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Reaction of Methyl-4-methylene-2,3-*O*-isopropylidene-β-D-ribofuranoside with *N*-Bromosuccinimide in Aqueous Tetrahydrofurane

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Abstract—Methyl-4-methylene-2,3-*O*-isopropylidene-β-D-ribofuranoside prepared from D-ribose reacted in a system NBS–THF–H_2O to give a mixture of stereoisomeric products of regioselective bromohydroxylation of a double bond. The reaction involved a hydrolysis of the glycoside bond, but the acetonide protective group was retained. The mechanism of the selective hydrolysis originating from the ring-chain tautomerism of bromohydrins obtained was proved by the ^{1}H NMR spectra of the stereoisomeric methyl-5-deoxy-5-bromo-4-hydroxy-2,3-*O*-isopropylidene-β-D-ribofuranosides. By crotonic cyclization of the formed masked 1,4-dicarbonyl compounds at heating in benzene in the presence of neutral Al_2O_3 a new chiral cyclopentenone block, 2-bromo-4,5-isopropylideneoxycyclopent-2-en-1-one, was obtained in a low yield.

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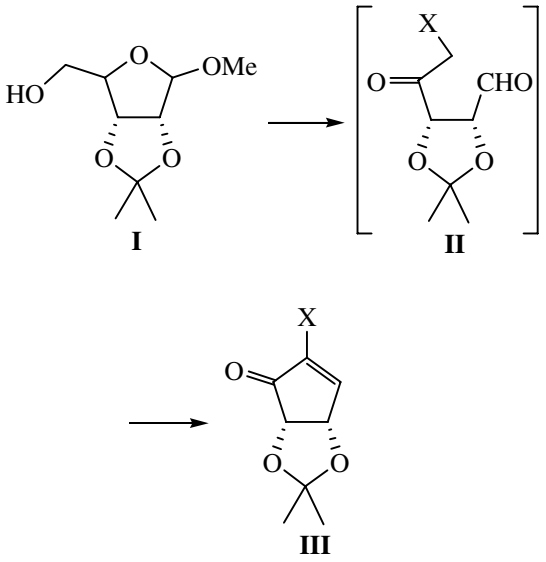
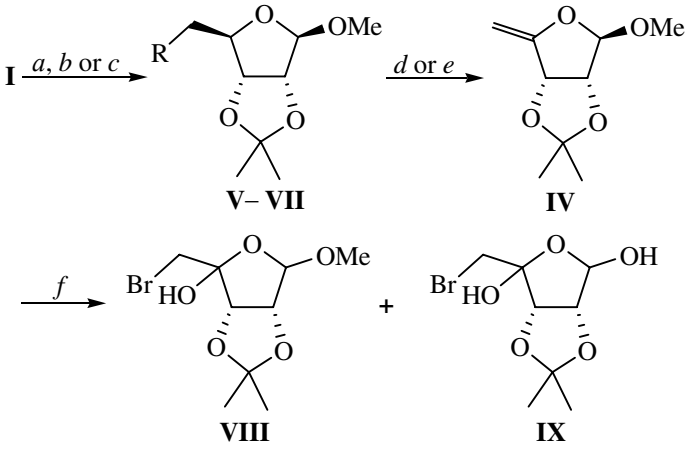
Chiral cyclopentenones prepared from sugars are used in the synthesis of cyclopentanoids (prostanoids, carbonucleosides etc) [1–5]. In extension of studies in this field we planned to prepare from an available D-ribose derivative **I** [6] chiral cyclopentenones **III** (X is an electron-acceptor group). As seen from the scheme, the key reaction stage is based on Knoevenagel intramolecular cyclization of compounds **II** containing an activated methylene group into bicyclic cyclopentenones **III** (iodine derivative **III** is mentioned in [7]).



Here we report on an approach tested for a hypothetical 1,4-ketoaldehyde **II** (X = Br). Taking into account that activated 1,4-α-hydroxy(halo)carbonyl compounds similar to substances **II** are prone to hydration, oligomerization, furanization, (and epimerization!) it seemed feasible to generate them prior to cyclization from enol ether **IV** available from methoxy derivative **I** [8]. For preparation of compound **IV** from alcohol **I** the latter was converted by known methods into bromide **V** and iodide **VI** [9], and also into tosylate **VII**. However at heating with DBU (80°C, benzene) bromide **V** did not changed, whereas under the same conditions iodide **VI** was converted enol ether **IV**. Regretfully, the R_f values of iodide **VI** and enol ether **IV** were too close hampering the reaction progress monitoring by TLC and chromatographic purification of the product from residual iodide **VI**. We avoided these difficulties by reacting tosylate **VII** with *t*-BuOK to obtain enol ether **IV** in 65–70% yield.

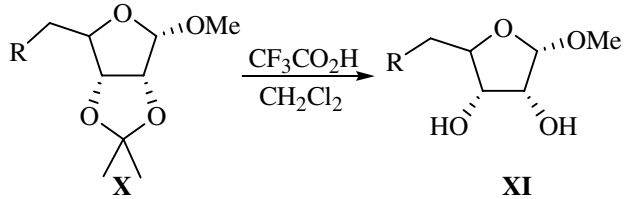
We regarded enol ethers as highly reactive latent equivalents of oxo functions convenient for regiodirected introduction of an electrophilic moiety X^+ into the α-position with respect to a carbonyl, and thus we studied a reaction of enol ether **IV** with *N*-bromosuccinimide. The bromohydroxylation in the presence of NBS in a mixture THF–H_2O (3:1) proceeded rapidly (10–15 min)



R = Br (**V**), I (**VI**), OTs (**VII**). Reagents and conditions: (*a*) 4.0 equiv CBr_4, 1.1 equiv PPh_3, MeCN, 20°C, 30 min (95%); (*b*) 2.0 equiv I_2, 1.25 equiv PPh_3, 1.5 equiv Im, PhMe, MeCN, 70°C, 20 min (76%); (*c*) 1.5 equiv TsCl, Py, 20°C, 20 h (80%); (*d*) 1.1 equiv DBU, 90°C, 30 min (68%); (*e*) 1.2 equiv *t*-BuOK, THT, 0 → 20°C, 1.5 h (67%); (*f*) 1.1 equiv NBS, THT–H_2O, 3:1, 20°C, 10 min (98%).

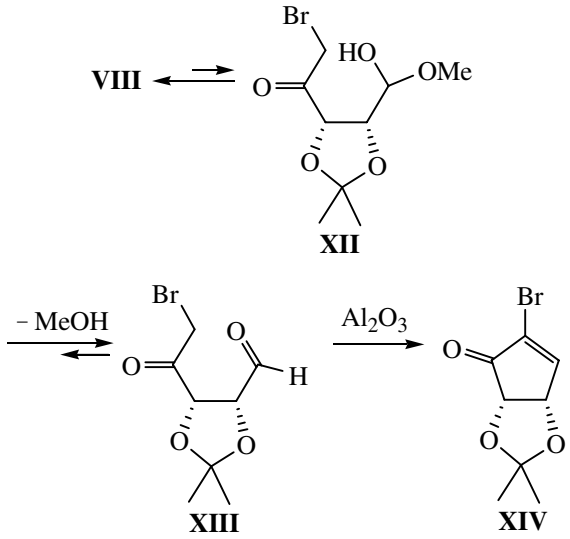
and yielded quantitatively isomeric mixtures of bromohydrins **VIII** and **IX** in a ratio 2:1. A striking feature of this reaction was the formation of deblocked acetal **IX** in considerable amounts within this short time. Methoxybromohydrin **VIII** was converted completely into the corresponding oxybromohydrin **IX** within 12 h at the use of 10 equiv of NBS.

The selective hydrolysis of the glycoside bond with the retention of the isopropylidene protection is obviously of a synthetic interest. The synthetic blocks of sugars containing in the structure both acetonide and methylacetal combination of protective groups, like in compounds **I, IV–VII**, are known to be most common among the hydrocarbon synthons. Usually under typical stringent conditions of water-acid hydrolysis an exhaustive hydrolysis occurs of both protective groups. We found in the literature only examples of selective hydrolysis of acetonide groups with retention of the other protection. In [10] α-D-ribofuranoside (**X**) was successfully converted into diol **XI** by a selective hydrolysis of the acetonide group in a mixture CF_3CO_2H–CH_2Cl_2 without affecting the glycoside. In the β-anomer the acetonide group proved to be stable. The selective hydrolysis of acetonide in compound **X** was ascribed to an anchimeric assistance to the hydrolysis of the oxygen atom of the *cis*-oriented glycoside methoxy group. Other examples of chemo- and regioselective deblocking of the acetonide protective group were described for polyhydroxy compounds at the use of heterogeneous catalyst $NaHSO_3 \cdot SiO_2$ [11], of $BiCl_3$ [12], $La(NO_3)_3 \cdot 6\,H_2O$ [13], etc. [12].



The selective hydrolysis of the C^1-glycoside bond we observed was likely to originate from the ring-chain tautomerism of bromohydrin **VIII**. As seen from the scheme, acyclic form **XII** is easily converted into aldehyde **XIII** whose hydrate gives bromohydrin **IX**.

This suggestion is supported by the data of ^{1}H NMR spectroscopy that has revealed the presence of four stereoisomeric methoxybromohydrins **VIII** which were isolated in pairs by column chromatography on SiO_2. The comprehensive analysis of the spectra of methoxybromohydrins **VIII** will be published elsewhere. We failed to isolate individual oxybromohydrins **IX**.



The intramolecular cyclization of compounds **VIII** and **IX** by aldol-crotonic route at heating in benzene in the presence of neutral Al_2O_3 [14] (under optimum conditions for 1,4-dioxo compounds like diol **XI**) led to the formation in low yields (10–20%) of target enone **XIV**. We plan to carry on the search for cyclization conditions of isomeric tetrahydrofurans **IX** by catalysis with protonic and Lewis acids.

EXPERIMENTAL

IR spectra were recorded on spectrophotometers UR-20 and Specord M-80 from films or mulls in mineral oil.

NMR spectra were registered on a spectrometer Bruker AM-300 at operating frequencies 300.13 (^{1}H) and 75.47 MHz (^{13}C)from solutions in $CDCl_3$ using solvent signals as internal reference (δ_H 7.27, δ_C 77.00 ppm). The reaction progress was monitored by TLC (Silufol, petroleum ether–ethyl acetate, CH_2Cl_2–MeOH), spots were visualized by 10% solution of anise aldehyde in ethanol with sulfuric acid added. The optical rotation was measur-ed on a polarimeter Perkin Elmer Polarimetre 241-M.

Methyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (I). To a mixture of 12.40 g of $CuSO_4$, 5.85 g (38.90 mmol) of D-ribose, 110 ml of anhydrous acetone, and 32 ml of anhydrous MeOH was added dropwise 0.2 ml of concn. H_2SO_4. The reaction mixture was stirred at 40°C for 48 h (TLC monitoring); $CuSO_4$ was filtered off, the precipitate was washed with a mixture acetone–MeOH, 1:1 v/v. The filtrate was neutralized with a saturated $NaHCO_3$ solution and evaporated. The residue was extracted with ethyl acetate, the extract was washed with H_2O, saturated solution of NaCl, dried with Na_2SO_4, and the solvent was evaporated in a vacuum. On distilling the residue we obtained 7.95 g (75%) of compound **I**, bp 110°C (2 mm Hg), R_f 0.44 (CH_2Cl_2–MeOH, 9:1), $[\alpha]_D^{20}$ –75° (*c* 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1020, 1056, 3485. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.32 s (3H, Me), 1.50 s (3H, Me), 3.25 d.d (1H, OH, $^3J_{OH,5B}$ 2.8, $^3J_{OH,5A}$ 10.0), 3.36 s (3H, OMe), 3.62 t.d (1H, H^{5A}, $^3J_{5A,4}$ 3.5, $^2J_{5A,5B} = {}^3J_{5A,OH}$ = 10.0), 3.70 d.d.d (1H, H^{5B}, $^3J_{5B,OH}$ 2.8, $^3J_{5B,4}$ 2.8, $^2J_{5B,5A}$ 10.0), 4.45 d.d (1H, H^4, $^3J_{4,5B}$ 2.8, $^3J_{4,5A}$ 3.5), 4.60 d (1H, H^2, $^3J_{2,3}$ 6.0), 4.83 d (1H, H^3, $^3J_{3,2}$ 6.0), 4.9 C (1H, H^1). ^{13}C NMR spectrum, δ, ppm: 24.60 (Me), 26.25 (Me), 55.35 (OMε), 63.64 (C^5), 81.40 (C^2), 85.65 (C^3), 88.16 (C^4), 109.79 (C^1), 112.00 (C$^{i\text{-Pr}}$). Found, %: C 52.79; H 7.88. $C_9H_{16}O_5$. Calculated, %: C 52.93; H 7.90.

Methyl-5-deoxy-5-bromo-2,3-*O*-isopropylidene-β-D-ribofuranoside (V). To a mixture of 0.50 g (2.45 mmol) of compound **I** and 0.97 g (3.70 mmol) of Ph_3P in anhydrous acetonitrile was added at room temperature 1.23 g (9.70 mmol) of CBr_4, and the mixture was stirred for 30 min (TLC monitoring). The precipitate was filtered off, the solution was evaporated, and the residue was subjected to chromatography on SiO_2 (CH_2Cl_2). Yield 0.62 g (95%), colorless oily substance, R_f 0.30 (petroleum ether–ethyl acetate, 9:1), $[\alpha]_D^{20}$ –74.2° (*c* 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1040, 1070, 1080, 1105. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.33 s (3H, Me), 1.49 s (3H, Me), 3.32 t (1H, H^{5A}, $^2J_{5A,5B}$ 10.0), 3.35 s (3H, OMe), 3.44 d.d (1H, H^{5B}, $^3J_{5B,4}$ 5.9, $^2J_{5B,5A}$ 10.0), 4.49 d.d (1H, H^4, $^3J_{4,5B}$ 5.9, $^3J_{4,5A}$ 10.0), 4.62 d (1H, H^2, $^3J_{2,3}$ 6.0), 4.77 d (1H, H^3, $^3J_{3,2}$ 6.0), 5.0 c (1H, H^1). ^{13}C NMR spectrum, δ, ppm: 24.90 (Me), 26.43 (Me), 32.48 (C^5), 55.13 (OMe), 82.59 (C^2), 85.13 (C^3), 86.63 (C^4), 109.53 (C^1), 112.71 (C$^{i\text{-Pr}}$). Found, %: C 40.39; H 5.54; Br 29.79. $C_9H_{15}BrO_4$. Calculated, %: C 40.47; H 5.66; Br 29.91.

Methyl-5-deoxy-5-iodo-2,3-*O*-isopropylidene-β-D-ribofuranoside (VI). To a stirred mixture of 1.00 g (4.89 mmol) of compound **I**, 1.60 g (6.11 mmol)of Ph_3P, and 0.49 g (7.33 mmol) of imidazole dissolved in a mixture of 15 ml of toluene and 2.5 ml of acetonitrile at 70°C was added by portions 1.56 g (9.75 mmol) of fine crystalline iodine. The reaction mixture was stirred for 20 min, diluted with ethyl acetate, washed with a saturated solution of $Na_2S_2O_3$ and with H_2O, and dried with Na_2SO_4. On evaporating the solvent in a vacuum the residue was subjected to chromatography on a column packed with SiO_2 (petroleum ether). Yield 1.18 g (76%), colorless oily substance, R_f 0.22 (petroleum ether–ethyl acetate, 9:1), $[\alpha]_D^{20}$ –79.8° (*c* 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1020, 1065, 1080, 1095. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.32 s (3H, Me), 1.47 s (3H, Me), 3.15 t (1H, H^{5A}, $^2J_{5A,5B}$ 10.0), 3.27 d.d (1H, H^{5B}, $^3J_{5B,4}$ 6.0, $^2J_{5B,5A}$ 10.0), 3.36 s (3H, OMe), 4.42 d.d (1H, H^4, $^3J_{4,5B}$ 6.0, $^3J_{4,5A}$ 10.0), 4.62 d (1H, H^2, $^3J_{2,3}$ 6.0), 4.74 d (1H, H^3, $^3J_{3,2}$ 6.0), 5.05 s (1H, H^1). ^{13}C NMR spectrum, δ, ppm: 6.64 (C^5), 24.82 (Me), 26.22 (Me), 54.98 (OMe), 82.77 (C^2), 85.10 (C^3), 87.15 (C^4), 109.40 (C^1), 112.30 (C$^{i\text{-Pr}}$). Found, %: C 34.58; H 4.95; I 40.23. $C_9H_{15}IO_4$. Calculated, %: C 34.41; H 4.81; I 40.40.

Methyl-2,3-*O*-isopropylidene-5-*O*-tosyl-β-D-ribofuranoside (VII). To a stirred solution of 2.0 g (9.79 mmol) of alcohol **I** in 15 ml of pyridine was added at 0°C by portions 2.8 g (14.69 mmol) of TsCl. The reaction mixture was stirred at room temperature for 20 h (TLC monitoring), then it was poured into cold water, the reaction product was extracted into chloroform, the extract was dried with Na_2SO_4, and evaporated. The residue was purified by column chromatography on SiO_2 (CH_2Cl_2) or by recrystallization from petroleum ether–ethyl acetate, 1:1, to obtain 2.8 g (80%) of tosylate **VII** as colorless crystals, mp 80–81°C, R_f 0.18 (petroleum ether–ethyl acetate, 8:2), $[\alpha]_D^{20}$ –48.7° (*c* 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 814, 838, 1090, 1180, 1354, 1594. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.21 s (3H, Me), 1.43 s (3H, Me), 2.44 s (3H, Me_{arom}), 3.22 s (3H, OMe), 3.97 d.d (1H, H^{5A}, $^3J_{5A,4}$ 7.2, $^2J_{5A,5B}$ 10.2), 4.03 d.d (1H,

H^{5B}, $^3J_{5B,4}$ 7.2, $^2J_{5B,5A}$ 10.2), 4.3 t (1H, H^4, $^3J_{4,5}$ 7.2), 4.52 d (1H, H^3, $^3J_{3,2}$ 5.9), 4.59 d (1H, H^2, $^3J_{2,3}$ 5.9), 4.92 s (1H, H^1), 7.35 d (2H, H^o, $^3J_{o,m}$ 8.3), 7.79 d (2H, H^m, $^3J_{m,o}$ 8.3). ^{13}C NMR spectrum, δ, ppm: 21.67 (Me_{arom}), 24.85 (Me), 26.32 (Me), 55.03 (OMe), 69.24 (C^5), 81.35 (C^3), 83.57 (C^4), 84.87 (C^2), 109.45 (C^1), 112.69 ($C^{i\text{-Pr}}$), 127.99 (C^o), 129.96 (C^m), 132.70 (C^θ), 145.12 (C^θ). Found, %: C 53.55; H 6.12; S 8.83. $C_{16}H_{22}O_7S$. Calculated, %: C 53.62; H 6.19; S 8.95.

Methyl-2,3-*O*-isopropylidene-4-methylene-β-D-erythrofuranoside (IV). *a*. A mixture of 0.20 g (0.64 mmol) of iodide **VI** and 0.1 g (0.70 mmol) of DBU was stirred at 90°C for 30 min. The reaction mixture was subjected to column chromatography on SiO_2 (petroleum ether–ethyl acetate, 98:2) to obtain 0.08 g (68%) of enol ether **IV**.

b. To a solution of 0.46 g (1.28 mmol) of tosylate **VII** in 15 ml of anhydrous THF was added at 0°C while stirring 0.22 g (1.92 mmol) of *t*-BuOK. The reaction mixture was stirred at room temperature for 1.5 h (TLC monitoring), the precipitate was filtered off, and the solution was evaporated in a vacuum. The residue was purified by column chromatography on SiO_2 (petroleum ether– ethyl acetate, 95:5). Yield 0.16 g (67%), R_f 0.22 (petroleum ether–ethyl acetate, 9:1), $[\alpha]_D^{20}$ +55.2° (*c* 1.15, $CHCl_3$). IR spectrum, ν, cm^{-1}: 890, 1060, 1085, 1670, 3085. ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.35 s (3H, Me), 1.48 s (3H, Me), 3.41 s (3H, OMe), 4.38 br.s (1H, H^{5A}), 4.49 d (1H, H^3, $^3J_{3,2}$ 5.90), 4.59 br.s (1H, H^{5B}), 5.95 d (1H, H^2, $^3J_{2,3}$ 5.90), 5.10 s (1H, H^1). ^{13}C NMR spectrum, δ, ppm: 25.73 (Me), 26.73 (Me), 55.65 (OMe), 78.69 (C^3), 82.66 (C^2), 88.70 (C^5), 108.35 (C^1), 113.20 ($C^{i\text{-Pr}}$), 161.23 (C^4). Found, %: C 57.98; H 7.39. $C_9H_{14}O_4$. Calculated, %: C 58.05; H 7.58.

Reaction of enol ether IV with *N*-bromosuccinimide. To a solution of 0.2 g (1.07 mmol) of enol ether **IV** in 7 ml of a mixture THF–H_2O, 3:1, was added 0.21 g (1.2 mmol) of NBS, and the stirring continued for 10 min (TLC monitoring). The reaction mixture was evaporated, the residue was extracted with $CHCl_3$, the extract was washed with a saturated NaCl solution, dried with Na_2SO_4, and evaporated in a vacuum. The residue was purified by column chromatography on SiO_2 (petroleum ether–ethyl acetate, 95:5) to isolate 0.2 g (66%) of a mixture of methoxybromohydrins **VIII** as two pairs of stereoisomers, and 0.09 g (32%) of compound **IX** as three stereoisomers in a ratio 4:2:1.8 (measured by integral intensities of CH_3 peaks in the ^{1}H NMR spectrum).

(4*S*)-Methyl-5-bromo-4-hydroxy-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (4*S*,β-VIII). R_f 0.3 (petroleum ether–ethyl acetate, 8:2, 2 runs). IR spectrum, ν, cm^{-1}: 682, 2986, 3420. ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.38 s (3H, Me), 1.56 s (3H, Me), 3.38 s (3H, OMe), 3.40 s (1H, OH), 3.64 d (1H, H^{5A}, $^2J_{5A,5B}$ 10.6), 3.69 d (1H, H^{5B}, $^2J_{5B,5A}$ 10.6), 4.63 d (1H, H^3, $^3J_{3,2}$ 5.9), 4.70 d (1H, H^2, $^3J_{2,3}$ 5.9), 4.95 s (1H, H^1). ^{13}C NMR spectrum, δ, ppm: 24.64 (Me), 25.96 (Me), 35.73 (C^5), 55.14 (OMe), 84.44 (C^3), 85.20 (C^2) 104.81 (C^1), 109.98 ($C^{i\text{-Pr}}$), 113.72 (C^4). Found, %: C 38.32; H 5.45; Br 28.37. $C_9H_{15}BrO_5$. Calculated, %: C 38.18; H 5.34; Br 28.22.

(4*R*)-Methyl-5-bromo-4-hydroxy-5-deoxy-2,3-*O*-isopropylidene-α-D-ribofuranoside (4*R*,α-VIII). ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.32 s (3H, Me), 1.47 s (3H, Me), 3.43 m (1H, H^{5A}), 3.45 s (3H, OMe), 3.65 d (1H, H^{5B}, $^2J_{5B,5A}$ 11.0), 4.42 d (1H, OH, $^4J_{OH,5A}$ 1.6), 4.69 d (1H, H^3, $^3J_{3,2}$ 5.67), 4.80 d (1H, H^2, $^3J_{2,3}$ 5.67), 5.03 s (1H, H^1). ^{13}C NMR spectrum, δ, ppm: 24.80 (Me), 26.16 (Me), 35.88 (C^5), 55.59 (OMe), 78.72 (C^3), 84.19 (C^2) 104.54 (C^1), 106.06 ($C^{i\text{-Pr}}$), 113.18 (C^4).

(4*S*)-Methyl-5-bromo-4-hydroxy-5-deoxy-2,3-*O*-isopropylidene-α-D-ribofuranoside (4*S*,α-VIII). ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.35 s (3H, Me), 1.48 s (3H, Me), 2.99 d (1H, OH, $^3J_{OH,1}$ 9.8), 3.40 s (3H, OMe), 3.60 d (1H, H^{5A}, $^2J_{5A,5B}$ 11.3), 3.61 d (1H, H^{5B}, $^2J_{5B,5A}$ 11.3), 4.68 d (1H, H^3, $^3J_{3,2}$ 5.6), 4.71 d (1H, H^2, $^3J_{2,3}$ 5.6), 5.35 d (1H, H^1, $^3J_{1,OH}$ 9.8). ^{13}C NMR spectrum, δ, ppm: 24.89 (Me), 26.25 (Me), 35.96 (C^5), 55.68 (OMe), 84.56 (C^3), 85.31 (C^2) 104.61 (C^1), 113.30 ($C^{i\text{-Pr}}$), 113.83 (C^4).

(4*R*)-Methyl-5-bromo-4-hydroxy-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (4R,β-VIII). ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.41 s (3H, Me), 1.55 s (3H, Me), 3.31 s (3H, OMe), 3.60 d (1H, H^{5A}, $^2J_{5A,5B}$ 11.3), 3.61 d (1H, H^{5B}, $^2J_{5B,5A}$ 11.3), 4.03 d (1H, OH, $^3J_{OH,1}$ 12.5), 4.58 d (1H, H^3, $^3J_{3,2}$ 5.9), 4.63 d.d (1H, H^2, $^3J_{2,1}$ 3.6, $^3J_{2,3}$ 5.9), 5.24 d.d (1H, H^1, $^3J_{1,2}$ 3.6, $^3J_{1,OH}$ 12.5). ^{13}C NMR spectrum, δ, ppm: 24.72 (Me), 25.05 (Me), 35.76 (C^5), 55.22 (OMe), 78.85 (C^2), 84.31(C^3), 104.96 (C^1), 106.11 ($C^{i\text{-Pr}}$), 110.09 (C^4).

5-Bromo-4-hydroxy-5-deoxy-2,3-*O*-isopropylidene-D-ribofuranose (IX). R_f 0.11 (petroleum ether–ethyl acetate, 8:2, 2 runs). IR spectrum, ν, cm^{-1}: 634, 2944, 3412. ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.32 s (3H, Me), 1.38 s (3H, Me), 1.40 s (3H, Me), 1.48 s (3H, Me), 1.55 s (3H, Me), 1.56 s (3H, Me), 3.60–3.75 m (6H, H^5), 4.60–4.85 m (6H, H^2, H^3), 5.40–5.50 m (3H, H^1).

^{13}C NMR spectrum, δ, ppm, major isomer: 24.66 (Me), 26.04 (Me), 35.80 (C^5), 82.93 (C^3), 84.39 (C^2), 103.68 (C^1), 106.10 (C^4), 113.18 ($C^{i\text{-Pr}}$); second isomer: 24.49 (Me), 25.82 (Me), 36.22 (C^5), 84.71 (C^3), 86.16 (C^2), 96.00 (C^1), 99.66 (C^4), 113.70 ($C^{i\text{-Pr}}$); minor isomer: 24.32 (Me), 25.60 (Me), 36.35 (C^5), 78.44 (C^3), 79.06 (C^2), 98.01 (C^1), 103.68 (C^4), 113.77 ($C^{i\text{-Pr}}$). Found, %: C 35.58; H 5.04; Br 29.53. $C_8H_{13}BrO_5$. Calculated, %: C 35.71; H 4.87; Br 29.69.

2-Bromo-4,5-*O*-isopropylidene-2-cyclopenten-1-one (XIV). To a dispersion of neutral Al_2O_3 in benzene was added under an argon atmosphere 0.68 g of a mixture of bromohydrins **VIII** and **IX** in benzene. The reaction mixture was stirred for 3 h at reflux, then Al_2O_3 was filtered off, and the solution was evaporated. The residue was subjected to a chromatography on a column packed with SiO_2 (petroleum ether–ethyl acetate, 95:5) to isolate 0.08 g (15%) of enone **XIV** as colorless crystals, mp 86.5–88°C, R_f 0.35 (petroleum ether–ethyl acetate, 7:3), $[\alpha]_D^{20}$ +4.4° (c 1.15, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1582, 1744. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.40 s (3H, Me), 1.42 s (3H, Me), 4.58 d (1H, H^5, $^2J_{5,4}$ 5.4), 5.23 d.d (1H, H^4, $^3J_{4,3}$ 3.6, $^3J_{4,5}$ 5.4), 7.59 d (1H, H^3, $^3J_{3,4}$ 3.6). ^{13}C NMR spectrum, δ, ppm: 26.33 (Me), 27.45 (Me), 75.29 (C^4), 77.52 (C^5), 115.91 ($C^{i\text{-Pr}}$), 128.52 (C^2), 157.10 (C^3), 195.45 (C^1). Found, %: C 41.11; H 3.78; Br 34.19. $C_8H_9BrO_3$. Calculated, %: C 41.23; H 3.89; Br 34.28.

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