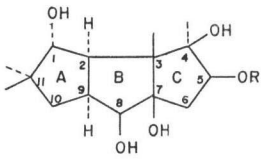
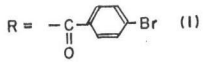
ABSOLUTE CONFIGURATION OF CORIOLIN, A SESQUITERPENE ANTIBIOTIC FROM *CORIOLUS CONSORS*

Sir:

Previously,[1] based on nmr analysis we reported the stereochemistry of the coriolins and pointed out the structural similarity of their skeleton to that of hirsutic acid.[2] In this communication we describe the result of the X-ray structure determination of hexahydrocoriolin, a hydrogenated product of coriolin, using a heavy atom derivative.





The crystals of hexahydrocoriolin *p*-bromobenzoate (**I**) grown from benzene solutions containing 5 % of methanol were colorless transparent prisms elongated along the c axis. Oscillation and Weissenberg photographs indicated the space group $P2_12_12_1$. The lattice constants and intensities were measured on a Rigaku four-circle X-ray diffractometer using Ni-filtered CuKα radiation. Crystal data are as follows: Orthorhombic, $P2_12_12_1$, a=11.403 $\pm$0.005, b=25.893$\pm$0.010, c=7.462$\pm$0.003Å, Z=4, Dx=1.415 g·cm^{-3}. Intensities of 1537 reflexions out of 2323 theoretically possible ones with 2θ values less than 135°, were obtained at the 3σ level using the $\omega-2\theta$ scanning method. The scanning speed was chosen to be 4°/min and the background was measured at both sides of each diffraction peak for 10 seconds.

The structure was solved by the heavy atom method and refined by the block-matrix least-squares method allowing anisotropic thermal vibrations for each atom. The final R value was 0.076. The absolute configuration was determined by the method of anomalous dispersion. The dispersion corrections for the bromine-scattering factor for CuKα radiation were $\Delta f'=-0.9$ and $\Delta f''=1.5$. Comparison of the observed and calculated intensities of 19 pairs of hk$l$ and h$\bar{k}l$ reflexions for l=1, 2, 3, indicated the absolute configuration as shown in Fig. 1. The final atomic parameters are listed in Table 1.

The bond lengths and angles are shown in Fig. 1. No abnormal values are found in the present structure. The mean C–C length and C–C–C angle involved in each five membered ring are: 1.566 Å, 104.8° for ring A, 1.583 Å, 105.0° for B and 1.566 Å, 103.6° for C. The torsion angles around the successive C–C bonds along the skeleton of the five membered ring are: C(1)-C(2)=−33.7°, C(2)-C(9)=14.9°, C(9)-C(10)=10.6°, C(10)-C(11)=−31.1°, C(11)-C(1)=41.0° in ring A, C(2)-C(3)=6.6°, C(3)-C(7)=−28.6°, C(7)-C(8)=39.5°, C(8)-C(9)=−34.4°, C(9)-C(2)=16.8° in B and C(3)-C(4)=44.7°, C(4)-C(5)=−44.8°, C(5)-C(6)=26.1°, C(6)-C(7)=2.0°, C(7)-C(3)=−28.9° in C, indicating that the conformation of ring A is a twist form while that of ring B is deformed envelope and ring C is envelope. The stereochemistry determined by the present

Fig. 1. Molecular structure of hexahydrocoriolin *p*-bromobenzoate showing absolute configuration, bond lengths and angles. The mean standard deviations σ(C-C) and $\sigma(\angle$C-C-C), are estimated to be 0.02Å and 1.2°

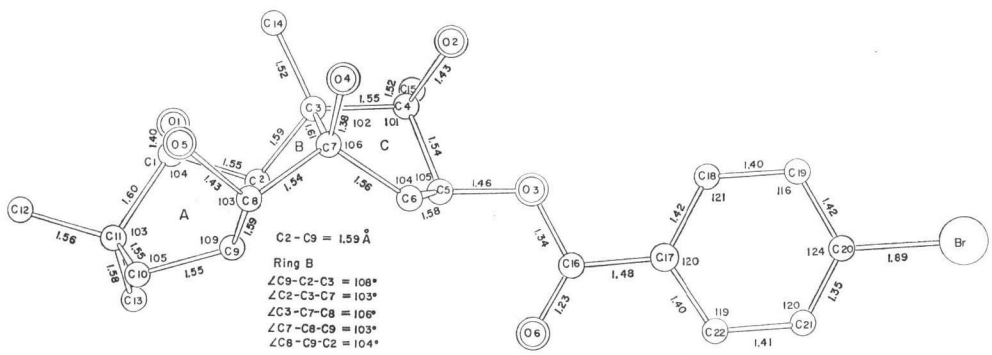


Table 1. Final atomic parameters

Temperature factors are of the form $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$
To represent the correct absolute configuration the x, y, z coordinates should be referred to the left hand coordinate system.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
BR	0.7722(2)	0.6030(1)	0.2678(3)	0.0120(2)	0.0003(0)	0.0268(4)	0.0004(1)	0.0008(3)	0.0000(1)
O(1)	0.6270(10)	0.1239(4)	0.5958(15)	0.0074(11)	0.0011(2)	0.0125(24)	0.0001(4)	0.0030(15)	0.0005(5)
O(2)	0.5053(8)	0.2911(3)	0.2361(19)	0.0051(8)	0.0008(1)	0.0228(27)	0.0002(3)	0.0000(18)	0.0008(7)
O(3)	0.7102(8)	0.3423(3)	0.2705(17)	0.0054(8)	0.0006(1)	0.0208(25)	−0.0003(3)	0.0002(18)	0.0007(6)
O(4)	0.5640(10)	0.2258(4)	−0.0706(14)	0.0094(12)	0.0013(2)	0.0087(23)	0.0002(4)	−0.0018(15)	0.0011(6)
O(5)	0.6563(11)	0.1280(4)	−0.0300(16)	0.0106(13)	0.0009(2)	0.0166(28)	−0.0011(4)	0.0022(17)	−0.0007(6)
O(6)	0.9093(9)	0.3451(3)	0.2702(21)	0.0062(9)	0.0008(1)	0.0283(32)	−0.0001(3)	0.0004(20)	0.0000(7)
C(1)	0.6696(14)	0.1218(5)	0.4199(24)	0.0054(14)	0.0006(2)	0.0169(36)	−0.0003(4)	−0.0003(21)	−0.0002(7)
C(2)	0.7052(13)	0.1750(5)	0.3430(19)	0.0041(13)	0.0008(2)	0.0105(28)	−0.0005(4)	0.0011(18)	0.0003(6)
C(3)	0.6038(12)	0.2081(4)	0.2524(25)	0.0051(12)	0.0007(2)	0.0144(34)	−0.0002(4)	0.0012(25)	0.0007(9)
C(4)	0.5972(14)	0.2640(5)	0.3253(23)	0.0054(13)	0.0006(2)	0.0175(39)	−0.0001(4)	0.0008(20)	0.0002(7)
C(5)	0.7151(11)	0.2861(4)	0.2619(24)	0.0034(10)	0.0006(2)	0.0189(34)	−0.0005(4)	0.0027(25)	−0.0005(8)
C(6)	0.7272(17)	0.2677(5)	0.0615(21)	0.0105(17)	0.0007(2)	0.0141(34)	−0.0004(5)	0.0044(25)	0.0003(7)
C(7)	0.6521(15)	0.2173(6)	0.0524(22)	0.0080(16)	0.0009(2)	0.0110(34)	−0.0003(5)	0.0007(21)	−0.0005(8)
C(8)	0.7312(17)	0.1706(5)	0.0095(22)	0.0095(18)	0.0008(2)	0.0133(33)	0.0002(6)	0.0013(25)	−0.0003(7)
C(9)	0.7983(13)	0.1607(5)	0.1926(23)	0.0054(14)	0.0009(2)	0.0184(39)	0.0001(4)	0.0054(20)	−0.0006(7)
C(10)	0.8376(15)	0.1041(5)	0.2207(28)	0.0105(16)	0.0003(2)	0.0250(46)	0.0016(5)	0.0011(28)	−0.0002(11)
C(11)	0.7871(15)	0.0885(5)	0.4059(22)	0.0070(15)	0.0006(2)	0.0159(34)	0.0006(5)	−0.0012(22)	−0.0003(7)
C(12)	0.7509(20)	0.0306(6)	0.4199(27)	0.0137(26)	0.0008(2)	0.0265(45)	0.0007(7)	0.0043(36)	0.0004(9)
C(13)	0.8736(15)	0.1017(7)	0.5649(26)	0.0068(16)	0.0014(3)	0.0228(43)	0.0011(6)	−0.0030(23)	0.0004(11)
C(14)	0.4852(12)	0.1818(5)	0.2520(28)	0.0038(11)	0.0011(2)	0.0177(35)	−0.0006(4)	0.0002(25)	0.0008(10)
C(15)	0.5767(17)	0.2686(6)	0.5254(24)	0.0101(20)	0.0012(3)	0.0111(36)	−0.0001(6)	0.0038(23)	0.0003(8)
C(16)	0.8138(13)	0.3668(5)	0.2699(26)	0.0080(15)	0.0007(2)	0.0156(36)	0.0001(4)	−0.0007(25)	−0.0001(9)
C(17)	0.8017(12)	0.4237(5)	0.2678(25)	0.0051(12)	0.0009(2)	0.0166(35)	−0.0001(4)	−0.0000(24)	−0.0009(9)
C(18)	0.6896(12)	0.4477(5)	0.2742(28)	0.0050(12)	0.0008(2)	0.0223(42)	−0.0000(4)	−0.0006(25)	0.0003(9)
C(19)	0.6787(14)	0.5013(5)	0.2639(32)	0.0086(16)	0.0010(2)	0.0264(49)	0.0008(5)	−0.0003(32)	−0.0009(11)
C(20)	0.7848(15)	0.5300(4)	0.2694(25)	0.0096(16)	0.0005(2)	0.0177(36)	−0.0002(4)	0.0006(31)	0.0002(8)
C(21)	0.8924(13)	0.5081(5)	0.2699(35)	0.0038(12)	0.0009(2)	0.0397(58)	−0.0001(4)	0.0015(31)	0.0004(12)
C(22)	0.9034(15)	0.4541(5)	0.2627(34)	0.0075(15)	0.0010(2)	0.0300(52)	−0.0000(5)	0.0012(36)	0.0002(13)

analysis is in complete agreement with that derived by the chemical method.[1]

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