# Novel Approach towards C–C-Linked Carbohydrate Dimers via Claisen Rearrangement of a Disaccharide Allyl Ketene Acetal

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**Abstract:** A disaccharide derivative was synthesised by coupling tri-*O*-benzyl-D-glucal with an allylic sugar alcohol in a glycosyloxyselenation reaction. Subsequent oxidation followed by *syn*-elimination of the selenoxide and in situ rearrangement of the intermediate allyl ketene acetal gave novel C–C-linked saccharide dimers.

**Key Words:** mimetics, carbohydrates, selenium, allyl ketene acetals, rearrangements

Oligosaccharides play a central role in intercellular communication and cell-mediated processes. The investigation of the structural features present in carbohydrate recognition and binding sites of antibodies and lectins is of crucial interest and requires the development of saccharide mimetics of naturally occurring carbohydrates.[1]

In recent years numerous efforts have been directed toward the synthesis of *C*-disaccharides, the chemical stability of which renders them particularly useful for imitating the biological and physical properties of the corresponding *O*-glycosides.[2] The replacement of the interglycosidic oxygen atom by carbonyl[3] and hydroxymethylene[4] groups has led to further interesting disaccharide analogues. A potential application field of these molecules includes inhibition of biosynthetic pathways of glycoproteins which may later result in novel antibacterial,[5] antiviral[6] or antitumoral agents.[7]

In a recent contribution from our laboratory we reported on the synthesis of divalent saccharide structures incorporating either a spiro or a methylene linkage via a ketene acetal Claisen rearrangement.[8] In this paper we reveal the first Claisen rearrangement of a disaccharide allyl ketene acetal incorporating both double bonds in endocyclic positions. The resulting dimeric saccharide structures feature a direct linkage of two pyranose rings without a methylene bridge. Similar compounds have hitherto been accessible only by acid-catalysed glycal dimerisation.[9]

A direct C–C bond formation between two pyranose rings can be achieved by the [3,3]-sigmatropic rearrangement of a disaccharide featuring an allyl ketene acetal substructure which incorporates the glycosidic bond.

To this end, we started from tri-*O*-acetyl-D-glucal (**1**), which was subjected to a Ferrier rearrangement[10] to give the 2,3-dideoxyhex-2-enopyranoside **2** (Scheme 1). Subsequent deacetylation[11] and silylation of the primary hydroxyl function delivered the allylic alcohol **4**, the α-anomer of which was coupled with tri-*O*-benzyl-D-glucal (**5**) in a glycosyloxyselenation reaction previously described by Sinaÿ et al.[12] The anomeric configuration at C-1′ of the isolated product **6** proved to be α which suggests a *trans*-diaxial nucleophilic opening of an intermediate seleniranium ion by the allylic alcohol **4**. Oxidation of the selenide **6** to the selenoxide **7** was accomplished with 30% hydrogen peroxide at –25 °C and delivered a mixture of products diastereomeric at selenium (ratio: **7a/7b** = 3:1). These compounds proved relatively stable owing to a kinetically retarded *syn*-elimination of phenylselenenic acid (PhSeOH)[13] toward the anomeric centre which considerably facilitated the chromatographic purification. A slow interconversion of the diastereomers at selenium due to hydration was likewise noted resulting in a ratio of **7a/7b** = 2:1 after one week in deuterated benzene.

Since a *syn*-elimination of PhSeOH towards C-3′ in **7a/b** is impossible due to the *trans*-diaxial arrangement, it was expected to proceed between C-1′ and C-2′ under enhanced thermal conditions[14] to give the corresponding allyl ketene acetal **8**. In order to subsequently effect the Claisen rearrangement of the reactive ketene acetal **8** in situ, the mixture of diastereomers **7a/b** was initially heated in *n*-butyl vinyl ether with diisopropylamine to 130 °C in a microwave device to give compounds **9a/b** in a moderate yield of 52%. Although *n*-butyl vinyl ether and related compounds are known to act as a scavenger for PhSeOH,[15] the formation of side products from the solvent, PhSeOH and diisopropylamine complicated purification and hence imposed a major drawback. Considerably better results were obtained by using toluene instead of *n*-butyl vinyl ether under similar conditions resulting in a maximum yield of 91% **9a/b**. The purpose of the added diisopropylamine was to convert PhSeOH into the selenenamide PhSeN(*i*-Pr)$_2$[13] and thus prevent it from attacking the double bond in the rearrangement products.

The inseparable mixture of lactones **9a/b** (ratio: **9a/9b** = 10:3) was thoroughly analysed primarily by means of NMR spectroscopy. Comparisons of coupling constants as well as known conformational structures of their

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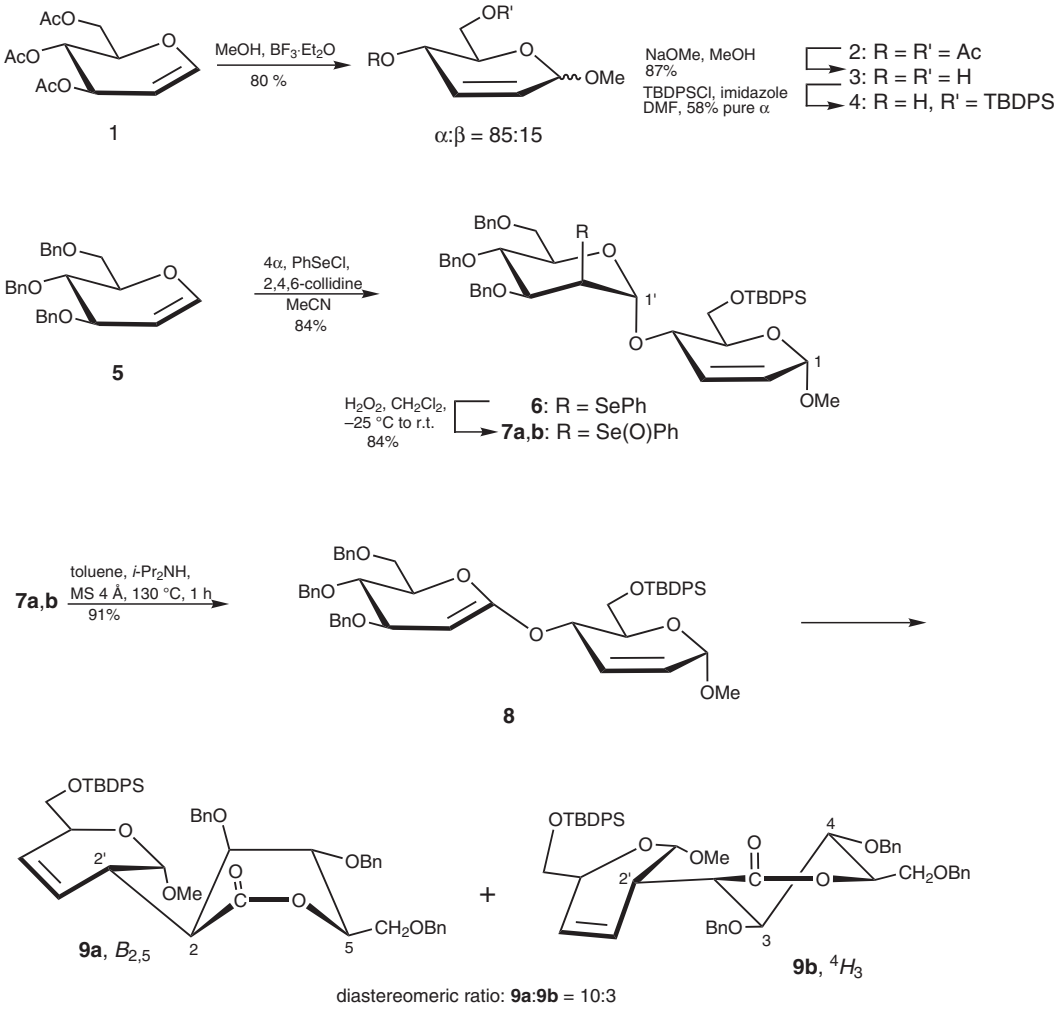


**Scheme 1**

parent compounds, δ-D-mannono-1,5-lactone and δ-D-glucono-1,5-lactone, argue for the proposed conformations of **9a** and **9b**. Both the 2-deoxymannonolactone and 2-deoxygluconolactone residues may either exhibit a half-chair ($^4H_3$) or a boat ($B_{2,5}$) structure since C-2 must be coplanar with the lactone group. δ-D-Mannono-1,5-lactone **10** indeed features the boat geometry, which is favoured over the boat form due to the *cis* arrangement of the hydroxyl group at C-2 and the hydroxymethylene group at C-5 (Figure 1).[16] By contrast, δ-D-glucono-1,5-lactone **11** occurs in a slightly distorted half-chair conformation[16,17] caused by the *trans* orientation of 2-OH and 5-$CH_2$OH. Furthermore, both of these structures enable bulky substituents at C-2 to adopt pseudoequatorial orientations. The measured coupling constants of **9a** and **9b** show similar values compared to those of the parent compounds, i.e. $^3J_{2,3}$ = 2.2 Hz in **9a** versus $^3J_{2,3}$ = 3.4 Hz in **10** and $^3J_{2,3}$ = 6.3 Hz in **9b** versus $^3J_{2,3}$ = 8.5 Hz in **11**.[18] Hence, **9a** features the boat geometry ($B_{2,5}$) and **9b** the half-chair geometry ($^4H_3$) of the respective lactone ring. The differences in the coupling constants may be attributed to the lack of oxygen at C-2 and the substitution pattern associated with slight conformational distortions.[19]

Regarding the 2′,3′,4′-trideoxyhex-3′-enopyranoside part the conformation in both compounds **9a** and **9b** most likely features a half-chair with the planar substructure incorporating C-2′ to C-5′.[20] Due to the axial nature of the methoxy group the configuration at C-2′ cannot be exactly deduced from the corresponding coupling constant ($^3J_{1',2'}$ = 4.1 Hz), however, a pseudoequatorial orientation is rather likely in order to minimise steric interactions of the lactone residue with the TBDPS group.

In this paper we have demonstrated the first Claisen rearrangement of a disaccharide ketene acetal with an allyl vinyl ether substructure incorporating the interglycosidic bond and both double bonds in endocyclic positions.

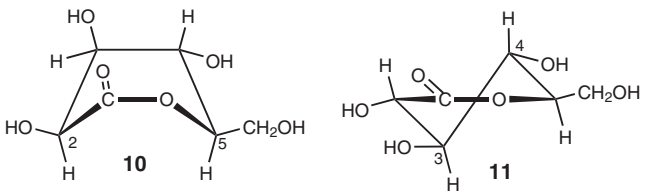


**Figure 1** Boat conformation ($B_{2,5}$) of δ-D-mannono-1,5-lactone **10** and half-chair conformation ($^4H_3$) of δ-D-glucono-1,5-lactone **11**

Within a synthetic sequence of six steps starting from protected D-glucal derivatives a mixture of diastereomeric target compounds **9a/b** could be isolated in an overall yield of 26%. These novel compounds exhibit a direct C–C bond between two pyranose rings and hence belong to a new class of C–C-disaccharides that are of particular interest with respect to saccharide mimetics and carbohydrate-based pharmaceuticals.

Anhyd solvents were purchased from the manufacturers Fluka and Merck. The protected D-glucal derivatives were purchased from Fluka and Sigma-Aldrich. Phenylselenyl chloride was purchased from Lancaster Synthesis. TLC was performed on silica gel 60-coated aluminum sheets (Merck or Macherey-Nagel), with detection by UV at 254 nm and by heating with $H_2SO_4$ (10% in EtOH). Flash chromatography was carried out on silica gel 60 (0.04–0.063 mm; Merck, Macherey-Nagel or ICN). Petroleum ether used refers to the fraction with bp 50–70 °C. The microwave experiments were performed in a CEM microwave system (Discover, 300 W maximum power output) by using sealed tubes with temperature control via infrared sensor. NMR spectra were recorded on a Bruker AMX-400 and DRX-500 NMR spectrometer ($^1$H: 400/500 MHz; $^{13}$C: 100 MHz) and analysed with the respective solvent peaks as references. Mass spectra were recorded with a Bruker Biflex III (MALDI-TOF, positive reflection mode, matrix: 2,5-dihydroxybenzoic acid). IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer. The optical rotations were measured on a Perkin-Elmer 243 or 341 polarimeter at 20 °C.

**(Methyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-4-yl)-3,4,6-tri-*O*-benzyl-2′-deoxy-2′-phenylselenyl-α-D-mannopyranoside (6)**

Under argon, a stirred solution of **5** (106 mg, 254 μmol) in MeCN (3 mL) was treated at 0 °C with PhSeCl (73 mg, 381 μmol) and 2,4,6-collidine (50 μL, 46 mg, 375 μmol). Subsequently a solution of **4** (71 mg, 178 μmol) in MeCN (2 mL) was added and stirring continued overnight. When TLC confirmed the complete conversion of **4**, the solvent was evaporated and the residue purified by column chromatography (petroleum ether–EtOAc, 7:1) to give **6** (145 mg, 84%) as a colourless syrup; $[\alpha]_{546}^{20}$ +79.2 ($c$ = 0.50, $CHCl_3$); $R_f$ 0.4 (petroleum ether–EtOAc, 3:1).

IR (film): 3030, 2930, 1454, 1428, 1112, 1049, 966, 753, 700 cm$^{-1}$.

$^1$H NMR (400 MHz, $C_6D_6$): δ = 1.20 (s, 9 H, $t$-$C_4H_9$), 3.30 (s, 3 H, $CH_3$), 3.55 (dd, $^2J_{6'a,6'b}$ = 10.9, $^3J_{5',6'b}$ = 1.5 Hz, 1 H, H-6′b), 3.74 (dd, $^2J_{6'a,6'b}$ = 10.9, $^3J_{5',6'a}$ = 3.8 Hz, 1 H, H-6′a), 3.93 (dd, $^3J_{1',2'}$ = 1.8 Hz, $^3J_{2',3'}$ = 4.3 Hz, 1 H, H-2′), 3.96–3.99 (m, $^3J_{4',5'}$ = 9.4, $^3J_{5',6'a}$ = 3.8, $^3J_{5',6'b}$ = 1.5 Hz, 1 H, H-5′), 4.03–4.10 (m, 2 H, H-6a/b), 4.11–4.15 (m, $^3J_{4,5}$ = 9.2, $^3J_{5,6a}$ = 2.3, $^3J_{5,6b}$ = 4.8 Hz, 1 H, H-5), 4.24 (dd, $^3J_{2',3'}$ = 4.3, $^3J_{3',4'}$ = 8.4 Hz, 1 H, H-3′), 4.28–4.36 (m, $^3J_{4',5'}$ = 9.4 Hz, 3 H, PhC$H_2$, H-4′), 4.42–4.48 (m, $^3J_{4,5}$ = 9.2 Hz, 2 H, PhC$H_2$, H-4), 4.56–4.60 (m, 2 H, PhC$H_2$), 4.72 (d, $^3J_{1,2}$ = 2.0 Hz, 1 H, H-1), 4.95 (d, 1 H, PhC$H_2$), 5.49 (d, $^3J_{1',2'}$ = 1.8 Hz, 1 H, H-1′), 5.56–5.60 (m, $^3J_{1,2}$ = 2.0, $^3J_{2,3}$ = 10.4 Hz, 1 H, H-2), 5.68 (d, $^3J_{2,3}$ = 10.4 Hz, 1 H, H-3), 6.91–6.96, 7.06–7.35, 7.60–7.62, 7.85–7.90 (4 m, 30 H, Ar).

$^{13}$C NMR (100 MHz, $C_6D_6$): δ = 19.64 (1 C, $C$Me$_3$), 27.17 [3 C, C($CH_3$)$_3$], 49.80 (1 C, C-2′), 55.48 (1 C, $CH_3$), 64.18 (1 C, C-6), 67.23 (1 C, C-4), 69.43 (1 C, C-6′), 71.11 (1 C, C-5), 71.66 (1 C, Ph$CH_2$), 73.44 (1 C, C-5′), 73.71, 75.17 (2 C, Ph$CH_2$), 75.90 (1 C, C-4′), 79.72 (1 C, C-3′), 95.67 (1 C, C-1), 97.71 (1 C, C-1′), 127.61–130.01, 135.18, 136.07, 136.32 (38 C, Ar).

MALDI-TOF: $m/z$ = 993.1 [M + Na]$^+$, 1009.1 [M + K]$^+$.

Anal. Calcd for $C_{56}H_{62}O_8SeSi$ (970.23): C, 69.32; H, 6.45. Found: C, 68.64; H, 6.71.

**(*R*/*S*)-(Methyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-4-yl)-3,4,6-tri-*O*-benzyl-2′-deoxy-2′-phenylselenoxyl-α-D-mannopyranosides (7a/b)**

A stirred solution of **6** (47 mg, 48 μmol) in $CH_2Cl_2$ (3 mL) was treated with 30% $H_2O_2$ (15 μL, 5.0 mg, 147 μmol) at –30 °C and the stirring was continued at –25 °C overnight. The next day, a second portion of 30% $H_2O_2$ (10 μL, 3.3 mg, 98 μmol) was added at –25 °C and the solution was allowed to warm to r.t. After evaporation of the solvent, the residue was purified by column chromatography (petroleum ether–EtOAc, 1:3) to give **7a/b** (mixture of diastereomers, 40 mg, 84%) as a colourless syrup; diastereomeric ratio: **a/b** = 3:1; $R_f$ 0.22, 0.26 (petroleum ether–EtOAc, 1:3).

IR (film): 3031, 2928, 2857, 1454, 1428, 1112, 1046, 967, 742, 700 cm$^{-1}$.

$^1$H NMR (400 MHz, $C_6D_6$): δ = 1.15, 1.20 (2 s, 2 × 9 H, 2 × $tert$-$C_4H_9$), 3.30, 3.31 (2 s, 2 × 3 H, 2 × $CH_3$), 3.56 (dd, $^3J_{1',2'}$ = 1.3, $^3J_{2',3'}$ = 4.8 Hz, 1 H, H-2′$_a$), 3.65 (dd, $^3J_{1',2'}$ = 3.3, $^3J_{2',3'}$ = 4.8 Hz, 1 H, H-2′$_b$), 5.35 (d, $^3J_{1',2'}$ = 3.3 Hz, 1 H, H-1′$_b$), 5.55–5.61 (m, $^3J_{2,3}$ = 10.4 Hz, 2 H, H-2$_{a/b}$), 5.74 (d, $^3J_{2,3}$ = 10.4 Hz, 1 H, H-3$_b$), 6.06 (d, $^3J_{2,3}$ = 10.4 Hz, 1 H, H-3$_a$), 6.17 (s, 1 H, H-1′$_a$).

$^{13}$C NMR (100 MHz, $C_6D_6$): δ = 27.07 [3 C, C($CH_3$)$_{3b}$], 27.16 [3 C, C($CH_3$)$_{3a}$], 55.49 (2 × 1 C, CH$_{3a/b}$), 64.13 (1 C, C-6$_b$), 64.25 (1 C, C-6$_a$), 65.83 (1 C, C-2′$_b$), 67.72 (1 C, C-2′$_a$), 68.93 (1 C, C-6′$_b$), 69.02 (1 C, C-6′$_a$), 71.07, 72.26, 72.56, 72.96, 73.18, 73.25, 74.24, 74.91, 75.32, 76.65, 78.02, 79.53, 79.56 (16 C, C-4$_{a/b}$, C-5$_{a/b}$, C-3′$_{a/b}$, C-4′$_{a/b}$, C-5′$_{a/b}$, Ph$CH_{2a/b}$), 93.28 (1 C, C-1′$_a$), 93.32 (1 C, C-1′$_b$), 95.72 (2 × 1 C, C-1$_{a/b}$), 127.44–130.75, 136.02, 136.05, 136.31 (2 × 38 C, C-2$_{a/b}$, C-3$_{a/b}$, Ar$_{a/b}$).

MALDI-TOF: $m/z$ = 1009.4 [M + Na]$^+$.

Anal. Calcd for $C_{56}H_{62}O_9SeSi$ (986.23): C, 68.20; H, 6.35. Found: C, 68.07; H, 6.93.

**2-Deoxy-2-[(3′*Z*)-methyl-6′-*O*-*tert*-butyldiphenylsilyl-2′,3′,4′-trideoxy-α-D-*ribo*- or -D-*xylo*-hex-3′-enopyranos-2′-yl]-D-mannono-1,5-lactone (9a) and 2-Deoxy-2-[(3′*Z*)-methyl-6′-*O*-*tert*-butyldiphenylsilyl-2′,3′,4′-trideoxy-α-D-*ribo*- or -D-*xylo*-hex-3′-enopyranos-2′-yl]-D-glucono-1,5-lactone (9b)**

A solution of **7a/b** (40 mg, 41 μmol) in toluene (6 mL) was stirred with molecular sieves 4 Å for 10 min. After addition of $i$-$Pr_2NH$ (243 μmol, 24.7 mg, 34 μL), the solution was heated to 130 °C for 1 h. Evaporation of the solvent and column chromatography of the residue (petroleum ether–EtOAc, 12:1) gave a diastereomeric mixture of **9a/b** (30.0 mg, 91%) as a colourless syrup; diastereomeric ratio **9a/9b** (2*S*/2*R*) = 10:3; $R_f$ 0.34 (petroleum ether–EtOAc, 3:1).

IR (film): 2927, 2856, 1457, 1114 cm$^{-1}$.

**2*S*-Diastereomer**

$^1$H NMR (500 MHz, $C_6D_6$): δ = 1.21 (s, 9 H, $t$-$C_4H_9$), 2.92 (dd, $^3J_{2,2'}$ = 11.0, $^3J_{2,3}$ = 2.2 Hz, 1 H, H-2), 3.10 (s, 3 H, $CH_3$), 3.47–3.51 (m, $^3J_{1',2'}$ = 4.4, $^3J_{2,2'}$ = 11.0 Hz, 1 H, H-2′), 3.91–3.97 (m, $^3J_{2,3}$ = 2.2 Hz, 1 H, H-3), 4.35 (d, $^3J_{1',2'}$ = 4.4 Hz, 1 H, H-1′), 5.85, 6.35 (2 d, $^3J_{3',4'}$ = 10.4 Hz, 2 × 1 H, H-3′, H-4′).

$^{13}$C NMR (100 MHz, $C_6D_6$): δ = 27.12 [3 C, C($CH_3$)$_3$], 35.41 (1 C, C-2′), 44.28 (1 C, C-2), 54.85 (1 C, $CH_3$), 66.95, 69.01, 70.23, 71.70, 73.60 (C-6, C-6′, Ph$CH_2$), 69.29, 74.43, 75.59, 78.38 (4 C, C-3, C-4, C-5, C-5′), 97.97 (1 C, C-1′), 126.24–130.02, 136.08–136.18 (32 C, C-3′, C-4′, Ar), 170.56 (1 C, C-1).

**2*R*-Diastereomer**

$^1$H NMR (500 MHz, $C_6D_6$): δ = 1.18 (s, 9 H, $t$-$C_4H_9$), 3.00 (dd, $^3J_{2,2'}$ = $^3J_{2,3}$ = 6.3 Hz, 1 H, H-2), 3.17–3.21 (m, $^3J_{1',2'}$ = 4.1, $^3J_{2,2'}$ = 6.3 Hz, 1 H, H-2′), 3.24 (s, 3 H, $CH_3$), 3.80 (dd, $^3J_{2,3}$ = 6.3, $^3J_{3,4}$ = 10.1 Hz, 1 H, H-3), 4.81 (d, $^3J_{1',2'}$ = 4.1 Hz, 1 H, H-1′), 5.81–5.91 (m, 2 H, H-3′, H-4′).

$^{13}$C NMR (100 MHz, $C_6D_6$): δ = 27.10 [3 C, C($CH_3$)$_3$], 39.20 (1 C, C-2′), 47.83 (1 C, C-2), 55.16 (1 C, $CH_3$), 66.73, 68.05, 68.88, 72.65, 73.36, 73.69 (C-6, C-6′, Ph$CH_2$), 69.47, 76.19, 77.26, 77.74 (4 C, C-3, C-4, C-5, C-5′), 98.51 (1 C, C-1′), 125.89–130.82, 136.36 (32 C, C-3′, C-4′, Ar), 168.60 (1 C, C-1).

MALDI-TOF: *m*/*z* = 835.3 $[M + Na]^+$, 851.2 $[M + K]^+$.

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