CRABTREE, G. W., DEXTER, D. L., SPREMULLI, E. N., CAMPBELL, D. E., CHU, S. H., QUEVEDO, W. C., CALABRESI, P. & PARKS, R. E. (1982). *Proc. Am. Assoc. Cancer Res.* **23**, 848.

GRAVES, B. J. & HODGSON, D. J. (1981). *Acta Cryst.* **B37**, 1576–1584.

GRAVES, B. J., HODGSON, D. J., KATZ, D. J., WISE, D. S. & TOWNSEND, L. B. (1978). *Biochim. Biophys. Acta,* **520**, 229–232.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98, 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

KAJANDER, E. O., KUBOTA, M., CARRERA, C. J., MONTGOMERY, J. A. & CARSON, D. A. (1986). *Cancer Res.* **46**, 2866–2870.

KOYAMA, G., NAKAMURA, H., UMEZAWA, H. & IITAKA, Y. (1976). *Acta Cryst.* **B32**, 813–820.

KOYAMA, G., UMEZAWA, H. & IITAKA, Y. (1974). *Acta Cryst.* **B30**, 1511–1516.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

PRUSINER, P., BRENNAN, T. & SUNDARALINGAM, M. (1973). *Biochemistry,* **12**, 1196–1201.

RAO, S. T. & SUNDARALINGAM, M. (1970). *J. Am. Chem. Soc.* **92**, 4963–4970.

SAENGER, W. (1984). *Principles of Nucleic Acid Structure,* p. 189. New York: Springer-Verlag.

SCHWALBE, C. H. & SAENGER, W. (1973). *J. Mol. Biol.* **75**, 129–143.

SINGH, C. (1965). *Acta Cryst.* **19**, 861–864.

SINGH, P. & HODGSON, D. J. (1974a). *J. Am. Chem. Soc.* **96**, 5276–5278.

SINGH, P. & HODGSON, D. J. (1974b). *J. Am. Chem. Soc.* **96**, 1239–1241.

SINGH, P. & HODGSON, D. J. (1974c). *Biochemistry,* **13**, 5445–5452.

SINGH, P. & HODGSON, D. J. (1975). Am. Crystallogr. Assoc. 25th Anniv. Meet., March 9–13, p. 13.

SINGH, P. & HODGSON, D. J. (1977a). *J. Am. Chem. Soc.* **99**, 4807–4815.

SINGH, P. & HODGSON, D. J. (1977b). *Acta Cryst.* **B33**, 3189–3194.

SPRANG, S., SCHELLER, R., ROHRER, D. & SUNDARALINGAM, M. (1978). *J. Am. Chem. Soc.* **100**, 2867–2872.

SUNDARALINGAM, M. (1966). *Acta Cryst.* **21**, 495–506.

SUNDARALINGAM, M. (1973). *Jerusalem Symposium Quantum Chemistry and Biochemistry,* Vol. 5, edited by E. D. BERGMANN & B. PULLMAN, p. 450. New York: Academic Press.

Structure of Dicyano-15-norcobyrinic Acid Heptamethyl Ester

BY ALAN R. BATTERSBY, INGEBORG GRGURINA AND PAUL R. RAITHBY*

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

AND ERNST EGERT, KLAUS HARMS AND GEORGE M. SHELDRICK

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany
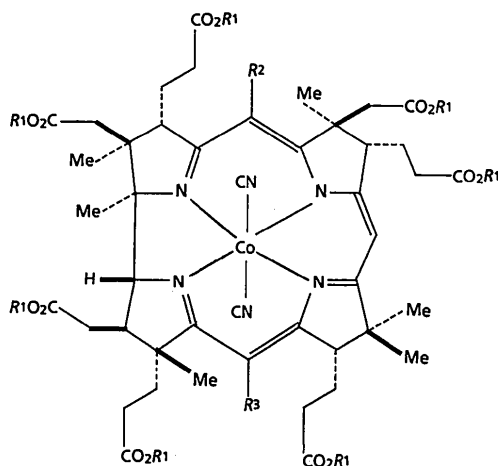
Abstract. [Co($C_{51}H_{71}N_4O_{14}$)(CN)$_2$], $M_r = 1075.09$, orthorhombic, $P2_12_12_1$, $a = 15.595 (2)$, $b = 18.672 (4)$, $c = 19.023 (5)$ Å, $V = 5539 (1)$ Å^3, $Z = 4$, $D_x = 1.289$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 3.086$ mm^{-1}, $F(000) = 2280$, $T = 293$ K, $R = 0.078$ for 3172 observed reflections [$F > 4\sigma(F)$] and 462 parameters. The molecular structure of the title complex closely resembles that of the parent cobyrinic acid heptamethyl ester. The corrin ring system is not planar, with a maximum deviation of 0.50 (3) Å [for C(11)] from the least-squares plane through the ring atoms, and the dihedral angles between the pyrrole rings lie in the range 7.5 (3)–15.0 (3)°. The replacement of the methyl group on C(19) in the parent complex by an H atom in the title complex has little effect on the local geometry. The side chains show some disorder.

---

* To whom correspondence should be addressed.

Introduction. Cobyrinic acid (1), which is a late biosynthetic precursor (Battersby & McDonald, 1982; Leeper, 1985, 1987) of vitamin B$_{12}$, is heavily C-methylated around the periphery of its macrocycle. The C-methyl groups coordinated to C(9) and C(19) [corresponding to C(5), C(15), respectively, on normal corrin numbering] stand apart from the rest by being sited on the chromophoric conjugated system. Analogues of the natural structure lacking one or both of these methyl groups have recently been prepared (Lewis, Nussberger, Kräutler & Eschenmoser, 1983; Nussbaumer & Arigoni, 1983) by chemical transformations of cobyrinic acid heptamethyl ester, cobester (2). These analogues are 15-norcobester (3), 5-norcobester (4) and 5,15-bisnorcobester (5). In relation to biosynthetic studies, the preparation of 15-norcobester (3) was repeated, and suitable crystals obtained for X-ray analysis. The structure was determined in order to analyse the

effect of the presence or absence of the methyl substitutents by comparison to the cobester itself (5) (Kamiya & Kennard, 1982).

(1) R^1 = H, R^2 = R^3 = Me
(2) R^1 = R^2 = R^3 = Me
(3) R^1 = R^2 = Me, R^3 = H
(4) R^1 = R^3 = Me, R^2 = H
(5) R^1 = Me, R^2 = R^3 = H

Experimental. Dark-red prismatic crystals of (3) were obtained by slow crystallization from acetone/ hexane. Crystal $0.49 \times 0.22 \times 0.13$ mm; Nicolet $R3m\mu$ diffractometer, graphite-monochromated Cu $K\alpha$ radiation; cell parameters refined from diffractometer angles for 25 centred reflections ($40 < 2\theta < 50°$). Intensity data collected by θ–2θ scans for 4502 reflections with $5 < 2\theta < 116°$ (h $-18/0$, k 0/21, l 0/21); three standard reflections measured every 100 reflections showed no significant crystal decay; absorption correction based on an ellipsoid model and 308 azimuthal scan data from six independent reflections; max. and min. transmission factors 0.822 and 0.589, $\mu R = 0.43$; 3172 unique reflections (R_{int} = 0.010) with $F > 4\sigma(F)$ were used in the analysis. Structure solved by a Patterson search using the corrin ring coordinates from (2) as the model, blocked-cascade least-squares refinement on F, anisotropic thermal parameters on Co, N, ordered O and cyanide C atoms. The side chains showed considerable positional disorder and high thermal parameters; where two positions for an atom could be located they were assigned a common temperature factor and occupancies were refined as k and $(1-k)$ respectively. H atoms were placed in idealized positions and allowed to ride on the relevant C atom, C—H 0.96 Å; each type of H was assigned a common isotropic thermal parameter. 462 parameters, $R = 0.078$, $wR = 0.093$, $w^{-1} = \sigma^2(F_o) + 0.0015F_o^2$, $S = 1.699$, $\Delta/\sigma = 0.036$ (mean) and 0.165 (max.), $\Delta\rho$ variations within 0.41 and -0.34 e Å^{-3}.

The structure was solved using *PATSEE* (Egert, 1986) and all other calculations performed using *SHELXTL* (Sheldrick, 1983). Neutral-atom scattering factors taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are given in Table 1,* and associated bond lengths and angles in Table 2. The structure of the molecule is shown in Fig. 1, and a packing diagram viewed down **a** is illustrated in Fig. 2.

---

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51981 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å$^2 \times 10^3$)*

	x	y	z	U
Co(1)	−2396 (1)	2530 (1)	−1810 (1)	35 (1)*
N(1)	−2302 (4)	1544 (3)	−1606 (3)	37 (2)*
N(2)	−1510 (4)	2308 (3)	−2450 (3)	35 (2)*
N(3)	−2455 (4)	3503 (4)	−2150 (3)	38 (2)*
N(4)	−3231 (4)	2670 (3)	−1072 (3)	35 (2)*
C(1)	−2643 (6)	1165 (4)	−1120 (4)	40 (2)
C(2)	−2521 (6)	363 (5)	−1231 (4)	46 (2)
C(3)	−1765 (6)	375 (5)	−1769 (5)	45 (2)
C(4)	−1868 (5)	1113 (4)	−2142 (4)	34 (2)
C(5)	−1100 (5)	1577 (4)	−2372 (4)	34 (2)
C(6)	−655 (5)	1476 (4)	−3110 (4)	41 (2)
C(7)	−506 (5)	2271 (4)	−3358 (5)	41 (2)
C(8)	−1221 (5)	2656 (4)	−2976 (4)	38 (2)
C(9)	−1555 (6)	3363 (4)	−3199 (5)	43 (2)
C(10)	−2111 (6)	3733 (5)	−2788 (5)	42 (2)
C(11)	−2516 (6)	4470 (5)	−2964 (4)	48 (2)
C(12)	−2805 (6)	4712 (5)	−2217 (5)	51 (3)
C(13)	−2933 (5)	4007 (4)	−1864 (5)	40 (2)
C(14)	−3527 (6)	3908 (5)	−1307 (5)	47 (2)
C(15)	−3630 (6)	3277 (5)	−939 (4)	42 (2)
C(16)	−4248 (6)	3216 (5)	−329 (5)	48 (2)
C(17)	−3892 (6)	2556 (6)	48 (5)	56 (3)
C(18)	−3406 (6)	2166 (5)	−550 (5)	44 (2)
C(19)	−3169 (6)	1480 (5)	−576 (5)	50 (2)
N(5)	−1129 (6)	3008 (5)	−654 (4)	65 (3)*
N(6)	−3854 (6)	2148 (6)	−2857 (5)	96 (4)*
C(20)	−1577 (6)	2831 (5)	−1103 (4)	41 (3)*
C(21)	−3297 (6)	2289 (5)	−2470 (5)	51 (3)*
O(1)	−804 (5)	69 (6)	899 (4)	109 (4)*
O(2)	−2164 (6)	−141 (7)	936 (5)	139 (5)*
O(3)	−911 (5)	−816 (4)	−3110 (4)	81 (3)*
O(4)	−245 (4)	−458 (4)	−2152 (4)	69 (3)*
O(5)	−585 (7)	511 (6)	−4560 (5)	139 (5)*
O(6)	−1174 (10)	1584 (5)	−4752 (4)	170 (7)*
O(7)	942 (12)	3366 (7)	−4433 (7)	232 (9)*
O(8)	1478 (9)	2449 (7)	−4843 (5)	153 (6)*
O(9)	−4437 (7)	5100 (7)	−3210 (5)	157 (6)*
O(10)	−3715 (6)	5166 (6)	−4187 (6)	144 (5)*
O(11)	−3032 (9)	6351 (11)	−1221 (9)	251 (11)*
O(12)	−3619 (12)	5690 (10)	−753 (18)	392 (20)*
O(13)	−2731 (11)	2830 (10)	2048 (7)	253 (10)*
O(14)	−1692 (16)	2797 (12)	1606 (13)	129 (5)
O(14')	−1770 (12)	1973 (11)	1863 (10)	129 (5)
C(22)	−2322 (6)	−54 (5)	−555 (5)	52 (3)
C(23)	−1538 (6)	208 (5)	−159 (5)	52 (3)
C(24)	−1562 (7)	5 (6)	605 (6)	71 (3)
C(25)	−791 (12)	−40 (9)	1638 (8)	143 (6)
C(26)	−3371 (6)	92 (5)	−1537 (5)	59 (3)
C(27)	−1753 (6)	−291 (5)	−2235 (5)	57 (3)
C(28)	−885 (7)	−523 (5)	−2483 (5)	57 (3)
C(29)	−125 (7)	−1069 (7)	−3384 (6)	79 (4)
C(30)	−435 (6)	1589 (5)	−1782 (5)	48 (2)
C(31)	158 (6)	1026 (5)	−3080 (5)	57 (3)
C(32)	−1295 (6)	1119 (5)	−3616 (5)	53 (3)
C(33)	−968 (8)	1046 (7)	−4381 (7)	86 (4)

Table 1 (cont.)

	x	y	z	U
C(34)	−748 (18)	1555 (14)	−5421 (11)	246 (12)
C(35)	366 (6)	2623 (5)	−3186 (5)	53 (2)
C(36)	1125 (8)	2450 (7)	−3656 (6)	85 (4)
C(37)	1130 (8)	2772 (7)	−4328 (7)	76 (4)
C(38)	1585 (12)	2774 (10)	−5502 (8)	152 (7)
C(39)	−1288 (7)	3606 (6)	−3926 (5)	70 (3)
C(40)	−1958 (7)	5025 (5)	−3329 (6)	62 (3)
C(41)	−3314 (7)	4282 (5)	−3410 (5)	61 (3)
C(42)	−3875 (8)	4910 (7)	−3568 (7)	88 (4)
C(43)	−4186 (13)	5801 (10)	−4418 (11)	176 (8)
C(44)	−2096 (7)	5137 (6)	−1828 (5)	63 (3)
C(45)	−2276 (8)	5320 (7)	−1041 (7)	97 (4)
C(46)	−2916 (20)	5740 (15)	−919 (15)	210 (12)
C(47)	−4247 (18)	6274 (12)	−868 (13)	262 (14)
C(48)	−5120 (7)	3020 (7)	−649 (7)	82 (4)
C(49)	−4348 (8)	3878 (6)	95 (6)	80 (4)
C(50)	−3256 (9)	2720 (7)	650 (7)	93 (4)
C(51)	−2780 (9)	2122 (8)	989 (7)	110 (5)
C(52)	−2346 (12)	2363 (10)	1691 (10)	148 (6)
C(53)	−1429 (21)	2200 (18)	2493 (14)	150 (10)
C(53')	−1273 (26)	3018 (22)	2356 (21)	150 (10)

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

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

Co(1)—N(1)	1·889 (6)	Co(1)—N(2)	1·888 (7)
Co(1)—N(3)	1·930 (7)	Co(1)—N(4)	1·933 (6)
Co(1)—C(20)	1·938 (9)	Co(1)—C(21)	1·937 (10)
N(1)—C(1)	1·280 (10)	N(1)—C(4)	1·465 (10)
N(2)—C(5)	1·515 (10)	N(2)—C(8)	1·274 (10)
N(3)—C(10)	1·396 (11)	N(3)—C(13)	1·317 (11)
N(4)—C(15)	1·316 (11)	N(4)—C(18)	1·396 (11)
C(1)—C(2)	1·526 (12)	C(1)—C(19)	1·444 (13)
C(2)—C(3)	1·561 (13)	C(2)—C(22)	1·535 (12)
C(2)—C(26)	1·533 (14)	C(3)—C(4)	1·558 (12)
C(3)—C(27)	1·528 (13)	C(4)—C(5)	1·542 (11)
C(5)—C(6)	1·577 (12)	C(5)—C(30)	1·528 (12)
C(6)—C(7)	1·574 (12)	C(6)—C(31)	1·523 (13)
C(6)—C(32)	1·539 (13)	C(7)—C(8)	1·513 (12)
C(7)—C(35)	1·546 (12)	C(8)—C(9)	1·481 (12)
C(9)—C(10)	1·356 (12)	C(9)—C(39)	1·514 (14)
C(10)—C(11)	1·550 (12)	C(11)—C(12)	1·558 (13)
C(11)—C(40)	1·521 (14)	C(11)—C(41)	1·547 (14)
C(12)—C(13)	1·491 (13)	C(12)—C(44)	1·550 (14)
C(13)—C(14)	1·420 (13)	C(14)—C(15)	1·379 (13)
C(15)—C(16)	1·512 (13)	C(16)—C(17)	1·530 (14)
C(16)—C(48)	1·534 (15)	C(16)—C(49)	1·485 (15)
C(17)—C(18)	1·548 (13)	C(17)—C(50)	1·546 (16)
C(18)—C(19)	1·335 (13)	N(5)—C(20)	1·151 (12)
N(6)—C(21)	1·170 (14)	O(1)—C(24)	1·314 (14)
O(1)—C(25)	1·420 (17)	O(2)—C(24)	1·162 (15)
O(3)—C(28)	1·311 (13)	O(3)—C(29)	1·414 (14)
O(4)—O(28)	1·187 (12)	O(5)—C(33)	1·213 (17)
O(6)—O(33)	1·269 (16)	O(6)—C(34)	1·438 (24)
O(7)—O(37)	1·165 (19)	O(8)—C(37)	1·272 (16)
O(8)—C(38)	1·404 (19)	O(9)—C(42)	1·166 (17)
O(10)—C(42)	1·297 (17)	O(10)—C(43)	1·460 (22)
O(11)—O(12)	1·776 (29)	O(11)—C(46)	1·290 (34)
O(12)—O(46)	1·145 (37)	O(12)—C(47)	1·481 (31)
O(13)—O(14)	1·826 (29)	O(13)—C(52)	1·258 (25)
O(14)—O(14')	1·619 (30)	O(14)—C(52)	1·312 (30)
O(14)—O(53')	1·623 (47)	O(14')—C(52)	1·201 (27)
O(14')—C(53)	1·379 (34)	C(22)—C(23)	1·518 (13)
C(23)—C(24)	1·502 (15)	C(27)—C(28)	1·497 (14)
C(32)—C(33)	1·549 (16)	C(35)—C(36)	1·517 (15)
C(36)—C(37)	1·412 (17)	C(41)—C(42)	1·494 (16)
C(44)—C(45)	1·560 (16)	C(45)—C(46)	1·291 (33)
C(50)—C(51)	1·487 (19)	C(51)—C(52)	1·563 (24)
C(53')—C(53)	1·568 (53)		

N(1)—Co(1)—N(2)	82·1 (3)	N(1)—Co(1)—N(3)	172·1 (3)
N(2)—Co(1)—N(3)	91·4 (3)	N(1)—Co(1)—N(4)	92·0 (3)
N(2)—Co(1)—N(4)	172·5 (3)	N(3)—Co(1)—N(4)	94·8 (3)
N(1)—Co(1)—C(20)	95·1 (3)	N(2)—Co(1)—C(20)	91·6 (3)
N(3)—Co(1)—C(20)	89·5 (3)	N(4)—Co(1)—C(20)	84·3 (3)
N(1)—Co(1)—C(21)	87·9 (3)	N(2)—Co(1)—C(21)	93·5 (4)
N(3)—Co(1)—C(21)	88·1 (3)	N(4)—Co(1)—C(21)	90·8 (3)
C(20)—Co(1)—C(21)	174·4 (4)	Co(1)—N(1)—C(1)	130·9 (6)
Co(1)—N(1)—C(4)	115·3 (5)	C(1)—N(1)—C(4)	113·1 (7)
Co(1)—N(2)—C(5)	116·3 (5)	Co(1)—N(2)—C(8)	130·8 (6)
C(5)—N(2)—C(8)	112·7 (7)	Co(1)—N(3)—C(10)	124·3 (5)

Table 2 (cont.)

Co(1)—N(3)—C(13)	124·1 (6)	C(10)—N(3)—C(13)	110·9 (7)
Co(1)—N(4)—C(15)	125·0 (6)	Co(1)—N(4)—C(18)	123·9 (5)
C(15)—N(4)—C(18)	110·6 (7)	N(1)—C(1)—C(2)	112·9 (7)
N(1)—C(1)—C(19)	121·9 (8)	C(2)—C(1)—C(19)	124·8 (8)
C(1)—C(2)—C(3)	99·8 (7)	C(1)—C(2)—C(22)	114·0 (7)
C(3)—C(2)—C(22)	113·9 (7)	C(1)—C(2)—C(26)	105·6 (7)
C(3)—C(2)—C(26)	114·2 (7)	C(22)—C(2)—C(26)	109·0 (7)
C(2)—C(3)—C(4)	103·6 (7)	C(2)—C(3)—C(27)	112·1 (7)
C(4)—C(3)—C(27)	117·2 (8)	N(1)—C(4)—C(3)	102·4 (6)
N(1)—C(4)—C(5)	104·3 (6)	C(3)—C(4)—C(5)	123·1 (7)
N(2)—C(5)—C(4)	101·9 (6)	N(2)—C(5)—C(6)	101·9 (6)
C(4)—C(5)—C(6)	121·8 (7)	N(2)—C(5)—C(30)	110·2 (7)
C(4)—C(5)—C(30)	109·1 (7)	C(6)—C(5)—C(30)	110·9 (7)
C(5)—C(6)—C(7)	102·7 (6)	C(5)—C(6)—C(31)	113·6 (7)
C(7)—C(6)—C(31)	114·1 (7)	C(5)—C(6)—C(32)	108·9 (7)
C(7)—C(6)—C(32)	108·5 (7)	C(31)—C(6)—C(32)	108·9 (7)
C(6)—C(7)—C(8)	101·2 (7)	C(6)—C(7)—C(35)	117·8 (7)
C(8)—C(7)—C(35)	110·2 (7)	N(2)—C(8)—C(7)	113·3 (7)
N(2)—C(8)—C(9)	123·6 (8)	C(7)—C(8)—C(9)	123·1 (7)
C(8)—C(9)—C(10)	121·0 (8)	C(8)—C(9)—C(39)	115·6 (8)
C(10)—C(9)—C(39)	123·3 (8)	N(3)—C(10)—C(9)	126·1 (8)
N(3)—C(10)—C(11)	107·7 (7)	C(9)—C(10)—C(11)	126·1 (8)
C(10)—C(11)—C(12)	100·2 (7)	C(10)—C(11)—C(40)	118·0 (8)
C(12)—C(11)—C(40)	112·6 (8)	C(10)—C(11)—C(41)	104·2 (7)
C(12)—C(11)—C(41)	109·5 (8)	C(40)—C(11)—C(41)	111·5 (8)
C(11)—C(12)—C(13)	101·2 (7)	C(11)—C(12)—C(44)	112·3 (8)
C(13)—C(12)—C(44)	109·5 (8)	N(3)—C(13)—C(12)	111·6 (7)
N(3)—C(13)—C(14)	125·8 (8)	C(12)—C(13)—C(14)	122·6 (8)
C(13)—C(14)—C(15)	124·5 (8)	N(4)—C(15)—C(14)	125·6 (8)
N(4)—C(15)—C(16)	112·5 (7)	C(14)—C(15)—C(16)	121·9 (8)
C(15)—C(16)—C(17)	101·0 (7)	C(15)—C(16)—C(48)	106·2 (8)
C(17)—C(16)—C(48)	108·4 (8)	C(15)—C(16)—C(49)	114·9 (8)
C(17)—C(16)—C(49)	117·0 (8)	C(48)—C(16)—C(49)	108·7 (9)
C(16)—C(17)—C(18)	102·2 (7)	C(16)—C(17)—C(50)	114·8 (9)
C(18)—C(17)—C(50)	108·8 (8)	N(4)—C(18)—C(17)	107·5 (7)
N(4)—C(18)—C(19)	124·5 (8)	C(17)—C(18)—C(19)	128·0 (9)
C(1)—C(19)—C(18)	125·1 (9)	Co(1)—C(20)—N(5)	175·9 (8)
Co(1)—C(21)—N(6)	178·5 (9)	C(24)—O(1)—C(25)	114·9 (11)
C(28)—O(3)—C(29)	116·6 (8)	C(33)—O(6)—C(34)	110·2 (15)
C(37)—O(8)—C(38)	122·3 (13)	C(42)—O(10)—C(43)	118·6 (12)
O(12)—O(11)—C(46)	40·1 (16)	O(11)—O(12)—C(46)	46·5 (17)
O(11)—O(12)—C(47)	75·8 (15)	C(46)—O(12)—C(47)	122·1 (24)
O(14)—O(13)—C(52)	45·9 (12)	O(13)—O(14)—O(14')	80·0 (14)
O(13)—O(14)—C(52)	43·5 (12)	O(14')—O(14)—C(52)	47·0 (13)
O(13)—O(14)—C(53')	86·8 (19)	O(14')—O(14)—C(53')	90·4 (20)
C(52)—O(14)—C(53')	111·2 (23)	O(14)—O(14')—C(52)	53·0 (14)
O(14)—O(14')—C(53)	86·6 (19)	C(52)—O(14')—C(53)	109·8 (22)
C(2)—C(22)—C(23)	114·6 (8)	C(22)—C(23)—C(24)	112·2 (8)
O(1)—C(24)—O(2)	121·2 (11)	O(1)—C(24)—C(23)	111·4 (9)
O(2)—C(24)—C(23)	127·1 (11)	C(3)—C(27)—C(28)	115·5 (8)
O(3)—C(28)—O(4)	123·5 (9)	O(3)—C(28)—C(27)	112·3 (8)
O(4)—C(28)—C(27)	124·2 (9)	C(6)—C(32)—C(33)	114·4 (8)
O(5)—C(33)—O(6)	128·4 (13)	O(5)—C(33)—C(32)	119·9 (11)
O(6)—C(33)—C(32)	111·6 (10)	C(7)—C(35)—C(36)	118·1 (8)
C(35)—c(36)—C(37)	116·6 (10)	O(7)—C(37)—O(8)	115·3 (13)
O(7)—C(37)—C(36)	124·0 (13)	O(8)—C(37)—C(36)	119·8 (12)
C(11)—C(41)—C(42)	113·7 (9)	O(9)—C(42)—O(10)	124·2 (13)
O(9)—C(42)—C(41)	124·2 (12)	O(10)—C(42)—C(41)	111·2 (11)
C(12)—C(44)—C(45)	116·3 (9)	C(44)—C(45)—C(46)	116·4 (16)
O(11)—C(46)—O(12)	93·5 (24)	O(11)—C(46)—C(45)	124·5 (25)
O(12)—C(46)—C(45)	137·7 (27)	C(17)—C(50)—C(51)	119·5 (11)
C(50)—C(51)—C(52)	111·8 (12)	O(13)—C(52)—O(14)	90·6 (18)
O(13)—C(52)—O(14')	129·1 (20)	O(14)—C(52)—O(14')	80·1 (18)
O(13)—C(52)—C(51)	117·0 (16)	O(14)—C(52)—C(51)	114·1 (18)
O(14')—C(52)—C(51)	112·4 (17)	O(14')—C(53)—C(53')	102·4 (24)
O(14)—C(53')—C(53)	80·5 (23)		

The overall structure of dicyano-15-norcobyrinic acid heptamethyl ester (3) is very similar to that of the parent cobester (2) (Kamiya & Kennard, 1982) except for the replacement of the methyl group at position C(19) in (2) by the H atom in (3). The coordination around the central metal is a distorted octahedron. Within the corrin ring system, the Co—N distances to N(1) and N(2) are *ca* 0·04 (1) Å shorter than to N(3) and N(4). The N(1)— Co(1)—N(2) angle in the five-membered metallocyclic ring is *ca* 11 (1)° more acute than the N—Co—N angles in the six-membered metallocyclic

rings. The Co—C(cyanide) distances are equivalent and the N≡C—Co—C≡N system is essentially linear. The Co(1) atom lies at the centre of the plane defined by the four corrin N atoms, but there is significant deviation of the N atoms from this least-squares plane [N(1), −0·076 (5); N(2), 0·076 (5); N(3), −0·066 (5); N(4), 0·066 (5) Å], consistent with the normal puckering observed in these systems (Kamiya & Kennard, 1982).

The bond parameters within the corrin ring in (3) follow the same trends as those observed in (2) (Kamiya & Kennard, 1982), and the replacement of the methyl group coordinated to C(19) in (2) by an H atom in (3) makes no significant difference. However, in both compounds (2) and (3) there is a significant difference in geometry around C(9) compared with that around C(19). While both C(9) and C(19) remain essentially planar there are differences

in the C—C—C(Me) angles. The C(8)—C(9)—C(39) angle is ca 8 (1)° narrower than the C(10)—C(9)—C(39) angle in (3) [there is also an 8 (1)° difference for the equivalent angles in (2)], so that the substitutent methyl group bends towards the less heavily substituted corrin ring carbon, C(7). In (2), the two C—C(19)—C(Me) angles are essentially equivalent and the substituent methyl group does not bend towards a monosubstituted corrin ring C atom, C(17), or a disubstituted corrin ring C atom, C(2). In (3) the substituent H atom was fixed on the bisector of the C(1)—C(19)—C(18) angle so that a true comparison is not valid; however, the C(1)—C(19)—C(18) angles in (3) and (2) are essentially equal, so that the other bond parameters may also be similar. There are no intramolecular short contacts involving C(39) in (3) or either of the methyl groups in (2), and the bending away of C(39) may help to reduce any steric congestion. In this context it would be interesting to determine the structure of (4) where there is a hydrogen bound to C(9).

The bond parameters within the pyrrole rings in (3) and the dihedral angles between them are not significantly different from those found in (2). This is consistent with the observations made previously (Kamiya & Kennard, 1982) that while the geometry of rings N(1)C(1)–C(4) and N(2)C(5)–C(8) is unaffected by the nature of the side chains or intermolecular packing forces, the geometry of rings N(3)C(10)–C(13) and N(4)C(15)–C(18) is much more variable, depending on the nature and distribution of the side chains. Since the substituents on (3) and (2) are so similar, the conformations of the pyrrole rings would be expected to be similar.

The side chains in (3) are flexible, and within the limits of the disorder, they take up conformations which lead to the most favourable packing arrangements. The molecules of (3) within the crystal structure are mainly held together by van der Waals contacts (Fig. 2), and similar side-chain conformations are observed in related structures where extensive hydrogen bonding is absent (Fischli & Daly, 1980; Schlingmann, Dresow, Koppenhagen, Becker & Sheldrick, 1980).
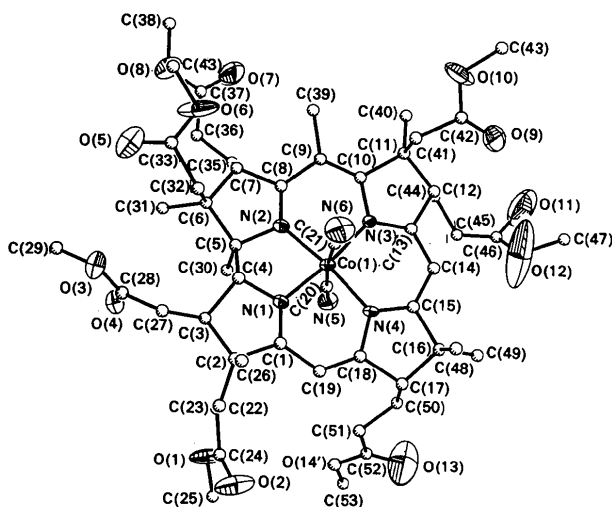
Fig. 1. The molecular structure of (3) showing the atomic labelling. The thermal ellipsoids are set at the 50% probability level.
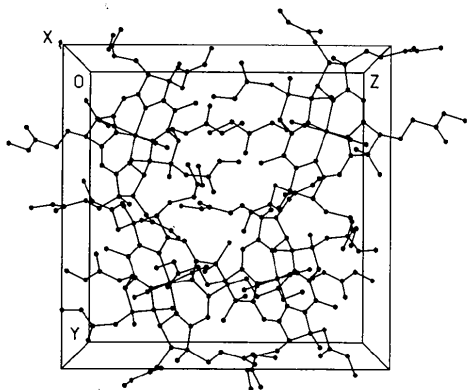

Fig. 2. A packing diagram showing the unit-cell contents viewed down the a axis.

References

BATTERSBY, A. R. & McDONALD, E. (1982). B_{12}, Vol. 1, edited by D. DOLPHIN, pp. 107–144. New York: Wiley.

EGERT, E. (1986). PATSEE. Patterson search program. Univ. of Göttingen, Federal Republic of Germany.

FISCHLI, A. & DALY, J. J. (1980). *Helv. Chim. Acta*, **63**, 1628–1643.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

KAMIYA, K. & KENNARD, O. (1982). *J. Chem. Soc. Perkin Trans.* 1, pp. 2279–2288.

LEEPER, F. J. (1985). *Nat. Prod. Rep.* **2**, 19–47, 561–580.

LEEPER, F. J. (1987). *Nat. Prod. Rep.* **4**, 441–483.

LEWIS, N. J., NUSSBERGER, R., KRÄUTLER, B. & ESCHENMOSER A. (1983). *Angew. Chem. Int. Ed. Engl.* **22**, 736–737.

NUSSBAUMER, C. & ARIGONI, D. (1983). *Angew. Chem. Int. Ed. Engl.* **22**, 737–738.

SCHLINGMANN, G., DRESOW, B., KOPPENHAGEN, V. B., BECKER, W. & SHELDRICK, W.S. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 321–322.

SHELDRICK, G. M. (1983). *SHELXTL Users Manual*, revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

An Aglycone Precursor of Anthracycline Antibiotics: C$_{23}$H$_{22}$O$_9$

BY O. JOHNSON AND D. W. JONES

Department of Chemistry and Chemical Technology, University of Bradford, Bradford BD7 1DP, England

Abstract. Methyl 5-(1,4-dihydroxy-9,10-dioxo-2-anthryl)-2,3-isopropylidene-α-D-lyxofuranoside, M_r = 442, trigonal, $P3_221$ (No. 154), a = 10·654 (2), c = 31·981 (4) Å, U = 3144 (2) Å^3, Z = 6, D_m = 1·40 (1) (carbon tetrachloride/*n*-pentane flotation), D_x = 1·38 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 1·02 cm^{-1}, $F(000)$ = 1392, T = 298 K, R (wR) = 0·026 (0·026) for 1379 reflections with $I > 3\sigma(I)$. In the crystal structure of this anthracyclinone precursor, in a relatively uncommon space group, there are intramolecular chelate hydrogen bonds with 2·54 (1) and 2·56 (1) Å O—O distances between ketone and hydroxyl groups on each side of the rigid planar quinizarin moiety and a 2·70 (1) Å intramolecular bond from O(15) on the bridging C atom to the ring O(17) atom of the isopropylidene-blocked lyxofuranose ring. Torsion angles at the new C(15)—O(15)H chiral C atom are 14·1 (4)° with C(2)—C(3) of the quinizarin and 64·3 (3)° with C(16)—C(17) in the bridge to the sugar.

Introduction. Structure analyses of precursors to synthetic anthracyclinone anti-cancer antibiotics can be helpful in establishing the diastereomeric products in stereospecific condensation reactions (Johnson, Jones, Mincher & Shaw, 1983). In its formation (Mincher, Shaw & Declercq, 1983), methyl 5-(1,4-dihydroxy-9,10-dioxo-2-anthryl-2,3-isopropylidene-α-D-lyxofuranoside forms a new chiral atom, C(15), linking the planar tricyclic quinizarin (or 1,4-dihydroxyanthraquinone) moiety to the furanose ring. If the persistence of the D sugar is accepted, the analysis confirms the prediction of an *S* isomer as predominant, in accord with an extension of Cram's rule (Cram & Elhafez, 1952) of asymmetric induction. It also provides an accurate determination of the dimensions of the quinizarin moiety.

Experimental. Dark-red well-formed rhombohedral crystals (provided by Dr D. J. Mincher). X-ray photographic study initially indicated a *C*-centred orthohexagonal cell with systematic absences in 00*l* reflections for *l* ≠ 3*n* consistent with 3$_1$, 3$_2$, 6$_2$ or 6$_4$ screw axes parallel to *c*. A second crystal mounted parallel to the 32 Å *c* axis gave 60° axial separations in Weissenberg photographs indicating a hexagonal axis system. The morphology of the well-developed rhombohedral crystals suggested point group 32. Crystal dimensions 0·3 × 0·3 × 0·4 mm. Enraf-Nonius CAD-4F diffractometer (Rothamstead Experimental Station) with graphite-monochromatized Mo $K\alpha$ X-radiation used to confirm cell dimensions (from 25 reflections with 18 < 2θ < 21°) and to collect intensity data from the unique part ($\frac{1}{6}$th) of reciprocal space: bisecting mode, ω–2θ scan, maximum time 90 s, 2θ range 2·5–50·0°, index range *h,k* −11*l*/−1 and *h,k* 0/11 for *l* 0/34; no significant decline in intensities of 4$\bar{4}$4 and 0,$\bar{3}$,10 standard reflections (remeasured every 3 h). 2903 measured data with 2557 observed. Observation of (formally Friedel) equivalent reflections among the data collected suggested the enantiomorphous pair of space groups $P3_121$ and $P3_221$ rather than $P3_112$ and $P3_212$.

Direct-methods solution by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) in $P3_121$ with 2508, formally unique, data led to the opposite enantiomer from that required based on the known sugar configuration. Coordinates inverted and space group changed to $P3_221$. The diffraction (Laue) symmetry of $P3_221$ is, however, $\bar{3}m$ and so the 2557 observed data were merged (neglecting the effects of anomalous scattering for such light atoms with Mo X-radiation and assuming $F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}$) to give 1514 averaged data (R_{int} =