scatter from the mean plane of the non-hydrogen atoms is ±0·010 (2) Å in the quinoline ring system, and ±0·006 (2) Å for the phenyl ring. The deviations of the H atoms from the planes are not significant. The phenyl ring axis has a slight bend out of the plane of the quinoline ring, C(12) lying 0·06 and C(15) lying 0·16 Å below the plane of the quinoline ring. The angle between plane normals is 71·9 (1)°. The tilt of the phenyl group is such that C(13) [2·66 (2) Å] and H(13) [2·71 (3) Å] are near H(8). The C(12)–H(8) distance is 2·50 (2) Å, and if the dihedral angle had been 90°, the p_z orbital of C(12) would be directed nearly straight at H(8). As it is, the π-electron cloud of the phenyl group is oriented to interact strongly with H(8). This shielding of H(8) results in a shift in its proton NMR spectrum from the δ 7·47–7·57 region observed for the unsubstituted quinoline to δ 6·64 for the 1-phenyl derivative. This behavior substantiates the explanation made earlier (Wawzonek, 1982) for the unusual NMR spectra for 6-phenyl and 6-(3-pyridyl)-4,5,10,11-tetrahydro-6*H*-indeno[1,2-*c*]isoquinoline-5,11-dione. H(7) in both of these compounds is shielded by the aryl groups and appeared as a doublet at δ 5·46 and 5·52, respectively.

The thermal motion parameters of the non-hydrogen atoms were fit by a model which assumed the whole molecule behaved as a rigid body, and the components of the tensors **T, L** and **S** (Schomaker & Trueblood, 1968) were found which best reproduced the individual atomic vibrational ellipsoids. The inclusion of **S** gave a significantly better fit. The values of the tensor components are $T(11,22,33,12,13,23) = 0·0349$ (14), 0·0415 (12), 0·0392 (13), −0·0038 (11), 0·0038 (12), 0·0039 (11) Å^2; L: 4·7 (7), 5·8 (1·3), 6·0 (9), −1·6 (6), 1·0 (6), 1·0 (8)°^{2}; S(12,13,21,23,31,32, 11–22, 11–33): 0·02 (2) −0·00 (2) −0·00 (2), −0·00 (2), 0·08 (2), 0·12 (2), 0·09 (3), 0·04 (3) Å°. The only significant **S** components are $S31$, $S32$ and ($S11$–$S22$).

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Absolute Configuration of the Brominated Product of Safracin A,* $C_{28}H_{35}BrN_4O_6$

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Abstract. $M_r = 603·53$, orthorhombic, $P2_12_12_1$, $a = 12·25$ (1), $b = 17·773$ (8), $c = 12·681$ (8) Å, $V = 2760$ (3) Å^3, $Z = 4$, $D_m = 1·43$, $D_x = 1·45$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 1·61$ mm^{-1}, $T = 298$ K, $F(000) = 1256$, $R = 0·050$ for 2299 observed reflexions. The compound is an antibiotic product which has antitumor activity. The structure is similar to that of saframycin C. However, the pyruvamide side chain and one of the *p*-quinone parts of the saframycins are substituted, respectively, by an alaninamide chain and a monophenol ring in the title compound. There is an unusually long C–C distance of 1·570 (9) Å.

Introduction. New antibiotic products which have antitumor activities were isolated from *Pseudomonas fluorescens* A_2-2 culture broth. The chemical structures of the main products were proposed to be (I) and (II) (see Fig. 1) from chemical and spectroscopic studies (Ikeda, Idemoto, Hirayama, Yamamoto, Iwao, Asao & Munakata, 1983; Ikeda, Matsuki, Ogawa & Munakata,

*IUPAC name: N^1-{(4-bromo-5,6,9,10,13,14,14a,15-octahydro-1-hydroxy-2,11-dimethoxy-3,12,16-trimethyl-10,13-dioxo-6,15-imino-7*H*-isoquino[3,2-*b*][3]benzazocin-9-yl)methyl}alaninamide.

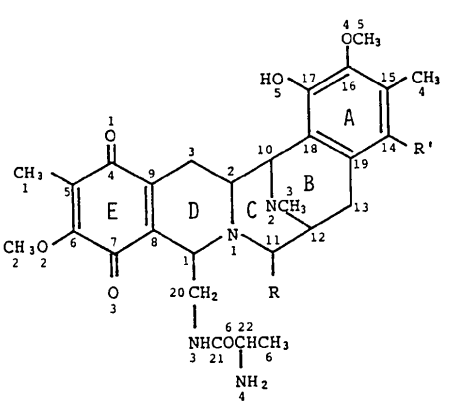
0108-2701/84/091578-03$01.50

1983; Ikeda, Shimada, Honjo, Okumoto & Munakata, 1983). Their chemical properties and biological activities were similar to those of the saframycins. In the case of the saframycins, the structure of saframycin C has been reported, but the absolute configuration was not determined (Arai, Takahashi, Kubo, Nakahara, Sato, Aiba & Tamura, 1979). Crystallization of the present products did not yield crystals suitable for X-ray diffraction study. Good crystals were only obtained by bromination of position 4 of compound (I). The X-ray diffraction study of the title compound was carried out to elucidate the precise and absolute molecular conformation.

Experimental. Brown plate crystals grown from acetone solution. Density measured by flotation in KI solution. A crystal ground manually to a sphere of diameter 0·52 mm; $\mu r = 0{\cdot}418$ for Mo $K\alpha$. Rigaku AFC-5 four-circle automated diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Cell parameters derived from least-squares treatment of the setting angles for 20 reflexions. 3069 reflexions measured, ω–2θ scan technique (12° min^{-1} for ω) up to $2\theta = 50°$, $0 \le h \le 14$, $0 \le k \le 21$, $0 \le l \le 15$. Three standard reflexions (200, 021, 004) measured every 100 reflexions, no significant variations. Data corrected for geometrical factors but not for absorption. 2299 independent reflexions [$F \ge \sigma(F)$] used for structure refinement. Br positions determined from Patterson map, 38 non-H atoms from successive block-diagonal least-squares procedures and Fourier syntheses, 35 H atoms from difference Fourier synthesis. All coordinates, anisotropic thermal parameters for non-H atoms and isotropic ones for H atoms refined by block-diagonal least squares; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1{\cdot}0$. Final $R = 0{\cdot}050$, $wR = 0{\cdot}051$, $S = 1{\cdot}69$, $(\Delta/\sigma)_{max} = 0{\cdot}35$ for non-H atoms, residual electron density of final difference Fourier synthesis $\le 0{\cdot}34$ e Å^{-3}. Absolute configuration determined by refinement of the enantiomeric structure ($R = 0{\cdot}076$) and by comparison of 11 Bijvoet pairs (Table 1). Atomic scattering factors involving the anomalous-dispersion factors f', f'' from *International Tables for X-ray Crystallography* (1974). Calculations performed on a FACOM M-200 computer at the Computer Center of Kyushu University using the *UNICS* III program system (Sakurai & Kobayashi, 1979).

Table 1. *Comparison of the ratios of structure factors for Bijvoet pairs*

	$\|F(hkl)\|/\|F(hk\bar{l})\|$			$\|F(hkl)\|/\|F(hk\bar{l})\|$	
h k l	Calc.	Obs.	h k l	Calc.	Obs.
1 1 1	1·081	1·056	3 1 6	0·903	0·870
2 1 1	0·918	0·903	3 1 11	0·848	0·956
2 1 2	0·929	0·948	5 1 2	0·747	0·828
2 1 5	0·922	0·933	6 1 3	0·842	0·878
3 1 2	0·889	0·918	2 2 1	0·947	0·913
3 1 4	0·928	0·970			



(I) R=H, R'=H (Safracin A)
(II) R=OH, R'=H (Safracin B)
(III) R=H, R'=Br (Title compound)

Fig. 1. Structures of safracins with the atom-numbering schemes.

Discussion. The final atomic parameters for the non-H atoms are given in Table 2.* Bond lengths and angles are in Table 3. A stereoscopic view of the molecular structure is shown in Fig. 2 with the atom-numbering scheme (*ORTEP*, Johnson, 1965). The molecules in the crystal are connected by N(4)···H(O5) hydrogen bonds and form molecular chains along the a axis. The N(4)···O(5) and N(4)···H(O5) distances are, respectively, 2·866 (8) and 1·88 (7) Å.

The main frame of the molecule consists of five condensed six-membered rings, as shown in Fig. 1. The frame is essentially the same as those of saframycins. However, one of the terminal p-quinone rings and the pyruvamide side chain of the saframycins are replaced, respectively, by a monophenol ring and an alaninamide side chain in the present compound. The main frame has the conformation with a creased hinge at the C(10)···C(12) axis. The dihedral angles between the terminal six-membered rings are 60° for the title compound and 75° for saframycin C. The methyl group of the alaninamide in the title compound and that of the pyruvamide moiety in saframycin C are inserted into the hinges to form close molecular conformations and hence good crystallinity. The unusually long C(2)–C(10) bond distances are 1·570 (9) Å for the title compound and 1·61 (3) Å for saframycin C. These may be due to concentrated strains of the frames. In

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, coordinates and isotropic thermal parameters for H atoms and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39458 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

fact, the fragmentations of the mass spectra occur at these points for safracins and saframycins (Ikeda, Matsuki, Ogawa & Munakata, 1983).

The authors are grateful to Professor Arai and Dr Tamura for supplying the atomic parameters of saframycin C.

Table 2. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2) *for non-*H *atoms, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Br	500 (1)	182 (1)	877 (1)	6·00 (2)
O(1)	−3600 (5)	3960 (3)	3175 (5)	5·58 (17)
O(2)	−2319 (5)	4115 (4)	6648 (5)	6·40 (20)
O(3)	−1667 (6)	2668 (3)	6422 (4)	6·06 (19)
O(4)	−1970 (5)	2149 (3)	−1066 (3)	4·46 (14)
O(5)	−3562 (4)	2032 (3)	419 (3)	4·12 (14)
O(6)	556 (6)	3115 (3)	4176 (4)	6·50 (19)
N(1)	−2207 (5)	1326 (3)	3722 (4)	2·83 (13)
N(2)	−3552 (5)	301 (3)	2583 (4)	3·78 (15)
N(3)	−176 (4)	2035 (3)	3577 (4)	3·48 (15)
N(4)	738 (7)	2334 (4)	1546 (5)	5·36 (21)
C(1)	−1829 (6)	1766 (4)	4620 (4)	3·07 (16)
C(2)	−3207 (6)	1593 (4)	3210 (5)	2·90 (16)
C(3)	−3103 (6)	2418 (4)	2907 (5)	3·11 (17)
C(4)	−3153 (5)	3660 (4)	3930 (6)	3·50 (18)
C(5)	−2965 (6)	4094 (4)	4918 (6)	3·92 (19)
C(6)	−2455 (6)	3764 (4)	5709 (6)	4·05 (20)
C(7)	−2075 (6)	2972 (4)	5653 (5)	3·47 (17)
C(8)	−2251 (5)	2557 (4)	4655 (5)	2·90 (16)
C(9)	−2796 (5)	2864 (4)	3859 (4)	2·62 (15)
C(10)	−3415 (5)	1087 (4)	2215 (5)	3·09 (17)
C(11)	−2330 (6)	539 (4)	4019 (6)	3·93 (19)
C(12)	−2511 (7)	59 (4)	3057 (5)	3·66 (18)
C(13)	−1541 (6)	66 (4)	2309 (6)	3·66 (18)
C(14)	−795 (5)	779 (4)	724 (5)	3·04 (16)
C(15)	−842 (6)	1262 (4)	−128 (5)	3·17 (17)
C(16)	−1799 (6)	1686 (4)	−204 (5)	3·03 (16)
C(17)	−2628 (5)	1628 (4)	532 (5)	2·76 (15)
C(18)	−2504 (5)	1151 (4)	1391 (5)	2·76 (15)
C(19)	−1598 (5)	701 (4)	1486 (5)	2·77 (15)
C(20)	−573 (6)	1765 (4)	4599 (5)	3·47 (17)
C(21)	330 (6)	2704 (4)	3459 (6)	3·86 (19)
C(22)	601 (7)	2933 (4)	2312 (6)	4·11 (20)
Me(1)	−3365 (7)	4884 (5)	4993 (8)	5·96 (27)
Me(2)	−1219 (9)	4305 (5)	6895 (7)	6·67 (31)
Me(3)	−3929 (7)	−194 (5)	1731 (6)	4·84 (22)
Me(4)	11 (6)	1316 (5)	−963 (7)	4·93 (22)
Me(5)	−1571 (9)	2897 (5)	−893 (7)	6·55 (30)
Me(6)	−269 (9)	3487 (5)	1929 (7)	6·00 (29)

Table 3. *Bond lengths* (Å) *and bond angles* (°) *involving non-*H *atoms*

Br–C(14)	1·918 (7)	C(3)–C(9)	1·492 (9)
O(1)–C(4)	1·225 (10)	C(4)–C(5)	1·489 (11)
O(2)–C(6)	1·355 (10)	C(4)–C(9)	1·483 (10)
O(2)–Me(2)	1·424 (13)	C(5)–C(6)	1·319 (11)
O(3)–C(7)	1·222 (9)	C(5)–Me(1)	1·490 (11)
O(4)–C(16)	1·384 (8)	C(6)–C(7)	1·484 (10)
O(4)–Me(5)	1·433 (11)	C(7)–C(8)	1·481 (9)
O(5)–C(17)	1·358 (8)	C(8)–C(9)	1·328 (9)
O(6)–C(21)	1·199 (9)	C(10)–C(18)	1·533 (9)
N(1)–C(1)	1·457 (8)	C(11)–C(12)	1·505 (10)
N(1)–C(2)	1·466 (9)	C(12)–C(13)	1·521 (11)
N(1)–C(11)	1·456 (9)	C(13)–C(19)	1·539 (10)
N(2)–C(10)	1·482 (9)	C(14)–C(15)	1·381 (9)
N(2)–C(12)	1·474 (10)	C(14)–C(19)	1·386 (9)
N(2)–Me(3)	1·468 (10)	C(15)–C(16)	1·397 (10)
N(3)–C(20)	1·465 (8)	C(15)–Me(4)	1·491 (11)
N(3)–C(21)	1·349 (9)	C(16)–C(17)	1·383 (9)
N(4)–C(22)	1·451 (10)	C(17)–C(18)	1·389 (9)
C(1)–C(8)	1·498 (10)	C(18)–C(19)	1·373 (9)
C(1)–C(20)	1·539 (11)	C(21)–C(22)	1·547 (11)
C(2)–C(3)	1·521 (10)	C(22)–Me(6)	1·530 (13)
C(2)–C(10)	1·570 (9)		
C(6)–O(2)–Me(2)	114·8 (7)	N(2)–C(10)–C(2)	107·8 (5)
C(16)–O(4)–Me(5)	112·3 (6)	N(2)–C(10)–C(18)	111·5 (6)
C(1)–N(1)–C(2)	116·0 (5)	C(2)–C(10)–C(18)	112·8 (5)
C(1)–N(1)–C(11)	110·3 (5)	N(1)–C(11)–C(12)	110·5 (6)
C(2)–N(1)–C(11)	109·8 (6)	N(2)–C(12)–C(11)	107·0 (6)
C(10)–N(2)–C(12)	107·8 (5)	N(2)–C(12)–C(13)	114·8 (5)
C(10)–N(2)–Me(3)	111·6 (5)	C(11)–C(12)–C(13)	112·7 (7)
C(12)–N(2)–Me(3)	113·4 (6)	C(12)–C(13)–C(19)	113·2 (6)
C(20)–N(3)–C(21)	122·6 (6)	Br–C(14)–C(15)	117·2 (5)
N(1)–C(1)–C(8)	114·6 (5)	Br–C(14)–C(19)	117·5 (5)
N(1)–C(1)–C(20)	107·7 (5)	C(15)–C(14)–C(19)	125·3 (6)
C(8)–C(1)–C(20)	110·3 (6)	C(14)–C(15)–C(16)	115·1 (6)
N(1)–C(2)–C(3)	110·7 (6)	C(14)–C(15)–Me(4)	124·5 (7)
N(1)–C(2)–C(10)	107·8 (5)	C(16)–C(15)–Me(4)	120·3 (6)
C(3)–C(2)–C(10)	111·3 (5)	O(4)–C(16)–C(15)	120·1 (6)
C(2)–C(3)–C(9)	109·2 (5)	O(4)–C(16)–C(17)	117·8 (6)
O(1)–C(4)–C(5)	120·1 (7)	C(15)–C(16)–C(17)	122·0 (6)
O(1)–C(4)–C(9)	120·0 (6)	O(5)–C(17)–C(16)	120·5 (6)
C(5)–C(4)–C(9)	120·0 (6)	O(5)–C(17)–C(18)	119·8 (6)
C(4)–C(5)–C(6)	118·9 (7)	C(16)–C(17)–C(18)	119·6 (6)
C(4)–C(5)–Me(1)	119·4 (7)	C(10)–C(18)–C(17)	120·0 (6)
C(6)–C(5)–Me(1)	121·7 (7)	C(10)–C(18)–C(19)	119·0 (6)
O(2)–C(6)–C(5)	121·5 (7)	C(17)–C(18)–C(19)	120·8 (6)
O(2)–C(6)–C(7)	116·1 (6)	C(13)–C(19)–C(14)	120·9 (6)
C(5)–C(6)–C(7)	122·3 (7)	C(13)–C(19)–C(18)	121·6 (6)
O(3)–C(7)–C(6)	120·6 (6)	C(14)–C(19)–C(18)	117·0 (6)
O(3)–C(7)–C(8)	121·4 (6)	N(3)–C(20)–C(1)	110·3 (5)
C(6)–C(7)–C(8)	117·9 (6)	O(6)–C(21)–N(3)	124·0 (7)
C(1)–C(8)–C(7)	116·3 (5)	O(6)–C(21)–C(22)	120·2 (7)
C(1)–C(8)–C(9)	122·5 (6)	N(3)–C(21)–C(22)	115·8 (6)
C(7)–C(8)–C(9)	121·2 (6)	N(4)–C(22)–C(21)	117·5 (6)
C(3)–C(9)–C(4)	118·8 (6)	N(4)–C(22)–Me(6)	109·9 (7)
C(3)–C(9)–C(8)	121·6 (6)	C(21)–C(22)–Me(6)	108·6 (7)
C(4)–C(9)–C(8)	119·6 (6)		

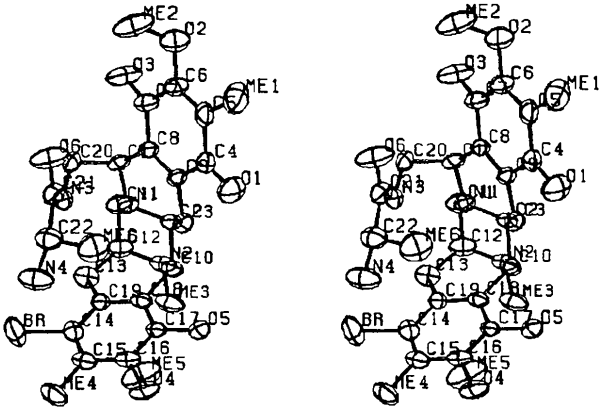


Fig. 2. A stereoview of the molecular conformation.

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