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Three Intermediates in the Synthesis of Chrysanthemic Acid

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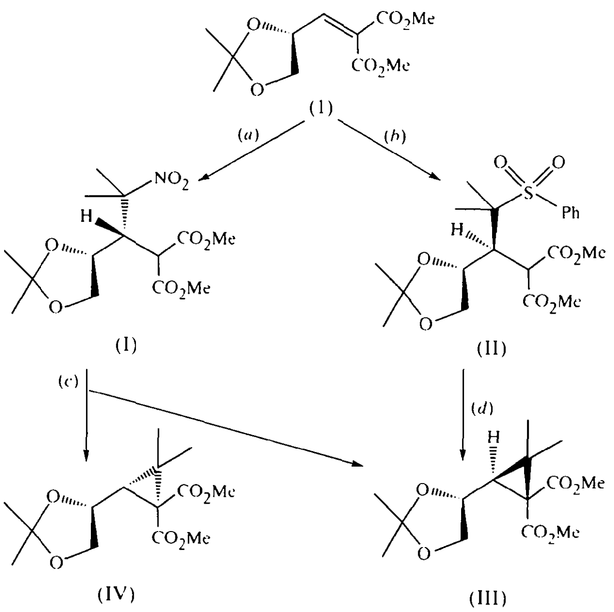
Abstract

The structures of three compounds, namely, dimethyl 2-{(1*S*)-1-[(4*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-methyl-2-nitropropyl}malonate [$C_{14}H_{23}NO_8$, (I)], dimethyl 2-{(1*S*)-1-[(4*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-methyl-2-(phenylsulfonyl)propyl}malonate [$C_{20}H_{28}O_8S$, (II)] and dimethyl (3*S*)-2,2-dimethyl-3-[(4*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]cyclopropane-1,1-dicarboxylate [$C_{14}H_{22}O_6$, (III)], which are intermediates in the synthesis of chrysanthemic acid, are presented and discussed.

Comment

Some esters of chrysanthemic acid are powerful insecticides (Elliott & Janes, 1978) and significant efforts have been made to design synthetic routes which produce them in high yield and with high enantiomeric purity. Dimethyl 2,2-dimethyl-3-(2,2-dimethyl-1,3-dioxolan-4-yl)cyclopropane-1,1-dicarboxylate, (III), is a valuable intermediate of chrysanthemic acid and we have studied a new diastereoselective synthesis (see scheme below) of this compound (Froidbize, 1997; Krief *et al.*, 1998). This synthesis uses the enantiomerically pure alkylidene malonate (1) (produced from D-mannitol) as the starting compound. During this study, it was necessary to unambiguously establish the relative stereochemistry of intermediate malonates (I) and (II), as well as the target molecule (III), and so their structures were determined by single-crystal X-ray diffraction.



(*a*) $LiC(CH_3)_2NO_2$, DMSO, 293 K, 24 h;
(*b*) $LiC(CH_3)_2SO_2Ph$, THF, 273 K, 2 h;
(*c*) Cs_2CO_3, DMSO, 353 K, 24 h;
(*d*) Cs_2CO_3, DMSO, 353 K, 8 h.

Compound (I) (Fig. 1) was obtained in 72% yield by a diastereoselective Michael addition of 2-lithio-2-nitropropane on alkylidene malonate (1). The absolute configuration of compound (1) being known, it was possible to establish the configuration of (I) to be (3*S*,4*S*). The dioxolane ring (C4–C6, O5, O6) is in the so-called 'envelope' conformation (Dunitz, 1979), with the O5 atom out of the plane defined by the other four atoms. The conformation around the C1—C3 single bond is energetically-disfavoured 'eclipsed', with the H1—C1 and C3—C2 bonds facing each other (Table 1). In contrast, the conformation around the C3—C2 single bond is 'staggered', the nitro group and the C1 atom being in *anti* positions. Consequently, the H1 atom, which is close to the two methyl groups of the nitropropyl substituent, is in a crowded environment.

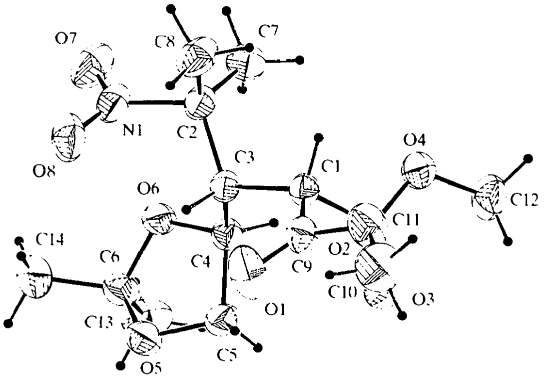


Fig. 1. The molecular structure of compound (I). Displacement ellipsoids are drawn at the 50% probability level and the H1 atom is linked to C1.

Compound (II) (Fig. 2) was obtained in 58% yield by a diastereoselective Michael addition of 2-lithio-2-phenylsulfonylpropane on compound (1). The absolute configuration of compound (II) is (3*S*,4*S*), for the same reason as for compound (I), and the dioxolane ring (C4–C6, O5, O6) is also in an 'envelope' conformation, with the C6 atom out of the plane defined by the other four atoms. The conformations around the C1—C3, C3—C2 and C3—C4 single bonds are all 'staggered' (Table 1). The H1 and C2 atoms are in *anti* positions. Consequently, the H1 atom is easily accessible.

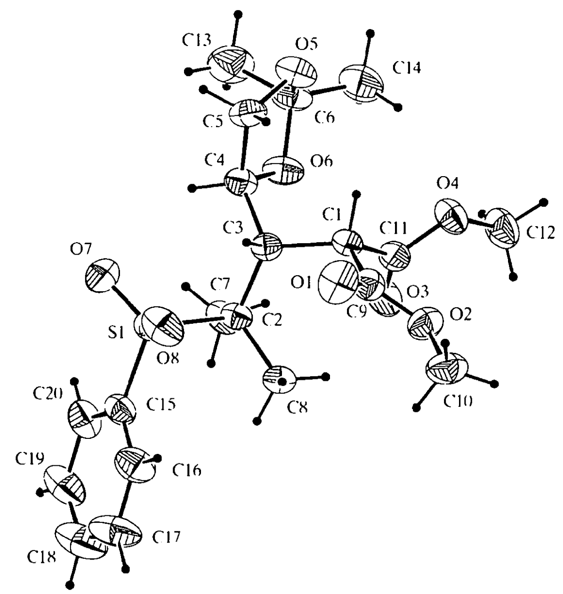


Fig. 2. The molecular structure of compound (II). Displacement ellipsoids are drawn at the 50% probability level and the H1 atom is linked to C1.

Compound (III) (Fig. 3) was obtained by two methods (see scheme above). If adduct (I) is heated with caesium carbonate in dimethylsulfoxide (DMSO), a 3:1 mixture of cyclopropanes (III) and (IV) is obtained in a 57% overall yield after 24 h (reaction *c*). However, if adduct (II) is treated in the same way, then cyclopropane (III) is obtained exclusively in 76% yield after 8 h (reaction *d*). The absolute stereochemistry of compound (III) is (3*S*,4*S*), the stereochemistry at the C4 atom being known, and the dioxolane ring (C4–C6, O5, O6) is in an 'envelope' conformation, with the C5 atom out of the plane defined by the other four atoms. The conformation around the C3—C4 single bond is 'staggered', with atoms H3 and H4 in *anti* positions (Table 1). The carbonyl O3 atom is agitated [U_{eq} = 0.0866 (9) Å^2].

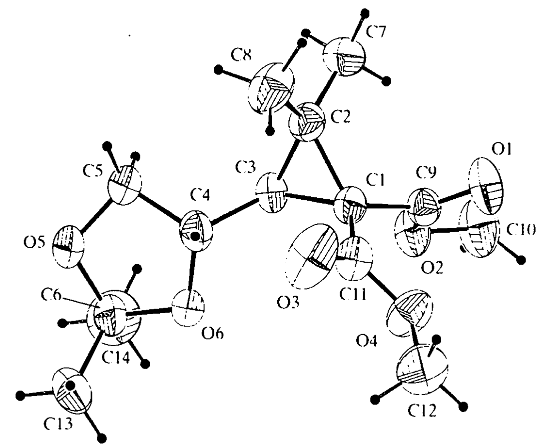


Fig. 3. The molecular structure of compound (III). Displacement ellipsoids are drawn at the 50% probability level.

The difference in reactivity of compounds (I) and (II) with caesium carbonate in DMSO can be partly explained by the difference in accessiblity of the acidic H1 atom, which is greater in compound (II) than in compound (I).

Experimental

The syntheses of compounds (I)–(IV) have been reported elsewhere (Krief *et al.*, 1998). Compounds (I)–(III) were all crystallized, without special care, by evaporation of diethyl ether solutions over a period of 14 h.

Compound (I)

Crystal data

$C_{14}H_{23}NO_8$
M_r = 333.33
Orthorhombic
$P2_12_12_1$
a = 8.003 (5) Å
b = 11.253 (5) Å
c = 18.461 (5) Å
V = 1662.6 (14) Å^3
Z = 4
D_x = 1.332 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 40–50°
μ = 0.933 mm^{-1}
T = 292 (2) K
Parallelepiped
0.45 × 0.20 × 0.20 mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2317 measured reflections
2140 independent reflections
2065 reflections with $I > 2\sigma(I)$

R_{int} = 0.098
θ_{max} = 71.80°
$h = 0 \rightarrow 9$
$k = -8 \rightarrow 13$
$l = 0 \rightarrow 22$
3 standard reflections frequency: 60 min intensity decay: 19%

Refinement

Refinement on F^2
$R(F)$ = 0.052
$wR(F^2)$ = 0.124
S = 1.062
2140 reflections
213 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0957P)^2 + 0.0501P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.194 e Å^{-3}
$\Delta\rho_{min}$ = −0.332 e Å^{-3}

H atoms treated by a mixture of independent and constrained refinement

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

$C_{20}H_{28}O_8S$
$M_r = 428.48$
Monoclinic
$P2_1$
$a = 10.693\ (1)$ Å
$b = 8.446\ (1)$ Å
$c = 11.992\ (1)$ Å
$\beta = 101.268\ (5)^\circ$
$V = 1062.16\ (18)$ Å^3
$Z = 2$
$D_x = 1.340$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40$–50°
$\mu = 1.736$ mm^{-1}
$T = 292\ (2)$ K
Irregular
$0.30 \times 0.18 \times 0.14$ mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3339 measured reflections
2234 independent reflections
2104 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.016$
$\theta_{\rm max} = 71.79^\circ$
$h = -12 \rightarrow 13$
$k = -10 \rightarrow 0$
$l = -14 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: 6.0%

Refinement

Refinement on F^2
$R(F) = 0.030$
$wR(F^2) = 0.077$
$S = 1.083$
2234 reflections
266 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.0142P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.125$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.250$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter $= -0.05\ (2)$

Compound (III)

Crystal data

$C_{14}H_{22}O_6$
$M_r = 286.32$
Orthorhombic
$P2_12_12_1$
$a = 7.3201\ (1)$ Å
$b = 10.719\ (1)$ Å
$c = 19.390\ (1)$ Å
$V = 1521.46\ (16)$ Å^3
$Z = 4$
$D_x = 1.250$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40$–50°
$\mu = 0.814$ mm^{-1}
$T = 292\ (2)$ K
Irregular
$0.18 \times 0.05 \times 0.04$ mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*NRCVAX*; Gabe *et al.*, 1989)
$T_{\rm min} = 0.853$, $T_{\rm max} = 0.997$
2444 measured reflections
2215 independent reflections
2016 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.050$
$\theta_{\rm max} = 71.86^\circ$
$h = -6 \rightarrow 9$
$k = -9 \rightarrow 13$
$l = -17 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 10%

Refinement

Refinement on F^2
$R(F) = 0.049$
$wR(F^2) = 0.142$
$S = 1.082$
2215 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2 + 0.3468P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.241$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.291$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (°)*

Compound (I)			
N1—C2—C3—C1	−165.31 (15)	H1—C1—C3—C2	4.5
Compound (II)			
S1—C2—C3—C1	144.55 (17)	H4—C4—C3—C1	170.5
H1—C1—C3—C2	173.9		
Compound (III)			
H3—C3—C4—H4	176.4		

For all compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *NONIUS*93 (Baudoux & Evrard, 1993) for (I) and (II); *NRCVAX* (Gabe *et al.*, 1989) for (III). Program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1993) for (I) and (II); *SHELXS*97 (Sheldrick, 1990) for (III). For all compounds, program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1167). Services for accessing these data are described at the back of the journal.

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Lignin Model Compounds: 4,4′-*O*-Dimethyldehydrodiacetovanillone and 4,4′-*O*-Diethyldehydrodiacetovanillone

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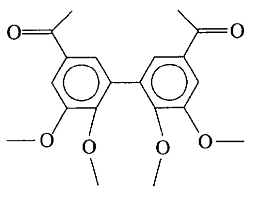
Abstract

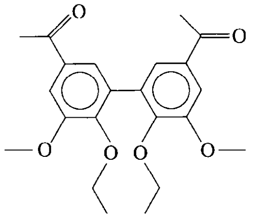
The title compounds, 5,5′-diacetyl-2,2′,3,3′-tetramethoxy-1,1′-biphenyl, $C_{20}H_{22}O_6$, and 5,5′-diacetyl-2,2′-diethoxy-3,3′-dimethoxy-1,1′-biphenyl (IUPAC nomenclature), $C_{22}H_{26}O_6$, correspond to the 5,5′-biphenyl-type lignin model compound. They were synthesized from dehydrodiacetovanillone by alkylation with CH_3I and C_2H_5I. In the former compound, all non-H atoms in the asymmetric unit are planar except for one C atom. In the latter compound, there are two molecules of different conformations, one of which is affected by disorder.

Comment

Lignin is a macromolecule which causes paper to yellow with age. It is a by-product of the cellulose industry and represents an important source for the production of aromatic substances. The main route for elucidation of the complex lignin structure has been the synthesis of small molecules followed by comparative NMR and IR studies of the model compound prepared and the lignin (Hergert, 1971; Drumond *et al.*, 1989, 1992). Structure determination by diffraction techniques can be helpful in interpreting NMR and IR spectra. The title compounds, (I) and (II), described herein were synthesized with the aim of studying dimeric model compounds related to 5,5′-arylpropanoid substructures (biphenyl derivatives) frequently found in lignins (Sarkanen & Ludwing, 1971; Adler, 1977; Chen, 1991).



(I)



(II)

The structure of 4,4′-*O*-dimethyldehydrodiacetovanillone, (I), is shown in Fig. 1. Half of the molecule constitutes an asymmetric unit. The average deviation of the aromatic ring C atoms from the best least-squares plane through the rings is 0.010 (2) Å. The dihedral angle between the two aromatic ring planes is 60.00 (7)°. All of the non-H atoms in the asymmetric unit are almost planar, except for C10, which deviates by 1.291 (3) Å from the best least-squares plane.

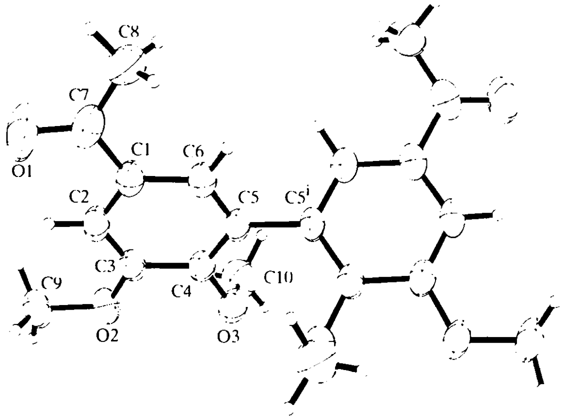


Fig. 1. The molecular structure of 4,4′-*O*-dimethyldehydrodiacetovanillone with ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.]

The structure of compound (II), 4,4′-*O*-diethyldehydrodiacetovanillone, is shown in Fig. 2. There are two molecules of different conformations in the asymmetric unit. The C(ring)—O(methoxy and/or ethoxy) bonds have a mean length of 1.371 (6) Å (external standard deviation estimate, *i.e.* calculated from the scatter of the data). The average bond distances and angles in the aromatic rings are 1.389 (9) Å and 120 (1)°, respectively. As expected, the four aromatic rings are planar, the maximum deviation from the best least-squares plane being 0.022 (2) Å. The dihedral angles between the aromatic rings are 114.9 (2) and 60.2 (1)° in molecules *A* and *B*, respectively. The structure of the *B* isomer is analogous to that of compound (I).

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† Deceased January 10, 1997.

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