Data collection

Enraf–Nonius CAD-4 diffractometer	1199 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.049$
Absorption correction: semi-empirical ψ scans (Spek, 1995b)	$\theta_{max} = 28.95°$
	$h = -12 \rightarrow 17$
	$k = -17 \rightarrow 13$
$T_{min} = 0.349$, $T_{max} = 0.386$	$l = -13 \rightarrow 25$
3030 measured reflections	3 standard reflections
1534 independent reflections	every 200 reflections intensity decay: 1.05%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$\Delta\rho_{max} = 0.334$ e Å^{-3}
$wR(F^2) = 0.067$	$\Delta\rho_{min} = -0.836$ e Å^{-3}
$S = 1.073$	Extinction correction: none
1534 reflections	Scattering factors from
89 parameters	International Tables for
H atoms refined	Crystallography (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j a_i.a_j.$$

	x	y	z	U_{eq}
Se	0.16480 (2)	0.05801 (3)	0.162402 (15)	0.02664 (10)
C1	0	0	0.1246 (2)	0.0224 (9)
C11	0.2174 (2)	−0.0361 (2)	0.10738 (13)	0.0224 (5)
C12	0.2865 (3)	0.0158 (3)	0.04703 (15)	0.0280 (6)
C13	0.3339 (3)	−0.0461 (3)	0.00977 (16)	0.0316 (6)
C14	0.3112 (3)	−0.1600 (3)	0.03236 (15)	0.0299 (6)
C15	0.2413 (3)	−0.2124 (3)	0.09203 (14)	0.0272 (6)
C16	0.1938 (3)	−0.1511 (3)	0.12988 (14)	0.0253 (5)

Table 2. *Selected geometric parameters (Å, °)*

Se—C11	1.928 (3)	C1—H1	1.10 (6)
Se—C1	1.9581 (16)		
C11—Se—C1	101.40 (11)	Se—C1—H1	111.49 (12)
Se—C1—Se'	107.38 (12)		

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SET4* in *CAD-4 Software*. Data reduction: *HELENA* (Spek, 1995a). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL97*.

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9-Methyl-8,11,12-trioxatricyclo[7.2.1.0²,⁷]-dodeca-2,4,6-trien-10-one

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Abstract

9-Methyl-8,11,12-trioxatricyclo[7.2.1.0²,⁷]dodeca-2,4,6-trien-10-one, $C_{10}H_8O_4$, was formed as an unexpected product of the reaction between salicylaldehyde and pyruvic acid. The main structural feature is the tricyclic system, which contains an O atom in each of the bridges.

Comment

The esterification of phenol and pyruvic acid is simple, according to the procedure of Hassner & Alexanian (1978), shown in reaction scheme (1).
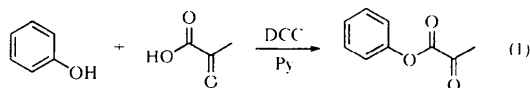
The dehydrating agent N,N-dicyclohexylcarbodiimide (DCC) leads to the formal loss of one equivalent of H_2O, but the regioselectivity of the O—C bond formation between salicylaldehyde, (I), and the activated pyruvic acid is different. The reaction does not lead to the corresponding ester. The title compound, (II), was synthesized as shown in reaction scheme (2) and isolated as a white crystalline solid.
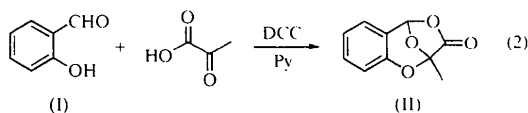
The phenolic O atom apparently does not attack the carboxyl group. Instead, the more exposed formyl O atom acts as a nucleophile. A conceivable mechanism for the consecutive steps is shown in reaction scheme (3).
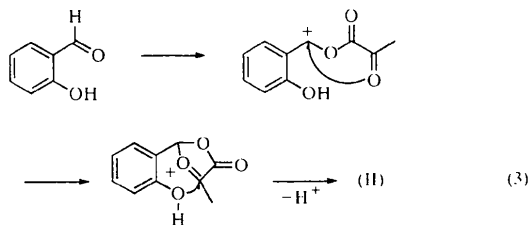
The non-aromatic part of compound (II) can be envisaged as a bicyclic system containing a twofold intramolecular O,O-acetal. The ready formation of an acetal came as a surprise, in particular since pyruvic acid is not known to be hydrated in solution to a significant degree under basic reaction conditions (Cooper & Redfield, 1975).

No comparable structures could be found in the Cambridge Structural Database (1997). In 3-chloromethyl-1,5,7-trimethyl-2,4,6,8-tetraoxatricyclo[3.3.1.0^{3,7}]nonane (Dodge, 1972), one can identify the same framework, but this latter structure contains only sp^3-C atoms, leading to a different geometry of the tricyclic system. We therefore prefer to compare the title structure

with values cited in the *International Tables for Crystallography* (1995, Vol. C). The C1—O7 distance of 1.386 (2) Å agrees well with the value for C_{ar}—O2 in aryl alkyl ethers (1.370 Å), as do the C_{sp^3}—O2 distances [1.407 (3)–1.454 (3) Å] with the cited value for dialkyl ethers (1.426 Å). The distances around C9 [1.347 (3) Å, *op. cit.* 1.336 Å; 1.191 (3) Å, *op. cit.* 1.208 Å] are also in good agreement with literature values.

In the crystal packing, no intermolecular contacts are shorter than normal van der Waals separations.

Experimental

The title compound was obtained by the reaction of salicylaldehyde (1.3 equivalents) and pyruvic acid (1 equivalent) according to Hassner's procedure [1 equivalent pyridine, 1 equivalent DCC, catalyst 4-dimethylaminopyridine (DMAP)]. After stirring for 6 h at 298 K, the urea was filtered and the solvent was evaporated. The crude product was distilled *in vacuo* in a Kugelrohr apparatus. The title compound was isolated as colourless needles [433 K, 0.1 mbar (1 mbar = 100 Pa)]. M.p.: 360–361 K (Gallenkamp, uncorrected). Elemental analysis for $C_{10}H_8O_4$: calculated C 62.50, H 4.20%; found C 62.63, H 4.23% (Perkin–Elmer 240). FT–IR (KBr, Nicolet 5DXC): ν = 3040 (m, C_{ar}H), 2995 (m, C_{al}H), 2940 (m, C_{al}H), 1810 (vs, C=O), 1620 (s, C=C), 1590 (s, C=C), 1480 (s, C=C), 1470 (s, C=C), 1400 (s), 1350 (s, OCOCH$_3$), 1270 (vs, C_{ar}OC), 1180 (s, C—O), 1110 (s, C—O), 1090 (s, C—O), 1025 (vs, C—O), 930 (vs), 915 (vs), 760 (vs, aromatic) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, Bruker WM300): δ = 1.88 (s, 3H, C11), 6.37 (s, 1H, C10), 6.91 (dd, ^3J = 8.3, ^4J = 1.0 Hz, 1H, aromatic H), 6.98 (ddd, ^3J = 7.6, ^3J = 7.6, ^4J = 1.0 Hz, 1H, aromatic H), 7.19 (dd, ^3J = 7.6, ^4J = 1.7 Hz, 1H, aromatic H), 7.35 (ddd, ^3J = 7.6, ^3J = 8.3, ^4J = 1.7 Hz, 1H, aromatic H). ^{13}C NMR (75.5 MHz, CDCl$_3$, Bruker WM300): δ = 18.5 (q, C11), 96.8 (s, C8), 99.7 (d, C10), 116.5 (d, C$_{ar}$), 120.5 (s, C6), 121.5 (d, C$_{ar}$), 124.9 (d, C$_{ar}$), 132.0 (d, C$_{ar}$), 151.1 (s, C1), 167.8 (s, C9). MS (IT, Varian GC1400), m/z (%): 192 (22) [M$^+$], 164 (6) [M$^+$ – CO], 148 (3) [M$^+$ – CO$_2$], 122 (100) [M$^+$ – CH$_2$COCO], 121 (50) [M$^+$ – CH$_3$COCO], 105 (18) [M$^+$ – CH$_3$COCOO], 78 (4) [C$_6$H$_6^+$], 77 (8) [C$_6$H$_5^+$], 76 (4) [C$_6$H$_4^+$], 65 (6) [C$_5$H$_5^+$], 51 (10) [C$_4$H$_3^+$], 50 (5) [C$_4$H$_2^+$], 43 (99) [OCOCH$_3^+$].
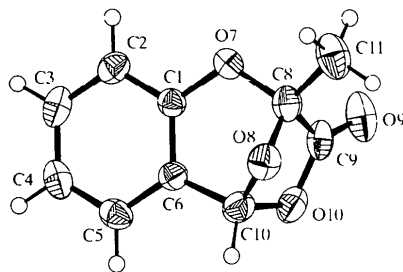

Fig. 1. *DIAMOND* plot (Brandenburg, 1996) of the title compound with the atomic numbering scheme. Displacement ellipsoids are shown at 50% probability.

Crystal data

$C_{10}H_8O_4$	Cu Kα radiation
M_r = 192.16	λ = 1.54178 Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
a = 5.838 (1) Å	θ = 40.34–46.44°
b = 7.231 (1) Å	μ = 0.978 mm^{-1}
c = 20.548 (1) Å	T = 223 (2) K
V = 867.4 (2) Å^3	Plate
Z = 4	0.50 × 0.50 × 0.20 mm
D_x = 1.471 Mg m^{-3}	Colourless
D_m not measured	

Data collection

Enraf–Nonius CAD-4	1051 reflections with
diffractometer	$I > 2\sigma(I)$

$\omega/2\theta$ scans

Absorption correction:
  empirical *via* ψ scan data
  (Fair, 1990)
  T_{min} = 0.941, T_{max} = 0.999
1068 measured reflections
1068 independent reflections

θ_{max} = 74.26°
$h = -7 \rightarrow 0$
$k = -9 \rightarrow 0$
$l = -25 \rightarrow 0$
3 standard reflections
  every 250 reflections
  intensity decay: 2.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.090
S = 1.132
1068 reflections
129 parameters
H atoms calculated and
  refined as riding atoms
  with U = 1.2(or 1.5)U_{host}
$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.1854P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001

$\Delta\rho_{max}$ = 0.192 e Å^{-3}
$\Delta\rho_{min}$ = -0.139 e Å^{-3}
Extinction correction:
  SHELXL93
Extinction coefficient:
  0.0160 (14)
Scattering factors from
  *International Tables for
  Crystallography* (Vol. C)
Absolute structure: Flack
  (1983)
Flack parameter = -0.2 (4)

Table 1. *Selected geometric parameters (Å, °)*

C1—O7	1.386 (2)	C8—C9	1.539 (3)
C1—C6	1.397 (3)	O8—C10	1.420 (3)
C6—C10	1.490 (3)	C9—O9	1.191 (3)
O7—C8	1.438 (2)	C9—O10	1.347 (3)
C8—O8	1.407 (3)	O10—C10	1.454 (3)
C1—O7—C8	115.59 (15)	C9—O10—C10	105.8 (2)
C8—O8—C10	101.8 (2)		

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Brandenburg, 1996). Software used to prepare material for publication: *SHELXL93*.

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sp-(R)-9-(o-tert-Butylphenyl)-9-hydroxy-N-[(S)-α-methylbenzyl]fluorene-2-carboxamide–Acetone: a Novel 1:1 Cavitate

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Abstract

Fractional crystallization of the two epimers sp-(R),(S)-9-(o-tert-butylphenyl)-9-hydroxy-N-[(S)-1-phenylethyl]-fluorene-2-carboxamide from acetone provided the title epimer as a 1:1 cavitate ($C_{32}H_{31}NO_2.C_3H_6O$) with the solvent acetone. Hydrogen bonding between the NH group of the host molecule and the O atom of a molecule of acetone takes place within a cavity of the host molecule, forming the novel cavitate. In addition, molecules of the host are connected to one another through hydrogen bonds between their respective OH groups as donors and amide O atoms as acceptors, forming molecular chains. To accommodate the molecule of acetone and its hydrogen bonding within the cavity, the o-tert-butylphenyl group of the title host, in contrast to that in its parent sp-9-(o-tert-butylphenyl)-9-fluorenol, is substantially rotated away from perpendicularity with the fluorene plane.

Comment

During the course of our investigations of the stereochemistry associated with reactions of sterically-hindered rotationally-restricted 9-arylfluorenes, it was necessary to prepare several enantiomerically pure 2-methyl-9-(o-tert-butylphenyl)fluorene compounds. This was accomplished subsequent to a multistep synthesis of the two epimeric sp-(R),(S)-9-(o-tert-butylphenyl)-9-hy-droxy-N-[(S)-α-methylbenzyl]fluorene-2-carboxamide, starting from commercially available 9-fluorenone-2-carboxylic acid and (S)-(−)-α-methylbenzylamine (see scheme below) (Hou, 1997). Of the two epimers, one was more readily isolated by fractional crystallization of the mixture from methanol, ethanol or acetone. ^{1}H NMR ($CDCl_3$) analysis of the crystals isolated from these solvents consistently exhibited the presence of a mole equivalent of the respective solvent. While the methanol and ethanol solvents evaporated from the crystals after a day or two, leaving an amorphous solid, the crystals obtained from acetone retained their transparency, and NMR indicated that acetone was still