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Crystal structure of (3*R*,5*R*,8*R*,9*R*,10*R*,12*R*,13*R*,14*R*)-4,4,8,10,14-pentamethyl-17-((*R*)-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol, C₃₀H₅₂O₃

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Abstract

C₃₀H₅₂O₃, orthorhombic, *P*₂₁₂₁₂₁ (no. 19), *a* = 6.71147(14) Å, *b* = 16.6565(4) Å, *c* = 25.0815(6) Å, *V* = 2803.85(11) Å³, *Z* = 4, *R*_{gt} (*F*) = 0.0405, *wR*_{ref} (*F*²) = 0.1092, *T* = 293(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Panaxadiol (PD, systematic name: (3*R*,5*R*,8*R*,9*R*,10*R*,12*R*,13*R*,14*R*)-4,4,8,10,14-pentamethyl-17-((*R*)-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol) was prepared

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Table 1: Data collection and handling.

Crystal:	Block, clear light colorless
Size:	0.26 × 0.20 × 0.18 mm
Wavelength:	Cu Kα radiation (1.54184 Å)
μ:	0.52 mm ^{−1}
Diffractometer, scan mode:	Xcalibur, ω-scans
θ _{max} , completeness:	66.5°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	19752, 4891, 0.035
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 4341
<i>N</i> (<i>param</i>) _{refined} :	309
Programs:	CrysAlis ^{PRO} [1], OLEX2 [2], SHELX [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O1	0.4441(3)	0.97618(14)	0.46135(8)	0.0789(6)
H1	0.4534	0.9641	0.4929	0.118*
O2	0.0044(3)	0.54840(10)	0.43154(8)	0.0746(6)
H2	0.0436	0.5023	0.4268	0.112*
O3	0.1903(3)	0.41538(10)	0.40036(7)	0.0603(5)
C1	0.1181(4)	0.85430(15)	0.46261(10)	0.0568(6)
H1A	0.0190	0.8229	0.4815	0.068*
H1B	0.2485	0.8348	0.4732	0.068*
C2	0.0984(5)	0.94224(16)	0.47921(11)	0.0677(7)
H2A	−0.0367	0.9602	0.4725	0.081*
H2B	0.1232	0.9468	0.5172	0.081*
C3	0.2426(5)	0.99614(16)	0.44937(10)	0.0625(7)
H3	0.2188	1.0518	0.4604	0.075*
C4	0.2185(4)	0.99093(14)	0.38859(10)	0.0547(6)
C5	0.2341(3)	0.90062(13)	0.37276(9)	0.0462(5)
H5	0.3674	0.8847	0.3847	0.055*
C6	0.2363(5)	0.88487(15)	0.31294(9)	0.0590(7)
H6A	0.1018	0.8884	0.2990	0.071*
H6B	0.3166	0.9254	0.2953	0.071*
C7	0.3215(4)	0.80196(15)	0.30132(10)	0.0595(7)
H7A	0.4583	0.7999	0.3137	0.071*
H7B	0.3225	0.7934	0.2631	0.071*
C8	0.2025(3)	0.73376(14)	0.32809(9)	0.0464(5)
C9	0.1693(3)	0.75457(13)	0.38828(8)	0.0407(5)
H9	0.3027	0.7523	0.4041	0.049*
C10	0.0916(3)	0.84108(13)	0.40186(9)	0.0454(5)
C11	0.0532(4)	0.68647(13)	0.41593(9)	0.0494(5)
H11A	0.0416	0.6990	0.4536	0.059*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H11B	−0.0805	0.6846	0.4012	0.059*
C12	0.1473(4)	0.60389(14)	0.41021(9)	0.0488(5)
H12	0.2698	0.6016	0.4314	0.059*
C13	0.1950(3)	0.58475(13)	0.35256(9)	0.0444(5)
H13	0.0678	0.5825	0.3334	0.053*
C14	0.3195(4)	0.65227(14)	0.32648(10)	0.0522(6)
C15	0.3577(7)	0.61599(18)	0.27084(13)	0.0898(11)
H15A	0.2453	0.6256	0.2474	0.108*
H15B	0.4764	0.6390	0.2549	0.108*
C16	0.3857(7)	0.52546(19)	0.28089(14)	0.0936(12)
H16A	0.5251	0.5110	0.2776	0.112*
H16B	0.3099	0.4946	0.2551	0.112*
C17	0.3110(4)	0.50781(15)	0.33783(10)	0.0584(6)
H17	0.4287	0.5059	0.3609	0.070*
C18	0.0054(4)	0.72609(17)	0.29697(11)	0.0623(7)
H18A	−0.0788	0.6874	0.3142	0.094*
H18B	0.0329	0.7089	0.2612	0.094*
H18C	−0.0606	0.7772	0.2962	0.094*
C19	−0.1314(4)	0.85203(16)	0.38880(13)	0.0650(7)
H19A	−0.1463	0.8649	0.3517	0.098*
H19B	−0.1850	0.8948	0.4101	0.098*
H19C	−0.2016	0.8032	0.3965	0.098*
C20	0.2053(4)	0.42574(16)	0.34304(10)	0.0615(7)
C21	−0.0015(6)	0.4274(2)	0.31784(15)	0.0933(12)
H21A	−0.0500	0.3735	0.3140	0.140*
H21B	0.0059	0.4525	0.2834	0.140*
H21C	−0.0906	0.4573	0.3403	0.140*
C22	0.3378(7)	0.35996(19)	0.31976(16)	0.0969(12)
H22A	0.3255	0.3605	0.2812	0.116*
H22B	0.4755	0.3716	0.3285	0.116*
C23	0.2856(9)	0.2767(2)	0.34023(17)	0.1126(15)
H23A	0.1531	0.2619	0.3283	0.135*
H23B	0.3793	0.2377	0.3261	0.135*
C24	0.2932(8)	0.27588(19)	0.40040(17)	0.1031(13)
H24A	0.4284	0.2868	0.4120	0.124*
H24B	0.2569	0.2229	0.4132	0.124*
C25	0.1534(6)	0.33782(17)	0.42477(14)	0.0836(10)
C26	−0.0634(8)	0.3155(3)	0.4201(3)	0.142(2)
H26A	−0.1442	0.3601	0.4311	0.213*
H26B	−0.0907	0.2701	0.4425	0.213*
H26C	−0.0933	0.3022	0.3837	0.213*
C27	0.2036(10)	0.3524(2)	0.48291(15)	0.132(2)
H27A	0.3405	0.3684	0.4859	0.198*
H27B	0.1826	0.3039	0.5028	0.198*
H27C	0.1194	0.3941	0.4968	0.198*
C28	0.3920(5)	1.03754(16)	0.36292(12)	0.0719(8)
H28A	0.5123	1.0067	0.3659	0.108*
H28B	0.4088	1.0880	0.3809	0.108*
H28C	0.3630	1.0470	0.3260	0.108*
C29	0.0258(5)	1.03250(17)	0.37134(14)	0.0777(9)
H29A	0.0034	1.0230	0.3341	0.116*
H29B	0.0370	1.0892	0.3776	0.116*
H29C	−0.0838	1.0114	0.3916	0.116*
C30	0.5238(4)	0.65862(18)	0.35466(17)	0.0828(10)
H30A	0.5039	0.6696	0.3919	0.124*
H30B	0.5997	0.7013	0.3389	0.124*
H30C	0.5947	0.6089	0.3507	0.124*

successively from *Panax ginseng* with 10% H₂SO₄, and purified by silica-gel column chromatography (petroleum ether: ethyl acetate = 8:1, v/v) to afford a white powder. After that, the pure product was obtained by recrystallization in ethyl acetate and dichloromethane as needle-shaped crystals. The mixture of PD in dichloromethane was treated with pyridinium chlorochromate at room temperature for 6 h to obtain the 3-oxo-PD. 3-Oxo-PD, aluminium isopropoxide and trace aluminium chloride was added to isopropyl alcohol and the mixture was refluxed (90 °C) for 4 h. After evaporation under vacuum, the residue was dissolved with ethyl acetate, and the organic solution was washed with water and brine, and finally dried over anhydrous sodium sulfate. After filtration, the filtrate was evaporated to dryness under vacuum and purified by silica-gel column chromatography (petroleum ether: ethyl acetate = 5:1, v/v). Suitable single crystals of the title compound were obtained by recrystallization in petroleum ether and ethyl acetate solution.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with O–H = 0.82 or 0.85 Å and U_{iso} (H) = 1.2 U_{eq} (O), H atoms on C atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms, with C–H = 0.96 Å, U_{iso} (H) = 1.5 U_{eq} (C) for methyl H atoms, and with C–H = 0.98 Å and 0.97 Å for methine and methylene H atoms, and both with U_{iso} (H) = 1.2 U_{eq} (C). The absolute configuration was derived from the synthesis and the configuration of the educts.

Comment

As a traditional Chinese medicine [4], ginseng is known for its wide spectrum of biological activities, such as anti-bacterium [5], anti-inflammatory [6, 7], anti-oxidation [8]. Ginsenosides are the major bioactive constituents in ginseng. And panaxadiol (PD) is a triterpenoid saponin monomer compound with a dammarane skeleton. It can be degraded by acid hydrolysate from natural panax ginseng saponin. PD has significant anti-tumor activity and regulation of cell cycle and apoptosis [9]. Some pharmacological activities are closely dependent on the stereoisomers [10], and the synthesis and crystal structure of derivatives driven from 20(R)-panaxadiol are of great significance.

The single-crystal measured is obtained by crystallization in petroleum ether and ethyl acetate solution. After oxidation and reduction, 3-β-OH-20R-PD is converted to 3-α-OH-20R-PD. The C3 carbon atom in the molecule is bonded to different groups, which are hydrogen atom, hydroxyl, methylene and quaternary atom, and C3 is a chiral center and in R-form. In addition, C5, C8, C9, C10, C12, C13, C14, C17, and C20 in the molecule are also chiral centers, and their configurations

are all *R*. The structure of the molecule is similar to the stereo configuration of the compound reported in the references [11–13]. The bond lengths and angles are all in the expected ranges.

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