Crystal structure of 3-acetoxy-16-bromo-17-ethylenedioxyandrost-5-ene, $C_{23}H_{33}BrO_4$

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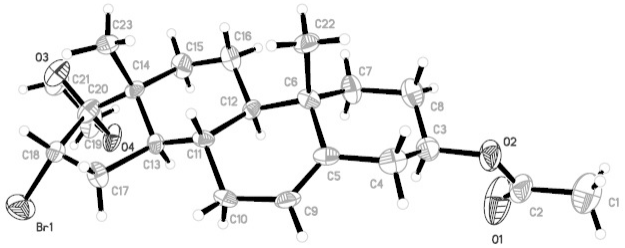

Abstract

$C_{23}H_{33}BrO_4$, monoclinic, $C2$ (no. 5), a = 10.314(2) Å, b = 7.590(2) Å, c = 28.312(6) Å, β = 99.79(3)°, V = 2184.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.0670, $wR_{ref}(F^2)$ = 0.1446, T = 293 K.

Table 1. Data collection and handling.

Crystal:	colourless prisms, size 0.30×0.30×0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	19.07 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4 diffractometer, $\omega 2\theta$
$2\theta_{max}$:	50.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2897, 2153
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1304
$N(param)_{refined}$:	256
Programs:	XCAD4 [5], PLATON [7], SHELXTL [8]

Source of material

The title compound was prepared by a literature method [1]. 3-acetoxy-17-ethylenedioxyandrost-5-ene (5g, 13mmol) was dissolved in freshly distilled anhydrous tetrahydrofuran (THF), 1,3-dibromo-5,5-dimethylhydantion (2.3g, 8mmol) in THF (15ml) was added and resulting mixture was stirred for 2 h. After cooling and filtrating, a crude compound was gained. The Pure compound was obstained by crystallization from a mixture of ethanol (8ml) and water (2ml). Prism shaped crystals of the pure product were obtained by slow evaporation of an ethanol solution at room temperature for about 20d.

Discussion

Experimental, clinical, and epidemiological studies have shown that steroid hormones, as well as their agonists and antagonists, produce salutary and in some cases, excellent results in the prevention and treatment of cancer. Several of these steroid hormones are in clinical use for the treatment of hormone-depended tumors (breast, prostate, ovarian, endometrium), as well as for the treatment of paraneoplastic syndromes and cancer symptoms. The molecule of the title compound is the key intermediate in the synthesis of steroid hormones.

The crystal structure analysis of the title compound revealed that the six-membered rings A(C3–C4–C5–C6–C7–C8), B(C6–C5–C9–C10–C11–C12) and C(C12–C11–C13–C14–C15–C16) are not planar, having total puckering amplitudes, respectively, have chair, flattened boat and chair conformations, while the two five-membered rings D(C14–C13–C17–C18–C19) and E(O3–C19–O4–C20–C21) have envelope conformations. Nearly similar conformational preferences are observable in steroid hormones [2]. Rings D and E have envelope conformations with atoms C14 and C19 displaced by 0.191(3) Å and 0.023(2) Å from the planes of the other four ring atoms, respectively. Rings D and E have pseudo twofold axis and pseudo mirror planes, respectively, running through atom C14 and the midpoint of the C17–C18 bond (for ring D) and atom C19 and the midpoint of C20–C21 bond (for ring E), as can be deduced from the torsion angles.

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*c*	0.2957	0.1699	1.0304	0.163
H(1B)	4*c*	0.1562	0.0850	1.0280	0.163
H(1C)	4*c*	0.1698	0.2890	1.0216	0.163
H(3A)	4*c*	0.2239	0.1041	0.8816	0.073
H(4A)	4*c*	0.5007	0.0893	0.9090	0.067
H(4B)	4*c*	0.4071	–0.0744	0.9075	0.067
H(7A)	4*c*	0.3372	0.4193	0.8059	0.072
H(7B)	4*c*	0.2391	0.2609	0.8049	0.072
H(8A)	4*c*	0.4064	0.3823	0.8883	0.068
H(8B)	4*c*	0.2534	0.4092	0.8779	0.068
H(9)	4*c*	0.4260	–0.2430	0.8434	0.060
H(10A)	4*c*	0.3575	–0.2430	0.7584	0.058
H(10B)	4*c*	0.5073	–0.2836	0.7740	0.058
H(11A)	4*c*	0.5697	–0.0193	0.7502	0.042
H(12A)	4*c*	0.3099	0.0949	0.7495	0.042
H(13A)	4*c*	0.3448	–0.0868	0.6844	0.039
H(15A)	4*c*	0.4208	0.3427	0.6518	0.068
H(15B)	4*c*	0.3018	0.2220	0.6588	0.068
H(16A)	4*c*	0.3630	0.3752	0.7277	0.071
H(16B)	4*c*	0.5106	0.3239	0.7299	0.071
H(17A)	4*c*	0.5896	–0.2571	0.6847	0.063
H(17B)	4*c*	0.4481	–0.3419	0.6734	0.063
H(18A)	4*c*	0.5831	–0.1891	0.6100	0.054
H(20A)	4*c*	0.1858	0.1438	0.5494	0.117
H(20B)	4*c*	0.2084	–0.0440	0.5283	0.117
H(21A)	4*c*	0.3866	0.0525	0.5051	0.098
H(21B)	4*c*	0.3648	0.2393	0.5266	0.098
H(22A)	4*c*	0.6374	0.1910	0.8131	0.082
H(22B)	4*c*	0.5935	0.2805	0.8577	0.082
H(22C)	4*c*	0.5716	0.3777	0.8081	0.082
H(23A)	4*c*	0.6677	0.0327	0.6503	0.083
H(23B)	4*c*	0.6576	0.1374	0.6973	0.083
H(23C)	4*c*	0.6321	0.2336	0.6476	0.083

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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)	4*c*	0.4001(1)	–0.3719(2)	0.57325(4)	0.114(1)	0.0696(8)	0.0721(7)	–0.024(1)	0.0118(6)	–0.0209(9)
C(1)	4*c*	0.205(1)	0.176(3)	1.0154(4)	0.10(1)	0.15(2)	0.080(9)	0.01(1)	0.023(7)	–0.01(1)
C(2)	4*c*	0.195(1)	0.152(2)	0.9640(4)	0.09(1)	0.06(1)	0.062(7)	0.009(9)	0.047(7)	–0.002(7)
C(3)	4*c*	0.306(1)	0.159(2)	0.8975(3)	0.039(6)	0.09(1)	0.061(6)	–0.022(7)	0.019(5)	–0.021(7)
C(4)	4*c*	0.419(1)	0.038(2)	0.8925(3)	0.054(7)	0.054(7)	0.057(6)	–0.003(6)	0.000(5)	0.010(5)
C(5)	4*c*	0.4295(9)	0.009(1)	0.8407(4)	0.034(6)	0.028(6)	0.058(6)	–0.004(5)	0.001(5)	0.004(5)
C(6)	4*c*	0.4335(9)	0.177(1)	0.8103(3)	0.023(5)	0.038(7)	0.047(5)	0.001(4)	–0.005(4)	–0.002(4)
C(7)	4*c*	0.324(1)	0.306(2)	0.8201(3)	0.063(8)	0.062(8)	0.054(6)	0.023(7)	0.006(5)	–0.006(6)
C(8)	4*c*	0.324(1)	0.330(2)	0.8735(3)	0.051(7)	0.057(8)	0.060(7)	0.021(6)	0.007(5)	–0.005(6)
C(9)	4*c*	0.431(1)	–0.149(2)	0.8227(4)	0.048(7)	0.041(7)	0.063(7)	–0.018(5)	0.016(5)	0.012(6)
C(10)	4*c*	0.441(1)	–0.193(1)	0.7736(3)	0.057(7)	0.039(7)	0.048(6)	–0.013(6)	0.009(5)	–0.007(5)
C(11)	4*c*	0.4747(8)	–0.040(1)	0.7425(3)	0.020(5)	0.023(6)	0.059(6)	–0.002(4)	0.003(4)	0.001(5)
C(12)	4*c*	0.4038(7)	0.124(2)	0.7561(2)	0.024(4)	0.042(5)	0.041(4)	0.005(6)	0.009(3)	0.002(6)
C(13)	4*c*	0.4406(9)	–0.072(1)	0.6912(3)	0.028(5)	0.035(6)	0.033(5)	0.005(5)	0.005(4)	0.000(4)
C(14)	4*c*	0.4732(8)	0.078(1)	0.6580(3)	0.016(4)	0.041(7)	0.055(5)	0.002(4)	0.010(4)	0.007(4)
C(15)	4*c*	0.395(1)	0.242(2)	0.6692(4)	0.055(7)	0.047(7)	0.068(8)	0.024(6)	0.011(6)	0.006(6)
C(16)	4*c*	0.421(1)	0.281(2)	0.7216(4)	0.061(8)	0.062(8)	0.054(7)	0.012(7)	0.008(6)	–0.009(6)
C(17)	4*c*	0.499(1)	–0.237(1)	0.6694(3)	0.052(7)	0.044(7)	0.058(6)	0.005(6)	0.001(5)	–0.007(5)
C(18)	4*c*	0.4925(9)	–0.195(1)	0.6162(3)	0.042(6)	0.042(6)	0.055(6)	0.001(5)	0.023(5)	–0.006(5)
C(19)	4*c*	0.4331(9)	–0.008(2)	0.6084(4)	0.022(5)	0.083(9)	0.053(6)	0.000(6)	0.007(4)	0.006(6)
C(20)	4*c*	0.249(1)	0.049(2)	0.5493(4)	0.066(8)	0.17(2)	0.049(7)	0.04(1)	–0.003(6)	–0.004(8)
C(21)	4*c*	0.372(1)	0.114(3)	0.5337(4)	0.075(8)	0.11(1)	0.066(7)	0.02(1)	0.021(6)	0.02(1)
C(22)	4*c*	0.5725(9)	0.265(2)	0.8236(3)	0.045(6)	0.060(8)	0.060(6)	–0.027(6)	0.014(5)	–0.003(6)
C(23)	4*c*	0.6219(8)	0.125(2)	0.6639(3)	0.040(6)	0.052(6)	0.078(6)	–0.016(8)	0.021(5)	–0.017(8)
O(1)	4*c*	0.0958(9)	0.150(3)	0.9369(3)	0.065(6)	0.26(2)	0.079(6)	0.02(1)	0.028(5)	0.00(1)
O(2)	4*c*	0.2997(7)	0.181(1)	0.9466(2)	0.072(5)	0.12(1)	0.058(4)	–0.034(5)	0.036(4)	–0.032(5)
O(3)	4*c*	0.4766(7)	0.083(1)	0.5713(2)	0.058(5)	0.097(9)	0.070(5)	–0.001(5)	0.022(4)	0.020(5)
O(4)	4*c*	0.2920(6)	–0.017(1)	0.5969(2)	0.033(4)	0.094(6)	0.059(4)	0.001(4)	0.016(3)	–0.010(4)

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