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Short Syntheses of Gabosine I and Gabosine G from δ-D-Gluconolactone

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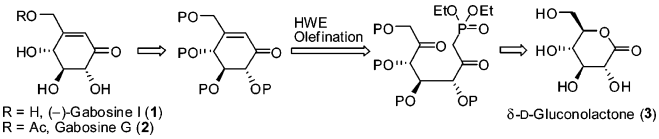

A short synthesis of gabosine I (**1**) from δ-D-gluconolactone (**3**) in four steps, involving a one-pot TPAP oxidation−K_2CO_3-mediated intramolecular Horner−Wadsworth−Emmons (HWE) olefination as the key step, is described. Regioselective acetylation of the primary alcohol in gabosine I (**1**) then furnished gabosine G (**2**).

Gabosines belong to a family of unusual, hydroxylated cyclohexenones and hexanones that may be classified as pseudo- or carbasugars (Figure 1).[1] They have been shown to display interesting bioactivities such as antibiotic,[1b] anticancer,[2] and DNA binding properties.[1c] Since the first isolation of gabosines from *Streptomyces* strains in 1974,[1a] twelve total syntheses have appeared. Four enantiospecific syntheses constructed the carbocyclic framework from carbohydrates by using either an intramolecular nitrile oxide cycloaddition,[3] a $SnCl_4$-promoted aldol-type cyclization of phenylsulfonyl enol silyl ether,[4] an intramolecular Nozaki−Kishi reaction,[5] or a ring-closing alkene metathesis[6] as the key step. Three other enantiospecific syntheses, including our earlier endeavor,[7] employed (−)-quinic acid as the chiral starting material.[8,9] The remaining five constructions of gabosines involved a racemic norbornyl route,[10] a chemoenzymatic synthesis from iodobenzene,[11] an asymmetric Diels−Alder reaction of chiral sulfinylacrylate with 2-methoxyfuran,[12] enantioselective acetylation of hydroxyketals,[13] and an enantioselective synthesis from [(*p*-tolylsulfinyl)methyl]-*p*-quinols[14] as the key strategies. In 1988, we reported a synthesis of (6*R*,7*S*)-asperlin from D-glucose using an intramolecular Horner−Wadsworth−Emmons (HWE) olefination as the key step.[15] Now, we extend the HWE strategy to a rapid entry to hydroxylated carbocycles from δ-D-gluconolactone, affording short syntheses of gabosines I (**1**) and G (**2**) in four and five steps, respectively. The fabrication of gabosine G (**2**) has not been addressed and this paper documents its first synthesis.

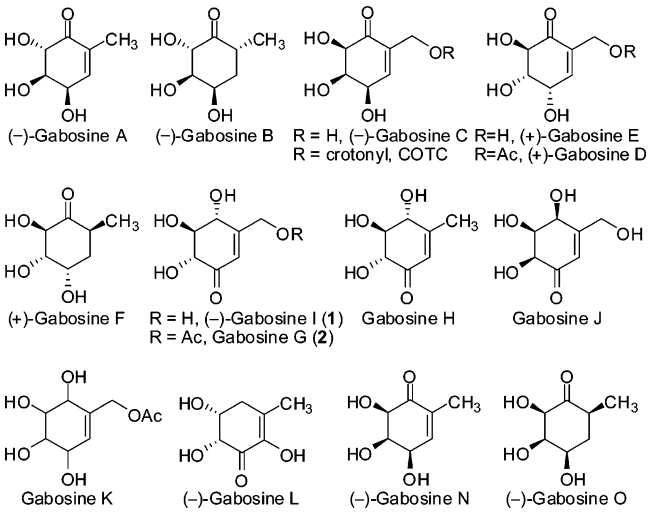

FIGURE 1. The gabosine family.

The first synthesis of garbosine I (**1**) was achieved by Lubineau and Billault in nine steps from tetra-*O*-benzyl-D-glucose.[5] Since tetra-*O*-benzyl-D-glucose was prepared from D-glucose in three steps,[16] the total number of synthetic steps to **1** from D-glucose is therefore 12. Protection of hydroxyls as benzyl ethers is common in syntheses involving carbohydrates.[5] However, in the present synthesis, the starting material is δ-D-gluconolactone (**3**) and direct benzylation of all the hydroxyl groups is not a trivial process. Furthermore, our experience has shown that deprotection of the four benzyl ethers in the presence

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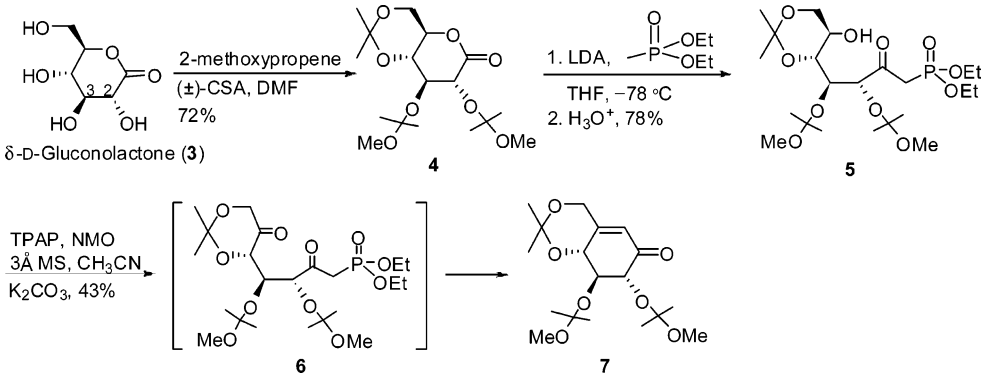
SCHEME 1. Synthesis of Enone 7

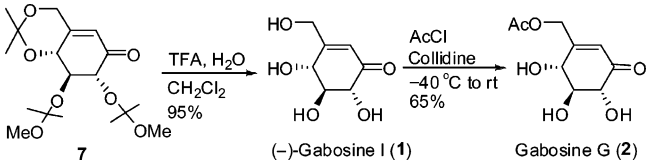


of an alkene functionality is not a high-yielding reaction. On the other hand, isopropylidene protecting groups could readily be installed and then removed easily via acid hydrolysis at the end of a synthesis.[17] Thus, acetalization of δ-D-gluconolactone (**3**) with an excess of 2-methoxypropene afforded an acid-sensitive, mixed acetal **4** in good yield (Scheme 1). Nucleophilic addition of lithiated diethyl methylphosphonate to the lactone carbonyl in **4** gave a β-ketophosphonate **5**, which then was subjected to an oxidation and intramolecular HWE cyclization sequence.[18,19] Phosphonate **5** exists as an acyclic hydroxy ketone instead of a cyclized pyranose ring as shown by ^{13}C NMR spectroscopy. Because of the acid labile mixed acetal protecting groups, the oxidation conditions for β-ketophosphonate **5** had to be mildly basic.

Various oxidation and cyclization conditions were attempted to yield enone **7** from β-ketophosphonate **5** and the results are shown in Table 1. Oxidation of **5** was initially carried out with PDC. Since the resultant 1,5-diketone **6** was too unstable for isolation, it was manipulated to the next step without purification. Hence, oxidation of **5** with PDC in the presence of pyridine followed by typical HWE reaction conditions,[20] entries 1a and 1b, furnished enone **7** in 20% and 32% yield, respectively. Potassium carbonate as base also caused cyclization to give enone **7** in 28% yield (entry 1c). Other literature conditions were studied, but no significant improvement was observed (entries 1d−f).[21−23]

Interestingly, oxidation of **5** with a catalytic amount of tetra-*n*-propylammonium perruthenate (TPAP) and *N*-methylmorpholine *N*-oxide (NMO) as oxidant not only provided 1,5-diketone **6**, but also induced **6** to undergo HWE olefination to give a 4% yield of enone **7** (entry 2a). Addition of lithium salt inhibited cyclization (entries 2b,c). Different bases were added in the same pot to promote the intramolecular alkenation. Amine bases were disappointing (entries 2d−f) and only very low yields of **7** were obtained. Among the inorganic bases used (entries 2g−i), potassium carbonate was found to be the best candidate to give enone **7** in 43% yield (entry 2i). (An unidentified mixture of compounds was isolated and the mixture contains phosphonate and isopropylidene groups as shown by ^{1}H and ^{13}C NMR spectroscopy. This mixture could not be induced to undergo alkenation under various conditions.) To the best of our knowledge, this is the first example of TPAP oxidation assisted by K_2CO_3 to induce HWE olefination in one pot. When a stoichiometric amount of TPAP was used, the oxidation−olefination sequence also occurred and gave **7** in 38% yield (entry 3). The reduced ruthenium(IV) species[24] was speculated to act as a base to induce cyclization. However, the high cost of TPAP prohibited its use in stoichiometric amount.

SCHEME 2. Syntheses of Gabosines I (1) and G (2)



With the blocked enone **7** in hand, we completed a new synthesis of (−)-gabosine I (**1**) by a facile acid hydrolysis in 95% yield (Scheme 2). The ^{1}H, ^{13}C NMR spectral data and

TABLE 1. Oxidation and Cyclization of Phosphonate 5 to Enone 7 under Various Conditions

oxidation conditions	cyclization conditions	yield of **7**	ref
1. PDC, 3 Å MS, pyridine, CH_2Cl_2	(a) LiCl, DBU, CH_3CN	20%	20
	(b) LiCl, DIPEA, CH_3CN	32%	20
	(c) K_2CO_3	28%	
	(d) LiCl, DBU, THF, −78 °C	21%	21
	(e) K_2CO_3, 18-crown-6, toluene	5%	22
	(f) NaH, THF, −40 °C	decomp	23
2. TPAP (0.05 equiv), NMO, 3 Å MS, CH_3CN	(a) without base	4%	
	(b) DBU, LiCl	NR[a]	
	(c) K_2CO_3, LiCl	NR[a]	
	(d) Et_3N	4%	
	(e) DIPEA	5%	
	(f) DBU	4%	
	(g) KO^{t}Bu	NR[a]	
	(h) NaOH	8%	
	(i) K_2CO_3	43%	
3. TPAP (1 equiv), 3 Å MS, CH_3CN		38%	

[a] NR = no reaction.

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specific optical rotation of **1** are in good agreement with the literature values.[1b]

Regioselective acetylation[25] of the primary alcohol in **1** then gave gabosine G (**2**) in 65% yield. Now, we document the first synthesis of gabosine G (**2**) with ^{1}H and ^{13}C NMR spectral data in accord with those reported in the literature; however, the specific optical rotation was not recorded.[1b] The absolute configuration of (−)-gabosine G ($[\alpha]^{20}_D$ −41.8 (*c* 1.34, MeOH)) is established as 2*R*,3*S*,4*R*.

In conclusion, the synthesis of gabosine I (**1**) was accomplished in four steps with 20.3% overall yield and that of gabosine G (**2**) was achieved in five steps with 13.2% overall yield from δ-D-gluconolactone (**3**) via a key one-pot TPAP oxidation−K_2CO_3-mediated HWE olefination. This construction, the shortest synthetic route reported for gabosines, not only underscores its potential to access other gabosines for biological evaluation, but also provides opportunities for the syntheses of polyhydroxylated cyclohexenoid natural products such as valienaminevalienamine[26] and the compounds containing it.[17,27] Research along this line is underway.

Experimental Section

Acetal 4. To a solution of δ-D-gluconolactone (**3**) (1.01 g, 5.69 mmol) in dry DMF (10 mL) at 0 °C were added 2-methoxypropene (2.5 mL, 26 mmol) and (±)-10-camphorsulfonic acid (36 mg, 0.15 mmol). The solution was stirred for 5 h at 0 °C, and was then quenched with saturated aq $NaHCO_3$ (10 mL). The resulting mixture was extracted with Et_2O (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and filtered. Concentration of the filtrate followed by flash chromatography (*n*-hexane:Et_2O 5:1) yielded mixed acetal **4** (1.48 g, 72%) as a colorless oil: $[\alpha]^{20}_D$ +22.6 (*c* 1.33, $CHCl_3$); R_f 0.5 (*n*-hexane:Et_2O, 1:1); IR (thin film) 2993, 1770, 1375, 1211, 1076, 1039, 832 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.37 (s, 3H), 1.40 (s, 3H), 1.43 (s, 3H), 1.44 (s, 3H), 1.48 (s, 3H), 3.22 (s, 6H), 3.76 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.78 (t, *J* = 10.5 Hz, 1H), 4.01 (dd, *J* = 5.4, 1.2 Hz, 1H), 4.06 (dd, *J* = 10.8, 5.4 Hz, 1H), 4.26 (d, *J* = 0.9 Hz, 1H), 4.70 (dt, *J* = 10.35, 5.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0 (CH_3), 25.1 (CH_3), 25.5 (CH_3), 25.5 (CH_3), 25.8 (CH_3), 29.3 (CH_3), 49.5 (CH_3), 50.2 (CH_3), 62.6 (CH_2), 67.6 (CH), 73.8 (CH), 74.2 (CH), 75.9 (CH), 100.3 (C), 101.7 (C), 103.2 (C), 169.8 (C); MS (FAB) *m*/*z* (rel intensity) 347 ([M − CH_3]$^+$, 41), 331 (36), 299 (100); HRMS (FAB) calcd for $C_{17}H_{30}O_8$ [M − CH_3]$^+$ 347.1700, found 347.1703.

Ulose 5. To a solution of diisopropylamine (1.88 mL, 13.4 mmol) in dry THF (10 mL) was added dropwise *n*-butyllithium in *n*-hexane (1.6 M solution, 8.4 mL, 13.4 mmol) at −78 °C under N_2. The reaction mixture was stirred for 15 min at −78 °C under N_2 and diethyl methylphosphonate (0.48 mL, 3.32 mmol) was then added. The reaction mixture was stirred for a further 30 min at −78 °C and was added slowly to a solution of lactone **4** (1.2 g, 3.31 mmol) in dry THF (10 mL) at −78 °C. Stirring was continued for an additional 1 h at the same temperature. The reaction was quenched with saturated aq NH_4Cl (10 mL) at −78 °C and was warmed to room temperature. The mixture was extracted with EtOAc (4 × 100 mL). The combined organic extracts were dried ($MgSO_4$) and filtered. Concentration of the filtrate gave an oily residue that crystallized on standing to afford ulose **5** (1.19 g, 78%) as colorless crystals: mp 89−90 °C; $[\alpha]^{20}_D$ −74.8 (*c* 0.75, $CHCl_3$); R_f 0.5 (EtOAc:acetone, 3:1); IR (thin film) 3380, 2991, 1721, 1382, 1205, 1061, 1026, 964, 891 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 3H), 1.27 (s, 3H), 1.29−1.35 (m, 9H), 1.41 (s, 3H), 1.50 (s, 3H), 1.62 (s, 3H), 1.83 (s, 1H), 2.84 (dd, *J* = 22.8, 13.8 Hz, 1H), 3.24 (s, 3H), 3.35 (s, 3H), 3.58−3.65 (m, 1H), 3.73−3.78 (m, 2H), 3.85−3.9 (m, 1H), 4.03−4.16 (m, 4H), 4.17−4.19 (m, 1H), 4.64 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.7 (CH_3), 16.8 (CH_3), 18.6 (CH_3), 23.2 (CH_3), 24.8 (CH_3), 24.9 (CH_3), 25.3 (CH_3), 28.6 (CH_3), 41.2 (CH_2) (d, J_{C-P} = 124 Hz), 50.1 (CH_3), 51.8 (CH_3), 62.4 (CH_2), 62.6 (CH_2), 62.7 (CH), 64.7 (CH_2), 71.2 (CH), 72.6 (CH), 75.6 (CH), 99.4 (C), 102.4 (C), 103.6 (C), 199.7 (C) (d, J_{C-P} = 21.9 Hz); MS (ESI) *m*/*z* (rel intensity) 537 ([M + Na]$^+$, 100); HRMS (ESI) calcd for $C_{22}H_{43}O_{11}P_1$ [M + Na]$^+$ 537.2435, found 537.2438.

Enone 7. To a mixture of ulose **5** (151 mg, 0.29 mmol), *N*-methylmorpholine *N*-oxide (NMO) (137 mg, 1.17 mmol), and 3 Å molecular sieves (MS) (251 mg) in dry CH_3CN (10 mL) were added tetra-*n*-propylammonium perruthenate (TPAP) (5 mg, 0.014 mmol) and K_2CO_3 (334 mg, 2.41 mmol) under N_2. After being stirred for 24 h at room temperature, the mixture was diluted with EtOAc (10 mL) then filtered through a pad of Celite and the residue was eluted with EtOAc:Et_3N (50:1, 50 mL). Concentration of the filtrate followed by flash chromatography (*n*-hexane:Et_2O:Et_3N, 2:1:0.01) gave enone **7** (44.1 mg, 43%) as a colorless oil: $[\alpha]^{20}_D$ −148 (*c* 1.02, $CHCl_3$); R_f 0.17 (*n*-hexane:Et_2O, 1:1); IR (thin film) 2921, 1684, 1383, 1221, 1119, 871 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41−1.43 (m, 15H), 1.52 (s, 3H), 3.29 (s, 3H), 3.39 (s, 3H), 3.99 (dd, *J* = 10.95, 8.1 Hz, 1H), 4.24 (d, *J* = 10.8 Hz, 1H), 4.37−4.49 (m, 2H), 4.55 (dd, *J* = 5.35, 1.5 Hz, 1H), 5.81 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8 (CH_3), 25.8 (CH_3), 25.9 (CH_3), 26.0 (CH_3), 26.0 (CH_3), 26.5 (CH_3), 50.6 (CH_3), 50.7 (CH_3), 62.0 (CH_2), 73.0 (CH), 74.8 (CH), 76.2 (CH), 101.0 (C), 102.6 (C), 102.9 (C), 121.5 (CH), 157.7 (C), 197.2 (C); MS (FAB) *m*/*z* (rel intensity) 327 ([M − OCH_3]$^+$, 10), 73 (100); HRMS (FAB) calcd for $C_{18}H_{30}O_7$ [M − OCH_3]$^+$ 327.1802, found 327.1812.

Gabosine I (1). To a solution of the enone **7** (44.1 mg, 0.12 mmol) in CH_2Cl_2 (3 mL) were added TFA (0.1 mL) and water (0.02 mL) at room temperature. The resulting solution was stirred for 2 h at room temperature. Concentration of the solution followed by flash chromatography ($CHCl_3$:MeOH, 8:1) yielded gabosine I (**1**) (20.4 mg, 95%) as a brownish oil: $[\alpha]^{20}_D$ −58.6 (*c* 0.79, MeOH) {lit.[1b] $[\alpha]^{20}_D$ −61.4 (*c* 1, MeOH)}; R_f 0.36 (^{t}BuOH:AcOH:H_2O 4:1:5, upper phase);[1b] ^{1}H NMR (300 MHz, CD_3OD) δ 3.59 (dd, *J* = 10.8, 8.4 Hz, 1H), 4.03 (d, *J* = 10.8 Hz, 1H), 4.29−4.37 (m, 2H), 4.51 (d, *J* = 17.7 Hz, 1H), 6.15 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 62.1 (CH_2), 73.7 (CH), 78.1 (CH), 79.5 (CH), 121.3 (CH), 168.1 (C), 199.5 (C); MS (ESI) *m*/*z* (rel intensity) 197 ([M + Na]$^+$, 100), 149 (10); HRMS (ESI) calcd for $C_7H_{10}O_5$ [M + Na]$^+$ 197.0420, found 197.0427.

Gabosine G (2). To a solution of gabosine I (**1**) (31.2 mg, 0.179 mmol) in collidine (3 mL) was added dropwise acetyl chloride (0.015 mL, 0.215 mmol) at −78 °C. The resulting white suspension was stirred at that temperature for 3 h, and then at room temperature for 12 h. Methanol (0.1 mL) was added to quench the reaction and the mixture was concentrated under high vacuum at 35 °C. The residue was flash chromatographed ($CHCl_3$:MeOH 20:1) to give gabosine G (**2**) (25.4 mg, 65%) as a brownish oil: $[\alpha]^{20}_D$ −41.8 (*c* 1.34, MeOH) {lit.[1b] no optical rotation reported}; R_f 0.6 (^{t}BuOH:AcOH:H_2O 4:1:5, upper phase);[1b] ^{1}H NMR (300 MHz, CD_3OD) δ 2.11 (s, 3H), 3.60 (dd, *J* = 11.1, 8.4 Hz, 1H), 4.03 (d, *J* = 10.8 Hz, 1H), 4.39 (d, *J* = 10.8 Hz, 1H), 4.89 (dt, *J* = 17.1, 1.2 Hz, 1H) (part of the peak was obscured by the solvent peak), 4.97 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.99 (q, *J* = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 20.6 (CH_3),

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63.7 (CH_2), 73.5 (CH), 78.0 (CH), 79.3 (CH), 122.5 (CH), 161.5 (C), 172.0 (C), 199.1 (C); MS (ESI)*m*/*z* (rel intensity) 239 ([M + Na]$^+$, 100); HRMS (ESI) calcd for $C_9H_{12}O_6$ [M + Na]$^+$ 239.0526, found 239.0530.

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Supporting Information Available: General procedures and copies of ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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