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3,4,4aα,10aα-Tetrahydro-7-nitro-2*H*,5*H*-[1]benzopyrano[2,3-*b*]pyran

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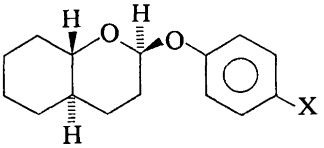
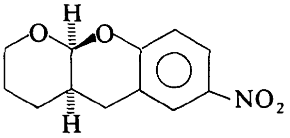
Abstract. $C_{12}H_{13}NO_4$, $M_r = 235\cdot24$, monoclinic, $P2_1/c$, $a = 6\cdot241$ (3), $b = 10\cdot418$ (5), $c = 17\cdot644$ (7) Å, $\beta = 103\cdot19$ (4)°, $Z = 4$, $U = 1117$ Å^3, $D_x = 1\cdot399$ Mg m^{-3}, $\mu = 0\cdot07$ mm^{-1} (Mo $K\alpha$). The structure was refined to $R = 0\cdot055$ for 1126 unique reflexions. The C—O lengths of the acetal group differ by 0·06 Å.

Introduction. The transmission of electronic effects between the O atoms of the acetal group appears to depend on the conformation about that centre (Jones, Kennard, Chandrasekhar & Kirby, 1979). The two acetal C—O lengths differ significantly in axial 2-phenoxy-*trans*-1-oxadecalin (I, X = H) (Jones, Kennard, Chandrasekhar & Kirby, 1978*a*), but not in the equatorial 2-phenoxy or 2-(4-nitrophenoxy) derivatives (Jones, Kennard, Chandrasekhar & Kirby, 1978*b*; Jones *et al.*, 1979). We expect to see larger differences for the axial 2-(4-nitrophenoxy) compound (I, X = NO_2); this compound is available (Chandrasekhar & Kirby, 1978), but we have been unable, despite many attempts, to grow suitable crystals.



(I)

A convenient alternative acetal with a 2-(4-nitrophenoxy) group axial on a pyranose ring is the tricyclic title compound (II), which we have shown (Kirby & Martin, 1978) to have normal reactivity. We report here its crystal and molecular structure.



(II)

Colourless needles, elongated along **a**, were obtained from dichloromethane/petroleum spirit. Intensities were measured on a Syntex $P2_1$ diffractometer, with monochromated Mo $K\alpha$ radiation and a crystal 0·75 × 0·1 × 0·1 mm. Systematic absences $0k0$, k odd and $h0l$, l odd indicated space group $P2_1/c$. 2300 reflexions were collected in the range $0 < 2\theta < 50°$. Lp corrections were applied; averaging of equivalent reflexions gave 1126 unique reflexions with $F > 4\sigma(F)$.

The structure was solved by multisolution $\sum_2$ sign expansion with 340 $E > 1\cdot2$. Isotropic least-squares refinement proceeded to $R = 0\cdot13$ and anisotropic to $R = 0\cdot11$, when a difference synthesis showed all the H atoms. In the final stages C—H lengths were fixed at 1·08 Å and H—C—H angles at 109·5°; an overall isotropic temperature factor for H atoms was employed. The final $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ was 0·0432,

Table 1. *Atom coordinates* (×10^4)

The overall isotropic temperature factor for H atoms is 0·070 (2) Å^2.

	x	y	z
O(1)	−4223 (3)	3727 (2)	1674 (1)
C(2)	−4101 (6)	4826 (3)	1194 (2)
C(3)	−1848 (5)	4968 (3)	1028 (2)
C(4)	−95 (5)	5015 (3)	1785 (1)
C(4a)	−336 (4)	3857 (3)	2294 (1)
C(5)	1200 (4)	3919 (3)	3103 (1)
C(5a)	439 (4)	4938 (2)	3588 (1)
C(6)	1836 (4)	5536 (3)	4205 (1)
C(7)	1041 (4)	6451 (3)	4637 (1)
C(8)	−1141 (4)	6817 (3)	4462 (1)
C(9)	−2549 (5)	6244 (3)	3842 (2)
C(9a)	−1773 (5)	5306 (3)	3417 (2)
O(10)	−3308 (3)	4778 (2)	2823 (1)
C(10a)	−2689 (4)	3730 (3)	2378 (2)
N(1)	2557 (4)	7055 (2)	5293 (1)
O(21)	4530 (3)	6855 (2)	5379 (1)
O(22)	1812 (4)	7748 (2)	5727 (1)
H(1)	3561	5288	4351
H(2)	−4259	6524	3686
H(3)	−2709	2819	2668
H(4)	1515	4998	1656
H(5)	−281	5888	2094
H(6)	−1729	7538	4805
H(7)	2845	4144	3046
H(8)	1204	3000	3386
H(9)	119	3027	2000
H(10)	−1532	4160	686
H(11)	−1790	5845	707
H(12)	−5298	4719	649
H(13)	−4471	5677	1489

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with a corresponding R of 0·0550. The weighting scheme was of the form $w = 1/[\sigma^2(F) + gF^2]$, where g refined to 6×10^{-5}, giving mean $w\Delta^2$ values virtually independent of $\sin\theta$ or $|F_o|$. A final difference map showed no peaks $>0{\cdot}23$ e Å^{-3}. Final atomic coordinates are given in Table 1, bond lengths and angles and torsion angles in Tables 2–4.* Diagrams of the structure are given in Figs. 1 and 2.

Discussion. The two C—O bonds to the acetal centre of (II) differ in length by 0·06 Å. This is the largest difference we have seen in this series of compounds, and contrasts with the non-significant difference observed for the related bicyclic acetal (III) with the O atom of the 4-nitrophenoxy group equatorial to the pyranose ring (Jones *et al.*, 1979).

Table 2. *Bond lengths* (Å)

C(2)–C(3)	1·507 (7)	C(2)–O(1)	1·436 (5)
C(3)–C(4)	1·522 (5)	C(4)–C(4a)	1·532 (6)
C(4a)–C(5)	1·528 (5)	C(4a)–C(10a)	1·515 (6)
C(5)–C(5a)	1·508 (6)	C(5a)–C(9a)	1·398 (5)
C(5a)–C(6)	1·377 (4)	C(6)–C(7)	1·381 (5)
C(7)–N(1)	1·460 (4)	C(7)–C(8)	1·380 (5)
C(8)–C(9)	1·374 (4)	C(9)–C(9a)	1·384 (5)
C(9a)–O(10)	1·364 (4)	C(10a)–O(1)	1·385 (4)
C(10a)–O(10)	1·448 (4)	N(1)–O(22)	1·219 (4)
N(1)–O(21)	1·224 (4)		

Table 3. *Bond angles* (°)

O(1)–C(2)–C(3)	111·7 (3)	O(1)–C(10a)–C(4a)	113·6 (3)
C(4)–C(3)–C(2)	110·4 (3)	C(4)–C(4a)–C(5)	112·9 (3)
C(4a)–C(4)–C(3)	110·0 (3)	C(5a)–C(5)–C(4a)	110·4 (3)
C(5a)–C(6)–C(7)	120·3 (3)	C(5a)–C(9a)–C(9)	121·8 (3)
C(6)–C(5a)–C(5)	122·9 (3)	C(6)–C(7)–C(8)	121·9 (3)
C(7)–C(8)–C(9)	118·5 (4)	C(7)–N(1)–O(21)	118·5 (3)
C(7)–N(1)–O(22)	118·8 (3)	C(9a)–C(5a)–C(6)	117·6 (3)
C(9a)–C(5a)–C(5)	119·6 (3)	C(9a)–C(9)–C(8)	119·9 (3)
C(9a)–O(10)–C(10a)	119·6 (3)	O(10)–C(9a)–C(5a)	122·8 (3)
O(10)–C(9a)–C(9)	115·4 (3)	O(10)–C(10a)–O(1)	105·9 (3)
O(10)–C(10a)–C(4a)	111·8 (3)	C(10a)–O(1)–C(2)	114·1 (3)
C(10a)–C(4a)–C(4)	110·7 (3)	C(10a)–C(4a)–C(5)	109·1 (3)
N(1)–C(7)–C(6)	119·0 (3)	N(1)–C(7)–C(8)	119·1 (3)
O(22)–N(1)–O(21)	122·7 (3)		

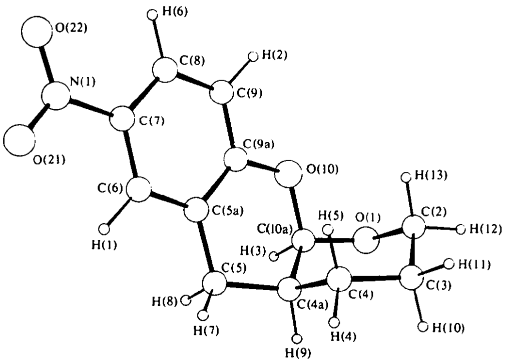

Fig. 1. The title compound, showing the atom numbering.

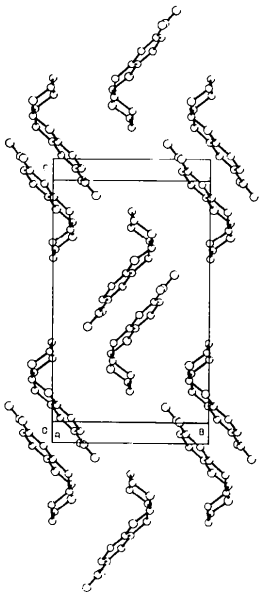

Fig. 2. Packing diagram projected down **a***; H atoms have been omitted for clarity.

Table 4. *Torsion angles* (°)

The sign convention is as defined by Klyne & Prelog (1960).

O(1)–C(10a)–C(4a)–C(4)	52·3 (4)	C(5a)–C(9a)–C(9)–C(8)	−1·6 (5)	O(10)–C(10a)–O(1)–C(2)	67·5 (4)
O(1)–C(10a)–C(4a)–C(5)	177·1 (3)	C(6)–C(5a)–C(5)–C(4a)	−155·5 (3)	O(10)–C(10a)–C(4a)–C(4)	−67·4 (4)
C(3)–C(4)–C(4a)–C(5)	−173·4 (3)	C(6)–C(5a)–C(9a)–C(9)	0·7 (5)	O(10)–C(10a)–C(4a)–C(5)	57·4 (4)
C(3)–C(4)–C(4a)–C(10a)	−50·7 (4)	C(6)–C(5a)–C(9a)–O(10)	−179·7 (3)	C(10a)–O(1)–C(2)–C(3)	57·0 (4)
C(4)–C(3)–C(2)–O(1)	−55·3 (4)	C(6)–C(7)–C(8)–C(9)	0·3 (5)	C(10a)–O(10)–C(9a)–C(5a)	4·5 (5)
C(4a)–C(4)–C(3)–C(2)	52·9 (4)	C(8)–C(7)–C(6)–C(5a)	−1·3 (5)	C(10a)–O(10)–C(9a)–C(9)	−175·9 (3)
C(4a)–C(10a)–O(1)–C(2)	−55·5 (3)	C(9a)–C(5a)–C(5)–C(4a)	24·7 (4)	N(1)–C(7)–C(6)–C(5a)	179·2 (3)
C(5)–C(5a)–C(6)–C(7)	−179·1 (3)	C(9a)–C(5a)–C(6)–C(7)	0·7 (5)	N(1)–C(7)–C(8)–C(9)	179·9 (3)
C(5)–C(5a)–C(9a)–C(9)	−179·5 (4)	C(9a)–C(9)–C(8)–C(7)	1·1 (5)	O(21)–N(1)–C(7)–C(6)	9·3 (5)
C(5)–C(5a)–C(9a)–O(10)	0·1 (5)	C(9a)–O(10)–C(10a)–O(1)	−158·1 (3)	O(21)–N(1)–C(7)–C(8)	−170·2 (3)
C(5a)–C(5)–C(4a)–C(4)	71·6 (4)	C(9a)–O(10)–C(10a)–C(4a)	−34·0 (4)	O(22)–N(1)–C(7)–C(6)	−171·6 (3)
C(5a)–C(5)–C(4a)–C(10a)	−51·9 (4)	O(10)–C(9a)–C(9)–C(8)	178·8 (3)	O(22)–N(1)–C(7)–C(8)	8·9 (5)

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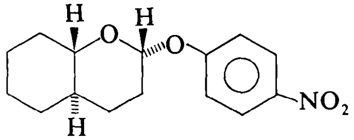
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33997 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(III)

The extra constraint of the third ring probably has only a minor effect on the bond lengths at the acetal centre; certainly the outer pair of C—O lengths of the C—O—C—O—C system are not significantly different from those in the bicyclic acetals (I) and (III). The low acetal bond angle [O(10)—C(10a)—O(1) = 105·9°] is close to that observed for the two equatorial compounds (I, X = H, NO_2) and in the range expected for an acetal adopting the *gauche,trans* conformation (Gorenstein & Kar, 1977).

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Structure of the Hydrogen Bromide Adduct of Spicatine, a Sesquiterpenoid Lactone

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Abstract. $C_{27}H_{33}BrO_{10}$, $P2_1$, a = 10·415 (5), b = 16·093 (2), c = 8·122 (3) Å, β = 96·96°, Z = 2, V = 1350 Å^3, $\rho_{\text{X-ray}}$ = 1·47 Mg m^{-3}, μ(Cu $K\alpha$) = 2·82 mm^{-1}. The final R value is 0·036 for 2401 independent observed reflexions. The seven-membered ring adopts a twist-chair conformation with the approximate C_2 axis through C(8). The γ-lactone ring has a twist conformation and is *trans*-fused to the cycloheptane ring, while the cyclopentene ring is a *cis*-fused C(1) envelope.

Introduction. Spicatine, $C_{22}H_{32}O_{10}$, is isolated both from *Liatris spicata* (L.) Kuntze and from *L. pycnostachya* (Michx.) Kuntze (Herz, Poplawski & Sharma, 1975). It is a sesquiterpene lactone of the guainolide type. Studies of this compound by spectroscopic and chemical methods were unsuccessful in determining the complete structure (Karlsson, Pilotti, Wiehager, Wahlberg & Herz, 1975). An X-ray analysis of the hydrogen bromide adduct of spicatine was therefore undertaken.

Three-dimensional data were collected from a parallelepiped crystal, with a volume of approximately 0·002 mm^3, using a computer-controlled Philips PW 1100 diffractometer [graphite monochromator, Cu $K\alpha$ radiation, $\theta/2\theta$ scan and stationary background measurements at ±0·75° (θ) from the peak maxima]. During the period of data collection, three reference reflexions (measured every 90 min) showed a linear intensity decrease with time of approximately 5%. Intensities were measured for all independent reflexions with $2\theta \leq 140°$. Only the 2401 most significant reflexions [$I_{\text{net}} \geq 4\sigma(I_{\text{net}})$] were used in the least-squares refinements.

Lorentz and polarization factors were applied, but no correction for absorption was made. Lattice constants were obtained from the least-squares refinement of the angular coordinates for 25 reflexions.

The structure was solved by a combination of a heavy-atom technique and a direct method. A Patterson map revealed the x and z coordinates of the Br atom. The y coordinate was fixed at 0·25 and was held fixed throughout the computations. Three cycles of

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