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The crystal structure of (3*S*,8*R*,10*R*,14*R*)-17-((2*S*,5*S*)-5-(2-hydroxypropan-2-yl)-2-methyltetrahydrofuran-2-yl)-4,4,8,10,14-pentamethyl-12-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate, C₃₂H₅₂O₅

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Abstract

C₃₂H₅₂O₅, monoclinic, *P*₂₁ (no. 4), *a* = 11.816(2) Å, *b* = 7.4064(15) Å, *c* = 17.101(3) Å, β = 97.01(3)°, *V* = 1485.5(5) Å³, *Z* = 2, *R*_{gt}(*F*) = 0.0543, *wR*_{ref}(*F*²) = 0.1501, *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.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.40 × 0.30 × 0.23 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.07 mm ^{−1}
Diffractometer, scan mode:	Bruker SMART, φ and ω
θ _{max} , completeness:	27.5°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	35271, 6062, 0.030
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 5664
<i>N</i> (<i>param</i>) _{refined} :	344
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

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	0.44583(16)	0.4324(3)	0.86271(10)	0.0521(5)
O2	0.2157(6)	0.1904(4)	0.38416(18)	0.170(3)
O3	0.11104(19)	0.5070(3)	0.14260(11)	0.0594(5)
O4	0.30274(16)	0.3679(5)	0.07513(13)	0.0710(6)
H4	0.310336	0.456081	0.104298	0.107*
O5	0.5566(2)	0.1878(5)	0.85784(14)	0.0835(8)
C1	0.2901(3)	0.3063(3)	0.66386(14)	0.0500(6)
H1A	0.225803	0.226221	0.650204	0.060*
H1B	0.353969	0.259458	0.639455	0.060*
C2	0.3213(3)	0.3058(4)	0.75344(15)	0.0551(6)
H2A	0.255643	0.342696	0.778528	0.066*
H2B	0.342196	0.184547	0.771071	0.066*
C3	0.4194(2)	0.4327(4)	0.77729(13)	0.0452(5)
H3	0.486289	0.389037	0.754301	0.054*
C4	0.3969(2)	0.6295(4)	0.75138(13)	0.0420(5)
C5	0.35894(17)	0.6254(3)	0.66065(12)	0.0346(4)
H5	0.425124	0.577294	0.638154	0.042*
C6	0.3400(2)	0.8135(3)	0.62347(13)	0.0436(5)
H6A	0.267630	0.861560	0.635310	0.052*
H6B	0.399906	0.894387	0.645853	0.052*
C7	0.3401(2)	0.8036(3)	0.53420(13)	0.0438(5)
H7A	0.414994	0.765672	0.522958	0.053*
H7B	0.326038	0.923309	0.512135	0.053*
C8	0.25020(16)	0.6727(3)	0.49352(12)	0.0324(4)
C9	0.25915(17)	0.4885(3)	0.53869(12)	0.0340(4)
H9	0.334641	0.441666	0.531206	0.041*
C10	0.25941(17)	0.4958(3)	0.63020(12)	0.0351(4)
C11	0.1747(3)	0.3494(4)	0.49748(15)	0.0591(7)
H11A	0.186867	0.233258	0.523325	0.071*
H11B	0.097274	0.387518	0.502091	0.071*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C12	0.1901(4)	0.3304(4)	0.41130(16)	0.0724(10)
C13	0.1789(2)	0.5028(3)	0.36621(13)	0.0403(5)
H13	0.104519	0.555166	0.372881	0.048*
C14	0.27240(17)	0.6324(3)	0.40627(12)	0.0370(4)
C15	0.2595(3)	0.7905(4)	0.34770(15)	0.0566(7)
H15A	0.328285	0.863029	0.352127	0.068*
H15B	0.195797	0.866929	0.357009	0.068*
C16	0.2378(3)	0.7002(5)	0.26586(15)	0.0568(7)
H16A	0.308059	0.694097	0.241994	0.068*
H16B	0.182489	0.769304	0.231485	0.068*
C17	0.1919(2)	0.5080(4)	0.27799(13)	0.0444(5)
H17	0.251355	0.421408	0.268322	0.053*
C18	0.1332(2)	0.7646(4)	0.49385(14)	0.0475(6)
H18A	0.128378	0.816596	0.544750	0.071*
H18B	0.073832	0.676589	0.482470	0.071*
H18C	0.124609	0.857718	0.454546	0.071*
C19	0.1424(2)	0.5484(5)	0.65466(15)	0.0519(6)
H19A	0.135350	0.677490	0.654934	0.078*
H19B	0.136042	0.502267	0.706415	0.078*
H19C	0.082853	0.498031	0.617852	0.078*
C20	0.0833(2)	0.4627(5)	0.22126(14)	0.0579(8)
C21	−0.0195(3)	0.5748(9)	0.2359(2)	0.0973(17)
H21A	0.001714	0.699825	0.240130	0.146*
H21B	−0.046423	0.536119	0.283892	0.146*
H21C	−0.078878	0.559278	0.192797	0.146*
C22	0.0568(3)	0.2594(6)	0.21771(18)	0.0796(12)
H22A	0.085225	0.200503	0.266861	0.096*
H22B	−0.024541	0.238095	0.206617	0.096*
C23	0.1187(3)	0.1929(6)	0.15105(18)	0.0678(8)
H23A	0.198639	0.170292	0.168650	0.081*
H23B	0.084105	0.083824	0.127608	0.081*
C24	0.1038(2)	0.3498(5)	0.09433(13)	0.0529(7)
H24	0.027067	0.343621	0.065371	0.063*
C25	0.1900(2)	0.3650(6)	0.03479(14)	0.0604(8)
C26	0.1830(4)	0.1974(9)	−0.0166(3)	0.1028(18)
H26A	0.237142	0.206728	−0.053985	0.154*
H26B	0.107559	0.186644	−0.044173	0.154*
H26C	0.200059	0.092699	0.015811	0.154*
C27	0.1691(3)	0.5357(9)	−0.0134(2)	0.0927(15)
H27A	0.173377	0.638288	0.021101	0.139*
H27B	0.094760	0.530539	−0.043134	0.139*
H27C	0.225788	0.546477	−0.048847	0.139*
C28	0.5107(3)	0.7311(5)	0.76732(17)	0.0655(9)
H28A	0.563614	0.683133	0.734311	0.098*
H28B	0.541138	0.716551	0.821614	0.098*
H28C	0.498491	0.857007	0.755991	0.098*
C29	0.3107(3)	0.7221(4)	0.79902(15)	0.0556(7)
H29A	0.286097	0.833933	0.774105	0.083*
H29B	0.346257	0.745623	0.851552	0.083*
H29C	0.246066	0.644540	0.801089	0.083*
C30	0.5184(2)	0.3066(5)	0.89477(15)	0.0553(7)
C31	0.5431(3)	0.3327(6)	0.98201(16)	0.0712(10)
H31A	0.588791	0.439043	0.992752	0.107*
H31B	0.583527	0.229608	1.005080	0.107*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H31C	0.472678	0.346285	1.004140	0.107*
C32	0.3910(2)	0.5503(7)	0.40207(17)	0.0714(11)
H32A	0.393825	0.431005	0.424198	0.107*
H32B	0.447888	0.624494	0.431311	0.107*
H32C	0.405429	0.544078	0.348093	0.107*

Source of material

A solution of 20(S),24(S)-epoxy-dammar-3,12,25-triol in dichloromethane was cooled to 270 K. A dichloromethane solution with *m*-CPBA was added slowly. After stirring for 1 h, isopropanol was added and stirred for another 1 h. The organic solvent was washed successively with saturated sodium bicarbonate solution, water and brine, and dried over sodium sulfate. The organic solvent was evaporated in vacuum, yielding a white solid. Acetic anhydride was added to a solution of the aforementioned intermediate in pyridine and was stirred for 11 h at room temperature. After evaporation under reduced pressure, the residue was dissolved with ethyl acetate and washed successively by water and brine, and dried over anhydrous sodium sulfate. The ethyl acetate was condensed in vacuo to yield a white solid. The objective compound was obtained from oxidation of the acetylated intermediate by 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) in dichloromethane at room temperature for about 1 h, which was purified by silica-gel column chromatography. Suitable crystals were obtained by slow evaporation in ethyl acetate.

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 $U_{iso}(H) = 1.2U_{eq}(O)$, 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, $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms, and with C–H = 0.98 Å and 0.97 Å for methine and methylene H atoms, and both with $U_{iso}(H) = 1.2U_{eq}$.

The absolute configuration was derived from the synthesis and the configuration of the educts.

Comment

20(S)-ocotillol-type saponin sharing a tetrahydrofuran ring and a dammarane skeleton, are a class of rare ginsenosides [5], which was achieved by base degradation from leaves and stems of *Panax quinquefolius* and they play a key role in neuroprotection [6], antibacterial [7] and antitumor activities [8]. It has been reported to possess good potential for myocardial ischemia and myocardial injury [9, 10].

It is also a potent approach to modify the structures of natural products and preparing a variety of derivatives for the search of new compounds. It is worth noting that our previous studies showed that similar compounds have corresponding stereoselective bioactivities [11–14]. Because of its potential medicinal value, synthesis and biological activity of 20(S)-ocotillol-type saponin and its derivatives have attracted much attention.

As shown in the figure, the bond angles of C30–O1–C3, O3–C20–C21 and O5–C30–O1 are 117.5(2)°, 107.7(3)° and 123.9(2)° respectively. The bond distance of O2–C12 is 1.190(5) Å. There are some intermolecular O–H···O hydrogen bonds. The bond lengths and angles are all in the expected ranges [15].

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