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REACTION OF ACYLATED METHYL ARABINOSIDES WITH HYDROGEN BROMIDE

KLAUS BOCK AND CHRISTIAN PEDERSEN

Department of Organic Chemistry, Technical University of Denmark, 2800 Lyngby (Denmark)

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ABSTRACT

Treatment of methyl tri-*O*-acetyl-β-D-arabinopyranoside (**1a**) with hydrogen bromide in benzene or in acetic acid gave, in addition to the pyranosyl bromide (**2a**), a considerable proportion of tri-*O*-acetyl-D-arabinofuranosyl bromide (**5**). Similar treatment of methyl tri-*O*-benzoyl-β-D-arabinopyranoside (**1b**) gave a good yield of the pyranosyl bromide (**2b**); no furanoid derivative was formed. Ring contraction also took place when methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-arabinopyranoside (**7**) was treated with hydrogen bromide, whereas the isomeric 3-*O*-acetyl-2,4-di-*O*-benzoyl compound (**12**) gave the pyranosyl bromide **13** in high yield. Thus, methyl pyranosides with an *O*-acetyl group at C-4 undergo ring contraction on treatment with hydrogen bromide. The corresponding compounds with *O*-benzoyl groups at C-4 gave pyranosyl bromides only.

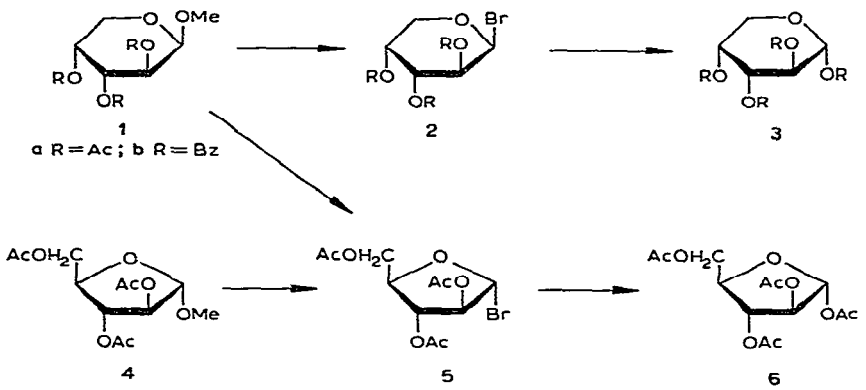
INTRODUCTION

The preparation of acylated glycosyl bromides by treatment of fully acylated pyranoses or furanoses with hydrogen bromide, usually in glacial acetic acid, is well known[1]. Since acylated methyl glycosides are sometimes more readily available than the fully acylated sugars, it is of interest to be able to prepare glycosyl bromides from glycosides. The reaction of acylated methyl glycosides with hydrogen bromide has, however, not been extensively investigated. Treatment of benzoylated methyl pentofuranosides with hydrogen bromide in acetic acid gave good yields of furanosyl bromides[2–5]; the corresponding acetates apparently have not been studied. The reaction of acylated methyl glycopyranosides with hydrogen bromide has been little studied[1], and Zemplén[6] reported that methyl tetra-*O*-acetyl-β-D-glucopyranoside did not give tetra-*O*-acetyl-α-D-glucopyranosyl bromide when treated with hydrogen bromide in acetic acid. We now report on the reaction of a number of acylated methyl β-D-arabinopyranosides with hydrogen bromide.

RESULTS AND DISCUSSION

Reaction of methyl tri-*O*-acetyl-β-D-arabinopyranoside (**1a**) with hydrogen bromide in benzene gave a mixture of unstable bromides which were at once converted

into the corresponding 1-acetates by treatment with silver acetate. Subsequent chromatography gave 28% of a mixture of the tetra-acetylated pyranose **3a** and the corresponding furanose **6** in a ratio of 3:2. The two products could not be separated but were identified on the basis of their n.m.r. spectra. In addition, a low yield of 2,3,5-tri-*O*-acetyl-D-arabinofuranose was obtained, probably formed by hydrolysis of the furanosyl bromide **5**. Thus, treatment of **1a** with hydrogen bromide in benzene gives some of the furanosyl bromide **5** in addition to the expected pyranosyl bromide **2a**. Similar results were obtained when **1a** was treated with hydrogen bromide in glacial acetic acid, but the amount of furanoid derivatives obtained was somewhat smaller.

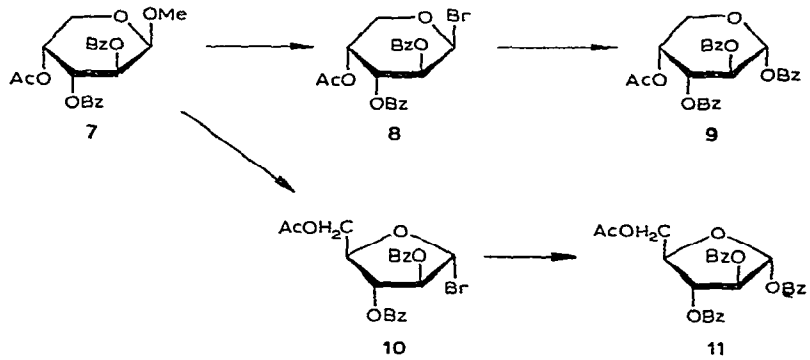


When the benzoylated methyl glycoside **1b** was treated with hydrogen bromide in benzene or in acetic acid, a high yield of tri-*O*-benzoyl-β-D-arabinopyranosyl bromide (**2b**) was obtained. No furanoid derivatives were found.

Treatment of methyl tri-*O*-acetyl-α-D-arabinofuranoside (**4**) with hydrogen bromide, followed by reaction with silver acetate, gave mainly furanoid derivatives; only traces of pyranoid derivatives could be detected. The total yields were rather low, probably due to the instability of the bromide **5**.

Tri-*O*-acetyl-β-D-arabinopyranosyl bromide (**2a**) did not undergo ring contraction when treated with hydrogen bromide in benzene or in glacial acetic acid. Hence the ring contraction with the methyl glycoside **1a** must take place before it is converted into the bromide **2a**. The conversion of **1a** into **4** may proceed *via* the protonated intermediates **15**, **16**, and **17**. The oxocarbonium ions **16** and **17** are probably relatively stable, whereas the corresponding bromocarbonium ions that might be formed from the bromide (**2a**) would be much less stable. Therefore, **2a** does not undergo ring contraction. The fact that the benzoate **1b** does not undergo ring contraction is probably because benzoyl groups have less tendency to migrate than acetyl groups. This view was confirmed by the results obtained on treatment of mixed esters with hydrogen bromide. Treatment of methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-arabinopyranoside (**7**) with hydrogen bromide in benzene, followed by reaction with silver benzoate, gave ~35% of furanoid derivatives, mostly 5-*O*-acetyl-1,2,3-tri-*O*-benzoyl-

α-D-arabinofuranose (**11**). In addition, the expected pyranoid derivative **9** was obtained. On the other hand, when methyl 3-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-arabinopyranoside (**12**) was treated with hydrogen bromide and silver acetate, the pyranoid derivative **14** was formed in high yield as the sole product. In the latter reaction, an *O*-benzoyl group is present at C-4 in the starting material, and this does not undergo acyl migration; therefore, no furanoid derivatives are formed.



The bromides **5** and **10** were only obtained as crude products due to their instability. The n.m.r. data (Table I) show that they must be arabinofuranosyl bromides. This is seen by comparison with the data for tri-*O*-benzoyl-α-D-arabinofuranosyl bromide (Table I) and from the results of Stevens and Fletcher[16]. Furthermore, treatment of the bromide **10** with methanol gave methyl 5-*O*-acetyl-2,3-di-*O*-benzoyl-α-D-arabinofuranoside, identical with a sample synthesized in an authentic manner (see Experimental).

Similar results were obtained with other methyl pentopyranosides. Acetylated methyl α-D-lyxopyranoside and methyl α-D-xylopyranoside gave considerable amounts of furanoid derivatives when treated with hydrogen bromide. This method therefore cannot be recommended for the preparation of acetylated pyranosyl bromides.

TABLE I

N.M.R. DATA[a] FOR ARABINOSE DERIVATIVES

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{1,3}$	$J_{1,4}$
7	5.19	5.66	5.85	5.56	3.85	4.05	3.5	10.5	3.5	2.0	1.3	13.0		
12	5.22	5.53	5.73	5.68	3.90	4.09	3.5	10.5	3.4	2.0	1.5	13.1		
[b]	5.15	5.6 — 5.8		4.33	3.80	4.00				2.0	1.3	12.8		
[c]	5.08	5.44	4.44	5.46	3.8 — 4.0		3.8	10.0	3.8					
9	6.25	5.91	5.69	5.59	4.30	4.03	5.5	7.2	3.3	5.0	2.8	12.2		
14	5.95	5.71	5.45	5.65	5.24	5.00	7.0	9.0	3.8	3.0	1.9			
4	4.93	5.07	5.00	4.25	4.44	4.22	~0	1.5	5.0	5.8	2.0	12.5		
6	6.21	5.23	5.08	4.35	4.29	4.38	0.8	1.7	4.6	5.4	3.0	12.6		
11	6.74	5.80	5.54	4.3 ———		4.8	0.5	1.0	3.2					
5	6.35	5.50	5.01	4.52	4.2 — 4.5		~0	0.9	4.5				0.8	0.6
10	6.60	5.93	5.49	4.72	4.49	4.63	~0	0.7	4.0	5.8	3.4	12.0	0.7	0.6
[d]	6.87	6.00	5.77	4.95	4.81	4.92	~0	0.8	4.4	5.0	2.5	12.2	0.7	0.7
[e]	5.12	5.52	5.46	4.32	3.95 – 4.05		0.4	1.6	4.8	4.0	4.0		0.6	
[f]	5.16	5.50	5.43	4.3 ———		4.7	0.4	1.3	4.4				0.6	

[a]Chemical shifts (δ values) for solutions in chloroform-*d*, and observed, first-order coupling constants (Hz). [b]Methyl 2,3-di-*O*-benzoyl-β-D-arabinopyranoside. [c]Methyl 2,4-di-*O*-benzoyl-β-D-arabinopyranoside. [d]Tri-*O*-benzoyl-α-D-arabinofuranosyl bromide in acetone-d_6. [e]Methyl 2,3-di-*O*-benzoyl-α-D-arabinofuranoside. [f]Methyl 5-*O*-acetyl-2,3-di-*O*-benzoyl-α-D-arabinofuranoside.

Szabó *et al.*[7] reported that dibromomethyl methyl ether reacted with a number of glycosides to give good yields of acetylated pyranosyl bromides. In agreement herewith, we found that treatment of **1a** with the latter reagent gave a good yield of tri-*O*-acetyl-β-D-arabinopyranosyl bromide (**2a**). It is, however, important that the reaction is carried out under the conditions specified by Szabó *et al.*[7]. Under other conditions, treatment of **1a** or **2a** with dibromomethyl methyl ether leads to formation of derivatives of 2-bromo-2-deoxy-D-xylopyranose. These results will be published in a forthcoming paper.

EXPERIMENTAL

Melting points are uncorrected. For thin-layer chromatography (t.l.c.), Silica Gel PF_{254} (Merck) was used, and preparative t.l.c. was conducted with 1-mm layers on 20 × 40 cm plates. Compounds were detected with u.v. light or by charring with a hot wire. N.m.r. spectra were recorded with Varian A-60 and HA-100 instruments, with tetramethylsilane as the internal reference.

Methyl tri-O-acetyl-α-D-arabinofuranoside (**4**). — Methyl tri-*O*-benzoyl-α-D-arabinofuranoside[2,8] (3.0 g) was kept overnight at room temperature in 1% methanolic sodium methoxide (30 ml). The solution was then neutralized with Amberlite IR-120(H^+) resin and evaporated. The residue was extracted with pentane, and the insoluble material was acetylated with acetic anhydride (5 ml) in pyridine (10 ml). Work-up in the usual way gave a syrupy product (1.79 g, 98%); a sample, purified

by preparative t.l.c. with ether–pentane (2:1), had $[\alpha]_D^{23}$ +68.0° (*c* 2.5, chloroform). The L enantiomer has been described by Williams and Jones[9].

Anal. Calc. for $C_{12}H_{18}O_8$: C, 49.66; H, 6.25. Found: C, 49.47; H, 6.12.

Dibenzoylation of methyl β-D-arabinopyranoside[10]. — A solution of methyl β-D-arabinopyranoside (1.119 g) in pyridine (6 ml) was cooled in ice while benzoyl chloride (1.55 ml, 2 equiv.) was added during 10 min. The mixture was then kept overnight at room temperature and worked up in the usual way to give methyl 2,3-di-*O*-benzoyl-β-D-arabinopyranoside[10] (1.045 g, 41%), m.p. 129–135° (from ethanol). Two additional recrystallizations from ethanol gave a product with m.p. 137–138°, $[\alpha]_D^{21}$ −214° (*c* 1.7, chloroform); lit.[10] for the L enantiomer, m.p. 141–142°, $[\alpha]_D^{20}$ +210°. The material in the mother liquor was separated into two fractions by preparative t.l.c. with ether–pentane (2:1). The fast-moving fraction gave methyl 2,4-di-*O*-benzoyl-β-D-arabinopyranoside as a syrup (190 mg, 7.5%). The product was identified by its n.m.r. spectrum (Table I). The next fraction gave an additional amount (523 mg, 20%) of the 2,3-dibenzoate, m.p. 133–135°.

Methyl 4-O-acetyl-2,3-di-O-benzoyl-β-D-arabinopyranoside (**7**). — Methyl 2,3-di-*O*-benzoyl-β-D-arabinopyranoside (935 mg) was acetylated conventionally with acetic anhydride (3 ml) in pyridine (5 ml). The syrupy product (1.03 g, 98%) had $[\alpha]_D^{20}$ −186.3° (*c* 2.5, chloroform).

Anal. Calc. for $C_{22}H_{22}O_8$: C, 63.77; H, 5.35. Found: C, 64.05; H, 5.03.

Methyl 3-O-acetyl-2,4-di-O-benzoyl-β-D-arabinopyranoside (**12**). — Conventional acetylation of methyl 2,4-di-*O*-benzoyl-β-D-arabinopyranoside (190 mg) gave 200 mg of product. Crystallization from ether–pentane gave **12** (135 mg, 64%), m.p. 86–87°, $[\alpha]_D^{21}$ −242.4° (*c* 0.5, chloroform).

Anal. Found: C, 63.57; H, 5.28.

5-O-Acetyl-1,2,3-tri-O-benzoyl-α-D-arabinofuranose (**11**). — Methyl α-D-arabinofuranoside[8,9] (1.09 g) was dissolved in pyridine (20 ml) and trityl chloride (2.0 g) was added. The mixture was stirred at room temperature for 48 h and then heated to 50° for 1 h. Benzoyl chloride (2.3 ml) was then added and the mixture was stirred for 24 h at room temperature. Work up in the usual manner gave crude methyl 2,3-di-*O*-benzoyl-5-*O*-trityl-α-D-arabinofuranoside (4 g).

This product (3.6 g) was boiled for 10 min with 80% aqueous acetic acid (40 ml). The solution was then diluted with ice–water and extracted with chloroform. The extract was washed with water and aqueous sodium hydrogen carbonate, dried, and evaporated. A solution of the product in tetrachloromethane (20 ml) was kept overnight at 5°. The triphenylmethanol was then filtered off, the solvent was evaporated, and the residue (2.31 g) was purified by preparative t.l.c. with ether–pentane (2:1). The slow-moving fraction gave syrupy methyl 2,3-di-*O*-benzoyl-β-D-arabinofuranoside (1 g, 48%), the structure of which was confirmed by its n.m.r. spectrum (Table I).

Acetylation of this product (873 mg) with acetic anhydride (2 ml) in pyridine (3 ml) gave crude methyl 5-*O*-acetyl-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (880 mg). The product, purified by preparative t.l.c. with ether–pentane (1:1), was a syrup, $[\alpha]_D^{24}$ −31.5° (*c* 5.4, chloroform). The n.m.r. data are given in Table I.

Anal. Calc. for $C_{22}H_{22}O_8$: C, 63.77; H, 5.35. Found: C, 63.52; H, 5.47.

A solution of the latter product (319 mg) in a mixture of dichloromethane (3 ml) and 30% hydrogen bromide in acetic acid (3 ml) was kept for 90 min at room temperature. It was then diluted with dichloromethane, washed with ice–water and aqueous sodium hydrogen carbonate, dried, and evaporated. The crude product (**10**, 312 mg; n.m.r. data given in Table I) was dissolved in acetonitrile and stirred with silver benzoate (1.0 g) overnight at room temperature. Filtration and evaporation gave a crude product (351 mg) which was purified by preparative t.l.c. with ether–pentane (2:1). The main fraction gave syrupy **11** (200 mg, 52%), $[\alpha]_D^{21}$ +23.4° (*c* 1.6, chloroform).

Anal. Calc. for $C_{28}H_{24}O_9$: C, 66.67; H, 4.80. Found: C, 66.45; H, 4.98.

Alternatively, the bromide **10** (175 mg) was treated with methanol (10 ml) containing silver carbonate (500 mg) at room temperature for 3 h. Filtration through activated carbon and evaporation gave a crude product which was dissolved in dichloromethane (3 ml), and a mixture (1 ml) of methanol, boron trifluoride etherate, and dichloromethane (1:1:8) was added. After 5 min at room temperature, the reaction mixture was diluted with dichloromethane and washed with aqueous sodium hydrogen carbonate. The solution was then dried and evaporated to give almost pure methyl 5-*O*-acetyl-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (145 mg). Preparative t.l.c. with ether–pentane (1:1) gave 100 mg (60%) of pure product as a syrup, $[\alpha]_D^{24}$ −30.8° (*c* 5.9, chloroform). An n.m.r. spectrum was identical with that of the product described above.

Tri-O-acetyl-β-D-arabinopyranosyl bromide (**2a**). — To a solution of **1a** (750 mg) in chloroform (5 ml) was added zinc chloride (150 mg) and dibromomethyl methyl ether[7] (1.0 ml). The mixture was kept at 70° for 1 h, and was then diluted with dichloromethane, washed with water and aqueous sodium hydrogen carbonate, and dried. Evaporation gave virtually pure **2a** (670 mg, 76%) as seen from an n.m.r. spectrum. No furanoid derivatives could be detected. Two recrystallizations from ether–pentane gave **2a** (310 mg, 36%), m.p. 137–138°, $[\alpha]_D^{21}$ −285° (*c* 1.4, chloroform); lit.[11] for the L enantiomer, m.p. 138–139°, $[\alpha]_D$ +287°.

Reactions with hydrogen bromide. — (*a*) Methyl tri-*O*-acetyl-β-D-arabinopyranoside[12] (**1a**) (300 mg) was dissolved in benzene (6 ml) and hydrogen bromide was passed through the solution for 1 h at room temperature. The solution was then evaporated, and the residue was dissolved in acetonitrile (10 ml) and stirred with silver acetate (2.0 g) for 2 h at room temperature. Filtration and evaporation then gave a product (270 mg) which was separated into two fractions by preparative t.l.c. with ether–pentane (1:1). The fast-moving fraction gave 92 mg (28%) of a 2:3 mixture of the furanose tetra-acetate **6** and the pyranose tetra-acetate **3a**. The two compounds could not be separated and they were identified by comparing the n.m.r. spectrum of the mixture with those of the authentic compounds. The slow-moving fraction gave 2,3,5-tri-*O*-acetyl-D-arabinofuranose (27 mg, 9%) which was identified by n.m.r. spectroscopy. Acetylation gave a mixture of **6** and the corresponding β anomer.

In another experiment, **1a** (408 mg) was dissolved in 4 ml of a 30% solution

of hydrogen bromide in glacial acetic acid. The solution was kept for 1 h at room temperature and was then evaporated, and the residue was treated with silver acetate as described above. Chromatography of the crude product gave 120 mg (27%) of a 1:4 mixture of **6** and **3**. In addition 2,3,5-tri-*O*-acetyl-D-arabinofuranose (89 mg) was isolated.

(*b*) *Methyl tri-*O*-benzoyl-β-*D*-arabinopyranoside*[13] (**1b**). A solution of **1b** (200 mg) in hydrogen bromide–acetic acid (2 ml) was kept for 1 h at room temperature. Evaporation left a crude product (220 mg) which was crystallized from ether–pentane to give tri-*O*-benzoyl-β-D-arabinopyranosyl bromide (**2b**) (180 mg, 82%), m.p. 138–140°. An additional recrystallization gave material having m.p. 145–146°, $[\alpha]_D^{21}$ −352° (*c* 4.3, chloroform); lit.[13] m.p. 147–148°, $[\alpha]_D$ −353°.

Treatment of **1b** with hydrogen bromide in benzene at 5° for 2 h gave **2b** (76%), m.p. 139–140°.

(*c*) *Methyl tri-*O*-acetyl-α-*D*-arabinofuranoside* (**4**). Hydrogen bromide was passed through a solution of **4** (733 mg) in benzene (10 ml) at 5° for 1 h. The benzene was then evaporated and the crude bromide[14] (**5**) (n.m.r. data given in Table I) was treated with silver acetate in acetonitrile as described above. The product (508 mg) was separated into two fractions by preparative t.l.c. with ether–pentane (2:1). The fast-moving fraction gave tetra-*O*-acetyl-α-D-arabinofuranose (**6**) as a syrup (220 mg, 27%), $[\alpha]_D^{23}$ +51.9° (*c* 1.6, chloroform).

Anal. Calc. for $C_{13}H_{18}O_9$: C, 49.05; H, 5.70. Found: C, 49.04; H, 5.77.

The second fraction gave 2,3,5-tri-*O*-acetyl-D-arabinofuranose (70 mg, 10%).

Treatment of **4** with hydrogen bromide in acetic acid, followed by reaction with silver acetate, gave **6** (40%) and tri-*O*-acetyl-D-arabinofuranose (21%).

(*d*) *Methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-β-*D*-arabinopyranoside* (**7**). Hydrogen bromide was passed through a solution of **7** (802 mg) in benzene (15 ml) for 2 h, and the solution was then kept overnight at 5°. Evaporation and treatment with silver benzoate in acetonitrile, as described above, gave a crude product (710 mg). This was separated into three fractions by preparative t.l.c. with ether–pentane (2:1). The fast-moving fraction gave 5-*O*-acetyl-1,2,3-tri-*O*-benzoyl-α-D-arabinofuranose (**11**) (263 mg, 27%). Additional purification by chromatography on a column of aluminia with ether–pentane (1:1) gave the pure product as a syrup, $[\alpha]_D^{24}$ +23.2° (*c* 1.6, chloroform).

Anal. Calc. for $C_{28}H_{24}O_9$: C, 66.67; H, 4.80. Found: C, 66.48; H, 4.96.

An n.m.r. spectrum showed that the product was identical with the authentic sample described above.

The next fraction (98 mg, 10%) was recrystallized from methanol to give 4-*O*-acetyl-1,2,3-tri-*O*-benzoyl-α-D-arabinopyranose (**9**), m.p. 118–119°, $[\alpha]_D^{23}$ −51.3° (*c* 1.2, chloroform).

Anal. Found: C, 66.52; H, 4.63.

The last fraction gave a product (66 mg, 9%) which was shown by n.m.r. spectroscopy to be 5-*O*-acetyl-2,3-di-*O*-benzoyl-D-arabinofuranose. Benzoylation gave a mixture of **11** and the corresponding β anomer.

(*e*) *Methyl 3-O-acetyl-2,4-di-O-benzoyl-β-D-arabinopyranoside* (**12**). Treatment of **12** (164 mg) with hydrogen bromide in benzene, followed by reaction with silver acetate, gave 1,3-di-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-arabinopyranose (**14**) (147 mg, 84%), m.p. 140–143°. The product was recrystallized from ether–pentane; m.p. 145–147°, $[\alpha]_D^{21}$ −154° (*c* 0.9, chloroform); lit.[15] m.p. 148–149°, $[\alpha]_D^{28}$ −153°.

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