34. Total Synthesis of L-Allose, L-Talose, and Derivatives[1])

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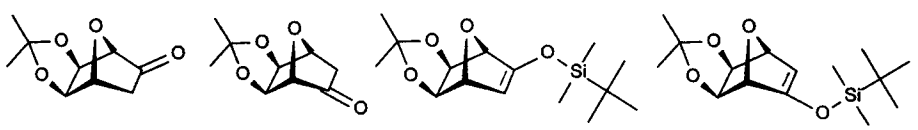
(19.X.88)

(1*S*,4*R*,5*S*,6*S*)-5-*exo*,6-*exo*-(Isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one ((−)-**1**) was transformed with high stereoselectivity to L-allose. Similarly, enantiomer (+)-**1** was transformed into L-talose. The ketones (+)-**1** and (−)-**1** were derived from furan and 1-cyanovinyl (1*S*)-camphanate and 1-cyanovinyl (1*R*)-camphanate, respectively.

The enantiomerically pure ketones (+)-**1** and (−)-**1** are readily available [1]. They have been transformed in a few synthetic steps into D- and L-ribose derivatives, respectively [1]. We report here on the highly stereoselective transformation of (−)-**1** into L-allose *(Scheme 1)* and of (+)-**1** into L-talose *(Scheme 2)*[2]).



(+)-**1** (1*R*) (-)-**1** (1*S*) (-)-**2** (+)-**2**

Applying the *Kiliani* reaction, D- and L-allose can be derived from D- [4] and L-ribose [5], respectively, in two steps. Other syntheses of D-allose starting with sucrose [6], D-glucose [7], or 2,3-*O*-isopropylidene-D-glyceraldehyde [8] have been reported. L-Allose derivatives can be obtained from D-mannofuranoside derivatives [9]. In 1970, a total synthesis of DL-allose was proposed [10]. L-Talose[3]) can be derived from L-lyxose [11]. A general method for the total synthesis of the eight L-hexoses has been proposed in 1983 by *Masamune, Sharpless,* and coworkers [12][4]).

Treatment of (+)-**1** and (−)-**1** with *N*-[(*tert*-butyl)dimethylsilyl]-*N*-methyltrifluoroacetamide and Et_3N in DMF [14] gave the corresponding enol ethers (−)-**2** (85%) and (+)-**2** (83%), respectively, and oxidation of (+)-**2** with 3-chloroperbenzoic

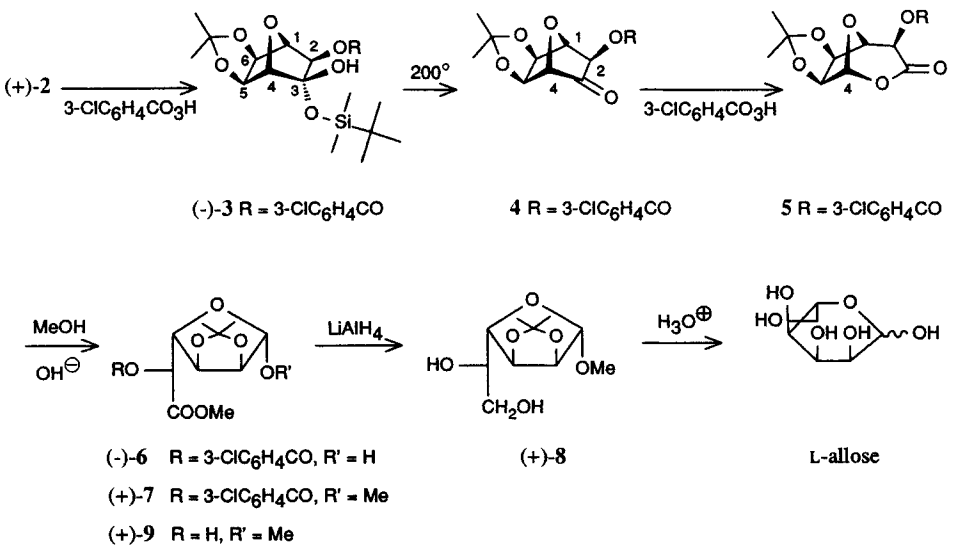
[1]) Enantiomerically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives ('naked sugars' [2]) as synthetic intermediates, Part IV. Part III, see [1].

[2]) D-Talose is a relatively common sugar, whereas D-allose is rare in nature, see [3].

[3]) D-Talose, see [11b]; 2,5-anhydro-3,4,6-tri-*O*-benzyl-L-talose dimethyl acetal has been derived from 2,5-anhydro-3,6-di-*O*-tosyl-L-idose [11c]; for a total synthesis of DL-talopyranose derivatives, see [11d].

[4]) For other total syntheses of carbohydrates, see [13].

Scheme 1



acid in THF (20°) led to the product of epoxide acidolysis, (−)-**3** (69%). On heating to 200° for 15 min, (−)-**3** yielded the protected α-hydroxyketone derivative **4** (*Scheme 1*)[5]). Addition of 1.1 equiv. of 3-chloroperbenzoic acid (20°, $CHCl_3$, 30 min) transformed **4** into lactone **5** which, in the presence of MeOH and K_2CO_3 (20°), gave selectively the diester (−)-**6**. Reactions (−)-**3**→**4**→**5**→(−)-**6** were carried out in 'one pot' with an overall yield of 78%. The methyl furanoside (+)-**7** (92%) was obtained on acidic methanolysis of (−)-**6**. Reduction of both ester functions in (−)-**6** with 4.2 equiv. of $LiAlH_4$ (THF, 20°, 15 min) afforded methyl 2,3-*O*-isopropylidene-β-L-allofuranoside ((+)-**8**; 71%) [16], which was found to be identical (mixed m.p., [α], *etc.*) with a sample of (+)-**8** derived from L-allose according to the procedure reported for the preparation of methyl 2,3-*O*-isopropylidene-β-D-allofuranoside[6]) [18a]. When only 2 equiv. of $LiAlH_4$ were used for the reduction of (+)-**7**, the methyl β-L-allofuranosiduronate derivative (+)-**9** [18b] was obtained selectively (80%, isolated). Acidic hydrolysis (2% H_2SO_4 in H_2O, 100°, 2 h) of (+)-**8** afforded L-allose [16]. D-Allose [3] and D-allofuranosiduronic-acid derivatives can be prepared in the same manner starting with ketone (+)-**1**.

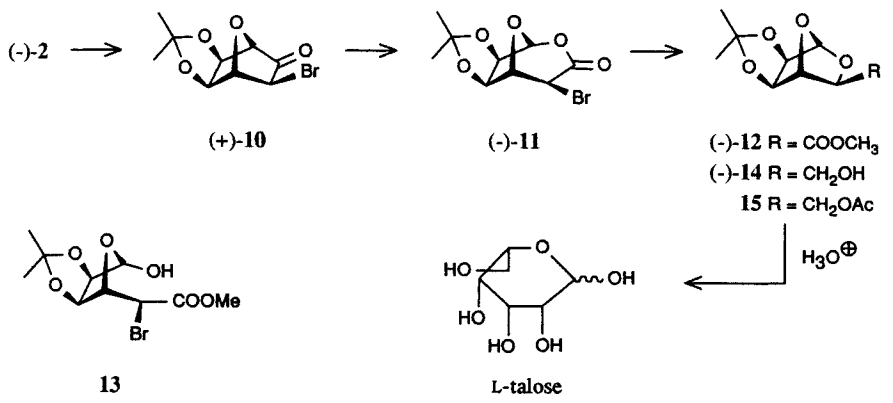
The structures of **3**–**9** were confirmed by their elemental analyses and spectral data. The 2-*exo* position of the 3-chlorobenzoate moiety in (−)-**3** was given by the vicinal coupling constant ^3J(H–C(1), H–C(2)) < 0.5 Hz [19], and the 3-*endo* position of the (*t*-Bu)Me_2SiO group was confirmed by the observation of NOE's in the 360-MHz ^{1}H-NMR spectrum ($CDCl_3$) between the signals of (*t*-Bu)*Me*$_2$SiO (0.08, 0.16 ppm), H_{endo}–C(5) (4.83 ppm), H_{endo}–C(2) (4.62 ppm), and OH (3.57 ppm). Irradiation of the signal at 4.12 ppm (H–C(4) of (−)-**3**) led to the observation of NOE's at 4.83 (H–C(5)) and 3.57 ppm (OH).

In the presence of 1.1 equiv. of Br_2 in CH_2Cl_2 (−50°), (−)-**2** gave the α-bromoketone (+)-**10** (78%; *Scheme 2*). *Baeyer-Villiger* oxidation of (+)-**10** with CF_3CO_3H (CH_2Cl_2,

[5]) For analogous reactions, see [15].

[6]) For D-isomers, see [17].

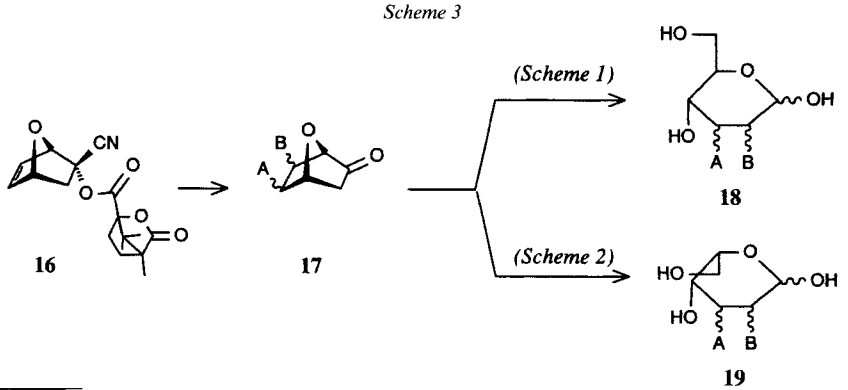
Scheme 2



Na_2HPO_4, 20°) afforded lactone (−)-**11** (85%). As for reaction **4**→**5**, the oxidation was highly selective yielding exclusively the product of O-insertion between the bridgehead center C(1) and the carbonyl group. Methanolysis of (−)-**11** in MeOH saturated with K_2CO_3 (20°, 45 min) gave (−)-**12** in 95% yield. The latter reaction implies the intermediacy of hemiacetal **13** which, in the presence of a base, undergoes intramolecular S_N2 displacement of the Br-atom giving (−)-**12**. This hypothesis was confirmed by the isolation of **13**, when (±)-**11** was treated with MeOH at 20° containing a small amount of $NaHCO_3$. On treatment with MeOH and K_2CO_3, **13** afforded (±)-**12**. Reduction of (−)-**12** with 2 equiv. of $LiAlH_4$ in THF (20°) furnished 1,4-anhydro-2,3-*O*-isopropylidene-α-L-talopyranose ((−)-**14**, 82%)[7]). Treatment with 1N HCl (20°, 4 d) afforded L-talose whose *N*-methyl-*N*-phenylhydrazone [21] was identical (mixed m.p.) with that obtained from an authentic sample of L-talose. D-Talose and its derivatives can be obtained in the same manner starting with ketone (−)-**1**.

One of the advantages of our synthetic method is that both the furanose and pyranose forms of the hexoses can be attained selectively. Partially protected sugars or hexoses with

Scheme 3



[7]) For analogous 1,4-anhydropyranoses, see *e.g.* [20]. The talopyranose (−)-**14** was also characterized as its 6-*O*-acyl derivative **15**.

different protective groups can be obtained with high selectivity. Since the 7-oxabicyclo[2.2.1]heptan-2-ones **17** (derived from the *Diels-Alder* adduct **16** of furan to 1-cyanovinyl (1*S*)-camphanate [22]) can be substituted at C(5) and C(6) by different groups A and B stereoselectively [23–25], our approach is, in principle, applicable to the stereoselective total synthesis of D-hexoses of type **18** and L-hexoses of type **19**. Moreover, starting with 1-cyanovinyl (1*R*)-camphanate [1] [22] and furan, the enantiomers of **18** and **19** are also accessible by our method.

We thank *F. Hoffmann-La Roche & Co. AG*, Basel, the *Swiss National Science Foundation*, and the *Fonds Herbette*, Lausanne, for generous support.

Experimental Part

General. See [1]. Silica gel used for column chromatography (FC = flash chromatography) and filtrations: *Merck 7734* or *9385*. None of the procedures reported here have been optimized.

*(+)-2-{[(*tert*-Butyl)dimethysilyl]oxy}-5,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]hept-2-ene* ((+)-**2**). Et_3N (1.6 ml, 21.6 mmol) and *N*-[(*tert*-butyl)dimethylsilyl]-*N*-methyltrifluoroacetamide (1.5 ml, 10.8 mmol) were added to a stirred soln. of (−)-**1** (1 g, 5.4 mmol) [1] in anh. DMF under Ar. The mixture was heated to 60° for 18 h. TLC (silica gel, AcOEt/petroleum ether 1:3, detection by vanillin): R_f ((+)-**2**) 0.68. The soln. was evaporated at 50°/0.05 Torr. The residue was purified by FC on silica gel (AcOEt/petroleum ether 1:3) yielding 1.38 g (85%), colorless oil. $[\alpha]_D^{25} = +29.0$ ($c = 1.44$, CH_2Cl_2). IR (KBr): 2930, 2855, 1620, 1470, 1370, 1320, 1260, 1200, 1180, 1065, 845. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.82 (*d*, ^3J(H−C(3), H−C(4)) = 2, H−C(3)); 4.69 (*dd*, ^3J = 2, ^4J(H−C(1), H−C(4)) = 1, H−C(4)); 4.54, 4.48 (2*d*, ^3J = 5.5, H−C(5), H−C(6)); 4.29 (*d*, ^4J = 1, H−C(1)); 1.50, 1.35 (2*s*, 2 Me); 0.91 (*s*, *t*-Bu); 0.19, 0.16 (2*s*, Me_2Si). ^{13}C-NMR ($CDCl_3$, 90 MHz): 162.06 (*s*, C(2)); 115.71 (*s*, quat. C); 102.01 (*d*, J = 173, C(3)); 82.30 (*d*, J = 162); 81.70 (2*d*, J = 167, C(5), C(6)); 79.53 (*d*, J = 161); 26.32, 25.65 (2*q*, J = 127, 2 Me); 25.40 (3*q*, J = 125, 3 Me); 18.01 (*s*, quat. C): −4.88, −5.14 (2*s*, 2 Me). MS (70 eV): 198 (6), 142 (13), 141 (16), 100 (100), 85 (46), 75 (36), 73 (36), 59 (21), 57 (28), 56 (29), 45 (21). Anal. calc. for $C_{15}H_{26}O_4Si$ (298.34): C 60.36, H 8.78, O 21,45, Si 9.41; found: C 60.72, H 8.80, O 20.28, Si 10.20.

*(−)-2-{[(*tert*-Butyl)dimethysilyl]oxy}-5,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]hept-2-ene* ((−)-**2**). Same procedure as for (+)-**2**, using (+)-**1** [1]. $[\alpha]_D^{23} = -29.4$ ($c = 1.55$, CH_2Cl_2). (±)-**2** derived from (±)-**1**: colorless crystals, m.p. 49.5–50.5°[8]).

*(−)-(1R,2R,3R,4S,5S,6S)-*endo*-{[(*tert*-Butyl)dimethylsilyl]oxy}-3-*exo*-hydroxy-5,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]hept-2-*exo*-yl 3-Chlorobenzoate* ((−)-**3**). At 20°, 3-$ClC_6H_4CO_3H$ (85%; 340 mg, 1.76 mmol) was added to a stirred soln. of (+)-**2** (0.5 g, 1.68 mmol) in anh. THF (10 ml). After stirring for 45 min at 20° (TLC control (silica gel, AcOEt/petroleum ether 1:2, detection by vanillin): R_f ((−)-**3**) 0.41), the solvent was evaporated and the residue filtered through a short column of silica gel cooled to 0° (150 g, AcOEt/petroleum ether 1:3), yielding 545 mg (69%), colorless oil. $[\alpha]_D^{23} = +31.4$ ($c = 1.75$, CH_2Cl_2). UV (CD_3CN): 232 (9410), 282 (1140), 291 (sh, 850). UV (EtOH): 232 (10380), 283 (1090), 290 (930). IR (KBr): 2365, 2920, 2880, 2845, 1722, 1420, 1370, 1273, 1248, 1110, 1065, 865, 833, 780, 740. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.03 (*dd*, J = 1.5, 2), 7.95 (*dt*, J = 8, 1.5), 7.58 (*ddd*, J = 8, 2, 1.5); 7.42 (*t*, J = 8)(4 arom. H); 4.83, 4.57 (2*d*, J = 5.5, H−C(5), H−C(6)); 4.62 (*s*, H_{endo}−C(2)); 4.39, 4.12 (2*d*, ^4J (H−C(1), H−C(4)) = 2, H−C(1), H−C(4)); 3.57 (*s*, OH); 1.49, 1.34 (2*s*, Me_2C); 0.91 (*s*, *t*-Bu); 0.16, 0.08 (2*s*, Me_2Si); irradiation at 0.08 and 0.16→NOE's at 4.62, 4.83, and 3.57; irradiation at 4.12 (H−C(4))→NOE's at 4.83 (H−C(5)) and 3.57 (OH) (the signal attributions were confirmed by the synthesis of (±)-(D)-**3**, see below). ^{13}C-NMR ($CDCl_3$, 90 MHz): 164.34 (*s*, OC=O); 134.94 (*s*, arom. C); 134.90 (*s*, arom. C); 133.79 (*d*, J = 167, arom. C); 130.75 (*s*, arom. C); 130.10 (*d*, J = 165, arom. C); 129.80 (*d*, J = 174, arom. C); 127.86 (*d*, J = 171, arom. C); 112.71 (*s*, quat. C); 86.44 (*d*, J = 162); 84.80 (*d*, J = 164); 79.20 (*d*, J = 157); 79.33 (*d*, J = 156); 79.20 (*d*, J = 160); 25.90, 25.86, 25.80, 25.74, 25.12 (5*q*, J = 125, 5 Me); −3.08, −3.25 (2*q*, J = 119, Me_2Si). MS (70 eV): 310 (1.2), 213 (2.3), 156 (64), 139 (74), 111 (99), 75 (100), 51 (58). Anal. calc. for $C_{22}H_{31}ClSiO_7$ (471.02): C 56.10, H 6.63, Cl 7.53, O 23.78, Si 5.96; found: C 55.99, H 6.58, Cl 7.94, O 23.18, Si 6.31.

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[8]) Prepared in our laboratory for the first time by Mr. *M. Bimwala*.

*(±)-2-*endo-*{[* tert-*Butyl)dimethylsilyl]oxy}-3-*exo-*hydroxy-5,6-*exo-*(isopropylidenedioxy)(2-*endo-*D)-7-oxabicyclo[2.2.1]hept-2-*exo-*yl 3-Chlorobenzoate* ((±)-(D)-**3**). A soln. of (±)-**1** (1 g, 5.4 mmol) in CD_3OD (5 ml) sat. with anh. K_2CO_3 was allowed to stand at 20° for 1 h. The mixture was filtered through silica gel and the solvent evaporated, yielding (±)-(3,3-D_2)-**1** (835 mg, 83.4%). This crude product was transformed, as described above, into (±)-(3-D)-**2** and oxidized with 3-$ClC_6H_4CO_3H$ to (±)-(D)-**3**. After recrystallization from hexane, m.p. 114.5–115° (dec.). ^{1}H-NMR (360 MHz): no *s* at 4.62.

*(1R,2R,4S,5S,6S)-5,6-*exo-*(Isopropylidenedioxy)-3-oxo-7-oxabicyclo[2.2.1]hept-2-*exo-*yl 3-Chlorobenzoate* (**4**). For 12 min, (–)-**3** (128 mg, 0.27 mmol) was heated to 200°. After cooling to 20°, crude **4** was washed with hexane (2 ml, twice) and dried *in vacuo:* 69 mg (74%), colorless oil. UV (EtOH): 230 (9160), 283 (1010), 292 (sh, 690). UV (CH_3CN): 232 (10320), 283 (1130), 290 (960). IR (KBr): 2975, 2930, 1770, 1720, 1420, 1370, 1280, 1255, 1120, 1070. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.0 (*dd, J* = 2, 1.5), 7.92 (*dt, J* = 8, 1.5), 7.55 (*ddd, J* = 2, 1.5, 8), 7.38 (*t, J* = 8)(4 arom. H); 4.81 (*s,* H_{endo}–C(3)); 4.77 (*d,* ^4J = 1.5, H–C(1) or H–C(4)); 4.73, 4.59 (2*d, J* = 5.5, H–C(5), H–C(6)); 4.44 (*d,* ^4J = 1.5, H–C(4) or H–C(1)); 1.51, 1.34 (2*s,* Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 202.93 (*s,* C(2)); 164.63 (*s,* OCO); 134.82 (*s,* arom. C); 133.83 (*d, J* = 167, arom. C); 130.30 (*s,* arom. C); 130.05 (*d, J* = 172, arom. C); 129.87 (*d, J* = 165, arom. C); 128.16 (*d, J* = 158, arom. C); 114.50 (*s,* quat. C); 84.21 (*d, J* = 167); 83.05 (*d, J* = 171); 79.72 (*d, J* = 158); 77.96 (*d, J* = 162); 69.68 (*d, J* = 153, C(3)); 25.71, 25.11 (2*q, J* = 128, 2 Me). MS (70 eV): 338 (0.18, M^+), 322 (2.5, M^+-15), 140 (30), 139 (27), 138 (100), 111 (29), 85 (68), 75 (41), 56 (34), 51 (40), 45 (75). Anal. calc. for $C_{16}H_{15}ClO_6$ (338.74): C 56.73, H 4.46, Cl 10.46, O 28.34; found: C 56.53, H 4.58, Cl 10.13, O 28.76.

(±)-**4** from (±)-**3**: recrystallization from petroleum ether. M.p. 135.5–136°.

*5-O-(3-Chlorobenzoyl)-2,3-*O*-isopropylidene-β-*L*-allofuranurono-6,1-lactone* (**5**). For 12 min, (–)-**3** (141 mg, 0.3 mmol) was heated to 200°. After cooling to 20°, $NaHCO_3$ (25 mg, 0.3 mmol) and 85% 3-$ClC_6H_4CO_3H$ (66 mg, 0.33 mmol) in $CHCl_3$ (4 ml) were added. After stirring at 20° for 15 min, the solvent was evaporated and the residue purified by filtration on silica gel (50 g, AcOEt/petroleum ether 1:2), yielding 72 mg (68%), colorless oil. UV (CH_3CN): 233 (9500), 282 (2350), 293 (sh, 1900). UV (EtOH): 232 (10060), 283 (2150), 293 (sh, 1650). IR (KBr): 2995, 2970, 2930, 1760, 1722, 1378, 1280, 1202, 1105, 1080, 985, 860, 740. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.06 (*dd, J* = 2, 1.5), 7.98 (*dt, J* = 8, 1.5), 7.59 (*ddd, J* = 8, 2, 1.5), 7.42 (*t, J* = 8)(4 arom. H); 5.88 (*d, J* = 1, H–C(1)); 5.48 (*s,* H–C(5)); 4.93, 4.86 (*d, J* = 5.5, H–C(2), H–C(3)); 4.72 (*d, J* = 1, H–C(4)); 1.50, 1.39 (2*s,* Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 163.84, 161.58 (2*s,* 2 COOR); 134.81 (*s,* arom. C); 134.01 (*d, J* = 168, arom. C); 130.14 (*d, J* = 170, arom. C); 130.00 (*s,* arom. C): 129.91 (*d, J* = 165, arom. C); 128.28 (*d, J* = 173, arom. C); 114.40 (*s,* quat. C); 104.28 (*d, J* = 188, C(1)); 83.72, 82.94, 79.26 (3*d, J* = 163, C(2), C(3), C(4)); 69.65 (*d, J* = 148, C(5)); 25.87, 24.96 (2*q, J* = 129, 2 Me). MS (70 eV): 356 (0.4, M^+), 354 (1.4, M^+), 341 (3.5, M^+-15), 339 (10, M^+-15), 141 (33, $^{37}ClPhCO^+$), 139 (100, $^{35}ClPhCO^+$), 113 (22), 111 (25), 100 (29), 85 (23), 75 (12), 59 (10). Anal. calc. for $C_{16}H_{15}ClO_7$ (354.74): C 54.17, H 4.26, Cl 9.99, O 31.57; found: C 53.68, H 4.37, Cl 10.20, O 31.75.

(±)-**5** from (±)-**3**: recrystallization from hexane. M.p. 141.5–142.5°.

*(–)-Methyl 5-*O*-(3-Chlorobenzoyl)-2,3-*O*-isopropylidene-β-*L*-allofuranuronate* ((–)-**6**). For 12 min, (–)-**3** (0.5 g, 1.06 mmol) were heated to 200° and then oxidized with 3-$ClC_6H_4CO_3H$ (1.1 mmol) in $CHCl_3$ (10 ml) containing $NaHCO_3$ (94 mg, 1.1 mmol) at 20° for 15–20 min. The solvent was evaporated and the residue taken up with MeOH (10 ml). $NaHCO_3$ (18 mg, 0.21 mmol) was added. After stirring at 20° for 1 h, the solvent was evaporated and the residue purified by column chromatography on silica gel (100 g, AcOEt/petroleum ether 1:2) yielding 320 mg (78%), colorless oil (anomeric mixture). Trituration with hexane gave pure β-L-anomer, colorless crystals. M.p. 102.5–103.5°. $[\alpha]_D^{25} = -0.54$ (*c* = 2.21, CH_2Cl_2). UV (CH_3CN): 231 (10200), 283 (1280), 290 (1100). UV (EtOH): 232 (10100), 283 (1200), 291 (1020). IR (KBr): 3460, 3060, 2980, 2960, 1730, 1720, 1437, 1225, 1200, 1120, 1065, 860, 748. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.05 (*dd, J* = 2, 1.5), 7.96 (*dt, J* = 8, 1.5), 7.58 (*ddd, J* = 8, 2, 1.5), 7.40 (*t, J* = 8)(4 arom. H); 5.50 (*d, J*(OH,H–C(1)) = 2, *J*(H–C(1), H–C(2)) ≈ 0, H–C(1), β-L-anomer); 5.30 (*d, J* = 8, H–C(5)); 4.91 (*dd, J* = 6, 1, H–C(3)); 4.68 (*d, J* = 6, H–C(2)); 4.60 (*dd, J* = 8, 1, H–C(4)); 3.80 (*s,* Me); 3.03 (*d, J* = 2, OH); 1.50, 1.34 (2*s,* Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 168.41, 164.35 (2*s,* 2 COOR); 134.78 (*s,* arom. C); 133.78 (*d, J* = 168, arom. C); 130.54 (*s,* arom. C); 130.06, 129.91 (2*d, J* = 164, 2 arom. C); 128.20 (*d, J* = 173, arom. C); 113.05 (*s,* quat. C); 103.46 (*d, J* = 175, C(1)); 85.77, 85.50, 82.14 (3*d, J* = 159, C(2), C(3), C(4)); 73.99 (*d, J* = 155, C(5)); 52.89 (*q, J* = 148, Me); 26.53, 25.08 (2*q, J* = 129, 2 Me). MS (70 eV): 387 (6, M^+), 385 (17, M^+), 282 (7), 173 (10), 141 (32, $^{37}ClPhCO^+$), 139 (100, $^{35}ClPhCO^+$), 111 (51), 98 (25), 85 (29), 75 (28), 59 (37), 45 (24). Anal. calc. for $C_{17}H_{19}ClO_8$ (386.78): C 52.79, H 4.95, Cl 9.17, O 33.09; found: C 52.80, H 5.03, Cl 8.79, O 33.38.

(±)-**6** from (±)-**3**: colorless crystals. M.p. 90.5–91.5°.

*(+)-Methyl (Methyl 5-*O*-(3-chlorobenzoyl)-2,3-*O*-isopropylidene-β-*L*-allofuranosid)uronate* ((+)-**7**). A soln. of (–)-**6** (400 mg, 1.03 mmol) and $MeSO_3H$ (70 µl, 1.08 mmol) in anh. MeOH (10 ml) and 2,2-dimethoxypropane

(4 ml) was allowed to stand at 20° for 8 h. Then, 5% aq. $NaHCO_3$ soln. (20 ml) was added and the mixture concentrated to *ca.* 10 ml. The mixture was extracted with CH_2Cl_2 (20 ml, 3 times), the combined extract washed with H_2O, dried ($MgSO_4$), and evaporated, and the residue purified by column chromatography on silica gel (100 g, AcOEt/petroleum ether 1:2), yielding 380 mg (92%), colorless oil. $[\alpha]_D^{25} = +42.9$ ($c = 1.44$, $CHCl_3$). IR (CH_2Cl_2): 2980, 2950, 2930, 1748, 1728, 1370, 1232, 1208, 1107, 1088, 862. ^{1}H-NMR (360 MHz, $CDCl_3$): 8.06 (*dd*, $J = 2, 1.5$), 7.99 (*dt*, $J = 8, 1.5$), 7.57 (*ddd*, $J = 8, 2, 1.5$), 7.41 (*t*, $J = 8$)(4 arom. H); 5.33 (*d*, $J = 6$, H–C(5)); 5.04 (*s*, H–C(1), β-L-anomer); 4.95 (*dd*, $J = 5.5, 1$, H–C(3)); 4.68 (*dd*, $J = 6, 1$, H–C(4)); 4.64 (*d*, $J = 5.5$, H–C(2)); 3.81 (*s*, MeOOC); 3.30 (*s*, MeO); 1.50, 1.35 (2*s*, Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 168.2, 164.4 (2*s*, 2 COOR); 134.7 (*s*, arom. C); 133.6 (*d*, $J = 167$, arom. C); 130.8 (*s*, arom. C); 130.0 (*d*, $J = 169$, arom. C); 129.8 (*d*, $J = 164$, arom. C); 128.1 (*d*, $J = 166$, arom. C); 112.9 (*s*, quat. C); 110.5 (*d*, $J = 173$, arom. C); 86.0 (*d*, $J = 155$); 85.4 (*d*, $J = 159$); 81.2 (*d*, $J = 158$); 73.5 (*d*, $J = 154$); 55.6 (*q*, $J = 144$, MeO); 52.6 (*q*, $J = 148$, COOMe); 26.5, 25.1 (2*q*, $J = 127$, 2 Me). MS (70 eV): 387 (2, M^+-15), 385 (7, M^+-15), 282 (5), 173 (13), 141 (34, ^{37}ClPhCO$^+$), 139 (100, ^{35}ClPhCO$^+$), 126 (9), 111 (15), 98 (8), 85 (21), 75 (20), 71 (19), 59 (35), 45 (28). Anal. calc. for $C_{18}H_{21}ClO_8$ (400.81): C 53.94, H 5.28, Cl 8.84, O 31.93; found: C 54.17, H 5.32, Cl 8.74, O 31.78.

(±)-**7** from (±)- **6**: colorless crystals. M.p. 51–52.5° (from hexane).

*(+)-Methyl 2,3-*O*-Isopropylidene-β-*L*-allofuranoside* ((+)-**8**). A mixture of (+)-**7** (70 mg, 0.175 mmol) and $LiAlH_4$ (28 mg, 0.74 mmol) in anh. THF (4 ml) was stirred at 20° for 15 min. MeOH (2 ml) was added and the mixture filtered through *Celite*. The solvent was evaporated, the residue dissolved in AcOEt (10 ml) and 0.5N HCl (10 ml), the aq. phase extracted with AcOEt (20 ml, 3 times), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by column chromatography on silica gel (80 g, AcOEt; R_f ((+)-**8**) 0.35) and recrystallization from Et_2O, yielding 29 mg (71%), colorless crystals. M.p. 94.5–95.5°. $[\alpha]_D^{25} = +70.0$ ($c = 1.2$, $CHCl_3$). IR (KBr): 3420, 2985, 2960, 2920, 1440, 1380, 1280, 1205, 1085, 1057, 1025, 965, 872. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.91 (*s*, H–C(1)); 4.84 (br. *d*, $J = 6$, ^3J(H–C(3), H–C(4)) < 1, H–C(3)); 4.53 (*d*, $J = 6$, H–C(2)); 4.21 (br. *d*, $J = 3.5$, H–C(4)); 3.72–3.62 (*m*, H–C(5), CH_2(6)); 3.36 (*s*, MeO); 2.59 (br. *s*, 2 OH); 1.42, 1.26 (2*s*, Me_2C); *cf.* [16]. ^{13}C-NMR ($CDCl_3$, 90 MHz): 112.25 (*s*, quat. C); 109.78 (*d*, $J = 173$, C(1)); 88.37 (*d*, $J = 149$); 85.57 (*d*, $J = 159$); 80.66 (*d*, $J = 158$); 72.52 (*d*, $J = 145$); 63.40 (*t*, $J = 142$, C(6)); 55.55 (*q*, $J = 144$, MeO); 26.33, 24.76 (2*q*, $J = 127$, 2 Me). MS (70 eV): 219 (30, M^+-15), 187 (14), 173 (17), 127 (14), 113 (20), 98 (18), 85 (52), 71 (20), 59 (100), 45 (48). Anal. calc. for $C_{10}H_{18}O_6$ (234.25): C 51.27, H 7.74, O 40.98; found: C 51.32, H 7.68, O 41.00.

An authentic sample of (+)-**8** was derived from L-allose according to [17] [18] and was identical with (+)-**8** obtained as described above (mixed m.p.).

*Methyl (Methyl 2,3-*O*-Isopropylidene-β-*L*-allofuranosid)uronate* ((+)-**9**). A mixture of (+)-**7** (70 mg, 0.175 mmol) and $LiAlH_4$ (14 mg, 0.36 mmol) in anh. THF (4 ml) was stirred at 20° for 10 min. MeOH (2 ml) was added and the mixture filtered through *Celite*. The soln. was concentrated to 2–3 ml, 0.5N HCl (20 ml) was added and the soln. extracted with CH_2Cl_2 (20 ml, 3 times). The combined extracts were dried ($MgSO_4$), evaporated, and purified by column chromatography on silica gel (10 g, AcOEt/petroleum ether 1:2, R_f ((+)-**9**) 0.34), yielding 36 mg (80%), colorless oil. $[\alpha]_D^{25} = +49.6$ ($c = 1.05$, $CHCl_3$). IR (CH_2Cl_2): 3520, 3390, 2980, 2940, 2840, 1740, 1438, 1373, 1205, 1090, 862. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.99 (*s*, H–C(1)); 4.88 (br. *d*, $J = 6$, H–C(3)); 4.59 (*d*, $J = 6$, H–C(2)); 4.56 (br. *d*, $J = 4.5$, H–C(4)); 4.31 (*d*, $J = 4.5$, H–C(5)); 3.80 (*s*, MeOOC); 3.42 (*s*, MeO); 1.47, 1.30 (2*s*, Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 171.18 (*s*, COOMe); 112.46 (*s*, quat. C); 110.48 (*d*, $J = 179$, C(1)); 89.07 (*d*, $J = 154$); 85.53 (*d*, $J = 158$); 83.56 (*d*, $J = 159$); 72.31 (*d*, $J = 149$); 55.78 (*q*, $J = 143$, MeO); 52.57 (*q*, $J = 148$, COOMe); 26.31, 24.73 (2*q*, $J = 128$, 2 Me). MS (70 eV): 247 (14, M^+-15), 231 (6), 215 (16), 173 (69), 113 (32), 98 (18), 85 (28), 71 (31), 59 (100), 45 (67). Anal. calc. for $C_{11}H_{18}O_7$ (262.26): C 50.38, H 6.92, O 42.70; found: C 51.04, H 6.84, O 42.12.

L-Allose. Same procedure as described in [16], starting with (+)-**8**.

*(+)-(1*R*,3*S*,4*S*,5*S*,6*R*)-3-*exo*-Bromo-5,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**10**). A soln. of Br_2 (0.19 ml, 3.6 mmol) in CH_2Cl_2 (50 ml) was added slowly to a soln. of (–)-**2** (1 g, 3.3 mmol) in CH_2Cl_2 (10 ml) at –50°. The temp. was allowed to rise to 20°, and sat. aq. $NaHCO_3$ soln. (20 ml) was added. The mixture was extracted with CH_2Cl_2 (50 ml, 3 times). The extracts were combined, dried ($MgSO_4$), and evaporated yielding yellowish crystals that can be used for the *Baeyer-Villiger* oxidation (+)-**10**→(–)-**11**. The crude (+)-**10** was purified by FC on silica gel (AcOEt/petroleum ether 1:3, R_f ((+)-**10**) 0.48), yielding 690 mg (78%), colorless crystals. M.p. 144.5–145.5°. $[\alpha]_D^{23} = +241.7$ ($c = 1.12$, $CHCl_3$). UV (EtOH): final abs., $\varepsilon_{210} = 850$. IR (KBr): 2990, 2940, 1780, 1380, 1275, 1205, 1140, 1065. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.75 (*d*, ^4J(H–C(1),H–C(4)) = 1.5 H–C(1)); 4.58, 4.53 (2*d*, $J = 5.5$, H–C(5), H–C(6)); 4.45 (*d*, $^4J = 1.5$, H–C(4)); 3.71 (*s*, H–C(3)); 1.51, 1.33 (2 *s*, Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 203.1 (*s*, C(2)); 114.8 (*s*, quat. C); 86.5, 83.5 (2*d*, $J = 173$, C(5), C(6)); 80.6 (*d*, $J = 159$); 77.8 (*d*, $J = 160$); 39.7 (*d*, $J = 128$, C(3)); 25.8, 25.3 (2*q*, $J = 125$, 2 Me). MS

(70 eV): 249 (16, $M^+ -15$), 247 (16, $M^+ -15$), 183 (24), 165 (48), 125 (38), 97 (100), 85 (51), 59 (69), 55 (72). Anal. calc. for $C_9H_{11}BrO_4$ (263.09): C 41.09, H 4.21, Br 30.37, O 24.32; found: C 41.17, H 4.27, Br 30.42, O 24.14.

(±)-**10** from (±)-**2**: recrystallization from Et_2O. M.p. 153–154.5° (dec.).

*(−)-5-Bromo-5-deoxy-2,3-*O*-isopropylidene-β-*D*-allofuranurono-6,1-lactone* ((−)-**11**). A soln. of CF_3CO_3H was prepared by stirring a mixture of $(CF_3CO)_2O$ (10 ml, 71 mmol) and 95% H_2O_2 (2.75 ml, 60 mmol) in anh. CH_2Cl_2 (15 ml). This soln. (18 ml, 43 mmol of CF_3CO_3H) was added dropwise to a stirred soln. of (+)-**10** (2 g, 7.2 mmol) and Na_2HPO_4 (2 g, 14.4 mmol) in anh. CH_2Cl_2 (40 ml) at 0°. After stirring at 20° for 18 h, a sat. aq. $NaHSO_3$ soln. was added at 0° until complete destruction of the excess of peracid. The org. phase was diluted with CH_2Cl_2 (200 ml) and washed with brine (50 ml, twice), dried ($MgSO_4$), and evaporated, and the residue recrystallized from Et_2O, yielding 1.8 g (85%), colorless crystals. M.p. 159–161°. $[\alpha]_D^{20} = -16.1$ ($c = 1.52$, CH_2Cl_2). UV (EtOH): final abs., $\varepsilon_{210} = 1060$. UV (isooctane): final abs., $\varepsilon_{210} = 950$. IR (KBr): 3030, 2990, 2930, 1750, 1370, 1205, 1105, 1085. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.82 (*s*, H–C(1)); 4.83, 4.69 (2*d*, $J = 8.5$, H–C(2), H–C(3)); 4.74 (*s*, H–C(4)); 4.30 (*s*, H–C(5)); 1.48, 1.34 (2*s*, Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 161,9 (*s*, C(6)); 114.4 (*s*, quat. C); 103.9 (*d*, $J = 192$, C(1)); 85.4, 79.7 (2*d*, $J = 160$, C(2), C(3)); 83.5 (*d*, $J = 180$, C(4)); 38.7 (*d*, $J = 155$, C(5)); 25.9, 25.1 (2*q*, $J = 126$, 2 Me). MS (70 eV): 265 (20, $M^+ - 15$), 263 (48, $M^+ - 15$), 129 (29), 85 (81), 59 (100). Anal. calc. for $C_9H_{11}BrO_5$ (279.09): C 38.73, H 3.97, Br 28.63, O 28.66; found: C 38.77, H 3.86, Br 28.67, O 28.70.

(±)-**11** from (±)-**10**: recrystallization from Et_2O. M.p. 177–179°.

*(−)-Methyl 1,5-Anhydro-2,3-*O*-isopropylidene-α-*L*-talofuranuronate* ((−)-**12**). A soln. of (−)-**11** (0.5 g, 1.8 mmol) in anh. MeOH (30 ml) saturated with anh. K_2CO_3 was stirred at 20° for 45 min. H_2O (100 ml) was added and the mixture extracted with CH_2Cl_2 (100 ml, 3 times). The combined extract was dried ($MgSO_4$) and evaporated yielding 390 mg (95%), colorless crystals. M.p. 98–100°. $[\alpha]_D^{23} = -14.3$ ($c = 1.1$, CH_2Cl_2). IR (KBr): 2980, 2960, 1730, 1440, 1380, 1270, 1205, 1090, 1020. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.65 (*s*, H–C(1)); 4.91 (*s*, H–C(4)); 4.44, 4.38 (2*d*, $J = 6$, H–C(2), H–C(3)); 3.91 (*s*, H–C(5)); 3.79 (*s*, COOMe); 1.45, 1.30 (2*s*, Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 169.50 (*s*, C(6)); 113.13 (*s*, quat. C); 101.04 (*d*, $J = 176$, C(1)); 81.04, 79.00 (2*d*, $J = 163$, C(2), C(3)); 80.96 (*s*, C(4)); 71.30 (*d*, $J = 154$, C(5)); 52.57 (*q*, $J = 148$, Me); 25.94, 25.47 (2*q*, $J = 128$, 2 Me). MS (70 eV): 215 (6, $M^+ - 15$), 144 (5), 127 (10), 126 (10), 112 (12), 98 (32), 85 (32), 71 (77), 59 (100). Anal. calc. for $C_{10}H_{14}O_6$ (230.22): C 52.17, H 6.13, O 41.69; found: C 52.27, H 6.17, O 41.56.

(±)-**12** from (±)-**11**: recrystallization from Et_2O. M.p. 134.5–135.5°.

*(±)-Methyl 5-Bromo-5-deoxy-2,3-*O*-isopropylidene-β-*DL*-allofuranuronate* (**13**). A soln. of (±)-**11** (100 mg, 0.36 mmol) and $NaHCO_3$ (10 mg) in anh. MeOH (5 ml) was allowed to stand at 20° for 2 h (TLC control (silica gel, AcOEt/petroleum ether 1:2, detection by vanillin): R_f (**13**) 0.3). H_2O (50 ml) was added and the mixture extracted with CH_2Cl_2 (20 ml, 3 times). The combined extract was dried ($MgSO_4$) and evaporated yielding 109 mg (98%), colorless crystals. M.p. 105.5–107°. IR (KBr): 3410, 2980, 2950, 1730, 1430, 1370, 1345, 1280, 1140, 1075. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.53 (*s*, H–C(1)); 4.94 (*dd*, $J = 6$, 1, H–C(3)); 4.68 (*d*, $J = 6$, H–C(2)); 4.62 (*dd*, $J = 11.5$, 1, H–C(4)); 4.33 (*d*, $J = 11.5$, H–C(5)); 3.83 (*s*, COOMe); 2.90 (*s*, OH); 1.51, 1.36 (2*s*, Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 168.61 (*s*, C(6)); 113.11 (*s*, quat. C); 103.17 (*d*, $J = 179$, C(1)); 87.54 (*d*, $J = 173$, C(4)); 85.53 (*d*, $J = 160$); 82.75 (*d*, $J = 157$); 53.14 (*q*, $J = 148$, Me); 44.80 (*d*, $J = 158$, C(5)); 26.47, 25.05 (2*q*, $J = 128$, 2 Me). MS (70 eV): 297 (15, $M^+ - 15$), 295 (17, $M^+ - 15$), 254 (4), 252 (4), 173 (9), 155 (24), 127 (29), 59 (100). Anal. calc. for $C_{10}H_{15}BrO_6$ (311.13): C 38.60, H 4.86, Br 25.68, O 30.85; found: C 38.70, H 4.85, Br 25.53, O 30.92.

*(−)-1,5-Anhydro-2,3-*O*-isopropylidene-α-*L*-talofuranose* ((−)-**14**). A suspension of $LiAlH_4$ (280 mg, 7.32 mmol) in THF (4 ml) was added slowly to a stirred soln. of (−)-**12** (790 mg, 3.66 mmol) in anh. THF (20 ml) at 20° under Ar. After stirring at 20° for 15 min, MeOH (10 ml) was added and the mixture filtered through *Celite*. The solvent was distilled off and the oily residue dissolved in 1N HCl (10 ml) and CH_2Cl_2 (10 ml). The mixture was extracted with CH_2Cl_2 (20 ml, 3 times), the combined extract was dried ($MgSO_4$) and evaporated, and the residue purified by sublimation at 70°/0.01 Torr, yielding 569 mg (82%), colorless crystals. M.p. 67–70°. $[\alpha]_D^{20} = -39.9$ ($c = 1$, $CHCl_3$). IR (KBr): 3400, 2990, 2970, 1370, 1205, 1090, 1065, 1040, 915. ^{1}H-NMR (360 MHz, C_6D_6): 5.46 (*s*, H–C(1)); 4.38 (*s*, H–C(4)); 4.12, 3.89 (2*d*, $J = 5.5$, H–C(2), H–C(3)); 3.40, 3.33 (2*dd*, $J = 11$, 6, CH_2(6)); 3.12 (*t*, $J = 6$, H–C(5)); 2.20 (*s*, OH); 1.69, 1.26 (2*s*, Me_2C). ^{13}C-NMR (C_6D_6/$CDCl_3$ 1:10, 360 MHz): 112.6 (*s*, quat. C); 100.16, (*s*, $J = 181$, C(1)); 81.26, 79.13 (2*d*, $J = 161$, C(2), C(3)); 78.63 (*d*, $J = 165$, C(4)); 73.50 (*d*, $J = 151$, C(5)); 63.04 (*t*, $J = 144$, C(6)); 25.86, 25.24 (2*q*, $J = 127$, 2 Me).

*6-*O*-Acetyl-1,5-anhydro-2,3-*O*-isopropylidene-α-*DL*-talofuranose* (**15**). A mixture of (±)-**14** (100 mg, 0.5 mmol), Ac_2O (3 ml), and pyridine (2 ml) was stirred at 20° for 4 h. The solvent was evaporated and the residue recrystallized from Et_2O/petroleum ether, yielding 106 mg (92%), colorless crystals. M.p. 81.5–84°. IR (KBr): 2980, 2935, 1740, 1375, 1240, 1220, 1090, 1070, 1045. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.35 (*s*, H–C(1)); 4.41 (*s*, H–C(4)); 4.21, 4.18 (2*d*, $J = 5.5$, H–C(2), H–C(3)); 3.86, 3.84 (2*dd*, $J = 11$, 6.5, CH_2(6)); 3.46 (*t*, $J = 6.5$, H–C(5)); 1.96 (*s*, MeCO); 1.33, 1.16 (2*s*, Me_2C). ^{13}C-NMR ($CDCl_3$, 90 MHz): 170.51 (*s*, MeCOO); 112.77 (*s*,

quat. C); 100.37 (*d*, J = 183, C(1)), 81.20 (*d*, J = 161); 79.05 (*d*, J = 159); 78.88 (*d*, J = 169); 71.02 (*d*, J = 150); 63.87 (*t*, J = 149, C(6)); 25.90, 25.33 (2*q*, 2 Me); 20.70 (*q*, MeCOO). MS (70 eV): 229 (3), 175 (4), 109 (19), 98 (12), 85 (12), 81 (14), 58 (13), 45 (100). Anal. calc. for $C_{11}H_{16}O_6$ (244.24): C 54.09, H 6.60, O 39.30; found: C 53.71, H 6.57, O 39.72.

L-*Talose. a)* A soln. of (−)-**14** (22.5 mg, 0.11 mmol) in 1N HCl (2 ml) was allowed to stand at 20° for 4 d. This soln. gave an $[\alpha]_D^{20} = -18.2$ (c = 1, H_2O). Commercial L-talose (*Sigma-Chemie*) treated under the same conditions gave $[\alpha]_D^{20} = -21.3$ (c = 1, H_2O). *Cf.* values for D-talose: $[\alpha]_D^{20} = +17.6$ (c = 1, H_2O) [20b] and +21 (c = 1, H_2O) [26].

b) A soln. of (−)-**14** (100 mg, 0.49 mmol) in 1N HCl (10 ml) was allowed to stand at 20° for 3 d. The soln. was filtered through ion-exchange resin (*Amberlite IRA-93*, 1.5 g) and the solvent evaporated. Reverse-phase chromatography (*Merck RP-8*, AcOEt/MeOH 10:1, R_f ((−)-talose) 0.37) gave 63 mg (71%) of slowly crystallizing sugar.

L-*Talose* N-*Methyl*-N-*phenylhydrazone*. *N*-Methyl-*N*-phenylhydrazine (66 µl, 0.54 mmol) was added to a soln. of L-talose (100 mg, 0.54 mmol) in anh. MeOH (4 ml). The soln. was concentrated to 0.5 ml and then absorbed on silica gel and washed with AcOEt. Extraction with MeOH (R_f of product 0.66), followed by recrystallization from MeOH/Et_2O (twice) gave 113 mg (72%), white crystals. M.p. 153–154°. $[\alpha]_D^{20} = +7.6$ (c = 1, MeOH). IR (KBr): 3400, 3360, 3320, 2935, 2890, 2520, 2500, 2470, 1595, 1500, 1095, 1070, 1020, 880, 740. ^{1}H-NMR (CD_3OD, 250 MHz): 7.25 (*m*, 4 arom. H); 6.96 (*d*, J(1,2) = 6, H–C(1)); 6.85 (*m*, 1 arom. H); 4.54 (*dd*, J(1,2) = 6, J(2,3) = 6, H–C(2)); 3.91 (*td*, J(5,6) = 6, J(4,5) = 1.5, H–C(5)); 3.87 (*dd*, J(2,3) = 6, J(3,4) = 8.5, H–C(3)); 3.65 (*dd*, J(3,4) = 8.5, J(4,5) = 1.5, H–C(4)); 3.62 (*d*, J(6.5) = 6, 2 H–C(6)); 3.31 (*s*, Me). ^{13}C-NMR (CD_3OD, 90 MHz): 149.9 (*s*, C(1)); 136.6 (*d*, J = 163, arom. C); 129.9 (2*d*, J = 158, 2 arom. C); 121.4 (*d*, J = 161, arom. C); 116.5, (*d*, J = 163, C(1)); 75.0 (*d*, J = 140); 74.7 (*d*, J = 145); 72.7 (*d*, J = 148); 72.1 (*d*, J = 142); 64.8 (*t*, J = 141, C(6)); 33.64 (*q*, J = 137, CH_3). MS (70 eV): 284 (2, $M^{+\cdot}$), 163 (10), 107 (100), 106 (96), 77 (66), 61 (26), 51 (81). Anal. calc. for $C_{13}H_{10}N_2O_5$ (284.31): C 54.92, H 7.09, N 9.85, O 28.14; found: C 54.94, H 7.14, N 9.73, O 28.19.

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