Crystal Structure of 12-Methoxy-8,8,21,21-tetramethyl-5-(3-methylbut-2,4-dienyl)-19-(3-methylpent-4-enyl)-3,7,20-trioxahehexacyclo[15.4.1.0<2,15>.0<2,19>.0<4,13>.0<6,11>]docosa-4(13),5,9,11,15-pentaene-14,18-dione

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The title compound was extracted from the natural product of plant origin. It crystallizes in tetragonal space group $P4_1$ or $P4_3$, with cell parameters $a = 15.795(2)\text{\AA}$, $c = 11.970(5)\text{\AA}$ and $Z = 4$. The structure exhibits intermolecular hydrogen bonds of the type $\text{C-H}\cdots\text{O}$.

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The cyclic oxide chroman may be regarded as the parent compound of a number of derivatives such as the chromones and coumarins.¹ A number of benzpyrone derivatives, like chromone, flavone and xanthone give rise to naturally occurring yellow dyes. Chromones are synthesized by a number of methods involving the ring-closure of *o*-hydroxyacetophenone derivatives.² For example, *o*-hydroxyacetophenone condenses in the presence of sodium with fatty acid esters to give diketones, which undergo ring-closure with concentrated mineral acids. The product is 2-methylchromone. The reverse process occurs when chromones are boiled with alkali. The heterocyclic ring is broken and a diketone is formed which is readily disrupted further, since the diketone undergoes both ketonic and acid hydrolysis. Chromones or benzo- γ -pyrones are widely distributed in plant life, mostly as pigments in plant leaves and flowers.

The title compound was extracted from the natural product. A schematic diagram of molecule under study is shown in Fig. 1. Thermal ellipsoids of the molecule at 50% probability are given in Fig. 2. Crystal and experimental data are listed in Table 1.

Fig. 1 Schematic diagram of the molecule.

Table 2 gives the fractional atomic coordinates and equivalent thermal parameters for all the refined atoms. Hydrogen atoms were placed at chemically acceptable positions. The absolute configuration of the molecule is unknown from chemical evidence and it has not been established by anomalous dispersion effects in diffraction measurements on the crystal. Therefore, an arbitrary choice of enantiomer has been made and the space group can be assigned as either $P4_1$ or $P4_3$. The bond distances and bond angles are in good agreement with the standard values. The packing of the molecules shown no stacking. The structure exhibits weak inter-molecular hydrogen bonds of type $\text{CH}\cdots\text{O}$. The intermolecular hydrogen bonds are: $\text{C20-H20}\cdots\text{O1}$ (3.43 Å, 172.08°), $\text{C27-H27}\cdots\text{O6}$ (3.40 Å, 145.82°) and $\text{C36-H36B}\cdots\text{O6}$ (3.37 Å, 155.81°) with symmetry codes $(y, 1-x, -1/4+z)$, $(-x, 1-y, -1/2+z)$, $(1-y, x, 1/4+z)$, respectively.

Fig. 2 ORTEP of the molecule at 50% probability.

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Table 1 Crystal data and structure refinement details

Empirical formula: C ₃₅ H ₄₀ O ₆
Formula weight: 556.67
Crystal system: tetragonal
Space group: <i>P</i> 4 ₁ or <i>P</i> 4 ₃
<i>a</i> = 15.795(2) Å
<i>c</i> = 11.970(5) Å
Volume = 2986.3(13) Å ³
<i>D</i> _x = 1.238 Mg/m ³
<i>R</i> = 0.0423
No. of reflections used = 4088
Measurements: Rigaku AFC7S
Program system: teXsan
Structure determination: SHELXS-97
Refinement: full matrix

Table 2 Atomic coordinates and equivalent thermal parameters of the non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O1	0.76240(19)	0.65258(19)	0.0884(2)	0.0521(8)
O2	0.88650(18)	0.59369(19)	-0.0649(2)	0.0485(8)
O3	1.0261(2)	0.7286(2)	-0.3602(3)	0.0616(9)
C4	0.8198(3)	0.5431(3)	-0.0198(4)	0.0433(11)
C5	0.9786(3)	0.6612(3)	-0.3249(4)	0.0480(12)
O6	0.8293(2)	0.3836(2)	-0.2463(3)	0.0674(10)
C7	0.9144(3)	0.5265(3)	-0.3577(4)	0.0506(12)
C8	0.8400(3)	0.5239(3)	0.1050(4)	0.0502(12)
C9	0.9551(3)	0.6613(3)	-0.2123(4)	0.0440(11)
C10	0.8376(3)	0.4514(3)	-0.1990(4)	0.0506(13)
C11	0.6747(4)	0.6218(3)	-0.2997(5)	0.0629(15)
C12	0.7396(3)	0.5966(3)	-0.0006(4)	0.0496(12)
O13	0.9038(2)	0.4589(2)	-0.4288(3)	0.0730(10)
C14	0.9069(3)	0.5908(3)	-0.1763(4)	0.0441(11)
C15	0.8858(3)	0.5231(3)	-0.2455(4)	0.0443(11)
C16	0.8228(3)	0.6106(3)	0.1632(4)	0.0528(12)
C17	0.9593(3)	0.5960(3)	-0.3974(4)	0.0484(12)
C18	0.7989(3)	0.4675(3)	-0.0880(4)	0.0468(11)
O19	0.6002(2)	0.5578(3)	0.0642(4)	0.0778(12)
C20	0.7381(3)	0.4179(3)	-0.0470(4)	0.0557(13)
C21	0.7833(3)	0.4498(3)	0.1423(4)	0.0608(14)
C22	0.8873(3)	0.8635(3)	-0.1312(5)	0.0653(14)
C23	0.7044(3)	0.4453(3)	0.0642(4)	0.0585(13)
C24	0.6663(3)	0.6048(3)	-0.1919(4)	0.0562(13)
C25	0.7799(4)	0.6053(4)	0.2775(4)	0.0707(16)
C26	0.6714(3)	0.5350(3)	0.0455(4)	0.0573(13)
C27	1.0260(3)	0.6714(4)	-0.5485(5)	0.0644(15)
C28	1.0278(4)	0.7491(4)	-0.4793(4)	0.0694(16)
C29	0.9018(3)	0.6636(3)	0.1719(5)	0.0647(14)
C30	0.7323(4)	0.6885(4)	-0.3494(6)	0.0875(19)
C32	0.9800(3)	0.7316(3)	-0.1327(4)	0.0511(12)
C33	0.9914(3)	0.6009(4)	-0.5120(4)	0.0601(14)
C34	0.9063(3)	0.7870(3)	-0.0979(4)	0.0566(13)
C35	0.9492(5)	0.8027(4)	-0.5037(6)	0.121(3)
C36	0.7075(3)	0.6511(3)	-0.0950(4)	0.0584(13)
C37	0.8211(5)	0.4464(5)	-0.4732(5)	0.103(2)
C38	1.1102(5)	0.7973(5)	-0.4931(6)	0.123(3)
C39	0.8111(4)	0.9097(4)	-0.0863(6)	0.096(2)
C40	0.6276(5)	0.5806(4)	-0.4762(5)	0.099(2)
C41	0.6242(5)	0.5732(4)	-0.3813(6)	0.097(2)
C42	0.9392(5)	0.9145(4)	-0.2140(6)	0.101(2)

Table 3 Bond lengths (Å)

Atom	Length	Atom	Length
O1-C12	1.430(5)	C11-C30	1.513(8)
O1-C16	1.467(5)	C12-C36	1.509(6)
O2-C14	1.372(6)	C12-C26	1.552(7)
O2-C4	1.429(5)	O13-C37	1.424(7)
O3-C5	1.369(5)	C14-C15	1.393(6)
O3-C28	1.462(6)	C16-C29	1.507(7)
C4-C18	1.484(6)	C16-C25	1.529(7)
C4-C12	1.540(6)	C17-C33	1.464(7)
C4-C8	1.556(6)	C18-C20	1.333(6)
C5-C17	1.381(6)	O19-C26	1.203(6)
C5-C9	1.399(7)	C20-C23	1.497(7)
O6-C10	1.218(5)	C21-C23	1.560(7)
C7-O13	1.374(5)	C22-C34	1.307(7)
C7-C17	1.391(6)	C22-C39	1.507(8)
C7-C15	1.419(7)	C22-C42	1.517(8)
C8-C21	1.539(7)	C23-C26	1.526(7)
C8-C16	1.560(6)	C24-C36	1.518(7)
C9-C14	1.416(6)	C27-C33	1.315(7)
C9-C32	1.515(6)	C27-C28	1.481(8)
C10-C15	1.473(7)	C28-C38	1.516(8)
C10-C18	1.484(7)	C28-C35	1.530(9)
C11-C24	1.325(7)	C32-C34	1.515(7)
C11-C41	1.477(9)	C40-C41	1.143(8)

Table 4 Bond angles (°)

Atom	Angle	Atom	Angle
C12-O1-C16	109.8(3)	C14-C15-C10	119.3(4)
C14-O2-C4	121.5(3)	C7-C15-C10	123.5(4)
C5-O3-C28	118.9(4)	O1-C16-C29	109.2(4)
O2-C4-C18	113.9(4)	O1-C16-C25	106.4(4)
O2-C4-C12	110.8(3)	C29-C16-C25	109.6(4)
C18-C4-C12	110.0(4)	O1-C16-C8	103.8(3)
O2-C4-C8	108.7(4)	C29-C16-C8	112.0(4)
C18-C4-C8	114.6(4)	C25-C16-C8	115.4(4)
C12-C4-C8	97.6(3)	C5-C17-C7	119.1(4)
O3-C5-C17	120.4(4)	C5-C17-C33	118.2(5)
O3-C5-C9	116.2(4)	C7-C17-C33	122.6(4)
C17-C5-C9	123.3(4)	C20-C18-C4	115.4(4)
O13-C7-C17	117.6(4)	C20-C18-C10	121.7(4)
O13-C7-C15	121.2(4)	C4-C18-C10	122.6(4)
C17-C7-C15	121.0(4)	C18-C20-C23	114.5(4)
C21-C8-C4	107.9(4)	C8-C21-C23	109.0(4)
C21-C8-C16	115.8(4)	C34-C22-C39	121.5(5)
C4-C8-C16	102.8(4)	C34-C22-C42	124.5(5)
C5-C9-C14	115.8(4)	C39-C22-C42	114.0(5)
C5-C9-C32	122.5(4)	C20-C23-C26	105.0(4)
C14-C9-C32	121.7(4)	C20-C23-C21	105.2(4)
O6-C10-C15	123.7(5)	C26-C23-C21	108.5(4)
O6-C10-C18	121.4(5)	C11-C24-C36	127.2(5)
C15-C10-C18	114.8(4)	O19-C26-C23	124.8(5)
C24-C11-C41	119.0(6)	O19-C26-C12	121.8(5)
C24-C11-C30	125.8(5)	C23-C26-C12	113.4(4)
C41-C11-C30	115.3(5)	C33-C27-C28	121.6(5)
O1-C12-C36	106.8(3)	O3-C28-C27	111.1(4)
O1-C12-C4	104.1(4)	O3-C28-C38	103.5(5)
C36-C12-C4	118.6(4)	C27-C28-C38	111.8(5)
O1-C12-C26	107.3(4)	O3-C28-C35	107.1(5)
C36-C12-C26	113.0(4)	C27-C28-C35	109.7(5)
C4-C12-C26	106.2(4)	C38-C28-C35	113.5(6)
C7-O13-C37	116.8(4)	C9-C32-C34	113.4(4)
O2-C14-C15	123.1(4)	C27-C33-C17	120.0(5)
O2-C14-C9	113.3(4)	C22-C34-C32	128.8(5)
C15-C14-C9	123.5(4)	C12-C36-C24	116.2(4)
C14-C15-C7	117.2(4)	C40-C41-C11	125.3(8)

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