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Crystal structure of (5*R*,10*R*)-2,7-dibromo-3,8-dihydroxy-5,10-dimethoxy-5,10-dihydrochromeno[5,4,3-*cde*]chromene sesquihydrate, $C_{16}H_{12}Br_2O_6 \cdot 1.5\,H_2O$

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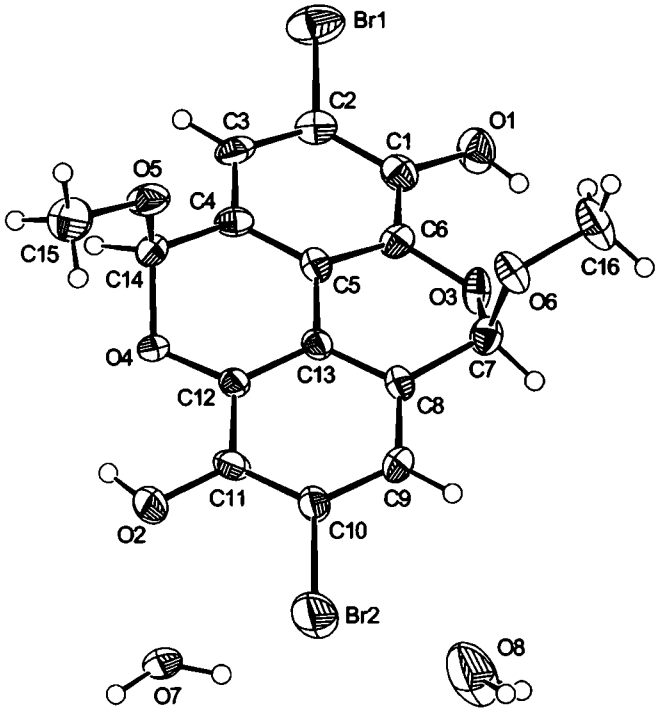

Abstract

$C_{16}H_{15}Br_2O_{7.5}$, orthorhombic, $P2_12_12$ (no. 18), a = 18.483(2) Å, b = 9.413(1) Å, c = 10.072(1) Å, V = 1752.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.083, $wR_{ref}(F^2)$ = 0.202, T = 293 K.

Source of material

The title compound was isolated from *Polysiphonia urceolata* collected from the coast of Qingdao, Shandong Province. Air-dried *Polysiphonia urceolata* (9.6 kg) was extracted with 95 % EtOH (30 L) at room temperature. Solvent was removed in vacuo and yielded a dark residue. The residue was suspended in water and then partitioned with EtOAc. The EtOAc fraction (200 g) was chromatographed over silica gel (2.0 kg, 100-200 mesh) column with a gradient increasing acetone (0-100 %) in chloroform (changing when the eluent being colorless). The 20 % acetone fraction (2.3 g) was subjected to silica gel (250 g, 200-300 mesh) column chromatograph eluted with petroleum ether/acetone (*v*/*v* 4:1) and purified through a sephadex LH-20 column (yield 62 mg). Colorless crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature from a solution containing petroleum ether and acetone in a 3:1 ratio.

Experimental details

The absolute structure was confirmed by the value of the Flack parameter of x = 0.00(9).

Discussion

The planar molecule of the title compound has been elucidated to have a symmetric tetracyclic structure by spectroscopic methods (including NMR, MS and optical rotation). In order to determine the stereochemistry of the two chiral centres at C7 and C14, we conducted the X-ray analysis. The diffraction analysis indicated an axial-symmetric molecule and both C7 and C14 to be *R*-configuration. This molecule has not the postulated planar structure, the benzene rings have a dihedral angle of 15.9°. Two hydroxyl groups form intramolecular hydrogen bonds with *ortho* oxygen atoms [d(O1–H1···O3) = 2.909 Å, d(O2–H2···O4) = 2.708 Å]. 1.5 water molecules are found per asymmetric unit. One water molecule is integrated with Br2 and O6 [d(O8–H19···Br2) = 2.881 Å, d(O8–H20···O6) = 2.103 Å]. O1 and O3 share one proton of the other water [d(O7–H18···O1) = 2.118 Å, d(O7–H18···O3) = 2.503 Å]. For a complete hydrogen bond pattern, the H atoms of the hydroxyl groups and the O7 water molecule occupy two different positions. A resolving of this disorder was ignored.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.07 × 0.37 × 0.52 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	46.65 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10632, 4044
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2323
$N(param)_{refined}$:	254
Programs:	SHELXS-97 [1], SHELXL-97 [2]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4c	–0.0095	0.7000	–0.0831	0.071
H(2)	4c	0.0989	0.4986	0.6934	0.076
H(3)	4c	–0.0824	0.9209	0.3509	0.045
H(9)	4c	0.2111	0.3562	0.2577	0.045
H(15A)	4c	0.0487	0.9004	0.7115	0.094
H(15B)	4c	0.1192	0.9806	0.6679	0.094
H(15C)	4c	0.1199	0.8148	0.6834	0.094
H(16A)	4c	0.2007	0.6028	–0.1113	0.096
H(16B)	4c	0.2275	0.7556	–0.0737	0.096
H(16C)	4c	0.1445	0.7251	–0.0885	0.096
H(7)	4c	0.144(5)	0.459(6)	0.056(8)	0.04(3)
H(14)	4c	–0.026(4)	0.795(8)	0.559(8)	0.02(2)
H(18)	4c	0.006(7)	0.587(6)	0.84(1)	0.07(4)
H(19)	4c	0.165(5)	0.21(1)	0.772(7)	0.06(4)
H(20)	4c	0.221(2)	0.23(2)	0.83(1)	0.11(5)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4c	–0.13262(6)	0.9801(1)	0.0888(1)	0.0688(7)	0.0451(6)	0.0764(8)	0.0094(5)	–0.0326(6)	0.0030(6)
Br(2)	4c	0.23683(7)	0.2480(2)	0.5202(1)	0.0942(9)	0.085(1)	0.0615(7)	0.0546(8)	0.0154(7)	0.0287(7)
O(1)	4c	–0.0376(3)	0.7565(8)	–0.0488(6)	0.051(4)	0.060(4)	0.031(4)	0.006(3)	–0.009(3)	–0.002(3)
O(2)	4c	0.1283(4)	0.4438(7)	0.6601(6)	0.075(5)	0.050(4)	0.027(3)	0.025(4)	0.004(3)	0.010(3)
O(3)	4c	0.0654(3)	0.5883(7)	0.0626(5)	0.041(3)	0.055(4)	0.021(3)	0.000(3)	–0.001(2)	–0.012(3)
O(4)	4c	0.0410(3)	0.6413(5)	0.5480(6)	0.052(4)	0.019(3)	0.027(3)	0.005(2)	0.004(3)	0.001(2)
O(5)	4c	0.0710(4)	0.8806(6)	0.5225(6)	0.067(4)	0.025(3)	0.039(4)	–0.001(3)	–0.015(3)	–0.004(3)
O(6)	4c	0.1861(3)	0.6500(7)	0.0781(6)	0.038(3)	0.053(4)	0.026(3)	–0.005(3)	0.000(3)	0.009(3)
O(7)	2b	0	½	0.8056(9)	0.074(6)	0.048(7)	0.020(5)	0.011(5)	0	0
O(8)	4c	0.1746(6)	0.259(2)	0.846(1)	0.098(7)	0.16(1)	0.076(7)	0.074(8)	0.025(6)	0.050(9)
C(1)	4c	–0.0247(4)	0.764(1)	0.081(1)	0.035(5)	0.037(5)	0.035(5)	–0.007(4)	–0.001(4)	0.003(5)
C(2)	4c	–0.0635(4)	0.8549(9)	0.1654(9)	0.028(4)	0.030(4)	0.043(5)	–0.004(4)	–0.010(4)	0.001(4)
C(3)	4c	–0.0540(5)	0.8609(8)	0.299(1)	0.046(5)	0.018(4)	0.049(6)	0.000(4)	0.001(4)	–0.002(4)
C(4)	4c	–0.0016(5)	0.7764(8)	0.3575(8)	0.031(4)	0.022(4)	0.042(5)	–0.006(3)	–0.002(4)	0.002(4)
C(5)	4c	0.0388(4)	0.6899(9)	0.2762(8)	0.031(5)	0.034(5)	0.026(5)	–0.003(4)	0.003(3)	0.002(4)
C(6)	4c	0.0277(4)	0.6840(9)	0.1404(9)	0.027(4)	0.028(4)	0.036(5)	–0.005(3)	–0.001(4)	–0.006(4)
C(7)	4c	0.1344(5)	0.5452(8)	0.1062(9)	0.034(4)	0.036(5)	0.032(5)	–0.004(4)	0.002(4)	–0.007(4)
C(8)	4c	0.1378(4)	0.5149(9)	0.2533(8)	0.028(4)	0.033(4)	0.023(4)	–0.004(4)	0.003(3)	0.001(3)
C(9)	4c	0.1806(5)	0.411(1)	0.3100(9)	0.042(5)	0.036(5)	0.036(5)	0.013(4)	0.010(4)	–0.002(4)
C(10)	4c	0.1774(5)	0.390(1)	0.4461(8)	0.040(5)	0.041(5)	0.029(5)	0.012(4)	0.007(4)	0.006(4)
C(11)	4c	0.1317(5)	0.4670(8)	0.5272(9)	0.038(4)	0.030(4)	0.037(5)	0.003(4)	0.004(4)	0.012(4)
C(12)	4c	0.0881(4)	0.5711(8)	0.4682(8)	0.038(5)	0.022(4)	0.023(4)	–0.004(3)	–0.002(4)	0.000(3)
C(13)	4c	0.0907(4)	0.5919(8)	0.3335(8)	0.037(5)	0.024(4)	0.023(4)	–0.007(3)	0.000(4)	0.000(3)
C(14)	4c	0.0171(5)	0.7791(9)	0.5018(9)	0.044(5)	0.029(5)	0.029(5)	0.009(4)	0.002(4)	–0.003(4)
C(15)	4c	0.0913(7)	0.895(1)	0.657(1)	0.104(9)	0.048(6)	0.036(6)	–0.008(6)	–0.020(6)	–0.013(5)
C(16)	4c	0.1900(6)	0.686(1)	–0.060(1)	0.071(8)	0.089(9)	0.031(6)	0.000(6)	0.008(5)	0.017(6)

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