

Discussion. In the crystal structure, as shown in Fig. 1, a three-dimensional network is formed by hydrogen bonds whose lengths and angles are given in Table 3. The hydrogen bond between sugar moieties is $O(3') \cdots O(2')$, which joins the molecules related by a screw axis. This hydrogen-bond scheme is similar to that in adenosine (Lai & Marsh, 1972) and inosine (Munns & Tollin, 1970). The N(3) atom does not participate in hydrogen bonding. Supposing that $O(3') \cdots O(2')$ is replaced by $O(5') \cdots O(2')$, the resulting hydrogen-bond scheme would become identical with that in nebularine (Takeda, Ohashi & Sasada, 1974). Distances between non-bonded atoms are not significantly shorter than the van der Waals contacts.

Table 4. *Deviations of the atoms from the least-squares planes* (Å)

Coordinates X, Y, Z are in Å referred to a, b and c .			
Ribose plane I:	$-0.1988X - 0.2701Y - 0.9421Z + 1.6480 = 0$		
	II: $-0.1683X - 0.3077Y - 0.9365Z + 1.5901 = 0$		
Purine plane III:	$-0.3097X + 0.7148Y - 0.6271Z + 0.1184 = 0$		
	Plane I	Plane II	Plane III
C(1')	-0.014*	0.000*	N(1) -0.009*
O(1')	0.023*	0.000*	C(2) -0.020*
C(2')	-0.599	-0.518	N(3) 0.009*
C(3')	0.013*	0.103	C(4) 0.009*
C(4')	-0.022*	0.000*	C(5) -0.004*
C(5')	-1.211	-1.206	C(6) 0.027*
			N(7) -0.014*
			C(8) -0.005*
			N(9) 0.007*
			C(10) 0.101
			C(1') 0.142

* Atoms defining the least-squares plane. The dihedral angle between the plane I and III is 62.7° .

The bond lengths and angles are shown in Fig. 2. Owing to the lack of the possible double-bond character between C(6) and the substitutional atom, the

bond alternation $C(2)=N(3)-C(4)=C(5)$ is not seen, as in nebularine. The purine ring is planar within 0.025 Å, as shown in Table 4. Closer examination shows, however, that the purine base has a tendency to bend. The dihedral angle between the five- and six-membered rings is 1.0° . C(2), C(6) and C(10) atoms are significantly deviated from the plane owing to the interaction between molecules. In the sugar ring there is a significantly large difference (0.050 Å) between the $C(4')-O(1')$ and $C(1')-O(1')$ lengths owing to the anomeric effect. The ring C-C bond distances and the $C(4')-C(5')$ bond distance are not different from those in other nucleosides. $C(2')-O(2')$ is shorter than $C(3')-O(3')$ and $C(5')-O(5')$, as observed in other nucleosides. The sugar puckering is $C(2')$ -endo referring to the least-squares plane of C(1'), C(3'), C(4') and O(1'), or $C(2')$ -endo-C(3')-exo referring to the plane of C(1'), O(1') and C(4'). The glycosidic torsional angle χ_{CN} [$C(8)-N(9)-C(1')-O(1')$] (Sundaralingam, 1969) is $+46.2^\circ$ and the conformation is *anti*. The torsional angles φ_{CO} [$C(3')-C(4')-C(5')-O(5')$] and φ_{OO} [$O(1')-C(4')-C(5')-O(5')$] are 55.3° and -64.6° , respectively, so that conformation about $C(4')-C(5')$ is *gauche-gauche* (Shefter & Trueblood, 1965).

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Crotocol, a Sesquiterpenoid Alcohol

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Abstract. $C_{15}H_{20}O_4$, M.W. 264, orthorhombic, space group $P2_12_12_1$, $a=6.915$ (2), $b=22.174$ (8), $c=8.477$ (2) Å (from Weissenberg and precession photographs), $Z=4$, $D_c=1.349$, $D_x=1.36$ g cm $^{-3}$ (by flotation). Crotocol is a diepoxide alcohol isolated from an antibiotic crotocin [Gyimesi, J. *Acta Chim. Acad. Sci.*

Hung. (1965). **45**, 323-328]. Proximity of the epoxide rings confirmed by X-ray analysis seems to explain the behaviour of crotocol in various chemical reactions.

Introduction. Intensities were measured by photometer on integrated equi-inclination Weissenberg photo-

graphs taken with Ni-filtered Cu $K\alpha$ ($\lambda=1.5418 \text{ \AA}$) radiation and the multiple-film technique. Photographs were taken for the layers: $0kl \rightarrow 4kl$ and $h0l \rightarrow h5l$. After data reduction and interlayer scaling 711 independent reflexions were obtained, 195 of which were too weak for observation. The phase problem was solved by *MULTAN* (Main, Woolfson & Germain, 1970) with 176 E values greater than 1.20. The E map computed from the set of phases with the second greatest ABSFOM of 1.06 gave the positions of 17 out of 19 non-hydrogen atoms. A subsequent Fourier synthesis revealed the positions of the missing two non-hydrogen atoms. At this stage R was 31 %.

Block-diagonal least-squares adjustment of the

atomic parameters converged to $R=12.8\%$ for the observed and 18% for the total 711 reflexions. Owing to the limited accuracy of the experimental data* H atoms were ignored. All calculations were performed on a CDC-3300 computer with scattering factors taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are given in Table 1. Bond distances and angles are presented in Table 2.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30842 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates and anisotropic thermal parameters ($\times 10^4$)

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are in the form:

$$\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)].$$

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O(1)	5121 (16)	3956 (7)	3080 (13)	90 (20)	43 (5)	88 (14)	-23 (24)	-96 (39)	14 (18)
C(2)	3986 (23)	3660 (10)	4268 (18)	110 (30)	36 (6)	75 (19)	-53 (30)	35 (53)	33 (25)
C(3)	2465 (23)	4000 (11)	5004 (19)	77 (30)	43 (7)	94 (22)	-42 (33)	12 (47)	-19 (24)
C(4)	676 (23)	3977 (11)	3758 (23)	83 (32)	44 (8)	173 (32)	68 (32)	32 (62)	-45 (32)
C(5)	1317 (22)	3455 (10)	2583 (21)	92 (30)	29 (6)	106 (22)	-53 (33)	-24 (53)	-6 (24)
C(6)	2396 (26)	3804 (10)	1208 (21)	130 (35)	17 (5)	140 (27)	13 (33)	-25 (64)	-38 (25)
C(7)	3189 (30)	3338 (11)	37 (21)	174 (40)	34 (7)	90 (24)	28 (37)	-76 (64)	-16 (27)
C(8)	4781 (30)	3574 (10)	9011 (22)	148 (39)	28 (7)	106 (24)	36 (36)	52 (69)	12 (27)
C(9)	5603 (25)	4186 (10)	9255 (24)	92 (35)	27 (6)	13 (28)	24 (34)	-42 (75)	39 (29)
C(10)	5206 (29)	4480 (10)	610 (25)	110 (36)	28 (6)	137 (29)	28 (34)	44 (75)	46 (27)
C(11)	3865 (25)	4237 (10)	1829 (19)	155 (36)	20 (5)	61 (19)	-1 (32)	-59 (59)	-20 (22)
C(12)	2843 (25)	3159 (10)	3394 (20)	159 (39)	30 (6)	102 (23)	48 (31)	-34 (63)	37 (24)
C(13)	3595 (27)	2485 (11)	3010 (34)	168 (41)	34 (7)	371 (54)	92 (39)	95 (105)	114 (33)
C(14)	9592 (25)	3096 (10)	2085 (24)	104 (33)	28 (7)	181 (31)	-38 (30)	-158 (61)	28 (30)
C(15)	906 (26)	4192 (11)	258 (23)	123 (37)	36 (7)	163 (29)	30 (32)	-131 (67)	80 (28)
C(16)	6825 (32)	4449 (13)	7920 (22)	177 (45)	49 (9)	81 (26)	71 (39)	52 (70)	58 (28)
O(17)	2345 (19)	2650 (8)	4448 (16)	189 (29)	51 (5)	180 (23)	-56 (26)	-32 (56)	46 (23)
O(18)	8989 (15)	3813 (7)	4719 (14)	105 (22)	44 (5)	135 (18)	-48 (23)	58 (41)	36 (20)
O(19)	5096 (18)	3141 (7)	342 (15)	87 (23)	37 (4)	138 (19)	23 (23)	21 (50)	24 (20)

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$) with their *e.s.d.*'s

O(1)—C(2)	1.43 (2)	O(1)—C(2)—C(3)	118 (2)	C(8)—C(7)—O(19)	62 (1)
C(2)—C(3)	1.44 (3)	O(1)—C(2)—C(12)	106 (1)	C(7)—C(8)—C(9)	121 (1)
C(2)—C(12)	1.55 (3)	C(3)—C(2)—C(12)	102 (2)	C(7)—C(8)—O(19)	56 (1)
C(3)—C(4)	1.63 (3)	C(2)—C(3)—C(4)	105 (2)	C(9)—C(8)—O(19)	115 (1)
C(4)—O(18)	1.47 (2)	C(3)—C(4)—O(18)	105 (1)	C(8)—C(9)—C(16)	117 (2)
C(4)—C(5)	1.59 (3)	C(3)—C(4)—C(5)	103 (2)	C(8)—C(9)—C(10)	119 (1)
C(5)—C(12)	1.42 (3)	C(5)—C(4)—O(18)	113 (1)	C(10)—C(9)—C(16)	124 (1)
C(5)—C(14)	1.50 (3)	C(4)—C(5)—C(6)	104 (2)	C(9)—C(10)—C(11)	123 (2)
C(5)—C(6)	1.59 (3)	C(4)—C(5)—C(12)	104 (2)	C(10)—C(11)—O(1)	106 (1)
C(6)—C(15)	1.56 (3)	C(4)—C(5)—C(14)	110 (1)	C(6)—C(11)—C(10)	114 (2)
C(6)—C(11)	1.49 (3)	C(6)—C(5)—C(12)	103 (2)	C(6)—C(11)—O(1)	112 (1)
C(6)—C(7)	1.53 (3)	C(6)—C(5)—C(14)	115 (1)	C(2)—O(1)—C(11)	112 (1)
C(7)—O(19)	1.41 (3)	C(12)—C(5)—C(14)	119 (1)	C(2)—C(12)—O(17)	112 (1)
C(7)—C(8)	1.50 (3)	C(5)—C(6)—C(7)	108 (2)	C(2)—C(12)—C(13)	127 (2)
C(8)—O(19)	1.50 (2)	C(5)—C(6)—C(11)	112 (1)	C(2)—C(12)—C(5)	106 (2)
C(8)—C(9)	1.49 (3)	C(5)—C(6)—C(15)	110 (2)	C(5)—C(12)—C(13)	125 (2)
C(9)—C(16)	1.53 (3)	C(7)—C(6)—C(11)	115 (2)	C(5)—C(12)—O(17)	118 (2)
C(9)—C(10)	1.35 (3)	C(7)—C(6)—C(15)	106 (2)	C(13)—C(12)—O(17)	59 (1)
C(10)—C(11)	1.49 (3)	C(11)—C(6)—C(15)	106 (2)	C(12)—C(13)—O(17)	56 (1)
C(11)—O(1)	1.51 (2)	C(6)—C(7)—C(8)	114 (1)	C(12)—O(17)—C(13)	65 (1)
C(12)—C(13)	1.62 (3)	C(6)—C(7)—O(19)	115 (2)	C(7)—O(19)—C(8)	62 (1)
C(12)—O(17)	1.48 (2)				
C(13)—O(17)	1.54 (3)				

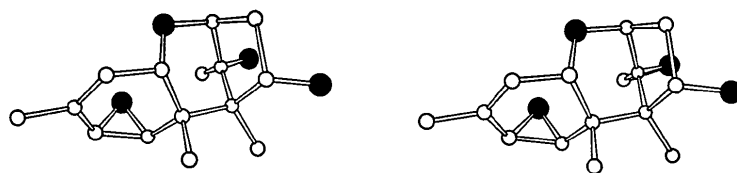
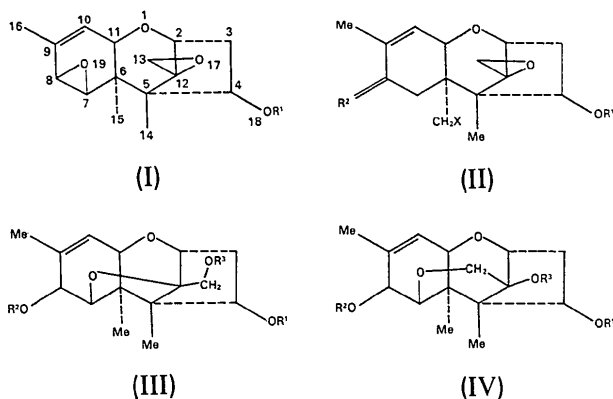


Fig. 1. An ORTEP stereo diagram of the title compound. Oxygen atoms are labelled with full circles.



- (I) $R^1=H$: crotocon, $R^1=CO-CH=CH-CH_3$: crotocon (atomic labelling is consistent with that used in Tables 1 and 2).
 (IIa) $R^2=O$, $X=H$; $R^1=H$: trichotecholone, $R^1=CO-CH=CH-CH_3$: trichotecin (Godtfredsen & Vangedal, 1964).
 (IIb) $R^2=2H$, $X=H$; $R^1=H$: trichodermol, $R^1=CO-CH_3$: trichodermin (Abrahamsson & Nilsson, 1966).
 (IIc) $R^2=2H$; $R^1=H$, $X=OH$: verrucarol, $R^1=X-OCO-C_{10}H_{14}O_3-CO$: verrucarin A (McPhail & Sim, 1966).
 (III) $R^1=R^2=R^3=H$: isocrotocon A (Gyimesi & Melera, 1967).
 (IV) $R^1=R^2=R^3=H$: isocrotocon B (Gyimesi & Melera, 1967).

Discussion. The title compound is the alcohol of an antifungal antibiotic, crotocon (I), isolated from a *Cephalosporium* strain (Gláz, Scheiber, Gyimesi, Horváth, Steczek, Szentirmai & Bohus, 1959). Molecular weights of both crotocon and crotocon were corroborated by crystal data (Kálmán, 1963) and they were shown later (Gyimesi, 1965) to have been isomers of the antibiotic trichotecin and its alcohol trichotecholone (IIa) (Freeman & Gill, 1950; Godtfredsen & Vangedal, 1964). Chemical and n.m.r. studies (Gyimesi & Melera, 1967) showed crotocon to be a diepoxide alcohol. Both epoxide groups can be destroyed easily and simultaneously by various chemicals, e.g. dilute acids at room temperature, to form new dilactones, (III) and (IV). These reactions pointed to a favourable proximity of the epoxide rings in (I). This, together with the structural model set up by Gyimesi & Melera

(1967), was confirmed by the X-ray analysis as shown in Fig. 1. The non-bonded distances C(12)–O(19) and C(13)–O(19) are 3.02 and 2.88 Å, respectively. Geometry of the trichotecane skeleton observed in crotocon is similar to those found by X-ray diffraction in other sesquiterpene antibiotics, e.g. trichodermin (IIb) (Abrahamsson & Nilsson, 1966) and verrucarin A (IIc) (McPhail & Sim, 1966).

Recently Adams & Hanson (1970) suggested that crotocon might be a precursor of trichotecin. If the above facts are taken into account, the isomerization of crotocon to trichotecin should only be an enzymatic process which protects the spiro ring of the trichotecane skeleton while the fused ring is transformed into a ketone group.

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