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Synthesis and Epimerisation Studies on Carbohydrate Derived Bicyclic Tetronate Esters: The Synthesis of Furanofurans Related to the Cytotoxic Metabolite Goniofufurone

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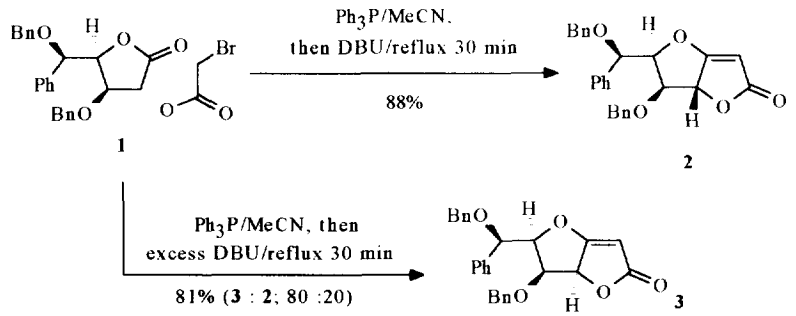
Abstract: The synthesis of the *D*-xylo- **12**. *D*-lyxo- **13**. *D*-ribo- **14** and *D*-arabino-furanofurans **15** was accomplished from the readily available butyrolactones **4** and **5** *via* a non-classical Wittig cyclisation/hydrogenation sequence: these compounds are analogues of the cytotoxic natural product goniofufurone. © 1997 Elsevier Science Ltd.

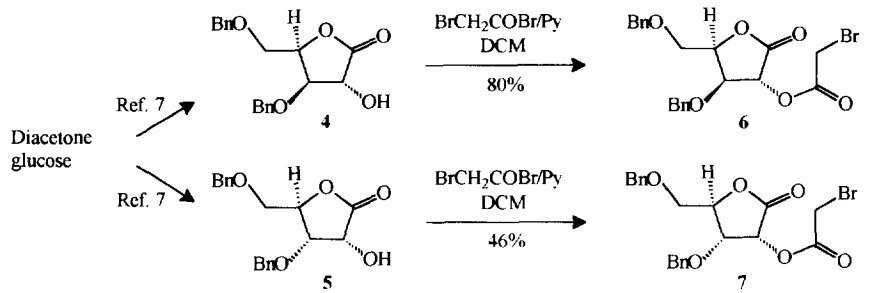
There has been considerable interest in the Wittig reaction as a synthetic procedure[2] and one particular aspect that we have studied extensively is the so-called "non-classical" Wittig reaction of stabilised phosphoranes with butyrolactones. This reaction,[3] when applied intramolecularly, has been used in the synthesis of the natural product goniofufurone[4] and has found other applications in synthesis.[5] During the synthesis of goniofufurone it was observed that the intermediate **1** when treated with triphenylphosphine followed by slightly less than one equivalent of DBU, cyclised to give **2** in excellent yield. However when the reaction was performed using an excess of DBU a different major product **3** was formed (80:20) in which the C-2 position of the sugar (as was) has epimerised. Furthermore upon treatment of **2** with a catalytic amount of DBU almost total epimerisation (95:05) of **2** into **3** was observed.



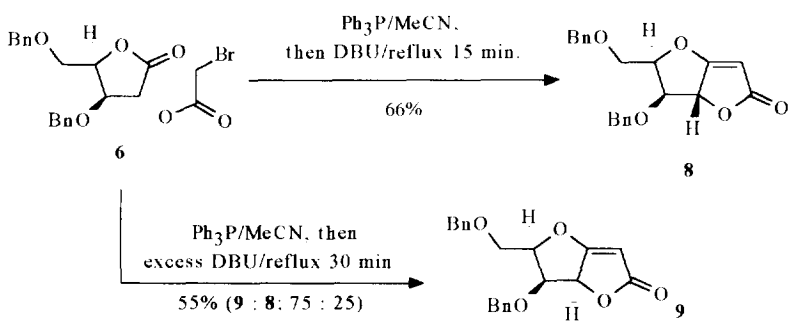
1 **2** **3**

This result is somewhat surprising as the favoured product **3** would appear to be the thermodynamically less stable product, in which all three substituents are on the same side of the tetrahydrofuran ring. We were thus keen to investigate this epimerisation further to test the generality of the epimerisation reaction and its use in the synthesis of analogues of goniofufurone.[6] In order to do this we chose the simpler systems based upon the *D*-xylo- and *D*-ribo-lactones **4** and **5**, which are both readily

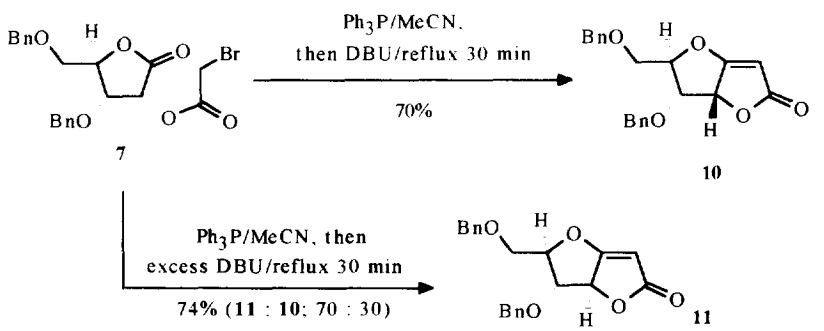
prepared from *D*-glucose.[7] The bromoacetylation of these derivatives was uneventful and proceeded in 80% and 46% yields to give **6** and **7** respectively.



The behaviour of the bromoacetates **6** and **7** to the cyclisation conditions were studied in turn. Reaction of **6** with triphenylphosphine in acetonitrile gave an intermediate phosphonium salt which was treated *in situ* with 0.8 equivalents of DBU and heated to reflux for 15 minutes; this led to the formation of the expected *D*-xylo-tetronate **8** in 66% yield. Upon repetition of this reaction using a slight excess (1.01-1.05 eqv.) of DBU, a mixture (25:75) of the previously observed tetronate **8** and the epimerised product, the *D*-lyxo-tetronate **9** were isolated in a combined yield of 55%. This result mirrors that observed in the goniofufurone chemistry and indeed when pure **8** was treated with a catalytic quantity of DBU in acetonitrile at reflux for 15 minutes, a 30:70 ratio of **8** : **9** was obtained.

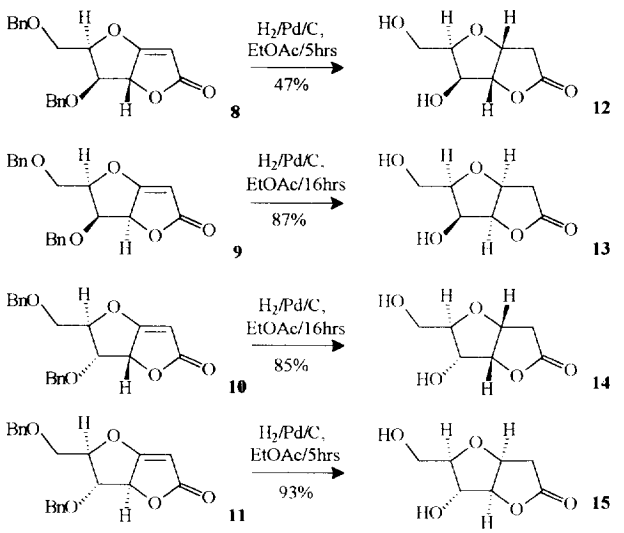


The Wittig cyclisation of the *D*-ribose derivative **7**, using 0.8 equivalents of DBU proceeded smoothly to give the *D*-ribo-tetronate **10**, as the only product in 70% yield. On repetition of the reaction using a slight excess of DBU, a second product, the *D*-arabino tetronate **11** was obtained along with the previously observed **10**. These were obtained as an inseparable 30 : 70 (**10** : **11**) mixture in 74% yield, which was shown to be the equilibrium ratio by similar epimerisation studies to those performed on the *D*-Xylo series.



At present we are unable to shed any light on the reasons for the selectivity observed in these reactions; molecular modelling (Hyperchem) of these compounds gave no clear insight as to a particular preference for either epimer in both the series that were studied.

However, with these bicyclic tetronates in hand we next investigated their conversion to the corresponding furanofurans. Thus hydrogenation of the tetronates **8-11** over palladium on charcoal gave the corresponding *D*-xylo-, *D*-lyxo-, *D*-ribo- and *D*-arabino- furanofurans **12-15**, respectively, in acceptable yields.



In conclusion we have prepared a series of structural analogues of the cytotoxic natural product goniofufurone from a common precursor (*D*-glucose).

Acknowledgements: The authors thank Glaxo Group Research for funding PRJ, the ERASMUS scheme and the EPSRC National Mass Spectrometry Service at Swansea.

Experimental

Column chromatography was carried out on Kieselgel (230-400 mesh) with the eluant specified in each case and tlc was conducted on precoated Kieselgel 60 F254 (Art. 5554; Merck) glass plates. All non-aqueous reactions were conducted in oven-dried apparatus under a static atmosphere of argon. Petrol refers to the 40-60 fraction. Dichloromethane, pyridine, diethyl ether and THF were dried and distilled before use using standard methods. Chemical shifts are reported as δ values relative to TMS. ^1H and ^{13}C nmr spectra were recorded in deuterochloroform on a Bruker AC250 spectrometer. IR were recorded as thin films (oils) or as chloroform solutions on a Perkin Elmer 1600 series instrument. Mass spectra were recorded on a VG Masslab Model 12/253 spectrometer using chemical ionisation (with ammonia as the reagent gas). Accurate mass determinations were recorded on a VG Analytical ZAB-E spectrometer using chemical ionisation (with ammonia as the reagent gas). M.p.s were recorded with a Gallenkamp MF370 apparatus and are uncorrected. Optical rotations were determined on a POLAAR 2001 instrument.

2-Bromoacetyl-3,5-di-*O*-benzyl-*D*-*xylo*-penta-1,4-lactone (6).

3,5-Di-O-benzyl-*D*-xylopenta-1,4-lactone **4** (3.10g, 9.5 mmol) was dissolved in cooled (0^oC), stirred diethyl ether (20ml) and pyridine (0.83g, 0,85 ml, 10.5 mmol) was added. Bromoacetyl bromide (2.13g, 0.92 ml 10.5 mmol) was then added and the mixture warmed to room temperature over 4 hours in the absence of light. Water (30ml) was added and the resulting mixture extracted with ether (3 x 25ml); the combined organic extracts were washed sequentially with water (25ml), saturated copper sulphate solution

(50ml), water (50ml), saturated sodium hydrogen carbonate (2 x 50ml), water (50ml) and brine (50ml). After drying ($MgSO_4$), evaporation and flash chromatography (ethyl acetate/petrol, 15:85), 2-bromoacetyl-3,5-di-O-benzyl-*D*-xylopenta-1,4-lactone **6** was obtained as an oil (3.40g, 80%). $[\alpha]_D^{24}$ = + 54.4° (C = 0.41 in $CHCl_3$).

^{1}H nmr; δ = 3.69 (2H, 2 x dd, J = 10.9, 2.7, 2.0Hz, CH_2), 3.84 (2H, s, CH_2), 4.51-4.68 (6H, m, 2 x CH, 2 x CH_2), 5.90 (1H, d, J = 7.7Hz, CH), 7.24-7.36 (10H, m, 2 x Ph). **^{13}C nmr**; δ = 24.86, 66.57, 73.04, 73.65 (4 x CH_2), 77.18, 77.69 (2 x CH), 127.57-128.65 (10 x Ph, CH), 136.79, 137.32 (2 x Ph, C), 165.86, 169.51 (2 x C=O). **IR**; ν max 1798,1754 (C=O). **MS(FAB)**; 471/473 (47%, 47% M + Na^+). **HRMS**; $C_{21}H_{22}O_6Br$ ($M+H^+$) requires 449.0600; found 449.0635.

2-Bromoacetyl-3,5-di-*O*-benzyl-*D*-*ribo*-penta-1,4-lactone (7).

Lactone **5** (1.18g, 3.59mmol) was dissolved in diethyl ether (25ml) and cooled (0°C); pyridine (297mg, 3.76mmol) and bromoacetyl bromide (794mg, 3.93mmol) were then added sequentially and the mixture warmed to room temperature over 16hrs in the absence of light. Water (50ml) was added and the resulting mixture extracted with ether (3 x 25ml); the combined organic extracts were washed sequentially with water (25ml), copper sulphate solution (saturated, 50ml), water (50ml), sodium hydrogen carbonate (saturated, 2 x 50ml), water (50ml) and brine (50ml). After drying ($MgSO_4$), evaporation and flash chromatography (ethyl acetate/petrol, 25:75 Rf = 0.27), **7** was obtained as an oil (0.75 g, 46%, $[a]_D^{24}$ +16° (*c* = 0.175).

^{1}H nmr; δ = 3.48 (1H, dd, J = 3.2, 10.9Hz, CH), 3.64 (1H, dd, J = 2.6, 10.9Hz, CH), 3.92 (2H, s, CH_2), 4.37-4.63 (6H, m, 2 x CH, 2 x CH_2), 5.58 (1H, d, J = 6.0Hz, CH), 7.22-7.38 (10H, m, Ph). **^{13}C nmr**; δ = 24.75 (CH_2), 68.46 (CH), 70.28 (CH_2), 73.14 (CH_2), 73.68 (CH_2), 75.54 (CH), 82.71 (CH), 127.64-128.57 (10 x Ph, CH), 136.29 (C), 137.24 (C), 170.11 (C), 175.50 (C). **IR**; ν max 3032, 2869, (C-H), 1793, 1750 (C=O). **MS(CI)**; 466/468 (20, 22%, $M+NH_4^+$). **HRMS**; $C_{21}H_{25}O_6NBr$ ($M+NH_4^+$) requires 466.0865; found 466.0865.

***(6R,7S,8R)*-7-Benzyloxy-6-benzyloxymethyl-1,5-dioxa-2-oxobicyclo[3.3.0.^{4,8}]oct-3-ene (8).**

Triphenylphosphine (0.1686g, 0.6367 mmol, 1.2 eqv.) was added to a stirred solution of **6** (0.2384g, 0.5306 mmol) in dry acetonitrile (2ml); the resultant solution was then warmed to 50°C to allow for the formation of the phosphonium salt (~2 hours, tlc analysis). After cooling (-15°C), DBU (64.3mg, 0.422 mmol, 0.8 eqv.) was added and the mixture stirred at this temperature for 10 min. before heating (80°C) for 15 min. The reaction was then cooled to 0°C, diluted with ether (30ml) and filtered through a short silica column, which was washed with further ether (3 x 30ml). Evaporation and flash chromatography (ethyl acetate/petrol, 20:80) gave **9** (98.1mg, 66%) as yellow crystalline solid; M.Pt. = 63°C, $[\alpha]_D^{24}$ = + 45.9° (C = 0.40 in $CHCl_3$).

^{1}H nmr; δ = 3.81, 3.85 (2H, 2 x dd, J = 11.6, 3.0, 2.8Hz, CH_2), 4.31 (1H, dd, J = 9.0, 8.1 CH), 4.56, 4.60 (2H, 2 x d, J = 12.0Hz, CH_2), 4.60,4.84 (2H, 2 x d, J = 11.8Hz, CH_2), 4.60, 4.84 (2H, 2 x d, J = 11.8Hz, CH_2), 4.94 (1H, ddd, J = 8.1, 3.0, 2.8Hz, CH), 5.04 (1H, d, J = 1.8Hz, vinyl CH), 5.53 (1H, dd, J = 9.0, 1.8Hz, CH), 7.25-7.38 (10H, m, 2 x Ph). **^{13}C nmr**; δ = 67.30, 72.26, 73.78 (3 x CH_2), 78.52, 81.98, 88.23, 89.67 (4 x CH), 127.61-128.58 (10 x Ph, CH), 136.56, 137.40 (2 x Ph, C), 174.32, 183.21 (2 x C). **IR**; ν max; 1771 (C=O), 1656 (C=C). **MS(CI)**, 370 (100%, M + NH_4^+), 353 (80%, M + H^+). **HRMS**; $C_{21}H_{21}O_5$ ($M+H^+$) requires 353.1389; found 353.1389.

***(6R,7S,8S)*-7-Benzyloxy-6-benzyloxymethyl-1,5-dioxa-2-oxobicyclo[3.3.0.^{4,8}]oct-3-ene (9).**

Triphenylphosphine (663.3mg, 2.529 mmol, 1.2 eqv.) was added to a stirred solution of **6** (946.3mg, 2.1062 mmol) in dry acetonitrile (10ml) and the resulting solution was stirred under an argon atmosphere at 50°C, until tlc (ethyl acetate/petrol, 25:75) showed full conversion to the phosphonium salt (~2 hours). The reaction mixture was cooled to 0°C and DBU (304.3mg, 1.999 mmol, 0.95 eqv.) was added. After stirring for 5 min., the reaction was heated at reflux for 30 min. and cooled again. Further DBU was added (ca 20mg) and the mixture reheated in the oil bath for a further 3 min whereupon a considerable darkening of the reaction was observed. The reaction was then cooled to 0°C, diluted with ether (30ml) and filtered through a silica plug, which was washed with further ether (3 x 30ml). Evaporation and chromatography (ethyl acetate/petrol, 20:80) of the filtrate gave a 30:70 mixture the

previously isolated **8** (170.6mg, 24%) and a new compound **9** (410.4 mg, 58%); M.Pt. = 90°C, $[\alpha]_D^{24}$ = + 13.0° (C = 0.40 in $CHCl_3$).

^{1}H nmr (C_6D_6); δ = 3.36 (1H, ddd, J = 3.9, 2.3, 0.7Hz, CH), 3.47, 3.60 (2H, 2 x dd, J = 10.8, 6.9, 5.0Hz, CH_2), 4.09 (1H, dd, J = 3.9, 1.8Hz, CH), 4.13, 4.22 (2H, 2 x d, J = 11.9Hz, CH_2), 4.14, 4.56 (2H, 2 x d, J = 11.7Hz, CH_2), 4.26 (1H, ddd, J = 6.9, 5.0, 2.3Hz, CH), 4.86 (1H, dd, J = 1.8, 0.7Hz, CH), 7.01-7.20 (10H, m, 2 x Ph). **^{13}C nmr**; δ = 67.14, 73.51, 74.59 (3 x CH_2), 73.61, 80.56, 86.76, 92.22 (4 x CH_2), 127.66-128.38 (10 x Ph, CH), 136.59, 137.23 (2 x Ph, C), 174.84, 182.96 (2 x C). **IR**; ν max; 1769 (C=O), 1652 (C=C). **MS(CI)**, 370 (100%, M + NH_4^+), 353 (55%, M + H^+). **HRMS**; $C_{21}H_{21}O_5$ ($M+H^+$) requires 353.1389; found 353.1389.

***(6R,7R,8R)*-7-Benzyloxy-6-benzyloxymethyl-1,5-dioxa-2-oxobicyclo[3.3.0.^{4,8}]oct-3-ene (10)**

Triphenylphosphine (307.8 mg, 1.18 mmol, 1.2 eqv.) was added to a stirred solution of **7** (0.439 g, 0.978 mmol) in dry acetonitrile (5 ml); the resultant solution was then warmed to 50°C to allow for the formation of the phosphonium salt (~1 hour, tlc). After cooling (-15°C, ice/salt), DBU (119.10 mg, 0.7823 mmol, 0.8 eqv.) was added and the mixture stirred for 10 min before heating (50°C) for 30 min. The reaction was then cooled to room temperature, diluted with ether (30ml) and filtered through a short silica column, which was washed with further ether. Evaporation and flash chromatography (ethyl acetate/petrol 20:80, Rf = 0.12) gave **10** (193.1mg, 70%) as a white crystalline solid (M.Pt = 85-87°C, $[a]_D^{24}$ +104° (*c* = 0.25, $CHCl_3$)).

^{1}H nmr; δ = 3.70 (1H, dd, J = 2.6, 11.4Hz, CH), 3.80 (1H, dd, J = 2.8, 11.4Hz, CH), 4.24, (1H, d, J = 4.6Hz, CH), 4.50-4.62 (3H, m, 3 x CH), 4.85 (1H, d, J = 11.5Hz, CH), 4.99 (1H, app t, J = 2.7Hz, CH), 5.13 (1H, finely split triplet/dd, J = <1.0Hz, vinyl CH), 5.39 (1H, dd, J = 1.7, 4.6Hz, CH), 7.26-7.41 (10H, m, Ph). **^{13}C nmr**; δ = 68.73 (CH_2), 73.40 (CH_2), 73.80 (CH_2), 75.31 (CH), 80.05 (CH), 87.66 (CH), 98.00 (CH), 127.68-128.67 (10 x Ph, CH), 136.82 (2 x C), 175.57 (C), 184.29 (C). **IR**; ν max; 2863 (CH), 1770 (C=O), 1655 (C=C). **MS(CI)**; 370 (100%, M+NH_4^+), 353 (40%, M+H^+). **HRMS**; $C_{21}H_{21}O_5$ ($M+H^+$) requires 353.1389; found 353.1389.

***(6R,7R,8S)*-7-Benzyloxy-6-benzyloxymethyl-1,5-dioxa-2-oxobicyclo[3.3.0.^{4,8}]oct-3-ene (11)**

Triphenylphosphine (112mg, 0.420 mmol, 1.2eqv.) was added to a solution of **7** (160mg, 0.356 mmol) in dry acetonitrile (4ml) and the resulting solution stirred under an argon atmosphere at 50°C, until tlc (ethyl acetate/petrol 25:75) showed full conversion of **7** to the corresponding phosphonium salt (~90 min.). The reaction mixture was then cooled to 0°C and DBU (54mg, 0.36mmol, 1 eqv.) was added. After stirring for 5 min., the reaction was heated at reflux for 30 min. then cooled to room temperature. The reaction was diluted with ether (30ml) and filtered through a silica plug, which was washed with further ether. Evaporation and chromatography (ethyl acetate/petrol 20:80, Rf = 0.12) of the filtrate gave a 30:70 mixture **10** and **11** (93.0mg, 74%).

^{1}H nmr (11); δ = 3.66 (1H, dd, J = 4.2, 12.2Hz, CH), 3.85 (1H, dd, J = 1.9, 12.2Hz, CH), 4.27, (1H, app t, J = 8.2Hz, CH), 4.48-4.59 (3H, m, 3 x CH), 4.82 (1H, d, J = 11.6Hz, CH), 4.86 (1H, obscured m, CH), 5.07 (1H, dd, J = 0.7, 1.8Hz, vinyl CH), 5.18 (1H, dd, J = 1.8, 8.2Hz, CH), 7.25-7.77 (10H, m, Ph). **^{13}C nmr**; δ = 67.29 (CH_2), 72.95 (CH_2), 73.56 (CH_2), 78.42 (CH), 83.32 (CH), 87.87 (CH), 90.84 (CH), 127.73-128.68 (10 x Ph, CH), 136.86 (C), 137.22 (C), 174.22 (C), 182.39 (C). **IR**; ν max; 2866 (CH), 1771 (C=O), 1659 (C=C).

Hydrogenation of tetronates 8-11.

The required tetronate (**8-11**) was dissolved in ethyl acetate (1-2 ml per mmol) and an equal weight of 10% palladium on charcoal added; the resultant mixture was then vigorously stirred under a hydrogen atmosphere for the required time (or until tlc had indicated the complete consumption of the starting material). Filtration and column chromatography (ethyl acetate) gave the goniofufurone analogues **12-15**.

Data for 12 (*D*-Xylo): *(4R,6R,7S,8S)*-7-Hydroxy-6-hydroxymethyl-1,5-dioxa-2-oxobicyclo-[3.3.0.^{4,8}]octane. 1.06 mmol scale, 47%, solid: M.Pt, 53-55°C, $[\alpha]_D^{24}$ +34.6° (*c* = 0.30, MeOH). **^{1}H nmr** ($CDCl_3$, CD_3OD); δ = 2.65 (1H, d, J = 18.7Hz, CH^3), 2.83 (1H, dd, J = 6.0, 18.7Hz, CH^3), 3.83, (1H, dd,

J = 11.8, 5.4Hz, CHOH), 3.88 (1H, dd, J = 11.8, 4.8Hz, CHOH), 4.06 (1H, ddd, J = 3.4, 4.8, 5.4 Hz, CH^6) 4.43 (3H, m, CH^7 + 2xOH) 4.90 (1H, dd, J = 0.5, 4.2Hz, CH^8) 5.01 (1H, dd, J = 4.2, 6.0Hz, CH^4). **^{13}C nmr**; δ = 35.91 (C3), 59.99 (CH_2OH), 74.06 (C7), 76.67 (C6), 80.61 (C4), 88.43 (C8), 176.60 (C2). **IR**; *ν* max; 3440 (O-H) 3020 (CH), 1788 (C=O).). **MS(CI)**; 192 ($M+NH_4^+$, 100%), 175 ($M+H^+$, 10%), 173 (M^+, 5%). **HRMS**; $C_7H_{14}O_5N$ ($M+NH_4^+$), requires 192.0872, Found 192.0871.

Data for 13 (*D*-Lyxo): *(4S,6R,7S,8R)*-7-Hydroxy-6-hydroxymethyl-1,5-dioxa-2-oxobicyclo-[3.3.0.^{4,8}]octane. 12.2 mmol scale, 87%, solid: M.Pt, 119-121°C, $[\alpha]_D^{24}$, -54.8° (*c* = 0.33, MeOH). **^{1}H nmr** (CD_3OD); δ = 2.60 (1H, dd, J = 18.5, 2.6Hz, CH^3), 2.83 (1H, dd, J = 7.2, 18.8Hz, CH^3), 3.67 (1H, dd, 6.8, 11.8 Hz, CHOH), 3.80 (1H, dd, 4.3, 11.8 Hz, CHOH), 3.78 (1H, ddd, J = 4.3, 4.8, 6.8Hz, CH^6) 4.40 (1H, dd, J = 5.2, 4.8Hz, CH^7) 4.60 (1H, ddd, J = 2.6, 6.1, 7.2Hz, CH^4), 4.84 (2H, br s, 2 x OH) 5.00 (1H, dd, J = 5.2, 6.1, CH^8). **^{13}C nmr**; δ = 37.18 (C3), 61.82 (CH_2OH), 72.27 (C7), 77.35 (C6), 83.94 (C4), 94.95 (C8), 178.43 (C2). **IR**; *ν* max; 3414 (O-H), 2920, 2849 (C-H), 1760 (C=O). **MS(CI)**; 192 (100%, $M+NH_4$). **HRMS**; $C_7H_{14}O_5N$ ($M+NH_4^+$), requires 192.0872, Found 192.0872.

Data for 14 (*D*-Ribo): *(4R,6R,7R,8S)*-7-Hydroxy-6-hydroxymethyl-1,5-dioxa-2-oxobicyclo-[3.3.0.^{4,8}]octane. 2.88 mmol scale, 85%, gum: ($[\alpha]_D^{24}$ +66.3° (*c* = 0.30, MeOH). **^{1}H nmr** ($CDCl_3$, CD_3OD); δ = 2.59 (1H, dd, J = 1.0, 18.7Hz, CH^3), 2.76 (1H, dd, J = 6.1, 18.7Hz, CH^3), 3.56, (1H, dd, J = 11.8, 3.5Hz, CHOH), 3.70 (3H, m, CH^6 + 2xOH) 3.78 (1H, dd, J = 11.8, 2.5Hz, CHOH), 4.10 (1H, dd, J = 4.4, 8.3Hz, CH^7) 4.75 (1H, ddd, J = 1.0, 4.5, 6.1Hz, CH^4) 4.87 (1H, dd, J = 4.4, 4.7 Hz, CH^8). **^{13}C nmr**; δ = 36.97 (C3), 60.54 (CH_2OH), 71.36 (C7), 75.71 (C6), 80.58 (C4), 83.86 (C8), 176.81 (C2). **IR**; *ν* max; 3418 (O-H), 1772 (C=O). **MS(CI)**; 192 (100%, $M+NH_4$). **HRMS**; $C_7H_{14}O_5N$ ($M+NH_4^+$) requires 192.0872, Found 192.0872.

Data for 15 (*D*-Arabino): *(4S,6R,7R,8R)*-7-Hydroxy-6-hydroxymethyl-1,5--dioxa-2-oxo-bicyclo[3.3.0.^{4,8}]octane. Performed on 30:70 mixture of **10** and **11** (0.350mmol total). We obtained the previously isolated **14**, 75% and **15**, 93% based on estimated content. Gum, $[\alpha]_D^{24}$; -29.2° (*c* = 0.25, MeOH). **^{1}H nmr** ($CDCl_3$, CD_3OD); δ = 2.60 (1H, d, J = 18.8Hz, CH^3), 2.71 (1H, dd, J = 4.0, 18.8Hz, CH^3), 3.15, (2H, br s, 2 x OH), 3.57 (1H, dd, 5.5, 12.0 Hz, CHOH), 3.68 (1H, dd, 3.9, 12.0 Hz, CHOH), 3.78 (1H, app.dt, J = 3.9, 5.5, CH^6) 4.16 (1H, d, J = 5.5 Hz, CH^7) 4.76 (2H, m, CH^4 & CH^8). **^{13}C nmr**; δ = 35.94 (C3), 61.62 (CH_2OH), 75.74 (C7), 77.25 (C6), 86.67 (C4), 90.67 (C8), 176.20 (C2). **IR**; *ν* max; 3433 (O-H), 2956, 2924, 2854 (C-H), 1777 (C=O). **MS(CI)**; 192 (30%, $M+NH_4$). **HRMS**; $C_7H_{14}O_5N$ ($M+NH_4^+$) requires 192.0872; found 192.0872.

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