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Structure of the Anthracycline Antibiotic Aranciamycin

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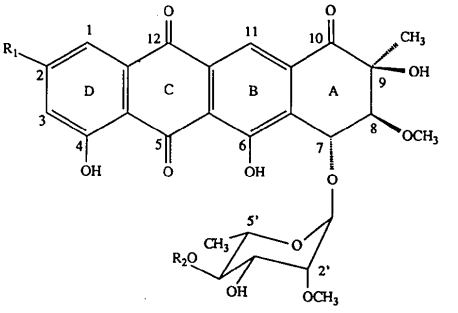
Abstract. 4-[(6-Deoxy-2-*O*-methyl-α-L-mannopyranosyl)oxy]-3,4-dihydro-2,5,7-trihydroxy-3-methoxy-2-methyl-1,6,11(2*H*)-naphthacenetrione, $C_{27}H_{28}O_{12}$, $M_r = 544.5$, orthorhombic, $P2_12_12_1$, $a = 8.029$ (1), $b = 8.224$ (1), $c = 37.261$ (6) Å, $V = 2460.4$ (6) Å^3, $Z = 4$, $D_x = 1.470$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.11$ mm^{-1}, $F(000) = 1144$, $T = 293$ K, $R = 0.069$ for 3186 observed reflections. The absolute configuration of this α-glycoside is 7*R*,8*S*,9*S*. Ring *A* adopts a half-chair conformation without an extra stabilizing intramolecular hydrogen bond from O(9) to O(7). The overall conformation is very similar to that found for the related antibiotic steffimycin B.

Introduction. The anthracycline antibiotic aranciamycin is produced by *Streptomyces echinatus* and consists of the aglycone aranciamycinone and the sugar 2-*O*-methyl-L-rhamnose. Aranciamycin shows weak antitumour activity and is closely related to steffimycin B. These antibiotics differ from the very well known anthracyclines (*e.g.* daunomycin, adriamycin, carminomycin) with respect to the substitution of ring *A* and the sugar moiety, which does not carry an amino group. The X-ray crystal-structure analysis confirms the structure elucidation by chemical and spectroscopic methods (Keller-Schierlein, Sauerbier, Vogler & Zähner, 1970; Keller-Schierlein & Müller, 1970; Zeeck, Schröder, Krone & Frobel, 1978).



Aranciamycin: R_1 = H; R_2 = H
Steffimycin B: R_1 = OCH_3; R_2 = CH_3

Experimental. Crystals grown from methanol were orange plates. A crystal 0.9 × 0.4 × 0.2 mm was mounted in a glass capillary and used to register 6292 profile-fitted intensities (Clegg, 1981) with $2\theta \leq 50°$ (h −9→9, k 0→9, l 0→44; $\sin\theta/\lambda = 0.59$ Å^{-1}) on a Stoe–Siemens four-circle diffractometer (ω-scan

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mode). 4341 reflections were unique ($R_{int} = 0.033$), of which 3186 with $|F| > 3\sigma(F)$ were used for all calculations, with programs *SHELXS*86 (Sheldrick, 1986) and *XLS* (Sheldrick, 1987). Cell constants were refined from 2θ values of 45 reflections in the range 19–22°. No crystal decay was observed. The structure was solved by direct methods; all H atoms were located in difference Fourier maps. Least-squares refinement (on F) included non-H atoms with anisotropic, and H atoms with fixed isotropic displacement parameters. A riding model was employed for all H atoms except the hydroxyl H atoms, whose bond distances were restrained (O—H = 0.90 Å). $R = 0.069$, $wR = 0.063$ $[w^{-1} = \sigma^2(F) + 0.0005F^2]$, for 380 parameters; $S = 1.62$; maximum $\Delta/\sigma = 0.02$; $\Delta\rho$ in the final difference map within 0.61 and -0.38 e Å^{-3}.

Final atomic coordinates for aranciamycin are presented in Table 1, bond lengths and angles in Table 2.* Fig. 1 displays the essential configurational and conformational features of the antibiotic. Since the sugar is known to be an L-rhamnose derivative the absolute configuration is 7*R*,8*S*,9*S*, as previously predicted by chemical methods.

Table 1. *Atomic coordinates* (x10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^3)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	1178 (7)	−179 (7)	2033 (1)	74 (2)
C(2)	269 (8)	789 (9)	1806 (1)	89 (3)
C(3)	161 (8)	2439 (9)	1837 (1)	86 (2)
C(4)	1048 (7)	3215 (7)	2111 (1)	64 (2)
O(4)	924 (5)	4844 (5)	2124 (1)	83 (2)
C(4*a*)	1972 (7)	2309 (6)	2358 (1)	54 (2)
C(5)	2858 (7)	3084 (5)	2648 (1)	53 (2)
O(5)	2863 (5)	4586 (3)	2677 (1)	72 (1)
C(5*a*)	3721 (6)	2085 (5)	2920 (1)	45 (1)
C(6)	4503 (6)	2825 (4)	3212 (1)	45 (1)
O(6)	4475 (5)	4454 (3)	3265 (1)	63 (1)
C(6*a*)	5374 (6)	1898 (5)	3464 (1)	42 (1)
C(7)	6247 (6)	2765 (5)	3774 (1)	47 (1)
C(8)	7536 (6)	1689 (6)	3945 (1)	62 (2)
O(8)	8829 (5)	1537 (5)	3683 (1)	94 (2)
C(81)	10435 (8)	1834 (9)	3779 (2)	100 (3)
C(9)	6870 (7)	−25 (5)	4036 (1)	57 (2)
O(9)	8208 (6)	−891 (4)	4189 (1)	91 (2)
C(91)	5396 (8)	−49 (5)	4289 (1)	67 (2)
C(10)	6355 (7)	−807 (5)	3684 (1)	52 (2)
O(10)	6595 (5)	−2243 (4)	3628 (1)	72 (1)
C(10*a*)	5432 (6)	221 (4)	3421 (1)	44 (1)
C(11)	4638 (6)	−525 (5)	3133 (1)	46 (1)
C(11*a*)	3809 (6)	387 (5)	2881 (1)	46 (1)
C(12)	2988 (7)	−427 (5)	2573 (1)	53 (2)
O(12)	3099 (5)	−1891 (3)	2532 (1)	73 (1)
C(12*a*)	2027 (6)	577 (6)	2313 (1)	54 (2)
O(7)	5012 (4)	3188 (3)	4035 (1)	49 (1)
C(1′)	4852 (6)	4854 (4)	4123 (1)	46 (1)
C(2′)	3166 (6)	4985 (5)	4300 (1)	55 (2)
O(2′)	2766 (5)	6626 (3)	4360 (1)	68 (1)
C(21′)	1779 (12)	7333 (9)	4103 (2)	148 (4)
C(3′)	3202 (7)	4119 (6)	4657 (1)	63 (2)
O(3′)	1656 (6)	4193 (6)	4842 (1)	99 (2)
C(4′)	4555 (7)	4837 (5)	4887 (1)	60 (2)
O(4′)	4730 (6)	3963 (5)	5218 (1)	96 (2)
C(5′)	6206 (6)	4725 (5)	4698 (1)	55 (2)
O(5′)	6136 (4)	5417 (3)	4344 (1)	47 (1)
C(6′)	7591 (8)	5664 (7)	4891 (2)	88 (2)

Discussion. The anthraquinone system is almost planar [the r.m.s. deviation of ring atoms is 0.036 Å, with maximum deviation of 0.078 Å for C(5)]. While rings *B* and *D* show nearly equal bond lengths, the C—C bonds to the carbonyl groups in ring *C* are much longer. As found for carminomycin (Von Dreele & Einck, 1977) and a series of dihydroxyanthraquinones (Ulicky, Kettmann, Soldanova & Betiba, 1987, and references cited therein), formation of intramolecular hydrogen bonds from the hydroxyl groups O(4)—H and O(6)—H to O(5) results in decreased C—C bond lengths for C(4a)—C(5) and C(5)—C(5a) compared to C(11a)—C(12) and C(12)—C(12a) (mean values 1.459 and 1.485 Å, respectively), short C—O distances (1.349 Å on average) to the hydroxyl groups and a long C═O distance [1.241 (5) Å] in the carbonyl group involved. The exocyclic C—C—O angles [C(3)—C(4)—O(4) 116.3 (5), C(6a)—C(6)—O(6) 116.8 (4)°] and the O···O distances [2.591 (8) and 2.546 (8) Å] are also typical of hydroxylated anthraquinones including the significant shortening of O(5)···O(6) compared to O(5)···O(4).

Ring *A* forms a half-chair with O(8) antiperiplanar to both O(7) and the methyl group at C(9). Stabilization by an O(9)—H···O(7) hydrogen bond as found in the crystal structures of daunomycin (Neidle & Taylor, 1977) and carminomycin (Von Dreele & Einck, 1977) is impossible here because of the different configuration at C(9), so that O(9), which is *trans* to O(7), occupies an equatorial (instead of an axial) position and forms an intramolecular hydrogen bond to O(10). In aranciamycin, the twist between the carbonyl group at C(10) and the anthraquinone part is thus more expressed than in steffimycin B (twist angles 12.1 and 8.5°, respectively).

The six-membered sugar ring is in the normal chair conformation and agrees well with the structure of α-L-rhamnose (Killean, Lawrence & Sharma, 1971; Takagi & Jeffrey, 1978). As in crystal structures of other anthracyclines the mean plane of the sugar residue is nearly perpendicular to the chromophore. The overall conformation of aranciamycin strongly resembles that of steffimycin B (Arora, 1985). A least-squares fit of all non-H atoms gives an r.m.s. deviation of 0.22 Å, which is reduced to 0.17 Å by omitting the C atoms of both methoxy groups.

All hydroxy groups participate in hydrogen bonding. The intermolecular hydrogen bonds O(3′)—H···O(4′) and O(4′)—H···O(9) with O···O 3.029 (8)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55472 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1002]

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1.372 (8)	C(1)—C(12*a*)	1.392 (6)
C(2)—C(3)	1.365 (8)	C(3)—C(4)	1.398 (8)
C(4)—O(4)	1.345 (6)	C(4)—C(4*a*)	1.398 (6)
C(4*a*)—C(5)	1.441 (6)	C(4*a*)—C(12*a*)	1.435 (6)
C(5)—O(5)	1.241 (5)	C(5)—C(5*a*)	1.477 (6)
C(5*a*)—C(6)	1.396 (6)	C(5*a*)—C(11*a*)	1.406 (5)
C(6)—O(6)	1.354 (4)	C(6)—C(6*a*)	1.396 (5)
C(6*a*)—C(7)	1.529 (5)	C(6*a*)—C(10*a*)	1.389 (5)
C(7)—C(8)	1.504 (6)	C(7)—O(7)	1.430 (5)
C(8)—O(8)	1.432 (6)	C(8)—C(9)	1.544 (7)
O(8)—C(81)	1.360 (7)	C(9)—O(9)	1.410 (6)
C(9)—C(91)	1.515 (7)	C(9)—C(10)	1.518 (6)
C(10)—O(10)	1.214 (5)	C(10)—C(10*a*)	1.491 (6)
C(10*a*)—C(11)	1.391 (5)	C(11)—C(11*a*)	1.375 (6)
C(11*a*)—C(12)	1.481 (6)	C(12)—O(12)	1.217 (5)
C(12)—C(12*a*)	1.489 (6)	O(7)—C(1′)	1.416 (4)
C(1′)—C(2′)	1.508 (6)	C(1′)—O(5′)	1.397 (5)
C(2′)—O(2′)	1.406 (5)	C(2′)—C(3′)	1.510 (7)
O(2′)—C(21′)	1.372 (7)	C(3′)—O(3′)	1.421 (6)
C(3′)—C(4′)	1.504 (7)	C(4′)—O(4′)	1.433 (5)
C(4′)—C(5′)	1.505 (7)	C(5′)—O(5′)	1.439 (5)
C(5′)—C(6′)	1.532 (7)		

C(12*a*)—C(1)—C(2)	117.6 (5)	C(3)—C(2)—C(1)	123.9 (6)
C(4)—C(3)—C(2)	118.9 (6)	O(4)—C(4)—C(3)	116.3 (5)
C(4*a*)—C(4)—C(3)	120.5 (5)	C(4*a*)—C(4)—O(4)	123.1 (5)
C(5)—C(4*a*)—C(4)	121.3 (4)	C(12*a*)—C(4*a*)—C(4)	117.9 (4)
C(12*a*)—C(4*a*)—C(5)	120.8 (4)	O(5)—C(5)—C(4*a*)	120.5 (4)
C(5*a*)—C(5)—C(4*a*)	120.0 (4)	C(5*a*)—C(5)—O(5)	119.5 (4)
C(6)—C(5*a*)—C(5)	120.3 (4)	C(11*a*)—C(5*a*)—C(5)	120.3 (4)
C(11*a*)—C(5*a*)—C(6)	119.4 (4)	O(6)—C(6)—C(5*a*)	122.5 (4)
C(6*a*)—C(6)—C(5*a*)	120.7 (3)	C(6*a*)—C(6)—O(6)	116.8 (4)
C(7)—C(6*a*)—C(6)	118.9 (3)	C(10*a*)—C(6*a*)—C(6)	118.8 (4)
C(10*a*)—C(6*a*)—C(7)	122.3 (4)	C(8)—C(7)—C(6*a*)	111.2 (3)
O(7)—C(7)—C(6*a*)	108.0 (4)	O(7)—C(7)—C(8)	109.4 (3)
O(8)—C(8)—C(7)	105.1 (4)	C(9)—C(8)—C(7)	113.0 (4)
C(9)—C(8)—O(8)	108.7 (4)	C(81)—O(8)—C(8)	119.5 (5)
O(9)—C(9)—C(8)	106.6 (4)	C(91)—C(9)—C(8)	114.7 (3)
C(91)—C(9)—O(9)	109.6 (4)	C(10)—C(9)—C(8)	107.0 (3)
C(10)—C(9)—O(9)	110.2 (3)	C(10)—C(9)—C(91)	108.7 (4)
O(10)—C(10)—C(9)	121.1 (4)	C(10*a*)—C(10)—C(9)	117.5 (3)
C(10*a*)—C(10)—O(10)	121.2 (4)	C(10)—C(10*a*)—C(6*a*)	120.3 (4)
C(11)—C(10*a*)—C(6*a*)	120.7 (4)	C(11)—C(10*a*)—C(10)	119.0 (3)
C(11*a*)—C(11)—C(10*a*)	120.6 (4)	C(11)—C(11*a*)—C(5*a*)	119.6 (4)
C(12)—C(11*a*)—C(5*a*)	120.5 (4)	C(12)—C(11*a*)—C(11)	119.9 (4)
O(12)—C(12)—C(11*a*)	120.8 (4)	C(12*a*)—C(12)—C(11*a*)	118.9 (4)
C(12*a*)—C(12)—O(12)	120.3 (4)	C(4*a*)—C(12*a*)—C(1)	121.1 (5)
C(12)—C(12*a*)—C(1)	119.6 (4)	C(12)—C(12*a*)—C(4*a*)	119.3 (4)
C(1′)—O(7)—C(7)	117.2 (3)	C(2′)—C(1′)—O(7)	104.6 (3)
O(5′)—C(1′)—O(7)	113.0 (3)	O(5′)—C(1′)—C(2′)	112.5 (3)
O(2′)—C(2′)—C(1′)	110.1 (4)	C(3′)—C(2′)—C(1′)	109.5 (4)
C(3′)—C(2′)—O(2′)	108.4 (4)	C(21′)—O(2′)—C(2′)	115.3 (4)
O(3′)—C(3′)—C(2′)	113.0 (4)	C(4′)—C(3′)—C(2′)	109.4 (4)
C(4′)—C(3′)—O(3′)	109.7 (4)	O(4′)—C(4′)—C(3′)	111.4 (4)
C(5′)—C(4′)—C(3′)	110.2 (3)	C(5′)—C(4′)—O(4′)	106.6 (4)
O(5′)—C(5′)—C(4′)	111.8 (3)	C(6′)—C(5′)—C(4′)	112.9 (4)
C(6′)—C(5′)—O(5′)	105.0 (4)	C(5′)—O(5′)—C(1′)	115.9 (3)

and 2.981 (8) Å, respectively, are important for the packing of the molecules (Fig. 2). The distance between the aromatic rings (3.45 Å) is shorter than in daunomycin–butanol [3.51 Å (Courseille, Busetta, Geoffre & Hospital, 1979)], but only the hydroxy and keto groups of the rings *C* and *D* overlap.

The crystal structure of aranciamycin underlines the close relationship to steffimycin B. Both antibiotics show the unusual behaviour that the aglycone is more active than the glycoside, while the aglycones of many other anthracyclines no longer show antitumour activity; *in vitro* tests against L1210 leukaemia cells yield $IC_{50} = 2.2$ $\mu g\,ml^{-1}$ for aranciamycin and 0.5 $\mu g\,ml^{-1}$ for aranciamycinone (Kraemer & Sedlacek, 1985). This may result from the different substitution of ring *A*, which carries four O atoms as potential binding partners, so that the sugar residue is no longer essential for DNA binding. Similar effects have been observed in the case of elloramycin/tetracenomycin antibiotics (Rohr & Zeeck, 1990).

From the crystal structure of the daunomycin–d(CGTACG) complex (Quigley, Wang, Ughetto, van der Marel, van Boom & Rich, 1980), Arora (1985) suggested a model for the intercalation of steffimycins into DNA, which accounts for the preference of A–T sequences and explains the weaker biological activity of steffimycins compared to daunomycin with weaker hydrogen bonding. However, since the biological properties of steffimycins and aranciamycin differ from those of other anthracyclines, one must be very careful when using the structure of a daunomycin complex in order to model the geometry of intercalation of this special group of antibiotics. Furthermore, recent structure determinations of daunomycin–DNA hexamer complexes (Nunn, van Meervelt, Zhang, Moore & Kennard, 1991, and references cited therein) and adducts (Gao, Liaw, Li, van der Marel, van Boom & Wang, 1991) have revealed a far more detailed picture of the conformational changes of both components upon complexation.

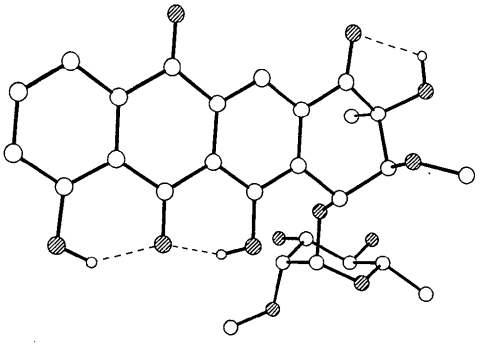

Fig. 1. The structure of aranciamycin in the crystal (O atoms fully shaded, only H atoms involved in intramolecular hydrogen bonds shown).

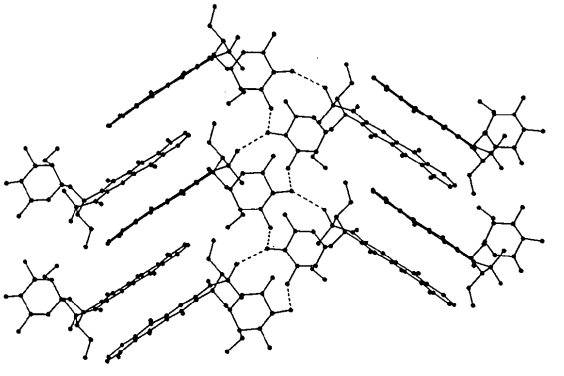

Fig. 2. Packing diagram along **b** with **c** horizontal and **a** vertical (intermolecular hydrogen bonds dashed).

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Structures of 1,2,3,4-Benzenetetracarboxylic Acid and 1,2,3,5-Benzenetetracarboxylic Acid Dihydrate

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Abstract. 1,2,3,4-Benzenetetracarboxylic acid (compound *A*), $C_{10}H_6O_8$, $M_r = 254.2$, triclinic, $P\bar{1}$, $a = 9.5616$ (1), $b = 8.4696$ (1), $c = 7.0568$ (1) Å, $\alpha = 106.806$ (1), $\beta = 100.192$ (1), $\gamma = 69.557$ (1)°, $V = 510.77$ (1) Å^3, $Z = 2$, $D_x = 1.65$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.39$ cm^{-1}, $F(000) = 260$, $T = 293$ K, final conventional $R = 0.036$, $wR = 0.039$ for 1699 'observed' reflections and 187 variables. 1,2,3,5-Benzenetetracarboxylic acid dihydrate (compound *B*), $C_{10}H_6O_8.2H_2O$, $M_r = 290.2$, triclinic, $P\bar{1}$, $a = 5.845$ (4), $b = 7.828$ (6), $c = 13.31$ (1) Å, $\alpha = 94.8$ (1), $\beta = 100.6$ (1), $\gamma = 93.63$ (9)°, $V = 594.6$ (9) Å^3, $Z = 2$, $D_x = 1.62$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.41$ cm^{-1}, $F(000) = 300$, $T = 293$K, final conventional $R = 0.070$, $wR = 0.072$ for 2354 'observed' reflections and 221 variables. The molecules in both structures are associated through their carboxylic groups forming a network of hydrogen bonds including water molecules in *B*. The molecules, O atoms excluded, are essentially planar in both compounds. The benzene rings show a week distortion towards a half-chair conformation for compound *A* and towards a slightly twisted boat conformation for *B*. The angles between the planes of the carboxyl groups and the least-squares plane of the C atoms of the ring are respectively 2.5 (2), 82.8 (1), 72.7 (1) and 14.7 (1)° for compound *A*, and 6.6 (3), 85.6 (3), 4.0 (3) and 5.8 (3)° for *B*.

Introduction. Benzenecarboxylic acids form a complete 'group' (12 members) of compounds whose physicochemical properties must depend on the

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