The hydroxyl group is *exo* to the nine-membered ring, confirming the results of a recent NMR study in solution (Anastassiou, 1983). The phenyl rings are planar (r.m.s. deviation from planarity 0·011 Å for molecule *A* and 0·006 Å for molecule *B*), with normal bond lengths and angles.

Analysis of the thermal-motion tensors in terms of the rigid-body model (Schomaker & Trueblood, 1968) results in reasonable agreement between the observed and calculated tensor components [$\langle(\Delta U_{ij}^2)\rangle^{1/2} =$ 0·0034 Å^2, $\langle\sigma(U_{ij})\rangle = 0{\cdot}0014$ Å^2; both molecules]. Bond lengths corrected for libration are listed in Table 2. Librational corrections to the bond angles are negligible.

An examination of intermolecular contact distances indicates that the crystal structure is built up of $C_{13}H_{12}O$ units linked into tetramers by O···O′ hydrogen bonds [O···O′ distances 2·714 (5) and 2·740 (5) Å; O—H···O′ angle 163 (2) and O···H′—O′ angle 158 (2)°]. The hydrogen-bonding scheme is incorporated in Fig. 2. With the exception of these O···O distances, all intermolecular contacts are of the normal van der Waals type.

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The Structure of Monacolin K,* $C_{24}H_{36}O_5$

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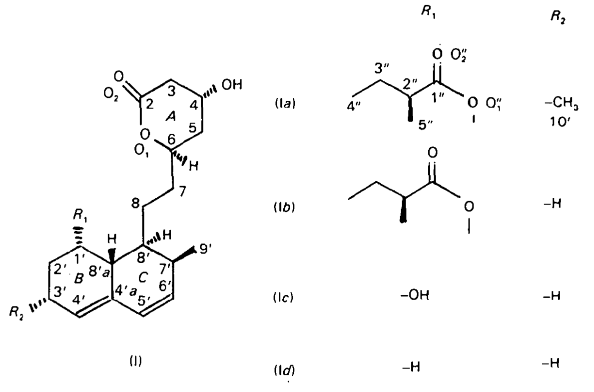
Abstract. $M_r = 404{\cdot}5$, orthorhombic, space group $P2_12_12_1$, $a = 22{\cdot}154$ (4), $b = 17{\cdot}321$ (3), $c = 5{\cdot}968$ (1) Å, $V = 2290{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}17$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 6{\cdot}1$ cm^{-1}, $F(000) = 880$, $T = 297$ K; $R = 0{\cdot}088$, $wR = 0{\cdot}082$ for 1515 observed reflections. The six-membered rings of the hexahydronaphthalene system containing a *transoid* conjugated diene are in a distorted half-chair form with an envelope conformation.

Introduction. In our continuing studies to detect specific inhibitors of cholesterol synthesis produced by microorganisms, the metabolite monacolin K (I*a*) was isolated from the culture of *Monascus ruber*. Some compounds (I*b,c,d*) isolated previously from the strains of *Penicillium citrium* had been recognized to have a similar biological activity to that of monacolin K (Endo, Kuroda, Tsujita, Terahara & Tamura, 1974, 1976).



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* (1*S*, 3*R*, 7*S*, 8*S*, 8a*R*)-1,2,3,7,8,8a-Hexahydro-3,7-dimethyl-8-{2-[(4*R*, 6*R*)-3,4,5,6-tetrahydro-4-hydroxy-2-oxo-2*H*-pyran-6-yl]-ethyl}-1-naphthyl (2*S*)-2-methylbutanoate.

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The structure of (*Ib*) (ML236B), one of these compounds, has already been studied by X-ray analysis (Tamura, 1974). The same compound, designated as compactin and isolated from a culture of *Penicillium brevicompactum* having antifungal activity, was reported by Brown, Smale, King, Hasenkamp & Thomson (1976). The structure of monacolin K was assumed to be very similar to that of ML236B on the basis of spectrometric measurements, with the former having one additional methyl group attached to a certain position of the latter; its position and stereochemistry, however, were not clear at this stage. The X-ray structure of monacolin K was thus investigated to establish the stereochemistry as part of the research programme on the structure–activity relationships of the inhibition of cholesterol synthesis.

Experimental. Colourless needle crystals obtained by slow evaporation of an ethanol solution, 0·5 × 0·3 × 0·1 mm, cell parameters by least squares from setting angles of 20 reflections, $30 \leq 2\theta \leq 50°$, Rigaku diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, intensities collected by 2θ–ω scan, decay of the crystal monitored every 51 reflections: no radiation damage; 2186 reflections measured, $2\theta \leq 128°$, $0 \leq h \leq 25$, $0 \leq k \leq 20$, $0 \leq l \leq 6$; Lorentz–polarization correction, no absorption correction; structure determined using *MULTAN* (Germain, Main & Woolfson, 1971); *E* map revealed 24 atoms at chemically reasonable positions among the 29 non-hydrogen atoms; refinement on *F* by successive Fourier syntheses and block-diagonal least-squares methods; difference Fourier map revealed positions for all H atoms; final cycles of least squares (non-hydrogen atoms anisotropic, H atoms isotropic) gave $R = 0·088$ and $wR = 0·082$ with $w = 1·0$, 1515 observations with $F_o \geq 2\sigma F_o$; final $\Delta\rho$ excursions $\geq 0·2$ e Å^{-3}, $(\Delta/\sigma)_{\max} = 0·56$; calculations carried out with the *UNICS* System on a CYBER70 computer at CRC Co., Ltd; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic positional parameters and B_{eq} values for non-hydrogen atoms are listed in Table 1.*

The additional methyl group is attached to the C(3′) position of ML236B. The chiral centre at this position is *R* while the C(2′) atom of the methylbutanoate side chain has been established as *S* by chemical degradation (Ogiso & Terahara, 1977). The absolute configuration determined for the present compound is shown in Fig. 1 [*ORTEP* (Johnson, 1965)].

Table 1. *Fractional atomic coordinates* (×10^4) *and thermal parameters with estimated standard deviations in parentheses*

B_{eq} according to Hamilton (1959).

	x	y	z	B_{eq}(Å^2)
O(1)	1917 (3)	1280 (4)	−2684 (12)	4·6
O(2)	2571 (3)	845 (5)	−5085 (17)	7·4
O(3)	718 (4)	253 (5)	−4355 (19)	9·0
O(1″)	665 (3)	3816 (3)	2742 (11)	3·6
O(2″)	−55 (3)	3861 (5)	160 (15)	6·4
C(2)	2113 (4)	733 (5)	−4109 (17)	4·3
C(3)	1781 (5)	−30 (6)	−4216 (19)	5·6
C(4)	1186 (5)	−75 (6)	−2964 (21)	5·3
C(5)	1232 (4)	362 (5)	−803 (17)	3·9
C(6)	1380 (4)	1202 (6)	−1282 (18)	4·2
C(7)	1521 (4)	1667 (5)	802 (18)	3·8
C(8)	1546 (4)	2540 (5)	371 (19)	4·3
C(1′)	1108 (4)	4149 (5)	1168 (16)	3·6
C(2′)	1055 (4)	5036 (5)	1173 (19)	4·4
C(3′)	1176 (4)	5399 (5)	3488 (17)	4·0
C(4′)	1666 (4)	4982 (5)	4722 (16)	3·7
C(4a′)	1913 (4)	4315 (5)	4135 (15)	3·2
C(5′)	2393 (4)	3966 (6)	5463 (17)	4·2
C(6′)	2631 (4)	3281 (6)	5041 (18)	4·3
C(7′)	2413 (4)	2773 (6)	3081 (18)	4·0
C(8′)	1768 (4)	3000 (5)	2351 (16)	3·3
C(8a′)	1727 (4)	3887 (5)	2023 (16)	3·4
C(9′)	2873 (4)	2750 (6)	1205 (20)	4·9
C(10′)	607 (5)	5459 (7)	4946 (24)	6·8
C(1″)	111 (4)	3690 (5)	2003 (21)	4·5
C(2″)	−274 (4)	3313 (6)	3748 (27)	6·7
C(3″)	−1 (6)	2502 (9)	4185 (30)	9·8
C(4″)	−282 (7)	2073 (11)	5879 (35)	12·0
C(5″)	−929 (5)	3283 (7)	3101 (31)	8·5

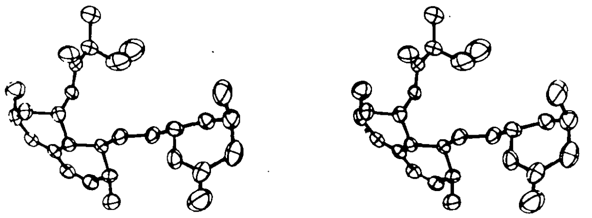
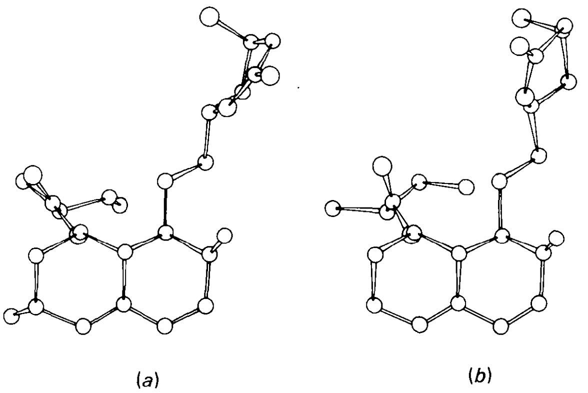


Fig. 1. A stereoscopic view showing thermal ellipsoids at the 50% probability level.



(*a*) (*b*)

Fig. 2. Projection of (*a*) the present compound and (*b*) ML236B (compactin) on their diene-system mean planes.

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* Lists of structure factors, anisotropic thermal parameters, Table 3 (deviations from least-squares planes) and Table 4 (selected torsion angles) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38905 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The C—C bond lengths of the *transoid* diene system in the hexahydronaphthalene ring are 1·325, 1·457 and 1·322 Å for C(4′)—C(4a′), C(4a′)—C(5′) and C(5′)—C(6′), respectively. These values are close to C—C single-bond (1·465 Å) and double-bond (1·336 Å) lengths (Sutton, 1965) involving sp^2-hybridized carbon in conjugated dienes: consequently there is less delocalization of electrons at the diene moiety in the present compound. The short C(3″)—C(4″) bond length (1·400 Å) in the side chain may be due to the effects of large thermal motion. The other bond lengths and angles between non-hydrogen atoms (Table 2) are in good agreement with expected values.

In a conjugated *transoid* diene system, atoms C(3′), C(4′), C(4a′), C(5′), C(6′), C(7′) and C(8a′) are approximately coplanar; however, a small deviation can be observed at C(7′) (0·10 Å) and C(8a′) (0·08 Å) due to a certain strain arising from the fused-ring system. C(1′) and C(8′) deviate below the mean plane of those seven atoms by 0·40 and 0·67 Å, and the C(2′) atom deviates above it by 0·24 Å. In the substituent groups attached to the hexahydronaphthalene ring, the atoms O(1″), C(9′) and C(10′) are in axial and C(8) in equatorial conformations.

Table 2. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

O(1)—C(2)	1·345 (12)	C(2′)—C(3′)	1·542 (15)
O(1)—C(6)	1·461 (12)	C(3′)—C(4′)	1·498 (13)
O(2)—C(2)	1·187 (13)	C(3′)—C(10′)	1·535 (16)
O(3)—C(4)	1·445 (15)	C(4′)—C(4a′)	1·325 (12)
O(1″)—C(1′)	1·477 (11)	C(4a′)—C(5′)	1·457 (13)
O(1″)—C(1″)	1·321 (11)	C(4a′)—C(8a′)	1·520 (13)
O(2″)—C(1″)	1·197 (15)	C(5′)—C(6′)	1·322 (14)
C(2)—C(3)	1·515 (14)	C(6′)—C(7′)	1·542 (14)
C(3)—C(4)	1·517 (16)	C(7′)—C(8′)	1·545 (12)
C(4)—C(5)	1·500 (16)	C(7′)—C(9′)	1·515 (15)
C(5)—C(6)	1·519 (14)	C(8′)—C(8a′)	1·551 (12)
C(6)—C(7)	1·515 (15)	C(1″)—C(2″)	1·498 (17)
C(7)—C(8)	1·534 (13)	C(2″)—C(3″)	1·551 (19)
C(8)—C(8′)	1·507 (14)	C(2″)—C(5″)	1·503 (16)
C(1′)—C(2′)	1·542 (13)	C(3″)—C(4″)	1·400 (25)
C(1′)—C(8a′)	1·531 (12)		
C(2)—O(1)—C(6)	124·0 (4)	C(3′)—C(4′)—C(4a′)	126·2 (16)
C(1′)—O(1″)—C(1″)	118·0 (11)	C(4′)—C(4a′)—C(5′)	121·3 (14)
O(2)—C(2)—C(3)	122·5 (11)	C(4′)—C(4a′)—C(8a′)	122·2 (11)
O(1)—C(2)—O(2)	118·1 (7)	C(5′)—C(4a′)—C(8a′)	116·5 (5)
O(1)—C(2)—C(3)	119·1 (9)	C(4a′)—C(5′)—C(6′)	124·1 (16)
C(2)—C(3)—C(4)	116·5 (9)	C(5′)—C(6′)—C(7′)	122·1 (12)
O(3)—C(4)—C(5)	110·1 (6)	C(6′)—C(7′)—C(8′)	111·1 (6)
C(3)—C(4)—C(5)	109·8 (6)	C(6′)—C(7′)—C(9′)	111·3 (3)
O(3)—C(4)—C(3)	108·7 (14)	C(8′)—C(7′)—C(9′)	114·9 (13)
C(4)—C(5)—C(6)	109·7 (11)	C(8)—C(8′)—C(8a′)	113·9 (10)
O(1)—C(6)—C(5)	111·9 (6)	C(7′)—C(8′)—C(8a′)	110·0 (3)
O(1)—C(6)—C(7)	104·7 (4)	C(8)—C(8′)—C(7′)	112·8 (6)
C(5)—C(6)—C(7)	113·6 (13)	C(4a′)—C(8a′)—C(8′)	111·3 (10)
C(6)—C(7)—C(8)	113·2 (12)	C(1′)—C(8a′)—C(4a′)	112·0 (6)
C(7)—C(8)—C(8′)	113·6 (13)	C(1′)—C(8a′)—C(8′)	112·8 (4)
O(1″)—C(1′)—C(2′)	109·7 (7)	O(1″)—C(1″)—O(2″)	123·6 (16)
O(1″)—C(1′)—C(8a′)	105·5 (9)	O(1″)—C(1″)—C(2″)	111·7 (17)
C(2′)—C(1′)—C(8a′)	111·3 (5)	O(2″)—C(1″)—C(2″)	124·7 (5)
C(1′)—C(2′)—C(3′)	113·3 (11)	C(1″)—C(2″)—C(3″)	106·8 (8)
C(2′)—C(3′)—C(10′)	113·1 (5)	C(1″)—C(2″)—C(5″)	112·8 (18)
C(2′)—C(3′)—C(4′)	111·7 (6)	C(3″)—C(2″)—C(5″)	112·9 (5)
C(4′)—C(3′)—C(10′)	110·4 (11)	C(2″)—C(3″)—C(4″)	115·3 (13)

Least-squares planes (with deviations of atoms) through the *A*, *B* and *C* rings are given in Table 3.* The six-membered ring *A* of the lactone group takes approximately an envelope form, with C(5) as the flap, but distorted slightly into a half-chair conformation. C(4) deviates −0·17 Å and C(5) 0·55 Å from the plane through the remaining four atoms. The hydroxyl group attached to C(4) in the axial position is on the same side as the H atom attached to C(6), with O(3)···H(6) = 2·53 (9) Å. The *B* and *C* rings are expected to take a cyclohexene-like, half-chair conformation (Eliel, Allinger, Angyal & Morrison, 1965). However, probably due to a certain strain at the ring junction, a half-chair with an envelope form is observed.

The projections of the mean-plane diene system of ML236B (compactin) and (I*a*) are shown in Fig. 2, and some selected torsion angles are listed in Table 4.* The torsion angles O(1″)—C(1″)—C(2″)—C(3″), O(2″)—C(1″)—C(2″)—C(5″), C(1″)—C(2″)—C(3″)—C(4″) and C(5″)—C(2″)—C(3″)—C(4″) of the methylbutanoate group in (I*a*) are −64·9, −9·6, 176·4 and −59·0°, and in compactin, −112·9, −53·1, 57·4 and 177·9°, respectively. A comparison of the torsion angles in the lactone and ideal six-membered rings shows that the lactone ring of (I*a*) takes an envelope form, and that of compactin, a half-chair form. The difference in intramolecular interaction between the methylbutanoate group and C(3′) α-substituent (H or CH$_3$) is probably responsible for the difference in the torsion angles about C(1″)—C(2″) and C(2″)—C(3″). However, it is difficult to explain the conformational difference in the lactone rings when that effect may be due to intermolecular packing forces or intramolecular atomic repulsion of the methylbutanoate.

It seems that the conformation of the hexahydronaphthalene is not affected by the methyl group attached to the C(3′) atom. The hexahydronaphthalene moiety in both compounds has a more or less rigid form, but the lactone ring and methylbutanoate side chain may have significant conformational flexibility causing some secondary pharmacological effect on the cholesterol synthesis inhibition.

Symmetry-related molecules are linked to form continuous chains by intermolecular OH···O ($-x$, $-\frac{1}{2}+y$, $-\frac{1}{2}-z$) hydrogen bonds [2·863 (15) Å] between the hydroxyl group attached to the lactone ring and the keto oxygen atom in the side chain. Other short intermolecular distances are observed for O(2)···O(3) ($\frac{1}{2}-x$, $-y$, $-\frac{1}{2}+z$), 3·183 (15) Å, and O(2″)···C(4) ($-x$, $\frac{1}{2}+y$, $-\frac{1}{2}-z$), 3·373 (16) Å.

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Acta Cryst. (1984). C**40**, 198–200

Structure and Absolute Configuration of (8*R*)-8-Benzyloxy-6-(1,3-dioxan-2-yl)-1,4-dithiaspiro[4.4]non-6-ene, $C_{18}H_{22}O_3S_2$

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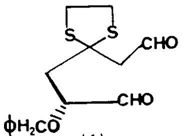
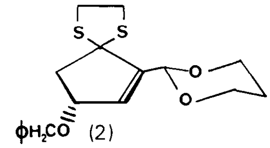
Abstract. $M_r = 350{\cdot}50$, monoclinic, $P2_1$, $a = 15{\cdot}399$ (4), $b = 7{\cdot}785$ (5), $c = 16{\cdot}128$ (4) Å, $\beta = 113{\cdot}01$ (2)°, $Z = 4$ (two independent molecules), $D_x = 1{\cdot}309$ Mg m^{-3}, $V = 1780$ (2) Å^3, μ(Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å) $= 1{\cdot}7$ mm^{-1}, $F(000) = 744$, $R = 0{\cdot}067$ for 1951 observed reflections. The two molecules of the unit cell are compared. Only van der Waals contacts are involved in the crystal packing.

Introduction. Synthetic approaches to enantiomerically pure substituted cyclopentanes are of great interest because they are decisive intermediates in the total synthesis of natural cyclopentane derivatives such as prostaglandins (Bindra & Bindra, 1977). Since our manifold interest in these compounds lies especially in their pharmacological activity, we needed cyclopentanes which are substituted in one proper natural configuration. Recently we have reported (Barrière, Chiaroni, Cléophax, Géro, Riche & Vuilhorgne, 1981) a short, flexible and stereocontrolled synthesis of cyclopentenes leading to 11α-hydroxy-13-oxaprostanoic acid (3), from (−)-quinic acid. The sequence implies generation of intermediates such as (2) (the title compound), obtained from an acyclic precursor (1) by an intramolecular aldolization dehydration reaction. The stereochemistry of the crystalline compound (2) was secured by the present X-ray analysis.



(1)



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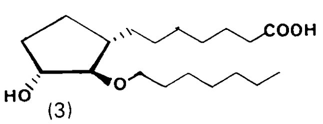

(3)

Experimental. Crystal 0·3 × 0·4 × 0·4 mm. Graphite-monochromated Cu $K\bar{\alpha}$ radiation, four-circle Philips PW 1100 diffractometer, θ–2θ scan-technique. Unit-cell dimensions refined from setting angles of 23 reflections. Three standard reflections measured every 2 h: no fluctuation in intensity. Two sets of equivalent reflections collected up to $2\theta = 135°$ ($-17 \le h \le 16$, $0 \le k \le 9$, $0 \le l \le 19$). 3670 *hkl* reflections, 3505 unique, 1951 considered as observed with $I > 2{\cdot}50\sigma(I)$; $\sigma(I)$ derived from counting statistics; $R_{\rm int} = 0{\cdot}076$ (from 103 multiple reflections). 3510 $\overline{hkl}$ unique reflections also recorded (of which 1948 'observed') for the absolute-configuration determination. Lp corrections, absorption ignored. Direct methods (*MULTAN*77; Main, Lessinger, Woolfson, Germain & Declercq, 1977). S atoms revealed on the best E map, other atoms from successive Fourier syntheses. Refinement by full-matrix least squares with anisotropic temperature factors (*ORION*; André, Fourme & Renaud, 1971); $\sum w|F_o - |F_c||^2$ minimized, $w = 1/\sigma^2(F_o)$. Not all H atoms on difference maps; therefore they were placed at idealized positions (C—H = 1·0 Å) and assigned the equivalent isotropic thermal factor of the bonded C atom. Absolute configuration determined by examination of several Bijvoet pairs. Final $R = 0{\cdot}067$, $R_w = 0{\cdot}076$ (for the 1951 *hkl* reflections), $S = 0{\cdot}72$. $(\Delta/\sigma)_{\max} = 0{\cdot}8$. Final difference-map excursions $\le 0{\cdot}33$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion terms for S from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction.

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