

**Brombyin-I [(*rel*)-4 $\beta$ -Acetyl-3-(1,3-benzodioxol-5-yl)-1,4,4a $\beta$ ,5,6,7,8,8a $\alpha$ -octahydronaphthalen-1 $\alpha$ -ol] and Brombyin-II [(*rel*)-4 $\beta$ -Acetyl-3 $\alpha$ -(1,3-benzodioxol-5-yl)-3,4,4a $\beta$ ,5,6,7,8,8a $\beta$ -octahydronaphthalene]: a Novel Type of Natural Product Isolated from the Stem Bark of *Brombya platynema*.  
F. Muell**

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Two naphthalene derivatives of a novel skeletal type have been isolated from the bark of *Brombya platynema* F. Muell (Rutaceae). They were identified by a combination of mass spectroscopy, 2-D NMR techniques, and X-ray studies, as (*rel*)-4 $\beta$ -acetyl-3-(1,3-benzodioxol-5-yl)-1,4,4a $\beta$ ,5,6,7,8,8a $\alpha$ -octahydronaphthalen-1 $\alpha$ -ol **1** and (*rel*)-4 $\beta$ -acetyl-3 $\alpha$ -(1,3-benzodioxol-5-yl)-3,4,4a $\beta$ ,5,6,7,8,8a $\beta$ -octahydronaphthalene **2**.

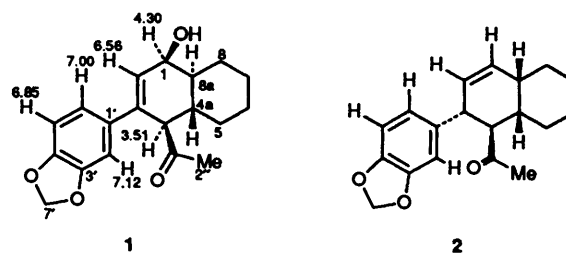
*Brombya platynema* F. Muell. (Rutaceae), is a tree endemic to the rainforests of northeast Queensland, Australia.<sup>1</sup> It has not been the subject of any previous phytochemical investigation, and we now wish to record the occurrence, within the stem bark of this species, of two novel naphthalene derivatives.

### Results and Discussion

Both compounds were obtained from the light petroleum extract of the stem bark, and were purified by silica gel chromatography, and recrystallisation. Compound **1** was identified by 2-D NMR spectroscopic methods, in conjunction with electron impact mass spectrometry (EIMS), and the structure was confirmed by X-ray analysis (Tables 4–6). The high resolution EIMS of **1** indicated that its molecular formula was C<sub>19</sub>H<sub>22</sub>O<sub>4</sub>. The <sup>1</sup>H NMR spectrum (Table 1) showed three aromatic protons, (2'-H, 5'-H, 6'-H), with couplings indicative of a 1,2,4 substitution pattern, and two weakly coupled protons ( $\delta_{\text{H}}$  5.93 and 5.95, *J* 1.2 Hz) were suggestive of a methylenedioxy group. These data collectively indicated the presence of a piperonyl moiety. A *J*-modulated <sup>13</sup>C NMR spectrum (Table 1) confirmed the methylenedioxy ( $\delta_{\text{C}}$  102.1) and revealed that the molecule contained, in addition to the piperonyl moiety, one olefinic C=CH bond, one ketonic carbonyl, four methine carbons, four methylene carbons, and a methyl group.

2-D HMBC (Heteronuclear Multiple Bond Coherence)<sup>2</sup> NMR reveals <sup>13</sup>C–<sup>1</sup>H couplings, over 2- or 3-bond distances (Table 2). Correlation (<sup>3</sup>*J*) of both the olefinic proton ( $\delta_{\text{H}}$  6.56) and 5'-H proton ( $\delta_{\text{H}}$  6.85) with the quaternary aromatic carbon at  $\delta_{\text{C}}$  136.2 required that the double bond was attached directly to the aromatic nucleus. The  $\delta_{\text{H}}$  6.56 proton resonated as a dd, (*J* 5.9, 1.9 Hz) and a <sup>1</sup>H–<sup>1</sup>H COSY experiment showed that its couplings were to the methine protons at  $\delta_{\text{H}}$  4.30 (*J* 5.9 Hz), and  $\delta_{\text{H}}$  3.51 (*J* 1.9 Hz). These latter two methine protons did not couple to each other, and it was therefore inferred that the 5.9 Hz coupling was between vicinal protons, whereas the 1.9 Hz coupling was transmitted through the double bond (<sup>4</sup>*J*).

Observation of the <sup>1</sup>H NMR spectrum also showed the presence of a methyl group ( $\delta_{\text{H}}$  2.01), attached to a quaternary carbon. Of the five quaternary centres in the molecule, four have already been assigned to the aromatic



nucleus and the olefinic bond, leaving only the carbonyl group, which must therefore be adjacent to the methyl. Furthermore, the COSY spectrum revealed a weak coupling between the signals at  $\delta_{\text{H}}$  3.51 and 2.01. This was confirmed by expansion of the proton spectrum, which showed the latter methyl signal actually to be a doublet, with a small coupling in the order of 0.3 Hz. The <sup>2</sup>*J* HMBC correlations of both the  $\delta_{\text{H}}$  3.51 and 2.01 resonances to the carbonyl carbon ( $\delta_{\text{C}}$  209.7) thus placed an acetyl group on the carbon bearing the  $\delta_{\text{H}}$  3.51 proton.

The chemical shift of the  $\delta_{\text{H}}$  4.30 proton, together with its appearance as a dd, suggested its oxymethine nature, with coupling to two vicinal protons at  $\delta_{\text{H}}$  6.56 and  $\delta_{\text{H}}$  ca. 1.4, as shown in the COSY spectrum (Table 3). The COSY spectrum further revealed that the  $\delta_{\text{H}}$  2.25 proton coupled to both this  $\delta_{\text{H}}$  ca. 1.4 proton, and also to the signal at  $\delta_{\text{H}}$  3.51. Thus, the presence of a 6-membered ring was indicated, and this was confirmed by the HMBC spectrum, which revealed common correlations of both the protons at  $\delta_{\text{H}}$  4.30 and 3.51 to a methine carbon at  $\delta_{\text{C}}$  34.5. The  $\delta_{\text{H}}$  2.25 proton resonated as a qd, or dddd, with three *J* ca. 10 Hz couplings, and one *J* ca. 3 Hz coupling. This was indicative of its axial stereochemistry at a ring-junction; the presence of three large *trans*-diaxial <sup>3</sup>*J* couplings revealed the *trans*-decalin nature of the ring-junction, and also placed the acetyl group in an equatorial position. Thus, four CH<sub>2</sub> carbons and an OH remained, to complete the molecular formula of C<sub>19</sub>H<sub>22</sub>O<sub>4</sub>, and they could be unambiguously placed to give the molecular structure shown. This structure, and its relative stereochemistry, were confirmed by X-ray studies (Fig. 1).

**Table 1**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data for compounds **1** and **2**.  $^{13}\text{C}$  spectra were run at 100 MHz,  $^1\text{H}$  spectra at 400 MHz. Data are for spectra in  $\text{C}_5\text{D}_5\text{N}$ , with  $\text{CDCl}_3$  data, if present, in parenthesis

	Compound 1			Compound 2		
	$\delta_{\text{C}}$	$\delta_{\text{H}}$	Multiplicity (J/Hz)	$\delta_{\text{C}}$	$\delta_{\text{H}}$	Multiplicity (J/Hz)
C-1	66.3 (CH)	4.30 (4.09)	dd ( $J$ 5.9, 3.3)	133.3 (CH)†	5.56 (5.48)	dt ( $J$ 9.9, 1.7)
C-2	130.7 (CH)	6.56 (6.26)	dd ( $J$ 6.0, 1.9)	129.6 (CH)†	5.78 (5.80)	ddd ( $J$ 9.9, 5.0, 2.7)
C-3	137.7 (C)	—	—	47.9 (CH)	3.72 (3.54)	ddd ( $J$ ca. 10, 5.0, ca. 2)
C-4	62.7(CH)	3.51 (3.29)	br d ( $J$ ca. 9.8)	54.9 (CH)	3.09 (3.00)	dd ( $J$ 11.5, 10.4)
C-4a	34.5 (CH)	2.25 ( <i>a</i> )	qd ( $J$ ca. 10, ca. 3)	37.4 (CH)***	<i>b</i>	
C-5	32.8 (CH <sub>2</sub> )	1.2, H $\alpha$ ( <i>a</i> )	multiplet	30.5 (CH <sub>2</sub> )††	<i>b</i>	
		ca. 2.0, H $\beta$ ( <i>a</i> )	multiplet		<i>b</i>	
C-6	26.8 (CH <sub>2</sub> )	1.7, H $\alpha$ ( <i>a</i> )	multiplet	29.2 (CH <sub>2</sub> )††	<i>b</i>	
		ca. 1.3, H $\beta$ ( <i>a</i> )	multiplet		<i>b</i>	
C-7	26.9 (CH <sub>2</sub> )	ca. 1.3, H $\alpha$ ( <i>a</i> )	multiplet	26.9 (CH <sub>2</sub> )††	<i>b</i>	
		ca. 1.8, H $\beta$ ( <i>a</i> )	multiplet		<i>b</i>	
C-8	29.4 (CH <sub>2</sub> )	ca. 1.8, H $\alpha$ ( <i>a</i> )	multiplet	21.7 (CH <sub>2</sub> )††	<i>b</i>	
		ca. 2.0, H $\beta$ ( <i>a</i> )	multiplet		<i>b</i>	
C-8a	42.9 (CH)	1.4 ( <i>a</i> )	multiplet	37.0 (CH)***	<i>b</i>	
C-1'	136.2 (C)	—	—	138.8 (C)	—	—
C-2'	107.8 (CH)	7.12 (6.76)	d ( $J$ 1.8)	109.1 (CH)**	6.87 (6.64)	d ( $J$ 1.7)
C-3'	148.9 (C)	—	—	148.9 (C)*	—	—
C-4'	148.0 (C)	—	—	147.3 (C)*	—	—
C-5'	109.0 (CH)	6.85 (6.73)	d ( $J$ 8.1)	108.9 (CH)**	6.88 (6.71)	d ( $J$ 7.9)
C-6'	120.8 (CH)	7.00 (6.81)	dd ( $J$ 8.1, 1.8)	121.8 (CH)	6.72 (6.56)	dd ( $J$ 7.9, 1.7)
C-7'	102.1 (CH <sub>2</sub> )	5.95 (5.95)	d ( $J$ 1.2)	102.0 (CH <sub>2</sub> )	5.99 (5.93)	d ( $J$ 1.2)
		5.93 (5.93)	d ( $J$ 1.2)		5.98 (5.93)	d ( $J$ 1.2)
C-1''	209.7 (C)	—	—	212.8 (C)	—	—
C-2''	26.7 (CH <sub>3</sub> )	2.01 (1.87)	s, 3 H	32.4 (CH <sub>3</sub> )	1.93 (1.87)	s, 3 H

\*, † Within any column, signals with equal numbers of \* or † are interchangeable. \*  $\text{CDCl}_3$  spectrum of **1** showed 5 H between  $\delta$  1.7–1.9, 1 H at  $\delta$  1.55, and 4 H between  $\delta$  1.2–1.4.  $^b$   $\text{C}_5\text{D}_5\text{N}$  spectrum of **2** showed 1 H at  $\delta$  2.25, 1 H at  $\delta$  2.01, 2 H at  $\delta$  1.65–1.7, 1 H at  $\delta$  1.57, and 5 H in the region  $\delta$  1.15–1.45, whereas  $\text{CDCl}_3$  spectrum of **2** showed 2–3 H between  $\delta$  2.1–2.3, 2 H between  $\delta$  1.7–1.9, 3 H between  $\delta$  1.4–1.6 and 2–3 H between  $\delta$  1.2–1.4.

**Table 2** HMQC and HMBC correlations between protons and carbons in **1** ( $\text{C}_5\text{D}_5\text{N}$ )

$^1\text{H}$	$^{13}\text{C}$		
	$^1\text{J}$ (HMQC)	$^2\text{J}$ (HMBC)	$^3\text{J}$ (HMBC)
7.12	107.8, CH		148.0, 137.7, 120.8
7.00	120.8, CH		148.0, 137.7, 107.8
6.85	109.0, CH		136.2, 148.9
6.56	137.7, CH	66.3	136.2, 62.7, 42.9
5.94	102.1, CH <sub>2</sub>		148.9, 148.0
4.30	66.3, CH	130.7	137.7, 34.5
3.51	62.7, CH	209.7, 137.7, 34.5	130.7, 32.8
2.25	34.5, CH		
2.01	26.7, CH <sub>3</sub>	209.7	
ca. 2.0, 1,2	32.8, CH <sub>2</sub>		
ca. 2.0, 1,8	29.4, CH <sub>2</sub>		
ca. 1.8, 1.7, 1.3 (2 H)	26.9, 26.8, both CH <sub>2</sub>		

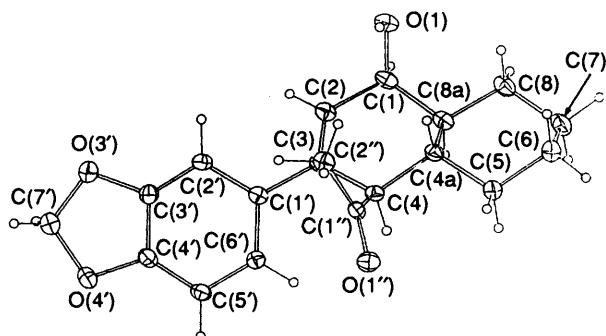
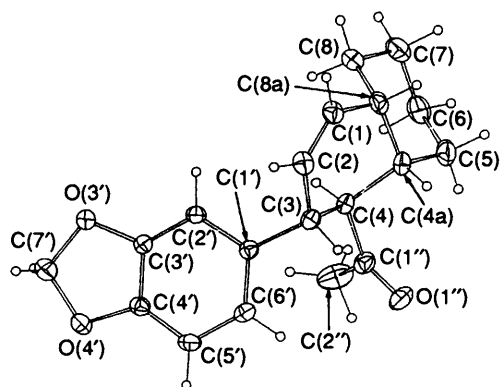
**Table 3**  $^1\text{H}$ – $^1\text{H}$  COSY correlations in **1** (400 MHz;  $\text{C}_5\text{D}_5\text{N}$ )

Proton	Neighbours
7.12 d	7.00
7.00 dd	7.12, 6.85
6.85 d	7.00
6.56 dd	4.30, 3.51
5.95 d	5.93
5.93 d	5.95
4.30 d	6.56, ca. 1.4
3.51 br d	6.56, 2.25, 2.01 (weak)
2.25 dddd	3.51, ca. 1.9, 1.4, 1.2
2.01 3 H, s	3.51 (weak)
ca. 1.9, 2 H, m	2.25, ca. 1.8, 1.7, 1.4, ca. 1.3, 1.2
ca. 1.8, 2 H, m	ca. 1.9, 1.4, ca. 1.3
1.7 m	ca. 1.9, ca. 1.8, ca. 1.3, 1.2
1.4 m	2.25, ca. 1.9, ca. 1.8
ca. 1.3 2 H, m	ca. 1.9, ca. 1.8, 1.7, 1.2
1.2 m	2.25, ca. 1.9, 1.7, ca. 1.3

A 400 MHz  $^1\text{H}$  NMR ( $\text{C}_5\text{D}_5\text{N}$ ) spectrum obtained for **2** revealed close similarities to that of **1** (Table 1). In this case, signals at  $\delta_{\text{H}}$  6.88, 6.87, 6.72, and a 2 H singlet at  $\delta_{\text{H}}$  6.0 were again indicative of a piperonyl moiety. The presence of a *cis*-double bond was revealed by a ca. 10 Hz coupling between olefinic signals at  $\delta_{\text{H}}$  5.56 and 5.78. A proton signal at  $\delta_{\text{H}}$  3.09 was assigned to C-4 ( $\alpha$  to carbonyl), and the two large (ca. 10–11 Hz) couplings of this proton were indicative of the *trans*-diaxial pattern of protons attached to C-3, C-4 and C-4a. The EIMS spectrum showed a molecular ion corresponding to  $\text{C}_{19}\text{H}_{22}\text{O}_3$  ( $m/z$  298), which was also the base peak. The presence of a fragment at  $m/z$  216, corresponding to  $\text{C}_{13}\text{H}_{12}\text{O}_3$ , revealed the loss of cyclohexene, and therefore suggested the presence of one perhydrogenated ring, as in **1**. Again, the structure and relative stereochemistry of **2** were confirmed by X-ray studies (Fig. 2, and Tables 4–6), although in this case, no 2-D NMR experiments were performed.

**Table 4** Non-hydrogen positional parameters for **1** and **2**

Atom	<b>1</b>			<b>2</b>		
	x	y	z	x	y	z
C(1)	1.024 4(3)	0.684 5(2)	0.566 7(1)	0.561 3(2)	0.230 0(2)	0.696 7(2)
O(1)	0.953 8(2)	0.801 4(2)	0.591 6(1)	—	—	—
C(2)	0.904 2(3)	0.572 1(2)	0.566 7(1)	0.595 7(2)	0.330 8(2)	0.692 0(2)
C(3)	0.929 4(3)	0.469 9(2)	0.608 5(1)	0.715 8(2)	0.367 6(2)	0.719 1(2)
C(4)	1.085 3(3)	0.460 9(2)	0.664 0(1)	0.787 2(2)	0.275 8(2)	0.783 0(2)
C(1')	1.034 6(3)	0.420 6(2)	0.732 2(1)	0.911 1(2)	0.306 2(2)	0.783 2(3)
O(1')	1.109 0(2)	0.333 2(2)	0.766 44(8)	0.955 2(1)	0.316 8(2)	0.687 5(2)
C(2')	0.891 6(4)	0.493 2(3)	0.756 9(2)	0.974 2(3)	0.327 3(5)	0.904 0(4)
C(5)	1.365 6(3)	0.565 5(3)	0.716 3(1)	0.839 2(3)	0.072 9(3)	0.758 9(3)
C(6)	1.472 8(4)	0.689 6(3)	0.722 9(2)	0.817 8(3)	0.029 3(3)	0.885 8(3)
C(7)	1.493 8(4)	0.742 0(3)	0.652 8(2)	0.695 3(3)	−0.002 7(2)	0.893 3(3)
C(8)	1.321 2(4)	0.768 6(3)	0.609 7(1)	0.617 5(3)	0.091 2(2)	0.856 8(3)
C(8a)	1.201 8(3)	0.651 3(2)	0.604 2(1)	0.637 2(2)	0.136 6(2)	0.729 0(2)
C(4a)	1.189 9(3)	0.588 9(2)	0.674 1(1)	0.761 4(2)	0.167 1(2)	0.717 1(2)
C(1'')	0.809 5(3)	0.357 4(2)	0.602 5(1)	0.724 5(2)	0.472 2(2)	0.792 7(2)
C(2'')	0.634 0(3)	0.376 1(2)	0.582 2(1)	0.656 4(2)	0.487 2(2)	0.891 3(2)
C(3')	0.532 1(3)	0.268 5(2)	0.575 3(1)	0.670 9(2)	0.581 0(2)	0.957 1(2)
O(3')	0.357 0(2)	0.263 2(2)	0.558 2(1)	0.612 7(1)	0.614 5(1)	1.056 0(1)
C(4')	0.595 0(3)	0.144 1(2)	0.586 0(1)	0.748 3(2)	0.658 4(2)	0.930 6(2)
O(4')	0.464 3(2)	0.055 0(2)	0.576 2(1)	0.744 0(1)	0.744 0(1)	1.011 2(2)
C(5')	0.764 3(3)	0.121 2(2)	0.605 9(1)	0.814 9(2)	0.646 6(2)	0.835 1(2)
C(6')	0.869 8(3)	0.230 7(2)	0.614 4(1)	0.801 1(2)	0.551 6(2)	0.766 2(2)
C(7')	0.318 4(4)	0.127 4(3)	0.547 5(3)	0.655 3(3)	0.719 5(3)	1.087 9(3)

**Fig. 1** X-Ray molecular structure of compound **1****Fig. 2** X-Ray molecular structure of compound **2**

Neither compound showed any optical rotation, in keeping with the centrosymmetric space group of both X-ray specimens. The biosynthesis of **1** and **2** is open to question, and must account for this racemic nature. Thus, although coupling of two cinnamate residues is possible, to give a novel 9-2', 7-7' neolignan linkage,<sup>3,4</sup> this would seem unlikely, given the perhydrogenated nature of one of the 6-membered rings, in each case. An alternative may be that

biosynthesis occurs *via* linkage of one cinnamate/cinnamaldehyde unit, with a 10-carbon acetate-derived chain, which has undergone decarboxylation.

### Experimental

IR and UV spectra were recorded on Perkin-Elmer 781 and 552 (UV-VIS) instruments, respectively. M.p. data (uncorr.) were obtained with a Reichert hot stage apparatus, and optical rotation measurements were taken on a Perkin-Elmer model 241 polarimeter ( $[\alpha]_D$  values are given in  $10^{-1}$  deg  $\text{cm}^2 \text{g}^{-1}$ ). NMR spectra were obtained on Bruker WH-250 and AMX-400 instruments ( $J$  values are given in Hz), and EIMS spectra were recorded on an AEIMS 902 double-focussing spectrometer, with a direct probe insert, and 70 eV electrons used, for ionisation. Unless otherwise specified, light petroleum refers to the fraction with 60–80 °C boiling range.

**Plant Material.**—The sample was collected from the Boonjie logging area of timber reserve 1230, in the Cook district of Queensland. A voucher specimen (TGH 15144) has been deposited at the Australian National Herbarium, Canberra, Australia.

**Extraction and Isolation.**—*Bromya platynema* bark (415 g) was ground to a fine powder, and extracted successively into light petroleum (40–60 °C),  $\text{CH}_2\text{Cl}_2$ , and MeOH, in a Soxhlet apparatus. The light petroleum extract yielded, after solvent evaporation, a total of 8.28 g of material, which was adsorbed onto silica gel (Merck type 7736, Keisigel 60 H), and applied to a vacuum liquid chromatography column. This column was eluted with increasing concentrations of EtOAc in hexane; **2** was thus obtained with 10% EtOAc as eluting solvent, and was recrystallised from MeOH–EtOAc, to give pure compound (110 mg). **1** was obtained from the fractions eluting in 50–60% EtOAc. These fractions were applied to a silica gel (Merck 7749, Keisigel 60 PF<sub>254</sub>) circular chromatography plate, eluting with  $\text{CHCl}_3$ –light petroleum mixtures. **1** was eluted by 70%  $\text{CHCl}_3$ –light petroleum, and was recrystallised from hexane–EtOAc, to give pure compound (18.5 mg).

**Table 5** Non-hydrogen bond angles for **1** and **2** (°)

Atoms	Bond angle (°)	
	1	2
O(1)–C(1)–C(2)	111.1(2)	—
O(1)–C(1)–C(8a)	113.5(2)	—
C(2)–C(1)–C(8a)	111.8(2)	123.9(2)
C(1)–C(2)–C(3)	124.8(2)	124.9(2)
C(2)–C(3)–C(4)	121.4(2)	110.3(2)
C(2)–C(3)–C(1')	121.8(2)	112.8(2)
C(4)–C(3)–C(1')	116.8(2)	111.7(2)
C(3)–C(4)–C(1')	110.8(2)	108.6(2)
C(3)–C(4)–C(4a)	113.7(2)	110.0(2)
C(1')–C(4)–C(4a)	109.1(2)	112.1(2)
C(4)–C(1')–O(1')	121.2(2)	120.4(2)
C(4)–C(1')–C(2')	117.8(2)	118.1(3)
O(1')–C(1')–C(2')	121.0(2)	121.5(3)
C(6)–C(5)–C(4a)	111.5(2)	113.7(3)
C(5)–C(6)–C(7)	110.8(2)	111.4(3)
C(6)–C(7)–C(8)	110.9(3)	110.9(3)
C(7)–C(8)–C(8a)	113.4(2)	112.8(3)
C(1)–C(8a)–C(8)	112.2(2)	111.6(2)
C(1)–C(8a)–C(4a)	110.5(2)	111.1(2)
C(8)–C(8a)–C(4a)	112.8(2)	112.1(2)
C(4)–C(4a)–C(5)	111.3(2)	115.2(2)
C(4)–C(4a)–C(8a)	110.1(2)	109.5(2)
C(5)–C(4a)–C(8a)	112.1(2)	110.5(2)
C(3)–C(1')–C(2')	120.8(2)	119.7(2)
C(3)–C(1')–C(6')	120.7(2)	120.8(2)
C(2')–C(1')–C(6')	118.5(2)	119.4(2)
C(1')–C(2')–C(3')	117.9(2)	117.2(2)
C(2')–C(3')–O(3')	128.1(2)	127.6(2)
C(2')–C(3')–C(4')	122.6(2)	122.7(2)
O(3')–C(3')–C(4')	109.3(2)	109.6(2)
C(3')–O(3')–C(7')	105.0(2)	105.9(2)
O(3')–C(7')–O(4')	107.9(3)	108.3(3)
C(7')–O(4')–C(4')	105.2(2)	105.9(2)
C(3')–C(4')–O(4')	110.2(2)	110.2(2)
C(3')–C(4')–C(5')	121.6(2)	121.5(2)
O(4')–C(4')–C(5')	128.1(2)	128.3(2)
C(4')–C(5')–C(6')	116.4(2)	116.7(2)
C(1')–C(6')–C(5')	123.0(2)	122.4(2)

(rel)-4 $\beta$ -Acetyl-3-(1,3-benzodioxol-5-yl)-1,4,4a $\beta$ ,5,6,7,8,8a $\alpha$ -octahydronaphthalen-1 $\alpha$ -ol **1**.—Clusters, m.p. 191–193 °C, from hexane–EtOAc; [ $\alpha$ ]<sub>D</sub> 0 (*c* 0.8, CHCl<sub>3</sub>);  $\lambda_{\max}$ /nm 297 (log  $\epsilon$  3.41), 263 (log  $\epsilon$  3.52);  $\nu_{\max}$ (KBr disc)/cm<sup>-1</sup> 3460, 1688, 1500, 1485, 1441, 1386, 1350, 1241, 1230, 1215, 1083, 1031, 923, 857 and 813; for <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data see Tables 1–3; *m/z* (EIMS, source temp. 120 °C) 314 (M<sup>+</sup> C<sub>19</sub>H<sub>22</sub>O<sub>4</sub>, 100%), 271 (C<sub>17</sub>H<sub>19</sub>O<sub>3</sub>, 23), 254 (C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>, 89), 253 (C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>, 31), 211 (C<sub>14</sub>H<sub>11</sub>O<sub>2</sub>, 23), 148 (C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>, 13) and 135 (C<sub>8</sub>H<sub>7</sub>O<sub>2</sub>, 41).

(rel)-4 $\beta$ -Acetyl-3 $\alpha$ -(1,3-benzodioxol-5-yl)-3,4,4a $\beta$ ,5,6,7,8,8a $\beta$ -octahydronaphthalene **2**.—Clusters, m.p. 130 °C, from MeOH–EtOAc; [ $\alpha$ ]<sub>D</sub> 0 (*c* 3.2, CHCl<sub>3</sub>);  $\lambda_{\max}$ /nm 284 (log  $\epsilon$  2.84), 230 (log  $\epsilon$  3.26);  $\nu_{\max}$ (KBr disc)/cm<sup>-1</sup> 1698, 1500, 1485, 1439, 1358, 1245, 1039, 939, 824 and 723; <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data see Tables 1–3; *m/z* (EIMS, inlet temp. 130 °C) 298 (M<sup>+</sup> C<sub>19</sub>H<sub>22</sub>O<sub>3</sub>, 100%), 255 (C<sub>17</sub>H<sub>19</sub>O<sub>2</sub>, 81), 254 (C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>, 10), 215 (C<sub>13</sub>H<sub>11</sub>O<sub>3</sub>, 15) and 135 (C<sub>8</sub>H<sub>7</sub>O<sub>2</sub>, 35).

**Crystal Data.**—**1**; C<sub>19</sub>H<sub>22</sub>O<sub>4</sub>, *M* = 314.4. Monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 7.937(4), *b* = 10.245(2), *c* = 19.637(11) Å,  $\beta$  = 98.65(6)°, *U* = 1579 Å<sup>3</sup>, *D*<sub>c</sub>(*Z* = 4) = 1.32 g cm<sup>-3</sup>; *F*(000) = 672.  $\mu_{\text{Mo}}$  = 1.0 cm<sup>-1</sup>; specimen: 0.60 × 0.35 × 0.22 mm. *N* = 2773, *N*<sub>o</sub> = 1959; *R* = 0.043, *R*' = 0.045. ENRAF-Nonius CAD-4 diffractometer.

**2**; C<sub>19</sub>H<sub>22</sub>O<sub>3</sub>, *M* = 298.4. Monoclinic, space group

**Table 6** Non-hydrogen bond lengths for **1** and **2** (Å)

Bond	Bond lengths (Å)	
	1	2
C(1)–O(1)	1.439(3)	—
C(1)–C(2)	1.496(3)	1.310(4)
C(1)–C(8a)	1.526(3)	1.488(4)
C(2)–C(3)	1.327(3)	1.505(3)
C(3)–C(4)	1.525(3)	1.549(3)
C(3)–C(1')	1.487(3)	1.517(3)
C(4)–C(1')	1.513(3)	1.517(3)
C(4)–C(4a)	1.549(3)	1.540(3)
C(1')–O(1')	1.217(3)	1.206(3)
C(1')–C(2')	1.497(4)	1.488(5)
C(5)–C(6)	1.524(4)	1.521(5)
C(5)–C(4a)	1.531(3)	1.531(4)
C(6)–C(7)	1.510(5)	1.514(5)
C(7)–C(8)	1.522(4)	1.515(4)
C(8)–C(8a)	1.524(4)	1.533(4)
C(8a)–C(4a)	1.529(3)	1.535(4)
C(1')–C(2')	1.404(3)	1.401(3)
C(1')–C(6')	1.391(3)	1.380(3)
C(2')–C(3')	1.362(3)	1.364(3)
C(3')–O(3')	1.381(3)	1.383(3)
C(3')–C(4')	1.374(3)	1.369(3)
O(3')–C(7')	1.433(4)	1.423(4)
C(7')–O(4')	1.419(4)	1.422(4)
O(4')–C(4')	1.374(3)	1.376(4)
C(4')–C(5')	1.362(4)	1.358(4)
C(5')–C(6')	1.395(4)	1.394(4)

*P*2<sub>1</sub>/*c*(C<sub>2h</sub>,<sup>5</sup> No. 14), *a* = 11.865(3), *b* = 12.327(5), *c* = 10.885(4) Å,  $\beta$  = 94.11(3)°, *U* = 1588 Å<sup>3</sup>. *D*<sub>c</sub>(*Z* = 4) = 1.25 g cm<sup>-3</sup>; *F*(000) = 640.  $\mu_{\text{Mo}}$  = 1.0 cm<sup>-1</sup>; specimen: cuboid,  $\approx$ 0.2 mm. *N* = 2819, *N*<sub>o</sub> = 1722; *R* = 0.040, *R*' = 0.038. Syntex *P*2<sub>1</sub> diffractometer.

**Structure Determination.**—Unique diffractometer data sets were measured at ca. 295 K within the limit  $2\theta_{\max} = 50^\circ$  (Monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å);  $2\theta/\theta$  scan mode). *N* Independent reflections were obtained, *N*<sub>o</sub> with *I* > 3 $\sigma$ (*I*) being considered 'observed' and used in the full matrix least squares refinements without absorption correction after solution of the structures by direct methods. Anisotropic thermal parameters were refined for C, O; hydrogen atoms were refined in (*x*, *y*, *z*) and *U*<sub>iso</sub>. Conventional residuals *R*, *R*' on |*F*| are quoted, statistical weights derivative of  $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004 \sigma^4(I_{\text{diff}})$  being employed. Neutral atom complex scattering factors were employed;<sup>5</sup> computation used the XTAL 3.0 program system<sup>6</sup> implemented by S. R. Hall. Pertinent results are given in Fig. 2 and Tables 4–6; material deposited at the C.C.D.C.\* comprises thermal and non-hydrogen atom parameters.

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\* For details of the C.C.D.C. deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

### References

- 1 A. Engler in *Die Natürlichen Pflanzenfamilien*, vol. 19a, p. 232, eds. A. Engler and K. Prantl., Engelmann, Leipzig, 1931.

- 2 A. Bax and M. F. Summers, *J. Am. Chem. Soc.*, 1986, **108**, 2093.  
3 O. R. Gottlieb, *Fortschr. Chem. Org. Naturst.*, 1978, **35**, 1.  
4 D. A. Whiting, *Nat. Prod. Rep.*, 1985, 191.  
5 *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

- 6 The XTAL User's Manual, Version 3.0. S. R. Hall and J. M. Stewart for Universities of Western Australia and Maryland, 1990.

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