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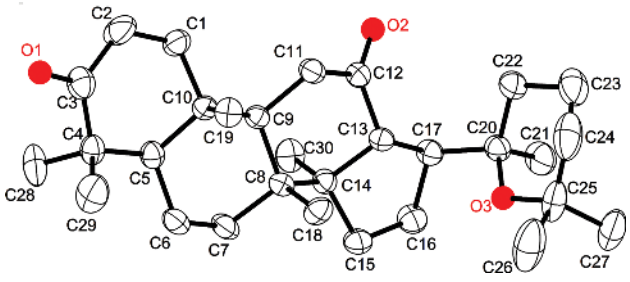
Crystal structure of (20*R*)-20,25-epoxy-dammaran-3,12-dione, $C_{30}H_{48}O_3$



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Abstract

$C_{30}H_{48}O_3$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 7.8710(16)$ Å, $b = 13.800(28)$ Å, $c = 24.561(49)$ Å, $V = 2667.9(9)$ Å^3, $Z = 4$. $R_{gt}(F) = 0.0488$, $wR_{ref}(F^2) = 0.1264$, $T = 293(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

(20*R*)-20,25-Epoxy-dammaran-3,12-dione {systematic name: (8*R*,9*R*,10*R*,13*R*,14*R*,17*S*)-4,4,8,10,14-pentamethyl-17-((*R*)-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)tetradecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,12(2*H*)-dione)} is synthesized by two-step oxidation reaction in turn.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.24 × 0.20 × 0.18 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.07 mm^{-1}
Diffractometer, scan mode:	Bruker P4, ω-scans
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	36598, 3755, 0.058
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3755
$N(param)_{refined}$:	306
Programs:	Bruker programs [1], SHELX [2, 3]

3-oxo-20(*R*)-panaxadiol was synthesized by Wu's method [4]. A solution of (20*R*)-panaxadiol in CH_2Cl_2 and pyridinium chlorochromate was stirred for 6 h at room temperature. The solvent was removed under reduced pressure to give a white solid. The white solid was dissolved in ethyl ether and washed with $NaHCO_3$, dried ($MgSO_4$) and concentrated under reduced pressure to give the crude product. The crude products were chromatographied using silica gel and eluted with [petroleum ether-EtOAc (8:1)] to give the pure product. (20*R*)-20,25-Epoxy-dammaran-3,12-dione is synthesized by reacting 3-oxo-20(*R*)-panaxadiol with DDQ in 1,4-dioxane at 110 °C temperature heating under reflux for 3 h. The mixture was concentrated in vacuo. The residue was dissolved in water and extracted with ethyl acetate. The organic phase was washed with water, dried over Na_2SO_4. The residue was separated by silica column chromatography [petroleum ether-EtOAc (8:1)] to give a white solid. (**m.p.**: 255–257 °C). Analysis calcd. for $C_{30}H_{48}O_3$: 456.36035; found: MS (ES^+): *m/z* 457.36740 ($M + 1$).

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C—H = 0.96–0.97 Å, with $U_{iso}(H) = 1.5\ U_{eq}(C)$ for methyl H atoms and 1.2 $U_{eq}(C)$ for all other H atoms. The absolute configuration was derived from the synthesis and the configuration of the educts.

Discussion

Panaxadiol (PD), one of the protopanaxadiol-type of ginsenoside with a dammarane skeleton can be obtained by acid hydrolysate. It has been reported to exhibits pharmacological

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

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.5403(4)	0.0979(3)	0.93692(15)	0.1245(16)
O2	−0.2557(2)	0.51504(19)	0.91667(10)	0.0612(7)
O3	−0.0353(3)	0.81548(16)	0.87134(9)	0.0503(6)
C1	0.1790(4)	0.2605(2)	0.93094(14)	0.0466(8)
H1A	0.1200	0.2839	0.9630	0.056*
H1B	0.0938	0.2385	0.9052	0.056*
C2	0.2866(5)	0.1760(3)	0.9469(2)	0.0754(12)
H2A	0.3114	0.1822	0.9854	0.091*
H2B	0.2184	0.1180	0.9425	0.091*
C3	0.4476(4)	0.1598(3)	0.91873(14)	0.0548(9)
C4	0.5020(4)	0.2195(2)	0.86911(13)	0.0452(8)
C5	0.3736(3)	0.3029(2)	0.85588(12)	0.0399(7)
H5	0.2856	0.2721	0.8336	0.048*
C6	0.4493(4)	0.3811(3)	0.81930(13)	0.0506(8)
H6A	0.5318	0.4185	0.8398	0.061*
H6B	0.5077	0.3509	0.7890	0.061*
C7	0.3111(4)	0.4487(3)	0.79765(12)	0.0493(8)
H7A	0.2330	0.4115	0.7754	0.059*
H7B	0.3633	0.4973	0.7745	0.059*
C8	0.2108(3)	0.4996(2)	0.84292(11)	0.0367(7)
C9	0.1455(3)	0.4205(2)	0.88304(11)	0.0334(6)
H9	0.0664	0.3817	0.8613	0.040*
C10	0.2768(3)	0.3450(2)	0.90543(11)	0.0356(7)
C11	0.0326(4)	0.4662(2)	0.92820(12)	0.0430(7)
H11A	−0.0176	0.4148	0.9498	0.052*
H11B	0.1032	0.5051	0.9521	0.052*
C12	−0.1071(3)	0.5289(2)	0.90503(12)	0.0391(7)
C13	−0.0461(3)	0.6048(2)	0.86643(11)	0.0353(6)
H13	0.0383	0.6437	0.8860	0.042*
C14	0.0494(3)	0.5526(2)	0.81925(11)	0.0364(7)
C15	0.0773(4)	0.6385(2)	0.78049(12)	0.0467(8)
H15A	0.1712	0.6784	0.7928	0.056*
H15B	0.1011	0.6160	0.7439	0.056*
C16	−0.0903(4)	0.6955(3)	0.78222(12)	0.0502(8)
H16A	−0.1662	0.6735	0.7536	0.060*
H16B	−0.0691	0.7641	0.7772	0.060*
C17	−0.1706(3)	0.6763(2)	0.83944(12)	0.0408(7)
H17	−0.2802	0.6438	0.8344	0.049*
C18	0.3301(3)	0.5741(2)	0.87046(14)	0.0474(8)
H18A	0.4415	0.5466	0.8742	0.071*
H18B	0.2864	0.5905	0.9058	0.071*
H18C	0.3364	0.6315	0.8485	0.071*
C19	0.3944(4)	0.3878(2)	0.94956(12)	0.0450(8)
H19A	0.3268	0.4167	0.9778	0.068*
H19B	0.4665	0.4361	0.9336	0.068*
H19C	0.4631	0.3371	0.9648	0.068*
C20	−0.1998(4)	0.7701(2)	0.87181(12)	0.0430(7)
C21	−0.3336(4)	0.8320(3)	0.84224(16)	0.0644(10)
H21A	−0.3686	0.8843	0.8655	0.097*
H21B	−0.4303	0.7925	0.8335	0.097*
H21C	−0.2856	0.8578	0.8094	0.097*
C22	−0.2601(5)	0.7509(3)	0.92976(13)	0.0587(9)
H22A	−0.3780	0.7306	0.9289	0.070*
H22B	−0.1938	0.6986	0.9453	0.070*
C23	−0.2436(6)	0.8396(3)	0.96542(15)	0.0798(13)
H23A	−0.3138	0.8916	0.9513	0.096*
H23B	−0.2808	0.8248	1.0021	0.096*
C24	−0.0601(7)	0.8700(3)	0.96583(17)	0.0900(15)
H24A	0.0078	0.8184	0.9815	0.108*
H24B	−0.0475	0.9268	0.9887	0.108*
C25	0.0072(5)	0.8932(3)	0.90871(18)	0.0675(11)
C26	0.2010(5)	0.8927(4)	0.9069(3)	0.110(2)
H26A	0.2420	0.8290	0.9155	0.166*
H26B	0.2444	0.9382	0.9330	0.166*
H26C	0.2385	0.9106	0.8711	0.166*
C27	−0.0591(6)	0.9906(3)	0.8879(2)	0.0827(13)
H27A	−0.0269	0.9988	0.8504	0.124*
H27B	−0.0113	1.0421	0.9092	0.124*
H27C	−0.1807	0.9921	0.8908	0.124*
C28	0.5037(5)	0.1462(3)	0.82144(15)	0.0714(12)
H28A	0.5336	0.1791	0.7884	0.107*
H28B	0.3931	0.1177	0.8176	0.107*
H28C	0.5856	0.0963	0.8287	0.107*
C29	0.6855(4)	0.2542(3)	0.8783(2)	0.0782(13)
H29A	0.6861	0.3055	0.9047	0.117*
H29B	0.7317	0.2775	0.8446	0.117*
H29C	0.7533	0.2012	0.8913	0.117*
C30	−0.0752(4)	0.4815(3)	0.79038(13)	0.0520(9)
H30A	−0.1704	0.5170	0.7763	0.078*
H30B	−0.1144	0.4340	0.8160	0.078*
H30C	−0.0175	0.4496	0.7610	0.078*

activities, such as anti-tumor, anti-HIV and regulating cell cycle and apoptosis [5–8]. Because of its wide biological properties and its potential medicinal value, the extraction, synthesis and biological activity of panaxadiol and its derivatives have attracted much attention. In this paper, we report the crystal structure of the title compound, whose partial synthesis methods have been reported in other journals [4].

In the molecule of the title compound, bond lengths and angles within the five-membered rings are very similar to those given in the literature for panaxadiol [9–13].

The structure of the title compound and panaxadiol are equivalent except for the substituents at C(3) and C(6). Two carbon-oxygen double bond exist in the compound which was synthesized by two-step oxidation reaction. Both the first ring and the third ring contain a carbon-oxygen double bond. The C—O bond distance (C3—O1) is 1.208(6) Å, The C—O bond distance (C12—O2) is 1.218(4) Å. The distance of C—O Bond (C20—O3) in Tetrahydropyran Ring is 1.438(4) Å and the distance of C—O Bond (C25—O3) is 1.452(5) Å. The C25—O3—C20—C22, O1—C3—C2—C1, O1—C3—C4—C28 and O2—C12—C11—C9 torsion angles are 43.1(4)°, 170.9(4)°, 68.3(4)° and

125.0(3)°, respectively. The C25—O3—C20—C22 torsion angle indicates that the C20 position is *R*-form.

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