

except C(10) and C(13) which are out of plane by  $-0.204$  and  $1.415$  Å respectively.

One of us (M.C.) is indebted to the D.A.W. der DDR and the Hungarian Academy of Sciences for providing the opportunity for studying the CORDAL method in Berlin.

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## 5,6:12,20-Diepoxy-19,20-methylimino-14,20-cyclo-*ent*-kaur-16-ene-2,11-diol: An Oxidation Product of Anopteryl Alcohol

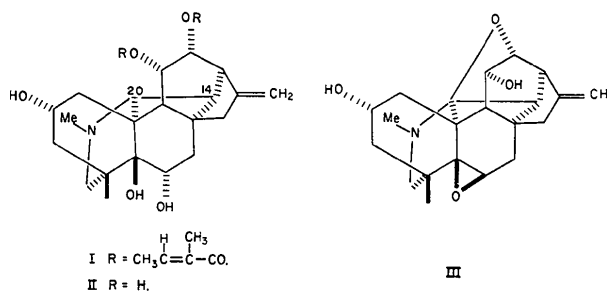
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**Abstract.**  $C_{21}H_{27}NO_4$ , orthorhombic,  $P2_12_12_1$ ;  $a = 9.892$  (1),  $b = 12.093$  (1),  $c = 14.545$  (1) Å;  $Z = 4$ ,  $D_x = 1.364$ ,  $D_m = 1.35$  g cm $^{-3}$ ;  $F(000) = 808$ ;  $U = 1739.9$  Å $^3$ ;  $\mu(\text{Cu } K\alpha) = 8.68$  cm $^{-1}$ ,  $\lambda = 1.5418$  Å. The atom fractional coordinates and individual isotropic temperature factors were refined by full-matrix least-squares methods to an  $R$  of 0.10 for 1328 structure magnitudes ( $F \geq 3\sigma_F$ ). The structure analysis has shown that the oxidation of anopteryl alcohol by potassium ferricyanide introduces an epoxide group across C(5) and C(6), and ring closure, through an ether link, between C(12) and C(20).

**Introduction.** On the basis of preliminary screening tests, the *Anopterus* alkaloids are potential anti-tumour agents. Anopterine itself (I) is the major alkaloid from the bark and leaves of the Queensland species *Anopterus macleayanus* F. Muell (family Escalloniaceae) and has also been isolated from the Tasmanian species *Anopterus glandulosus* Labill. Its structure, an *ent* kaurane derivative with a bond linking C(20) to C(14) (see I), was inferred from spectral data and an X-ray structural study of a crystalline azomethine iodide derived from *O,O,O,O*-tetraacetylanopteryl alcohol (Denne, Johns, Lamberton, Mathieson & Soares, 1972).



The title compound (III) was produced as part of a chemical study of the *Anopterus* alkaloids, by oxidation of anopteryl alcohol (II) with potassium ferricyanide in ethanol (Lamberton, 1975). The present crystal structure analysis was undertaken to elucidate the unexpected changes in the ring skeleton on oxidation, which were indicated by proton and  $^{13}\text{C}$  magnetic resonance studies, but not understood at the time.

The crystal used had dimensions  $0.25 \times 0.62 \times 0.25$  mm and was mounted about the  $b$  axis on a Picker diffractometer. A set of 1634 unique reflexions were measured to a  $\sin \theta/\lambda$  limit of  $0.58$  Å $^{-1}$  with Ni-filtered Cu  $K\alpha$  radiation in the  $\theta$ - $2\theta$  scanning mode: of these, 306 had intensities less than  $3\sigma_F$  and were coded as

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'unobserved'. The 335 reflexion was monitored for crystal deterioration every 50 reflexions (4.5 h) and its intensity decreased 4% over the collection period. The measured intensities were corrected for this deterioration before application of the Lp factors. Weights were taken as unity for the 'observed' reflexions and zero otherwise.

The solution and refinement of the structure were undertaken with the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Six reflexions, origin-enantiomorph definition and two others, were used to initiate the tangent refinement. The 169 reflexions with  $E \geq 1.50$  gave an  $R_{\text{Karié}}$  of 0.19 and  $\sum E_{\text{obs}}/\sum E_{\text{calc}}$  of 0.89. The  $E$  map calculated with this set revealed 21 atom sites. The remaining atoms were located with difference electron density syntheses. Refinement was continued with full-matrix least-squares methods. The variables were an overall scale, the individual isotropic temperature factors of the non-hydrogen atoms and their positional parameters.

The H atoms were located from difference electron density maps in conjunction with known molecular geometry. The two hydroxyl protons, on O(2) and O(11), were located from the final difference electron density map.

The last refinement cycle, which yielded a reliability index,  $R$ , of 0.10, was carried out without the two hydroxyl hydrogens and omitted reflexions with  $\sin \theta/\lambda \leq 0.12$  (20). The restricted data set was considered ad-

visible as the intense low-order reflexions consistently calculated high, which suggested that the crystal probably exhibited extinction. All the final parameter shifts were less than half their estimated standard deviations. A list of the atomic parameters with standard deviations is given in Table 1.\*

**Discussion.** The molecule comprises one three-membered ring, three five-membered rings and five six-membered rings fused into a rigid and approximately spherical shape. A stereoscopic projection is shown in Fig. 1, and the torsion angles involving ring atoms are listed in Table 2. The strained nature of the molecule is apparent, for example in the skew form of ring C(5)-C(6)-C(7)-C(8)-C(9)-C(10) and the extreme chair form of ring C(8)-C(9)-C(11)-C(12)-C(13)-C(14). The unexpected features revealed by this study are the epoxide formation across the C(5)-C(6) bond and the ring closure between C(20) and the O on C(12). However, the observed structure does provide a satisfactory interpretation of the NMR spectra.

The bond lengths and angles derived from the coordinates of Table 1 are listed in Tables 3 and 4. The

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31890 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Anopteryl alcohol oxidation product; atomic parameters with estimated standard deviations in parentheses*

Fig. 1 illustrates the atom-numbering sequence. The H atoms are labelled according to the number of the atoms to which each is attached: where necessary to differentiate an additional symbol (*A, B, C*) is appended.

	$x$ ( $\times 10^4$ )	$y$ ( $\times 10^4$ )	$z$ ( $\times 10^4$ )	$U$ ( $\text{\AA}^2$ ) ( $\times 10^3$ )		$x$ ( $\times 10^3$ )	$y$ ( $\times 10^3$ )	$z$ ( $\times 10^3$ )	$U$ ( $\text{\AA}^2$ ) ( $\times 10^2$ )
C(1)	1783 (10)	1018 (8)	2116 (7)	2.5 (2)	H(1) <i>A</i>	81	126	196	3.5
C(2)	2734 (12)	2019 (9)	2003 (8)	3.4 (3)	H(1) <i>B</i>	205	44	159	3.5
C(3)	2716 (12)	2752 (9)	2848 (8)	3.5 (3)	H(2)	242	248	142	3.5
C(4)	2705 (11)	2161 (8)	3802 (7)	2.2 (2)	H(3) <i>A</i>	354	327	281	3.5
C(5)	1600 (10)	1266 (8)	3784 (7)	2.2 (2)	H(3) <i>B</i>	185	326	279	3.5
C(6)	917 (11)	980 (8)	4655 (7)	2.5 (2)	H(6)	116	153	525	3.5
C(7)	528 (11)	-215 (9)	4810 (7)	2.8 (2)	H(7) <i>A</i>	79	-44	546	3.5
C(8)	1175 (10)	-987 (9)	4109 (7)	2.3 (2)	H(7) <i>B</i>	-53	-26	477	3.5
C(9)	846 (10)	-575 (8)	3102 (6)	2.2 (2)	H(9)	-16	-31	302	3.5
C(10)	1824 (10)	435 (8)	3043 (6)	1.9 (2)	H(11)	66	-221	260	3.5
C(11)	1258 (11)	-1537 (9)	2467 (7)	2.8 (3)	H(12)	299	-248	216	3.5
C(12)	2745 (11)	-1823 (9)	2611 (7)	2.9 (3)	H(13)	397	-244	371	3.5
C(13)	3000 (11)	-2133 (9)	3604 (7)	2.9 (3)	H(14)	316	-94	471	3.5
C(14)	2711 (10)	-984 (9)	4056 (7)	2.5 (2)	H(15) <i>A</i>	61	-231	503	3.5
C(15)	753 (12)	-2199 (9)	4337 (8)	3.3 (3)	H(15) <i>B</i>	-16	-241	402	3.5
C(16)	1871 (12)	-2895 (9)	3972 (8)	3.2 (3)	H(17) <i>A</i>	120	-416	409	3.5
C(17)	1932 (15)	-3999 (12)	3902 (10)	5.6 (4)	H(17) <i>B</i>	266	-406	365	3.5
C(18)	2499 (12)	3049 (9)	4547 (7)	3.3 (3)	H(18) <i>A</i>	249	268	518	3.5
C(19)	4001 (12)	1548 (10)	4036 (8)	3.4 (3)	H(18) <i>B</i>	160	347	446	3.5
C(20)	3160 (10)	-162 (8)	3286 (7)	2.2 (2)	H(18) <i>C</i>	327	362	454	3.5
C(21)	5560 (13)	37 (11)	3735 (9)	4.7 (3)	H(19) <i>A</i>	398	128	471	3.5
O(2)	4099 (8)	1673 (7)	1786 (5)	4.3 (2)	H(19) <i>B</i>	482	211	399	3.5
O(5)	198 (7)	1608 (6)	3916 (5)	2.7 (2)	H(21) <i>A</i>	578	-61	331	3.5
O(11)	970 (8)	-1254 (6)	1498 (5)	3.2 (2)	H(21) <i>B</i>	548	-23	440	3.5
O(20)	3550 (7)	-838 (6)	2506 (5)	2.7 (2)	H(21) <i>C</i>	639	58	371	3.5
N(1)	4300 (9)	599 (7)	3414 (6)	2.7 (2)	H(O2)	450	110	215	3.5
					H(O11)	13	-106	155	3.5

mean C-C, C-O and C-N bond lengths are 1.53, 1.46 and 1.48 Å respectively, with variations from the mean of approximately  $\pm 0.02$  Å. These values, and the short C-C bond of the epoxide group, are within the range expected for the particular bond type (Kennard, Watson, Allen, Isaacs, Motherwell, Pettersen & Town, 1972). Similarly the bond angles have acceptable values and their average standard deviation is  $1.3^\circ$ .

Table 2. Torsion angles for five- and six-membered rings ( $^\circ$ )

C(1)C(2)C(3)C(4)	41.2	C(4)C(5)C(20)C(20)	64.1
C(2)C(3)C(4)C(5)	-48.8	C(5)C(10)C(20)N(1)	-54.8
C(3)C(4)C(5)C(10)	58.9	C(10)C(20)N(1)C(19)	49.1
C(4)C(5)C(10)C(1)	-61.6	C(20)N(1)C(19)C(4)	-50.0
C(5)C(10)C(1)C(2)	53.5	N(1)C(19)C(4)C(5)	54.2
C(10)C(1)C(2)C(3)	-43.1	C(19)C(4)C(5)C(10)	-64.0
C(5)C(6)C(7)C(8)	12.0	C(9)C(11)C(12)C(13)	58.5
C(6)C(7)C(8)C(9)	-53.7	C(11)C(12)C(13)C(14)	-66.3
C(7)C(8)C(9)C(10)	74.9	C(12)C(13)C(14)C(8)	81.2
C(8)C(9)C(10)C(5)	-56.9	C(13)C(14)C(8)C(9)	-83.8
C(9)C(10)C(5)C(6)	21.6	C(14)C(8)C(9)C(11)	69.5
C(10)C(5)C(6)C(7)	4.2	C(8)C(9)C(11)C(12)	-57.4
C(10)C(9)C(11)C(12)	50.5	C(8)C(14)C(20)C(10)	9.8
C(9)C(11)C(12)O(20)	-53.4	C(14)C(20)C(10)C(9)	-39.4
C(11)C(12)O(20)C(20)	67.2	C(20)C(10)C(9)C(8)	54.9
C(12)O(20)C(20)C(10)	-81.5	C(10)C(9)C(8)C(14)	-48.0
O(20)C(20)C(10)C(9)	72.6	C(9)C(8)C(14)C(20)	23.5
C(20)C(10)C(9)C(11)	-56.4		
C(8)C(15)C(16)C(13)	4.6	C(13)C(14)C(20)O(20)	3.3
C(15)C(16)C(13)C(14)	18.0	C(14)C(20)O(20)C(12)	28.0
C(16)C(13)C(14)C(8)	-33.3	C(20)O(20)C(12)C(13)	-49.9
C(13)C(14)C(8)C(15)	36.8	O(20)C(12)C(13)C(14)	50.0
C(14)C(8)C(15)C(16)	-26.5	C(12)C(13)C(14)C(20)	-31.2

Table 3. Anopteryl alcohol oxidation product: bond lengths (Å)

C(1)-C(2)	1.542	C(9)-C(10)	1.561
-C(10)	1.522	-C(11)	1.539
C(2)-C(3)	1.516	C(10)-C(20)	1.547
-O(2)	1.447	C(11)-C(12)	1.525
C(3)-C(4)	1.560	-O(11)	1.478
C(4)-C(5)	1.539	C(12)-C(13)	1.513
-C(18)	1.540	-O(20)	1.441
-C(19)	1.519	C(13)-C(14)	1.564
C(5)-C(6)	1.476	-C(16)	1.544
-C(10)	1.490	C(14)-C(20)	1.563
C(5)-O(5)	1.459	C(15)-C(16)	1.488
C(6)-C(7)	1.512	C(16)-C(17)	1.340
C(7)-C(8)	1.524	C(19)-N(1)	1.492
C(8)-C(9)	1.581	C(20)-N(1)	1.467
-C(14)	1.521	C(21)-N(1)	1.495
-C(15)	1.560		

Table 4. Anopteryl alcohol oxidation product: bond angles ( $^\circ$ )

Central atom	Bonded atoms		Central atom	Bonded atoms	
C(1)	C(2), C(10)	116.2	C(10)	C(1), C(5)	109.0
C(2)	C(1), C(3)	111.4		-C(1), C(9)	113.2
	-C(1), O(2)	111.4		-C(1), C(20)	116.2
	-C(3), O(2)	110.9		-C(5), C(9)	113.3
C(3)	C(2), C(4)	117.0		-C(5), C(20)	106.1
C(4)	C(3), C(5)	108.2		-C(9), C(20)	98.7
	-C(3), C(18)	107.9	C(11)	C(9), C(12)	110.1
	-C(3), C(19)	114.6		-C(9), O(11)	110.2
	-C(5), C(18)	114.1		-C(12), O(11)	111.7
	-C(5), C(19)	105.1	C(12)	C(11), C(13)	110.4
	-C(18), C(19)	107.1		-C(11), O(20)	109.4

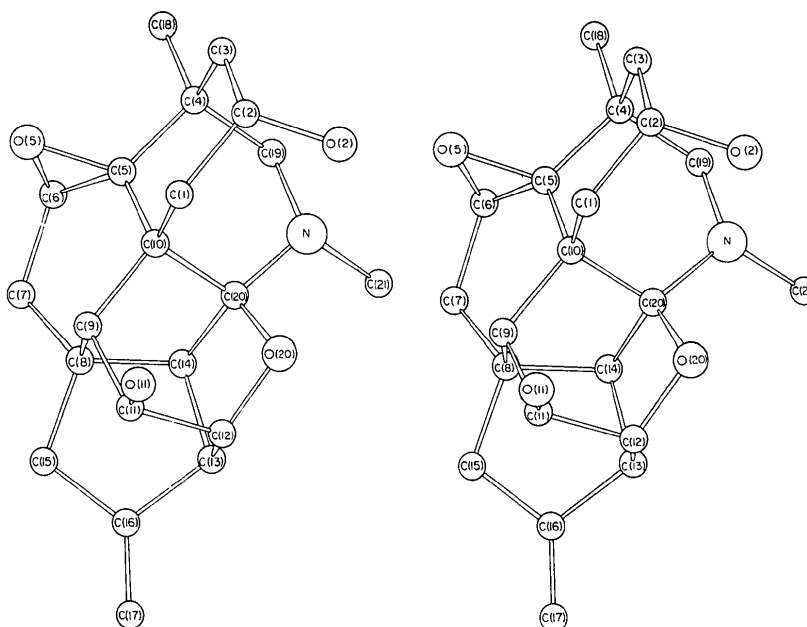


Fig. 1. Anopteryl alcohol oxidation product: stereoscopic projection (ORTEP, Johnson, 1965).

Table 4 (cont.)

C(5)-C(4), C(6)	118.4	-C(13), O(20)	102.3
-C(4), C(10)	112.3	C(13)-C(12), C(14)	98.7
-C(4), O(5)	118.3	-C(12), C(16)	111.0
-C(6), C(10)	122.1	-C(14), C(16)	104.6
-C(6), O(5)	61.3	C(14)-C(8), C(13)	101.6
-C(10), C(5)	115.3	-C(8), C(20)	108.8
C(6)-C(5), C(7)	117.9	-C(13), C(20)	102.2
-C(5), O(5)	58.8	C(15)-C(8), C(16)	104.8
-C(7), O(5)	118.1	C(16)-C(13), C(15)	108.9
C(7)-C(6), C(8)	112.3	-C(13), C(17)	122.4
C(8)-C(7), C(9)	109.9	-C(14), C(17)	128.6
-C(7), C(14)	116.8	C(19)-C(4), N(1)	114.0
-C(7), C(15)	108.7	C(20)-C(10), C(14)	102.6
-C(9), C(14)	99.1	-C(10), O(20)	108.2
-C(9), C(15)	116.0	-C(10), N(1)	113.1
-C(14), C(15)	106.3	-C(14), O(20)	106.1
C(9)-C(8), C(10)	99.7	-C(14), N(1)	121.8
-C(8), C(11)	105.2	-O(20), N(1)	104.4
-C(10), C(11)	113.3	O(5)-C(5), C(6)	59.9
		O(20)-C(12), C(20)	103.6
		N(1)-C(19), C(20)	114.1
		-C(19), C(21)	108.9
		-C(20), C(21)	113.3

Table 5. Intramolecular hydrogen-bond contacts  $\leq 3.30 \text{ \AA}$ 

	H...X	A-H...X
O(2)-H(O2)...N(1)	1.94 Å	136°
O(2)-H(O2)...O(20)	2.57	128
O(11)-H(O11)...O(5)	2.90	80

Molecular packing in the crystal appears to be governed by van der Waals interactions. The relevant contact distances and angles for the two H atoms capable of acting as hydrogen-bond donors are listed in Table 5. There is a weak intramolecular hydrogen bond between H(O2) and N(1). The H(O11) atom does not bond at all as the only contact within 3.3 Å which is suitable as an acceptor is poorly placed with respect to angle.

We thank Dr J. A. Lambertson, Division of Applied Organic Chemistry, CSIRO, for supplying the crystalline material and for helpful discussion.

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### 1-Phthalimido-1-deoxy-2,3:4,6-di-O-isopropylidene- $\alpha$ -L-sorbofuranose

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**Abstract.**  $C_{20}H_{23}NO_7$ , orthorhombic,  $P2_12_12_1$ ;  $a = 11.776$  (1),  $b = 18.162$  (2),  $c = 9.143$  (1) Å;  $Z = 4$ ,  $D_c = 1.32$ ,  $D_m = 1.33$  g cm $^{-3}$ . Full-matrix least-squares refinement led to an  $R$  of 0.051. The molecular conformation in the crystal is the same as the preferred conformation in solution. Potential-energy calculations show that attractive London dispersion forces favor this conformation.

**Introduction.** NMR studies (Glass & Williams, 1972) of the title compound (I) demonstrated the importance of the conformation illustrated in Fig. 1. Especially revealing was the intramolecular shielding of the hydrogens of the methyl group placed above the phthalimide

ring. It was suggested that the preference for this conformation may be due to a stabilizing interaction between the O atoms of the 1,3-dioxane ring and the carbonyl carbons of the phthalimide moiety. Analogous interactions are the subject of considerable interest. Furthermore, such interactions may be of biological significance, for example in the binding of barbiturates (Voet, 1972) and the teratogenic properties of thalidomide (Jönsson, 1972). Thus an X-ray crystallographic structural analysis was performed on (I) to determine the significance of the interaction.

Preliminary X-ray photographs showed orthorhombic symmetry and the following systematic absences were observed:  $h00$  when  $h = 2n + 1$ ,  $0k0$  when  $k = 2n + 1$ , and  $00l$  when  $l = 2n + 1$ . The space group is thus determined to be  $P2_12_12_1$ . Twelve reflections were centered on a Picker four-angle diffractometer and a least-

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