Asymmetric Diels–Alder Reactions. Part 6.[1] Regio- and Stereo-selective Cycloadditions of 5-(2',3',4',6'-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-1,4-naphthoquinone[2]

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The title naphthoquinone **1d** underwent reaction with cyclopentadiene to give a cycloadduct, established as (1*R*,4*S*,4a*R*,9a*S*)-1,4,4a,9a-tetrahydro-5-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-1,4-methano-9,10-anthraquinone **9a** by X-ray crystallographic analysis. Single cycloadducts, assigned the structures **4d**, **4e** and **17** were also isolated from the reactions of the naphthoquinone **1d** with (*E*)-1-methoxy-3-trimethylsiloxybuta-1,3-diene **2b**, (*E*)-3-methyl-1-trimethylsiloxybuta-1,3-diene **2f** and (*E*)-2-methyl-1-trimethylsiloxybuta-1,3-diene **16**. A 2:1 mixture of cycloadducts, formulated as the regioisomers **4g** and **3f**, arose in the reaction of the dienophile **1d** with (*E*)-1-acetoxy-3-methylbuta-1,3-diene **2g**.

The sugar auxiliary was readily detached from the oxidation product of compound **9a**, *i.e.* (1*R*,4*S*)-1,4-dihydro-5-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-1,4-methano-9,10-anthraquinone **18b**, by acidic hydrolysis to give the aglycone **18a**.

An X-ray crystallographic analysis of compound **1d** revealed that the quinone ring adopts a boat-like geometry in which the carbonyl oxygen atoms shield the *syn*-face of the C(2)–C(3) double bond. *endo*-Addition of dienes to the *anti*-face provides an explanation for the high diastereofacial reactivity of the naphthoquinone **1d**.

Diels–Alder reactions of juglone **1a** and its derivatives have played an important role in the synthesis of quinonoid natural products and their relatives. Not surprisingly, therefore, much attention has been devoted to controlling the regio- and stereochemical outcome of such reactions.

In an early study, Muxfeldt *et al.*[3] noted that the diene **2a** reacted with juglone **1a** to give a 3:1 mixture of the (±)-cycloadducts **3a** and **4a** and with juglone acetate **2b** to afford a 1:3 mixture of the (±)-cycloadducts **3b** and **4b**. Trost *et al.*[4] observed that the regiochemistry of the cycloaddition of the diene **2a** with juglone **1a** was markedly improved in the presence of boron trifluoride [to a >20:1 mixture of the (±)-cycloadducts **3a** and **4a**]. Enhanced regioselectivity could also be achieved by the use of more polarised dienes as demonstrated by Boeckman *et al.*;[5] thus, Danishefsky's diene **2b** was found to react with juglone **1a** to give only the (±)-cycloadduct **3c** and with juglone methyl ether **1c** to afford only the (±)-cycloadduct **4c** (in practice, the cycloadducts were not isolated but subjected to base-induced aromatisations).

Two strategies have been developed to control the absolute stereochemical outcome of cycloaddition reactions involving juglone **1a** and its relatives. In one strategy, enantiopure dienes of type **2** (R^1 = a detachable chiral auxiliary) are used to promote the reactions. In the other strategy, enantiopure Lewis acids are employed.

The use of enantiopure dienes was established by Trost and his co-workers[6] and by ourselves.[7] Thus, the American workers developed the diene **2c** and showed that it reacted with juglone **1a** in the presence of tetra-acetyl diborate to give the cycloadduct **3d** as the sole product. We introduced the diene **2d** and demonstrated that it afforded largely the cycloadduct **5a** with juglone **1a** in the presence of tetraacetyl diborate.

The employment of enantiopure Lewis acids to promote cycloadditions of juglone **1a** and its relatives has been progressed by the groups of Kelly[8] and Yamamoto.[9] Thus, the American workers found that the complex generated by treatment of the binaphthol **6** with diborane, acetic acid and juglone **1a** underwent reaction with the diene **2a** to give the cycloadduct **5b** (>98% e.e.). The Japanese group established that the complex formed from juglone **1a**, trimethyl borate and the diamide **7** reacted with the diene **2e** to furnish the cycloadduct **3e** (92% e.e.). The ability of bovine serum albumin to catalyse the Diels–Alder reaction between juglone **1a** and 1-methoxycyclohexa-1,3-diene to give a 2.5:1 mixture of cycloadducts (the major one with 38% e.e.) was noted by Colonna and his co-workers.[10]

In this paper we report a third strategy for controlling the absolute stereochemical outcome of cycloadditions of juglone derivatives. It involves the use of dienophiles of type **1** (R = a detachable enantiopure auxiliary).

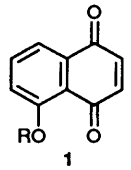
Results and Discussion

Prompted by our finding[11,12] that the 2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl auxiliary can confer a notable diastereofacial reactivity on 1-oxybuta-1,3-dienes in Diels–Alder reactions, we decided to investigate the dienophilic reactivity of the juglone glucoside **1d**.

Initially, compound **1d** was prepared (78% yield after crystallisation) by the reaction of juglone **1a**[13] and the acetobromoglucose **8**[14] in quinoline in the presence of silver(I) oxide (conditions prescribed by Müller[15] for the preparation of hydroxyanthraquinone glucosides). However, the reaction was somewhat capricious (it is noteworthy that Thomson and Hayes[16] reported that the reaction was unsuccessful) and better, and reproducible, results were obtained by using acetonitrile as the solvent and subjecting the mixture to sonication.† Following a chromatographic work-up and crystallisation, the glucoside **1d** was isolated in 82% yield.

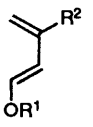
To establish its diastereofacial reactivity, the dienophile **1d** was treated with cyclopentadiene[17] in benzene at ambient temperature. Essentially a single cycloadduct was produced which was isolated in 83% yield after crystallisation. Clearly, the

† We thank Dr. A. Whiting for suggesting these conditions.

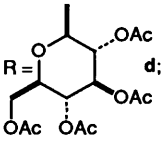
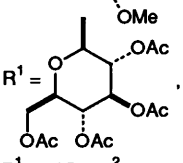


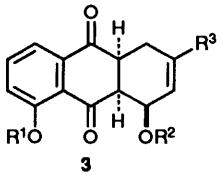
1

a; R = H
b; R = Ac
c; R = Me

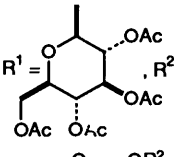


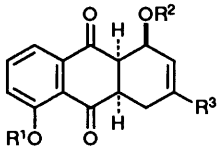
2

a; R^1 = Ac, R^2 = H
b; R^1 = Me, R^2 = $OSiMe_3$
c; R^1 = CO–(Ph, H, OMe), R^2 = H
d; R = 
d; R^1 =  , R^2 = Me
e; R^1 = $SiEt_3$, R^2 = H
f; R^1 = $SiMe_3$, R^2 = Me
g; R^1 = Ac, R^2 = Me

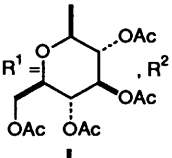
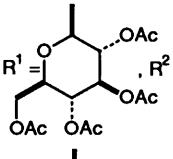
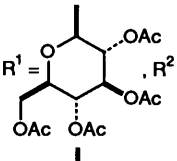
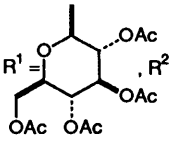


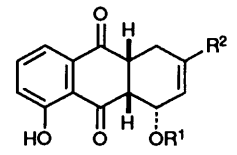
3

a; R^1 = H, R^2 = Ac, R^3 = H
b; R^1 = Ac, R^2 = Ac, R^3 = H
c; R^1 = H, R^2 = Me, R^3 = $OSiMe_3$
d; R^1 = H, R^2 = CO–(Ph, H, OMe), R^3 = H
e; R^1 = H, R^2 = $SiEt_3$, R^3 = H
f; R^1 =  , R^2 = Ac, R^3 = Me



4

a; R^1 = H, R^2 = Ac, R^3 = H
b; R^1 = Ac, R^2 = Ac, R^3 = H
c; R^1 = Me, R^2 = Me, R^3 = $OSiMe_3$
d; R^1 =  , R^2 = Me, R^3 = $OSiMe_3$
e; R^1 =  , R^2 = $SiMe_3$, R^3 = Me
f; R^1 =  , R^2 = H, R^3 = Me
g; R^1 =  , R^2 = Ac, R^3 = Me



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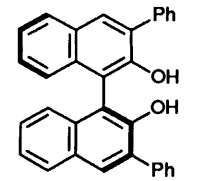
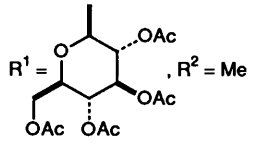
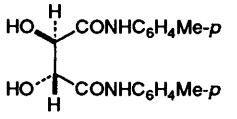


6

a; R^1 =  , R^2 = Me
b; R^1 = Ac, R^2 = H



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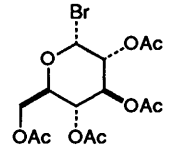

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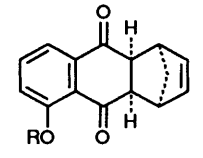

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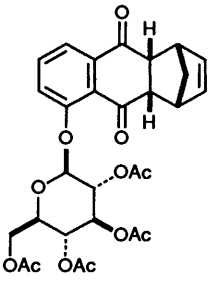

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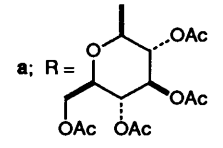
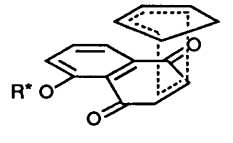
a; R = 
b; R = H



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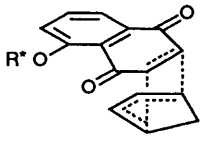
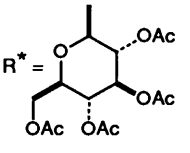
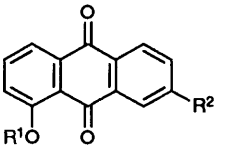
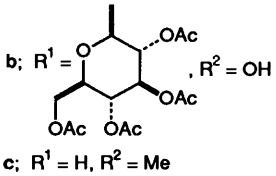
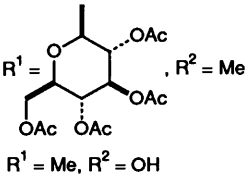


12

R* = 



13

a; R^1 = H, R^2 = OH
b; R^1 =  , R^2 = OH
c; R^1 = H, R^2 = Me
d; R^1 =  , R^2 = Me
e; R^1 = Me, R^2 = OH

sugar, even though remote from the reacting centre (a 1,6-relationship exists between the closest stereogenic and reacting centres), exerts a pronounced stereodirecting influence.

On the assumption that an *endo*-transition state is involved, the cycloadduct must possess the stereostructure **9a** or **10**. That the former structure was the correct one was established by an X-ray crystallographic analysis. The molecular structure (see Experimental section for crystal data and other information),

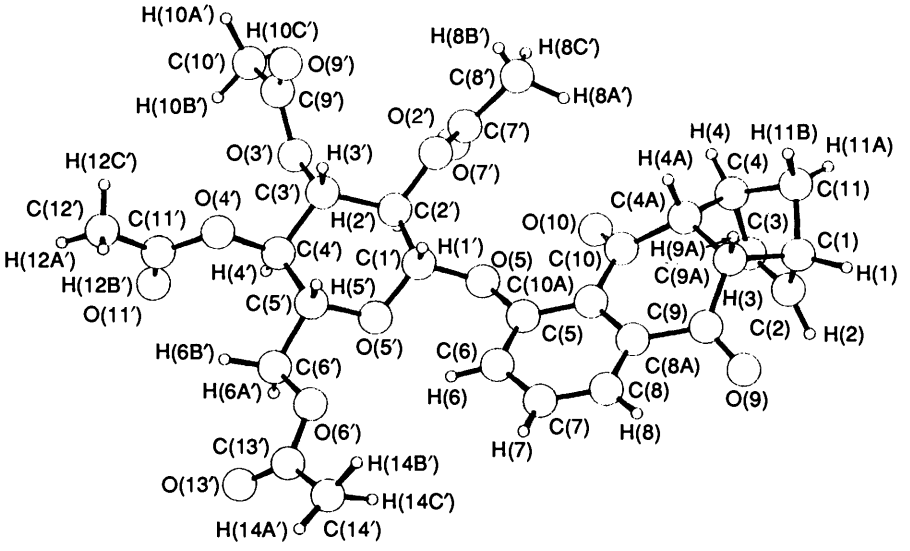


Fig. 1 Molecular structure of compound **9a**

Table 1 Fractional atomic co-ordinates ($\times 10^4$) for compound **9a** with estimated standard deviations (esds) in parentheses.

Atom	*x*	*y*	*z*
C(1)	12 324(7)	834(2)	6 053(2)
C(2)	10 349(8)	700(3)	5 704(1)
C(3)	8 911(8)	1 164(3)	5 833(2)
C(4)	9 878(6)	1 623(2)	6 276(1)
C(4A)	10 054(5)	1 194(2)	6 840(1)
C(5)	6 405(5)	131(1)	7 790(1)
O(5)	4 829(3)	598(1)	7 900(1)
C(6)	6 479(6)	−485(2)	8 079(1)
C(7)	8 028(7)	−952(2)	7 934(2)
C(8)	9 469(6)	−816(2)	7 519(2)
C(8A)	9 466(5)	−199(2)	7 237(1)
C(9)	11 131(5)	−64(2)	6 795(1)
O(9)	11 990(5)	−526(1)	6 547(1)
C(9A)	11 741(5)	654(2)	6 687(1)
C(10)	7 943(5)	952(1)	7 059(1)
O(10)	6 351(4)	1 293(1)	6 999(1)
C(10A)	7 920(5)	290(1)	7 374(1)
C(11)	12 211(7)	1 599(2)	6 086(2)
C(1′)	4 143(5)	689(2)	8 468(1)
C(2′)	2 953(5)	1 353(1)	8 492(1)
O(2′)	4 412(4)	1 889(1)	8 378(1)
C(3′)	1 972(5)	1 448(2)	9 088(1)
O(3′)	384(3)	1 978(1)	9 052(1)
C(4′)	842(5)	816(1)	9 305(1)
O(4′)	490(3)	903(1)	9 915(1)
C(5′)	2 198(5)	197(2)	9 216(1)
O(5′)	2 743(3)	163(1)	8 616(1)
C(6′)	1 073(6)	−459(2)	9 358(2)
O(6′)	2 699(4)	−969(1)	9 307(1)
C(7′)	3 960(8)	2 328(2)	7 955(1)
O(7′)	2 300(6)	2 336(1)	7 710(1)
C(8′)	5 904(13)	2 753(3)	7 824(3)
C(9′)	710(7)	2 565(2)	9 335(2)
O(9′)	2 278(6)	2 666(1)	9 610(1)
C(10′)	−1 128(9)	3 028(2)	9 247(2)
C(11′)	−1 475(5)	771(2)	10 131(1)
O(11′)	−2 946(4)	621(1)	9 838(1)
C(12′)	−1 463(8)	827(3)	10 770(2)
C(13′)	2 172(8)	−1 600(2)	9 416(2)
O(13′)	394(7)	−1 742(1)	9 553(2)
C(14′)	3 980(11)	−2 075(2)	9 367(3)

together with its crystallographic labelling, is shown in Fig. 1. Refined atomic co-ordinates are included in Table 1, bond lengths in Table 2 and bond angles in Table 3.

Clearly, the transition state **11** leading to the cycloadduct **9a** is preferred to its diastereoisomeric counterpart **12** which would lead to the cycloadduct **10**. Possible explanations for this preference will be considered later.

Table 2 Bond lengths (Å) for compound **9a** with esds in parentheses.

C(1)–C(2)	1.503(6)	C(1)–C(9A)	1.556(5)
C(1)–C(11)	1.518(6)	C(2)–C(3)	1.323(7)
C(3)–C(4)	1.499(6)	C(4)–C(4A)	1.563(4)
C(4)–C(11)	1.529(6)	C(4A)–C(9A)	1.545(5)
C(4A)–C(10)	1.496(4)	C(5)–O(5)	1.377(3)
C(5)–C(6)	1.392(4)	C(5)–C(10A)	1.390(4)
O(5)–C(1′)	1.396(3)	C(6)–C(7)	1.383(5)
C(7)–C(8)	1.347(6)	C(8)–C(8A)	1.385(4)
C(8A)–C(9)	1.487(4)	C(8A)–C(10A)	1.407(4)
C(9)–O(9)	1.207(4)	C(9)–C(9A)	1.493(5)
C(10)–O(10)	1.213(4)	C(10)–C(10A)	1.500(4)
C(1′)–C(2′)	1.514(4)	C(1′)–O(5′)	1.405(4)
C(2′)–O(2′)	1.425(4)	C(2′)–C(3′)	1.523(4)
O(2′)–C(7′)	1.341(4)	C(3′)–O(3′)	1.450(4)
C(3′)–C(4′)	1.525(4)	O(3′)–C(9′)	1.349(4)
C(4′)–O(4′)	1.440(3)	C(4′)–C(5′)	1.506(4)
O(4′)–C(11′)	1.355(4)	C(5′)–O(5′)	1.433(3)
C(5′)–C(6′)	1.516(4)	C(6′)–O(6′)	1.440(4)
O(6′)–C(13′)	1.317(5)	C(7′)–O(7′)	1.185(6)
C(7′)–C(8′)	1.512(9)	C(9′)–O(9′)	1.189(5)
C(9′)–C(10′)	1.487(7)	C(11′)–O(11′)	1.183(4)
C(11′)–C(12′)	1.484(5)	C(13′)–O(13′)	1.193(7)
C(13′)–C(14′)	1.477(8)		

Based upon the aforecited result and the finding of Boeckman *et al.*[5] mentioned earlier, we hoped that Danishefsky's diene **2b**[18] would react with the dienophile **1d** in a fully regio- and stereo-selective manner. Gratifyingly, a single cycloadduct (92% yield), formulated as compound **4d**, emerged when the reaction was conducted in benzene.

The regiostructure of the cycloadduct **4d** was established by its conversion into the dihydroxyanthraquinone **13a**.[19] Thus, when treated in chloroform with a few drops of conc. hydrochloric acid, compound **4d** was transformed into the hydroxyanthraquinone **13b** (93% yield after crystallisation); hydrolysis of the last-cited compound was effected with hot ethanolic hydrochloric acid to give the dihydroxyanthraquinone **13a** (88% yield after crystallisation). The melting point and 300 MHz ^{1}H NMR spectrum of the last-cited material matched those of an independently prepared sample of 1,7-dihydroxyanthraquinone **13a** (obtained by subjecting the cycloadduct of juglone methyl ether **1c** and Danishefsky's diene **2b** to an aromatisation–demethylation sequence) but differed

Table 3 Bond angles (°) for compound **9a** with esds in parentheses

C(2)–C(1)–C(9A)	105.9(3)	C(2)–C(1)–C(11)	99.5(3)
C(9A)–C(1)–C(11)	99.9(3)	C(1)–C(2)–C(3)	108.5(4)
C(2)–C(3)–C(4)	107.5(4)	C(3)–C(4)–C(4A)	105.6(3)
C(3)–C(4)–C(11)	99.8(3)	C(4A)–C(4)–C(11)	99.0(3)
C(4)–C(4A)–C(9A)	103.5(2)	C(4)–C(4A)–C(10)	113.3(3)
C(9A)–C(4A)–C(10)	117.5(3)	O(5)–C(5)–C(6)	121.6(3)
O(5)–C(5)–C(10A)	117.8(2)	C(6)–C(5)–C(10A)	120.7(3)
C(5)–O(5)–C(1′)	118.8(2)	C(5)–C(6)–C(7)	119.5(3)
C(6)–C(7)–C(8)	120.7(3)	C(7)–C(8)–C(8A)	120.8(3)
C(8)–C(8A)–C(9)	118.9(3)	C(8)–C(8A)–C(10A)	120.2(3)
C(9)–C(8A)–C(10A)	120.9(3)	C(8A)–C(9)–O(9)	120.3(3)
C(8A)–C(9)–C(9A)	117.8(3)	O(9)–C(9)–C(9A)	121.9(3)
C(1)–C(9A)–C(4A)	102.6(3)	C(1)–C(9A)–C(9)	115.8(3)
C(4A)–C(9A)–C(9)	116.5(3)	C(4A)–C(10)–O(10)	120.7(3)
C(4A)–C(10)–C(10A)	116.9(3)	O(10)–C(10)–C(10A)	122.3(3)
C(5)–C(10A)–C(8A)	118.1(2)	C(5)–C(10A)–C(10)	122.8(3)
C(8A)–C(10A)–C(10)	119.1(2)	C(1)–C(11)–C(4)	95.2(3)
O(5)–C(1′)–C(2′)	107.4(2)	O(5)–C(1′)–O(5′)	109.0(2)
C(2′)–C(1′)–O(5′)	109.1(3)	C(1′)–C(2′)–O(2′)	108.9(3)
C(1′)–C(2′)–C(3′)	109.9(2)	O(2′)–C(2′)–C(3′)	109.6(2)
C(2′)–O(2′)–C(7′)	118.9(3)	C(2′)–C(3′)–O(3′)	108.3(2)
C(2′)–C(3′)–C(4′)	112.7(2)	O(3′)–C(3′)–C(4′)	107.2(3)
C(3′)–O(3′)–C(9′)	119.4(3)	C(3′)–C(4′)–O(4′)	107.2(2)
C(3′)–C(4′)–C(5′)	111.2(3)	O(4′)–C(4′)–C(5′)	108.6(2)
C(4′)–O(4′)–C(11′)	118.6(2)	C(4′)–C(5′)–O(5′)	107.9(2)
C(4′)–C(5′)–C(6′)	113.9(3)	O(5′)–C(5′)–C(6′)	106.3(2)
C(1′)–O(5′)–C(5′)	110.5(2)	C(5′)–C(6′)–O(6′)	104.7(3)
C(6′)–O(6′)–C(13′)	118.2(3)	O(2′)–C(7′)–O(7′)	122.9(4)
O(2′)–C(7′)–C(8′)	109.7(4)	O(7′)–C(7′)–C(8′)	127.2(4)
O(3′)–C(9′)–O(9′)	122.1(3)	O(3′)–C(9′)–C(10′)	110.3(3)
O(9′)–C(9′)–C(10′)	127.6(3)	O(4′)–C(11′)–O(11′)	123.1(3)
O(4′)–C(11′)–C(12′)	110.4(3)	O(11′)–C(11′)–C(12′)	126.5(3)
O(6′)–C(13′)–O(13′)	120.6(4)	O(6′)–C(13′)–C(14′)	113.4(4)
O(13′)–C(13′)–C(14′)	126.0(4)		

from those of 1,6-dihydroxyanthraquinone **14a**[5] (obtained by aromatisation of the cycloadduct of juglone **1a** and Danishefsky's diene **2b**).

Selective cleavage of the trimethylsilyl ether moiety of compound **4d** was effected by using dilute hydrochloric acid in tetrahydrofuran (THF), the ketone **15** being isolated in 96% yield after crystallisation.

Full regio- and stereo-selectivity was also achieved in the reaction of the juglone glucoside **1d** with the diene **2f**[20] in benzene, affording the cycloadduct **4e** in 93% yield after crystallisation.

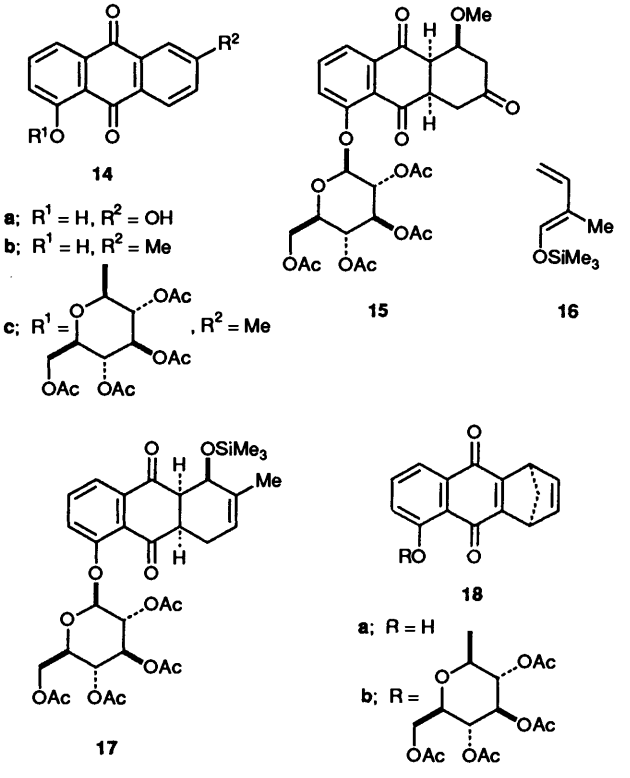
The regiochemistry of the cycloaddition was secured by transforming the cycloadduct **4e** into the hydroxymethylanthraquinone **13c**.[21] Thus, in chloroform containing a few drops of conc. hydrochloric acid, compound **4e** was converted into the methylanthraquinone **13d** (92% yield after crystallisation) which underwent hydrolysis in hot ethanolic hydrochloric acid to give the hydroxymethylanthraquinone **13c** (84% yield after crystallisation). The melting point and 300 MHz ^{1}H NMR spectrum of the last-cited material matched that of an independently prepared sample of 1-hydroxy-7-methylanthraquinone **13c** (obtained by subjecting the cycloadduct of juglone methyl ether **1c** and the diene **2f** to an oxidative aromatisation–demethylation sequence).

Cleavage of the trimethylsilyl ether moiety of compound **4e** was effected by the action of dilute hydrochloric acid in THF; after crystallisation, the alcohol **4f** was isolated in 92% yield.

The diene **2g**,[22] which is less polarised than its relative **2f**, reacted with the juglone glucoside **1d** in benzene to give a 2:1 mixture of cycloadducts, presumed to be the regioisomers **4g** and **3f**. Fractional crystallisation of the mixture provided the major cycloadduct **4g** in 42% yield. Its regiochemistry was established by conversion into the hydroxymethylanthraquinone **13c** under hydrolytic conditions.

A single cycloadduct, formulated as compound **17**, was obtained (90% yield after crystallisation) from the reaction of the juglone glucoside **1d** with the diene **16**[23] in benzene.

The regiochemistry of the cycloaddition was corroborated by transforming the cycloadduct **17** into the hydroxymethylanthraquinone **14b**.[21,24] Thus, under the usual conditions, the cycloadduct **17** afforded the methylanthraquinone **14c** (95% yield after crystallisation) and thence the hydroxymethylanthraquinone **14b** (92% yield after crystallisation). The melting point and 300 MHz ^{1}H NMR spectrum of compound **14b** matched that of an independently prepared sample (obtained by subjecting the cycloadduct of juglone **1a** and the diene **2f** to the action of Et_3N in CH_2Cl_2 and crystallisation of the product).



The possibility of detaching the sugar auxiliary from the cycloadduct **9a**, without damage to the induced stereochemistry, was examined. When the cycloadduct **9a** was heated in ethanolic hydrochloric acid, work-up (by partitioning the mixture between CH_2Cl_2 and H_2O and evaporation of the organic phase) led mainly to a 4:1:1 mixture of compound **9b**, compound **18a** and an unidentified material according to 300 MHz ^{1}H NMR spectroscopy. The use of trifluoroacetic acid at room temperature gave, after silica gel chromatography, the aglycone **9b** in a slightly impure state in *ca.* 26% yield. The 300 MHz ^{1}H NMR spectrum of the sample matched that of racemic material[25] (prepared in 75% yield after crystallisation from the reaction of juglone **1a** with cyclopentadiene).

No problems were encountered when the quinone **18b** (prepared in 72% yield after crystallisation by treatment of the cycloadduct **9a** in CH_2Cl_2 with Et_3N and O_2) was subjected to the action of hot ethanolic hydrochloric acid. Work-up afforded the quinone **18a** in 92% yield. The spectroscopic properties of compound **18a**, which showed $[\alpha]_D$ +20 ($CHCl_3$), matched those of racemic material [prepared by oxidation of the (±)-cycloadduct **9b**].

In addition to their synthetic value, the aforecited findings are of considerable mechanistic interest. Clearly, a substantive stereoinduction phenomenon is implicated. Earlier, we noted[11,12] that dienes of type **19** reacted with dienophiles of type **20** to give predominantly cycloadducts of type **21**. To

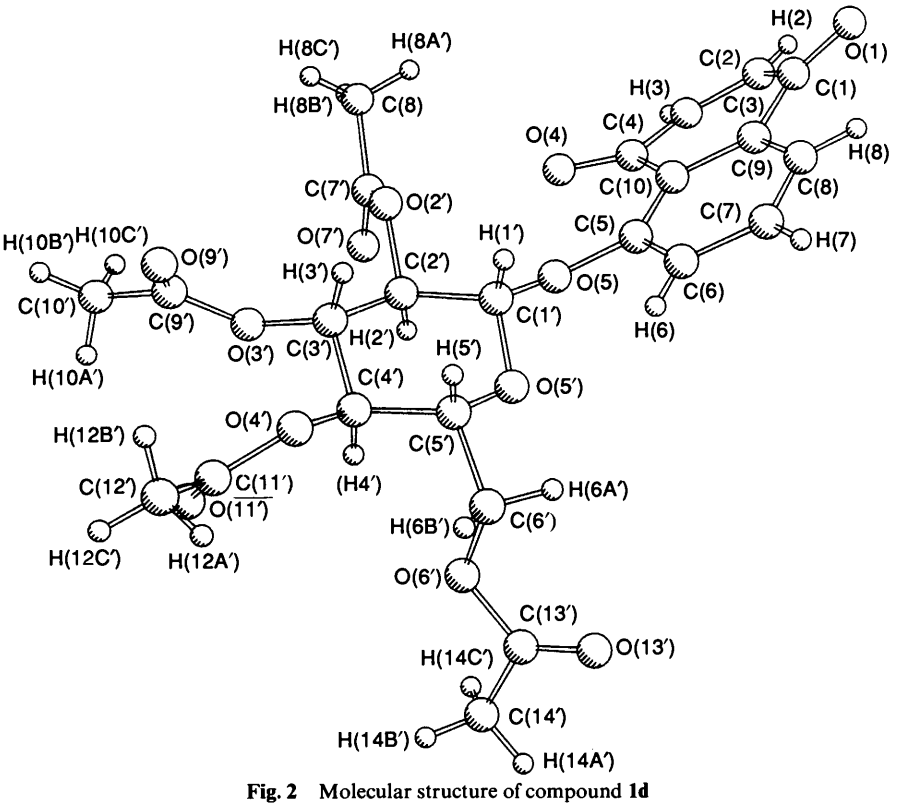
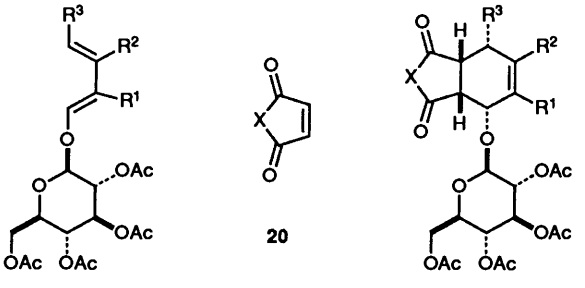
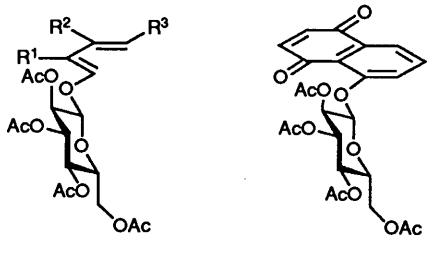


Fig. 2 Molecular structure of compound **1d**

account for the 1,3-stereoinduction, we suggested that the dienes reacted mainly by way of conformers of type **22**. The major cycloadducts were considered to arise by *endo*-addition of the dienophiles to the least-hindered 'top' faces of these conformers.



19 **20** **21**



22 **23**

Initially, we attempted to extrapolate the 1,3-stereoinduction model to the 1,6-stereoinduction situation. Thus, on the assumption that O(5) would approximate sp^2-hybridisation, that a near-orthogonal relationship would exist between O(5)–C(5) and O(5')–C(1') (to maximise the *exo*-anomeric effect[26]) and that there would be a near-planar arrangement of the aromatic ring and the C(1')–O(5) bond (to maximise conjugation), the juglone glycoside **1d** was expected to favour the conformer **23** [or a version in which the C(1')–O(5) bond would be slightly twisted from the plane of the aromatic ring so as to relieve the H(1')–H(6) interaction]. Were conformer **23** to be the reactive one, *endo*-addition of cyclopentadiene to the 'top' face of the C(2)–C(3) double bond might be slightly preferred to the corresponding addition to the 'bottom' face.* Such a situation would lead to the cycloadduct **10** in preference to its diastereoisomer **9a**—a prediction opposite to the experimental result! Clearly, the origins of the 1,6- and 1,3-stereoinductions are unrelated.

In the hope that its solid-state structure would reveal 'preorganization' which might shed some light on the diastereoselection process, the juglone glycoside **1d** was subjected to an X-ray crystallographic analysis. The structure (see Experimental section for crystal data and other information) is shown in Fig. 2 together with its crystallographic labelling. Refined atomic co-ordinates are given in Table 4, bond lengths in Table 5 and bond angles in Table 6.

Clearly, in the crystal state, the conformer **23** is modified by twisting (35°) the plane of the aromatic ring with respect to the C(1')–O(5) bond [presumably, to minimize the van der Waal's interaction between H(1') and H(6)]. Of particular interest is that the twisting takes place in a clockwise direction [when viewed along the O(5)–C(5) bond] and places a quinone carbonyl oxygen [O(4)] close to the carbonyl carbon [C(7')] of the 2'-*O*-acetyl group of the sugar [the interatomic distance between O(4) and C(7') is 3.11 Å]. In consequence, the quinone

* Earlier, we suggested[12] that dienophiles added preferentially to the 'top' face of dienes of type **22** to avoid the development of a 1,3-*syn* interaction with the O(5')–C(1') bond. It would be necessary to invoke a related 1,6-*syn* interaction (which, clearly, would be less effective) in the case of the conformer **23**.

Table 4 Fractional atomic co-ordinates for compound **1d** with esds in parentheses

Atom	*x*	*y*	*z*
O(1)	−0.1109(2)	0.0193	0.1096(9)
O(4)	0.0063(2)	0.374(1)	0.308(1)
O(5)	0.0533(1)	0.119(1)	0.3680(6)
C(1)	−0.0859(3)	0.089(2)	0.189(1)
C(2)	−0.0913(3)	0.252(2)	0.241(1)
C(3)	−0.0610(3)	0.338(1)	0.296(1)
C(4)	−0.0201(2)	0.280(1)	0.299(1)
C(5)	0.0205(2)	0.028(1)	0.319(1)
C(6)	0.0230(2)	−0.137(1)	0.312(1)
C(7)	−0.0093(3)	−0.226(1)	0.265(1)
C(8)	−0.0439(3)	−0.153(2)	0.223(1)
C(9)	−0.0471(2)	0.012(2)	0.2335(9)
C(10)	−0.0148(2)	0.106(1)	0.285(1)
O(2′)	0.0997(1)	0.307(1)	0.1851(5)
O(3′)	0.1800(1)	0.296(1)	0.2799(6)
O(4′)	0.2056(1)	−0.054(1)	0.3201(5)
O(5′)	0.1059(1)	−0.036(1)	0.4467(6)
O(6′)	0.1685(1)	−0.165(1)	0.6644(6)
O(7′)	0.0965(2)	0.518(1)	0.3477(8)
O(9′)	0.2119(2)	0.226(1)	0.0684(8)
O(11′)	0.2480(2)	0.112(1)	0.4483(7)
O(13′)	0.1432(2)	−0.368(1)	0.7924(7)
C(1′)	0.0891(2)	0.064(1)	0.326(1)
C(2′)	0.1161(2)	0.208(1)	0.311(1)
C(3′)	0.1563(2)	0.154(1)	0.269(1)
C(4′)	0.1718(2)	0.026(1)	0.3836(9)
C(5′)	0.1420(2)	−0.105(1)	0.400(1)
C(6′)	0.1543(2)	−0.236(1)	0.517(1)
C(7′)	0.0908(2)	0.460(2)	0.221(1)
C(8′)	0.0727(3)	0.543(2)	0.078(1)
C(9′)	0.2051(2)	0.320(1)	0.168(1)
C(10′)	0.2246(3)	0.479(1)	0.193(1)
C(11′)	0.2420(2)	−0.002(1)	0.365(1)
C(12′)	0.2723(2)	−0.104(2)	0.297(1)
C(13′)	0.1624(3)	−0.250(2)	0.796(1)
C(14′)	0.1829(2)	−0.176(2)	0.936(1)

Table 5 Bond lengths (Å) for compound **1d** with esds in parentheses

O(1)–C(1)	1.21(1)	O(5′)–C(1′)	1.411(9)
O(4)–C(4)	1.20(1)	O(5′)–C(5′)	1.440(8)
O(5)–C(5)	1.398(9)	O(6′)–C(6′)	1.441(9)
O(5)–C(1′)	1.375(8)	O(6′)–C(13′)	1.35(1)
C(1)–C(2)	1.45(1)	O(7′)–C(7′)	1.19(1)
C(1)–C(9)	1.50(1)	O(9′)–C(9′)	1.19(1)
C(2)–C(3)	1.32(1)	O(11′)–C(11′)	1.190(9)
C(3)–C(4)	1.48(1)	O(13′)–C(13′)	1.19(1)
C(4)–C(10)	1.47(1)	C(1′)–C(2′)	1.53(1)
C(5)–C(6)	1.38(1)	C(2′)–C(3′)	1.51(1)
C(5)–C(10)	1.39(1)	C(3′)–C(4′)	1.51(1)
C(6)–C(7)	1.37(1)	C(4′)–C(5′)	1.51(1)
C(7)–C(8)	1.36(1)	C(5′)–C(6′)	1.52(1)
C(8)–C(9)	1.39(1)	C(7′)–C(8′)	1.49(1)
C(9)–C(10)	1.40(1)	C(9′)–C(10′)	1.50(1)
O(2′)–C(2′)	1.435(9)	C(11′)–C(12′)	1.49(1)
O(2′)–C(7′)	1.35(1)	C(13′)–C(14′)	1.47(1)
O(3′)–C(3′)	1.439(9)		
O(3′)–C(9′)	1.334(9)		
O(4′)–C(4′)	1.469(8)		
O(4′)–C(11′)	1.353(9)		

ring adopts a boat-like geometry with the two carbonyl oxygens [O(1) and O(4)] facing 'upwards'. The overall effect is that the face of the C(2)–C(3) double bond *syn* to O(1) and O(4) is shielded.

In spite of the usual concerns (that solid-state structures may not be relevant in solution and that ground-state conformations may have no bearing on reactive conformations), it is noteworthy that the diastereofacial reactivity of the juglone glycoside **1d** can be correctly predicted from its crystal-state conformation.

Table 6 Bond angles (°) for compound **1d** with esds in parentheses

C(5)–O(5)–C(1′)	116.8(6)	O(5′)–C(1′)–C(2′)	108.0(6)
O(1)–C(1)–C(2)	122(1)	O(2′)–C(2′)–C(1′)	108.2(6)
O(1)–C(1)–C(9)	121(1)	O(2′)–C(2′)–C(3′)	108.9(6)
C(2)–C(1)–C(9)	117.1(9)	C(1′)–C(2′)–C(3′)	110.0(6)
C(1)–C(2)–C(3)	121(1)	O(3′)–C(3′)–C(2′)	104.5(6)
C(2)–C(3)–C(4)	123(1)	O(3′)–C(3′)–C(4′)	111.8(6)
O(4)–C(4)–C(3)	119.2(9)	C(2′)–C(3′)–C(4′)	110.7(6)
O(4)–C(4)–C(10)	124.2(8)	O(4′)–C(4′)–C(3′)	110.0(6)
C(3)–C(4)–C(10)	116.5(8)	O(4′)–C(4′)–C(5′)	104.3(6)
O(5)–C(5)–C(6)	120.3(8)	C(3′)–C(4′)–C(5′)	111.3(6)
O(5)–C(5)–C(10)	118.3(7)	O(5′)–C(5′)–C(4′)	108.8(6)
C(6)–C(5)–C(10)	121.2(8)	O(5′)–C(5′)–C(6′)	108.8(6)
C(5)–C(6)–C(7)	120.2(8)	C(4′)–C(5′)–C(6′)	115.1(6)
C(6)–C(7)–C(8)	120.0(8)	O(6′)–C(6′)–C(5′)	109.2(7)
C(7)–C(8)–C(9)	120.2(8)	O(2′)–C(7′)–O(7′)	124.3(8)
C(1)–C(9)–C(8)	118.8(9)	O(2′)–C(7′)–C(8′)	110.5(8)
C(1)–C(9)–C(10)	120.4(8)	O(7′)–C(7′)–C(8′)	125.2(9)
C(8)–C(9)–C(10)	120.8(8)	O(3′)–C(9′)–O(9′)	124.5(9)
C(4)–C(10)–C(5)	124.0(8)	O(3′)–C(9′)–C(10′)	109.4(8)
C(4)–C(10)–C(9)	118.6(8)	O(9′)–C(9′)–C(10′)	125.9(8)
C(5)–C(10)–C(9)	117.4(7)	O(4′)–C(11′)–O(11′)	123.2(8)
C(2′)–O(2′)–C(7′)	117.8(7)	O(4′)–C(11′)–C(12′)	110.5(8)
C(3′)–O(3′)–C(9′)	117.7(6)	O(11′)–C(11′)–C(12′)	126.2(8)
C(4′)–O(4′)–C(11′)	118.5(6)	O(6′)–C(13′)–O(13′)	122.2(9)
C(1′)–O(5′)–C(5′)	111.0(5)	O(6′)–C(13′)–C(14′)	110.4(9)
C(6′)–O(6′)–C(13′)	115.7(7)	O(13′)–C(13′)–C(14′)	127(1)
O(5)–C(1′)–O(5′)	110.0(6)		
O(5)–C(1′)–C(2′)	107.9(6)		

With a view to shedding some light on the conformational behaviour of the juglone glycoside **1d** in solution, a nuclear Overhauser effect difference (NOED) spectroscopic study was undertaken (in $CDCl_3$). Irradiation of H(1′) led to a 8.6% enhancement of H(6) and irradiation of H(6) caused a 5.8% enhancement of H(1′). The results are not inconsistent with the adoption, in deuteriochloroform, of a conformation akin to that observed in the crystal state.

Experimental

Dry solvents, referred to in the ensuing experiments, were prepared as follows: benzene was distilled from sodium wire; acetonitrile was distilled from calcium hydride. Light petroleum refers to that fraction boiling in the range 30–40 °C.

Sonications were carried out in a Sonicleaner Type 6442AE bath (Dawe Ultrasonics Ltd.) filled with water. For other instrumental and for chromatographic details, see earlier papers.[11,12,27] Optical rotations, measured at *ca.* 20 °C, are given in 10^{-1} deg cm^2 g^{-1}, UV extinction coefficients (ε) are presented in cm^2 mmol^{-1} and coupling constants (*J*) and separations are shown in Hz.

Preparation of 5-(2′,3′,4′,6′-*Tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-1,4-*naphthoquinone* **1d**.—Silver(I) oxide (3.48 g, 15 mmol) was added to a solution of juglone **1a**[13] (1.74 g, 10 mmol) and the acetobromoglucose **8**[14] (4.93 g, 12 mmol) in dry acetonitrile (25 cm^3) and the mixture was subjected to sonication for 3 h. Celite was added and the mixture was filtered through silica gel which was then washed with dichloromethane (200 cm^3) and diethyl ether (200 cm^3). Concentration of the combined filtrate and washings gave an orange residue which was subjected to silica-gel chromatography (using a 8 cm × 8 cm sinter funnel) [CH_2Cl_2 (200 cm^3) and then CH_2Cl_2–Et_2O (1:1; 200 cm^3) as eluents]. Crystallisation of the chromatographed material from dichloromethane–diethyl ether gave the *title compound* **1d** (4.13 g, 82%) as pale yellow needles; m.p. 147–148 °C; $[\alpha]_D$ −80 (1.5% in $CHCl_3$); ν_{max}(KBr)/cm^{-1}

1755 and 1745 (ester C=O), 1670 (quinone C=O); λ_{max}-(EtOH)/nm 204 (ε 31 200), 242 (17 500) and 368 (3300); δ_H(300 MHz; $CDCl_3$) 2.056, 2.06, 2.08 and 2.13 (each 3 H, s, 4 × $MeCO_2$), 3.85–3.91 (1 H, m, 5'-H), 4.21 (1 H, dd, *J* 12.5 and 2.5, 6'-H), 4.27 (1 H, dd, *J* 12.5 and 5.5, 6'-H), 5.14 (1 H, d, *J* 8, 1'-H), 5.20 (1 H, t, *J* 10, 4'-H), 5.32 (1 H, t, *J* 10, 3'-H), 5.46 (1 H, dd, *J* 10 and 8, 2'-H), 6.84 and 6.89 (each 1 H, d, *J* 10.5, 2- and 3-H), 7.52 (1 H, dd, *J* 8.5 and 1, 6-H), 7.67 (1 H, dd, *J* 8.5 and 7.5, 7-H) and 7.90 (1 H, dd, *J* 7.5 and 1, 8-H) (in an NOED spectroscopic study, irradiation of the signal at δ_H 5.14 resulted in enhancements of 5, 9 and 9% of the signals at δ_H 5.32, 3.88 and 7.52; irradiation of the signal at δ_H 7.52 caused 6 and 8% enhancements of those at δ_H 5.14 and 7.67); *m/z* (FAB) 506 (MH_2^+, 40%) and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 57.4; H, 4.9. $C_{24}H_{24}O_{12}$ requires C, 57.1; H, 4.8%).

Crystal Data for Compound **1d**.—$C_{24}H_{24}O_{12}$, *M*, 504.45. Monoclinic, a = 34.173(6), b = 8.379(7), c = 8.468(8) Å, β = 93.51(4)°, V = 2430(3) Å^3 (by least-squares refinement of 25 accurately centred reflections, λ = 0.71069 Å), space group *C*2 (No. 5), Z = 4, D_x = 1.384 g cm^{-3}. Pale yellow tablets. Crystal dimensions: 0.3 × 0.2 × 0.2 mm, μ(Mo-Kα) = 1.05 cm^{-1}.

Data collection and processing. Rigaku AFC6S diffractometer, $\omega/2\theta$ mode with ω scan width = 1.21 + 0.30tanθ and ω scan speed 4 deg min^{-1} {with 2 rescans of weak reflections [$I < 10\sigma(I)$]}, graphite-monochromated Mo-Kα radiation; 2331 reflections measured ($0 < \theta < 25°$), 2290 unique [merging R = 0.021 after absorption correction (max., min. transmission factors = 1.0, 0.96)], giving 1270 with $I > 3\sigma(I)$. Intensity standards measured repeatedly during data collection showed no significant drift.

Structure analysis and refinement. Direct methods (MITHRIL)[28] revealed all non-hydrogen atoms. Full-matrix least-squares refinement (TEXSAN)[29] with all non-hydrogen atoms anisotropic and hydrogen atoms attached to central sugar ring isotropic with rest in calculated positions with fixed isotropic vibrational parameters. The weighting scheme $\omega = 1/[\sigma^2(F_o) + 0.03F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R_w values are 0.045, 0.049. Neutral atom scattering factors[30] were used throughout. All calculations were carried out on a Digital Vax station 3520. Fractional atomic co-ordinates are presented in Table 4, bond lengths in Table 5 and bond angles in Table 6.* The molecule and its atomic labelling is displayed in Fig. 2.

Preparation of (1R,4S,4aR,9aS)-1,4,4a,9a-*Tetrahydro*-5-(2',3',4',6'-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*-1,4-*methano*-*anthracene*-9,10-*quinone* **9a**.—Cyclopentadiene[17] (0.807 g, 12 mmol) was added to a solution of the naphthoquinone **1d** (1.00 g, 2 mmol) in benzene (50 cm^3) and the mixture was stirred for 24 h. Evaporation and crystallisation of the residue from dichloromethane–light petroleum gave the *title compound* **9a** (0.942 g, 83%) as colourless needles; m.p. 152–154 °C; $[\alpha]_D$ −114 (0.5% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1755 and 1745 (ester C=O), 1690 (quinone C=O); λ_{max}(EtOH)/nm 228 (ε 25 000) and 318 (3100); δ_H(300 MHz; $CDCl_3$) 1.46 and 1.54 [each 1 H, br d (separation 9) and dt (*J* 9, 1.5 and 1.5), 11-H_2], 2.05, 2.06, 2.07 and 2.16 (each 3 H, s, 4 × $MeCO_2$), 3.36 and 3.44 (each 1 H, dd *J* 9 and 3.5, 4a-and 9a-H), 3.50–3.57 (2 H, m, 1- and 4-H), 3.84 (1 H, ddd, *J* 10, 5 and 2.5, 5'-H), 4.19 (1 H, dd, *J* 12.5 and 2.5, 6'-H), 4.27 (1 H, dd, *J* 12.5 and 5, 6'-H), 5.08 (1 H, d, *J* 8, 1'-H), 5.18 (1 H, t, *J* 10, 4-H'), 5.27–5.38 (2 H, m, 2'- and 3'-H), 5.86 and 5.98 (each 1 H, dd, *J* 5.5 and 2.5, 2- and 3-H), 7.41 (1 H, dd, *J* 8 and 1, 6-H), 7.54 (1 H, t, *J* 8, 7-H) and 7.67 (1 H, dd, *J* 7.5 and 1, 8-H); *m/z* (Cl; NH_3) 524 (97%), 331 ($C_{14}H_{19}O_9^+$, 92), 213 (55) and 61 (100) (Found: C, 61.4; H, 5.6. $C_{29}H_{30}O_{12}$ requires C, 61.1; H, 5.3%).

Crystal Data for Compound **9a**.—$C_{29}H_{30}O_{12}$, *M*, 568.5. Orthorhombic, a = 6.270(3), b = 19.811(9), c = 23.162(6) Å, V = 2877 Å^3 (by least-squares refinement of 25 accurately centred reflections, λ = 0.71069 Å), space group $P2_12_12_1$ (No. 19), Z = 4, D_x = 1.31 g cm^3. Tablets. Crystal dimensions: 0.3 × 0.2 × 0.2 mm, μ(Mo-Kα) = 0.64 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.70 + 0.35tanθ and ω scan speed 0.5 to 5 deg min^{-1}, graphite-monochromated Mo-Kα radiation; 4023 unique reflections measured ($0 < \theta < 25°$), Lorentz-polarisation corrections applied but absorption effects ignored, 2965 observed reflections with $F > 3\sigma(F)$. Intensity standards measured repeatedly during data collections showed no significant drift.

Structure analysis and refinement. Direct methods (MULTAN-80)[31] located all non-hydrogen atoms. Blocked- matrix least-squares refinement (SHELX-76)[32] with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic. The weighting scheme $w = 1.603/[\sigma^2(F_o) + 0.002F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R_w values are 0.043, 0.041. Neutral atom scattering factors[30] were used throughout. All calculations were carried out on the University of Manchester Computing Centre Amdahl 5760 computer. Fractional atomic co-ordinates are presented in Table 1, bond lengths in Table 2 and bond angles in Table 3. The molecule and its atomic labelling is displayed in Fig. 1.

Preparation of (1S,4aR,9aR)-1,4,4a,9a-*Tetrahydro*-1-*methoxy*-5-(2',3',4',6'-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-3-*trimethylsiloxy*-9,10-*anthraquinone* **4d**.—Danishefsky's diene **2b**[18] (0.089 g, 0.5 mmol) was added to a stirred solution of the naphthoquinone **1d** (0.100 g, 0.2 mmol) in dry benzene (5 cm^3). Evaporation, after 24 h, addition of diethyl ether to the residue and filtration gave the *title compound* **4d** (0.124 g, 92%) as an off-white solid; m.p. 182–183 °C (decomp.); $[\alpha]_D$ +51 (2.2% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1760 and 1745 (ester C=O), 1705 and 1695 (quinone C=O); λ_{max}(EtOH)/nm 225 (ε 29 800), 253sh (7600) and 317 (3200); δ_H(300 MHz; $CDCl_3$) 0.28 (9 H, s, Me_3Si), 2.04, 2.05, 2.06 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.92 (3 H, s, MeO), 2.98 (1 H, br d, separation 18, 4-Hα), 3.21 (1 H, dd, *J* 6 and 4, 9a-H), 3.36 (1 H, t, *J* 6.5, 4a-H), 3.81–3.86 (1 H, m, 5'-H), 4.16 (1 H, dd, *J* 6 and 3.5, 1-H), 4.25 (2 H, d, separation 4, 6'-H_2), 4.94 (1 H, d, *J* 7.5, 1'-H), 5.13–5.21 (2 H, m, 2- and 2'-H), 5.25 (1 H, t, *J* 9, 4-H), 5.37 (1 H, t, *J* 9, 3'-H), 7.52-7.59 (2 H, m, 7- and 8-H) and 7.88 (1 H, dd, *J* 6.5 and 2.5, 6-H) (the signal for 4-Hβ was obscured by the $MeCO_2$ signals); δ_H(300 MHz; C_6D_6) 0.46 (9 H, s, Me_3Si), 1.87, 1.91, 1.97 and 2.15 (each 3 H, s, 4 × $MeCO_2$), 2.08 (1 H, dd, *J* 18 and 8, 4-Hα), 2.82 (1 H, br t, separation 7, 4a-H), 2.89 (3 H, s, MeO), 3.20 (1 H, dd, *J* 6 and 4, 9a-H), 3.34 (1 H, d, *J* 18, 4-Hβ), 3.49 (1 H, ddd, *J* 10.5 and 2.5, 5'-H), 4.25 (1 H, dd, *J* 12 and 2.5, 6'-H), 4.35–4.41 (2 H, m, 6'- and 1-H), 5.04 (1 H, d, *J* 7.5, 1'-H), 5.26 (1 H, br d, *J* 5.5, 2-H), 5.48 (1 H, t, *J* 10, 4'-H), 5.67 (1 H, t, *J* 9, 3'-H), 5.81 (1 H, dd, *J* 9 and 8, 2'-H), 7.28 (1 H, t, *J* 8, 7-H), 7.53 (1 H, dd, *J* 8 and 1, 8-H) and 8.32 (1 H, dd, *J* 8 and 1, 6-H); *m/z* (FAB) 699 (MNa^+, 3%), 331 ($C_{14}H_{19}O_9^+$, 20) and 169 (100).

Reaction of the Cycloadduct **4d** *with Hydrochloric Acid.*—(*a*) Conc. hydrochloric acid (5 drops) was added to a stirred solution of the cycloadduct **4d** (0.200 g, 0.3 mmol) in chloroform (5 cm^3). After 1 h, the mixture was diluted with dichloro-

* *Supplementary data* (see Section 5.6.3 of Instructions for Authors in the January issue). Vibrational parameters for non-hydrogen atoms, fractional atomic co-ordinates and vibrational parameters for hydrogen atoms, and bond lengths and bond angles involving hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.

methane (50 cm^3) and washed twice with water. Evaporation of the dried ($MgSO_4$) organic phase and crystallisation of the residue from chloroform–methanol gave *7-hydroxy-1-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyloxy)-9,10-anthraquinone* **13b** (0.157 g, 93%) as a bright yellow solid; m.p. 149–150 °C; $[\alpha]_D$ −60 (1% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1750br (ester C=O) and 1675 (quinone C=O); λ_{max}(EtOH)/nm 214 (ε 12 500), 238 (7700), 270 (12 500) and 352 (2800); δ_H(300 MHz; $CDCl_3$) 2.067, 2.073, 2.09 and 2.17 (each 3 H, s, 4 × $MeCO_2$), 3.90 (1 H, ddd, *J* 10, 5 and 2.5, 5′-H), 4.23 (1 H, dd, *J* 12.5 and 2.5, 6′-H), 4.30 (1 H, dd, *J* 12.5 and 5, 6′-H), 5.18 (1 H, d, *J* 8, 1′-H), 5.23 (1 H, t, *J* 9.5, 4′-H), 5.35 (1 H, t, *J* 9, 3′-H), 5.50 (1 H, dd, *J* 9.5 and 8, 2′-H), 6.37 (1 H, br s, OH), 7.19 (1 H, dd, *J* 8.5 and 2.5, 6-H), 7.54 (1 H, dd, *J* 8.5 and 1, 2-H), 7.64 (1 H, d, *J* 2.5, 8-H), 7.70 (1 H, t, *J* 8.5, 3-H), 8.11 (1 H, dd, *J* 7.5 and 1, 4-H) and 8.18 (1 H, d, *J* 8.5, 5-H); *m/z* (FAB) 593 (MNa^+, 2%), 571 (MH^+, 2), 331 ($C_{14}H_{19}O_9^+$, 80) and 169 (100) (Found: C, 59.2; H, 4.7. $C_{28}H_{26}O_{13}$ requires C, 58.9; H, 4.6%).

(*b*) A mixture of the anthraquinone **13b** (0.114 g, 0.2 mmol), ethanol (5 cm^3) and hydrochloric acid (*ca.* 1 mol dm^{-3}; 5 cm^3) was heated under reflux for 30 min. Dichloromethane (50 cm^3) was added to the cooled solution and the mixture was washed with water (× 3). Evaporation of the dried ($MgSO_4$) organic phase and crystallisation of the residue from chloroform–methanol gave a yellow solid (0.042 g, 88%) which was identified as 1,7-dihydroxy-9,10-anthraquinone **13a** on the basis of its m.p. of 292–293 °C (lit.,[19] 293–294 °C) and its ^1H NMR spectrum [δ_H(300 MHz; $CDCl_3$) 7.68 (1 H, dd, *J* 9 and 7, 3-H), 7.83 (1 H, dd, *J* 7.5 and 1, 4-H), 8.25 (1 H, d, *J* 8.5, 5-H) and 12.53 (1 H, s, 1-OH) (the signals for 2-, 6- and 8-H were obscured by the $CHCl_3$ signal); δ_H(300 MHz; CD_3COCD_3) 7.47 (1 H, dd, *J* 7.5 and 2, 2-H), 7.50 (1 H, dd, *J* 8 and 2.5, 6-H), 7.50 (1 H, s, 7-OH), 7.83 (1 H, d, *J* 2.5, 8-H), 7.92 (1 H, dd, *J* 7.5 and 2, 4-H), 7.96 (1 H, t, *J* 7.5, 3-H) and 8.32 (1 H, d, *J* 8.5, 5-H)].

Preparation of 1,7-*Dihydroxy*-9,10-*anthraquinone* **13a**.—A mixture of silver(I) oxide (2.78 g, 12 mmol) and juglone **1a**[13] (0.522 g, 3 mmol) in dichloromethane (10 cm^3) was subjected to sonication for 10 min. Iodomethane (4.26 g, 30 mmol) was added to the mixture which was stirred vigorously in the dark for 24 h. The mixture was filtered through a bed of Celite and the filtrate concentrated. Crystallisation of the residue from ethanol gave 5-methoxy-1,4-naphthoquinone **1c** (0.541 g, 96%) as yellow needles; m.p. 186 °C (lit.,[33] 187 °C); δ_H(300 MHz; $CDCl_3$) 4.01 (3 H, s, MeO), 6.87 (2 H, s, 2- and 3-H), 7.32 (1 H, dd, *J* 7.5 and 1.5, 6-H), 7.69 (1 H, t, 7.5, 7-H) and 7.74 (1 H, dd, *J* 7.5 and 1.5, 8-H).

A solution of the naphthoquinone **1c** (0.188 g, 1 mmol) and Danishefsky's diene **2b**[18] (0.230 g, 1.3 mmol) in dry benzene (10 cm^3) was heated under reflux for 24 h. Evaporation left a yellow residue which was dissolved in chloroform (5 cm^3). Conc. hydrochloric acid (5 drops) was added to the stirred solution which, after 1 h, was diluted with dichloromethane (25 cm^3) and washed twice with water. Concentration of the dried ($MgSO_4$) organic phase and recrystallisation of the residue from ethanol gave 7-hydroxy-1-methoxy-9,10-anthraquinone **13e** (0.210 g, 83%) as a yellow microcrystalline solid; m.p. 186–187 °C (sublim.) (lit.,[5] 185–186 °C); δ_H(300 MHz; $CDCl_3$) 4.07 (3 H, s, MeO), 7.22 (1 H, dd, *J* 8.5 and 2.5, 6-H), 7.33 (1 H, dd, *J* 8.5 and 1, 2-H), 7.74 (1 H, t, *J* 8.5, 3-H), 7.97 (1 H, dd, *J* 7.5 and 1, 4-H), 8.03 (1 H, d, *J* 2.5, 8-H) and 8.19 (1 H, d, *J* 8.5, 5-H).

A solution of the methoxy derivative **13e** (0.128 g, 0.5 mmol) in dichloromethane (5 cm^3) was added to a stirred solution of boron tribromide (0.250 g, 1 mmol) in dichloromethane (5 cm^3) under argon. After 24 h, the solution was poured onto saturated aqueous sodium hydrogen carbonate (100 cm^3) and the mixture was extracted with diethyl ether. The organic phase was washed twice with water, dried ($MgSO_4$) and concentrated. Crystallisation of the residue from chloroform–methanol gave the title compound **13a** (0.089 g, 74%) as a yellow solid; m.p. 289–290 °C (lit.,[19] 293–294 °C). The 300 MHz ^1H NMR spectrum of the sample matched that of the product obtained by hydrolysis of compound **13b**.

Preparation of 1,6-*Dihydroxy*-9,10-*anthraquinone* **14a**.—A solution of Danishefsky's diene **2b**[18] (0.230 g, 1.3 mmol) and juglone **1a**[13] (0.174 g, 1 mmol) in dry benzene (5 cm^3) was heated under reflux for 2 h. Evaporation left an orange residue which was dissolved in dichloromethane (5 cm^3). Triethylamine (1 cm^3) was added to the solution which, after 5 min, was diluted with dichloromethane (25 cm^3) and washed with hydrochloric acid (*ca.* 1 mol dm^{-3}) and water. Evaporation of the dried ($MgSO_4$) organic layer and crystallisation of the residue from chloroform–methanol gave the title compound **14a** (0.195 g, 81%) as a yellow microcrystalline solid; m.p. 270–273 °C (sublim.) [lit.,[5] 272–275 °C); δ_H(300 MHz; CD_3COCD_3) 7.47–7.52 (3 H, m, 2- and 7-H, 6-OH), 7.79 (1 H, d, *J* 2.5, 5-H), 7.90–7.96 (2 H, m, 3- and 4-H) and 8.38 (1 H, d, *J* 8.5, 8-H); δ(300 MHz; $CDCl_3$) 6.15 (1 H, br s, 7-OH), 7.30 (1 H, dd, *J* 8.5 and 2, 2-H), 7.65 (1 H, t, *J* 8, 3-H), 7.66 (1 H, d, *J* 2.5, 5-H), 7.81 (1 H, dd, *J* 7.5 and 1, 4-H), 8.26 (1 H, d, *J* 8.5, 8-H) and 12.76 (1 H, s, 1-OH) (the 7-H signal was partly obscured by the $CHCl_3$ signal).

Preparation of (1S,4aR,9aR)-1,2,4a,9a-*Tetrahydro*-1-*methoxy*-5-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-*anthracene*-3(4H),9,10-*trione* **15**.—The cycloadduct **4d** (0.135 g, 0.2 mmol) was added to a stirred ice-cooled solution of THF (8 cm^3) and hydrochloric acid (0.1 mol dm^{-3}; 2 cm^3). After 30 min, the mixture was diluted with dichloromethane (50 cm^3) and washed twice with water. Evaporation of the dried ($MgSO_4$) organic layer and crystallisation of the residue from dichloromethane–diethyl ether gave the *title compound* **15** (0.115 g, 96%) as white crystals; m.p. 188–189 °C; $[\alpha]_D$ −115 (0.2% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1750br (ester C=O), 1720 (ketone C=O) and 1695 (quinone C=O); λ_{max}(EtOH)/nm 226 (ε 29 400) and 316 (2800); δ(300 MHz; $CDCl_3$) 2.038, 2.042, 2.07 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.34 (1 H, dd, *J* 15.5 and 7, 4-Hβ), 2.46 (1 H, dd, *J* 15.5 and 3, 2-Hβ), 2.87 (1 H, dt, *J* 15.5, 1.5 and 1.5, 2-Hα), 2.98 (3 H, s, MeO), 3.31 (1 H, dt, *J* 15.5, 1.5 and 1.5, 2-Hα), 3.47 (1 H, dd, *J* 7 and 2.5, 9a-H), 3.62 (1 H, dt, *J* 7, 7 and 1.5, 4a-H), 3.81 (1 H, dt, *J* 9.5, 4 and 4, 5′-H), 4.19–4.24 (2 H, m, 6′-H_2), 4.96 (1 H, d, *J* 8, 1′-H), 5.14–5.34 (3 H, m, 2′-, 3′- and 4′-H), 7.57-7.63 (2 H, m, 6- and 7-H) and 7.90 (1 H, dd, *J* 7 and 3, 8-H); *m/z* (FAB) 935 [$M(C_{14}H_{19}O_9)^+$, 7%], 627 (MNa^+, 9), 605 (MH^+, 2) and 331 ($C_{14}H_{19}O_9^+$, 100) (Found: C, 57.7; H, 5.0. $C_{29}H_{32}O_{14}$ requires C, 57.6; H, 5.3%).

Preparation of (1S,4aR,9aR)-1,4,4a,9a-*Tetrahydro*-3-*methyl*-5-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-1-*trimethylsiloxy*-9,10-*anthraquinone* **4e**.—A mixture of the diene **2f**[20] (0.470 g, 3 mmol) and the naphthoquinone **1d** (1.00 g, 2 mmol) in dry benzene (50 cm^3) was stirred for 24 h. Evaporation and crystallisation of the residue from dichloromethane–diethyl ether gave the *title compound* **4e** (1.23 g, 93%) as a pale yellow solid; m.p. 157–158 °C; $[\alpha]_D$ +75 (0.1% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1750 (ester C=O) and 1700 (quinone C=O); λ_{max}(EtOH)/nm 226 (ε 30 800), 254 (7200) and 316 (3200); δ_H(300 MHz; $CDCl_3$) −0.32 (9 H, s, Me_3Si), 1.79 (3 H, br s, 3-Me), 2.044, 2.047, 2.07 and 2.09 (each 3 H, s, 4 × $MeCO_2$), 2.90 (1 H, br d, separation 18, 4-Hβ), 3.17 (1 H, dd, *J* 6 and 4, 9a-H), 3.31 (1 H, br t, separation 6, 1-H), 3.78–3.83 (1 H, m, 5′-H), 4.22 (1 H, dd, *J* 12 and 3, 6′-H), 4.26 (1 H, dd, *J* 12 and 5, 6′-H), 4.41 (1 H, br t, separation 4.5, 1-H), 4.95 (1 H, d, *J* 7.5, 1′-H), 5.18 (1 H, t, *J* 9, 4′-H), 5.25 (1 H, t, *J* 9, 3′-H), 5.30 (1 H, dd, *J* 9 and 7.5, 2′-H), 7.49–7.61 (2 H, m, 6- and 7-H) and 7.87 (1 H, dd, *J* 7 and 2, 8-H); δ_H(300 MHz; C_6D_6) −0.03 (9 H, s,

Me_3Si), 1.77 (3 H, br s, 3-Me), 1.88, 1.92, 1.97 and 2.18 (each 3 H, s, 4 × $MeCO_2$), 2.86 (1 H, br t, separation 6, 4a-H), 3.09 (1 H, br d, separation 18, 4-Hβ), 3.17 (1 H, dd, *J* 6 and 4, 9a-H), 3.50 (1 H, ddd, *J* 10, 5 and 2.5, 5'-H), 4.28 (1 H, dd, *J* 12 and 2.5, 6'-H), 4.40 (1 H, dd, *J* 12 and 5, 6'-H) 4.64 (1 H, br t, separation 4.5, 1-H), 5.03 (1 H, d, *J* 7.5, 1'-H), 5.48 (1 H, t, *J* 10, 4'-H), 5.58–5.63 (1 H, m, 2-H), 5.69 (1 H, t, *J* 9, 3'-H), 5.83 (1 H, dd, *J* 9.5 and 7.5, 2'-H), 7.34 (1 H, t, *J* 8, 7-H), 7.61 (1 H, dd, *J* 8 and 1, 6-H) and 8.31 (1 H, dd, *J* 8 and 1, 8-H); *m/z* (FAB) 683 (MNa$^+$, 1%), 331 ($C_{14}H_{19}O_9^+$, 60) and 169 (100) (Found: C, 58.2; H, 6.2. $C_{32}H_{40}O_{13}Si$ requires C, 58.2; H, 6.1%).

Reaction of the Cycloadduct **4e** *with Hydrochloric Acid.*—(*a*) Conc. hydrochloric acid (5 drops) was added to a stirred solution of the cycloadduct **4e** (0.330 g, 0.5 mmol) in chloroform (5 cm^3). After 1 h, dichloromethane (50 cm^3) was added to the mixture which was washed twice with water. Evaporation of the dried ($MgSO_4$) organic phase and crystallisation of the residue from ethanol gave 7-*methyl*-1-(2',3',4',6'-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-9,10-*anthraquinone* **13d** (0.261 g, 92%) as an off-white solid; m.p. 180 °C; $[\alpha]_D$ −82 (0.1% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1760br and 1730 (ester C=O), 1680 (quinone C=O); λ_{max}(EtOH)/nm 211 (ε 28 200), 257 (37 400) and 345 (5000); δ_H(300 MHz; $CDCl_3$) 2.06, 2.079, 2.082 and 2.19 (each 3 H, s, 4 × $MeCO_2$), 2.52 (3 H, s, 7-Me), 3.88 (1 H, ddd, *J* 10, 5 and 2.5, 5'-H), 4.22 (1 H, dd, *J* 12.5 and 2.5, 6'-H), 4.29 (1 H, dd, *J* 12.5 and 5, 6'-H), 5.19 (1 H, d, *J* 7.5, 1'-H), 5.22 (1 H, t, *J* 10, 4'-H), 5.35 (1 H, t, *J* 9, 3'-H), 5.49 (1 H, dd, *J* 9.5 and 7.5, 2'-H), 7.53–7.58 (2 H, m, 2- and 6-H), 7.69 (1 H, t, *J* 8.5, 3-H), 8.01 (1 H, br s, 8-H), 8.12 (1 H, dd, *J* 7.5 and 1, 4-H) and 8.13 (1 H, d, *J* 8, 5-H); *m/z* (FAB) 591 (MNa$^+$, 1%), 570 (MH$_2^+$, 1), 568 (M^+, 1), 331 ($C_{14}H_{19}O_9^+$, 60) and 169 (100) (Found: C, 61.1; H, 5.1. $C_{29}H_{28}O_{12}$ requires C, 61.3; H, 4.9%).

(*b*) A mixture of the anthraquinone **13d** (0.144 g, 0.2 mmol), ethanol (5 cm^3) and hydrochloric acid (*ca.* 1 mol dm^{-3}; 5 cm^3) was heated under reflux for 30 min. The mixture was allowed to cool and the yellow precipitate collected by filtration. Recrystallisation of the material from ethanol gave a yellow solid (0.040 g, 83%) which was identified as 1-hydroxy-7-methyl-9,10-anthraquinone **13c** on the basis of its melting point of 180–181 °C (lit.,[21] 183–184 °C) and its ^{1}H NMR spectrum [δ_H(300 MHz; $CDCl_3$) 2.55 (3 H, s, 7-Me), 7.30 (1 H, dd, *J* 8.5 and 1, 2-H), 7.61 (1 H, dm, separation 8, 6-H), 7.68 (1 H, t, *J* 8, 3-H), 7.83 (1 H, dd, *J* 7.5 and 1, 4-H), 8.11 (1 H, br s, 8-H), 8.20 (1 H, d, *J* 8, 5-H) and 12.65 (1 H, s, 1-OH)].

Preparation of 1-*Hydroxy*-7-*methyl*-9,10-*anthraquinone* **13c**.—A mixture of the diene **2f**[20] (0.230 g, 1.5 mmol) and the naphthoquinone **1c** (0.188 g, 1 mmol) in dry benzene (10 cm^3) was stirred for 24 h. Evaporation left a yellow residue which was dissolved in dichloromethane (5 cm^3). Triethylamine (1 cm^3) was added to the stirred solution which, after 1 h, was diluted with dichloromethane (25 cm^3) and washed with hydrochloric acid (*ca.* 1 mol dm^{-3}) and water. Evaporation of the dried ($MgSO_4$) organic phase left a yellow residue which was dissolved in dichloromethane (10 cm^3). The solution was added to a stirred solution of boron tribromide (0.250 g, 1 mmol) in dichloromethane (10 cm^3) under argon. After 24 h, the solution was poured onto saturated aqueous sodium hydrogen carbonate (100 cm^3) and the mixture was extracted with diethyl ether. The organic phase was washed twice with water, dried ($MgSO_4$) and concentrated. Crystallisation of the residue from chloroform–methanol gave 1-hydroxy-7-methyl-9,10-anthraquinone **13c** (0.234 g, 71%) as a yellow solid; m.p. 180–181 °C (lit.,[21] 183–184 °C). The 300 MHz ^{1}H NMR spectrum of the sample matched that of the product obtained by hydrolysis of compound **13d**.

Preparation of (1S,4aR,9aR)-1,4,4a,9a-*Tetrahydro*-1-*hydroxy*-3-*methyl*-5-(2',3',4',6'-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-9,10-*anthraquinone* **4f**.—The cycloadduct **4e** (0.746 g, 1.13 mmol) was added to a stirred ice-cooled solution of THF (20 cm^3) and hydrochloric acid (*ca.* 1 mmol dm^{-3}; 5 cm^3). After 30 min, dichloromethane (50 cm^3) was added to the mixture which was washed twice with water. Evaporation of the dried ($MgSO_4$) organic phase and crystallisation of the residue from dichloromethane–diethyl ether–light petroleum gave the *title compound* **4f** (0.614 g, 92%) as a white solid; m.p. 182–183 °C; $[\alpha]_D$ −74 (0.4% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3460br (OH), 1750br (ester C=O) and 1690 (quinone C=O); λ_{max}(EtOH)/nm 226 (ε 30 100) and 318 (3200); δ_H(300 MHz; $CDCl_3$) 1.74 (3 H, s, 3-Me), 2.05, 2.06, 2.07 and 2.13 (each 3 H, s, 4 × $MeCO_2$), 2.51 (1 H, br dd, separation 18.5 and 4, 4-Hα), 2.73 (1 H, br d, separation 8.5, 9a-H), 3.29–3.38 (2 H, m, 4-Ha and 4-Hβ), 3.85 (1 H, dt, *J* 9.5, 3.5 and 3.5, 5'-H), 4.24 (2 H, d, separation 4, 6'-H_2), 4.41 (1 H, br s, 1-H), 5.10 (1 H, d, *J* 7.5, 1'-H), 5.18 (1 H, t, *J* 9.5, 4'-H), 5.35 (1 H, t, *J* 9, 3'-H), 5.36 (1 H, dd, *J* 9 and 7.5, 2'-H), 5.65 (1 H, br s, 2-H), 7.52 (1 H, dd, *J* 8.5 and 1, 6-H) 7.61 (1 H, t, *J* 8.5, 7-H) and 7.85 (1 H, dd, *J* 8.5 and 1, 8-H); *m/z* (FAB) 611 (MNa$^+$, 1%), 331 ($C_{14}H_{19}O_9^+$, 60) and 169 (100) (Found: C, 59.0; H, 5.5. $C_{29}H_{32}O_{13}$ requires C, 59.2; H, 5.4%).

Preparation of (1S,4aR,9aR)-1-*Acetoxy*-1,4,4a,9a-*tetrahydro*-3-*methyl*-5-(2',3',4',6'-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-9,10-*anthraquinone* **4g**.—A mixture of the diene **2g**[22] (0.300 g, 2.4 mmol) and the naphthoquinone **1d** (1.00 g, 2.0 mmol) in dry benzene (50 cm^3) was stirred for 2 d. Evaporation of the solvent left a residue which comprised a 2:1 mixture of the cycloadducts **4g** and **3f** by 300 MHz ^{1}H NMR spectroscopy [the ratio was estimated from the integrals of the doublets at δ 2.92 (*J* 18) and 3.05 (*J* 18) ascribed to 4-Hβ of the cycloadducts **4g** and **3f**]. Crystallisation of the mixture from dichloromethane–diethyl ether gave the *title compound* **4g** (0.533 g, 42%) as a white solid; m.p. 168–169 °C; $[\alpha]_D$ +83 (0.3% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1750br (ester C=O) and 1700 (ketone C=O); λ_{max}(EtOH)/nm 226 (ε 30 600) and 317 (3400); δ_H(300 MHz; $CDCl_3$) 1.42 (3 H, s, 1-$MeCO_2$), 1.82 (3 H, s, 3-Me), 2.05, 2.08 and 2.09 (6, 3 and 3 H, each s, 4 × $MeCO_2$), 2.92 (1 H, br d, separation 18.5, 4β-H), 3.36–3.45 (2 H, m, 4α- and 9a-H), 3.84 (1 H, ddd, *J* 9.5, 4.5 and 3, 5'-H), 4.24–4.26 (2 H, m, 6'-H_2), 4.98 (1 H, *J* 7.5, 1'-H), 5.15–5.38 (3 H, m, 2'-, 3'- and 4'-H), 5.33-5.38 (1 H, m, 2'-H), 5.42 (1 H, br t, separation 3.5, 1-H), 5.65 (1 H, br s, 2-H), 7.55–7.63 (2 H, m, 6- and 7-H) and 7.87 (1 H, dd, *J* 6.2 and 2, 8-H) (the 4-Hα signal was obscured by the $MeCO_2$ signals); *m/z* (FAB) 653 (MNa$^+$, 1%), 629 (M^+ − H, 1), 331 ($C_{14}H_{19}O_9^+$, 65) and 169 (100) (Found: C, 59.4; H, 5.5. $C_{31}H_{34}O_{14}$ requires C, 59.0; H, 5.4%).

Reaction of the Cycloadduct **4g** *with Hydrochloric Acid.*—Conc. hydrochloric acid (5 drops) was added to a stirred solution of the cycloadduct **4g** (0.126 g, 0.2 mmol) in chloroform (5 cm^3). After 1 h, the mixture was diluted with dichloromethane (50 cm^3) and washed twice with water. Evaporation of the dried ($MgSO_4$) organic phase left a yellow residue which was dissolved in a mixture of ethanol (5 cm^3) and hydrochloric acid (*ca.* 1 mol dm^{-3}; 5 cm^3). The solution was heated under reflux for 30 min and allowed to cool. The yellow precipitate was collected by filtration and recrystallised from ethanol to give 1-hydroxy-7-methyl-9,10-anthraquinone **13c** (0.041 g, 85%) (identified by 300 MHz ^{1}H NMR spectroscopy) as a yellow solid; m.p. 180 °C (lit.,[21] 183–184 °C).

Preparation of (1R,4aR,9aR)-1,4,4a,9a-*Tetrahydro*-2-*methyl*-5-(2',3',4',6'-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-1-*trimethylsiloxy*-9,10-*anthraquinone* **17**.—A mixture of the diene **16**[23] (0.047 g, 0.3 mmol) and the naphthoquinone **1d** (0.100 g, 0.2 mmol) in dry benzene (2 cm^3) was stirred for 24 h.

Evaporation, addition of diethyl ether to the residue and filtration gave the *title compound* **17** (0.119 g, 90%), as a pale yellow solid; m.p. 139–140 °C, $[\alpha]_D$ +57 (1% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1760br (ester C=O), 1720, 1695 and 1670 (quinone C=O); λ_{max}(EtOH)/nm 226 (ε 26 200) 255sh (8300) and 318 (2900); δ_H(300 MHz; $CDCl_3$) −0.34 (9 H, s, Me_3Si), 1.71 (3 H, br s, 2-Me), 2.041, 2.043, 2.06 and 2.10 (each 3 H, s, 4 × $MeCO_2$), 3.04 (2 H, br d, separation 18, 4-Hβ), 3.20–3.28 (2 H, m, 4a- and 9a-H), 3.80–3.86 (1 H, m, 5′-H), 4.21–4.29 (2 H, m, 6′-H_2), 4.95 (1 H, d, *J* 7.5, 1′-H), 5.15–5.37 (4 H, m, 1′-, 2′-, 3′- and 4′-H), 5.55 (1 H, br s, 3-H), 7.54–7.60 (2 H, m, 6- and 7-H) and 7.88–7.91 (1 H, m, 8-H) (the 4-Hα signal was obscured by the $MeCO_2$ signals); δ_H(300 MHz; C_6D_6) −0.07 (9 H, s, Me_3Si), 1.79 (3 H, br d, separation 1, 2-Me), 1.88, 1.92, 1.98 and 2.17 (each 3 H, s, 4 x $MeCO_2$), 2.81 (1 H, br t, separation 6.5, 4a-H), 3.19 (1 H, dd, *J* 8 and 3.5, 9a-H), 3.26 (1 H, dm, separation 18, 4-Hβ), 3.48 (1 H, ddd, *J* 10, 5 and 2.5, 5′-H), 4.28 (1 H, dd, *J* 12 and 2.5, 6′-H), 4.39 (1 H, dd, *J* 12 and 5, 6′-H), 4.45 (1 H, d, *J* 3.5, 1-H), 5.00 (1 H, d, *J* 7.5, 1′-H), 5.49 (1 H, t, *J* 10, 4′-H), 5.56 (1 H, br s, 3-H), 5.67 (1 H, t, *J* 9.5, 3′-H), 5.84 (1 H, *J* 9.5 and 7.5, 2′-H), 7.35 (1 H, t, *J* 8, 7-H), 7.65 (1 H, dd, *J* 8.5 and 1, 6-H) and 8.30 (1 H, dd, *J* 7.5 and 1, 8-H) (the 4-Hα signal was obscured by the $MeCO_2$ signals); *m*/*z* (FAB) 683 (*M*HNa^+, 3%), 661 (*M*H_2^+, 2), 331 ($C_{14}H_{19}O_9^+$, 70) and 169 (100) (Found: C, 57.9; H, 5.8; Si, 3.7. $C_{32}H_{40}O_{13}Si$ requires C, 58.2; H, 6.1; Si, 4.2%).

Reaction of the Cycloadduct **17** *with Hydrochloric Acid.*—(*a*) Conc. hydrochloric acid (5 drops) was added to a stirred solution of the cycloadduct **17** (0.330 g, 0.5 mmol) in chloroform (5 cm^3). After 1 h, the mixture was diluted with dichloromethane (50 cm^3) and washed twice with water. Evaporation of the dried ($MgSO_4$) organic phase and crystallisation of the residue from ethanol gave 6-*methyl*-1-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-9,10-*anthraquinone* **14c** (0.269 g, 95%) as an off-white solid; m.p. 190–192 °C; $[\alpha]_D$ −78 (0.2% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1755br and 1730 (ester C=O), 1675 (quinone C=O); λ_{max}(EtOH)/nm 211 (ε 32 000), 257 (39 700) and 346 (5300); δ_H(300 MHz; $CDCl_3$) 2.06, 2.07, 2.08 and 2.19 (each 3 H, s, 4 × $MeCO_2$), 2.51 (3 H, s, 6-Me), 3.87 (1 H, ddd, *J* 10, 5 and 2.5, 5′-H), 4.22 (1 H, dd, *J* 12 and 2.5, 6′-H), 4.29 (1 H, dd, *J* 12 and 5, 6′-H), 5.35 (1 H, t, *J* 9, 3′-H), 5.48 (1 H, dd, *J* 9.5 and 7.5, 2′-H), 7.56–7.61 (2 H, m, 2- and 7-H), 7.69 (1 H, t, *J* 8.5, 3-H), 8.03 (1 H, br s, 5-H) and 8.11–8.14 (2 H, m, 4- and 5-H); *m*/*z* (FAB) 591 (*M*Na^+, 1%), 569 (*M*H^+, 1), 331 ($C_{14}H_{19}O^+$, 60) and 169 (100) (Found: C, 61.0; H, 5.0. $C_{29}H_{28}O_{12}$ requires C, 61.3; H, 4.9%).

(*b*) A mixture of the anthraquinone **14c** (0.114 g, 0.2 mmol), ethanol (5 cm^3) and hydrochloric acid (*ca.* 1 mol dm^{-3}; 5 cm^3) was heated under reflux for 30 min. The mixture was allowed to cool and the yellow precipitate was collected by filtration. Recrystallisation of the material from ethanol gave 1-hydroxy-6-methyl-9,10-anthraquinone **14b** (0.044 g, 92%) as a yellow solid; m.p. 153 °C (lit.,[21,24] 147 °C); δ_H(300 MHz; $CDCl_3$) 2.55 (3 H, s, 6-Me), 7.31 (1 H, dd, *J* 8.5 and 1, 2-H), 7.61 (1 H, dm, separation 8, 7-H), 7.67 (1 H, t, *J* 8, 3-H), 7.83 (1 H, dd, *J* 7.5 and 1, 4-H), 8.10 (1 H, br s, 5-H), 8.21 (1 H, d, *J* 8, 8-H) and 12.69 (1 H, s, 1-OH).

Reaction of the Cycloadduct **9a** *with Trifluoroacetic Acid.*—A solution of the cycloadduct **9a** (0.490 g, 0.86 mmol) in trifluoroacetic acid (5 cm^3) was stirred for 5 h. Dichloromethane (50 cm^3) was added to the mixture which was washed with water (× 3). Evaporation of the dried ($MgSO_4$) organic phase left a brown residue which was subjected to silica gel chromatography [Et_2O–CH_2Cl_2 (1:1) as eluent]. The resultant brown oil (0.054 g, *ca.* 26%) was predominantly (1*R*,4*S*,4a*R*,9a*S*)-1,4,4a,9a-tetrahydro-5-hydroxy-1,4-methano-9,10-anthraquinone **9b**; $[\alpha]_D$ −47 (0.5% in CH_2Cl_2); δ_H(300 MHz; $CDCl_3$) *inter alia* 1.53 and 1.58 (each 1 H, br dt and dt, *J* 9, 1.5 and 1.5, CH_2), 3.39 and 3.47 (each 1 H, dd, *J* 9 and 4, 4a- and 9a-H), 3.64–3.69 (2 H, m, 1- and 4-H), 6.01 (2 H, t, separation 2, 2- and 3-H), 7.19 (1 H, dd, *J* 8 and 1.5, 6-H), 7.54 (1 H, dd, *J* 8 and 1.5, 8-H), 7.60 (1 H, t, *J* 8, 7-H) and 12.61 (1 H, s, 5-OH).

Preparation of (1R*,4S*,4aR*,9aS*)-1,4,4a,9a-*Tetrahydro*-5-*hydroxy*-1,4-*methano*-9,10-*anthraquinone* **9b**.—(*a*) A solution of cyclopentadiene[17] (0.888 g, 13.5 mmol) and juglone **1a**[13] (1.00 g, 5.7 mmol) in benzene (5 cm^3) was heated under reflux for 1 h. Evaporation and crystallisation of the residue from ethanol gave the title compound **9b** (1.03 g, 75%) as white needles; m.p. 133 °C (lit.,[25] 133–134 °C). The 300 MHz ^{1}H NMR spectrum of the sample matched that of the aglycone obtained by hydrolysis of the glycoside **9a**.

Preparation of (1R,4S)-1,4-*Dihydro*-5-(2′,3′,4′,6′-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)-1,4-*methano*-9,10-*anthraquinone* **18b**.—A solution of the cycloadduct **9a** (2.39 g, 4.2 mmol) in dichloromethane (25 cm^3) and triethylamine (25 cm^3) was stirred under an oxygen atmosphere for 5 d. Evaporation, subjection of the residue to silica gel chromatography [Et_2O–CH_2Cl_2 (1:1) as eluent] and crystallisation of the chromatographed material from dichloromethane–diethyl ether gave the *title compound* **18b** (1.71 g, 72%) as yellow needles; m.p. 188 °C (decomp.); $[\alpha]_D$ −72 (0.3% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1755 and 1745sh (ester C=O), 1700 and 1660 (quinone C=O); λ_{max}(EtOH)/nm 203 (ε 22 700), 229 (17 100), 275 (7300) and 333 (2200); δ(300 MHz; $CDCl_3$) 2.054, 2.065, 2.07 and 2.17 (each 3 H, s, 4 × $MeCO_2$), 2.27 (1 H, br d, separation 7, 11-H), 2.32 (1 H, dt, *J* 7, 1.5 and 1.5, 11-H), 3.85 (1 H, ddd, *J* 10, 5 and 3, 5′-H), 4.17–4.22 (3 H, m, 1-, 4- and 6′-H), 4.26 (1 H, dd, *J* 12.5 and 5, 6′-H), 5.11 (1 H, d, *J* 7.5, 1′-H), 5.19 (1 H, t, *J* 10, 4′-H), 5.32 (1 H, t, *J* 9, 3′-H), 5.44 (1 H, dd, *J* 9.5 and 7.5, 2′-H), 6.83–6.87 (2 H, m, 2- and 3-H), 7.48 (1 H, dd, *J* 8.5 and 1.5, 6-H), 7.59 (1 H, t, *J* 8.5, 7-H) and 7.88 (1 H, dd, *J* 7.5 and 1.5, 8-H); *m*/*z* (FAB) 331 ($C_{14}H_{19}O_9^+$, 100) and 169 (100) (Found: C, 61.2; H, 5.0. $C_{29}H_{28}O_{12}$ requires C, 61.3; H, 4.9%).

Hydrolysis of the Glycoside **18b**.—A mixture of the glycoside **18b** (1.70 g, 3 mmol), ethanol (25 cm^3) and hydrochloric acid (*ca.* 1 mol dm^{-3}; 25 cm^3) was heated under reflux for 30 min. The cooled mixture was extracted with dichloromethane and the extract was washed with water. Evaporation of the dried ($MgSO_4$) organic phase and crystallisation of the residue from hexanes gave (1R,4S)-1,4-*dihydro*-5-*hydroxy*-1,4-*methano*-9,10-*anthraquinone* **18a** (0.659 g, 92%) as orange crystals; m.p. 150–151 °C; $[\alpha]_D$ +20 (0.2% in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1665 and 1635 (quinone C=O); λ_{max}(EtOH)/nm 209 (ε 18 000), 213sh (17 300), 283 (9400) and 435 (3600); δ(300 MHz; $CDCl_3$) 2.33 and 2.40 (each 1 H, dt, *J* 7, 1.3 and 1.5, CH_2), 4.23–4.26 (2 H, m, 1- and 4-H), 6.89–6.91 (2 H, m, 2- and 3-H), 7.21 (1 H, dd, *J* 8 and 1.5, 6-H), 7.55 (1 H, t, *J* 8, 7-H), 7.61 (1 H, dd, *J* 8 and 1.5, 8-H) and 12.08 (1 H, s, 5-OH); *m*/*z* (EI) 238 (*M*$^+$, 100) (Found: C, 75.6; H, 4.4. $C_{15}H_{10}O_3$ requires C, 75.6; H, 4.2%).

Preparation of (1R*,4S*)-1,4-*Dihydro*-5-*hydroxy*-1,4-*methano*-9,10-*anthraquinone* **18a**.—(*a*) A solution of (±)-compound **9b** (0.570 g, 2.4 mmol) in dichloromethane (10 cm^3) and triethylamine (10 cm^3) was stirred under an argon atmosphere for 5 d. Evaporation, subjection of the residue to silica gel column chromatography [Et_2O–CH_2Cl_2 (1:1) as eluent] and crystallisation of the chromatographed material from hexanes gave the title compound **18a** (0.476 g, 84%) as orange crystals; m.p. 155 °C. The IR, 300 MHz ^{1}H NMR and EI mass spectra of the sample matched those of the aglycone obtained by hydrolysis of the glycoside **18b**.

(*b*) A solution of (±)-compound **9b** (0.120 g, 0.5 mmol) in benzene (5 cm^3) was stirred with manganese(IV) oxide (0.435 g,

5 mmol) for 7 d under an oxygen atmosphere. The mixture was diluted with dichloromethane and filtered through a bed of Celite. Evaporation of the filtrate and crystallisation of the residue from hexanes gave the title compound **18a** (0.087 g, 73%) identified by its melting point (m.p. 153 °C) and 300 MHz ^{1}H NMR spectrum.

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