THE EPOXIDE RING OPENING OF 2-O-ACYL-1,6 : 3,4-DIANHYDRO-β-D-GALACTOPYRANOSES

M.Prystaš, H.Gustafsson* and F.Šorm

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague 6

Received July 14th, 1970

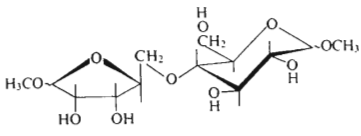
Reaction of 2-O-acyl-1,6 : 3,4-dianhydro-β-D-galactopyranoses *IX* and *X* with anhydrous hydrogen chloride in benzene afforded the chlorohydrins *XIII* and *XIV* of a *galacto*-configuration. Treatment of galactopyranoses *IX* and *X* with alcohols in the presence of boron trifluoride etherate led to 2-O-acyl-1,6-anhydro-β-D-gulopyranosides *XXVII* and *XXIII*, characterised in the form of triacyl derivatives *XXVI* and *XXIV* or as the free 1,6-anhydro-β-D-gulopyranose (*XXV*). The same compounds *XXIII* and *XXVII* are also formed by simple action of Lewis acid and the subsequent hydrolysis. Participation of acyl groups is assumed in both reactions mentioned.

In connection with the proposed synthesis of exotoxin from *Bacillus thuringiensis*, we were interested[1] particularly in the preparation of the unusual sugar fragment containing an ethereal linkage which connects the methyl riboside and the methyl glucoside fragment at positions 5 and 4, respectively. This sugar fragment was obtained in our Institute[2,3] by the action of methanolic hydrogen chloride on exotoxin and shown to represent an anomeric mixture according to the formula *I*, the anomer with the β- and α-configuration at the anomeric centers 1 and 1′, resp., being the predominant component. The structure of the fragment *I* was confirmed[2,3] by hydrolysis and the subsequent conversion to the corresponding flavazole and substituted ribonolactone as well as by the formation of the acetonide triacetate *II* the NMR spectrum of which was successfully used to determine the configuration at anomeric centers. In the synthesis of the fragment derivative *II*, use was made of the *trans*-diaxial opening of the epoxide ring of 1,6 : 3,4-dianhydro-β-D-galactopyranoses *IV* and *VII* carrying at position 2 the non-participating benzyl and *p*-toluenesulfonyl group, resp. The epoxide ring opening of compound *IV* was readily

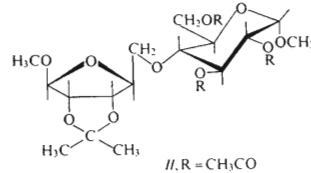
* Domicile address: Chemical Institute, University of Uppsala, Sweden.

accomplished under alkaline conditions, namely, with sodium in dimethyl sulfoxide while the analogous reaction of compound *VII* with the carbonate *VI* was performed under the acidic catalysis of boron trifluoride etherate. Compounds *V* and *VIII* were then converted in several steps to the required compound *II* which was in every respect identical with a specimen obtained from the naturally occurring material.

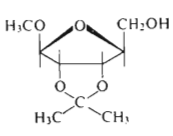
Investigations on the epoxide ring opening of dianhydropyranoses have been now extended on substances carrying participating groups in the neighborhood of the epoxide ring. As the starting material, 2-O-acetyl- (*IX*) and 2-O-benzoyl-1,6 : 3,4-dianhydro-β-D-galactopyranose (*X*) has been used. The epoxides *IX* and *X*, obtained by acylation in pyridine of the readily accessible free 1,6:3,4-dianhydro-β-D-galactopyranose[4], were subjected to the action of anhydrous hydrogen chloride in benzene as solvent to afford chlorohydrins which were ascribed the structure of 2-O-acetyl-



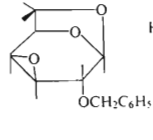
I



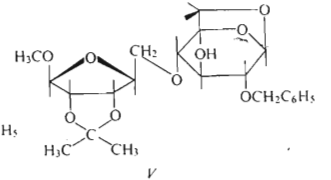
II, R = CH_3CO



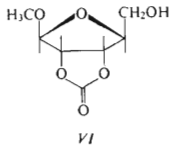
III



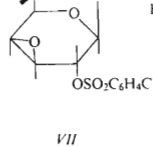
IV



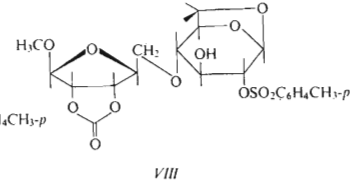
V



VI



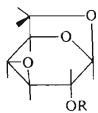
VII



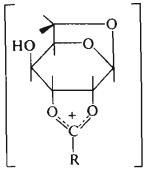
VIII

(*XIII*) and 2-O-benzoyl-3-chloro-3-deoxy-1,6-anhydro-β-D-galactopyranose (*XIV*) on the basis of NMR spectra. Since both chlorohydrins XIII and *XIV* possess the *galacto*-configuration, the epoxide ring opening of compounds *IX* and *X* must necessarily proceed under the participation of vicinal acyl groups *via* the cyclic ion *XI* and *XII*. Nucleophilic attack of the chloride ion from the most accessible side opens the cyclic ions *XI* and *XII* under the formation of *cis*-chlorohydrins *XIII* and *XIV*. When the neighborhood of the epoxide ring is occuppied by a group of a low participating ability as in the case of methyl 3,4-anhydro-α-D-galactopyranoside[5] (*XV*), both possible *trans*-chlorohydrins *XVI* and *XVII* are formed as expected.

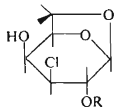
Compound *XIII* was converted into 2,4-di-O-acetyl-3-chloro-3-deoxy-1,6-anhydro-β-D-galactopyranose (*XVIII*) and then into 4-O-benzoyl (*XIX*) and 4-O-*p*-toluenesulfonyl derivative *XX* with resolved NMR spectra. For the same reason, the



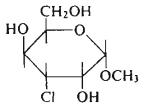
IX, R = CH_3CO
X, R = C_6H_5CO



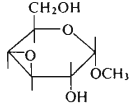
XI, R = CH_3
XII, R = C_6H_5



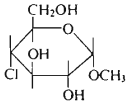
XIII, R = CH_3CO
XIV, R = C_6H_5CO



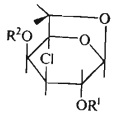
XVI



XV



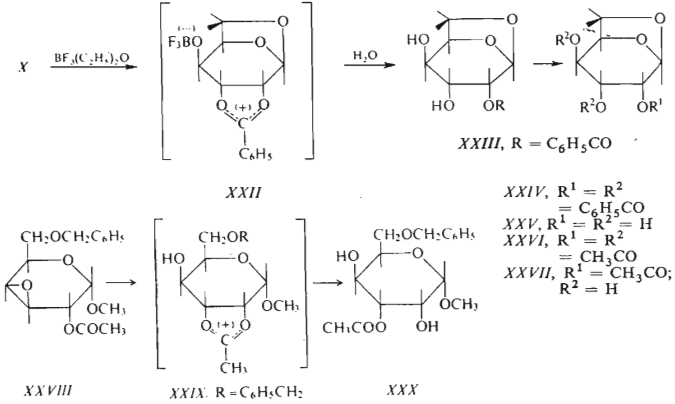
XVII



XVIII, $R^1 = R^2 = CH_3CO$
XIX, $R^1 = CH_3CO$; $R^2 = C_6H_5CO$
XX, $R^1 = CH_3CO$; $R^2 = p\text{-}CH_3C_6H_4SO_2$
XXI, $R^1 = R^2 = C_6H_5CO$

chlorohydrin *XIV* was converted into 2,4-di-O-benzoyl-3-chloro-3-deoxy-1,6-anhydro-β-D-galactopyranose (*XXI*).

We were also interested in the epoxide ring opening of the benzoyl derivative *X* by the action of boron trifluoride etherate. Surprisingly enough, even a catalytic amount of boron trifluoride etherate reacts with the benzoate *X* in benzene to afford after a brief hydrolysis an excellent yield of a compound which was ascribed the structure of 2-O-benzoyl-1,6-anhydro-β-D-gulopyranose (*XXIII*) on the basis of NMR spectra and chemical evidence (*vide infra*). Compound *XXIII* was converted to the known[6] tribenzoate (*XXIV*) and triacetate (*XXVI*) of 1,6-anhydro-β-D-gulopyranose, and the free 1,6-anhydro-β-D-gulopyranose (*XXV*). Also in this epoxide ring opening we assume participation of the benzoyl group under the formation of the cyclic ion *XXII* (Scheme 1). Its hydrolysis may afford the isomeric 3-O-benzoyl-1,6-anhydro-β-D-gulopyranose in addition to the 2-O-benzoyl derivative *XXIII* but we have always isolated only the latter compound. Similarly, reaction of the benzoyl epoxide *X* with boron trifluoride etherate in the presence of alcohols afforded the identical gulose derivative *XXIII* in excellent yields. Consequently, a *trans*-diequatorial epoxide ring opening takes place under the conditions stated. A similar epoxide ring opening under acidic conditions has been studied by Buchanan and Fletcher[7]. Thus, refluxing of the acetyl epoxide *XXVIII* in 80% aqueous acetic acid led to the acetate *XXX*. The authors assume participation of the acetyl group under the formation of the cyclic ion *XXIX* and migration of the acetyl group. The steric course of this epoxide ring opening is thus identical with our case.



SCHEME 1

The analogous reaction of the acetyl epoxide *IX* and boron trifluoride etherate afforded a small amount of an acetyl 1,6-anhydro-β-D-gulopyranose of the most probable structure *XXVII*. Compound *XXVII* was isolated in the form of crystalline 1,6-anhydro-β-D-gulopyranose triacetate (*XXVI*). The reaction mixture contained an additional poorly polar substance as the principal product, melting unsharply above 240°C, $[\alpha]_D^{25}$ +85·2° (chloroform), and giving the same elemental analysis as the starting acetyl derivative *IX*. The isolation was performed by column chromatography on silica gel. As shown by mass spectrum, the substance possesses the double molecular weight when compared with that of compound *IX*. No conclusions, however, could be drawn from the infrared and NMR spectrum.

EXPERIMENTAL

Melting points were taken on a heated microscope stage. Analytical samples were dried for 8 hours at 20°C/0.2 Torr unless stated otherwise.

2-O-Acetyl-1,6 : 3,4-dianhydro-β-D-galactopyranose (*IX*)

A mixture of 1,6 : 3,4-dianhydro-β-D-galactopyranose[4] (2·88 g; 20 mmol), pyridine (30 ml), and acetic anhydride (3 ml) was allowed to stand at room temperature for 15 hours, the residue coevaporated with four 30 ml portions of toluene and finally dissolved in chloroform (50 ml). The chloroform solution was washed with 0·3% aqueous hydrochloric acid (150 ml), dried, and evaporated under diminished pressure. The residue was purified on a column of neutral aluminum oxide (100 g; Brockmann activity III) with the use of 20 : 1 benzene–ethyl acetate. The eluate (250 ml) was evaporated under diminished pressure, the residue dissolved in hot benzene (12 ml), the solution diluted gradually with light petroleum (30 ml), and kept at 0°C overnight to afford 3·25 g (88%) of the acetate *IX*, m.p. 118°C. Optical rotation: $[\alpha]_D^{25}$ −48·4° (*c* 0·51; chloroform). Infrared spectrum: ν(C=O) at 1 762 and 1 739 cm^{-1}. For $C_8H_{10}O_5$ (186·2) calculated: 51·61% C, 5·41% H; found: 51·70% C, 5·31% H.

2-O-Benzoyl-1,6 : 3,4-dianhydro-β-D-galactopyranose (*X*)

A solution of 1,6 : 3,4-dianhydro-β-D-galactopyranose[4] (4 g; 27·8 mmol) in pyridine (40 ml) was treated in one lot with benzoyl chloride (4·5 ml), the reaction mixture cooled down, allowed to stand at room temperature overnight, evaporated under diminished pressure, and the residue diluted with water (200 ml) and benzene (100 ml). The organic layer was washed with 2% aqueous hydrochloric acid and water (200 ml), dried, evaporated under diminished pressure, the residue dissolved in hot toluene (10 ml), and the solution diluted gradually with light petroleum (30 ml) to afford 6·35 g (93%) the benzoate *X*, m.p. 126–128°C. Recrystallisation from the same solvent mixture raised the m.p. value to 127–128°C. Optical rotation: $[\alpha]_D^{25}$ −43·9° (*c* 0·51; chloroform). Infrared spectrum: ν(C=O) at 1 723 cm^{-1}. NMR spectrum (deuteriochloroform): δ 5·37 (s, 1-H, $J_{1,2}$ = 0·7), 5·08 (s, 2-H, $J_{2,3}$ = 0·6), 3·23 (q, 3-H, $J_{3,4}$ = 4·0), 3·67 (t, 4-H, $J_{4,5}$ = 4·9), 4·90 (t, 5-H, $J_{5,6en}$ = 0·6 and $J_{5,6ex}$ = 4·9), 4·06 (d, 6en-H, $J_{6en,ex}$ = 6·5 c.p.s.) and 3·57 p.p.m. (q, 6ex-H). For $C_{13}H_{12}O_5$ (248·2) calculated: 62·90% C, 4·87% H; found: 62·81% C, 4·85% H.

Epoxide Ring Opening of 2-O-Acetyl-1,6 : 3,4-dianhydro-β-D- galactopyranose (*IX*)

A. *With boron trifluoride etherate.* A mixture of the acetyl derivative *IX* (740 mg; 4 mmol), boron trifluoride etherate (40 mg; 0·28 mmol), and benzene (45 ml) was allowed to stand at room temperature for 1 ½ hours and decomposed with 1% aqueous potassium hydrogen carbonate (20 ml). The aqueous solution was extracted with five 20 ml portions of chloroform, the extract dried, and evaporated under diminished pressure. The residue was chromatographed on a column of silica gel (15 g; deactivated with 10% of water) with the use of 7 : 3 benzene–ethyl acetate (100 ml), 1 : 1 benzene–ethyl acetate (100 ml; fractions 1—19), and ethyl acetate (120 ml; fractions 20—44). The chromatographically homogeneous fractions 28—30 (thin-layer chromatography on loose silica gel: R_F value 0·08 in benzene–ethyl acetate 1 : 1) contain compound *XXVII* (55 mg). The oily residue was coevaporated with pyridine (10 ml) and then mixed with pyridine (5 ml) and acetic anhydride (0·25 ml). The mixture was allowed to stand at room temperature for 10 hours, evaporated under diminished pressure, the residue coevaporated with three 10 ml portions of toluene, and the residue chromatographed on a column of silica gel (5 g; deactivated with 10% water) with the use of 4 : 1 benzene–ethyl acetate (50 ml; fractions 1—10). The chromatographically homogeneous fractions (thin-layer chromatography on loose silica gel: R_F value 0·3 in the same solvent mixture) were evaporated under diminished pressure and the residue crystallised from ether to afford 71 mg 1,6-anhydro-β-D-gulopyranose triacetate (*XXVI*), m.p. 114—115°C, undepressed on admixture with an authentic sample.[6] Optical rotation: $[\alpha]_D^{25}$ +22·5° (*c* 0·50; chloroform). Infrared spectrum: ν(C=O) at 1 753 cm^{-1}. For $C_{12}H_{16}O_8$ (288·3) calculated: 50·00% C, 5·59% H; found: 50·03% C, 5·66% H. The original benzenic solution was dried and applied to a column of silica gel (30 g) of the above activity. The column was eluted with benzene (100 ml) and 9 : 1 benzene–ethyl acetate (250 ml; fractions 1—25). The homogeneous fractions 14—22 were evaporated under diminished pressure and the solid residue crystallised from a mixture of benzene and light petroleum. Mother liquors were processed as usual. Overall yield, 397 mg (54%) of compound *XXXI*, melting unsharply above 240°C. Optical rotation: $[\alpha]_D^{25}$ +85·2° (*c* 0·50; chloroform). Infrared spectrum: ν(C=O) is absent. For $C_8H_{10}O_5$ (186·2) calculated: 51·61% C, 5·41% H; found: 51·76% C, 5·47% H.

B. *With anhydrous hydrogen chloride.* A mixture of the acetyl derivative *IX* (372 mg; 2·00 mmol), benzene (20 ml), and ethereal 7M-HCl (2 ml) was allowed to stand at room temperature for 15 hours, evaporated under diminished pressure, the residue dissolved in chloroform (40 ml), the solution washed with water (5 ml), dried, evaporated under diminished pressure, and the residue chromatographed on a column of silica gel (40 g; deactivated by the addition of 10% water). The column was washed successively with 19 : 1 benzene–ethyl acetate (250 ml) and 4 : 1 benzene–ethyl acetate (350 ml; fractions 1—28). The homogeneous fractions 18—26 (thin-layer chromatography on silica gel: R_F value 0·15 in 4 : 1 benzene–ethyl acetate and 0·5 in 1 : 1 benzene–ethyl acetate) were combined, evaporated under diminished pressure, and the residue crystallised from 1 : 2 ether–light petroleum to afford 287 mg (64%) of the chlorohydrin *XIII*, m.p. 107—108°C (did not change on recrystallisation). NMR spectrum in deuteriochloroform: δ 5·43 (m, 1-H, $J_{1,2}$ = 1·4), 5·11 (m, 2-H, $J_{2,3}$ = 0·5), 4·20—4·40 (m, 3-H, 4-H), 4·46 (d, 5-H), 4·49 (d, 6en-H, $J_{5,6}$en = 0·4, $J_{6en,6ex}$ = 7·8), and 3·67 p.p.m. (q, 6ex-H, $J_{5,6ex}$ = 4·9 c.p.s.). For $C_8H_{11}ClO_5$ (222·6) calculated: 43·17% C, 4·98% H, 15·93% Cl; found: 43·16% C, 4·97% H, 15·87% Cl.

2,4-Di-O-acetyl-3-chloro-3-deoxy-1,6-anhydro-β-D-galactopyranose (*XVIII*)

A solution of the chlorohydrin *XIII* (145 mg; 0·65 mmol) in pyridine (3 ml) was treated with acetic anhydride (0·3 ml), the reaction mixture allowed to stand at room temperature for 10 hours, evaporated under diminished pressure, the residue coevaporated with three 10 ml portions

of toluene, and finally chromatographed on a column of silica gel (10 g; deactivated by the addition of 12% water). The column was eluted with benzene (60 ml; fractions 1–12) and then 9 : 1 benzene–ethyl acetate (80 ml; fractions 13–23). The homogeneous fractions 14–16 were combined, evaporated under diminished pressure, and the residue crystallised from ether–light petroleum (2 : 5) to afford a 96% yield of the diacetate *XVIII*, m.p. 104–105°C. Infrared spectrum: ν(C=O) at 1754 and 1738 cm^{-1}. For $C_{10}H_{13}ClO_6$ (264·7) calculated: 45·38% C, 4·93% H, 13·40% Cl; found: 45·63% C, 4·89% H, 13·22% Cl.

2-O-Acetyl-4-O-benzoyl-3-chloro-3-deoxy-1,6-anhydro-β-D-galactopyranose (*XIX*)

A mixture of the chlorohydrin *XIII* (100 mg), benzoyl chloride (0·10 ml), and pyridine (3 ml) was allowed to stand at room temperature for 15 hours and then decomposed by a drop of water. After 10 minutes, the mixture was evaporated under diminished pressure, the residue dissolved in chloroform (10 ml), the solution washed with 1% aqueous sodium hydrogen sulfate until acid to the Congo Red paper, and then with saturated aqueous potassium hydrogen carbonate. After drying, the solution was evaporated under diminished pressure and the residue chromatographed on a column of silica gel (10 g; deactivated by the addition of 10% water). The column was eluted with benzene (100 ml) and then 19 : 1 benzene–ethyl acetate (100 ml; fractions 1–11). The chromatographically homogeneous fractions 2–5 (thin-layer chromatography on silica gel with binder: R_F values 0·25 and 0·42 in benzene–ethyl acetate 20 : 1 and 10 : 1, resp.) were combined, evaporated under diminished pressure, and the residue coevaporated with three 10 ml portions of benzene to afford 105 mg of the product *XIX* in the form of a solid foam. The analytical sample was dried for two days at room temperature and 0·5 Torr over concentrated sulfuric acid and potassium hydroxide pellets. NMR spectrum (deuteriochloroform): δ 5·50 (m, 1-H, $J_{1,2}$ = 1·4), 5·14 (m, 2-H, $J_{2,3}$ = 1·4), 4·54 (m, 3-H, $J_{3,4}$ = 6·2), 5·44 (m, 4-H, $J_{4,5}$ = = 4·5), 4·66 (m, 5-H, $J_{5,6en}$ = 0·5 and $J_{5,6ex}$ = 0·5), 4·66 (m, 6en-H, $J_{6en,6ex}$ = 7·7 c.p.s.) and 3·78 p.p.m. (q, 6ex-H). For $C_{15}H_{15}ClO_6$ (326·8) calculated: 55·12% C, 4·62% H, 10·86% Cl; found: 55·46% C, 4·77% H, 10·45% Cl.

2-O-Acetyl-4-O-*p*-toluenesulfonyl-3-chloro-3-deoxy-1,6-anhydro-β-D-galactopyranose (*XX*)

A mixture of the chlorohydrin *XIII* (115 mg), *p*-toluenesulfonyl chloride (160 mg) and pyridine (2 ml) was heated at 65°C for 4 hours and then processed similarly to the preceding paragraph to afford 102 mg of glassy compound *XX*. Thin-layer chromatography on silica gel with binder: R_F values 0·16 and 0·30 in benzene–ethyl acetate 20 : 1 and 10 : 1, resp. NMR spectrum (deuteriochloroform): δ 5·40 (m, 1-H, $J_{1,3}$ = 1·3), 5·05 (m, 2-H, $J_{2,3}$ = 1·3), 4·11 (dq, 3-H, $J_{3,4}$ = 5·9), 4·98 (t, 4-H, $J_{4,5}$ = 4·2), 4·48 (t, 5-H, $J_{5,6en}$ = 9·1 and $J_{5,6ex}$ = 5·0), 4·54 (d, 6en-H, $J_{6en,ex}$ = = 8·2 c.p.s.) and 3·66 p.p.m. (q, 6ex-H). For $C_{15}H_{17}ClO_7S$ (376·9) calculated: 47·80% C, 4·55% H, 8·51% S; found: 48·35% C, 4·86% H, 8·30% S.

Epoxide Ring Opening of 2-O-Benzoyl-1,6 : 3,4-dianhydro-β-D-galactopyranose (*X*)

A. *With boron trifluoride etherate.* A mixture of the benzoyl epoxide *X* (397 mg; 2·0 mmol), benzene (20 ml, and 1% benzenic boron trifluoride etherate (1·8 ml; 0·126 mmol) was allowed to stand at room temperature for 20 hours, decomposed with water (1 ml), washed with three 3 ml portions of water, the aqueous washings combined, and extracted with five 5 ml portions of chloroform. The chloroform extracts were dried, evaporated under diminished pressure, and the residue crystallised from 1 : 4 chloroform–ethanol to afford 2-O-benzoyl-1,6-anhydro-β-D-gulopyranose (*XXIII*), m.p. 151–152°C (after drying for 2 hours at 90°C/0·1 Torr). The

mother liquors were processed as usual; overall yield of compound *XXIII*, 74%. Optical rotation: $[\alpha]_D^{25} + 96°$ (*c* 0·30; chloroform). Infrared spectrum; ν(C=O) at 1721 cm^{-1} and ν(O—H) bonded at 3585 and 3460 cm^{-1}. NMR spectrum (deuteriochloroform): δ 5·49 (d, 1-H, $J_{1,2} = 2·3$), 5·22 (q, 2-H, $J_{2,3} = 4·0$), 3·90—4·10 (m, 3-H and 4-H), 4·48 (m, 5-H, $J_{4,5} = 3·6$, $J_{5,6en} = 1·0$, $J_{5,6ex} = 5·0$) 4·08 (d, 6en-H, $J_{6en,6ex} = 7·7$ c.p.s.) and 3·63 p.p.m. (q, 6ex-H). For $C_{13}H_{14}O_6$ (266·3) calculated: 58·65% C, 5·30% H; found 58·72% C, 5·27% H.

An analogous reaction of the benzoyl epoxide *X* with methanol (10 mol %; 200 mol %) in the presence of boron trifluoride etherate (3 mol %) in benzene afforded compound *XXIII* in the yield of 42 and 51%, respectively.

B. *With anhydrous hydrogen chloride.* A mixture of the epoxide *X* (500 mg), ethereal 7M-HCl (2 ml), and benzene (20 ml) was allowed to stand at room temperature for 15 hours, evaporated under diminished pressure, the residue dissolved in benzene (10 ml), the solution washed with three 10 ml portions of water, dried, and applied to a column of silica gel (40 g; deactivated by the addition of 11% water). The column was eluted successively with benzene (200 ml), 20 : 1 benzene–ethyl acetate (250 ml; fractions 1—19), and 9 : 1 benzene–ethyl acetate (280 ml; fractions 20 to 39). The chromatographically homogeneous fractions 24—33 (thin-layer chromatography on silica gel with binder: R_F value 0·35 in 4 : 1 benzene–ethyl acetate) were combined, evaporated under diminished pressure, and the residue crystallised from a mixture of ether and light petroleum (0°C; 10 hours) to afford the compound *XIV* (460 mg; 81%), m.p. 87—90°C. Infrared spectrum: ν(C=O) at 1724 cm^{-1}. NMR spectrum (deuteriochloroform): δ 5·53 (m, 1-H, $J_{1,2} = 1·3$), 5·33 (m, 2-H, $J_{2,3} = 1·5$), 4·15—4·45 (m, 3-H and 4-H), 4·48 (d, 5-H, $J_{5,6en} = 0·4$ and $J_{5,6ex} = 5·0$), 4·50 (d, 6en-H, $J_{6en,6ex} = 7·8$ c.p.s.) and 3·68 (q, 6ex-H). For $C_{13}H_{13}ClO_5$ (284·7) calculated: 54·84% C, 4·60% H, 12·45% Cl; found: 54·91% C, 4·68% H, 12·49% Cl.

2,4-Di-O-benzoyl-3-chloro-3-deoxy-1,6-anhydro-β-D-galactopyranose (*XXI*)

A mixture of the chlorohydrin *XIV* (350 mg), benzoyl chloride (0·30 ml), and pyridine (3 ml) was allowed to stand at room temperature for 10 hours, decomposed with water (2 drops), and evaporated under diminished pressure. The residue was dissolved in benzene (10 ml), the solution washed with 1% aqueous sodium hydrogen sulfate until acid to the Congo Red paper and then with saturated aqueous potassium hydrogen carbonate (5 ml), dried, and applied to a column of silica gel (15 g; deactivated by the addition of 10% water). The elution was performed with benzene (90 ml; fractions 1—25). The chromatographically homogeneous fractions 11—16 (thin-layer chromatography on silica gel with binder: R_F value 0·25 in benzene) were combined, evaporated under diminished pressure, and the residue coevaporated with anhydrous benzene (10 ml) to afford compound *XXI* (87%; an oil). Optical rotation: $[\alpha]_D^{25} + 1·3°$ (*c* 0·47; chloroform). Infrared spectrum: ν(C=O) at 1725 cm^{-1}. For $C_{20}H_{17}ClO_6$ (388·8) calculated: 61·78% C, 4·41% H; found: 62·31% C, 4·58% H.

2,3,4-Tri-O-benzoyl-1,6-anhydro-β-D-gulopyranose (*XXIV*)

A mixture of the monobenzoate *XXIII* (100 mg), benzoyl chloride (0·20 ml), and pyridine (4 ml) was allowed to stand at room temperature for one day, decomposed with water (0·1 ml), and evaporated under diminished pressure. The residue was dissolved in chloroform (10 ml), the solution washed with 1% aqueous sodium hydrogen sulfate until acid to the Congo Red paper and then with saturated aqueous potassium hydrogen carbonate, dried and applied to a column of neutral aluminum oxide (7 g; Brockmann activity II—III). Elution was performed with 30 : 1 benzene–ethyl acetate (50 ml). The eluate was evaporated under diminished pressure and the residue crystallised from a mixture of chloroform and ethanol to afford 92% of the tribenzoate

XXIV, m.p. 158—160°C. Optical rotation: $[\alpha]_D^{25}$ +213·9° (*c* 0·49; chloroform), in accordance with the reported[6] value. NMR spectrum in deuteriochloroform: δ 5·60—6·00 (m, 1,2,3,4-H), 4·91 (t, 5-H, $J_{4,5}$ = 3·8, $J_{5,6en}$ = 0·6, and $J_{5,6ex}$ = 4·8), 4·33 (d, 6en-H, $J_{6en,6ex}$ = 8·0 c.p.s.), and 3·84 p.p.m. (q, 6ex-H). For $C_{27}H_{22}O_8$ (474·5) calculated: 68·35% C, 4·67% H; found: 68·47% C, 4·78% H.

1,6-Anhydro-β-D-gulopyranose (*XXV*)

The ester *XXIII* (825 mg) was dissolved in methanol (25 ml) and methanolic 1M-$NaOCH_3$ (0·2 ml), the reaction mixture allowed to stand at room temperature for 4 hours, neutralised by the addition of Amberlite IRC-50 (H^+) ion exchange resin, filtered, the filtrate evaporated under diminished pressure, the residue coevaporated with three 10 ml portions of 50% aqueous ethanol, and finally crystallised from ethanol (2 ml) to afford 90% of compound *XXV*, m.p. 154—155°C. Optical rotation: $[\alpha]_D^{25}$ +48·6° (water, *c* 0·50), in accordance with literature[6]. For $C_6H_{10}O_5$ (162·1) calculated: 44·45% C, 6·22% H; found: 44·62%, 6·27% H.

The authors wish to thank Dr M. Masojídková for measurement and interpretation of NMR spectra (Varian HA-100). Infrared spectra were taken on a UR-10 spectrophotometer. Elemental analyses were performed in the Analytical Department (Dr J. Horáček, Head) of this Institute by Mrs V. Rusová and Mrs E. Šípová.

REFERENCES

1. Prystaš M., Šorm F.: This Journal *36*, 1448 (1971).
2. Farkaš J., Šebesta K., Horská K., Samek Z., Dolejš L., Šorm F.: This Journal *34*, 1118 (1969).
3. Farkaš J., Šebesta K., Horská K., Samek Z., Dolejš L., Šorm F.: Unpublished results.
4. Höök J. E., Lindberg B.: Acta Chem. Scand. *20*, 2363 (1966).
5. Buchanan J. G.: J. Chem. Soc. *1958*, 2511.
6. Stewart L. C., Richtmyer N. K.: J. Am. Chem. Soc. *77*, 1021 (1955).
7. Buchanan J. G., Fletcher R.: J. Chem. Soc. *1965*, 6316.

Translated by J. Plíml.