Pergamon

Tetrahedron: *Asymmetry* 13 (2002) 2223–2228

TETRAHEDRON: *ASYMMETRY*

Stereochemistry of the Diels–Alder cyclization of sugar-derived dienes with active dienophiles

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Received 2 August 2002; accepted 24 September 2002

Abstract—The high-pressure intermolecular Diels–Alder reactions of sugar-derived dienes with *N*-phenylmaleimide are described and the crystal structure of a representative adduct is presented. The sugar matrix can be removed from the molecule, allowing the preparation of enantiomerically pure *iso*-indole derivatives. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

One of the most useful methods for the preparation of cyclohexane derivatives is undoubtedly the Diels–Alder reaction.[1] The intramolecular version of this reaction leads to bicyclic adducts. For the preparation of enantiomerically pure compounds (being the obvious targets in stereoselective synthesis), the 'chiron approach'[2] is particularly useful, especially when sugars are used as starting materials. Sugars are readily available and contain a number of defined stereogenic centers. Moreover, stereospecific transformations on a sugar backbone are well documented.

Recently, we elaborated a convenient route to enantiomerically pure, highly oxygenated carbobicyclic compounds (decalins and [4.3.0]nonanes]) from sugar organotin derivatives. These reactions are based on the controlled decomposition of sugar allyltin reagents[3] (**1**; as an example the D-*galacto*-configured derivative is shown in Fig. 1), followed by transformations of the resulting dienoaldehyde **2** either into

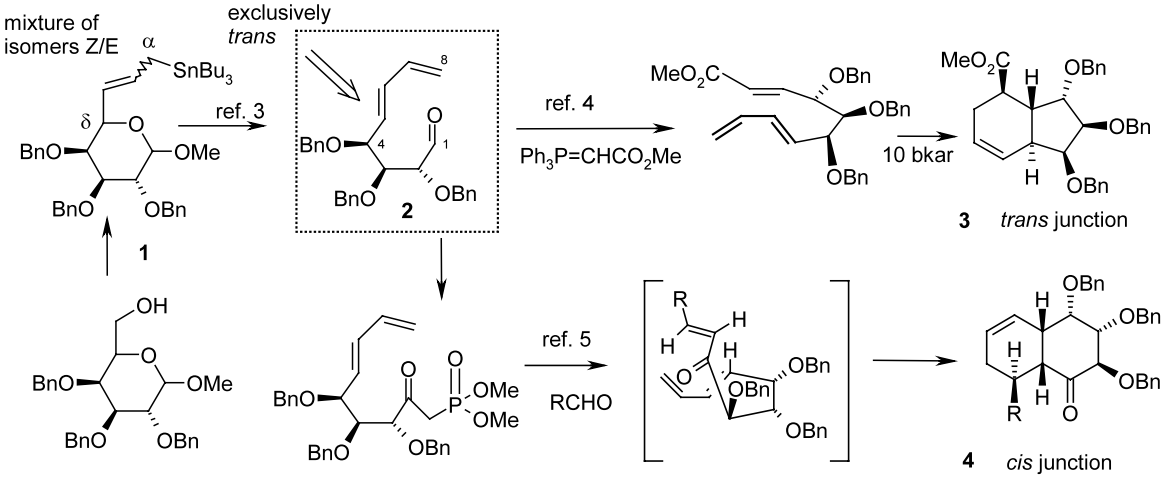

Figure 1. Application of sugar allyltin derivatives in a highly stereoselective synthesis of carbobicyclic derivatives.

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PII: S0957-4166(02)00583-9

bicyclo[4.3.0]nonene[4] **3** or bicyclo[4.4.0]decene[5] (decaline, **4**) derivatives (Fig. 1). Both types of compound could be prepared with very high degrees of selectivity.

Herein, the application of the Diels–Alder reaction of sugar-derived dienes in an inter-molecular mode is reported.

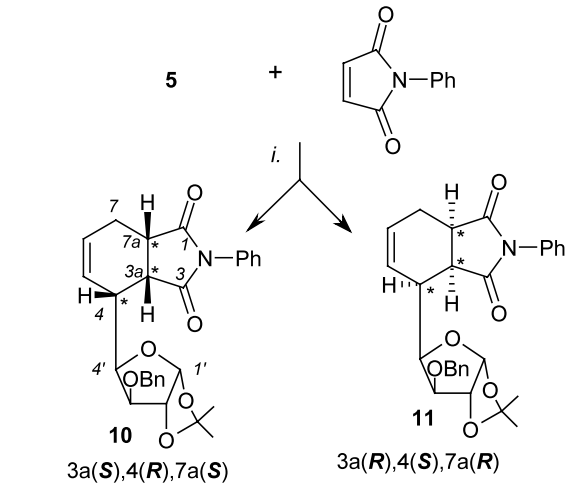
2. Results and discussion

The dienes **5**[6] and **6**[6]—readily prepared from the corresponding sugar allyltin derivatives **7** and **8** (Scheme 1)—were selected for the present study. These compounds have the *opposite* configuration at the α-position to the diene function. Both derivatives were reacted with the active dienophile, *N*-phenylmaleimide **9**, under high pressure conditions.[7]

Reaction of the diene **5** with dienophile **9** afforded two (of the four possible) stereoisomers, **10** and **11**, in a 4:1 ratio (Scheme 2). The relative configuration between the newly created stereogenic centers (C3a, C4 and C7a) was assigned from the NMR spectra; NOESY experiments conducted on **10** and **11** indicated a *cis* relationship between H-1 and H-2 protons in both compounds. However, precise determination of the configurations at these centers, i.e. differentiation between **10**/**11**, was not possible from the NMR experiments. The configuration of these centers in adduct **10** (the major isomer obtained in reaction of **5** with **9**) was therefore determined as 3a*S*,4*R*,7a*S* by X-ray measurements (see Fig. 2). Consequently, the configuration of the second *cis* isomer **11** had to be 3a*R*,4*S*,7a*R*.

Reaction of the diene **6** with olefin **9** was performed analogously and afforded two adducts in a 3:1 ratio. Again, the *cis* geometry between the H-3a and H-4 protons in both adducts **12** and **13** was assigned on the basis of the NOESY experiments. The absolute configuration at the newly created stereogenic centers (C-3a, C-7 and C-7a) in these two products was eventually determined by chemical degradation (see Scheme 3) either to compound **14** or its enantiomer, *ent*-**14**.

To prepare the standard derivative **14** of *known* configuration at the C-3a, C-4 and C-7a centers, the sugar component of compound **10** (the structure of which was determined by X-ray crystallographic analysis) was transformed by a simple sequence of reactions:



Scheme 2. *Reagents and conditions*: (i) **9**, toluene–benzene, 4:1, 10 kbar, 86%.

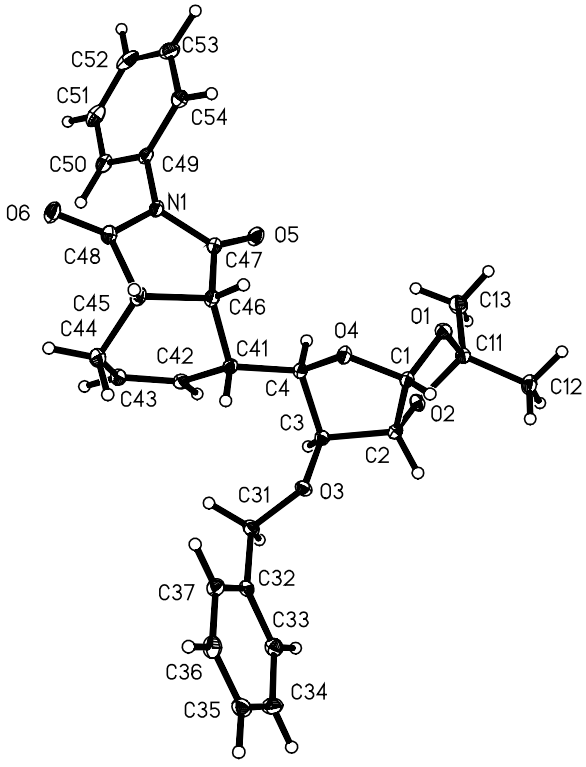
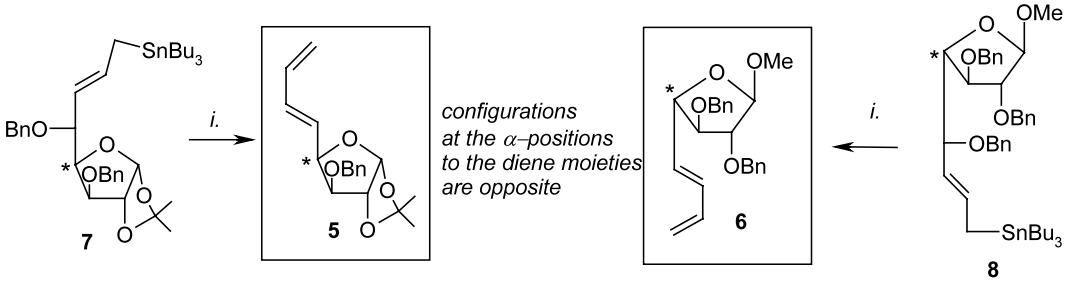


Figure 2. X-Ray structure of **10**.

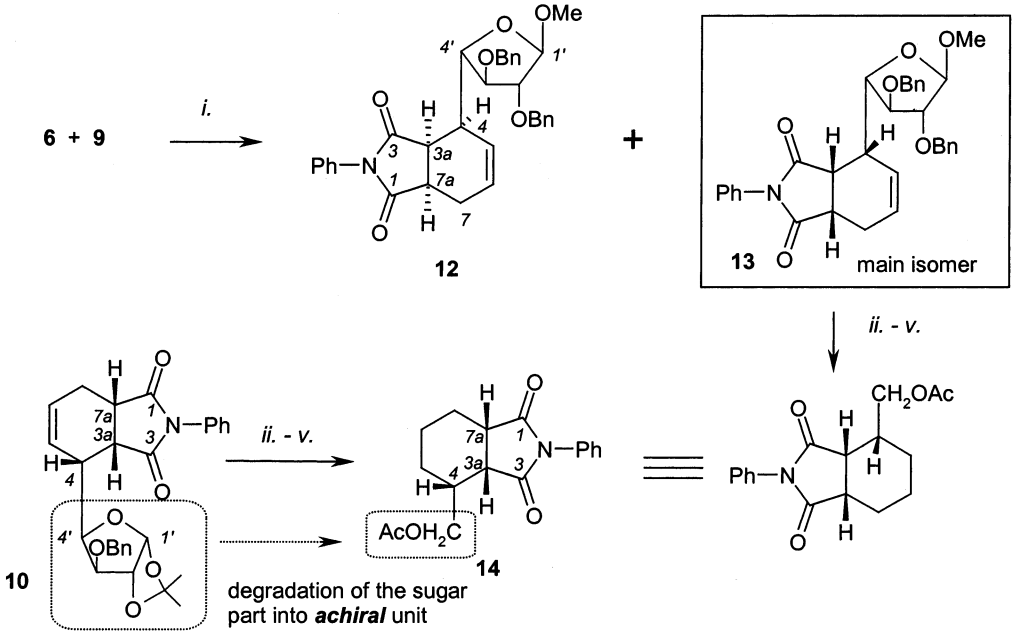


Scheme 1. *Reagents and conditions*: (i) $ZnCl_2$ Ref. 6.

(i) hydrogenolysis, (ii) hydrolysis, (iii) periodate cleavage, (iv) reduction, and finally (v) acetylation (see Scheme 3 and Section 4) into the achiral acetoxymethylene group. The thus obtained levorotatory enantiomer **14** ($[\alpha]_D$ −12.1 (*c* 3.6, $CHCl_3$)) served as the standard for determination of the configuration of adducts **12** and **13**.

The sequence of reactions used for the preparation of **10** was then performed for **13**—the major isomer isolated from reaction of the diene **6** with **9**. We expected, that the degradation should provide dextrorotatory isomer of 4-acetoxymethyl-2-phenyl-hexahydroisoindole-1,3-dione (*ent*-**14**), since the configuration at the C-4′ center of the diene **6** is *opposite* to that in the diene **5**. However, to our surprise, the degradation of **13** afforded the levorotatory compound **14** ($[\alpha]_D$ −10.4 (*c* 1.1, $CHCl_3$)) and not its enantiomer! (Scheme 3).

Careful analysis of the transition states of the cycloaddition process allows this unexpected result to be explained: Only the *endo* addition—leading to the *cis* adduct—has to be considered (Fig. 3). In reaction of the *xylo*-diene



Scheme 3. *Reagents and conditions*: (i) **9**, toluene–benzene, 4:1, 10 kbar, 83%; (ii) H_2/Pd; (iii) THF/H_2O (4:1), cat. H_2SO_4, 40°C, 24 h; (iv) $NaIO_4$ then $NaBH_4$; (v) Ac_2O, Et_3N, CH_2Cl_2, DMAP.

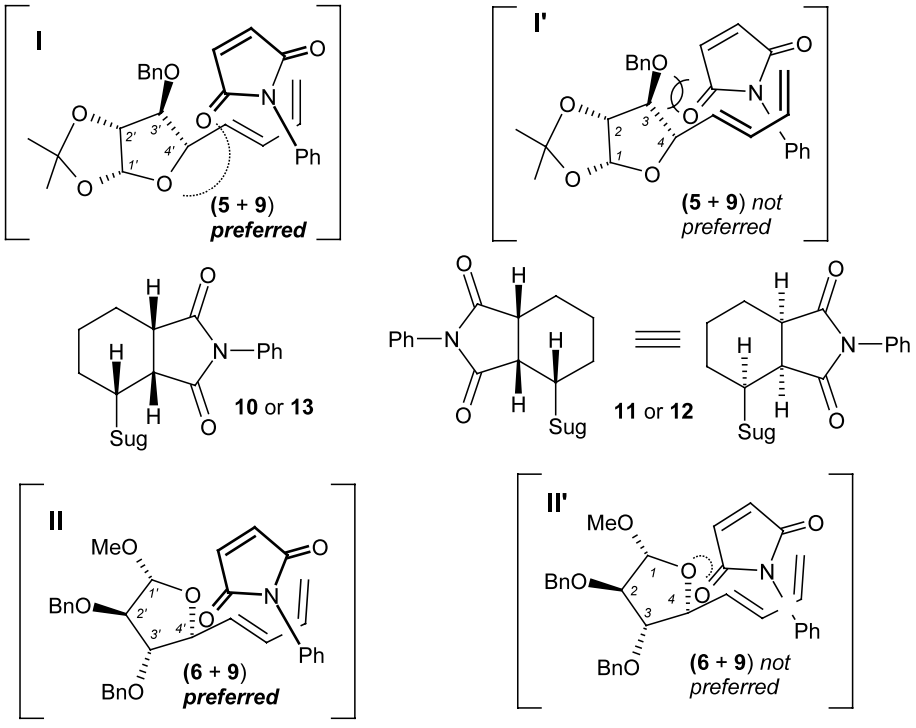


Figure 3. Transition states for addition of **5** or **6** to **9**.

5 with olefin **9** the corresponding transition states may be depicted as **I** and **I′**. There is an unfavorable coulombic interaction between the carbonyl oxygen of the dienophile and the ring oxygen atom of the sugar fragment of the diene (transition state **I**). However, in the alternative transition state **I′** there is severe coulombic and steric interaction of the carbonyl oxygen atom of **9** with the benzyloxy group placed at the C-3′ position of the sugar. Consequently, the reaction proceeds via transition state **I** providing the adduct **10** as the major isomer.

In reaction of the diene **6** (with the *opposite* configuration at the C-4 center of the sugar unit) the *endo* attack of **9** on the diene proceeds via transition state **II** [no steric interaction with the C-3(OBn)], to afford the *iso*-indole derivative **13** *with the same absolute configuration* at the newly created stereogenic centers as **10**. The alternative **II′** is less favored due to severe coulombic repulsion between the carbonyl group of **9** and the ring oxygen of the sugar component of **6**.

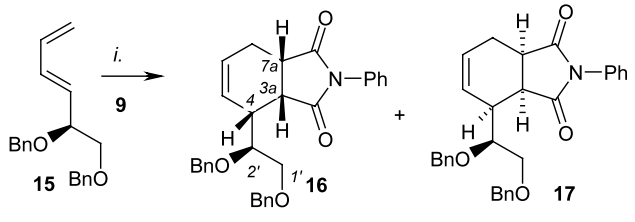
Although the attack of the dienophile onto a diene system occurring from the side occupied by a ring oxygen atom (**I** or **II′**) faced the same (or similar) coulombic repulsion, the attack from the opposite side (**I′** or **II**) *is strongly influenced by the substituent at the C-3 position of the sugar ring* (see Fig. 3). Therefore, the C-α (to the reacting diene system) stereogenic center (opposite in **5** and **6**) is not as important, at least in the case of the process described here.

Reaction of *N*-phenylmaleimide **9** with the less hindered diene supported this assumption to some extent. High pressure cycloaddition of **9** with **15**[6] afforded two cycloadducts, **16** and **17** in equal amounts (Scheme 4).

Again, the *cis*-relationship between the C-4 and C-3a centers in both adducts was assigned on the basis of NOESY NMR experiments.[†]

3. Conclusion

The high pressure reactions of sugar-derived dienes (readily obtained from the corresponding sugar allyltin derivatives) with *N*-phenylmaleimide provided the 4-substituted-3a,4,7,7a-tetrahydro-*iso*-indole-1,3-dione derivatives. Only two (of the four possible isomers) are formed in a ratio of ca. 4:1. The *cis* relationship between all three newly created stereogenic centers in the products arises from the *endo* transition states of the cyclization process. Rather surprisingly, dienes substituted with the D-*xylo*- and L-*arabino* tetrose units, having the *opposite* configuration at the C-α center (**5** and **6**, respectively), afforded (as the major products) *iso*-indole derivatives with *the same absolute configuration* at the bicyclic system.



Scheme 4. *Reagents and conditions*: (i) toluene–benzene, 4:1, 10 kbar, 24 h.

[†] The absolute configuration was not determined, however, it may be tentatively assigned as 3a*S*,4*R*,7a*S* to **16** and 3a*S*,4*R*,7a*S* to **17** on the basis of the similarity of the ^{1}H NMR spectra of the corresponding isomers (**16**/**12** and **17**/**13**; see Section 4).

4. Experimental

4.1. General

NMR spectra were recorded with a Bruker AM 500 or Varian Gemini 200 spectrometers for solutions in $CDCl_3$ (internal Me_4Si) unless otherwise stated. All resonances were assigned by COSY (^{1}H–^{1}H and ^{1}H–^{13}C) correlations. Mass spectra [LSIMS (m-nitrobenzyl alcohol was used as a matrix to which sodium acetate was added) or EI] were recorded with a AMD-604 (AMD Intectra GmbH, Germany) mass spectrometer. Specific rotations were measured with a JASCO DIP Digital Polarimeter for chloroform solution at rt. Column chromatography was performed on silica gel (Merck, 70–230 mesh). Organic solutions were dried over anhydrous magnesium sulfate.

4.2. Reaction of dienes with *N*-phenylmaleimide under high pressure

A solution of the diene[6] **5**, **6**, or **15** (2 mmol) and *N*-phenylmaleimide (2 mmol) in toluene–benzene mixture (4:1 v/v; 11 mL) was placed in a piston–cylinder type apparatus[8] and kept under 10 kbar hydrostatic pressure for 24 h. After this time the solvent was evaporated to dryness and the residue was chromatographed using hexane–ethyl acetate, 5:1→3:1) to afford pure products.

- Reaction of **5** with **9** afforded **10** (68%) and **11** (18%).
- Reaction of **6** with **9** afforded **12** (22%) and **13** (61%).
- Reaction of **15** with **9** afforded **16** (38%) and **17** (34%). This reaction was performed on a 1 mmol scale.

4.2.1. 4-(3′-*O*-Benzyl-1′,2′-*O*-isopropylidene-α-D-*xylo*-tetros-4-yl)-2-phenyl-(3a*S*,4*R*,7a*S*)-tetrahydro-*iso*-indole-1,3-dione, 10. $[\alpha]_D$ −4.2 (*c* 1.5); mp = 186–187°C; ^{1}H NMR δ: 5.99 (m, H-6), 5.96 (d, $J_{1',2'}$ 3.7, H-1′), 5.68 (dt, $J_{4,5} = J_{5,7}$ 3.5, $J_{5,6}$ 9.3, H-5), 5.06 (dd, $J_{3',4'}$ 3.0, $J_{4',4}$ 11.1, H-4′), 4.66 (d, $J_{2',3'}$ 0, H-2′), 4.01 (d, H-3′), 3.61 (dd, $J_{3a,4}$ 5.3, $J_{3a,7a}$ 9.0, H-3a), 3.30 (m, $J_{7,7a}$ 1.3, H-7a), 2.86 (m, H-4), 2.81 (ddd, $J_{6,7}$ 6.8, $J_{7,7}$ 15.5, H-7), 2.29 (m, second H-8), 1.55 and 1.34 [$C(CH_3)_2$]; ^{13}C NMR δ: 178.8 and 176.7 (2×C=O), 129.3–126.5 (C_{arom}, C-5,6), 112.1 [$C(CH_3)_2$], 104.7 (C-1′), 81.9, 80.9 and 78.4 (C-2′,3′,4′), 71.8 (CH_2Ph), 41.0 and 39.6 (C-7a,3a), 35.2 (C-4), 26.9 and 26.6 [$C(CH_3)_2$], 25.0 (C-7); HRMS (LSIMS) m/z: 476.2077 [$C_{28}H_{30}NO_6$ (M+H$^+$) requires 476.2073]. NOE: H4–H3a, H3a–H-7a.

4.2.2. 4-(3′-*O*-Benzyl-1′,2′-*O*-isopropylidene-α-D-*xylo*-tetros-4-yl)-2-phenyl-(3a*R*,4*S*,7a*R*)-tetrahydro-*iso*-indole-1,3-dione, 11. $[\alpha]_D$ −40.3 (*c* 1.3); mp = 189–190°C; ^{1}H NMR δ: 6.13 (dt, $J_{4,5}=J_{5,7}$ 3.4, $J_{5,6}$ 9.3, H-5), 5.99 (m, H-6), 5.97 (d, $J_{1',2'}$ 4.0, H-1′), 4.79 (dd, $J_{3',4'}$ 3.1, $J_{4',4}$ 10.5, H-4′), 4.70 (d, $J_{2',3'}$ 0, H-2′), 4.37 (d, H-3′), 3.12 (ddd, $J_{7,7a}$ 1.4, and 7.7, $J_{3a,7a}$ 9.1, H-7a), 2.96 (dd, $J_{3a,4}$ 5.7, H-3a), 2.78 (ddd, $J_{6,7}$ 7.0, $J_{7,7}$ 15.4, H-7), 2.76 (m, H-4), 2.21 (m, H-7), 1.50 and 1.33 [C(CH_3)$_2$]; ^{13}C NMR δ: 178.7 and 176.9 (2×C=O), 131.7 and 129.3–126.5 (C_{arom}, C-5,6), 111.6 [*C*(CH_3)$_2$], 104.8 (C-1′), 82.4, 81.5 and 80.0 (C-2′,3′,4′), 71.4 (*C*H_2Ph), 40.7 and 40.2 (C-3a,7a), 35.0 (C-4), 26.8 and 26.3 [C(*C*H_3)$_2$], 24.5 (C-7); HRMS (LSIMS) *m*/*z*: 476.2069 [$C_{28}H_{29}NO_6$ (M+H$^+$) requires 476.2073]. Anal. calcd for $C_{28}H_{30}NO_6$ (475.54): C, 70.72; H, 6.15; N, 2.94. Found: C, 70.59; H, 6.18; N, 2.99. NOE: H4–H3a, H3a–H-7a.

4.2.3. 4-(Methyl 2′,3′-di-*O*-benzyl-β-L-arabino-tetrosid-4-yl)-2-phenyl-3a*S*,4*R*,7a*S*)-tetrahydro-*iso*-indole-1,3-dione, 13. $[\alpha]_D$ −106.0 (*c* 1); ^{1}H NMR δ: 5.97 (m, H-5,6), 4.98 (s H-1′), 4.72 (dd, $J_{3',4'}$ 6.1, $J_{4',4}$ 11.1 H-4′), 4.03 (d, $J_{2',3'}$ 1.8, H-2′), 3.73 (dd, H-3′), 3.63 (dd, $J_{4,3a}$ 5.8, $J_{7a,3a}$ 11.1, H-3a), 3.43 (OCH_3), 3.26 (m, H-7a), 2.81 and 2.18 (2×m, both H-7), 2.52 (m, H-4); ^{13}C NMR δ: 178.9 and 176.2 (2×C=O), 129.0–126.5 (C-5,6 and Ph), 106.0 (C-1′), 88.8, 87.7 and 79.1 (C-2′,3′,4′), 72.1 and 72.0 (2×*C*H_2Ph), 54.2 (OCH_3), 41.4, 41.1 and 39.9 (C-4,3a,7a), 24.9 (C-7); HRMS (LSIMS) *m*/*z*: 562.2191 [$C_{33}H_{33}NNaO_6$ (M+Na$^+$) requires 562.2206]. NOE: H4–H3a, H3a–H-7a.

4.2.4. 4-(Methyl 2′,3′-di-*O*-benzyl-β-L-arabino-tetrosid-4-yl)-2-phenyl-(3a*R*,4*S*,7a*R*)-tetrahydro-*iso*-indole-1,3-dione, 12. $[\alpha]_D$ 82.2 (*c* 1.4); ^{1}H NMR δ: 6.02 (m, H-6), 5.88 (m, H-5), 4.81 (d, $J_{1',2'}$ 1.8, H-1′), 4.63 (dd, $J_{3',4'}$ 7.1, $J_{4',4}$ 4.9, H-4′), 4.01 (dd, $J_{2',3'}$ 3.9, H-2′), 3.85 (dd, H-3′), 3.21 (m, H-7a), 3.20 (OCH_3), 3.15 (dd, $J_{4,3a}$ 6.8, $J_{3a,7a}$ 9.4, H-3a), 2.77–2.67 (m, H-4,7), 2.29 (m, second H-7); ^{13}C NMR δ: 129.4–126.5 (C-5,6 and Ph), 107.3 (C-1′), 88.2, 84.3 and 80.1 (C-2′,3′,4′), 72.2 and 71.9 (2×*C*H_2Ph), 55.5 (OCH_3), 42.1, 39.7 and 37.4 (C-4,3a,7a), 23.3 (C-7); HRMS (LSIMS) *m*/*z*: 562.2191 [$C_{33}H_{33}NNaO_6$ (M+Na$^+$) requires 562.2206]. NOE: H4–H3a, H3a–H-7a.

4.2.5. 4-[1′,2′(*S*)-Di-*O*-benzyloxyethane-2′-yl)-2-phenyl-(3a*S*,4*R*,7a*S*)-tetrahydro-*iso*-indole-1,3-dione, 16. $[\alpha]_D$ −87.3 (*c* 2.1); ^{1}H NMR δ: 6.00 (m, H-6), 5.88 (m, H-5), 4.41 (ddd, *J* 11.2, 3.1, and 4.0, H-2′), 3.78 (m, H-3a and H-1′), 3.64 (dd, $J_{1',1'}$ 10.8, second H-1′), 3.27 (m, H-7a), 2.80 (ddd, $J_{7,7a}$ 1.2 and 7.4 $J_{7,7}$ 15.2, H-7), 2.68 (m, H-4), 2.22 (m, second H-7); ^{13}C NMR δ: 179.1 and 177.6 (2×C=O), 130.2(C-5), 127.5 (C-6), 77.5 (C-2′), 73.3 and 72.5 (2×*C*H_2Ph), 70.5 (C-1′), 40.5 (C-3a), 40.1 (C-7a), 38.9 (C-4), 25.4 (C-7); HRMS (LSIMS) *m*/*z*: 490.1966 [$C_{30}H_{29}O_4NNa$ (M+Na$^+$) requires 490.1994]. NOE: H4–H3a, H4–H7a (weak), H3a–H-7a.

4.2.6. 4-[1′,2′(*S*)-Di-*O*-benzyloxyethane-2′-yl)-2-phenyl-(3a*R*,4*S*,7a*R*)-tetrahydro-*iso*-indole-1,3-dione 17. $[\alpha]_D$ +11.5 (*c* 2.1); ^{1}H NMR δ: 6.04 (dt, $J_{5,6}$ 9.3, $J_{4,5}=J_{5,7}$ 3.2, H-5), 5.98 (m, H-6), 4.20 (m, H-2′), 3.94 (m, both H-1′), 3.27 (m, H-3a and H-7a), 2.82 (m, H-4), 2.77 and 2.23 (2m, both H-7); ^{13}C NMR δ: 178.9 and 177.5 (2×C=O), 131.7 (C-5), 127.3 (C-6), 78.4 (C-2′), 73.4 and 72.0 (2×*C*H_2Ph), 68.1 (C-1′), 41.3 (C-3a), 40.8 (C-7a), 37.8 (C-4,), 24.6 (C-7); HRMS (LSIMS) *m*/*z*: 490.1982 [$C_{30}H_{29}O_4NNa$ (M+Na$^+$) requires 490.1994]. NOE: H4–H3a, H4–H7a.

4.3. Degradation of compound 10, the major isomer from reaction of 5 with 9

Major stereoisomer **10** (100 mg) was dissolved in ethyl acetate (10 mL) and hydrogenated under standard conditions (H_2/Pd, overnight). The catalyst was filtered off through Celite and the solvent was evaporated to dryness. The ^{13}C NMR spectrum of the pure intermediate thus obtained indicated the saturation of the C5–C6 double bond and removal of the benzyl protecting group from the C-3′ position of the sugar moiety. ^{13}C NMR δ: 179.1 and 176.9 (2×C=O), 112.3 (*C*Me_2), 104.1 (C-1′), 85.3, 80.0 and 74.1 (C-2′,3′,4′) 41.1, 40.5 and 33.1 (C-4,3a,7a), 27.5 and 27.3 (C*Me*$_2$), 25.6, 22.6, 20.5 (C-5,6,7).

This crude product was dissolved in THF (10 mL), sulfuric acid (10% solution in water, 2 mL) was added and the mixture was heated under reflux for 24 h. After cooling to rt, the acid was carefully neutralized with triethylamine and mixture was poured into ether (10 mL) and water (10 mL). Sodium periodate (300 mg) was added, the mixture was vigorously stirred for 1 h and partition between ether (20 mL) and water (10 mL). The organic lawyer was separated washed with water, dried and concentrated. The crude product was dissolved in THF/MeOH (5 mL, 3:1 v/v) and reduced with sodium borohydride (50 mg) under standard conditions. Acetylation of the crude material with Ac_2O/py, followed by chromatographic purification (hexane–ethyl acetate, 5:1→3:1) afforded **14** (30 mg).

4.3.1. 4-(Acetoxymethyl)-2-phenyl-(3a*S*,4*R*),7a*S*)tetrahydro-*iso*-indole-1,3-dione, 14. $[\alpha]_D$ −12.1 (*c* 3.6), ^{13}C NMR δ: 170.8 (×2) and 170.1 (3×C=O), 67.1 (*C*H_2OAc), 44.6 and (2×) 39.8 (C-3a,4,7a), 24.9 and (2×) 23.9 (C-5,6,7), 21.0 (CO*C*H_3); HRMS *m*/*z*: 370.1299 [$C_{18}H_{21}NO_6$ [M+HCOOH+Na$^+$) requires 370.1267].

4.4. Degradation of compound 13, the major isomer from reaction of 6 with 9

This reaction was performed as detailed above for compound **10**. The product had identical spectral data as **14** (^{13}C NMR and MS); $[\alpha]_D$ −10.4 (*c* 1, $CHCl_3$).

4.5. Crystal structure data for compound 10

For crystal structure data for compound **10**, see Table 1.

Table 1. Crystal structure data for compound **10**

Empirical formula	$C_{28}H_{29}NO_6$
Formula weight	475.52
Temperature (K)	100(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	10.9059(7)
b (Å)	5.4735(5)
c (Å)	20.3267(13)
β (°)	101.067(5)
V (Å^{-3})	1190.81(15)
Z	2
D_c (Mg m^{-3})	1.326
μ (mm^{-1})	0.093
$F(000)$	504
Crystal size (mm)	$0.15\times0.15\times0.15$
Diffractometer	Kuma KM4CCD
Theta range for data collection (°)	3.75–28.49
Ranges of h,k,l	$-14\rightarrow14$, $-7\rightarrow7$, $-26\rightarrow26$
Reflections collected	14909
Independent reflections (R_{int})	5521 (0.0180)
Completeness to $2\theta=28.49$	94.6%
Data/parameters	5521/433
Goodness-of-fit (F^2)	1.031
Final R_1/wR_2 indices ($I>2\sigma_I$)	0.0283/0.0663
Extinction coefficient	0.0188(17)
Largest diff. peak/hole (e Å^{-3})	0.241/−0.168

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure of **10** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 192616.

References

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