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endo-(1′*R*,2′*R*,5′*S*,7′*R*,9′*S*)-2-(9′-Benzyloxy-2′-phenyl-3′,6′-dioxabicyclo[3.2.2]nonan-7′-yl)-7-bromo-5,8-dimethoxynaphthalen-1-yl acetate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.009 Å
R factor = 0.036
wR factor = 0.114
Data-to-parameter ratio = 7.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, (1), is the product of a model synthesis of an analogue of the antibiotic medermycin, and is thought to be the result of an unusual 1,6-hydride shift.

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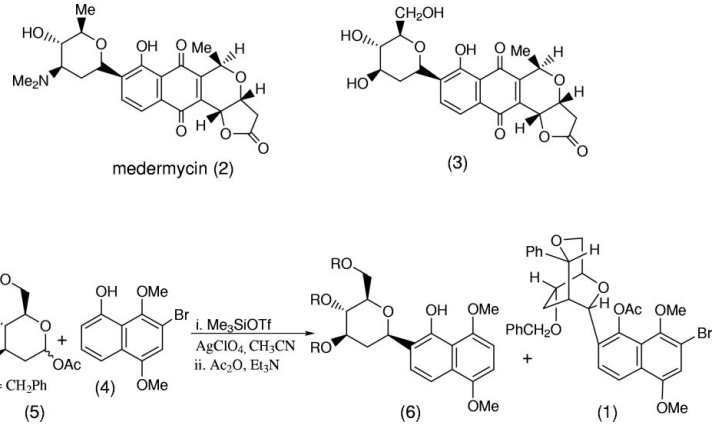
Comment

Recent synthetic effort has been directed towards the synthesis of the pyranonaphthoquinone antibiotic medermycin (2) which was isolated from Streptomyces tanashiensis and contains a C-glycoside linkage to a 2-deoxy sugar (Takano *et al.*, 1976). As part of this programme we embarked on model studies directed towards the synthesis of the 2-deoxyglucosyl analogue of medermycin, (3). The key step in the approach to (3) involved the direct C-glycosylation of 3-bromonaphthol, (4), with a 2-deoxyglucosyl donor, (5) (Brimble & Brenstrum, 2000) (see Scheme) which was expected to afford the desired C-glycoside, (6). Unfortunately this critical C-glycosylation reaction afforded predominantly C-glycoside (1) wherein extensive rearrangement of the 2-deoxyglucosyl moiety had taken place. The structure of this rearranged C-glycoside was established by X-ray crystallography of the acetate derivative of the initial glycosylation product (Fig. 1).



The structure of this rearranged C-glycoside (1) clearly shows that extensive rearrangement of the carbohydrate skeleton has taken place. This rearrangement has been proposed to occur *via* an unusual 1,6-hydride shift similar to that observed by Steel *et al.* in the dimerization of tri-*O*-benzyl-D-glucal (Byerley *et al.*, 1998). The X-ray structure also clearly establishes that the naphthalene ring is *endo* to the bicylic ring system

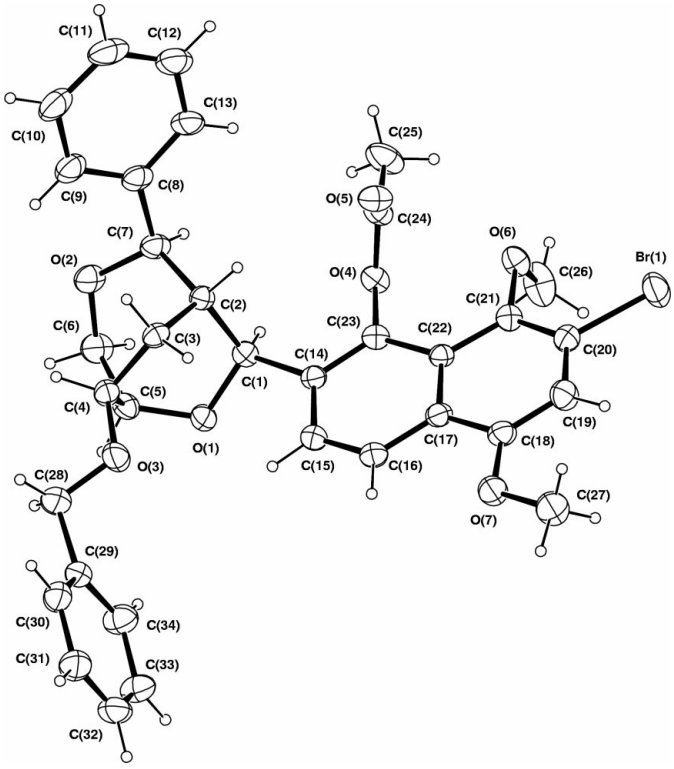


Figure 1
*ORTEP*II (Johnson, 1976, Hall *et al.*, 1999) projection of (1) with displacement ellipsoids shown at the 20% probability level.

Experimental

Trimethylsilyl trifluoromethanesulfonate (51 ml, 0.266 mmol) and silver perchlorate (2 mg, 5 mol%) were added to a stirred solution of 3-bromo-1,4-dimethoxy-5-hydroxynaphthalene, (4) (50 mg, 0.177 mmol), and tri-*O*-benzyl-2-deoxy-D-glucosyl acetate, (5) (101 mg, 210 mmol), in dry acetonitrile (5 ml) at 273 K. The mixture was stirred for 1 h then quenched with aqueous bicarbonate solution (5 ml). The reaction mixture was extracted with dichloromethane (3 × 50 ml), washed with water (100 ml) and dried (magnesium sulfate). The solvent was removed at reduced pressure and the oily residue purified by flash chromatography using hexane-ethyl acetate (4:1) as eluent to give a mixture of a rearranged C-glycoside and *b*-C-glycoside (6) (71 mg, 6:1). This mixture of glycosides was subjected to HPLC.

Triethylamine (0.50 ml, 3.59 mmol), acetic anhydride (0.25 ml, 2.65 mmol) and a catalytic quantity of dimethylaminopyridine were added to a solution of the above rearranged C-glycoside (98 mg, 0.166 mmol) in dichloromethane (2 ml). The solution was stirred overnight then the solvent removed at reduced pressure. The residue was purified by flash chromatography using hexane-ethyl acetate (4:1) to give the acetate (1) (99 mg, 94%) which was recrystallized from hexane-ethyl acetate to give pale-brown needles (m.p. 477–478 K).

Crystal data

$C_{34}H_{33}BrO_7$
M_r = 633.51
Orthorhombic, $P2_12_12_1$
a = 19.5150 (10) Å
b = 23.667 (2) Å
c = 6.541 (2) Å
V = 3021.0 (10) Å^3
Z = 4
D_x = 1.393 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 26.6–30.2°
μ = 2.25 mm^{-1}
T = 294 (2) K
Acicular, pale brown
0.55 × 0.13 × 0.08 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.715, T_{max} = 0.835
2962 measured reflections
2962 independent reflections
2068 reflections with $I > 2\sigma(I)$
θ_{max} = 65.0°
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 7$
3 standard reflections
every 150 reflections
intensity decay: 2.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.114
S = 1.02
2962 reflections
382 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.6329P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Absolute structure: Flack (1983) and Bernardinelli & Flack(1985); no Friedel pairs
Flack parameter = −0.06 (3)

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995); data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); structure solution: *SIR*92 (Altomare *et al.*, 1993); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* (Molecular Structure Corporation, 1997).

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