–C(8)); 1.62 (*dd*, ^2J = 13.5, ^3J = 3.2, H_{endo}–C(8)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 166.1 (*s*, COO); 165.9 (*s*, C(4)); 133.5, 130.6, 129.6, 128.6, 128.5, 128.3 (6*d*, ^1J(C,H) = 160, arom. CH); 129.2, 127.0 (2*s*, arom. C); 81.5 (*d*, ^1J(C,H) = 165); 80.8, 80.6, 75.6, 71.9 (4*d*, ^1J(C,H) = 160); 34.3 (*t*, ^1J(C,H) = 135, C(8)). CI-MS (NH_3): 336 (3, $[M + 1]^+$), 335 (2, $M^{+\cdot}$), 213 (10), 105 (100), 77 (38). Anal. calc. for $C_{20}H_{17}NO_4$ (335.36): C 71.63, H 5.11, N 4.18; found: C 71.52, H 5.09, N 4.26.

*(1S,2R,6R,7R,9R)-4-Phenyl-3,10-dioxa-5-azatricyclo[5.2.1.0^{2,6}]dec-4-en-9-*endo*-yl Benzoate* ((–)-**7**). A mixture of (–)-**6** (104 mg, 0.45 mmol), pyridine (2 ml), and benzoyl chloride (105 µl, 0.90 mmol) was stirred at 20° for 15 h. The solvent was evaporated and the residue purified as above by FC: 129 mg (86%). Recrystallization from Et_2O at 4° gave 65 mg (43%) of colorless crystals. M.p. 153–155.5°. $[\alpha]_{589}^{25} = -185$, $[\alpha]_{577}^{25} = -193$, $[\alpha]_{546}^{25} = -221$, $[\alpha]_{435}^{25} = -423$, $[\alpha]_{405}^{25} = -549$ (c = 1.0, CH_2Cl_2).

*(1RS,2SR,6SR,7SR,9SR)-4-Phenyl-3,10-dioxa-5-azatricyclo[5.2.1.0^{2,6}]dec-4-en-9-*endo*-yl Acetate* ((±)-**15**). A mixture of (±)-**6** (100 mg), Ac_2O (4 ml), pyridine (2 ml), and 4-(dimethylamino)pyridine (10 mg) was stirred at 20° for 15 h. The solvent was evaporated, the residue taken with toluene (5 ml), and the solvent evaporated. The latter operation was repeated twice and the residue purified by FC (silica gel, AcOEt/Et_2O 1:1, R_f 0.51 (UV)): 45 mg (75%) of (±)-**15**. Colorless crystals. M.p. 182–187°. UV (MeCN): 243 (10000), 206 (10700). IR (KBr): 2980, 1730, 1640, 1575, 1490, 1450, 1355, 1325, 1245, 1235, 1150, 1055, 1025, 1000, 900, 860, 790, 775, 695, 670. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.95–7.92 (*m*, 2 H); 7.52–7.37 (*m*, 3 H); 5.15 (*d*, ^1J = 7.0, H–C(2)); 5.04 (*ddd*, ^3J = 10.0, 5.5, 3.5, H–C(9)); 4.87 (br. *d*, ^3J = 5.5, H–C(1)); 4.57 (br. *d*, ^3J = 5.5, H–C(7)); 4.55 (*d*, ^3J = 7.0, H–C(6)); 2.39 (*ddd*, ^2J = 13.5, ^3J = 10.0, 5.5, H_{exo}–C(8)); 2.12 (*s*, Ac); 1.45 (*dd*, ^2J = 13.5, ^3J = 3.5, H_{endo}–C(8)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.3 (*s*, COO); 166.0 (*s*, C(4)); 131.4, 128.4, 128.2 (3*d*, ^1J(C,H) = 160); 127.0 (*s*); 81.3, 80.6 (2*d*, ^1J(C,H) = 165, C(2), C(9)); 80.3 (*d*, ^1J(C,H) = 160, C(1)); 75.5 (*d*, ^1J(C,H) = 155, C(7)); 71.3 (*d*, ^1J(C,H) = 160, C(6)); 34.1 (*t*, ^1J(C,H) = 135, C(8)); 20.8 (*q*, ^1J(C,H) = 130, Me). CI-MS (NH_3): 274 (5, $[M + 1]^+$), 273 (10, $M^{+\cdot}$), 213 (24), 184 (43), 158 (24), 145 (11), 106 (14), 105 (100), 81 (10), 77 (17). Anal. calc. for $C_{15}H_{15}NO_4$ (273.29): C 65.93, H 5.53, N 5.12; found: C 65.99, H 5.41, N 5.28.

7α-Bromo-3aβ,4,5,6,7,7aβ-hexahydro-4α-hydroxy-2-phenyl-1,3-benzoxazol-6β-yl Benzoate (**8**), *6α-Bromo-3aβ,4,5,6,7,7aβ-4α-hydroxy-2-phenyl-1,3-benzoxazol-7β-yl* (**9**), *and 4β,6α-Dibromo-3aβ,4,5,6,7,7aβ-hexahydro-2-phenyl-1,3-benzoxazol-7β-yl Benzoate* (**11**). BBr_3 (60 µl, 0.623 mmol) was added to a stirred soln. of (±)-**7** (120 mg, 0.358 mmol) in CH_2Cl_2 (20 ml) at –78°. After stirring at 0° for 4 h, the mixture was poured in a sat. aq. $NaHCO_3$ soln. at 0°. The mixture was extracted with CH_2Cl_2 (25 ml, 4 times), the combined extract dried ($MgSO_4$) and evaporated, and the residue purified by column chromatography (silica gel, AcOEt/Et_2O 1:1). The 1st fraction (R_f 0.72 (UV)) gave 39 mg (23%) of **11**, the 2nd (R_f 0.35 (UV)) 45 mg (30%) of **8**, and the 3rd (R_f 0.15 (UV)) 25 mg (17%) of **9**. When the same reaction was carried out with anh. CH_2Cl_2, no **11** was obtained, and **8** and **9** were isolated in 55 and 41% yield, resp.

Data of **8**: M.p. 147–148° (from CH_2Cl_2/Et_2O). IR (KBr): 3380, 3060, 2960, 2920, 1720, 1635, 1600, 1575, 1490, 1450, 1365, 1265, 1100, 1065, 1030, 990, 925, 865, 835, 770, 695. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.05–7.99 (*m*, 4 H); 7.64–7.39 (*m*, 6 H); 5.54 (*ddd*, ^3J(C(6),H–C(7)) = 3.0, ^3J(H_α–C(5),H–C(6)) = 6.5, ^3J(H_β–C(5),H–C(6)) = 3.5, H–C(6)); 4.95 (*dd*, ^3J(H–C(3a),H–C(7a)) = 9.5, ^3J(H–C(7a),H–C(7)) = 7.2, H–C(7a)); 4.61 (br. *dd*, ^3J(H–C(3a),H–C(7a)) = 9.5, ^3J(H–C(3a),H–C(4)) = 4.0, H–C(3a)); 4.47 (br. *dd*, ^3J(H–C(7),H–C(7a)) = 7.2, ^3J(H–C(6),H–C(7)) = 3.0, H–C(7)); 4.37 (*ddd*, ^3J(H–C(4),H_α–C(5)) ≈ ^3J(H–C(4),H_β–C(5)) ≈ 5.0, ^3J(H–C(3a),H–C(4)) = 4.0, H–C(4)); 2.35 (*ddd*, ^2J = 15.5, ^3J = 6.5, 5.0, H_α–C(5)); 2.16 (*dddd*, ^2J = 15.5, ^3J = 5.0, 3.5, ^4J(H_β–C(5),H–C(3a)) ≤ 1, H_β–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 166.3 (*s*, COO); 165.8 (*s*, C(2)); 133.4, 132.3, 129.6 (3*d*, ^1J(C,H) = 160, arom. CH); 129.9 (*s*, arom. C); 128.7, 128.5, 128.4 (3*d*, ^1J(C,H) = 160); 126.9 (*s*); 82.2 (*d*, ^1J(C,H) = 160); 71.3 (*d*, ^1J(C,H) = 150); 70.1, 68.5 (2*d*, ^1J(C,H) = 155); 64.2 (*d*, ^1J(C,H) = 155, C(4)); 33.6 (*t*, ^1J(C,H) = 130, C(5)). CI-MS (NH_3): 418 (6, $[M(^{81}Br) + 1]^+$), 416 (7, $M^{+\cdot}$), 355 (6, $[M(^{81}Br) - Br + NH_3 + H]^+$), 354 (30), 322 (7), 232 (15), 231 (28), 203 (7), 202 (20), 117 (14), 105 (100), 91 (16), 77 (74), 71 (15).

Data of **9**: Colorless crystals. M.p. 204–205°. IR (KBr): 3180, 2920, 2850, 1720, 1645, 1600, 1490, 1450, 1360, 1315, 1270, 1175, 1115, 1090, 1070, 1025, 990, 955, 705. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.16–8.12 (*m*, 2 H); 8.00–7.96 (*m*, 2 H); 7.67–7.41 (*m*, 6 H); 5.61 (br. *dd*, ^3J(H–C(6),H–C(7)) = 10.5, ^3J(H–C(7),H–C(7a)) = 7.0, H–C(7)); 4.88 (br. *dd*, ^3J(H–C(3a),H–C(7a)) = 8.5, ^3J(H–C(7),H–C(7a)) = 7.0, H–C(7a)); 4.58 (br. *dd*, ^3J(H–C(3a),H–C(7a)) = 8.5, ^3J(H–C(3a),H–C(4)) = 5.0, H–C(3a)); 4.17 (*dddd*, ^3J(H–C(4),OH) = 8.0 (vanishes with D_2O), ^3J(H–C(4),H_β–C(5)) = 10.0, ^3J(H–C(3a),H–C(4)) = 5.0, ^3J(H–C(4),H_α–C(3)) = 4.5, H–C(4)); 4.06 (*ddd*, ^3J(H–C(6),H–C(7)) ≈ ^3J(H_β–C(5),H–C(6)) ≈ 10.5, ^3J(H_α–C(5),H–C(6)) = 5.0, H–C(6)); 3.10 (*d*, ^3J(OH, H–C(4)) = 8.0, OH); 2.68 (br. *ddd*, ^2J = 13.5, ^3J = 5.0, 4.5, H_α–C(5)); 2.30 (*ddd*, ^2J = 13.5,

^3J = 10.5, 10.0, H_β–C(5)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 165.6, 165.2 (2*s*, COO, C(2)); 133.4, 132.2, 130.0, 128.8, 128.6, 128.5 (6*d*, ^1J(C,H) = 160, arom. CH); 129.7, 126.9 (2*s*, arom. C); 81.3, 77.2 (2*d*, ^1J(C,H) = 155); 69.4, 67.1 (2*d*, ^1J(C,H) = 145); 43.1 (*d*, ^1J(C,H) = 150); 39.0 (*t*, ^1J(C,H) = 135, C(5)). CI-MS (NH_3): 418 (3, $[M(^{81}Br) + H]^+$), 416 (4), 336 (2), 215 (13), 214 (58), 186 (4), 184 (2), 146 (12), 105 (100), 77 (26).

Data of **11**: Colorless crystals. M.p. 140–143°. IR (KBr): 2980, 2950, 1725, 1635, 1490, 1450, 1320, 1290, 1260, 1200, 1100, 1055, 1025, 975, 890, 815, 780, 705, 690. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.21–8.16 (*m*, 2 H); 7.97–7.93 (*m*, 2 H); 7.68–7.41 (*m*, 6 H); 5.47 (*dd*, ^3J(H–C(6),H–C(7)) = 10.5, ^3J(H–C(7),H–C(7a)) = 7.0, H–C(7)); 5.05 (*dd*, ^3J(H–C(3a),H–C(7a)) = 7.5, ^3J(H–C(7),H–C(7a)) = 7.0, H–C(7a)); 4.92 (*ddd*, ^3J(H–C(4),H_α–C(5)) ≈ ^3J(H–C(4),H_β–C(5)) ≈ 3.5, ^3J(H–C(3a),H–C(4)) = 2.5, H–C(4)); 4.77 (*ddd*, ^3J(H–C(3a),H–C(7a)) = 7.5, ^3J(H–C(3a),H–C(4)) = 2.5, ^4J(H–C(3a),H_β–C(5)) = 1.5, H–C(3a)); 4.60 (*ddd*, ^3J(H_α–C(5),H–C(6)) = 11.0, ^3J(H–C(6),H–C(7)) = 10.5, ^3J(H_β–C(5),H–C(6)) = 4.0, H–C(6)); 2.79 (*dddd*, ^2J = 15.0, ^3J = 4.0, 3.5, ^4J = 1.5, H_β–C(5)); 2.66 (*ddd*, ^2J = 15.0, ^3J = 11.0, 3.5, H_α–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 165.6, 165.2 (2*s*, COO, C(2)); 133.4, 132.3, 130.0, 128.7, 128.6, 128.5 (6*d*, ^1J(C,H) = 160, arom. CH); 129.6, 127.0 (2*s*, arom. C); 80.9 (*d*, ^1J(C,H) = 160); 77.2 (*d*, ^1J(C,H) = 155); 73.0 (*d*, ^1J(C,H) = 150); 47.8 (*d*, ^1J(C,H) = 160); 43.9 (*d*, ^1J(C,H) = 155); 38.9 (*t*, ^1J(C,H) = 135). CI-MS (NH_3): 482 (12, $[M(^{2\,81}Br) + H]^+$), 481 (6, M^+), 480 (18), 479 (3), 478 (12), 401 (3), 400 (7, $[M - {}^{81}Br]^+$), 399 (3), 398 (5), 279 (9), 278 (42), 277 (7), 276 (52), 106 (10), 105 (100), 77 (67). Anal. calc. for $C_{20}H_{17}Br_2NO_3$ (479.18): C 50.13, H 3.58, Br 33.35, N 2.92; found: C 49.50, H 3.43, Br 32.99, N 2.77.

6β-(Benzoyloxy)-4β-bromo-3aβ,4,5,6,7,7aβ-hexahydro-2-phenyl-1,3-benzoxazol-7α-yl Acetate (**16**). A degassed (vacuum line, freeze-thaw cycles) mixture of (±)-**7** (84 mg, 0.25 mmol) and 33% HBr in AcOH (10 ml) in a *Pyrex* tube was sealed under vacuum. After heating to 60° for 3 days in the dark, the tube was frozen in liq. N_2 and opened. The solvent was evaporated, the residue taken with toluene (5 ml), and the solvent evaporated. The latter operation was repeated twice (complete elimination of HBr). The residue was purified by FC (silica gel, AcOEt/light petroleum ether 3:5; R_f 0.56 (UV)): 65 mg (56%) of **16** which was recrystallized from CH_2Cl_2/Et_2O (20°). Colorless crystals. M.p. 135–137°. UV (MeCN): 226 (16800), 204 (15900). IR (KBr): 3080, 2970, 1760, 1710, 1645, 1605, 1585, 1495, 1455, 1430, 1370, 1280, 1225, 1045, 1030, 930, 905, 845, 710, 695. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.08–7.97 (*m*, 4 H); 7.63–7.42 (*m*, 6 H); 6.19 (*dd*, ^3J(H–C(6),H–C(7)) = 8.2, ^3J(H–C(7),H–C(7a)) = 3.5, H–C(7)); 5.44 (*ddd*, ^3J(H–C(6),H–C(7)) = 8.2, ^3J(H_α–C(5),H–C(6)) = 8.0, ^3J(H_β–C(5),H–C(6)) = 3.5, H–C(6)); 5.10 (*dd*, ^3J(H–C(3a),H–C(7a)) = 9.0, ^3J(H–C(7),H–C(7a)) = 3.5, H–C(7a)); 4.90 (br. *dd*, ^3J(H–C(3a),H–C(7a)) = 9.0, ^3J(H–C(3a),H–C(4)) = 4.0, ^4J(H–C(3a),H_β–C(5)) = 1.0, H–C(3a)); 4.26 (*ddd*, ^3J(H–C(4),H_β–C(3)) = 6.0, ^3J(H–C(3a),H–C(4)) ≈ ^3J(H–C(4),H_α–C(5)) ≈ 4.0, H–C(4)); 2.82 (*ddd*, ^2J = 16.0, ^3J = 8.0, 4.0, H_α–C(5)); 2.25 (*dddd*, ^2J = 16.0, ^3J = 6.0, 3.5, ^4J = 1.0, H_β–C(5)); 2.11 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.3, 165.8 (2*s*, COO); 165.1 (*s*, C(2)); 133.4, 132.3, 129.8, 128.8, 128.6, 128.5 (6*d*, ^1J(C,H) = 160, arom. CH); 129.5, 126.3 (2*s*, arom. C); 77.8, 72.4, 68.4 (3*d*, ^1J(C,H) = 155); 69.4 (*d*, ^1J(C,H) = 150); 43.3 (*d*, ^1J(C,H) = 158, C(4)); 29.7 (*t*, ^1J(C,H) = 133, C(5)); 20.9 (*q*, ^1J(C,H) = 130, Me). CI-MS (NH_3): 460 (1, $[M(^{81}Br) + H]^+$), 458 (18, M^+), 400 (5), 398 (5), 255 (11), 196 (12), 106 (11), 105 (100), 91 (16), 77 (18). Anal. calc. for $C_{22}H_{20}BrNO_5$ (458.32): C 57.66, H 4.40, N 3.06; found: C 56.98, H 4.41, N 3.26.

*(3a*RS*,4*RS*,6*SR*,7*RS*,7a*SR*)-4β-Bromo-3aβ,4,5,6,7,7aβ-hexahydro-2-phenyl-1,3-benzoxazole-6β,7α-diyl Diacetate* ((±)-**17**). A mixture of (±)-**7** (109 mg, 0.472 mmol) and 33% HBr/AcOH (10 ml) was degassed on the vacuum line and sealed in a *Pyrex* tube. After heating to 60° for 3 days in the dark, the tube was frozen in liq. N_2 and opened. The solvent was evaporated, the residue taken with toluene (5 ml), and the solvent evaporated. The latter operation was repeated twice. The residue was purified by FC (silica gel, AcOEt/light petroleum ether 3:5; R_f 0.48 (UV)): 93 mg (56%) of (±)-**17**. Colorless crystals. M.p. 137–140° (from CH_2Cl_2/Et_2O at 20°). UV (MeCN): 241 (9000), 206 (10000). IR (KBr): 3060, 2960, 1735, 1640, 1490, 1450, 1430, 1370, 1250, 1230, 1090, 1040, 935, 785, 695. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.97–7.93 (*m*, 2 H); 7.57–7.40 (*m*, 3 H); 5.91 (*dd*, ^3J(H–C(7),H–C(7a)) = 3.5, ^3J(H–C(6),H–C(7)) = 8.0, H–C(7)); 5.18 (*ddd*, ^3J(H–C(6),H–C(7)) ≈ ^3J(H_α–C(5),H–C(6)) = 8.0, ^3J(H_β–C(5),H–C(6)) = 4.0, H–C(6)); 5.04 (*dd*, ^2J(H–C(3a),H–C(7a)) = 9.0, ^3J(H–C(7),H–C(7a)) = 3.5, H–C(7a)); 4.81 (br. *dd*, ^3J(H–C(3a),H–C(7a)) = 9.0, ^3J(H–C(3a),H–C(4)) = 4.0, ^4J(H–C(3a),H_β–C(5)) = 1.0, H–C(3a)); 4.18 (*ddd*, ^3J(H–C(4),H_β–C(5)) = 7.0, ^3J(H–C(4),H_α–C(5)) ≈ ^3J(H–C(3a),H–C(4)) ≈ 4.0, H–C(4)); 2.72 (*ddd*, ^2J = 16.0, ^3J = 8.0, 4.0, H_α–C(5)); 2.11 (*m*, ^2J = 16.0, ^3J = 7.0, 4.0, ^4J = 1.0, H_β–C(5)); 2.13, 2.09 (2*s*, 2 Ac). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 170.2, 170.19 (2*s*, 2 CO); 165.0 (*s*, C(2)); 132.2, 128.5, 128.48 (3*d*, ^1J(C,H) = 160, arom. CH); 126.3 (*s*, arom. C); 77.5 (*d*, ^1J(C,H) = 160); 72.3 (*d*, ^1J(C,H) = 155); 69.4 (*d*, ^1J(C,H) = 150); 67.6 (*d*, ^1J(C,H) = 155); 43 (*d*, ^1J(C,H) = 157, C(4)); 34.8 (*t*, ^1J(C,H) = 133, C(5)); 21.0, 20.9 (2*q*, ^1J(C,H) = 130, 2 Me). CI-MS (NH_3): 399 (26), 398 (62, $[M(^{81}Br) + H]^+$), 396 (47, M^+), 338 (83), 337 (82), 336 (100), 335 (48, $[M - OAc]^+$), 317 (12, $[M - Br]^+$), 316 (62), 296 (50), 295 (83), 294 (40), 293 (100), 117 (35), 105 (71). Anal. calc. for $C_{17}H_{18}BrNO_5$ (396.25): C 51.53, H 4.58, Br 20.17, N 3.53; found: C 51.51, H 4.65, Br 20.19, N 3.59.

(−)-(3aS,4S,6R,7S,7aR)-4β-Bromo-3aβ,4,5,6,7,7aβ-hexahydro-2-phenyl-1,3-benzoxazole-6β,7α-diyl Diacetate ((−)-**17**). Prepared from (−)-**6** as described above. Colorless oil. $[\alpha]_{589}^{25} = -59$, $[\alpha]_{577}^{25} = -62$, $[\alpha]_{546}^{25} = -66$, $[\alpha]_{435}^{25} = -108$, $[\alpha]_{405}^{25} = -135$ ($c = 1.0$, CH_2Cl_2).

(1RS,2SR,3RS,4SR,5SR)-4-Amino-5-bromocyclohexane-1,2,3-triol Hydrochloride (**18**). A mixture of **16** (54 mg, 0.14 mmol) and 5N HCl (5 ml) was heated under reflux for 3 h. After cooling to 20°, the mixture was extracted with CH_2Cl_2 (5 ml, 4 times) and the combined org. extract dried ($MgSO_4$) and evaporated: 17 mg (100%) of benzoic acid. The aq. phase was evaporated: 31 mg (87%) of **18**. Colorless oil, pure by NMR. ^{1}H-NMR (250 MHz, MeOD): 4.36 (*ddd*, $^3J(H_{ax}$–C(6),H–C(5)) = 12.5, ^3J(H–C(4),H–C(5)) = 11.0, $^3J(H_{eq}$–C(6),H–C(5)) = 4.5, H–C(5)); 4.20 (*dd*, ^3J = 3.0, 2.5, H_{eq}–C(3)); 3.84 (*ddd*, ^3J(H–C(1),H_{ax}–C(6)) = 11.5, ^3J(H–C(2),H–C(1)) = 9.5, ^3J(H–C(1),H_{eq}–C(6)) = 5.0, H–C(1)); 3.56 (*dd*, ^3J(H–C(4),H–C(5)) = 11.0, ^3J(H–C(4),H–C(3)) = 2.5, H–C(4)); 3.47 (*dd*, ^3J = 9.5, 3.0, H–C(2)); 2.58 (*ddd*, ^2J = 12.5, ^3J = 5.0, 4.5, H_{eq}–C(6)); 1.91 (*ddd*, ^2J = 12.5, ^3J = 12.5, 11.5, H_{ax}–C(6)). ^{13}C-NMR (62.9 MHz, MeOD): 75.7 (*d*, ^1J(C,H) = 140); 71.8 (*d*, ^1J(C,H) = 150); 69.2, 59.3 (2*d*, ^1J(C,H) = 145); 45.7 (*d*, ^1J(C,H) = 155); 42.5 (*t*, ^1J(C,H) = 135). CI-MS (NH_3): 228 (27, [$M(^{81}Br) - Cl]^+$), 227 (5), 226 (35), 88 (100), 72 (66).

(1RS,2SR,3RS,4SR,5SR)-4-Amino-5-bromocyclohexane-1,2,3-triol (**19**). Hydrochloride **18** (50 mg) was deposited on a column of *Dowex* (500 × 4) with a little MeOH and eluted with pure MeOH (20 ml), then with H_2O (20 ml), and finally with 5% aq. NH_3 soln. (20 ml). The last fraction was decolorized with charcoal and filtration on *Celite*, yielding 38 mg (88%) of colorless oil. Crystallization from MeOH/Et_2O (20°) gave 30 mg (70%) of **19**. Colorless crystals. M.p. 160° (dec.). IR (KBr): 3400, 1640, 1520, 1060. ^{1}H-NMR (250 MHz, MeOD): 4.22 (*ddd*, ^3J(H–C(4),H–C(5)) = 10.5, $^3J(H_{ax}$–C(6),H–C(5)) = 13.0, $^3J(H_{eq}$–C(6),H–C(5)) = 4.5, H–C(5)); 4.06 (*dd*, ^3J = 3.0, 2.5, H_{eq}–C(3)); 3.80 (*ddd*, ^3J = 11.5, 9.5, 4.8, H_{ax}–C(1)); 3.39 (*dd*, ^3J = 9.5, 3.0, H_{ax}–C(2)); 3.01 (*dd*, ^3J(H–C(4),H–C(5)) = 10.5, ^3J(H–C(4),H–C(3)) = 2.5, H_{ax}–C(4)); 2.54 (*ddd*, ^2J = 12.5, ^3J = 4.8, 4.5, H_{eq}–C(6)); 1.87 (*ddd*, ^2J = 12.5, ^3J = 13.5, 11.5, H_{ax}–C(6)). ^{13}C-NMR (62.9 MHz, MeOD): 76.4 (*d*, ^1J(C,H) = 140); 73.0, 69.5 (2*d*, ^1J(C,H) = 145); 59.8 (*d*, ^1J(C,H) = 140); 50.7 (*d*, ^1J(C,H) = 150); 42.9 (*t*, ^1J(C,H) = 130).

(3aRS,6RS,7RS,7aRS)-6β-(Benzoyloxy)-3aβ,6,7,7aβ-tetrahydro-2-phenyl-1,3-benzoxazol-7α-yl Acetate (**20**). A mixture of **16** (93 mg, 0.20 mmol), toluene (10 ml), and DBU (60 µl, 0.41 mmol) was heated under reflux for 2 h. After solvent evaporation, the residue was purified by FC (silica gel, AcOEt/light petroleum ether 3:5; R_f 0.19 (UV)): 72 mg (94%) of **20**. Colorless oil. IR (CH_2Cl_2): 1740, 1715, 1635, 1365, 1215, 1105, 1040, 1020, 855. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.06–7.96 (*m*, 4 H); 7.63–7.40 (*m*, 6 H); 6.01 (*dddd*, ^3J = 10.5, 3.5, ^4J(H–C(4),H–C(6)) = 2.0, ^4J(H–C(4),H–C(7a)) = 0.5, H–C(4)); 5.90 (*dddd*, ^3J = 8.5, 2.0, ^4J = 2.0, ^5J(H–C(3a),H–C(6)) = 2.0, H–C(6)); 5.85 (*ddd*, ^3J = 10.5, 2.0, ^4J(H–C(3a),H–C(5)) = 1.5, H–C(5)); 5.63 (*dd*, ^3J = 8.5, 3.0, H–C(7)); 5.06 (br. *dd*, ^3J = 8.0, 3.0, ^4J = 0.5, H–C(7a)); 4.91 (*dddd*, ^3J(H–C(3a), H–C(7a)) = 8.0, ^3J(H–C(3a),H–C(4)) = 3.5, ^4J(H–C(3a),H–C(5)) = 1.5, ^{5}J(H–C(3a),H–C(6)) = 2.0, H–C(3a)); 2.09 (*s*, Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.5, 165.8 (2*s*, 2 CO); 164.8 (*s*, C(2)); 133.3, 131.9, 129.7, 128.5, 128.38, 128.37 (6*d*, ^1J(C,H) = 160, arom. CH); 129.5, 127.1 (2*s*, arom. C); 128.0 (*d*, ^1J(C,H) = 165, C(5)); 126.7 (*d*, ^1J(C,H) = 168, C(4)); 77.4 (*d*, ^1J(C,H) = 157); 70.6 (*d*, ^1J(C,H) = 150); 67.9 (*d*, ^1J(C,H) = 155); 65.0 (*d*, ^1J(C,H) = 150); 20.9 (*q*, ^1J(C,H) = 130). CI-MS (NH_3): 378 (75, [M + H]$^+$), 377 (11, M^+), 317 (17), 256 (15), 255 (63), 213 (11), 196 (19), 195 (22), 105 (100), 86 (11), 82 (11), 77 (47).

(3aRS,6RS,7RS,7aRS)-3aβ,6,7,7aβ-Tetrahydro-2-phenyl-1,3-benzoxazole-6β,7α-diyl Diacetate ((±)-**21**). Prepared from (±)-**17** (87 mg, 0.22 mmol) as described above (R_f 0.21 (UV)): 66 mg (95%) of (±)-**21**. Colorless oil. IR (CH_2Cl_2): 2920, 1740, 1635, 1215, 1040, 1020, 855. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.07–7.93 (*m*, 2 H); 7.55–7.39 (*m*, 3 H); 5.97 (*dddd*, ^3J(H–C(4),H–C(5)) = 10.0, ^3J(H–C(3a),H–C(4)) = 3.5, ^4J(H–C(4),H–C(6)) = 2.0, ^4J(H–C(4),H–C(7a)) = 0.5, H–C(4)); 5.73 (*ddd*, ^3J = 10.0, 2.0, ^4J(H–C(3a),H–C(5)) = 1.5, H–C(5)); 5.65 (*dddd*, ^3J(H–C(6),H–C(7)) = 8.5, ^3J(H–C(5),H–C(6)) = 2.0, ^4J(H–C(4),H–C(6)) = 2.0, ^5J(H–C(3a),H–C(6)) = 2.0, H–C(6)); 5.39 (*dd*, ^3J = 8.5, 3.5, H–C(7)); 5.01 (br. *dd*, ^3J = 8.0, 3.5, ^4J = 0.5, H–C(7a)); 4.86 (*dddd*, ^3J = 8.0, 3.5, ^4J = 1.5, ^5J = 2.0, H–C(3a)); 2.13, 2.10 (2*s*, 2 Ac). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 170.5, 170.3 (2*s*, 2 CO); 164.7 (*s*, C(2)); 131.8, 128.4, 128.5 (3*d*, ^1J(C,H) = 160, arom. CH); 128.0 (*d*, ^1J(C,H) = 170, C(5)); 127.1 (*s*, arom. C); 126.5 (*d*, ^1J(C,H) = 170, C(4)); 77.2 (*d*, ^1J(C,H) = 160); 70.6, 67.1, 64.8 (3*d*, ^1J(C,H) = 150); 21.0 (2*q*, ^1J(C,H) = 130, 2 Me). CI-MS (NH_3): 318 (4), 317 (20), 316 (100, [M + H]$^+$), 315 (3, M^+), 256 (18), 255 (31), 214 (21), 213 (25), 196 (35), 110 (20), 105 (69), 86 (21), 84 (30), 77 (52). Anal. calc. for $C_{17}H_{17}NO_5$ (315.33): C 64.75, H 5.43, N 4.44; found: C 64.45, H 5.45, N 4.35.

(3aR,6R,7R,7aR)-3aβ,6,7,7aβ-Tetrahydro-2-phenyl-1,3-benzoxazole-6β,7α-diyl Diacetate ((−)-**21**). Prepared from (−)-**7** as described above. Colorless crystals. M.p. 133–135°. $[\alpha]_{589}^{25} = -257$, $[\alpha]_{577}^{25} = -270$, $[\alpha]_{546}^{25} = -309$, $[\alpha]_{435}^{25} = -578$, $[\alpha]_{405}^{25} = -740$ ($c = 1.0$, CH_2Cl_2). IR (KBr): 2960, 1750, 1735, 1640, 1450, 1365, 1235, 1215, 1045, 980, 695.

(1RS,2SR,3RS,4RS)-4-Aminocyclohex-5-ene-1,2,3-triol Hydrochloride ((±)-**1**·HCl). A mixture of (±)-**21** (55 mg, 0.18 mmol) and 5N HCl (5 ml) was heated under reflux for 2 h. After cooling to 20°, the mixture was extracted with CH_2Cl_2 (5 ml, 4 times) and the combined extract dried ($MgSO_4$) and evaporated: 17 mg (100%) of benzoic acid. The aq. phase was evaporated: 23 mg (100%) of (±)-**1**·HCl, pure by ^{1}H-NMR. Colorless oil. ^{1}H-NMR (250 MHz, MeOD): 6.03 (*ddd*, ^3J = 10.0, 3.0, ^4J(H–C(4),H–C(6)) = 2.0, H–C(6)); 5.74 (*m*, ^3J(H–C(6),H–C(5)) = 10.0, ^3J(H–C(4),H–C(5)) = 3.0, ^3J(H–C(1),H–C(5)) = 1.5, ^3J(H–C(3),H–C(5)) = 1.0, H–C(5)); 4.29 (*ddd*, ^3J(H–C(2),H–C(1)) = 6.0, ^3J(H–C(1),H–C(6)) = 3.0, ^3J(H–C(1),H–C(5)) = 1.5, ^5J(H–C(4),H–C(1)) = 1.0, H–C(1)); 4.20 (br. *dd*, ^3J = 4.5, 2.5, ^3J = 1.0, H–C(3)); 3.97 (*m*, ^3J = 4.5, 3.0, ^4J = 2.0, ^5J = 1.0, H–C(4)); 3.78 (*dd*, ^3J = 6.0, 2.0, H–C(2)). ^{13}C-NMR (62.9 MHz, MeOD): 135.1, 123.2 (2*d*, ^1J(C,H) = 165, C(5), C(6)); 75.2, 69.9, 68.0, 51.1 (4*d*, ^1J(C,H) = 145). CI-MS (NH_3): 146 (11), 110 (8), 109 (6), 105 (5), 99 (10), 98 (9), 86 (8), 85 (100).

(1RS,2SR,3RS,4RS)-4-Aminocyclohex-5-ene-1,2,3-triol ((±)-**1**). (±)-**1**·HCl (23 mg) was deposited on a *Dowex* (500 × 4) column with a minimum of MeOH and eluted with MeOH (20 ml), then with H_2O (20 ml), and finally with 5% aq. NH_3 soln. (20 ml). The last fraction was decolorized with acidic charcoal (*Fluka 05100*) and filtration on *Celite* and evaporated: 17 mg (74%) of colorless oil. Crystallization from MeOH/Et_2O (20°) gave 13 mg (57%) of (±)-**1**. Hygroscopic, colorless crystals. ^{1}H-NMR (250 MHz, MeOH): 5.99 (*ddd*, ^3J = 10.0, 3.0, ^4J = 2.0, H–C(6)); 5.72 (*m*, ^3J = 10.0, 3.0, ^4J = 1.5, 1.0, H–C(5)); 4.28 (*dddd*, ^3J = 6.0, 3.0, ^4J = 1.5, ^5J = 1.0, H–C(1)); 4.17 (br. *dd*, ^3J = 4.5, 2.0, ^4J = 1.0, H–C(3)); 3.90 (*m*, ^3J(H–C(3),H–C(4)) = 4.5, ^3J(H–C(4),H–C(5)) = 3.0, ^4J(H–C(4),H–C(6)) = 2.0, ^5J(H–C(1),H–C(4)) = 1.0, H–C(4)); 3.76 (*dd*, ^3J = 6.0, 2.0, H–C(2)). ^{13}C-NMR (100.6 MHz, MeOD): 134.5, 124.4 (2*d*, ^1J(C,H) = 163, C(5), C(6)); 75.4, 70.0, 68.7, 51.1 (4*d*, ^1J(C,H) ≈ 143). CI-MS (NH_3): 146 (17, $[M + H]^+$), 110 (10), 99 (14), 98 (16), 85 (100), 82 (11), 81 (13).

(–)-(1R,2S,3R,4R)-4-Aminocyclohex-5-ene-1,2,3-triol (= *(–)-Conduramine* C_1; (–)-**1**). Prepared from (–)-**21** as described above. Very hygroscopic solid. M.p. 90–92° ([10]: 148–150°). $[\alpha]_{589}^{25} = -114$, $[\alpha]_{577}^{25} = -120$, $[\alpha]_{546}^{25} = -133$, $[\alpha]_{435}^{25} = -223$, $[\alpha]_{405}^{25} = -273$ (c = 0.5, MeOH; [10]: $[\alpha]_{589}^{25} = -221$ (c = 0.79, MeOH)).

The data for (–)-**1** obtained here did not vary as a function of the reaction time and concentrations, this seems to exclude the possibility of racemization of (–)-**1** under the acidic conditions for its preparation. The deviations between *Johnson*'s data and ours can be attributed to the extremely hygroscopic character of this compound.

(1RS,2SR,3RS,4RS)-4-(Acetamido)cyclohex-5-ene-1,2,3-triyl Triacetate ((±)-**22**). A mixture of (±)-**1** (75 mg, 0.517 mmol), pyridine (4 ml), and Ac_2O (4 ml) was stirred at 20° for 15 h. The solvent was evaporated, the residue taken without toluene (10 ml), and the solvent evaporated. The latter operation was repeated twice and the residue purified by FC (silica gel, AcOEt; R_f 0.23 (*Pancaldi*)): 153 mg (95%) of (±)-**22**. Colorless oil. IR (CH_2Cl_2): 3440, 1950, 1740, 1675, 1500, 1365, 1251, 1155, 1040, 950. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.75 (*ddd*, ^3J(H–C(5),H–C(6)) = 10.2, ^3J(H–C(1),H–C(6)) = 2.0, ^4J(H–C(4),H–C(6)) = 2.5, H–C(6)); 5.71 (*d*, ^3J(H–C(4),NH) = 9.2, NH); 5.64 (*m*, ^3J(H–C(5),H–C(6)) = 10.2, ^3J(H–C(4),H–C(5)) = 2.5, ^4J(H–C(1),H–C(5)) = 2.0, H–C(5)); 5.57–5.51 (*m*, 2 H, ^3J = 7.7, 6.0, 2.0, 2.5, ^4J = 2.0, ^5J = 1.0, H–C(1), H–C(3)); 5.16 (*dd*, ^3J(H–C(1),H–C(2)) = 7.7, ^3J(H–C(2),H–C(3)) = 2.0, H–C(2)); 5.08 (*dddd*, ^3J(H–C(4),NH) = 9.2, ^3J(H–C(3),H–C(4)) = 6.0, ^3J(H–C(4),H–C(5)) = 2.5, ^4J(H–C(4),H–C(6)) = 2.0, ^5J(H–C(1),H–C(4)) = 1.0, H–C(4)); 2.13, 2.07, 2.03, 1.98 (4*s*, 4 Ac). ^{13}C-NMR (100.6 MHz, MeOD): 170.4, 170.0, 169.7, 169.3 (4*s*, 4 CO); 129.1 (*d*, ^1J(C,H) = 172, C(6)); 126.4 (*d*, ^1J(C,H) = 170, C(5)); 71.4 (*d*, ^1J(C,H) = 150); 69.9 (*d*, ^1J(C,H) = 152); 68.9 (*d*, ^1J(C,H) = 167, C(1), C(2), C(3)); 46.3 (*d*, ^1J(C,H) = 140, C(4)); 23.1, 20.9, 20.8, 20.7 (4*q*, ^1J(C,H) = 130, 4 Me). CI-MS (NH_3): 331 (19, $[M + NH_3]^+$), 314 (35, $[M + H]^+$), 254 (63), 238 (100), 151 (48), 133 (16), 126 (23), 109 (52). Anal. calc. for $C_{14}H_{19}NO_7$ (313.31): C 53.67, H 6.11, N 4.47; found: C 53.55, H 6.12, N 4.44.

(1R,2S,3R,4R)-4-(Acetamido)cyclohex-5-ene-1,2,3-triyl Triacetate ((–)-**22**). Prepared from (–)-**21** as described above, once using 5N HCl, and a second time using 2.5N HCl (heating under reflux, 2 h) for the hydrolysis of (–)-**21**. Colorless crystals. M.p. 143–145°. $[\alpha]_{589}^{25} = -181$ (c = 1.0, CH_2Cl_2).

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