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Novel Protein Kinase C Inhibitor K-252a

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Abstract. Methyl (8*R**,9*S**,11*S**)-2,3,8,9,10,11-hexahydro-9-hydroxy-8-methyl-8,11-epoxy-1-oxo-1*H*-2,7*b*,11*a*-triazadibenzo[*a*,*g*]cycloocta[*c*,*d*,*e*]trindene-9-carboxylate,‡ $C_{27}H_{21}N_3O_5.2CH_3OH$, $M_r = 531{\cdot}57$, monoclinic, $P2_1$, $a = 14{\cdot}040$ (1), $b = 7{\cdot}005$ (1), $c = 13{\cdot}283$ (1) Å, $\beta = 106{\cdot}38$ (1)°, $V = 1253{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}408$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 6{\cdot}780$ cm^{-1}, $F(000) = 560$, $T = 295$ K, $R = 0{\cdot}052$ for 2613 unique significant reflections. The molecule, which is a novel strong inhibitor of protein kinase C, adopts a unique skeletal structure composed of eight rings.

Introduction. The novel compound K-252a was isolated from *Nocardiopsis* sp. K252 and found to be a strong inhibitor of protein kinase C (Kase, Iwahashi & Matsuda, 1986). As the activity of K252a is stronger than that of chlorpromazine we were prompted to establish the structure of the molecule.

Experimental. Pale-yellow prismatic crystals [m.p. 535–546 K (dec)] were obtained from acetone–methanol solution. Single crystal with dimensions of 0·3 × 0·3 × 0·4 mm was sealed in a glass capillary for the data collection. Cell dimensions by least-squares refinement of 25 θ values measured on an Enraf–Nonius CAD-4 diffractometer. Intensity measurements with ω–2θ scan mode up to $\theta = 75{\cdot}0°$ ($-17 \le h \le 17$, $0 \le k \le 8$, $0 \le l \le 16$), max. scan time 100 s, no significant changes in three standard reflections monitored every 3600 s; 2909 unique reflections, 2613 with $I > 3\sigma(I)$ used for refinement. No corrections for absorption or secondary extinction. Lorentz and polarization corrections; structure solved by *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), full-matrix least-squares refinement on F. All hydrogen atoms except those of solvent molecules located in difference Fourier map and refined, anisotropic and isotropic temperature factors for non-hydrogen and hydrogen atoms, respectively. Final $R = 0{\cdot}052$, $wR = 0{\cdot}052$, unit weights, number of variables 469, max. $\Delta/\sigma = 0{\cdot}02$ for non-H atoms, highest peak in a final difference synthesis 0·22 e Å^{-3}. The absolute configuration {$[\alpha]_D = -23{\cdot}2°$ (c 0·5, $CHCl_3$)} was not determined. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974), calculations carried out on a PDP 11/34A with *SDP-Plus* V.1·0 (Frenz, 1982).§

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‡ Methyl (2'*R**,3'*S**,5'*S**)-*N*,*N*'-(3-hydroxy-2-methyltetrahydro-2,5-furandiyl)-5-oxo-5,7-dihydroisoindolo[5,4-*b*:6,7-*b*']diindole-3'-carboxylate.

§ Lists of structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43026 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. Tables 1 and 2 list atomic parameters and molecular geometry, respectively. Fig. 1 is an *ORTEP*II drawing (Johnson, 1976) of the molecule, and Fig. 2 shows the chemical structure. The molecule adopts a unique skeletal structure in which eight rings are fused. The aromatic system consisting of three six-membered rings and three five-membered hetero rings is slightly bent and the dihedral angle between the two terminal benzene rings is 7·5°. The 2-pyrrolidone ring is planar. Both the seven-membered ring and the tetrahydrofuran ring take envelope conformations.

The bond lengths and angles observed in the indolo[2,3-*a*]carbazole part are generally in agreement with the corresponding values in staurosporin (Furusaki, Hashiba, Matsumoto, Hirano, Iwai & Ōmura, 1982). Although in staurosporin the indolo-[2,3-*a*]carbazole part adopts approximately a C_{2v} symmetry, in K-252a the deviation from C_{2v} symmetry is more noteworthy. The bond lengths around the N(3) atom are significantly longer than the corresponding values around the N(1) atom. The close contact between the C(25) and C(24) atoms [3·164 (3) Å] may explain the long distances around the N(3) atom. The C(17)–C(18) bond is significantly longer than the C(15)–C(16) bond. This may be due to the repulsions between the N(3) and O(3) atoms [N(3)···O(3) = 2·774 (2) Å, N(3)–C(18)–C(17)–O(3) = 40·0 (3)°], and between the C(25) and C(26) atoms [C(25)···C(26) = 2·901 (2) Å, C(25)–C(18)–C(17)–C(26) = 38·2 (3)°]. The O(2)–C(15) bond is significantly longer than the O(2)–C(18) bond.

The bond angles O(1)–C(10)–C(9), C(10)–C(9)–C(7), and C(9)–C(7)–C(6) are significantly larger than O(1)–C(10)–N(2), C(11)–C(12)–C(13), and C(12)–C(13)–C(20), respectively. These bond-angle asymmetries may result from the rather small steric hindrance between the O(1) atom and the C(1)–H(C1)

Table 1. *Positional parameters and equivalent isotropic temperature factors of non-*H *atoms with their e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å²)
O(1)	0·2125 (1)	0·300	0·1560 (2)	4·78 (5)
O(2)	0·7430 (1)	0·3988 (3)	0·3575 (1)	3·01 (3)
O(3)	0·8177 (1)	0·0013 (4)	0·2297 (2)	3·55 (4)
O(4)	0·9348 (2)	0·1899 (5)	0·4800 (2)	5·13 (6)
O(5)	0·9920 (1)	0·1159 (4)	0·3443 (2)	3·92 (4)
N(1)	0·5977 (1)	0·2603 (4)	0·3717 (2)	3·07 (4)
N(2)	0·2548 (2)	0·3071 (5)	0·0012 (2)	4·06 (5)
N(3)	0·6887 (1)	0·3092 (4)	0·1792 (1)	2·79 (4)
C(1)	0·3497 (2)	0·2264 (5)	0·3914 (2)	3·54 (5)
C(2)	0·3636 (2)	0·2032 (5)	0·4981 (2)	3·86 (5)
C(3)	0·4586 (2)	0·2003 (5)	0·5677 (2)	3·93 (6)
C(4)	0·5421 (2)	0·2173 (5)	0·5341 (2)	3·43 (5)
C(5)	0·5282 (2)	0·2395 (4)	0·4265 (2)	2·90 (4)
C(6)	0·4331 (2)	0·2470 (4)	0·3546 (2)	2·99 (5)
C(7)	0·4462 (2)	0·2736 (4)	0·2514 (2)	2·89 (5)
C(8)	0·5496 (2)	0·2794 (4)	0·2661 (2)	2·76 (4)
C(9)	0·3840 (2)	0·2903 (5)	0·1476 (2)	3·05 (4)
C(10)	0·2747 (2)	0·2982 (5)	0·1064 (2)	3·55 (5)
C(11)	0·3419 (2)	0·3118 (5)	−0·0365 (2)	3·44 (5)
C(12)	0·4242 (2)	0·3012 (4)	0·0644 (2)	2·95 (4)
C(13)	0·5264 (2)	0·3037 (4)	0·0796 (2)	2·79 (4)
C(14)	0·5903 (2)	0·2987 (4)	0·1819 (2)	2·70 (4)
C(15)	0·7044 (2)	0·2451 (5)	0·4064 (2)	3·02 (5)
C(16)	0·7433 (2)	0·0597 (5)	0·3702 (2)	3·36 (5)
C(17)	0·8182 (2)	0·1246 (4)	0·3118 (2)	2·87 (4)
C(18)	0·7761 (2)	0·3284 (4)	0·2729 (2)	2·73 (4)
C(19)	0·6876 (2)	0·3092 (4)	0·0728 (2)	2·90 (4)
C(20)	0·5881 (2)	0·3083 (4)	0·0099 (2)	2·92 (4)
C(21)	0·5665 (2)	0·3066 (5)	−0·1002 (2)	3·69 (5)
C(22)	0·6439 (2)	0·3056 (6)	−0·1440 (2)	4·31 (6)
C(23)	0·7417 (2)	0·3035 (6)	−0·0815 (2)	4·40 (6)
C(24)	0·7657 (2)	0·3045 (6)	0·0269 (2)	3·81 (5)
C(25)	0·8505 (2)	0·4740 (5)	0·2556 (2)	3·65 (5)
C(26)	0·9210 (2)	0·1472 (5)	0·3902 (2)	3·19 (5)
C(27)	1·0925 (2)	0·1355 (8)	0·4105 (3)	5·44 (9)
OM(1)*	0·0896 (2)	0·5696 (6)	0·2055 (2)	6·70 (7)
OM(2)*	0·9549 (2)	0·8635 (6)	0·1309 (2)	5·78 (7)
CM(1)*	0·1508 (4)	0·637 (1)	0·3022 (3)	7·4 (1)
CM(2)*	1·0084 (4)	1·014 (2)	0·0836 (5)	10·5 (2)

* Solvent atoms are asterisked.

Table 2. *Bond lengths* (Å) *and angles* (°); *numbers in parentheses are e.s.d.'s in the least significant digits*

O(1)–C(10)	1·233 (3)	O(2)–C(15)	1·440 (2)
O(2)–C(18)	1·420 (2)	O(3)–C(17)	1·389 (2)
O(4)–C(26)	1·191 (3)	O(5)–C(26)	1·326 (2)
O(5)–C(27)	1·443 (2)	N(1)–C(5)	1·379 (2)
N(1)–C(8)	1·382 (2)	N(1)–C(15)	1·442 (2)
N(2)–C(10)	1·348 (3)	N(2)–C(11)	1·446 (3)
N(3)–C(14)	1·394 (2)	N(3)–C(18)	1·488 (2)
N(3)–C(19)	1·408 (2)	C(1)–C(2)	1·384 (3)
C(1)–C(6)	1·398 (2)	C(2)–C(3)	1·392 (3)
C(3)–C(4)	1·373 (3)	C(4)–C(5)	1·395 (3)
C(5)–C(6)	1·406 (3)	C(6)–C(7)	1·445 (2)
C(7)–C(8)	1·410 (2)	C(7)–C(9)	1·413 (2)
C(8)–C(14)	1·398 (2)	C(9)–C(10)	1·477 (2)
C(9)–C(12)	1·378 (3)	C(11)–C(12)	1·504 (2)
C(12)–C(13)	1·392 (2)	C(13)–C(14)	1·402 (2)
C(13)–C(20)	1·435 (2)	C(15)–C(16)	1·537 (3)
C(16)–C(17)	1·542 (2)	C(17)–C(18)	1·576 (3)
C(17)–C(26)	1·531 (2)	C(18)–C(25)	1·523 (3)
C(19)–C(20)	1·411 (2)	C(19)–C(24)	1·398 (3)
C(20)–C(21)	1·408 (2)	C(21)–C(22)	1·369 (3)
C(22)–C(23)	1·390 (4)	C(23)–C(24)	1·383 (3)

C(15)–O(2)–C(18)	110·2 (2)	C(26)–O(5)–C(27)	115·9 (2)
C(5)–N(1)–C(8)	109·3 (1)	C(5)–N(1)–C(15)	130·5 (2)
C(8)–N(1)–C(15)	119·9 (1)	C(10)–N(2)–C(11)	114·3 (2)
C(14)–N(3)–C(18)	124·9 (1)	C(14)–N(3)–C(19)	107·2 (1)
C(18)–N(3)–C(19)	127·8 (1)	C(2)–C(1)–C(6)	118·8 (2)
C(1)–C(2)–C(3)	120·9 (2)	C(2)–C(3)–C(4)	122·0 (2)
C(3)–C(4)–C(5)	117·2 (2)	N(2)–C(10)–C(9)	106·0 (2)
N(2)–C(11)–C(12)	101·7 (2)	C(9)–C(12)–C(11)	109·4 (2)
C(9)–C(12)–C(13)	121·6 (2)	C(11)–C(12)–C(13)	129·0 (2)
C(12)–C(13)–C(14)	119·4 (2)	C(12)–C(13)–C(20)	133·8 (2)
C(14)–C(13)–C(20)	106·8 (1)	N(3)–C(14)–C(8)	131·1 (2)
N(3)–C(14)–C(13)	109·9 (1)	C(8)–C(14)–C(13)	119·0 (2)
O(2)–C(15)–N(1)	106·8 (2)	O(2)–C(15)–C(16)	106·2 (1)
N(1)–C(15)–C(16)	113·0 (2)	C(15)–C(16)–C(17)	105·2 (2)
C(13)–C(20)–C(19)	107·2 (1)	C(13)–C(20)–C(21)	132·7 (2)
C(19)–C(20)–C(21)	120·1 (2)	C(20)–C(21)–C(22)	118·5 (2)
C(21)–C(22)–C(23)	121·0 (2)	C(22)–C(23)–C(24)	122·1 (2)
C(19)–C(24)–C(23)	117·6 (2)	O(4)–C(26)–O(5)	124·8 (2)
O(4)–C(26)–C(17)	124·3 (2)	O(5)–C(26)–C(17)	110·9 (2)
N(1)–C(5)–C(4)	129·5 (2)	N(1)–C(5)–C(6)	108·4 (2)
C(4)–C(5)–C(6)	122·1 (2)	C(1)–C(6)–C(5)	119·1 (2)
C(1)–C(6)–C(7)	133·5 (2)	C(5)–C(6)–C(7)	107·4 (1)
C(6)–C(7)–C(8)	105·8 (1)	C(6)–C(7)–C(9)	136·6 (2)
C(8)–C(7)–C(9)	117·5 (2)	N(1)–C(8)–C(7)	109·1 (1)
N(1)–C(8)–C(14)	129·0 (2)	C(7)–C(8)–C(14)	121·9 (2)
C(7)–C(9)–C(10)	131·0 (2)	C(7)–C(9)–C(12)	120·4 (2)
C(10)–C(9)–C(12)	108·6 (2)	O(1)–C(10)–N(2)	125·6 (2)
O(1)–C(10)–C(9)	128·4 (2)	O(3)–C(17)–C(16)	111·0 (2)
O(3)–C(17)–C(18)	112·8 (2)	O(3)–C(17)–C(26)	113·2 (2)
C(16)–C(17)–C(18)	100·7 (1)	C(16)–C(17)–C(26)	109·5 (2)
C(18)–C(17)–C(26)	108·9 (2)	O(2)–C(18)–N(3)	108·5 (1)
O(2)–C(18)–C(17)	103·4 (1)	O(2)–C(18)–C(25)	106·2 (2)
N(3)–C(18)–C(17)	109·7 (2)	N(3)–C(18)–C(25)	111·9 (2)
C(17)–C(18)–C(25)	116·5 (2)	N(3)–C(19)–C(20)	108·8 (2)
N(3)–C(19)–C(24)	130·5 (2)	C(20)–C(19)–C(24)	120·6 (2)

group [O(1)···C(1) = 3·219 (3), O(1)···H(C1) = 2·20 (3) Å]. The short distance of 2·20 Å is due to the relatively long H(C1)–C(1) bond of 1·24 (1) Å. If an ideal value of 1·10 Å is adopted as the H(C1)–C(1) bond, the relevant distance is 2·36 Å.

There is an intramolecular hydrogen bond between the O(3) and O(5) atoms [O(3)···O(5) = 2·618 (3) Å, O(3)–H(O3) = 1·04 (2) Å, H(O3)···O(5) = 2·00 (2) Å, O(3)–H(O3)···O(5) = 115 (2)°].

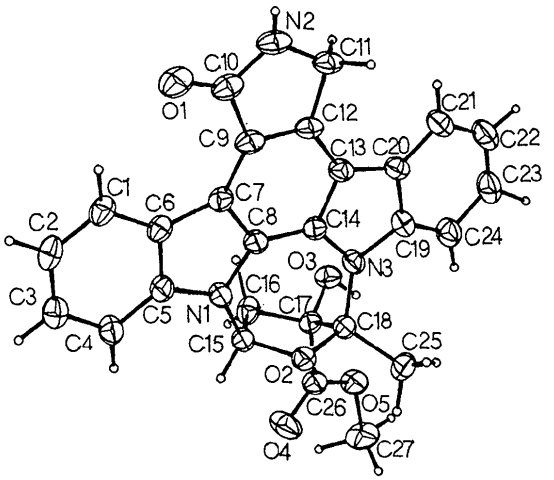

Fig. 1. View of the title compound, K-252a, showing atom numbering.

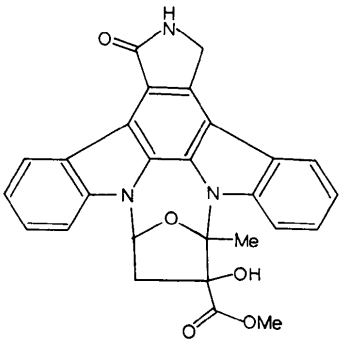

Fig. 2. Chemical structure of the molecule.

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Structure of 6-Fluoro-10,10′-diphenyl-9-phenanthrone (1), 7-Chloro-10,10′-diphenyl-9-phenanthrone (2) and 3-Methoxy-10,10′-diphenyl-9-phenanthrone (3)

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Abstract. (1): $C_{26}H_{17}FO$, $M_r = 364·4$, orthorhombic, *Iba*2, $a = 17·274$ (3), $b = 13·748$ (1), $c = 15·877$ (2) Å, $V = 3770$ Å^3, $Z = 8$, $D_x = 1·28$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å (graphite-crystal monochromator), $\mu = 0·8$ cm^{-1}, $F(000) = 1520$, $T = 293$ K, final $R = 0·036$ for 1900 unique observed reflections. (2): $C_{26}H_{17}ClO$, $M_r = 380·9$, orthorhombic, $P2_12_12_1$, $a = 9·027$ (2), $b = 12·517$ (2), $c = 16·874$ (2) Å, $V = 1907$ Å^3, $Z = 4$, $D_x = 1·33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å (graphite-crystal monochromator), $\mu = 2·1$ cm^{-1}, $F(000) = 792$, $T = 293$ K, final $R = 0·046$ for 2280 unique observed reflections. (3): $C_{27}H_{20}O_2$, $M_r = 376·5$, monoclinic, $P2_1/n$, $a = 14·647$ (1), $b = 9·666$ (1), $c = 15·102$ (1) Å, $\beta = 112·950$ (3)°, $V = 1969$ Å^3, $Z = 4$, $D_x = 1·27$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å (Ni filter), $\mu = 5·8$ cm^{-1}, $F(000) = 792$, $T = 293$ K, final $R = 0·039$ for 3324 unique observed reflections. The molecular structures of three chemically related compounds are compared: in the three compounds there are no significant differences between comparable bond lengths and angles. The sp^3 C atom

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