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X-ray Structure of Two Analogues of the Carbohydrate Moiety of the Polyoxins

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The structures of two isomeric sugars, $C_{22}H_{29}NO_9$, have been studied by X-ray diffraction. Isomer (*D*) was shown to be ethyl 5-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-formylamino-1,2-*O*-isopropylidene-*D*-glycero-*L*-talohexofuranuronate and crystallizes in the space group $P2_12_12_1$, with $a = 18.40$ (1), $b = 14.82$ (1), $c = 8.65$ (1) Å, $Z = 4$. Isomer (*C*) was shown to be ethyl 5-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-formylamino-1,2-*O*-isopropylidene-*L*-glycero-*D*-allo-heptofuranuronate and crystallizes in $P2_1$ with $a = 19.50$ (1), $b = 8.50$ (1), $c = 14.99$ (1) Å, $\beta = 109.0$ (1)°, $Z = 4$. The structures were refined to $R(D) = 0.05$, $R(C) = 0.07$. Packing forces cause the distortions which lead to the crystallographic dimerization.

Introduction

The discovery of the naturally occurring polyoxins (Suhadolnik, 1970) has led to interest in C–C linked sugar α -amino acids, and several compounds with C^α of an α -amino acid moiety attached to C(1), C(2), C(3) or C(4) of furanosyl sugars have been reported (Bischofberger, Brink, De Villiers, Hall & Jordaan, 1977, and references therein). Recently, similar compounds with an α -amino acid moiety attached to C(5)

of a furanosyl sugar have been prepared (Hall, Bischofberger, Brink, De Villiers & Jordaan, to be published) by reacting 3-*O*-benzyl-1,2-*O*-isopropylidene- α -*D*-ribo-pentodialdo-1,4-furanose with ethyl isocyanoacetate in ethanol in the presence of sodium cyanide. Hydrolysis of the two oxazoline derivatives obtained (Hoppe, 1974) gave two ethyl 3-*O*-benzyl-6-deoxy-6-formylamino-1,2-*O*-isopropylidene-heptofuranuronates [*A*] and [*B*] which were separated by column chromatography. Acetylation, with acetic

anhydride in pyridine, of (A) and (B) gave the crystalline 5-O-acetates (C) and (D), respectively.

The reaction sequence, which can be regarded as a chain-extension in the carbohydrate series, introduces two new centres of chirality at C(5) and C(6) of the heptofuranuronates [(A) and (B)] and their derivatives. Attempts to establish the chirality at these centres by chemical and spectroscopic methods were unsuccessful.

Experimental

Colourless needles of (C) and (D) were grown from their saturated solution in a 1:1 mixture of ethyl acetate and hexane. The crystals were mounted on a Philips PW 1100 four-circle diffractometer, equipped with a graphite monochromator, for the refinement of cell constants and data collection (Mo K α radiation).

Crystal data

(D): Space group $P2_12_12_1$, $a = 18.40$ (1), $b = 14.82$ (1), $c = 8.65$ (1) Å, $Z = 4$, $F(000) = 960$, $\mu = 0.61$ cm $^{-1}$, 2975 reflexions.

(C): Space group $P2_1$, $a = 19.50$ (1), $b = 8.50$ (1), $c = 14.99$ (1) Å, $\beta = 109.0$ (1)°, $Z = 4$, $F(000) = 960$, $\mu = 0.62$ cm $^{-1}$, 2354 reflexions.

Reflexions were scanned in the ω - 2θ mode in steps of 0.03° to cover 1°, and a background count was accumulated on both sides of each peak over the same period as the duration of the peak scan. Data reduction consisted of background and Lp corrections only. Before refinement all unobserved reflexions with $|F| < 3\sigma(F)$ were eliminated. Both structures were solved with *SHELX-76* (Sheldrick, 1976). The structure of (D) was obtained by a standard multiresolution approach which showed up the atoms of the two five-membered rings. The rest of the structure was developed by difference syntheses. The structure of (C) was obtained by incorporating phase information from a two-dimensional analysis into the starting set of phases (Boeyens, 1977).

The asymmetric unit of (D) was small enough to allow anisotropic refinement of all non-hydrogen atoms, but for (C) only the N and O atoms were treated in this way. In both cases the H atoms, which were located on difference maps, were refined with a common isotropic temperature factor. At the termination of refinement $R(D) = 0.05$, $R(C) = 0.07$.

Table 1. Structure (D): final fractional atomic coordinates ($\times 10^4$)

The estimated standard deviations, in parentheses, refer to the last significant digit.

	x	y	z		x	y	z
O(1)	4808 (2)	556 (2)	4238 (4)	H(1)	4969 (25)	1945 (33)	4359 (58)
O(2)	5285 (2)	425 (2)	1817 (3)	H(2)	5588 (27)	1823 (32)	1756 (55)
O(3)	4449 (2)	1122 (2)	508 (3)	H(3)	4527 (26)	2288 (33)	652 (54)
O(4)	4010 (1)	1646 (2)	3388 (3)	H(4)	3637 (26)	630 (34)	1723 (58)
O(5)	2596 (1)	1826 (2)	2624 (3)	H(5)	3292 (26)	2737 (33)	1444 (56)
O(6)	1650 (2)	2371 (2)	821 (4)	H(6)	3162 (27)	1692 (33)	-914 (59)
O(7)	2671 (2)	3184 (2)	975 (4)	H(8.1)	1882 (30)	3798 (33)	-2161 (64)
O(8)	2630 (3)	3268 (2)	3329 (5)	H(8.2)	2417 (31)	4106 (33)	-2613 (67)
O(9)	2672 (3)	474 (2)	2513 (4)	H(9.1)	2586 (27)	4703 (31)	944 (57)
N	2472 (2)	844 (2)	-15 (4)	H(9.2)	1805 (28)	4059 (35)	816 (60)
C(1)	4742 (2)	1411 (3)	3602 (5)	H(9.3)	1875 (28)	5138 (35)	-594 (57)
C(2)	5096 (2)	1348 (3)	1990 (5)	H(11.1)	1895 (29)	2630 (36)	5477 (58)
C(3)	4475 (2)	1610 (3)	896 (4)	H(11.2)	2302 (27)	1678 (32)	5951 (60)
C(4)	3794 (2)	1401 (3)	1842 (4)	H(11.3)	1545 (28)	1915 (34)	4613 (60)
C(5)	3142 (2)	1986 (3)	1445 (4)	H(12)	2218 (26)	-242 (35)	-1095 (61)
C(6)	2814 (2)	1718 (3)	-115 (4)	H(14.1)	5782 (26)	-685 (35)	4853 (65)
C(7)	2288 (2)	2440 (3)	-670 (5)	H(14.2)	6099 (27)	138 (35)	4298 (63)
C(8)	2284 (4)	4001 (4)	-1453 (8)	H(14.3)	6261 (27)	-917 (33)	3017 (60)
C(9)	2101 (4)	4554 (5)	-177 (11)	H(15.1)	4521 (28)	-1288 (34)	3847 (62)
C(10)	2414 (3)	2520 (3)	3543 (5)	H(15.2)	4990 (27)	-1443 (33)	2007 (58)
C(11)	1942 (4)	2195 (5)	4861 (7)	H(15.3)	4273 (29)	-756 (33)	2203 (63)
C(12)	2453 (3)	303 (3)	-1253 (6)	H(16.1)	5053 (27)	928 (33)	-2497 (69)
C(13)	5157 (3)	-64 (3)	3238 (5)	H(16.2)	5472 (29)	1365 (33)	-1137 (61)
C(14)	5876 (3)	-347 (5)	3910 (8)	H(18)	3796 (26)	1907 (33)	-3250 (58)
C(15)	4678 (4)	-857 (5)	2882 (10)	H(19)	3785 (26)	3397 (34)	-4618 (61)
C(16)	5002 (3)	1392 (3)	-1590 (6)	H(20)	4612 (27)	4601 (34)	-4281 (60)
C(17)	4872 (2)	2321 (3)	-2262 (4)	H(21)	5656 (26)	4501 (33)	-2648 (59)
C(18)	4246 (3)	2472 (3)	-3121 (5)	H(22)	5771 (27)	2823 (33)	-1452 (59)
C(19)	4137 (3)	3310 (4)	-3811 (6)	H(N)	2290 (27)	654 (33)	847 (62)
C(20)	4652 (4)	3983 (3)	-3657 (6)				
C(21)	5264 (4)	3848 (4)	-2795 (7)				
C(22)	5373 (3)	2995 (4)	-2077 (6)				

Table 2. *Structure (C): final fractional atomic coordinates ($\times 10^4$)*

	Molecule (C')			Molecule (C'')		
	x	y	z	x	y	z
O(1)	-2028 (5)	0	-2580 (7)	-6649 (4)	88 (10)	-8386 (7)
O(2)	-2038 (5)	2637 (10)	-2683 (7)	-6508 (4)	2738 (9)	-8144 (6)
O(3)	-727 (4)	4092 (9)	-2363 (5)	-5153 (4)	4206 (9)	-7522 (5)
O(4)	-867 (4)	-41 (9)	-2664 (5)	5390 (4)	49 (9)	7737 (5)
O(5)	671 (4)	2386 (8)	-1417 (5)	-4006 (4)	2313 (9)	-6021 (5)
O(6)	1775 (5)	-1286 (12)	-563 (6)	-3029 (5)	-940 (14)	-4916 (6)
O(7)	1504 (5)	-425 (13)	-2036 (6)	-3104 (4)	-1049 (12)	-6413 (6)
O(8)	972 (5)	3339 (12)	-2641 (7)	-3379 (5)	3289 (11)	-6897 (7)
O(9)	-12 (7)	-2772 (18)	-250 (7)	-4830 (6)	-2906 (11)	-5402 (8)
N	438 (5)	-298 (11)	-497 (6)	-4508 (5)	-330 (10)	-5386 (6)
C(1)	-1600 (7)	301 (17)	-3137 (10)	-6005 (7)	468 (16)	-8528 (9)
C(2)	-1652 (7)	2107 (18)	-3271 (10)	-5991 (6)	2258 (15)	-8570 (9)
C(3)	-842 (6)	2619 (16)	-2875 (9)	-5237 (6)	2718 (15)	-7952 (8)
C(4)	-498 (6)	1318 (16)	-2169 (8)	-5079 (6)	1392 (15)	-7189 (8)
C(5)	288 (6)	1094 (15)	-1982 (8)	-4296 (6)	1077 (14)	-6706 (8)
C(6)	567 (6)	-450 (16)	-1394 (8)	-4188 (6)	-451 (14)	-6116 (8)
C(7)	1355 (7)	-755 (17)	-1251 (9)	-3384 (7)	-829 (16)	-5723 (9)
C(8)	2248 (8)	-661 (24)	-2024 (12)	-2319 (8)	-1290 (20)	-6165 (11)
C(9)	2739 (11)	525 (27)	-1506 (14)	-1938 (10)	133 (23)	-6073 (12)
C(10)	982 (7)	3436 (18)	-1855 (10)	-3545 (6)	3371 (16)	-6216 (9)
C(11)	1340 (9)	4738 (22)	-1157 (12)	-3382 (8)	4611 (19)	-5456 (10)
C(12)	168 (7)	-1430 (18)	-112 (10)	-4807 (6)	-1561 (17)	-5086 (10)
C(13)	-2393 (7)	1380 (18)	-2404 (9)	-6957 (6)	1451 (16)	-8082 (8)
C(14)	-2252 (8)	1549 (22)	-1369 (9)	-6950 (9)	1268 (22)	-7114 (11)
C(15)	-3181 (8)	1305 (23)	-2990 (11)	-7728 (9)	1707 (21)	-8787 (12)
C(16)	-1090 (9)	5411 (21)	-2925 (12)	-4891 (8)	5361 (19)	-8034 (10)
C(17)	-776 (7)	5889 (16)	-3696 (9)	-5366 (7)	5568 (16)	-9034 (9)
C(18)	-1131 (8)	5620 (20)	-4638 (11)	-6023 (7)	6366 (18)	-9239 (10)
C(19)	-836 (9)	6089 (22)	-5316 (12)	-6494 (8)	6413 (21)	-10150 (10)
C(20)	-215 (9)	6905 (23)	-5038 (13)	-6317 (8)	5794 (19)	-10870 (11)
C(21)	-183 (10)	7121 (23)	-4125 (12)	-5666 (8)	4982 (21)	-10688 (10)
C(22)	-109 (8)	6635 (19)	-3429 (11)	-5192 (7)	4947 (19)	-9759 (9)
H(1)	-1743 (53)	-64 (143)	-3774 (76)	-5921 (62)	419 (164)	-9192 (87)
H(2)	-1926 (50)	2302 (131)	-4047 (69)	-6201 (61)	2696 (162)	-9215 (85)
H(3)	-568 (51)	2571 (131)	-3385 (68)	-4864 (63)	2392 (160)	-8268 (81)
H(4)	-667 (49)	1227 (136)	-1602 (69)	-5362 (58)	1567 (159)	-6749 (78)
H(5)	391 (49)	925 (131)	-2640 (67)	-4041 (60)	997 (156)	-7245 (81)
H(6)	210 (55)	-1237 (134)	-1804 (71)	-4432 (61)	-1289 (159)	-6594 (83)
H(8.1)	2271 (8)	-746 (24)	-2733 (12)	-2211 (8)	-1998 (20)	-6703 (11)
H(8.2)	2437 (8)	-1748 (24)	-1652 (12)	-2122 (8)	-1891 (20)	-5495 (11)
H(9.1)	3281 (11)	337 (27)	-1528 (14)	-1369 (10)	-117 (23)	-5930 (12)
H(9.2)	2748 (11)	517 (27)	-781 (14)	-2002 (10)	898 (23)	-5531 (12)
H(9.3)	2539 (11)	1647 (27)	-1823 (14)	-2153 (10)	702 (23)	-6751 (12)
H(11.1)	1576 (9)	5453 (22)	-1577 (12)	-3001 (8)	5281 (19)	-5688 (10)
H(11.2)	1756 (9)	4397 (22)	-512 (12)	-3113 (8)	4159 (19)	-4756 (10)
H(11.3)	926 (9)	5405 (22)	-989 (12)	-3827 (8)	5360 (19)	-5446 (10)
H(12)	113 (49)	-1133 (133)	727 (67)	-4833 (59)	-996 (160)	-4368 (78)
H(14.1)	-2499 (8)	519 (22)	-1180 (9)	-6345 (63)	1114 (160)	-6555 (81)
H(14.2)	-2510 (8)	2593 (22)	-1217 (9)	-7253 (67)	673 (173)	-6830 (93)
H(14.3)	-1681 (8)	1571 (22)	-966 (9)	-7036 (70)	2167 (177)	-6836 (90)
H(15.1)	-3193 (49)	1373 (137)	-3645 (72)	-7667 (58)	1943 (159)	-9344 (85)
H(15.2)	-3425 (60)	657 (142)	-2822 (73)	-7840 (67)	1165 (173)	-8572 (86)
H(15.3)	-3536 (59)	2325 (144)	-3036 (69)	-8266 (60)	2482 (160)	-8659 (77)
H(16.1)	-1535 (60)	5143 (139)	-3298 (74)	-4953 (63)	6487 (175)	-7645 (85)
H(16.2)	-951 (51)	5804 (129)	-2300 (75)	-4457 (66)	5131 (163)	-8147 (82)
H(18)	-1648 (8)	5025 (20)	-4849 (11)	-6165 (7)	6936 (18)	-8679 (10)
H(19)	-1104 (9)	5815 (22)	-6052 (12)	-7015 (8)	6976 (21)	-10289 (10)
H(20)	-18 (9)	7403 (23)	-5571 (13)	-6677 (8)	5926 (19)	-11586 (11)
H(21)	713 (10)	7660 (23)	-3933 (12)	-5534 (8)	4379 (21)	-11245 (10)
H(22)	187 (8)	6845 (19)	-2693 (11)	-4664 (7)	4418 (19)	-9616 (9)
H(N)	576 (49)	518 (126)	-162 (64)	-4472 (58)	469 (151)	-5048 (78)

Table 4. Bond angles involving non-hydrogen atoms ($^{\circ}$)

	(D)	(C')	(C'')	Average
C(1)—O(1)—C(13)	113.0 (3)	113.0 (9)	110.7 (10)	112.2 (3)
C(2)—O(2)—C(13)	110.7 (3)	111.0 (10)	110.5 (9)	110.7 (3)
C(3)—O(3)—C(16)	113.1 (3)	113.7 (9)	112.2 (10)	113.0 (3)
C(1)—O(4)—C(4)	109.0 (3)	110.6 (9)	111.3 (9)	110.3 (3)
C(5)—O(5)—C(10)	117.6 (3)	116.4 (9)	117.2 (9)	117.1 (3)
C(7)—O(7)—C(8)	118.9 (4)	117.6 (10)	118.7 (10)	118.4 (4)
C(6)—N—C(12)	120.1 (4)	123.8 (11)	123.0 (10)	122.3 (4)
O(1)—C(1)—O(4)	111.3 (4)	111.8 (11)	112.0 (11)	111.7 (4)
O(1)—C(1)—C(2)	105.4 (3)	103.6 (12)	105.6 (11)	104.9 (3)
O(4)—C(1)—C(2)	107.5 (3)	106.5 (11)	105.2 (9)	106.4 (3)
O(2)—C(2)—C(1)	104.9 (3)	105.2 (12)	104.2 (12)	104.8 (3)
O(2)—C(2)—C(3)	111.2 (3)	110.7 (11)	110.0 (10)	110.6 (3)
C(1)—C(2)—C(3)	103.1 (3)	102.3 (11)	105.1 (9)	103.5 (3)
O(3)—C(3)—C(2)	115.1 (3)	114.1 (11)	117.3 (10)	115.5 (3)
O(3)—C(3)—C(4)	109.2 (3)	107.6 (9)	110.3 (9)	109.0 (3)
C(2)—C(3)—C(4)	103.2 (3)	103.0 (11)	100.4 (9)	102.2 (3)
O(4)—C(4)—C(3)	102.7 (3)	101.0 (8)	102.2 (8)	102.0 (3)
O(4)—C(4)—C(5)	106.5 (3)	108.0 (10)	108.3 (10)	107.6 (3)
C(3)—C(4)—C(5)	114.2 (3)	114.8 (11)	114.3 (10)	114.4 (3)
O(5)—C(5)—C(4)	107.1 (3)	108.7 (10)	108.5 (10)	108.1 (3)
O(5)—C(5)—C(6)	107.7 (3)	106.8 (8)	104.7 (8)	106.4 (3)
C(4)—C(5)—C(6)	111.3 (3)	111.2 (11)	110.9 (10)	111.1 (3)
N—C(6)—C(5)	110.6 (3)	108.2 (10)	111.5 (10)	110.1 (3)
N—C(6)—C(7)	111.9 (3)	111.1 (9)	111.8 (9)	111.6 (3)
C(5)—C(6)—C(7)	110.3 (3)	112.0 (11)	109.3 (10)	110.5 (3)
O(6)—C(7)—O(7)	124.9 (4)	124.4 (13)	122.1 (12)	123.8 (4)
O(6)—C(7)—C(6)	127.1 (4)	125.3 (14)	126.7 (13)	126.4 (4)
O(7)—C(7)—C(6)	107.9 (3)	110.2 (10)	111.2 (9)	109.8 (3)
O(7)—C(8)—C(9)	112.0 (5)	113.3 (17)	112.4 (14)	112.6 (5)
O(5)—C(10)—O(8)	122.5 (4)	124.9 (13)	122.4 (11)	123.3 (4)
O(5)—C(10)—C(11)	110.2 (4)	108.7 (13)	106.9 (12)	108.6 (4)
O(8)—C(10)—C(11)	127.2 (5)	126.4 (15)	130.5 (13)	128.0 (5)
O(9)—C(12)—N	126.7 (4)	121.1 (14)	124.0 (14)	123.9 (4)
O(1)—C(13)—O(2)	105.6 (3)	104.1 (11)	105.6 (10)	105.1 (3)
O(1)—C(13)—C(14)	110.1 (5)	109.5 (11)	111.1 (12)	
O(1)—C(13)—C(15)	111.5 (5)	109.4 (12)	108.0 (10)	
O(2)—C(13)—C(14)	109.0 (4)	107.1 (12)	109.9 (11)	109.6 (2)
O(2)—C(13)—C(15)	108.3 (5)	111.5 (12)	109.3 (11)	
C(14)—C(13)—C(15)	112.1 (5)	114.7 (13)	112.8 (13)	113.2 (5)
O(3)—C(16)—C(17)	113.0 (3)	113.9 (14)	113.8 (11)	113.6 (3)
C(16)—C(17)—C(18)	118.9 (4)	122.7 (13)	120.3 (13)	
C(16)—C(17)—C(22)	120.8 (4)	118.3 (12)	121.7 (13)	120.5 (3)
C(18)—C(17)—C(22)	120.2 (4)	119.0 (15)	118.0 (11)	
C(17)—C(18)—C(19)	119.5 (5)	121.2 (14)	120.1 (14)	
C(18)—C(19)—C(20)	120.2 (5)	118.1 (16)	121.6 (14)	
C(19)—C(20)—C(21)	120.9 (5)	123.4 (20)	119.6 (13)	120.0 (2)
C(20)—C(21)—C(22)	118.9 (5)	118.4 (17)	118.0 (15)	
C(17)—C(22)—C(21)	120.3 (5)	119.3 (13)	122.4 (14)	

(Cremer & Pople, 1975) was developed. This involves transformation to a set of molecular axes defined in such a way that x and y are in the mean plane with y along the projection of the positional vector \mathbf{R}_1 in the plane. The z coordinates directly define the deviations of the atoms from the plane. These puckering coordinates are listed in Table 6 with the endocyclic torsion angles. These refer to the bonds following each atom in a clockwise progression. The puckering parameters $q(2)$ and $P(2)$ (Table 6) for five-membered rings are a puckering amplitude (\AA) and a phase angle ($^{\circ}$) which refer to a pseudo-rotational cycle with reference point at the 0E envelope conformation. Table 6 shows that

the sugar rings of (D) and (C') are much alike and close to the 4E conformation which occurs at $P(2) = 324^{\circ}$ (Altona & Sundaralingam, 1972). (C'') is slightly different and corresponds better to the 3T conformation (306°). Both conformations are reasonably close to one of the regions (270 – 306°) favoured by a large number of sugar rings (Altona & Sundaralingam, 1972).

(ii) Conformation of the isopropylidene rings

The puckering parameters and torsion angles for these rings are also listed in Table 6. The closest correspondence occurs once again for the rings of (D) and

Table 5. A selection of torsion angles to describe the molecular conformations ($^{\circ}$)

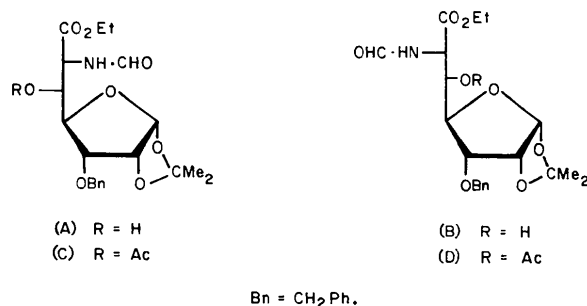
	(D)	(C')	(C'')
O(1)-C(1)-C(2)-O(2)	-4.3	-6.5	-18.7
C(1)-C(2)-O(2)-C(13)	6.6	15.7	15.4
C(2)-C(1)-O(1)-C(13)	0.5	-4.7	15.4
O(1)-C(13)-O(2)-C(2)	-6.4	-18.3	-6.6
O(2)-C(13)-O(1)-C(1)	3.5	14.1	-6.2
O(4)-C(1)-C(2)-C(3)	-2.0	-4.2	-15.8
C(1)-C(2)-C(3)-C(4)	23.3	26.6	33.1
C(2)-C(1)-O(4)-C(4)	-22.1	-22.1	-10.7
C(1)-O(4)-C(4)-C(3)	37.0	39.1	31.7
O(4)-C(4)-C(3)-C(2)	-36.4	-39.2	-39.1
O(4)-C(1)-O(1)-C(13)	-115.8	-119.0	-98.5
O(1)-C(1)-O(4)-C(4)	92.9	90.4	103.5
C(3)-C(2)-O(2)-C(13)	117.4	125.5	127.5
O(2)-C(2)-C(3)-C(4)	-88.7	-85.1	-78.5
O(4)-C(4)-C(5)-O(5)	56.6	175.3	170.0
O(5)-C(5)-C(4)-C(3)	169.3	-72.9	-76.9
O(4)-C(4)-C(5)-C(6)	174.2	58.0	55.5
C(3)-C(4)-C(5)-C(6)	-73.2	169.8	168.6
O(5)-C(5)-C(6)-N	47.9	-57.5	-54.6
N-C(6)-C(5)-C(4)	-69.3	60.9	62.2
O(5)-C(5)-C(6)-C(7)	-76.5	65.3	69.4
C(4)-C(5)-C(6)-C(7)	166.4	-176.2	-173.7
C(5)-C(6)-N-C(12)	149.1	-135.8	-146.7
C(7)-C(6)-N-C(12)	-87.5	100.8	90.7
O(7)-C(7)-C(6)-N	169.9	161.3	-175.5
O(7)-C(7)-C(6)-C(5)	-66.6	40.2	60.6
O(6)-C(7)-C(6)-C(5)	113.6	-143.3	-120.0
O(6)-C(7)-C(6)-N	-9.9	-22.2	3.9
C(2)-C(3)-O(3)-C(16)	74.5	60.4	98.4
C(4)-C(3)-O(3)-C(16)	-169.9	173.9	-147.5
C(3)-O(3)-C(16)-C(17)	70.4	68.8	-58.0

(C'). The conformation of the (D) ring is close to 2E (252°) and that of (C') is close to 1T (234°). These are both 180° away from and hence enantiomorphs of the second preferred region at $54-90^{\circ}$ (Altona & Sundaralingam, 1972). The (C'') isopropylidene ring has the same 3T conformation as the (C'') sugar ring.

(iii) Orientation of the side chains

The centres at C(5) and C(6) both have *S* chirality (Cahn, Ingold & Prelog, 1956) in the (D) molecule and

R chirality in both (C) molecules. The change of chirality at C(5) is shown by the torsion angles around C(4)-C(5) (Table 5). To observe the change at C(6), compare the angles O(5)-C(5)-C(6)-N and O(5)-C(5)-C(6)-C(7). The two chemically different molecules can thus be named systematically as: (C) ethyl 5-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-formylamino-1,2-*O*-isopropylidene-*L*-glycero-*D*-allo-heptofuranuronate; (D) ethyl 5-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-formylamino-1,2-*O*-isopropylidene-*D*-glycero-*L*-talo-heptofuranuronate. The structural formulae are:



The most obvious difference between the two molecules in (C) is the orientation of their benzyl groups. In (C'), as in (D), it is tilted away from the isopropylidene ring, but in (C'') it is directed towards the isopropylidene. This is brought about by a relative rotation of some 127° about O(3)-C(16) (Table 5).

(iv) Hydrogen bonding

The only hydrogen bond in any of these structures occurs between each NH group and the carbonyl O(9) of a 2_1 -related molecule (Table 7). This is the most important intermolecular interaction and leads to the formation of screw-related parallel stacks interconnected by hydrogen bonds. These paired stacks are the basic building units in the structure and all the observed deformations occur to ensure close-packing without affecting the integrity of these units.

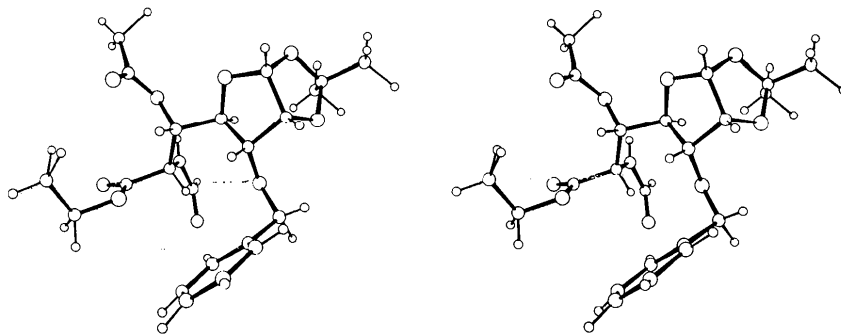


Fig. 2. Stereoscopic drawing of the (D) molecule.

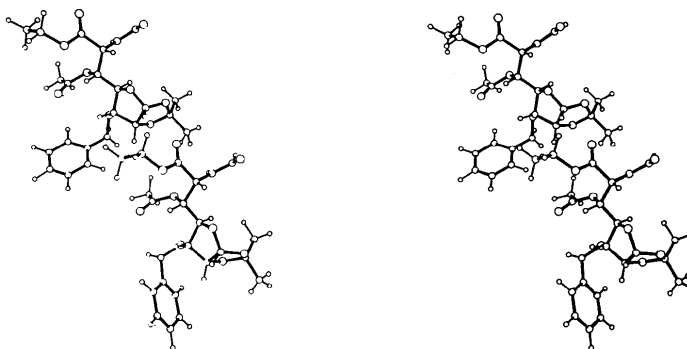


Fig. 3. Stereoscopic drawing of the two molecules in the asymmetric unit of (C).

Table 6. Conformational details of the five-membered rings

	Puckering coordinates (Å)									Endocyclic torsion angles (°)		
	x			y			z			(D)	(C')	(C'')
	(D)	(C')	(C'')	(D)	(C')	(C'')	(D)	(C')	(C'')			
Sugar ring												
O(4)	0	0	0	1.1933	1.1723	1.1920	+0.1724	+0.1761	+0.1237	-22.1	-22.1	-10.7
C(1)	1.1608	1.1729	1.1906	0.4368	0.4331	0.4067	-0.0523	-0.0422	+0.0239	-2.0	-4.2	-15.8
C(2)	0.7473	0.7495	0.7095	-1.0486	-1.0536	-1.0266	-0.0878	-0.1078	-0.1623	23.3	26.6	33.1
C(3)	-0.7596	-0.7719	-0.7494	-0.9993	-0.9788	-1.0052	+0.1944	+0.2167	+0.2388	-36.4	-39.2	-39.1
C(4)	-1.1484	-1.1504	-1.1507	0.4178	0.4269	0.4331	-0.2267	-0.2428	-0.2240	37.0	39.1	31.7
									<i>q</i> (2) (Å)	0.36	0.39	0.39
									<i>P</i> (2) (°)	319	316	300
Isopropylidene ring												
O(1)	0	0	0	1.1874	1.1751	1.1923	-0.0083	-0.0519	+0.0636	3.5	14.1	-6.2
C(13)	1.1695	1.1740	1.1757	0.3894	0.3534	0.3527	+0.0288	+0.0927	+0.0009	-6.4	-18.3	-6.6
O(2)	0.7070	0.6994	0.6871	-0.9796	-0.9592	-0.9822	-0.0384	-0.0980	-0.0650	6.6	15.7	15.4
C(2)	-0.7097	-0.6964	-0.7187	-1.0347	-1.0190	-1.0054	+0.0333	+0.0660	+0.1043	-4.3	-6.5	-18.7
C(1)	-1.1668	-1.1770	-1.1441	0.4375	0.4498	0.4425	-0.0155	-0.0087	-0.1037	0.5	-4.7	15.4
									<i>q</i> (2) (Å)	0.06	0.16	0.17
									<i>P</i> (2) (°)	258	239	306

Table 7. Interatomic distances (Å) pertaining to the N—H...O hydrogen bonds

	(D)	(C')	(C'')
N—H(N)	0.86 (5)	0.85 (10)	0.84 (13)
O(9)...H(N)	2.19	2.27	2.19
O(9)...N	2.93	2.92	2.88

Discussion of the structures

The most interesting crystallographic feature of the structures is the occurrence of two molecules of (C) in the asymmetric unit. The system of hydrogen bonds has already been implicated as the cause of this. In (D) the paired stacks pack without any steric hindrance and all the molecules are crystallographically equivalent. However, because of the different stereochemistry at C(6) this is no longer possible in (C). In stacks

containing the molecules (C') the orientation of the benzyl groups is about the same as in (D) and in the crystal they occur together with stacks of the crystallographically different (C'') molecules in a pseudo *B*-centred arrangement.

(C'') differs from (C') mainly in the orientation of the benzyl groups and the conformation of the five-membered rings. Some of the closest intramolecular contacts in (C'') occur between the five-membered rings and the phenyl ring. This suggests that the different conformation of the rings is caused by the changed orientation of the benzyl group.

A three-dimensional model of the structure shows that replacement of the (C'') stacks by (C') stacks would lead to steric interference between the C(9) atoms of one paired stack with the benzyl groups of another. More comfortable packing results from the interleaving of (C') stacks with stacks of (C'').

There is no obvious steric effect that would impair

the packing of equivalent paired stacks of the (C'') type. The inference is that (C') is of lower energy than (C'') and that it is energetically favourable to convert half of the molecules into (C'') to relieve packing strain, but unfavourable to convert them all into (C''). The result is a molecular complex in which the total molecular and packing strain energy is a minimum.

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Positional Disorder and Non-Stoichiometry in $\text{Cu}_{2-x}\text{Mo}_3\text{S}_4$ Compounds. I. Single-Crystal Studies of $\text{Cu}_{2-x}\text{Mo}_3\text{S}_4$ ($x = 1.1, 0.62, 0.53, 0.17$) at Room Temperature

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The results of an X-ray investigation of $\text{Cu}_{2-x}\text{Mo}_3\text{S}_4$ alloys as a function of the Cu concentration are reported. The structure is described in terms of a model consisting of rigid Mo_6S_8 building blocks with a rhombohedral stacking. The building blocks are cubes of S atoms which are centred by an octahedron formed by Mo atoms. At room temperature, the Cu atoms are found in tetrahedral interstices of the S atom network. 12 of these holes are very close together and form a cluster. These cluster sites correspond to two sixfold equivalent crystallographic positions which are filled to a different extent if the Cu content of the compound is increased. The maximum possible Cu occupation is four atoms per cluster which corresponds to the formula $\text{Cu}_2\text{Mo}_3\text{S}_4$. The Mo:S ratio was found to be constant in all compounds. Analyses of the thermal parameters suggest that the Mo_6 octahedra form stable units which vibrate preferentially around and along the ternary axis and that the Cu atoms of the first site undergo large anisotropic oscillations (r.m.s. amplitude = 0.3 Å) in the direction of the Cu atoms of the second site and *vice versa*. Cu atoms on peripheral sites that belong to adjacent clusters are separated by only 2.1–2.4 Å. Ionic d.c. conduction is therefore possible. Variations in the interatomic distances with increasing Cu content correspond to a general expansion of the structure except for the Mo–Mo contacts which decrease. This contraction is interpreted by assuming partially filled *d* orbitals localized on the Mo atoms which become more populated with increasing Cu concentration, the latter element acting as an electron donor. The ionic formula $\text{Cu}_x^+[\text{Mo}_6^{2+}\text{S}_8^{2-}]^{4-}$ is proposed.

Introduction

Ternary Mo sulphides of formula $M_x\text{Mo}_3\text{S}_4$, $M =$ transition element, metal or rare-earth element,

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$0 < x \leq 2$ (Chevrel, Sergent & Prigent, 1971; Fischer, Treyvaud, Chevrel & Sergent, 1975), are of interest because of their outstanding physical properties at low temperatures. The compounds are generally good superconductors (Matthias, Marezio, Corenzwit, Cooper & Barz, 1972), yield exceptionally high critical fields (Fischer, 1974) and have a marked pressure