Highly Stereoselective Total Syntheses of 2,5-Anhydro-3-deoxy- and -4-deoxy-D-hexonic Acids and of the Related Deoxyadenosines-C[1]

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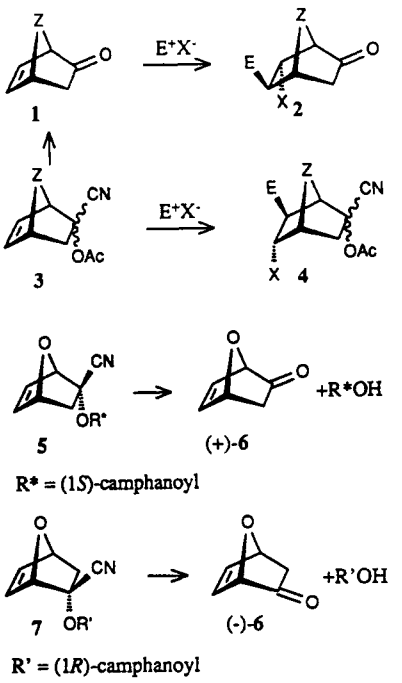
Received October 5, 1989

(1*R*,2*S*,4*R*)-2-Cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl (1*S*')-camphanate (**5**) has been converted into 2,5-anhydro-3-deoxy-D-*ribo*-hexonic acid (**8**, eight steps, 38%) and 2,5-anhydro-3-deoxy-D-*xylo*-hexonic acid (**9**, seven steps, 40%). Similarly, (1*S*,4*S*)-7-oxabicyclo[2.2.1]hept-5-en-3-one ((−)-**6**, derived from (1*S*,2*R*,4*S*)-2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl (1*R*')-camphanate (**7**)) was converted into 2,5-anhydro-4-deoxy-D-*ribo*-hexonic acid (**10**, nine steps, 29%) and 2,5-anhydro-4-deoxy-D-*xylo*-hexonic acid (**11**, eight steps, 31%). The methods exploit the high regioselectivity of the electrophilic additions of the C=C double bonds in 7-oxabicyclo-[2.2.1]hept-5-en-2-yl derivatives **5** and **7** ("naked sugars") and the high exo-face preference for the hydride reduction of 5- and 6-chloro-7-oxabicyclo[2.2.1]hept-5-en-2-ones (**21**, **35**). 2'-Deoxyadenosine-C (**12**) and cordycepin-C (**14**) were derived from **8** and **10**, respectively. Similarly, the corresponding 2'- and 3'-epimers **13** and **15** (C-nucleosides deriving from 2-deoxy- and 3-deoxy-β-D-*threo*-pentofuranose, respectively) were obtained in few steps and with high stereoselectivity from **9** and **11**, respectively.

Under kinetically controlled conditions, the bicyclic homoconjugated ketones **1** add soft electrophiles, EX, to give the corresponding adducts **2** with high regioselectivity.[3,4] The nucleophile's (X^-) preference for carbon center C(6) was attributed to the electron-releasing effect of the carbonyl function in positively charged intermediates due to the favorable n(CO) ↔ σC(2),C(1) ↔ pC(6) hyperconjugative interaction.[5-7] In contrast, the synthetic precursors **3** of ketones **1** were found to add EX with opposite regioselectivity and to give the corresponding adducts **4** (Scheme I).[3,4] This principle has now been applied to the optically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives **5**, (+)-**6**, (−)-**6**, and **7** ("naked sugars"),[8,9] which are obtained readily from furan and 1-cyanovinyl camphanates.[10,11] It has allowed us to develop simple and highly stereoselective total syntheses of all four isomeric 2,5-anhydro-3-deoxy- and -4-deoxy-D-hexonic acids **8**–**11**. The latter were converted in two steps and without epimerization at the anomeric center of the pentose moiety into "deoxyadenosines-C" **12**–**15**, C-nucleosides that derive formally from the corresponding 2-deoxy-D-*erythro*-, 2-deoxy-D-*threo*-, 3-deoxy-D-*erythro*-, and 3-deoxy-D-*threo*-pentofuranoses.

Scheme I



Starting with 2-deoxy-D-*erythro*-pentose, Igolen and co-workers[12] prepared 2'-deoxyadenosine-C (**12**) in seven steps (3.9% overall yield) via the mixture of α- and β-furanoside cyanides **17** and the corresponding imidazoles **18** following an approach similar to that they had developed for the synthesis of adenosine-C (**16**).[13] El Khadem and El Ashry[14] transformed D-xylose (15 steps, 6.2% overall yield) into cordycepin-C (**14**) according to a method similar to that reported earlier by Bobek and Farkas[15] for the synthesis of adenosine-C and which implies the pyrolysis at 220–225 °C of amide **19** obtained by condensation of

(1) A preliminary communication of this work has been presented at the Journées de Chimie Organique (JCO 89), Société Française de Chimie, Palaiseau, France, Sept 9, 1989; communication A 213. Enantiomerically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives ("naked sugars") as synthetic intermediates, Part IX. For Part VIII, see: Bimwala, R. M.; Vogel, P. *Helv. Chim. Acta* **1989**, *72*, 1825.

(2) Present address: Department of Chemistry, Duke University, Durham, NC 27706.

(3) Carrupt, P.-A.; Vogel, P. *Tetrahedron Lett.* **1982**, *23*, 2563–2566; *Helv. Chim. Acta* **1989**, *72*, 1008–1028.

(4) Black, K. A.; Vogel, P. *J. Org. Chem.* **1986**, *51*, 5341–5348.

(5) Carrupt, P.-A.; Vogel, P. *Tetrahedron Lett.* **1984**, *25*, 2879–2882.

(6) Carrupt, P.-A.; Vogel, P. *J. Phys. Org. Chem.* **1988**, *1*, 287–298.

(7) Carrupt, P.-A.; Gabioud, R.; Rubello, A.; Vogel, P.; Honegger, E.; Heilbronner, E. *Helv. Chim. Acta* **1987**, *70*, 1540–1550.

(8) Warm. A.; Vogel, P. *J. Org. Chem.* **1986**, *51*, 5348–5353.

(9) Vogel, P.; Auberson, Y.; Bimwala, M.; de Guchteneere, E.; Vieira, E.; Wagner, J. In *Trends in Synthetic Carbohydrate Chemistry*; Horton, D., Hawkins, L. D., McGarvey, G. J., Eds. ACS Symposium Series 386; American Chemical Society: Washington, DC, 1989; Chapter 13, pp 197–241.

(10) Vieira, E.; Vogel, P. *Helv. Chim. Acta* **1983**, *66*, 1865–1871.

(11) Warm, A.; Vogel, P. *Helv. Chim. Acta* **1987**, *70*, 690–700. See also: Black, K. A.; Vogel, P. *Ibid.* **1984**, *67*, 1612–1615. Saf, R.; Faber, K.; Penn, G.; Griengl, H. *Tetrahedron* **1988**, *44*, 389–392.

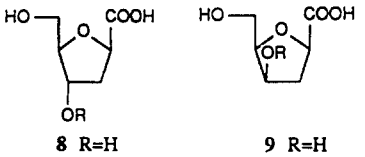
(12) Kolb, A.; Gouyette, C.; Huynh-Dinh, T.; Igolen, J. *Tetrahedron* **1975**, *31*, 2914–2920.

(13) Huynh-Dinh, T.; Kolb, A.; Gouyette, C.; Igolen, J. *J. Heterocycl. Chem.* **1975**, *12*, 111–117.

(14) El Khadem, H. S.; El Ashry, E. S. H. *Carbohydr. Res.* **1973**, *29*, 525–527; **1974**, *32*, 339–348.

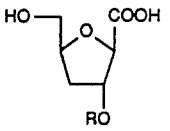
(15) Bobek, M.; Farkas, J. *Collect. Czech. Chem. Commun.* **1969**, *34*, 247–252.

0022-3263/90/1955-2451$02.50/0

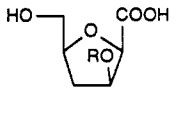


8 R=H
32 R=Bn

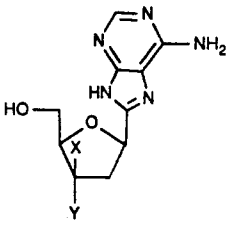
9 R=H
27 R=Bn



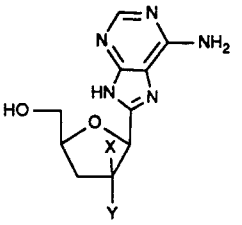
10 R=H
49 R=Bn



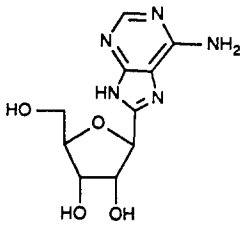
11 R=H
40 R=Bn



12 X=H, Y=OH
13 X=OH, Y=H

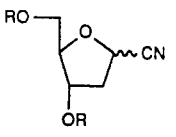


14 X=H, Y=OH
15 X=OH, Y=H

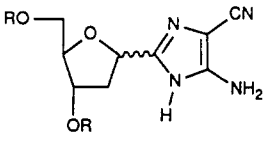


16 ("adenosine-C")

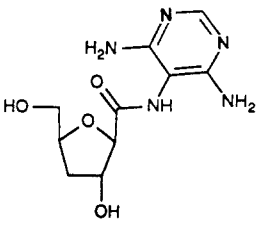
10 with 4,5,6-triaminopyrimidine.[16] In the case of the synthesis of **16**, this latter technique led to epimerization at the "anomeric" center.[15] C-Nucleosides **13** and **15** are unknown compounds.



17



18

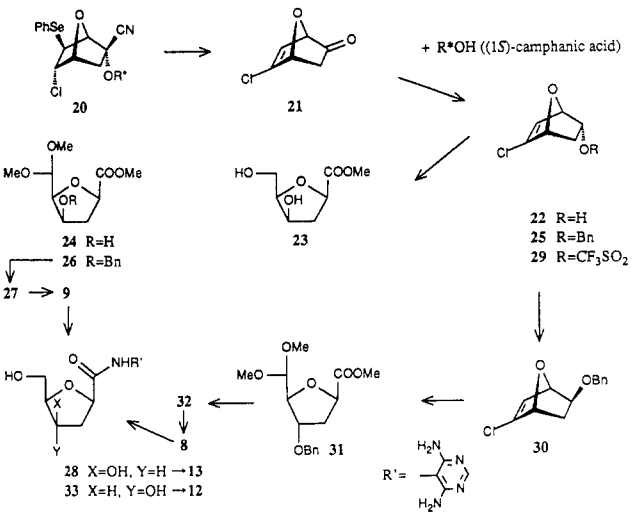


19

Results

One-pot transformation of the "naked sugar" **5** into chloro enone **21** (Scheme II) was achieved in 94% yield via adduct **20**, oxidative elimination of the benzeneselenyl moiety with H_2O_2, and saponification of the camphanate. At this stage, (1*S*)-camphanic acid (chiral auxiliary) was recovered with a yield better than 85%.[8] Reduction of ketone **21** with $NaBH_4$ in MeOH at −10 °C afforded the endo alcohol **22** (85%)[17] contaminated with less than 3% of the exo isomer. Ozonolysis[18,19] of the chloroalkene **22**

Scheme II

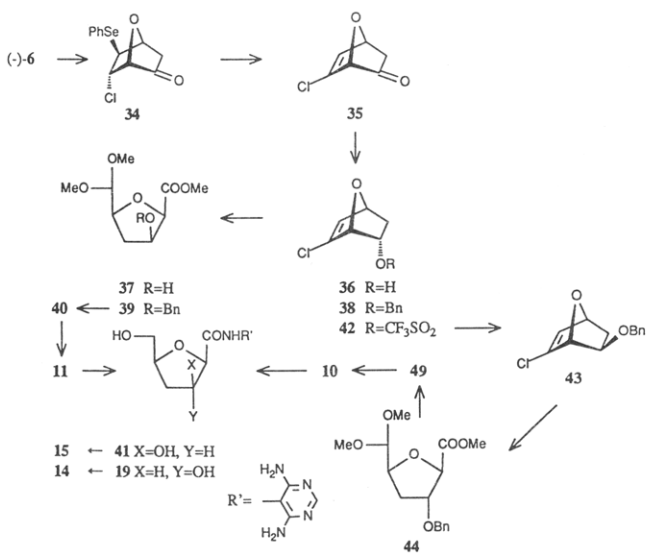


in MeOH followed by a workup with $NaBH_4$[18] led to the expected methyl 2,5-anhydro-D-hexonate (**23**) in mediocre yield (40–50%). The use of Me_2S in the workup of the ozonolysis product led to the formation of acetal–ester **24** in 88% yield. Under the same conditions, the benzyl ether **25** (derived from **22**) gave the fully protected methyl 2,5-anhydro-4-deoxy-L-*xylo*-hexuronate **26** in 90% yield. When the ozonolysis was carried out at a temperature above −65 °C, the benzyl ether was partially oxidized into the corresponding benzoate. Acidic hydrolysis (THF/H_2O/H_2SO_4, 70 °C) followed by treatment with $NaBH_3CN$ (20 °C) afforded the partially protected 2,5-anhydro-4-deoxy-D-*xylo*-hexonic acid (**27**) in 88% yield. Hydrogenolysis of the benzyl ether (H_2/Pd/C, THF/H_2O) gave **9** (95%). Condensation with 4,5,6-triaminopyrimidine gave amide **28** (55%), which on heating in DMF (130 °C) in the presence of CsF[16] afforded the new C-nucleoside **13** in 94% yield.

Mitsunobu[20] substitution of the endo alcohol **22** (PhCOOH, Ph_3P, diethyl azodicarboxylate) failed to give the corresponding *exo*-benzoate. However, treatment of **22** with $(CF_3SO_2)_2O$ and pyridine[21] yielded triflate **29** (85%), which was displaced smoothly by BnOLi in THF/HMPT to give the exo benzylic ether **30** (74%). Ozonolysis of **30** in MeOH (−78 °C) followed by a workup with Me_2S afforded **31** (86%), which was hydrolyzed and reduced (as for **26** → **27**) into **32** (94%). Hydrogenolysis of **32** furnished 2,5-anhydro-3-deoxy-D-*ribo*-hexonic acid (**8**) (96%). Condensation with 4,5,6-triaminopyrimidine gave amide **33**, which, on heating with CsF/DMF (130 °C),[16,23] was dehydrated into the known 2′-deoxyadenosine-C (**12**)[12] (Scheme II).

(16) For a shorter and highly stereoselective synthesis of cordycepin-C, see: Gasparini, F.; Vogel, P. *Helv. Chim. Acta* **1989**, *72*, 271–277.
(17) Durgnat, J.-M.; Vogel, P. Unpublished.
(18) Gensler, W. J.; Chan, S.; Ball, D. B. *J. Am. Chem. Soc.* **1975**, *97*, 436–437. Gensler, W. J.; Chan, S.; Ruchirawat, S. *J. Org. Chem.* **1981**, *46*, 1750–1752. Gensler, W. J.; Chan, S.; Ball, D. B. *Ibid.* **1981**, *46*, 3407–3415.
(19) For other examples of chloroalkene ozonolysis, see: Keul, H.; Griesbaum, K. *Can. J. Chem.* **1980**, *58*, 2049–2054. Schneider, H.; Griesbaum, K. *Tetrahedron Lett.* **1979**, 57–58. Griesbaum, K.; Keul, H. *Angew. Chem.* **1975**, *87*, 748–749. Schulte-Hostede, S.; Gäb, S.; Korte, F. *Chem. Ber.* **1978**, *111*, 2646–2655. Gäb, S.; Nitz, S.; Parlar, H.; Korte, F. *Angew. Chem.* **1976**, *88*, 479–480.
(20) Mitsunobu, O. *Synthesis* **1981**, 1–28.
(21) Binkley, R. W.; Ambrose, M. G.; Hehemann, D. G. *J. Org. Chem.* **1980**, *45*, 4387–4391.
(22) de Guchteneere, E.; Vogel, P. In preparation.
(23) Boiling 4,5,6-triamino-*N*-acylpyrimidines in 1.5 N NaOH is known to induce the formation of the corresponding purines.[24] Under these conditions, our amides gave low yields of the expected C-nucleosides together with products of decomposition.
(24) Smith, C. V. Z.; Robins, R. K.; Tolman, R. L. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1855–1858.

Scheme III



The addition of PhSeCl to enone (−)-**6** gave exclusively adduct **34**. Treatment with *m*-chloroperoxybenzoic acid (mCPBA) afforded chloro enone **35**,[4] which was reduced ($NaBH_4$/MeOH, −10 °C) into endo alcohol **36** (88%)[22] (less than 2% of the corresponding exo isomer was formed by 360-MHz ^1H NMR of the crude reaction mixture). When the same procedures were followed as those presented for the syntheses of **12** and **13** (Scheme II), the new C-nucleoside **15** and cordycepin-C (**14**)[14] were obtained in good yields (Scheme III; see Experimental Section).

Electrochemically induced oxidative decarboxylation[25] in MeOH of the deoxy-D-hexonic acids **8**–**11** furnished the corresponding methyl deoxy-D-pentofuranosides **45** (90%), **46** (93%), **47** (87%), and **48** (95%). Hydrolysis (0.25 M H_2SO_4/H_2O, 80 °C) afforded 2-deoxy-D-*erythro*-pentose (73%),[26] 2-deoxy-D-*threo*-pentose (90%),[27] 3-deoxy-D-*erythro*-pentose (61%),[28] and 3-deoxy-D-*threo*-pentose (86%),[29] respectively, whose characteristics were identical with those reported in the literature for these carbohydrates.[30]

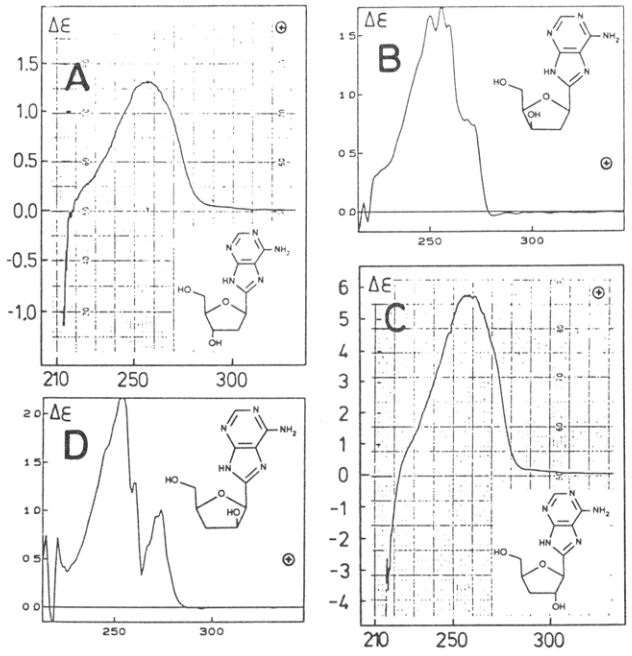


Figure 1. CD spectra of C-nucleosides **12** (A, in H_2O), **13** (B, in H_2O), **14** (C, in MeOH) and **15** (D, in MeOH).

The structures of all the new compounds presented here were established by their elemental analysis, spectral data, mode of formation, and reactivity. The CD spectra of the new C-nucleosides **13** and **15** had the same signs and were similar (see Figure 1) to those measured for **12**[12] and **14**, thus confirming the β relative configuration of the "anomeric centers". It is interesting to note that while the mass spectra of amides **19**, **28**, **33**, and **41** displayed base peaks at m/e = 125 amu corresponding to the 4,5,6-tri-

(25) Iwasaki, T.; Horikawa, H.; Matsumoto, K.; Miyoski, M. *J. Org. Chem.* **1977**, *42*, 2419–2423. Kitagawa, I.; Kamigauchi, T.; Ohmori, H.; Yoshikawa, M. *Chem. Pharm. Bull.* **1980**, *28*, 3078–3086. Kitagawa, I.; Yoshikawa, M.; Kamigauchi, T.; Shirakawa, K.; Ikeda, Y. *Ibid.* **1981**, *29*, 2571–2581. Nishitani, T.; Horikawa, H.; Iwasaki, T.; Matsumoto, K.; Inoue, I.; Miyoshi, M. *J. Org. Chem.* **1982**, *47*, 1706–1712. Wuts, P. G. M.; Sutherland, C. *Tetrahedron Lett.* **1982**, *23*, 3987–3990. Renaud, P.; Seebach, D. *Synthesis* **1986**, 424–425. See also ref 26b.

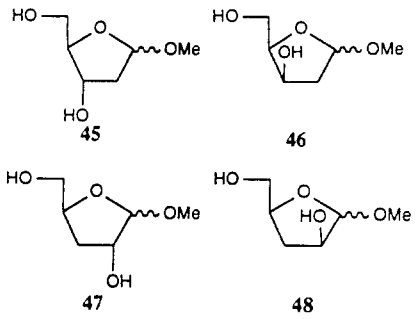
(26) For syntheses of 2-deoxy-D-*erythro*-pentose starting with D-arabinose, see: (a) Deriaz, R. E.; Overend, W. G.; Stacey, M.; Teece, E. G.; Wiggins, L. F. *J. Chem. Soc.* **1949**, 1879–1883 (four steps, 8.3% overall yield). (b) Wong, M. Y. H.; Gray, G. R. *J. Am. Chem. Soc.* **1978**, *100*, 3548–3553 (six steps, 30%). Starting with D-glucose: (c) Hauske, J. R.; Rappoport, H. *J. Org. Chem.* **1979**, *44*, 2472–2476 (six steps, 28%). Starting with D-mannitol: (d) Harada, T.; Mukaiyama, T. *Chem. Lett.* **1981**, 1109–1110 (eight steps, 12.6%). (e) Murakami, M.; Mukaiyama, T. *Ibid.* **1982**, 241–244 (five steps, 8.3%). (f) Hoffmann, R. W.; Endesfelder, A.; Zeiss, H.-J. *Carbohydr. Res.* **1983**, *123*, 320–325 (five steps, 3%). (g) Kozikowski, A. P.; Ghosh, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 5788–5789 (six steps, <12%). For a synthesis of 2-deoxy-L-*erythro*-pentose starting with 2-deoxy-D-*lyxo*-hexose (four steps, 55%), see: (h) Schimmel, S. D.; Bevill, R. D. *Anal. Biochem.* **1970**, *37*, 385–394. For syntheses of 2-deoxy-D,L-*erythro*-pentose, see: (i) Weygand, F.; Leube, H. *Chem. Ber.* **1956**, *89*, 1914–1917. (j) Fraser, M. M.; Raphael, R. A. *J. Chem. Soc.* **1955**, 4280. (k) Torssell, K. B. G.; Hazell, A. C.; Hazell, R. G. *Tetrahedron* **1985**, *41*, 5569–5575. See also: (l) Nakamura, Y. *Noguchi Kenkyusho Jiho* **1983**, *23*, 31–38; *Chem. Abstr.* **1984**, *101*, 73018; *Chem. Abstr.* **1985**, *102*, 113874.

(27) For syntheses of 2-deoxy-D-*threo*-pentose starting with D-xylose, see: (a) Levene, P. A.; Mori, T. *J. Biol. Chem.* **1929**, *83*, 803–816. (b) Overend, W. G.; Shafizadeh, F.; Stacey, M. *J. Chem. Soc.* **1950**, 1027–1029. (c) Dyatkina, N. B.; Azhayev, A. V. *Synthesis* **1984**, 961–963 (six steps, 37%). (d) Fleet, G. W. J.; Chan Son, J. *Tetrahedron Lett.* **1987**, *28*, 3615–3618. (e) Giese, B.; Gröninger, K. S.; Witzel, T.; Korth, H. G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 233–243 (two steps, less than 34%). Reference 26b. Starting with D-glucose: Weygand, F.; Wolz, H. *Chem. Ber.* **1952**, *85*, 256–260 (seven steps, 18%).

(28) For syntheses of 3-deoxy-D-*erythro*-pentose (cordycepose) starting with D-arabinose, see: (a) Kent, P. W.; Stacey, M.; Wiggins, L. F. *J. Chem. Soc.* **1949**, 1232–1235. (b) Allerton, R.; Overend, W. G. *Ibid.* **1951**, 1480–1484. (c) Pettersson, L.; Frejd, T.; Magnusson, G. *J. Org. Chem.* **1984**, *49*, 4540–4541 (six steps, 46%). Starting with D-xylose: (d) Anderson, C. D.; Goodman, L.; Baker, B. R. *J. Am. Chem. Soc.* **1959**, *81*, 898–902. (e) Walton, E.; Holly, F. W.; Boxer, G. E.; Nutt, R. R.; Jenkins, S. R. *J. Med. Chem.* **1965**, *8*, 659–663 (seven steps, 22%). (f) Nair, V.; Sinhababu, A. K. *J. Org. Chem.* **1978**, *43*, 5013–5017 (eight steps, 42%). (g) Witczak, Z. J.; Whistler, R. L. *Carbohydr. Res.* **1982**, *110*, 326–329 (six steps, 22.7%). See also: (h) De Bernardo, S.; Tengi, J. P.; Sasso, G. J.; Weigele, M. *J. Org. Chem.* **1985**, *50*, 3457–3462. Starting with D-glucose: (i) Szabó, P.; Szabó, L. *J. Chem. Soc.* **1965**, 2944–2945 (eight steps, 8%). Starting with 2,3-*O*-isopropylidene-D-glyceraldehyde: (j) Schreiber, S. L.; Goulet, M. T. *Tetrahedron Lett.* **1987**, *28*, 1043–1046. Starting with furan: (k) Ito, Y.; Shibata, T.; Arita, M.; Sawai, H.; Ohno, M. *J. Am. Chem. Soc.* **1981**, *103*, 6739–6741. (l) Ohno, M.; Ito, Y.; Arita, M.; Shibata, T.; Adachi, K.; Sawai, H. *Tetrahedron* **1984**, *40*, 145–152 (five steps, <8%, 77% ee). Starting with α-bromoacetic acid: (m) Solladié, G.; Hutt, J. *Tetrahedron Lett.* **1987**, *28*, 797–800. For syntheses of L-cordycepose, see: (n) Mukherjee, S.; Todd, A. R. *J. Chem. Soc.* **1947**, 969–973. Reference 27c.

(29) For syntheses of 3-deoxy-D-*threo*-pentose starting with D-xylose, see: (a) Casini, G.; Goodman, L. *J. Am. Chem. Soc.* **1964**, *86*, 1427–1431. (b) Lemieux, R. U.; Watanabe, K. A.; Pavia, A. A. *Can. J. Chem.* **1969**, *47*, 4413–4426. (c) El Khadem, H. S.; Audichya, T. D.; Withee, M. J. *Carbohydr. Res.* **1974**, *34*, 329–337 (five steps, 17.2%). (d) Lerner, L. M. *Ibid.* **1984**, *132*, 168–172. Starting with α-bromoacetic acid: ref 28. Starting with β-D-*arabino*-furanosyltheophylline: (e) Davoll, J.; Lythgoe, B.; Tripett, S. *J. Chem. Soc.* **1951**, 2230–2233. (f) Brown, D. M.; Parihar, D. B.; Todd, A.; Varadarajan, S. *Ibid.* **1958**, 3028–3035. For synthesis of 3-deoxy-D,L-*threo*-pentose starting with 3-(trifluoroacetoxy)-2*H*-tetrahydropyran (two steps, <35%), see: (g) Buddrus, J.; Herzog, H.; Bauer, H. *Liebigs Ann. Chem.* **1983**, 1950–1958. Buddrus, J.; Herzog, H. *Chem. Ber.* **1979**, *112*, 1260–1266.

(30) Manasinghe, V. R. N. In *Carbohydrates*; Collins, P. M., Ed.; Chapman and Hall: London, 1987.



aminopyrimidine moiety, the 2′-deoxyadenosines-C (**12** and **13**) showed base peaks at m/e = 162 amu and the 3′-deoxyadenosines-C (**14** and **15**) at m/e = 164 amu.

Discussion

C-Glycosides and C-nucleosides of D-ribose have already been prepared from 7-oxabicyclo[2.2.1]heptene derivatives.[31] Apart from the synthesis of (±)-2-deoxyshowdomycin proposed by Just and Lim,[32] which implies the chromatographic separation of two isomeric 7-oxabicyclo[2.2.1]heptan-2-*exo*-ols, and our first total synthesis of cordycepin-C (**14**)[16] based on the stereoselective $LiAlH_4$ reduction of (1*R*,4*R*,5*R*,6*R*)-5-*exo*,6-*exo*-epoxy-2,2-dimethoxy-7-oxabicyclo[2.2.1]heptane, no general method had been reported thus far for the total synthesis of 2,5-anhydro-3-deoxy- and -4-deoxy-D-hexonic acids and of the corresponding deoxyadenosines-C. Our approach is simple and highly stereoselective. It uses inexpensive starting materials, and the chiral auxiliaries ((1*S*)- and (1*R*)-camphanic acids) are recovered at an earlier stage of the synthesis. The method can be applied to the total syntheses of 2,5-anhydro-3-deoxy- and -4-deoxy-L-hexonic acids and of the enantiomers of C-nucleosides **12**–**15**. The use of CsF to induce water elimination from the amide precursors **19**, **28**, **33**, and **41** avoids the extreme temperature conditions required normally to generate the purinyl heterocycles and thus limits the relative importance of concurrent epimerizations at the "anomeric centers" of the C-nucleosides. With the ready access to hexonic acid derivatives **8**–**11** and their partially protected derivatives **27**, **32**, **40**, and **49**, respectively, other heterocyclic moieties can be constructed around the carboxylic group, in principle,[15,33] and thus make possible the preparation of a large variety of unusual C-nucleosides and C-glycosides.

Conclusion

The new C-nucleosides **13** and **15** deriving formally from 2-deoxy- and 3-deoxy-β-D-*threo*-pentofuranoses, respectively, have been prepared in nine steps (23% overall yield) and 11 steps (9.6%) from the optically pure (1*R*,2*S*,4*R*)-2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl (1*S*′)-camphanate (**5**) and (1*S*,2*R*,4*S*)-2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl (1*R*′)-camphanate (**7**), respectively, in highly stereoselective fashion. In similar ways, the known 2′-deoxyadenosine-C (**13**) and cordycepin-C (**14**) were derived from **5** (12 steps, 17.5%) and **7** (12 steps, 7.2%). Our syntheses exploit the control by remote substituents of the regioselectivity of electrophilic addition of the C=C double bond in 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives.

Experimental Section

Melting points (uncorrected) were determined on a Tottoli (SMP-20) apparatus, and for bulb-to-bulb distillations (Büchi apparatus), the temperature reported refers to the oven temperature. UV–visible absorption spectra were recorded with a Hewlett-Packard 8450 A spectrometer; the IR, with Beckmann IR 4230 or Perkin-Elmer 1430 spectrometers. MS (mass spectra) were measured with Finnigan 1020 or Nermag R10-10C instruments in the electron-ionization mode (70 eV) or the chemical-ionization mode (NH_3). Optical rotations were measured with a Perkin-Elmer 241 polarimeter. The dichroism spectra were recorded on Jobin-Yvon Mark III and Mark V dichrographs. Routine ^1H NMR spectra were obtained on Bruker WH-250 FT (250 MHz) or WH-360 FT (360 MHz) spectrometers (Aspect 2000 computer, 32K memory space). ^{13}C NMR spectra were obtained on the same instruments (62.9 and 90.55 MHz). Chemical shifts are reported in parts per million downfield from tetramethylsilane (Me_4Si), using either Me_4Si (δ_H 0.00, δ_C 0.00) or the solvent's residual proton signal ($CHCl_3$, δ_H 7.24, δ_C 77.0; benzene-d_5, δ_H 7.15, δ_C 128.5; CD_3COCHD_2, δ_H 1.95, δ_C 29.8; CD_2HCN, δ_H 2.05, δ_C 1.3; or CD_3SOCHD_2, δ_H 2.50, δ_C 39.5) as internal reference. Also reported are the apparent multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), number of protons (when appropriate), coupling constants (hertz), and tentative structural assignments. Other spectral data and elemental analysis are provided as supplementary material.

Solvents were either reagent or technical grade (Fluka, Aldrich, or Merck) and when necessary were purified and dried by distillation from an appropriate desiccant under an atmosphere of N_2. Concentration of solution after reactions and extractions involved use of a rotatory evaporator operating at a reduced pressure of approximately 20 Torr. Liquid/solid flash chromatographies used columns of silica gel (0.040–0.63 μm, Merck) or Lobar columns (Merck SiO_2 or RP-8).

(1*R*,2*R*,4*R*)-5-Chloro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (22). $NaBH_4$ (2.6 g, 6.89 mmol) was added portionwise to a stirred solution of **21**[8] (5 g, 34.64 mmol) in MeOH (50 mL) cooled to −10 °C. After stirring at −10 °C for 30 min, CH_3COOH (3 mL) was added dropwise. CH_2Cl_2 (80 mL) was added and the solution washed with H_2O (40 mL, twice) and brine (40 mL). After drying ($MgSO_4$), the solvent was evaporated in vacuo (<20 °C), yielding 4.31 g (85%), white crystals, mp 35–38 °C: ^1H NMR (250 MHz, $CDCl_3$) δ 6.24 (d, J = 2.0, HC(6)), 5.68 (ddd, J = 4.5, 2.0, 1.0, HC(1)), 5.72 (d, J = 5.0, HC(4)), 5.6 (ddd, J = 8.0, 4.5, 2.5, HC(2)), 2.36 (ddd, J = 12.0, 8.0, 5.0, $H_{exo}C(3)$), 1.22 (dd, J = 12.0, 2.5, $H_{endo}C(3)$); $[\alpha]^{25}_{365}$ +573°, $[\alpha]^{25}_{436}$ +327°, $[\alpha]^{25}_{546}$ +176°, $[\alpha]^{25}_{578}$ +153°, $[\alpha]^{25}_{589}$ +146° (c = 11.1 g/dm^3, CH_2Cl_2).

Dimethyl Acetal of Methyl 2,5-Anhydro-4-deoxy-D,L-*xylo*-hexuronate ((±)-24). O_3 (3%) in O_2 was bubbled through a solution of (±)-**22**[17] (0.43 g, 2.9 mmol) in anhydrous MeOH (8 mL) cooled to −78 °C until persistence of the blue color. N_2 was bubbled through the solution to eliminate the excess of O_3. After the addition of Me_2S (1.61 mL, 14.7 mmol) and of methyl orthoformate, the mixture was allowed to warm up to 20 °C and to stand for 4 h. Solid $NaHCO_3$ was added until pH = 7 and the solvent evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (15 mL) and the solution washed with H_2O (5 mL, twice). The aqueous phases were combined and extracted with CH_2Cl_2 (5 mL, twice). The organic phases were combined and washed with brine (5 mL). After drying ($MgSO_4$), the solvent was evaporated in vacuo, yielding 548 mg (85%), colorless oil: ^1H NMR (360 MHz, $CDCl_3$) δ 4.72 (d, J = 7.0, HC(1)), 4.6 (dd, J = 9.5, 2.2, HC(5)), 4.4 (m, HC(3)), 3.9 (dd, J = 7.0, 3.2, HC(2)), 3.8 (s, COOMe), 3.5 (s, 2 MeO), 2.44 (ddd, J = 14.0, 9.5, 4.5, HC(4)), 2.3 (ddd, J = 14.0, 2.2, 1.0, HC(4)).

(1*R*,4*R*,5*R*)-5-*endo*-(Benzyloxy)-2-chloro-7-oxabicyclo-

(31) Just, G.; Martel, A. *Tetrahedron Lett.* **1973**, 1517–1520. Just, G.; Martel, A.; Grozinger, K.; Ramjeesingh, M. *Can. J. Chem.* **1975**, *53*, 131–137. Just, G.; Liak, T. J.; Lim, M. I.; Potvin, P.; Tsantrizos, Y. S. *Ibid.* **1980**, *58*, 2024. Fourney, J.-L.; Henry, G.; Jovin, P. *J. Am. Chem. Soc.* **1977**, *99*, 6753–6754. Kozikowski, A. P.; Ames, A. *Ibid.* **1981**, *103*, 3923–3924. Ito, Y.; Shibata, T.; Arita, M.; Sawai, H.; Ohno, M. *Ibid.* **1981**, *103*, 6739–6741. Ohno, M.; Ito, Y.; Arita, M.; Shibata, T.; Adachi, K.; Sawai, H. *Tetrahedron* **1984**, *40*, 145–152. See also: Sato, T.; Ito, R.; Hayakawa, Y.; Noyori, R. *Tetrahedron Lett.* **1978**, 1829–1832. Noyori, R.; Sato, T.; Hayakawa, Y. *J. Am. Chem. Soc.* **1978**, *100*, 2561–2563. Sato, T.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 2535–2538. Noyori, R.; Sato, T.; Kobayaski, H. *Ibid.* **1980**, *21*, 2569–2572. Noyori, R.; Kobayaski, H.; Sato, T. *Ibid.* **1980**, *21*, 2573–2576. Reference 18.

(32) Just, G.; Lim, M.-I. *Can. J. Chem.* **1977**, *55*, 2993–2997.

(33) For example, ribavirin analogues: Buffel, D. K.; Simons, B. P.; Deceuninck, J. A.; Hoornaert, G. J. *J. Org. Chem.* **1984**, *49*, 2165–2168. Tiazofurin analogues: Hennen, W. J.; Hinshaw, B. C.; Riley, T. A.; Wood, S. G.; Robins, R. K. *Ibid.* **1985**, *50*, 1741–1746. See also: El Khadem, H. S.; Kawai, J.; Swartz, D. L. *Carbohydr. Res.* **1989**, *189*, 149–160.

[2.2.1]hept-2-ene (25). A solution of alcohol **22** (1.544 g, 10.53 mmol) in anhydrous DMF (12 mL) was added dropwise under an Ar atmosphere to a stirred suspension of NaH (347 mg, 11.6 mmol, 80% in oil) in anhydrous DMF (4 mL) cooled to −12 °C. The mixture was allowed to reach 20 °C with stirring. After the end of the H_2 evolution, the mixture was cooled to −12 °C and a solution of benzyl bromide (1.37 g, 11.5 mmol) in anhydrous DMF (3 mL) was added dropwise with stirring. The temperature was allowed to reach 20 °C, and the mixture was stirred overnight. The mixture was poured into ether (80 mL) and the solution washed with H_2O (30 mL, twice) and then with brine (30 mL, twice). After drying ($MgSO_4$), the solvent was evaporated in vacuo below 20 °C. The residue was filtered through a column of silica gel (l = 40 cm, i.d. = 2 cm); AcOEt/petroleum ether, 1:4 v/v), yielding 2.1 g (84%), colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.37–7.20 (m, C_6H_5), 6.06 (d, J = 2.0, HC(3)), 4.8 (ddd, J = 4.0, 2.0, 1.0, HC(4)), 4.62 (dd, J = 4.8, 1.0, HC(1)), 4.51 and 4.41 (2 d, J = 12.0, CH_2Ph), 4.25 (ddd, J = 8.0, 4.0, 2.5, HC(5)), 2.12 (ddd, J = 12.0, 8.0, 4.8, H_{exo}C(6)), 1.3 (dd, J = 12.0, 2.5, H_{endo}C(6)); $[\alpha]^{25}_{365}$ +521.7°, $[\alpha]^{25}_{436}$ +305.6°, $[\alpha]^{25}_{546}$ +169.4°, $[\alpha]^{25}_{578}$ +147.1°, $[\alpha]^{25}_{589}$ +140.6° (c = 1.125 g/dm^3; CH_2Cl_2).

(±)-5-*endo*-(Benzyloxy)-2-chloro-7-oxabicyclo[2.2.1]-hept-2-ene ((±)-25). The same procedure was followed as for **25**, starting with (±)-**22**:[17] mp 35–36 °C.

Dimethyl Acetal of Methyl 2,5-Anhydro-3-*O*-benzyl-4-deoxy-L-*xylo*-hexuronate (26). O_3 (3%) in O_2 was bubbled through a solution of **25** (290 mg, 1.22 mmol) in anhydrous MeOH (10 mL) cooled to −78 °C until persistence of the blue color. The excess of O_3 was removed by bubbling of N_2, and Me_2S (0.88 mL, 12 mmol) and then methyl orthoformate (0.66 mL, 6 mmol) were added. The solution was allowed to warm up to 20 °C and stirred for 4 h. The solution was neutralized by addition of solid $NaHCO_3$ with vigorous stirring. The solvent was evaporated in vacuo and the residue dissolved in ether (40 mL). The solution was washed with H_2O (10 mL) and then with brine (10 mL). After drying ($MgSO_4$), the solvent was evaporated in vacuo, yielding 360 mg (95%), colorless oil that could be crystallized from ether/petroleum ether, mp 59–61 °C: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.38–7.22 (m, C_6H_5), 4.71 (d, J = 7.8, HC(1)), 4.66 (dd, J = 9.0, 2.0, HC(5)), 4.53 and 4.37 (2 d, J = 11.5, CH_2Ph), 4.12 (t, J = 4.0, HC(3)), 3.97 (dd, J = 7.8, 4.0, HC(2)), 2.66 (dd, J = 13.0, 2.0, HC(4)), 2.21 (ddd, J = 13.0, 9.0, 4.0, HC(4)); $[\alpha]^{25}_{365}$ −201.2°, $[\alpha]^{25}_{436}$ −127.1°, $[\alpha]^{25}_{546}$ −74.2°, $[\alpha]^{25}_{578}$ −64.9°, $[\alpha]^{25}_{589}$ −62.5° (c = 1.46 g/dm^3, CH_2Cl_2).

2,5-Anhydro-4-*O*-benzyl-3-deoxy-D-*xylo*-hexonic Acid (27). A mixture of **26** (0.99 g, 3.19 mmol), THF (50 mL), H_2O (9 mL), and 15% aqueous H_2SO_4 (5 mL) was heated to 70 °C for 20 h. After cooling to −5 °C, $NaBH_3CN$ (473 mg, 6.4 mmol, 85%) was added and the mixture stirred at 20 °C for 1 h. The mixture was poured into AcOEt (70 mL) and the solution washed with brine (30 mL). The aqueous phase was extracted with AcOEt (10 mL). The organic phases were combined and dried ($MgSO_4$), and the solvent was evaporated in vacuo, yielding 750 mg (94%), colorless oil: ^{1}H NMR (250 MHz, CD_3OD) δ 7.43–7.26 (m, C_6H_5), 5.0 (s, OH), 4.64 and 4.44 (2 d, J = 11.5, CH_2Ph), 4.58 (dd, J = 9.0, 3.5, HC(2)), 4.24 (ddd, J = 4.5, 4.5, 2.0, HC(4)), 4.12 (ddd, J = 6.0, 5.5, 4.5, HC(5)), 3.92 (dd, J = 11.5, 6.0, HC(6)), 3.85 (dd, J = 11.5, 5.5, HC(6)), 2.6 (ddd, J = 13.5, 3.5, 2.0, HC(3)), 2.43 (ddd, J = 13.5, 9.0, 4.5, HC(3)); $[\alpha]^{25}_{365}$ −146.5°, $[\alpha]^{25}_{436}$ −92.1°, $[\alpha]^{25}_{546}$ −52.6°, $[\alpha]^{25}_{578}$ −46.5°, $[\alpha]^{25}_{589}$ −44.7° (c = 1.14 g/dm^3, EtOH).

(±)-2,5-Anhydro-4-*O*-benzyl-3-deoxy-D,L-*xylo*-hexonic Acid ((±)-27). The same procedure was followed as for **27**, starting with (±)-**25**: colorless crystals, mp 46–48 °C.

2,5-Anhydro-3-deoxy-D-*xylo*-hexonic Acid (9). A mixture of **27** (790 mg, 3.13 mmol), THF (16 mL), H_2O (4 mL), and 10% Pd/C (1.6 g) was pressured (1 bar) with H_2 and stirred for 4 h (control by TLC on reverse phase, MeOH/H_2O, 3:1 v/v, R_f (**27**) = 0.8, R_f (**9**) = 0.95). The catalyst was removed by filtration and the solvent evaporated in vacuo, yielding 431 mg (85%), colorless oil that solidifies at −20 °C. Recrystallization from EtOH/ether gave colorless crystals, mp 130–132 °C: ^{1}H NMR (250 MHz, CD_3OD) δ 5.0 (s, OH), 4.53 (dd, J = 9.5, 4.5, HC(2)), 4.41 (ddd, J = 5.5, 4.0, 2.5, HC(4)), 4.0 (ddd, J = 5.0, 5.0, 4.0, HC(5)), 3.85 (d, J = 5.0, H_2C(6)), 2.58 (ddd, J = 13.5, 9.5, 5.5, HC(3)), 2.23 (ddd, J = 13.5, 4.5, 2.5, HC(3)); $[\alpha]^{25}_{365}$ −146.5°, $[\alpha]^{25}_{436}$ −92.1°, $[\alpha]^{25}_{546}$ −52.6°, $[\alpha]^{25}_{578}$ −46.5°, $[\alpha]^{25}_{589}$ −44.7° (c = 1.14 g/dm^3, EtOH).

(±)-2,5-Anhydro-3-deoxy-D,L-*xylo*-hexonic Acid ((±)-9). The same procedure was followed as for **9**, starting with (±)-**27**: colorless crystals, mp 131–133 °C.

2,5-Anhydro-3-deoxy-*N*-(4′,6′-diaminopyrimidin-5′-yl)-D-*xylo*-hexonamide (28). A mixture of **9** (180 mg, 1.1 mmol), 1 N HCl (5 mL), and (4,5,6-triaminopyrimidine sulfate)·H_2O (265 mg, 1.1 mmol) was heated to 100 °C for 16 h. After treatment with charcoal, the solvent was evaporated in vacuo. The residue was dissolved in H_2O (2 mL) and filtered through a Dowex column (50 W × 8); elution with H_2O was continued until pH ~6. The acidic eluate was eliminated and the elution continued with 3% aqueous NH_3 (50 mL). The alkaline eluate was concentrated in vacuo. The residue was purified by column chromatography (Lobar B, RP-8, two columns in series, MeOH/H_2O, 3:1 v/v), yielding 180 mg 55%), colorless crystals, mp 231–234 °C dec: ^{1}H NMR (250 MHz, D_2O) δ 8.3 (s, HC(2′)), 5.17 (dd, J = 9.5, 2.0, HC(2)), 4.91 (dd, J = 4.0, 3.0, HC(4)), 4.8 (s, NH_2, OH), 4.58 (ddd, J = 6.5, 5.0, 3.0, HC(5)), 4.37 (m, H_2C(6)), 3.04 (ddd, J = 14.0, 9.5, 4.0, HC(3)), 2.78 (ddd, J = 14.0, 2.0, 1.0, HC(3)); MS (70 eV) m/z (relative intensity) 269 ($M^{\bullet+}$, 29), 191 (4), 180 (8), 176 (5), 164 (5), 153 (7), 152 (64), 135 (12), 126 (11), 125 (100); $[\alpha]^{25}_{365}$ +148.1°, $[\alpha]^{25}_{436}$ +93.0°, $[\alpha]^{25}_{546}$ +54.8°, $[\alpha]^{25}_{578}$ +47.4°, $[\alpha]^{25}_{589}$ +45.2° (c = 0.27 g/dm^3, H_2O).

(±)-2,5-Anhydro-3-deoxy-*N*-(4′,6′-diaminopyrimidin-5′-yl)-D,L-*xylo*-hexonamide ((±)-28). The same procedure was followed as for **28**, starting with (±)-**9**: mp 220–225 °C dec.

(1*R*)-1-*C*-(6′-Amino-7′*H*-purin-8′-yl)-1,4-anhydro-2-deoxy-D-*threo*-pentitol (13). A mixture of **28** (145 mg, 0.54 mmol, dried over P_4O_{10}, 10^{-2} Torr), anhydrous DMF (5 mL), and anhydrous CsF (330 mg, 2.1 mmol) was heated to 135–140 °C for 12 h. After cooling to 20 °C, the mixture was filtered through silica gel (MeOH) and the solvent was evaporated in vacuo. The residue was purified by column chromatography (Lobar B, Merck SiO_2, MeOH/CH_2Cl_2, 1:2 v/v) yielding 128 mg (94%), colorless crystals, mp 258–260 °C dec: UV (MeOH) 211 (19 800), 264 (12 700); CD (see Figure 1) $\Delta\epsilon_{256}$ = +174 (c = 0.36 g/dm^3, H_2O); IR (KBr) 3300 (br), 1665, 1610, 1590, 1500, 1450, 1370; ^{1}H NMR (250 MHz, D_2O) δ 8.5 (s, HC(2′)), 5.5 (dd, J = 9.0, 5.0, HC(1)), 4.98 (ddd, J = 6.0, 4.0, 2.5, HC(3)), 4.8 (s, NH_2, OH), 4.5 (ddd, J = 7.0, 4.5, 4.0, HC(4)), 4.36 (dd, J = 12.0, 4.5, HC(5)), 4.28 (dd, J = 12.0, 7.0, HC(5)), 3.23 (ddd, J = 14.0, 9.0, 6.0, HC(2)), 2.66 (ddd, J = 14.0, 5.0, 2.5, HC(2)); ^{13}C NMR (62.9 MHz, D_2O) δ 155.3, 154.2, 152.4 (3 s), 152.4 (d, ^1J(C,H) = 200), 116.3 (s), 84.4, 73.7, and 71.6 (3 d, ^1J(C,H) = 150), 60.7 (t, ^1J(C,H) = 145), 40.5 (t, ^1J(C,H) = 135); MS (70 eV) m/z (relative intensity) 251 ($M^{\bullet+}$, 11.5), 208 (2), 204 (1), 203 (2), 164 (6), 163 (11), 162 (100), 161 (11); $[\alpha]^{25}_{436}$ +79.2°, $[\alpha]^{25}_{546}$ +44.1°, $[\alpha]^{25}_{578}$ +39.0°, $[\alpha]^{25}_{589}$ +37.0° (c = 0.265 g/dm^3, H_2O); HR-MS ($C_{10}H_{13}N_5O_3$) calcd 251.101 99, found 251.100 200 (ref I$_2$).

(±)-(1*RS*)-1-*C*-(6′-Amino-7′*H*-purin-8′-yl)-1,4-anhydro-2-deoxy-D,L-*threo*-pentitol ((±)-13). The same procedure was followed as for **13**, starting with (±)-**28**: mp 243–245 °C dec.

(1*R*,2*S*,4*S*)-6-Chloro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (36). $NaBH_4$ (8.2 g, 216 mmol) was added portionwise to a stirred solution of **35**[4] (15.7 g, 108.6 mmol) in MeOH (150 mL) cooled to −10 °C. After stirring at −10 °C for 30 min, CH_3COOH (6 mL) was added dropwise. CH_2Cl_2 (300 mL) was added and the solution washed with a saturated aqueous solution of $NaHCO_3$ (160 mL), H_2O (160 mL), and then brine (160 mL). After drying ($MgSO_4$), the solvent was evaporated in vacuo (<20 °C), yielding 14 g (88%), colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.4 (d, J = 2.0, HC(6)), 4.94 (ddd, J = 4.5, 2.0, 1.0, HC(4)), 4.68 (d, J = 4.5, HC(1)), 4.6 (ddd, J = 8.0, 4.5, 2.0, HC(2)), 2.34 (ddd, J = 12.0, 8.0, 4.5, H_{exo}C(3)), 1.17 (dd, J = 12.0, 2.0, H_{endo}C(3)); $[\alpha]^{25}_{365}$ −423°, $[\alpha]^{25}_{436}$ −240°, $[\alpha]^{25}_{546}$ −128°, $[\alpha]^{25}_{578}$ −111°, $[\alpha]^{25}_{589}$ 106° (c = 18.7 g/dm^3, CH_2Cl_2).

Dimethyl Acetal of Methyl 2,5-Anhydro-3-deoxy-D,L-*xylo*-hexuronate ((±)-37). The same procedure was followed as for (±)-**24**, starting with (±)-**36**: yield 65%, colorless oil; ^{1}H NMR (250 MHz, CD_3OD) δ 4.59 (m, HC(5)), 4.56 (d, J = 6.0, HC(1)), 4.53 (d, J = 5.0, HC(5)), 4.14 (ddd, J = 8.5, 6.0, 5.0, HC(2)), 3.8 (s, COOMe), 3.56, 3.53 (2 s, 2 MeO), 2.36 (ddd, J = 14.0, 8.5, 6.0, HC(3)), 2.05 (dd, J = 14.0, 5.0, 3.0, HC(3)).

(1*R*,4*S*,6*S*)-6-*endo*-(Benzyloxy)-2-chloro-7-oxabicyclo-[2.2.1]hept-2-ene (38). The same procedure was followed as for **25**, starting with **36**: mp 46–48 °C; ^{1}H NMR (360 MHz, $CDCl_3$)

δ 7.41–7.27 (m, C_6H_5), 6.37 (d, J = 1.8, HC(3)), 4.96 (dd, J = 4.5, 1.8, HC(4)), 4.87 (d, J = 4.0, HC(1)), 4.65 and 4.52 (2 d, J = 11.5, CH_2Ph), 4.34 (ddd, J = 8.0, 4.0, 2.2, HC(6)), 2.28 (ddd, J = 12.0, 8.0, 5.0, H_{exo}C(5)), 1.31 (dd, J = 12.0, 2.2, H_{endo}C(5)); $[\alpha]^{25}_{365}$ −467.9°, $[\alpha]^{25}_{436}$ −276.6°, $[\alpha]^{25}_{546}$ −153.9°, $[\alpha]^{25}_{578}$ −133.6°, $[\alpha]^{25}_{589}$ −128.2° (c = 1.465 g/dm³, CH_2Cl_2).

Dimethyl Acetal of Methyl 2,5-Anhydro-4-*O*-benzyl-3-deoxy-L-*xylo*-hexuronate (39). The same procedure was followed as for **26**, starting with **38**: yield 90%, colorless oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.4–7.27 (m, C_6H_5), 4.64 (d, J = 6.0, HC(1)), 4.61 and 4.53 (d, J = 12.0, CH_2Ph), 4.57 (d, J = 7.0, HC(5)), 4.41 (q, J = 5.5, HC(2)), 4.12 (q, J = 7.0, HC(4)), 3.76 (s, COOMe), 3.55 and 3.42 (2 s, 2 MeO), 2.27–2.14 (m, H_2C(3)); $[\alpha]^{25}_{436}$ +3.9°, $[\alpha]^{25}_{546}$ +3.95°, $[\alpha]^{25}_{578}$ +3.9°, $[\alpha]^{25}_{589}$ +3.6° (c = 1.52 g/dm³, CH_2Cl_2).

2,5-Anhydro-3-*O*-benzyl-4-deoxy-D-*xylo*-hexonic Acid (40). The same procedure was followed as for **27**, starting with **39**: yield 88%, colorless oil; ^{1}H NMR (250 MHz, CD_3OD) δ 7.42–7.26 (m, C_6H_5), 5.1 (s, OH), 4.64 and 4.55 (2 d, J = 13.0, CH_2Ph), 4.6 (d, J = 3.5, HC(2)), 4.48 (ddd, J = 6.0, 6.0, 3.5, HC(3)), 4.24 (m, HC(5)), 3.74 (dd, J = 11.5, 5.5 HC(6)), 3.7 (dd, J = 11.5, 4.0, HC(6)), 2.25 (ddd, J = 14.0, 8.0, 6.0, HC(4)), 2.08 (ddd, J = 14.0, 6.0, 3.5, HC(4)); $[\alpha]^{25}_{365}$ +28.7°, $[\alpha]^{25}_{436}$ +21.1°, $[\alpha]^{25}_{546}$ +14°, $[\alpha]^{25}_{578}$ +12.5°, $[\alpha]^{25}_{589}$ +12.2° (c = 1.22 g/dm³, EtOH).

2,5-Anhydro-4-deoxy-D-*xylo*-hexonic Acid (11). The same procedure was followed as for **9**, starting with **40**: yield 95%, colorless oil that can be crystallized from EtOH/ether, mp 123–125 °C; ^{1}H NMR (250 MHz, CD_3OD) δ 5.0 (s, OH), 4.59 (ddd, J = 5.0, 4.5, 3.0, HC(3)), 4.47 (d, J = 4.5, HC(2)), 4.25 (ddd, J = 8.5, 5.0, 4.5, 3.0, HC(5)), 3.77 (dd, J = 11.5, 3.0, HC(6)), 3.67 (dd, J = 11.5, 4.5, HC(6)), 2.41 (ddd, J = 13.5, 8.5, 5.0, HC(4)), 1.91 (ddd, J = 13.5, 5.0, 3.0, HC(4)); $[\alpha]^{25}_{365}$ +114.1°, $[\alpha]^{25}_{436}$ +74.9°, $[\alpha]^{25}_{546}$ +45.4°, $[\alpha]^{25}_{578}$ +40.2°, $[\alpha]^{25}_{589}$ +38° (c = 1.02 g/dm³, EtOH).

(±)-2,5-Anhydro-4-deoxy-D,L-*xylo*-hexonic Acid ((±)-11). The same procedure was followed as for **11**, starting with (±)-**40**: mp 150–151 °C.

2,5-Anhydro-4-deoxy-*N*-(4′,6′-diaminopyrimidin-5′-yl)-D-*xylo*-hexonamide (41). A mixture of **11** (450 mg, 2.77 mmol), 1 N HCl (12 mL), and (4,5,6-triaminopyrimidine sulfate)·H_2O (670 mg, 2.77 mmol) was heated to 90 °C for 16 h. After treatment with charcoal and filtration, the solvent was evaporated in vacuo. The residue was dissolved in H_2O (3 mL) and filtered through a column of Dowex 50 W × 8. Elution was started with H_2O, until pH ∼6. The acidic eluate was discarded. Elution with 3% aqueous NH_3 (120 mL) gave, after solvent evaporation in vacuo, 513 mg of a residue, which was purified by chromatography on a column (Lobar B, RP-8, two columns in series, MeOH/H_2O, 3:1 v/v), yielding 300 mg (37%) of **41**·H_2O, colorless crystals, mp 80–85 °C (loss of H_2O, then dec): ^{1}H NMR (250 MHz, CD_3OD) δ 7.89 (s, HC(2′)), 4.9 (s, NH_2, OH), 4.65 (ddd, J = 5.5, 4.0, 2.0, HC(3)), 4.52 (d, J = 4.0, HC(2)), 4.37 (dq, J = 9.0, 4.5, HC(5)), 3.79 (d, J = 4.5, H_2C(6)), 2.46 (ddd, J = 14.0, 9.0, 5.5, HC(4)), 1.95 (ddd, J = 14.0, 4.5, 2.0, HC(4)); MS (70 eV) m/z (relative intensity) 269 (M^+, 49), 196 (9), 193 (5), 182 (15), 165 (5), 154 (5), 152 (63), 126 (16), 125 (100); $[\alpha]^{25}_{365}$ +89.9°, $[\alpha]^{25}_{436}$ +74.5°, $[\alpha]^{25}_{546}$ +51.9°, $[\alpha]^{25}_{578}$ +47.2°, $[\alpha]^{25}_{589}$ +44.9° (c = 0.345 g/dm³, MeOH).

(±)-2,5-Anhydro-4-deoxy-*N*-(4′,6′-diaminopyrimidin-5′-yl)-D,L-*xylo*-hexonamide ((±)-41). The same procedure was followed as for **41**, starting with (±)-**11**: colorless crystals, mp 220–225 °C dec.

(1*S*)-1-*C*-(6′-Amino-7′*H*-purin-8′-yl)-1,4-anhydro-3-deoxy-D-*threo*-pentitol (15). A mixture of **41** (250 mg, 0.93 mmol, dried over P_4O_{10}, 10^{-2} Torr), anhydrous DMF (10 mL), and anhydrous CsF (423 mg, 2.8 mmol) was heated to 135–140 °C for 48 h. After cooling to 20 °C, the mixture was filtered through SiO_2 (MeOH) and the solvent evaporated in vacuo. The residue was purified by column chromatography (Lobar B, RP-8, MeOH/H_2O, 3:1 v/v), yielding 210 mg (84%) of **15**·H_2O: colorless crystals, mp 130–133 °C (loss of H_2O, then dec; UV (MeOH) 210 (16 000), 265 (11 350); CD (see Figure 1) $\Delta\epsilon_{254}$ = +2.17, $\Delta\epsilon_{274}$ = +1.01 (c = 0.48 g/dm³, H_2O); IR (KBr) 3400 (br), 1650, 1610, 1590, 1490, 1450, 1420, 1370; ^{1}H NMR (250 MHz, CD_3OD) δ 8.22 (s, HC(2′)), 5.11 (d, J = 4.0, HC(1)), 4.8 (br s, NH_2, OH), 4.65 (ddd, J = 5.5, 4.0, 2.5, HC(2)), 4.37 (dddd, J = 8.5, 5.0, 4.5, 3.0, HC(4)), 3.91 (dd, J = 11.5, 3.0, HC(5)), 3.79 (dd, J = 11.5, 4.5, HC(5)), 2.53 (ddd, J = 13.5, 8.5, 5.5, HC(3)), 2.06 (ddd, J = 13.5, 5.5, 2.5, HC(3)); MS (70 eV) m/z (relative intensity) 251 (M^+, 10), 204 (4), 203 (9), 192 (4), 178 (22), 176 (13), 165 (17), 164 (100), 163 (8), 162 (5), 149 (13); $[\alpha]^{25}_{436}$ +123.3°, $[\alpha]^{25}_{546}$ +72.6°, $[\alpha]^{25}_{578}$ +63.9°, $[\alpha]^{25}_{589}$ +60.6° (c = 0.31 g/dm³, MeOH); HR-MS ($C_{10}H_{13}N_5O_3$) calcd 251.101 99, found 251.103 678 (ref I$_2$).

(±)-(1*RS*)-1-*C*-(6′-Amino-7′*H*-purin-8′-yl)-1,4-anhydro-3-deoxy-D,L-*threo*-pentitol ((±)-15). The same procedure was followed as for **15**, starting with (±)-**41**: mp 227–230 °C dec.

(1*R*,2*R*,4*R*)-5-Chloro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Trifluoromethanesulfonate (29). A solution of $(CF_3SO_2)_2O$ (2.9 mL, 17.6 mmol) in anhydrous CH_2Cl_2 (25 mL) was added dropwise to a vigorously stirred solution of pyridine (1.67 mL, 20.74 mmol) in anhydrous CH_2Cl_2 (50 mL) cooled to −10 °C. A white precipitate was formed, and the mixture was stirred at −10 °C for an additional 10 min. A solution of **22** (1.52 g, 10.37 mmol) in anhydrous CH_2Cl_2 (25 mL) was then added dropwise, and the mixture was stirred at −10 °C for 90 min. The mixture was poured into ice-cold H_2O (200 mL). The aqueous phase was extracted with CH_2Cl_2 (100 mL). The organic phases were combined and washed with 5% aqueous cold $NaHCO_3$ (50 mL), then with ice-cold H_2O (50 mL), and with brine (50 mL). After drying ($MgSO_4$), the solvent was evaporated in vacuo (<20 °C). The residue was filtered through basic alumina (Merck, activity I; CH_2Cl_2). The solvent was evaporated in vacuo, yielding 2.45 g (85%), colorless, unstable oil that solidifies at −20 °C: ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.2 (d, J = 2.0, HC(6)), 5.45 (ddd, J = 8.0, 4.0, 2.5, HC(2)), 5.15 (ddd, J = 4.0, 2.0, 0.8, HC(1)), 4.8 (dd, J = 4.5, 0.8, HC(4)), 2.52 (ddd, J = 13.0, 8.0, 4.5, H_{exo}C(3)), 1.64 (dd, J = 13.9, 2.5, H_{endo}C(3)).

(1*R*,4*R*,5*S*)-5-*exo*-(Benzyloxy)-2-chloro-7-oxabicyclo-[2.2.1]hept-2-ene (30). A solution of 1.6 M BuLi in hexane (13 mL, 20.8 mmol) was added dropwise to a stirred solution of benzylic alcohol (2.16 mL, 20.8 mmol) in THF (14 mL) cooled to −78 °C. After the end of the addition, the temperature was allowed to reach 0 °C and the mixture stirred for 10 min under an Ar atmosphere. The solution was then cooled to −78 °C, and a solution of **29** (2.9 g, 10.4 mmol) in anhydrous THF (6 mL) was added dropwise. The mixture was allowed to reach 20 °C, HMPA (6 mL) was added dropwise, and the mixture was stirred overnight. After the addition of ether (100 mL), the solution was washed with H_2O (30 mL, twice) and then with brine (30 mL) and dried ($MgSO_4$). The solvent was eliminated by distillation under reflux at atmospheric pressure. The residue was purified by flash chromatography on a column of silica gel (AcOEt/petroleum ether, 1:4 v/v), yielding 1.83 g (74%), colorless oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.4–7.3 (m, C_6H_5), 6.01 (d, J = 2.0, HC(3)), 4.97 (dd, J = 2.0, 1.0, HC(4)), 4.76 (dd, J = 4.5, 1.0, HC(1)), 4.59 (s, CH_2Ph), 3.86 (dd, J = 6.5, 2.0, HC(5)), 1.93 (dd, J = 12.0, 6.5, H_{endo}C(6)), 1.75 (ddd, J = 12.0, 4.5, 2.0, H_{exo}C(6)); $[\alpha]^{25}_{436}$ +41.2°, $[\alpha]^{25}_{546}$ +22.2°, $[\alpha]^{25}_{578}$ +19.2°, $[\alpha]^{25}_{589}$ +18.2° (c = 1.55 g/dm³, CH_2Cl_2).

(±)-5-*exo*-(Benzyloxy)-2-chloro-7-oxabicyclo[2.2.1]hept-2-ene ((±)-30). The same procedure was followed as for **30**, starting with (±)-**22**: mp 48–50 °C.

Dimethyl Acetal of Methyl 2,5-Anhydro-3-*O*-benzyl-4-deoxy-L-*ribo*-hexuronate (31). The same procedure was followed as for the preparation of **26**, starting with **30**: yield 86%, colorless oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.38–7.27 (m, C_6H_5), 4.7 (dd, J = 10, 6.5, HC(5)), 4.56 and 4.50 (2 d, J = 12.0, CH_2Ph), 4.34 (d, J = 4.5, HC(1)), 4.24 (ddd, J = 6.0, 1.5, 1.5, HC(3)), 4.19 (dd, J = 4.5, 1.5, HC(2)), 3.76 (s, COOMe), 3.49 and 3.47 (2 s, 2 MeO), 2.38 (ddd, J = 13.0, 6.5, 1.5, HC(4)), 2.14 (ddd, J = 13.0, 10.0, 6.0, HC(4)); $[\alpha]^{25}_{365}$ +31.4°, $[\alpha]^{25}_{436}$ +22°, $[\alpha]^{25}_{546}$ +14°, $[\alpha]^{25}_{578}$ +12.7°, $[\alpha]^{25}_{589}$ +12.3 (c = 1.6 g/dm³, CH_2Cl_2).

2,5-Anhydro-4-*O*-benzyl-3-deoxy-D-*ribo*-hexonic Acid (32). The same procedure was followed as for **27**, starting with **31**: yield 94%, colorless oil; ^{1}H NMR (250 MHz, CD_3OD) δ 7.43–7.28 (m, C_6H_5), 5.0 (s, OH), 4.64 (dd, J = 9.5, 7.0, HC(2)), 4.61 and 4.56 (2 d, J = 11.5, CH_2Ph), 4.17 (m, HC(4), HC(5)), 3.64 (d, J = 5.5, H_2C(6)), 2.46 (ddd, J = 13.0, 7.0, 2.0, HC(3)), 2.14 (ddd, J = 13.0, 9.5, 5.5, HC(3)); $[\alpha]^{25}_{365}$ +57.2°, $[\alpha]^{25}_{436}$ +37.6°, $[\alpha]^{25}_{546}$ +22.7°, $[\alpha]^{25}_{578}$ +20.4°, $[\alpha]^{25}_{589}$ +18.4° (c = 1.275 g/dm³, EtOH).

2,5-Anhydro-3-deoxy-D-*ribo*-hexonic Acid (8). The same procedure was followed as for **9**, starting with **32**: yield 96%, colorless crystals, mp 109–111 °C; ^{1}H NMR (250 MHz, CD_3OD) δ 5.1 (s, OH), 4.66 (t, J = 8.0, HC(2)), 4.32 (ddd, J = 6.0, 3.5, 3.0, HC(4)), 3.97 (ddd, J = 4.5, 4.5, 3.0, HC(5)), 3.68 (dd, J = 12.0,

4.5, HC(6)), 3.61 (dd, J = 12.0, 4.5, HC(6)), 2.3 (ddd, J = 13.5, 7.0, 3.5, HC(3)), 2.19 (ddd, J = 13.5, 8.5, 6.0, HC(3)); $[\alpha]^{25}_{365}$ +90.3°, $[\alpha]^{25}_{436}$ +59.2°, $[\alpha]^{25}_{546}$ +35.9°, $[\alpha]^{25}_{578}$ +31.7°, $[\alpha]^{25}_{589}$ +30.3° (c = 1.325 g/dm^3, MeOH).

2,5-Anhydro-3-deoxy-*N*-(4′,6′-diaminopyrimidin-5′-yl)-D-*ribo*-hexonamide (33). The same procedure was followed as for **41**, starting with **32**, with heating to 95 °C for 16 h: yield 70% **33**·H_2O, colorless crystals, mp 178–180 °C: ^{1}H NMR (250 MHz, CD_3OD) δ 7.89 (s, HC(2′)), 4.9 (s, NH_2, OH), 4.84 (t, J = 8.0, HC(2)), 4.41 (dt, J = 6.0, 3.0, HC(4)), 4.07 (q, J = 3.0, HC(5)), 3.89 (dd, J = 12.0, 3.0, HC(6)), 3.77 (dd, J = 12.0, 3.0, HC(6)), 2.46 (ddd, J = 13.0, 8.0, 6.0, HC(3)), 2.35 (ddd, J = 13.0, 8.0, 3.0, HC(3)); $[\alpha]^{25}_{365}$ +373.8°, $[\alpha]^{25}_{436}$ +216.3°, $[\alpha]^{25}_{546}$ +121.8°, $[\alpha]^{25}_{578}$ +106.1°, $[\alpha]^{25}_{589}$ +101.5° (c = 0.325 g/dm^3, MeOH).

(±)-2,5-Anhydro-3-deoxy-*N*-(4′,6′-diaminopyrimidin-5′-yl)-D,L-*ribo*-hexonamide ((±)-33). The same procedure was followed as for **33**, starting with (±)-**32**: mp 150–155 °C dec.

(1*R*)-1-*C*-(6′-Amino-7′*H*-purin-8′-yl)-1,4-anhydro-2-deoxy-D-*erythro*-pentitol (12). A 5:1 mixture of **33** and 4,5,6-triaminopyrimidine (220 mg, 0.75 mmol), anhydrous DMF (7 mL), and anhydrous CsF (621 mg, 4.08 mmol) was heated to 120 °C for 48 h. After cooling to 20 °C, the precipitate was filtered off (rinsing with MeOH) and the solvent evaporated in vacuo. The residue was purified by column chromatography on silica gel (Lobar B, MeOH/CH_2Cl_2, 1:2 v/v), yielding 130 mg (70%), colorless crystals, mp 242–245 °C dec. Recrystallization from EtOH/H_2O gave **12**·H_2O, mp 194–197 °C (lit.[12] mp 192 °C): UV (MeOH) 264 (15090), 211 (18320); CD (see Figure 1) $\Delta\epsilon_{257}$ = +1.3 (c = 0.32 g/dm^3, MeOH); IR (KBr) 3300 (br), 1660, 1600, 1500, 1420, 1370, 1330, 1220, 1170, 1090; ^{1}H NMR (250 MHz, CD_3OD) δ 8.22 (s, HC(2′)), 5.4 (dd, J = 9.0, 6.5, HC(1)), 4.47 (ddd, J = 5.5, 3.0, 2.5, HC(3)), 4.08 (ddd, J = 4.0, 3.0, HC(4)), 3.83 (dd, J = 12.0, 4.0, HC(5)), 3.76 (dd, J = 12.0, 4.5, HC(5)), 2.44 (ddd, J = 13.0, 6.5, 2.5, HC(2)), 2.35 (ddd, J = 13.0, 9.0, 5.5, HC(2)); MS (70 eV) m/z (relative intensity) 251 (M^+, 10), 220 (2), 208 (2), 195 (1), 178 (7), 164 (17), 162 (100), 149 (5), 135 (7); HR-MS ($C_{10}H_{13}N_5O_3$) calcd 251.101 99, found 251.101 939 and 251.102 436 (ref I$_2$).

(±)-(1*RS*)-1-*C*-(6′-Amino-7′*H*-purin-8′-yl)-1,4-anhydro-2-deoxy-D,L-*erythro*-pentitol ((±)-12). The same procedure was followed as for **12**, starting with (±)-**33**: mp 242–245 °C dec.

(1*R*,2*S*,4*S*)-6-Chloro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Trifluoromethanesulfonate (42). The same procedure was followed as for the preparation of **29**, starting with **36**: yield 85%, colorless oil that solidifies at −20 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.5 (d, J = 2.0, HC(5)), 5.47 (ddd, J = 8.0, 4.0, 2.0, HC(2)), 5.08 (ddd, J = 4.5, 2.0, 1.0, HC(4)), 4.96 (d, J = 4.0, HC(1)), 2.57 (ddd, J = 13.0, 8.0, 4.5, H_{exo}C(3)), 1.64 (dd, J = 13.0, 2.0, H_{endo}C(3)).

(1*R*,4*S*,6*R*)-6-*exo*-(Benzyloxy)-2-chloro-7-oxabicyclo-[2.2.1]hept-2-ene (43). The same procedure was followed as for **30**, starting with **42**: yield 88%, colorless oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.42–7.28 (m, C_6H_5), 6.21 (d, J = 1.5, HC(3)), 5.06 (dd, J = 4.5, 1.5, HC(4)), 4.73 (s, HC(1)), 4.65 and 4.6 (2 d, J = 12.0, CH_2Ph), 3.97 (dd, J = 6.5, 2.5, HC(6)), 1.94 (dd, J = 12.0, 6.5, H_{endo}C(5)), 1.81 (ddd, J = 12.0, 4.5, 2.5, H_{exo}C(5)); $[\alpha]^{25}_{365}$ −202°, $[\alpha]^{25}_{436}$ −116.8°, $[\alpha]^{25}_{546}$ −63.8°, $[\alpha]^{25}_{578}$ −55.1°, $[\alpha]^{25}_{589}$ −52.9° (c = 1.68 g/dm^3, CH_2Cl_2).

Dimethyl Acetal of Methyl 2,5-Anhydro-4-*O*-benzyl-3-deoxy-L-*ribo*-hexuronate (44). The same procedure was followed as for **26**, starting with **43**: yield 82%, colorless oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.38–7.26 (m, C_6H_5), 4.63 (s, HC(5)), 4.61 and 4.55 (2 d, J = 12.0, CH_2Ph), 4.44 (d, J = 6.5, HC(1)), 4.38 (m, HC(2)), 4.26 (d, J = 5.5, HC(4)), 3.78 (s, COOMe), 3.46 and 3.40 (2 s, 2 MeO), 2.18 (dd, J = 13.0, 5.5, HC(3)), 1.91 (ddd, J = 13.0, 9.5, 5.5, HC(3)); $[\alpha]^{25}_{365}$ −144.2°, $[\alpha]^{25}_{436}$ −88°, $[\alpha]^{25}_{546}$ −50.2°, $[\alpha]^{25}_{578}$ −43.9°, $[\alpha]^{25}_{589}$ −42.2° (c = 1.475 g/dm^3, CH_2Cl_2).

2,5-Anhydro-3-*O*-benzyl-4-deoxy-D-*ribo*-hexonic Acid (49). The same procedure was followed as for **27**, starting with **44**: yield 90%, colorless oil.[16]

2-Deoxy-D-*erythro*-pentose. MeONa (0.3 mL, 5.4 M) in anhydrous MeOH was added to a solution of **8** (290 mg, 1.79 mmol) in MeOH (15 mL). Two graphite electrodes were introduced, and 8.95 mF (200 mA, 133 mA/cm^2) of electricity was passed through the solution. After neutralization with Dowex 50 W × 8, the mixture was filtered and the solvent evaporated in vacuo, yielding 240 mg (90%) of methyl furanosides **45**, colorless oil. This product (210 mg, 1.42 mmol) was dissolved in 0.25 M aqueous H_2SO_4 (8 mL) and heated to 90 °C for 30 min. After cooling to 20 °C, the solution was neutralized with Amberlite IRA 93. After filtration, the solvent was evaporated in vacuo, yielding 160 mg (73%), yellowish oil: $[\alpha]^{25}_{365}$ −158°, $[\alpha]^{25}_{436}$ −103.9°, $[\alpha]^{25}_{546}$ −60.8°, $[\alpha]^{25}_{578}$ −52.8°, $[\alpha]^{25}_{589}$ −52.0° (c = 1.05 g/dm^3, H_2O, after 24 h at 25 °C) (lit.[26b] $[\alpha]^{25}_{589}$ −55.2° (c = 1, H_2O)). (*p*-Toluylsulfonyl)hydrazone: mp 162–163 °C (lit.[34] mp 163–163.5 °C). Benzylphenylhydrazone: mp 126–127 °C (lit.[27a] mp 128 °C).

2-Deoxy-D-*threo*-pentose. The same procedure was followed as above, starting with **9**: yield 84%, colorless oil that can be crystallized from MeOH/ether, mp 84–88 °C; $[\alpha]^{25}_{365}$ −4.8°, $[\alpha]^{25}_{436}$ −3.2°, $[\alpha]^{25}_{546}$ −2.5°, $[\alpha]^{25}_{578}$ −2.1°, $[\alpha]^{25}_{589}$ −1.9° (c = 0.525 g/dm^3, H_2O). Benzylphenylhydrazone: mp 115–116 °C (lit.[35] mp 115–116 °C, lit.[27a] mp 114–115 °C).

3-Deoxy-D-*erythro*-pentose. The same procedure was followed as above, starting with **10**. The crude sugar was purified by column chromatography (Lobar B, RP-8, MeOH/H_2O, 3:1 v/v): yield 61%, colorless oil; $[\alpha]^{25}_{365}$ −18.8°, $[\alpha]^{25}_{436}$ −12.9°, $[\alpha]^{25}_{546}$ −7.2°, $[\alpha]^{25}_{578}$ −6.8°, $[\alpha]^{25}_{589}$ −6.5° (c = 1.54 g/dm^3, H_2O) (lit.[28a] $[\alpha]^{25}_{589}$ −6.3° (c = 1.3 g/dm^3, H_2O)). (*p*-Toluylsulfonyl)hydrazone: mp 144–145 °C (lit.[28i] mp 143–144 °C).

3-Deoxy-D-*threo*-pentose. The same procedure was followed as above, starting with **11**: yield 82%, colorless oil; $[\alpha]^{25}_{365}$ −15.0°, $[\alpha]^{25}_{436}$ −8.5°, $[\alpha]^{25}_{546}$ −3.8°, $[\alpha]^{25}_{578}$ −2.8°, $[\alpha]^{25}_{589}$ −3.3° (c = 1 g/dm^3, H_2O). Benzylphenylhydrazone: mp 85–86 °C (two recrystallizations from ether) (lit.[35] mp 86–86.5 C).

Acknowledgment. We are grateful to Hoffmann-La Roche and Co., AG (Basel), E. I. du Pont de Nemours and Co. (Wilmington, DE), the Fonds Herbette (Lausanne), and the Swiss National Science Foundation for financial support. We thank Marie-Christine Giddey for her technical assistance and Dr. Daniel Stahl, EPFL, for the HR-MS measurements.

Registry No. **5**, 88764-13-0; (+)-**6**, 88708-22-9; (−)-**6**, 94482-75-4; **7**, 125133-06-4; (±)-**8**, 125024-40-0; (+)-**8**, 77909-74-1; (±)-**9**, 125024-41-1; (−)-**9**, 125024-65-9; **10**, 51450-17-0; (±)-**11**, 125024-42-2; (+)-**11**, 125024-66-0; (±)-**12**, 50664-25-0; (+)-**12**, 50664-25-0; (+)-**12**·H_2O, 125024-62-6; (±)-**13**, 125024-67-1; (+)-**13**, 125024-67-1; (±)-**15**, 125024-68-2; (+)-**15**, 125024-68-2; (+)-**15**·H_2O, 125024-64-8; (+)-**19**, 51450-18-1; (±)-**21**, 105183-28-6; (+)-**21**, 105497-54-9; (±)-**22**, 125024-43-3; (+)-**22**, 125133-07-5; (±)-**23**, 125024-44-4; (±)-**24**, 125024-45-5; (±)-**25**, 125024-46-6; (+)-**25**, 125133-08-6; (±)-**26**, 125024-47-7; (−)-**26**, 125024-69-3; (±)-**27**, 125024-48-8; (−)-**27**, 125024-70-6; (±)-**28**, 125024-49-9; (+)-**28**, 125024-71-7; (±)-**29**, 125024-50-2; (+)-**29**, 125133-09-7; (±)-**30**, 125024-51-3; (+)-**30**, 125133-10-0; (±)-**31**, 125024-52-4; (+)-**31**, 125024-72-8; (±)-**32**, 125024-53-5; (+)-**32**, 125024-73-9; (±)-**33**, 125024-54-6; (+)-**33**, 125024-74-0; (+)-**33**·H_2O, 125024-63-7; **35**, 125133-11-1; (±)-**35**, 105183-29-7; (±)-**36**, 125024-55-7; (−)-**36**, 125133-12-2; (±)-**37**, 125024-56-8; (+)-**37**, 125024-75-1; (±)-**38**, 125024-57-9; (−)-**38**, 125133-13-3; (±)-**39**, 125024-58-0; (+)-**39**, 125024-76-2; (±)-**40**, 125024-59-1; (+)-**40**, 125024-77-3; (±)-**41**, 125024-60-4; (+)-**41**, 125024-78-4; (+)-**41**·H_2O, 125024-61-5; **42**, 125024-79-5; (−)-**43**, 125133-14-4; (−)-**44**, 125024-80-8; α-**45**, 51255-17-5; β-**45**, 51255-18-6; α-**46**, 96038-80-1; β-**46**, 96039-31-5; α-**47**, 42890-91-5; β-**47**, 4395-36-2; α-**48**, 53081-35-9; β-**48**, 53081-41-7; **49**, 122825-56-3; 2-deoxy-D-*erythro*-pentose, 533-67-5; 2-deoxy-D-*erythro*-pentose (*p*-tolylsulfonyl)hydrazone, 109285-84-9; 2-deoxy-D-*erythro*-pentose (benzylphenyl)hydrazone, 115002-60-3; 2-deoxy-D-*threo*-pentose, 5284-18-4; 2-deoxy-D-*threo*-pentose (benzylphenyl)-hydrazone, 107280-91-1; 3-deoxy-D-*erythro*-pentose, 3396-73-4; 3-deoxy-D-*erythro*-pentose (*p*-tolylsulfonyl)hydrazone, 3396-74-5; 3-deoxy-D-*threo*-pentose, 55658-87-2; 3-deoxy-D-*threo*-pentose (benzylphenyl)hydrazone, 107280-92-2.

Supplementary Material Available: UV, IR, ^{13}C NMR, and mass spectral data and elemental analyses of all new compounds (**8**, **9**, **11**, (±)-**24**, **25–33**, (±)-**37**, and **38–44**) (6 pages). Ordering information is given on any current masthead page.

(34) David, S.; Jaymond, P. *Bull. Soc. Chim. Fr.* **1959**, 157.
(35) Casini, G.; Goodman, L. *J. Am. Chem. Soc.* **1964**, *86*, 1427–1431.