Crystal structure of 12*a*-hydroxy-2,3,9-trimethoxy-12-oxo-6,6*a*,12,12*a*-tetrahydrochromeno[3,4-*b*]chromen-11-yl 4-methylbenzenesulfonate, $C_{26}H_{24}O_{10}S$

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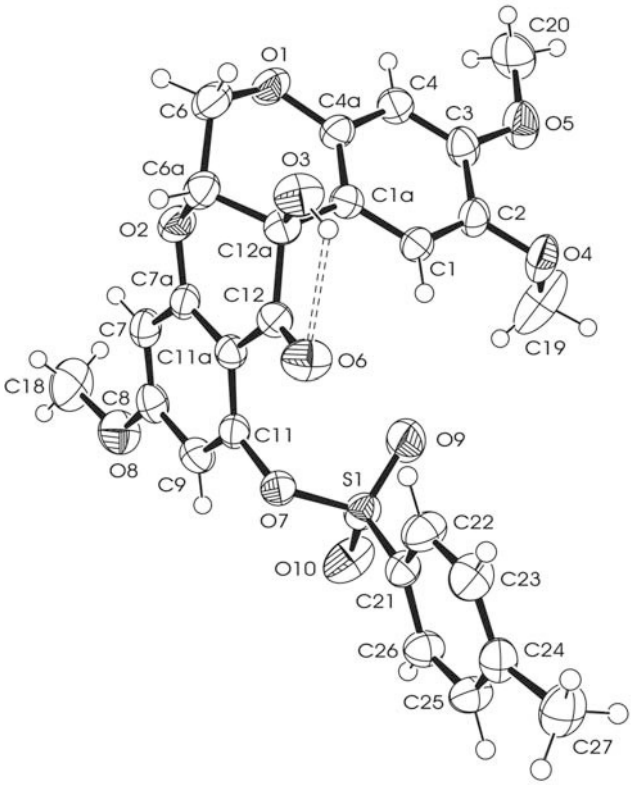

Abstract

$C_{26}H_{24}O_{10}S$, monoclinic, $P2_1$ (no. 4), a = 8.4239(4) Å, b = 16.9458(6) Å, c = 8.8568(4) Å, β = 105.480(1)°, V = 1218.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.100, T = 296 K.

Source of material

The product was obtained *via* a sulfonation reaction of toluenesulfonyl chloride and 6-deoxyclitoriacetal in the present of K_2CO_3 as a base. To a solution of anhydrous potassium carbonate (0.92 g, 6.55 mmol) and *p*-toluenesulfonyl chloride (0.51 g, 2.66 mmol), a solution of 6-deoxyclitoriacetal (0.50 g, 1.33 mmol) in dry acetone (10 ml) were added. The mixture was stirred under reflux for 24 h. Upon cooling the precipitate was filtered off, washed with acetone (20 ml), the filtrates were vacuum evaporated and the residue was purified by column chromatography using a mixture of hexane/ethyl acetate (50/50, *v*/*v*) as the eluent to give a yellow solid. This compound was obtained in a yield of 94 %. ^{1}H NMR and MS (ES) data are available in the CIF.

Experimental details

H atoms were positioned geometrically and refined using riding model with d(C—H) = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C) for aromatic CH; 0.97 Å and U_{iso}(H) = 1.2 U_{eq}(C) for CH_2; d(C—H) = 0.96 Å and U_{iso}(H) = 1.5 U_{eq}(C) for CH_3, d(O—H) = 0.82 Å and U_{iso}(H) = 1.2 U_{eq}(O) for the OH group. The highest residual electron density peak and the deepest hole are located at 0.27 Å and –0.19 Å from S1, respectively. The absolute configuration was determined from the anomalous X-ray scattering from the sulfur atom. The absolute configuration at the chiral C6A and C12A was both determined to be *R* and consistent with the previously reported structure [1]. The Flack absolute configuration parameter was 0.13(7). 2750 Friedel pairs were used to determine the absolute configuration.

Discussion

The chromanone moiety plays an important role in strong cytotoxicity of human tumor cells [2]. 6-Deoxyclitoriacetal, extracted from the roots of *Stemona Collinsae* Craib, exhibits strong cytotoxicity against various human carcinomas [1]. In order to enhance its cytotoxicity, 6-deoxyclitoriacetal was modified with methanesulfonyl chloride to give 6-deoxyclitoriacetal methanesulfonate.

The geometric parameters in the title crystal structure agree with the reported values of similar structure [3]. The chroman-4-one unit is fused with the chroman ring, making a dihedral angle of 82.84(4)°. The benzyl ring makes a dihedral angle of 11.1(1)° with the benzene ring of the chromanone unit. The pyrone and dihydropyran rings adopt a distorted half-chair conformation. One of methoxy group in the chroman ring is co-planar with the benzene ring (r.m.s deviation = 0.031 Å), the other methoxy group is nearly perpendicular to the benzene ring [dihedral angle = –99.6(3)°]. The molecular structure is stabilized by weak intramolecular O–H···O interactions. The crystal structure is devoid of any classical hydrogen bonds. However, non-classical inter- and intramolecular hydrogen-bonding interactions of the type C–H···O are present in the title crystal structure.

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Table 1. Data collection and handling.

Crystal:	pale yellow prism, size 0.30 × 0.35 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.92 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEXII CCD, φ/ω
$2\theta_{max}$:	63.7°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9141, 4167
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3552
$N(param)_{refined}$:	339
Programs:	SHELXS-97, SHELXL-97 [4], ORTEP-III [5]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*a*	1.0214	0.3657	0.3812	0.042
H(4)	2*a*	1.3884	0.2497	0.8074	0.050
H(6A)	2*a*	1.0363	0.3653	1.0238	0.058
H(6B)	2*a*	0.9392	0.3046	0.8995	0.058
H(6A1)	2*a*	0.8423	0.4321	0.8279	0.050
H(7)	2*a*	1.2036	0.6068	0.8927	0.050
H(9)	2*a*	1.0577	0.7004	0.4595	0.051
H(18A)	2*a*	1.3504	0.7963	0.9063	0.112
H(18B)	2*a*	1.4125	0.7089	0.9133	0.112
H(18C)	2*a*	1.2456	0.7284	0.9516	0.112
H(19A)	2*a*	1.3745	0.3359	0.1597	0.142
H(19B)	2*a*	1.4691	0.3367	0.3380	0.142
H(19C)	2*a*	1.3295	0.3985	0.2719	0.142
H(20A)	2*a*	1.6482	0.1519	0.6267	0.099
H(20B)	2*a*	1.5073	0.1443	0.7110	0.099
H(20C)	2*a*	1.6250	0.2177	0.7435	0.099
H(22)	2*a*	0.6857	0.4658	0.1236	0.058
H(23)	2*a*	0.4789	0.4377	–0.0993	0.060
H(25)	2*a*	0.6191	0.6210	–0.3192	0.055
H(26)	2*a*	0.8224	0.6519	–0.0943	0.050
H(27A)	2*a*	0.3435	0.4570	–0.3654	0.088
H(27B)	2*a*	0.4720	0.4793	–0.4578	0.088
H(27C)	2*a*	0.3455	0.5425	–0.4324	0.088
H(3)	2*a*	0.7287	0.3322	0.5224	0.075

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}
C(1)	2*a*	1.0942(2)	0.3419(1)	0.4667(2)	0.0355(9)	0.0364(9)	0.0290(8)	–0.0006(7)	0.0013(7)	–0.0033(7)
C(1A)	2*a*	1.0665(2)	0.3489(1)	0.6146(2)	0.0326(8)	0.0328(8)	0.0322(8)	–0.0017(7)	0.0053(7)	–0.0014(7)
C(2)	2*a*	1.2266(3)	0.3006(1)	0.4442(2)	0.0390(9)	0.045(1)	0.0323(9)	0.0029(8)	0.0047(8)	–0.0090(8)
C(3)	2*a*	1.3370(3)	0.2639(1)	0.5732(3)	0.0376(9)	0.044(1)	0.042(1)	0.0042(8)	0.0023(8)	–0.0109(9)
C(4)	2*a*	1.3139(3)	0.2722(1)	0.7213(3)	0.0397(9)	0.043(1)	0.035(1)	0.0069(9)	–0.0020(8)	–0.0009(8)
C(4A)	2*a*	1.1788(3)	0.3143(1)	0.7414(2)	0.0409(9)	0.039(1)	0.0295(9)	–0.0005(8)	0.0049(7)	0.0003(7)
C(6)	2*a*	1.0177(3)	0.3477(2)	0.9162(3)	0.056(1)	0.057(1)	0.037(1)	0.001(1)	0.019(1)	0.007(1)
C(6A)	2*a*	0.9456(3)	0.4148(1)	0.8075(3)	0.042(1)	0.048(1)	0.037(1)	0.0015(9)	0.0157(8)	0.0015(9)
C(7)	2*a*	1.1437(3)	0.6031(1)	0.7883(3)	0.043(1)	0.045(1)	0.0349(9)	0.0013(9)	0.0084(8)	–0.0094(9)
C(7A)	2*a*	1.0512(2)	0.5358(1)	0.7335(2)	0.0390(9)	0.039(1)	0.0290(9)	0.0024(8)	0.0099(7)	–0.0048(7)
C(8)	2*a*	1.1455(3)	0.6639(1)	0.6863(3)	0.044(1)	0.038(1)	0.046(1)	–0.0012(8)	0.0100(9)	–0.0121(9)
C(9)	2*a*	1.0542(3)	0.6596(1)	0.5289(3)	0.049(1)	0.0335(9)	0.044(1)	0.0011(8)	0.0101(9)	–0.0023(8)
C(11)	2*a*	0.9601(2)	0.5942(1)	0.4803(2)	0.0355(8)	0.038(1)	0.0304(8)	0.0059(7)	0.0061(7)	–0.0041(7)
C(11A)	2*a*	0.9541(2)	0.5294(1)	0.5785(2)	0.0319(8)	0.0351(9)	0.0330(9)	0.0038(7)	0.0083(7)	–0.0021(7)
C(12)	2*a*	0.8597(2)	0.4572(1)	0.5283(2)	0.0304(8)	0.0377(9)	0.0360(9)	0.0017(7)	0.0081(7)	0.0006(8)
C(12A)	2*a*	0.9123(2)	0.3870(1)	0.6381(2)	0.0339(8)	0.0372(9)	0.0370(9)	–0.0031(8)	0.0096(7)	0.0014(8)
C(18)	2*a*	1.3170(5)	0.7423(2)	0.8876(4)	0.085(2)	0.070(2)	0.065(2)	–0.028(2)	0.011(2)	–0.028(2)
C(19)	2*a*	1.3645(4)	0.3451(4)	0.2637(4)	0.061(2)	0.182(5)	0.043(1)	–0.025(2)	0.017(1)	–0.013(2)
C(20)	2*a*	1.5690(4)	0.1806(2)	0.6655(4)	0.049(1)	0.070(2)	0.073(2)	0.021(1)	0.005(1)	–0.003(2)
C(21)	2*a*	0.7763(2)	0.5602(1)	0.0336(2)	0.0383(9)	0.039(1)	0.0319(8)	–0.0005(8)	0.0062(7)	–0.0024(7)
C(22)	2*a*	0.6727(3)	0.4965(2)	0.0341(3)	0.057(1)	0.048(1)	0.040(1)	–0.011(1)	0.011(1)	0.005(1)
C(23)	2*a*	0.5505(3)	0.4794(2)	–0.0998(3)	0.052(1)	0.050(1)	0.049(1)	–0.015(1)	0.013(1)	–0.004(1)
C(24)	2*a*	0.5328(3)	0.5237(2)	–0.2354(3)	0.0341(9)	0.049(1)	0.042(1)	0.0017(9)	0.0070(8)	–0.0084(9)
C(25)	2*a*	0.6338(3)	0.5893(1)	–0.2308(3)	0.047(1)	0.049(1)	0.037(1)	0.0015(9)	0.0045(8)	0.0069(9)
C(26)	2*a*	0.7556(3)	0.6080(1)	–0.0967(3)	0.042(1)	0.040(1)	0.042(1)	–0.0038(9)	0.0074(8)	0.0040(9)
C(27)	2*a*	0.4125(3)	0.4983(2)	–0.3865(3)	0.044(1)	0.078(2)	0.048(1)	–0.003(1)	0.000(1)	–0.013(1)
O(1)	2*a*	1.1694(2)	0.3197(1)	0.8930(2)	0.0566(9)	0.060(1)	0.0296(7)	0.0116(8)	0.0082(6)	0.0069(7)
O(2)	2*a*	1.0631(2)	0.4781(1)	0.8413(2)	0.0549(9)	0.0458(8)	0.0316(7)	–0.0032(7)	0.0073(6)	–0.0008(6)
O(3)	2*a*	0.7813(2)	0.3319(1)	0.6148(2)	0.0405(8)	0.0517(9)	0.055(1)	–0.0133(7)	0.0096(7)	0.0050(8)
O(4)	2*a*	1.2462(2)	0.2923(1)	0.2957(2)	0.0519(9)	0.075(1)	0.0350(8)	0.0075(9)	0.0079(7)	–0.0168(8)
O(5)	2*a*	1.4607(2)	0.2214(1)	0.5408(2)	0.0478(9)	0.072(1)	0.053(1)	0.0228(9)	0.0026(7)	–0.0144(9)
O(6)	2*a*	0.7477(2)	0.4493(1)	0.4101(2)	0.0420(8)	0.053(1)	0.0503(9)	–0.0077(7)	–0.0044(7)	0.0043(8)
O(7)	2*a*	0.8596(2)	0.59256(9)	0.3245(2)	0.0382(7)	0.0411(8)	0.0332(6)	0.0062(6)	0.0044(5)	–0.0005(6)
O(8)	2*a*	1.2310(3)	0.7321(1)	0.7253(2)	0.066(1)	0.047(1)	0.060(1)	–0.0142(9)	0.0049(9)	–0.0138(8)
O(9)	2*a*	1.0375(2)	0.5012(1)	0.2312(2)	0.059(1)	0.073(1)	0.050(1)	0.028(1)	0.0096(8)	–0.0029(9)
O(10)	2*a*	1.0387(2)	0.6421(1)	0.1651(2)	0.053(1)	0.085(2)	0.047(1)	–0.028(1)	0.0045(8)	0.0021(9)
S(1)	2*a*	0.95058(6)	0.57375(3)	0.19087(6)	0.0361(2)	0.0485(3)	0.0345(2)	0.0005(2)	0.0050(2)	–0.0013(2)

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