

## Five bicyclo[3.3.0]octa-2,6-dienes

Andrés Vega,<sup>a\*</sup> Oscar Donoso-Tauda,<sup>a</sup> Andres Ibañez<sup>b</sup>  
and Carlos A. Escobar<sup>a</sup>

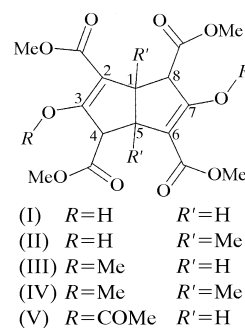
<sup>a</sup>Laboratorio de Recursos Naturales, Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales, Universidad Andrés Bello, Av. República 275, Santiago, Chile, and <sup>b</sup>Centro de Investigación Interdisciplinaria Avanzada en Ciencia de los Materiales, CIMAT, Universidad de Chile, Santiago, Chile  
Correspondence e-mail: andresvega@unab.cl

A series of five compounds containing the bicyclo[3.3.0]octa-2,6-diene skeleton are described, namely tetramethyl *cis,cis*-3,7-dihydroxybicyclo[3.3.0]octa-2,6-diene-2,4-*exo*,6,8-*exo*-tetracarboxylate, C<sub>16</sub>H<sub>18</sub>O<sub>10</sub>, (I), tetramethyl *cis,cis*-3,7-dihydroxy-1,5-dimethylbicyclo[3.3.0]octa-2,6-diene-2,4-*exo*,6,8-*exo*-tetracarboxylate, C<sub>18</sub>H<sub>22</sub>O<sub>10</sub>, (II), tetramethyl *cis,cis*-3,7-dimethoxybicyclo[3.3.0]octa-2,6-diene-2,4-*exo*,6,8-*exo*-tetracarboxylate, C<sub>18</sub>H<sub>22</sub>O<sub>10</sub>, (III), tetramethyl *cis,cis*-3,7-dimethoxy-1,5-dimethylbicyclo[3.3.0]octa-2,6-diene-2,4-*exo*,6,8-*exo*-tetracarboxylate, C<sub>20</sub>H<sub>26</sub>O<sub>10</sub>, (IV), and tetramethyl *cis,cis*-3,7-diacetoxylbicyclo[3.3.0]octa-2,6-diene-2,4-*exo*,6,8-*exo*-tetracarboxylate, C<sub>20</sub>H<sub>22</sub>O<sub>12</sub>, (V). The bicyclic core is substituted in all cases at positions 2, 4, 6 and 8 with methoxycarbonyl groups and additionally at positions 3 and 7 with hydroxy [in (I) and (II)], methoxy [in (III) and (IV)] or acetoxy [in (V)] groups. The conformations of the methoxycarbonyl groups at positions 2 and 4 are *exo* for all five compounds. Each C<sub>5</sub> ring of the bicyclic skeleton is almost planar, but the rings are not coplanar, with dihedral angles of 54.93 (7), 69.85 (5), 64.07 (4), 80.74 (5) and 66.91 (7)° for (I)–(V), respectively, and the bicyclooctadiene system adopts a butterfly-like conformation. Strong intramolecular hydrogen bonds exist between the –OH and C=O groups in (I) and (II), with O···O distances of 2.660 (2) and 2.672 (2) Å in (I), and 2.653 (2) and 2.635 (2) Å in (II). The molecular packing is stabilized by weaker C–H···O(=C) interactions, leading to dimers in (I)–(III) and to a chain structure in (V). The structure series presented in this article shows how the geometry of the cycloocta-2,6-diene skeleton changes upon substitution in different positions and, consequently, how the packing is modified, although the intermolecular interactions are basically the same across the series.

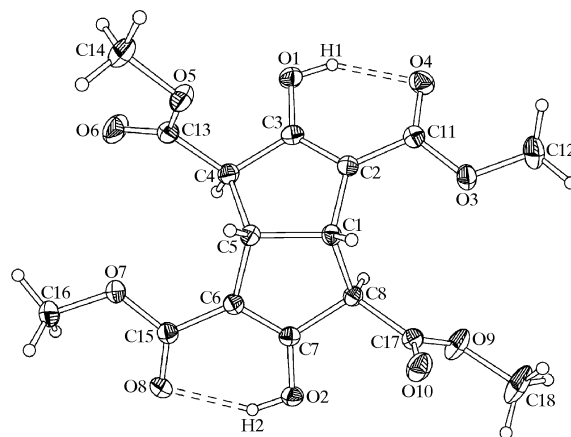
### Comment

The Weiss reaction is a very general, versatile and simple route to bicyclo[3.3.0]octa-2,6-dienes, which starts from  $\alpha$ -diketones reacting with 3-oxoglutarate esters. Although this is a widely

used synthetic route, few of the bicyclic compounds derived from it, depicted in the scheme, have been fully structurally characterized. The structure of the related red Vossen's salt, synthesized in 1910 (Vossen, 1910; Schroeter, 1922), was reported only in 2002 (Djaidi *et al.*, 2002). The structures of the two possible epimers when  $R = \text{H}$ ,  $R'_1 = \text{CH}_3$  and  $R'_2 = \text{C}_2\text{H}_5$  have been reported (Williams *et al.*, 1997). The structure of (I) has been previously described in a PhD thesis (Djaidi, 2006), although to the best of our knowledge and from the latest version of the Cambridge Structural Database (Version 5.29; Allen, 2002), it has been not published. From the synthetic viewpoint, this tetraester could be easily hydrolyzed and decarboxylated in acid media, leading to bicyclo[3.3.0]octane-3,7-diones (Bertz *et al.*, 1982; Docken, 1981), a versatile starting point for the synthesis of a wide variety of compounds (Gupta *et al.*, 1991).

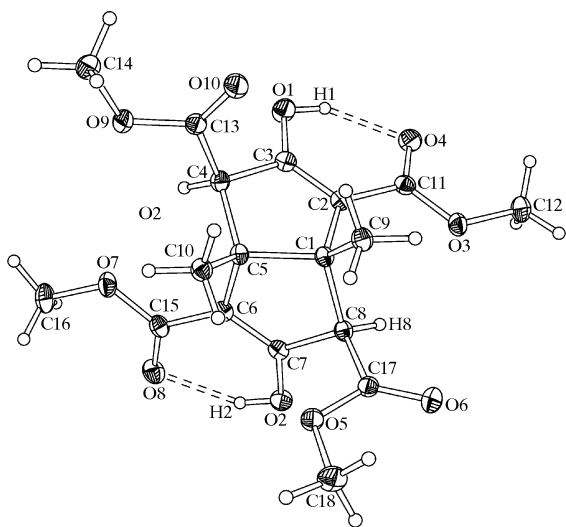


The series of compounds (I)–(V) (Figs. 1–5) are constructed from the central bicyclo[3.3.0]octa-2,6-diene core, with numbering for the nomenclature and the substitution as shown in the scheme. The structure contains two nonconjugated C=C double bonds at positions 2 and 6 and four methoxycarbonyl groups at positions 2, 4, 6 and 8. As expected from considering conjugation between the double bonds at positions 2 and 6 and the methoxycarbonyl groups at positions 2 and 4, these groups are coplanar with their anchoring carbon rings, with (C1/C3)–C2–C11–(O3/O4) and (C5/C7)–C6–C15–(O7/O8) torsion angles (Tables 1, 3, 5, 7 and 8) of less



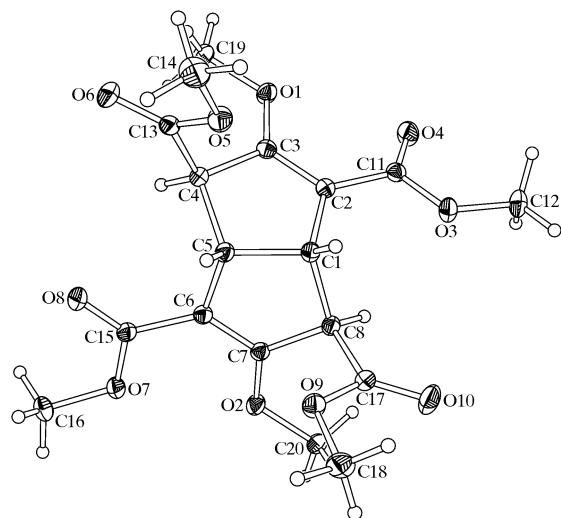
**Figure 1**  
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 33% probability level and H atoms are shown as spheres of arbitrary radii.

than 5°, except for (III) in which some of these angles are *ca* 15°. Given the planar nature of the methoxycarbonyl groups, two distinct orientations are possible for the methoxy groups at positions 2 and 6, either towards the ‘bridgehead’ side, *i.e.* internal, or towards the hydroxy group (positions 3 and 7), *i.e.* external. Both (I) and (II) have internal methoxy groups at the 2 and 6 positions, similar to both epimers of Williams *et al.* (1997). In contrast, the compounds with substituted hydroxy groups at positions 3 and 7 [*viz.* (III), (IV) and (V)] have an alternate pattern, with one internal and one external methoxy group. This situation can be rationalized in terms of the tendency of the OH group to form a hydrogen bond with the methoxycarbonyl C=O group in preference to a methoxy group. Strong intramolecular hydrogen bonds exist between



**Figure 2**

The molecular structure of (II), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 33% probability level and H atoms are shown as spheres of arbitrary radii.

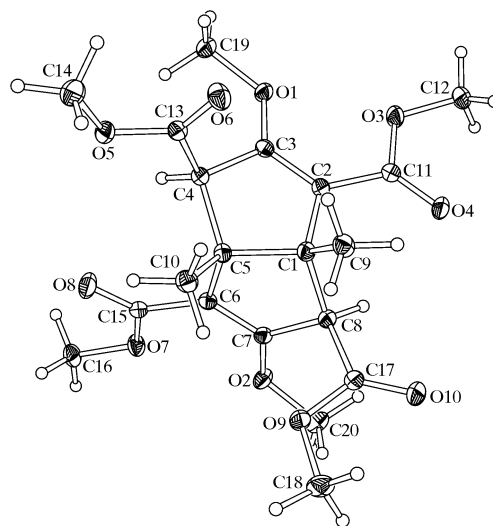


**Figure 3**

The molecular structure of (III), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 33% probability level and H atoms are shown as spheres of arbitrary radii.

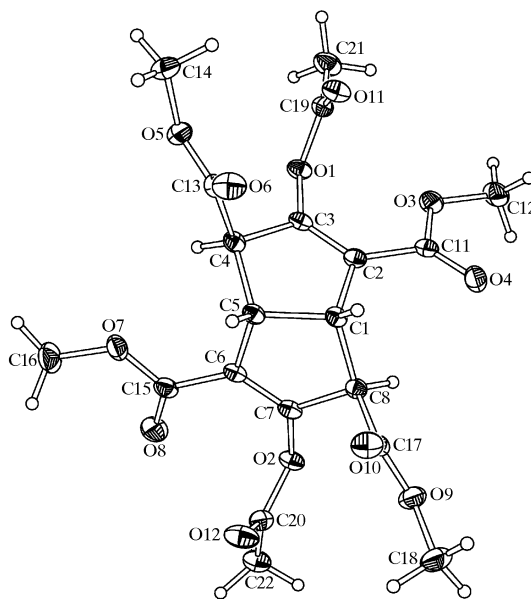
the OH and C=O groups (Desiraju, 2002), with O...O distances of 2.660 (2) and 2.672 (2) Å in (I), and 2.653 (2) and 2.635 (2) Å for (II).

Each of the two fused C<sub>5</sub> rings in the bicyclic core is almost planar, as indicated by the C–C–C–C torsion angles. As the rings are fused through *sp*<sup>3</sup>-like hybridized C atoms they are not coplanar and define dihedral angles of 54.93 (7), 69.85 (5), 64.07 (4), 80.74 (5) and 66.91 (7)° for (I)–(V), respectively, with the bicyclic core conformation best described as butterfly. The positions of the methoxycarbonyl groups on positions 4 and 8 are *exo* in all cases. Additionally, the groups located at positions 1 and 5 [H for (I), (III) and (V), and CH<sub>3</sub> for (II) and



**Figure 4**

The molecular structure of (IV), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 33% probability level and H atoms are shown as spheres of arbitrary radii.

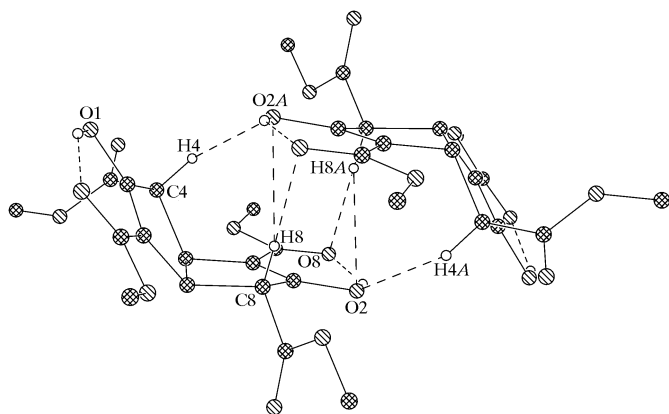


**Figure 5**

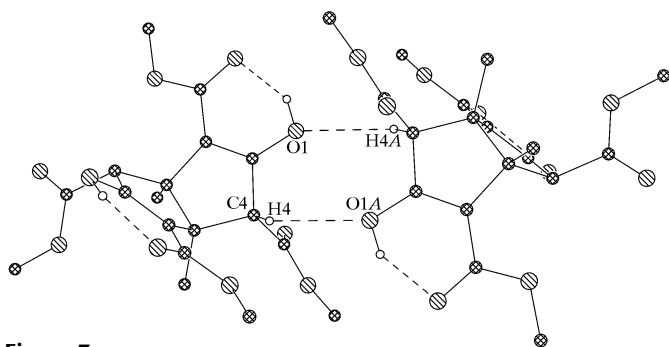
The molecular structure of (V), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 33% probability level and H atoms are shown as spheres of arbitrary radii.

(IV)] lie at opposite sides of the plane that bisects the carbon unit parallel to the C1–C5 bond, with C10–C5–C1–C9 torsion angles of 25.7 (2) and 25.0 (2)° for (II) and (IV), respectively. For compounds (I)–(IV), the groups connected to atoms O1 and O2 [H for (I) and (II), and CH<sub>3</sub> for (III) and (IV)] are almost coplanar with their rings; according to the C–C–O–C torsion angle data, the substituents are inclined at less than 15° for (III) and (IV). In (V), the acetyl group is perpendicular to each pentacyclic unit, with torsion angles close to 90°.

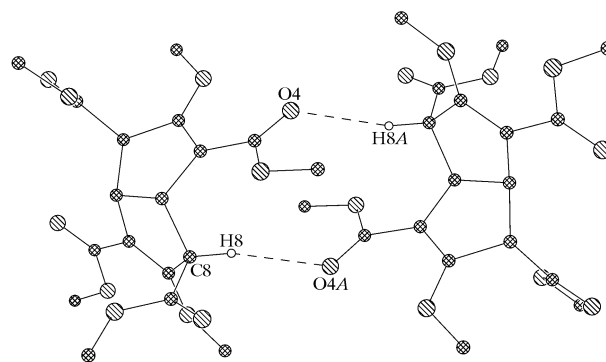
The *endo* H atoms H4 and H8 play an important role in determining the packing of the five compounds, since they define hydrogen bonds with C=O or OH oxygens on adjacent molecules. In this way, molecules of (I) form dimers through the interaction of atoms H4 and H8 with hydroxy atom O2A, and of atom H8 with carbonyl atom O8A [the suffix *A* denotes the symmetry code ( $-x, -y + 2, -z$ ); Fig. 6 and Table 2]. The butterfly wings of the two molecules in these dimers remain parallel, with a separation of *ca* 3.1 Å. The interactions of atom H4 with hydroxy atom O1( $-x + 1, -y, -z$ ) in (II) and of atom H8 with carbonyl atom O4( $-x + 1, -y + 1, -z + 2$ ) in (III) lead in the same way to intermolecular dimers (Figs. 7 and 8, and Tables 4 and 6), but with no parallelism between the



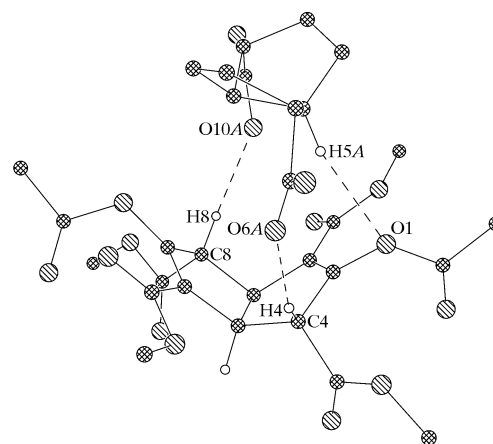
**Figure 6**  
The molecular packing for (I) [symmetry code: (A)  $-x, -y + 2, -z$ ]. C atoms are drawn as cross-hatched circles, O atoms as shaded circles and H atoms as open circles. Some of the H atoms have been omitted for clarity.



**Figure 7**  
The molecular packing for (II) [symmetry code: (A)  $-x + 1, -y, -z$ ]. Atoms are represented as in Fig. 6. Some of the H atoms have been omitted for clarity.



**Figure 8**  
The molecular packing for (III) [symmetry code: (A)  $-x + 1, -y + 1, -z + 2$ ]. Atoms are represented as in Fig. 6. Some of the H atoms have been omitted for clarity.



**Figure 9**  
The molecular packing for (V) [symmetry code: (A)  $x, -y + \frac{3}{2}, -z - \frac{1}{2}$ ]. Atoms are represented as in Fig. 6. Some of the H atoms and some atoms not involved in the interactions shown have been omitted for clarity.

butterfly wings. The interactions of atoms H4 and H8 with carbonyl atoms O6A and O10A, respectively, in addition to the interaction of atom O1 with H5A, leads to a chain structure for (V) [the suffix *A* denotes the symmetry code ( $x, -y + \frac{3}{2}, -z - \frac{1}{2}$ ); Fig. 9 and Table 9]. The molecules are positioned in a concave-to-convex arrangement. As the molecules are not planar, the direction of each of the vicinal chains is opposite. This interaction between the *endo* bicyclic atoms H4 and H8 with other O atoms in the vicinal molecule is not present for (IV), where the packing just contains C<sub>methyl</sub>–H···O contacts.

## Experimental

The synthesis of (I) followed the previously reported protocol of Bertz *et al.* (1982), slightly modified in order to avoid the formation of sticky by-products. The sodium salt C<sub>16</sub>H<sub>16</sub>O<sub>10</sub>Na<sub>2</sub> (26.86 g, 0.065 mol) was dissolved in the minimum amount of distilled water (*ca* 150 ml). Under vigorous stirring, 1 M acetic acid solution was added dropwise (*ca* 1 ml min<sup>-1</sup>); a white solid began to appear, which redissolved quickly (dropwise addition of the acid avoids formation of the sticky product), with 128 ml of 1 M acetic acid added in total.

The white solid formed was filtered off and redissolved in ethyl acetate, and the resulting solution was dried (MgSO<sub>4</sub>), filtered and concentrated under vacuum to obtain a white solid. Recrystallization from acetone gave colorless prismatic crystals in 98% yield [m.p. 383.1–383.8 K; literature m.p. 374–376 K (Bertz *et al.*, 1982)]. The synthesis of (II) followed the same procedure as described for (I) but starting from C<sub>18</sub>H<sub>20</sub>O<sub>10</sub>Na<sub>2</sub>. Recrystallization from acetone gave colorless crystals (m.p. 427.1–428.3 K; yield 83%). Compound (I) (6.00 g, 0.016 mol) or (II) (6.0 g, 0.016 mol) was suspended in dry diethyl ether and then treated dropwise with excess diazomethane dissolved in diethyl ether [prepared from *N*-nitrosomethylurea and KOH according to Arndt (1943)]. The excess diazomethane was allowed to react for 12 h until no more of reactant (I) or (II) was visible by thin-layer chromatography (aluminium foil, silica gel 60 F<sub>254</sub>, ethyl acetate–hexane 1:3). The solution was evaporated under vacuum to give a light-yellow solid, which was redissolved in methanol (250 ml) and allowed to crystallize, yielding 4.87 g of colorless crystals of (III) (m.p. 411.9–413.2 K; yield 76.1%) or 1.87 g of colorless crystals of (IV) (m.p. 440.7–442.3 K; yield 87.4%). For the synthesis of (V), a mixture of acetic acid (40 ml) and acetic anhydride (10 ml, 0.085 mol) was added to (I) (15.38 g, 0.042 mol) and the resulting mixture refluxed [the solid compound (I) dissolves upon heating]. After 40 min, the heat was removed and distilled water (10 ml) was added to the reactor (in small portions with care). The mixture was allowed to cool to room temperature and extracted with ethyl acetate (3 × 50 ml). The extract was dried with MgSO<sub>4</sub>. Evaporation under vacuum led to 10.2 g of a white powdered solid, which was recrystallized from acetone to give X-ray quality colorless crystals of (V) (m.p. 369.7–371.2 K; yield 53.4%). When the procedure was applied to (II), no acetylated products were observed.

### Compound (I)

#### Crystal data

C<sub>16</sub>H<sub>18</sub>O<sub>10</sub>  $V = 1711.5 (4) \text{ \AA}^3$   
 $M_r = 370.30$   $Z = 4$   
 Monoclinic,  $P2_1/n$  Mo  $K\alpha$  radiation  
 $a = 12.1198 (18) \text{ \AA}$   $\mu = 0.12 \text{ mm}^{-1}$   
 $b = 12.5461 (19) \text{ \AA}$   $T = 150 (2) \text{ K}$   
 $c = 12.4089 (19) \text{ \AA}$   $0.55 \times 0.21 \times 0.13 \text{ mm}$   
 $\beta = 114.896 (2)^\circ$

#### Data collection

Siemens SMART CCD area-detector diffractometer 11440 measured reflections  
 3025 independent reflections  
 Absorption correction: part of the refinement model ( $\Delta F$ ) (SADABS; Bruker, 1999) 2583 reflections with  $I > 2\sigma(I)$   
 $T_{\min} = 0.935$ ,  $T_{\max} = 0.984$   $R_{\text{int}} = 0.028$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$  H atoms treated by a mixture of independent and constrained refinement  
 $wR(F^2) = 0.103$   $\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$   
 $S = 1.04$   $\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$   
 3025 reflections  
 247 parameters

**Table 1**

Selected torsion angles ( $^\circ$ ) for (I).

C1–C2–C3–C4	−0.85 (19)	C3–C2–C11–O3	−174.64 (14)
C2–C3–C4–C5	8.92 (18)	C3–C2–C11–O4	4.1 (2)
C5–C6–C7–C8	−5.02 (19)	C5–C6–C15–O7	3.1 (2)
C6–C7–C8–C1	13.33 (17)	C5–C6–C15–O8	−179.52 (15)
C1–C2–C11–O3	1.6 (2)	C7–C6–C15–O7	−173.64 (14)
C1–C2–C11–O4	−179.69 (15)	C7–C6–C15–O8	3.7 (2)

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 $\cdots$ O4	0.89 (2)	1.89 (2)	2.6720 (18)	146 (2)
O2–H2 $\cdots$ O8	0.85 (2)	1.91 (2)	2.6597 (17)	146 (2)
C8–H8 $\cdots$ O8 <sup>i</sup>	1.00	2.62	3.602 (2)	169
C4–H4 $\cdots$ O2 <sup>i</sup>	1.00	2.53	3.237 (2)	128

Symmetry code: (i)  $-x, -y + 2, -z$ .

### Compound (II)

#### Crystal data

C<sub>18</sub>H<sub>22</sub>O<sub>10</sub>  $\gamma = 109.208 (1)^\circ$   
 $M_r = 398.36$   $V = 917.90 (11) \text{ \AA}^3$   
 Triclinic,  $P\bar{1}$   $Z = 2$   
 $a = 9.3037 (6) \text{ \AA}$  Mo  $K\alpha$  radiation  
 $b = 10.2495 (7) \text{ \AA}$   $\mu = 0.12 \text{ mm}^{-1}$   
 $c = 10.6378 (7) \text{ \AA}$   $T = 150 (2) \text{ K}$   
 $\alpha = 95.155 (1)^\circ$   $0.55 \times 0.42 \times 0.39 \text{ mm}$   
 $\beta = 103.114 (1)^\circ$

#### Data collection

Siemens SMART CCD area-detector diffractometer 5494 measured reflections  
 3209 independent reflections  
 Absorption correction: part of the refinement model ( $\Delta F$ ) (SADABS; Bruker, 1999) 2900 reflections with  $I > 2\sigma(I)$   
 $T_{\min} = 0.938$ ,  $T_{\max} = 0.955$   $R_{\text{int}} = 0.011$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$  H atoms treated by a mixture of independent and constrained refinement  
 $wR(F^2) = 0.095$   $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$   
 $S = 1.03$   $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$   
 3209 reflections  
 267 parameters

**Table 3**

Selected torsion angles ( $^\circ$ ) for (II).

C1–C2–C3–C4	−2.47 (17)	C3–C2–C11–O4	−2.9 (2)
C2–C3–C4–C5	−10.61 (15)	C5–C6–C15–O7	2.9 (2)
C5–C6–C7–C8	−0.16 (17)	C5–C6–C15–O8	−176.92 (13)
C6–C7–C8–C1	−13.05 (15)	C7–C6–C15–O7	179.87 (12)
C1–C2–C11–O3	1.6 (2)	C7–C6–C15–O8	0.1 (2)
C1–C2–C11–O4	−177.43 (13)	C9–C1–C5–C10	−25.72 (16)
C3–C2–C11–O3	176.19 (12)		

**Table 4**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 $\cdots$ O4	0.89 (2)	1.85 (2)	2.6354 (16)	146 (2)
O2–H2 $\cdots$ O8	0.89 (2)	1.86 (2)	2.6533 (15)	146.8 (18)
C4–H4 $\cdots$ O1 <sup>i</sup>	0.98	2.56	3.2533 (18)	128

Symmetry code: (i)  $-x + 1, -y, -z + 1$ .

### Compound (III)

#### Crystal data

C<sub>18</sub>H<sub>22</sub>O<sub>10</sub>  $V = 1832.15 (11) \text{ \AA}^3$   
 $M_r = 398.36$   $Z = 4$   
 Monoclinic,  $P2_1/n$  Mo  $K\alpha$  radiation  
 $a = 13.4118 (4) \text{ \AA}$   $\mu = 0.12 \text{ mm}^{-1}$   
 $b = 8.3693 (3) \text{ \AA}$   $T = 150 (2) \text{ K}$   
 $c = 17.4894 (6) \text{ \AA}$   $0.48 \times 0.43 \times 0.42 \text{ mm}$   
 $\beta = 111.049 (1)^\circ$

### Data collection

Siemens SMART CCD area-detector diffractometer  
Absorption correction: part of the refinement model ( $\Delta F$ ) (*SADABS*; Bruker, 1999)  
 $T_{\min} = 0.923$ ,  $T_{\max} = 0.930$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.095$   
 $S = 1.03$   
3200 reflections

8916 measured reflections  
3200 independent reflections  
2987 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.011$

259 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{\AA}^{-3}$

**Table 5**

Selected torsion angles ( $^\circ$ ) for (III).

C1–C2–C3–C4	0.61 (15)	C3–C2–C11–O4	–16.2 (2)
C2–C3–C4–C5	–9.33 (14)	C5–C6–C15–O7	–176.66 (10)
C5–C6–C7–C8	3.01 (15)	C5–C6–C15–O8	1.25 (19)
C6–C7–C8–C1	–11.00 (13)	C7–C6–C15–O7	–7.57 (19)
C1–C2–C11–O4	166.75 (12)	C7–C6–C15–O8	170.33 (13)
C1–C2–C11–O3	–12.78 (16)	C2–C3–O1–C19	–176.97 (12)
C3–C2–C11–O3	164.30 (12)	C6–C7–O2–C20	–171.39 (12)

**Table 6**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (III).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C8–H8 $\cdots$ O4 <sup>i</sup>	1.00	2.47	3.4489 (15)	166

Symmetry code: (i)  $-x + 1, -y + 1, -z + 2$ .

### Compound (IV)

#### Crystal data

$C_{20}H_{26}O_{10}$   
 $M_r = 426.41$   
Monoclinic,  $P2_1/n$   
 $a = 11.6352$  (4)  $\text{\AA}$   
 $b = 13.3095$  (4)  $\text{\AA}$   
 $c = 13.2262$  (4)  $\text{\AA}$   
 $\beta = 96.369$  (1) $^\circ$

$V = 2035.55$  (11)  $\text{\AA}^3$   
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.11 \text{ mm}^{-1}$   
 $T = 150$  (2) K  
 $0.60 \times 0.29 \times 0.14 \text{ mm}$

#### Data collection

Siemens SMART CCD area-detector diffractometer  
Absorption correction: part of the refinement model ( $\Delta F$ ) (*SADABS*; Bruker, 1999)  
 $T_{\min} = 0.936$ ,  $T_{\max} = 0.985$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.112$   
 $S = 1.01$   
3594 reflections

12490 measured reflections  
3594 independent reflections  
3089 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$

279 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$

**Table 7**

Selected torsion angles ( $^\circ$ ) for (IV).

C1–C2–C3–C4	–0.89 (17)	C5–C6–C15–O7	174.57 (12)
C2–C3–C4–C5	–12.71 (16)	C5–C6–C15–O8	–5.3 (2)
C5–C6–C7–C8	–1.57 (17)	C7–C6–C15–O7	–13.8 (2)
C6–C7–C8–C1	–11.98 (16)	C7–C6–C15–O8	166.27 (16)
C1–C2–C11–O4	2.1 (2)	C9–C1–C5–C10	–25.03 (18)
C1–C2–C11–O3	–177.17 (12)	C2–C3–O1–C19	–167.08 (14)
C3–C2–C11–O3	–5.4 (2)	C6–C7–O2–C20	–164.46 (14)
C3–C2–C11–O4	173.92 (15)		

### Compound (V)

#### Crystal data

$C_{20}H_{22}O_{12}$   
 $M_r = 454.38$   
Monoclinic,  $P2_1/c$   
 $a = 10.0095$  (5)  $\text{\AA}$   
 $b = 20.9263$  (12)  $\text{\AA}$   
 $c = 10.1881$  (6)  $\text{\AA}$   
 $\beta = 90.507$  (1) $^\circ$

$V = 2133.9$  (2)  $\text{\AA}^3$   
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.12 \text{ mm}^{-1}$   
 $T = 150$  (2) K  
 $0.34 \times 0.12 \times 0.12 \text{ mm}$

#### Data collection

Siemens SMART CCD area-detector diffractometer  
Absorption correction: part of the refinement model ( $\Delta F$ ) (*SADABS*; Bruker, 1999)  
 $T_{\min} = 0.983$ ,  $T_{\max} = 0.986$

13188 measured reflections  
3766 independent reflections  
2596 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.057$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.146$   
 $S = 0.91$   
3766 reflections

295 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$

**Table 8**

Selected torsion angles ( $^\circ$ ) for (V).

C1–C2–C3–C4	3.1 (3)	C3–C2–C11–O4	170.1 (3)
C2–C3–C4–C5	–13.2 (3)	C5–C6–C15–O7	–5.0 (3)
C5–C6–C7–C8	3.1 (3)	C5–C6–C15–O8	175.8 (3)
C6–C7–C8–C1	–12.5 (3)	C7–C6–C15–O7	173.4 (2)
C1–C2–C11–O3	173.1 (2)	C7–C6–C15–O8	–5.9 (4)
C1–C2–C11–O4	–7.6 (4)	C2–C3–O1–C19	–78.7 (3)
C3–C2–C11–O3	–9.2 (4)	C6–C7–O2–C20	–70.4 (3)

**Table 9**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (V).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4–H4 $\cdots$ O6 <sup>i</sup>	1.00	2.35	3.290 (3)	156
C8–H8 $\cdots$ O10 <sup>i</sup>	1.00	2.33	3.138 (3)	137
C5–H5 $\cdots$ O1 <sup>ii</sup>	1.00	2.63	3.614 (3)	168

Symmetry codes: (i)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (ii)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ .

The hydroxy H atoms (where present) were located in a Fourier map and refined with isotropic displacement parameters. For all other H atoms, the H-atom positions were calculated after each cycle of refinement with *SHELXTL-NT* (Bruker, 1999) using a riding model for each structure, with C–H distances in the range 0.96–1.00  $\text{\AA}$ .  $U_{\text{iso}}(\text{H})$  values were set equal to  $1.5U_{\text{eq}}$  of the parent C atom for the methyl groups and  $1.2U_{\text{eq}}(\text{C})$  for the other H atoms.

For all compounds, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1999); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

The authors gratefully acknowledge generous financial support from FONDECYT (grant No. 11060176) and Universidad Andr s Bello (grant Nos. DI-UNAB-20-06/R and DI-UNAB-22-06/I).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3136). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Arndt, F. (1943). *Org. Synth. Coll.* **2**, 461.
- Bertz, S. H., Rihs, G. & Woodward, R. B. (1982). *Tetrahedron*, **38**, 63–70.
- Bruker (1999). *SAINTE-NT* (Version 6.02), *SHELXTL-NT* (Version 6.10) and *SADABS* (Version 2.05). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). *SMART-NT*. Version 5.624. Bruker AXS Inc., Madison, Wisconsin, USA.
- Desiraju, G. R. (2002). *Acc. Chem. Res.* **35**, 565–573.
- Djaidi, D. (2006). PhD thesis, University of New South Wales, Sydney, Australia.
- Djaidi, D., Bishop, R., Craig, D. C. & Scudder, M. L. (2002). *New J. Chem.* **26**, 614–616.
- Docken, A. M. (1981). *J. Org. Chem.* **46**, 4096–4097.
- Gupta, A. K., Fu, X., Snyder, J. P. & Cook, J. M. (1991). *Tetrahedron*, **47**, 3665–3710.
- Schroeter, G. (1922). *Liebigs Ann. Chem.* **426**, 1–17.
- Vossen, G. (1910). Inaugural dissertation, University of Bonn, Germany.
- Williams, R. V., Gadgil, V. R., Vij, A., Cook, J. M., Kubiak, G. & Huang, Q. (1997). *J. Chem. Soc. Perkin Trans. 1*, pp. 1425–1428.