

Crystallography (1974, Vol. IV) on a NOVA 4S computer.

Final atomic coordinates are given in Table 1.* Bond lengths and angles are shown in Table 2. Asymmetry parameters of the cyclopropane ring are given in Table 3. Ball and stick drawings of the molecules with the numbering schemes are shown in Figs. 1 and 2. Crystal packing is displayed in Figs. 3 and 4.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54388 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Related literature. The structures of (1) and (2) have been previously deduced by NMR studies (Díaz, Ontiveros, Salazar, Negrón & Joseph-Nathan, 1981). Gas-phase studies on 1,1-difluorocyclopropane (Perreta & Laurie, 1975).

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Bis(carbodifluoro) Derivative of Anhydroparthenin*

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Abstract. (3*S*,6*S*,6*aS*,9*aR*)-6,6*a*-Difluoromethano-2',2'-difluoro-6,7-dimethyl-2,3,3*a*,4,5,6,6*a*,7,8,9,9*a*,-9*b*-dodecahydrospiro[azuleno[4,5-*b*]furan-3,1'-cyclopropane]-2,9-dione, C₁₇H₁₆F₄O₃, *M_r* = 344.31, monoclinic, *C*2, *a* = 19.271 (7), *b* = 6.430 (2), *c* = 12.456 (4) Å, β = 91.70 (3)°, *V* = 1542.6 (1) Å³, *Z* = 4, *D_x* = 1.48 g cm⁻³, λ(Cu Kα) = 1.54178 Å, μ = 11.23 cm⁻¹, *F*(000) = 712, *T* = 296 K, *R* = 0.046 for 1020 observed reflections [*F_o* > 3σ(*F_o*)]. The X-ray analysis enabled us to correct the configuration of the difluorocyclopropane attached to C(1), C(10) previously assigned on the basis of NMR studies. The configuration is 1*S*,5*R*,10*S*,11*S* relative to 7*S* as has been found in most of the pseudoguaianolides isolated so far. Cyclopentenone, cycloheptane and γ-lactone rings adopt envelope, twist-boat and half-chair conformations, respectively. Average bond length asymmetry in cyclopropane: distal bond 1.570 (6), vicinal bonds 1.474 (5) and 1.441 (6) Å. Packing entirely due to van der Waals forces.

Experimental. Title compound was crystallized from an acetone-isopropyl ether solution and yielded light-yellow crystals. Crystal used for data collection 0.12 × 0.24 × 0.28 mm, Nicolet *P3/F* diffractometer

with Ni-filtered Cu radiation. Lattice parameters from 25 machine-centered reflections with 9.18 < 2θ < 28.68°; 1074 reflections with 3 < 2θ < 110° were measured, 1051 unique, *R_{int}* = 0.042, 23 unobserved [*F_o* < 3σ(*F_o*)], index ranges: *h* 0 to 20; *k* 0 to 6; *l* ± 13. θ/2θ scan mode, scan range [2θ(*Kα*₁) – 1.0] to [2θ(*Kα*₂) + 1.0]°, variable scan speed (min. 2.0, max. 29.3° min⁻¹), two standards (202, 312) monitored every 50 measurements, decay 3%, *Lp* corrections, absorption corrections ignored. Space group from systematic absences: *hkl* with *h* + *k* odd, *C*2 or *C*2/*m*; successful structure solution and refinement proved *C*2 to be correct. Structure solved by direct methods using *SHELXTL* (Sheldrick, 1983), origin definition by fixing the *y* coordinate of F(1). Block-matrix least-squares refinement of 217 parameters based on *F*, including positional and anisotropic temperature parameters for non-H atoms and a scale factor. H atoms in idealized positions with fixed *U* = 0.06 Å². Function minimized ∑*w*(Δ*F*)²; *w* = [σ²(*F_o*) + 0.043(*F_o*)²]⁻¹. In last cycle (Δ/σ)_{max} = 0.52, residual electron density –0.26 and 0.21 e Å⁻³. Final *R* = 0.046, *wR* = 0.051 and *S* = 1.06, no extinction correction. Complex atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations performed on a Data General NOVA 4S computer with the *SHELXTL* program package.

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Table 1. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
F(1)	6598 (1)	1880	1220 (2)	73 (1)
F(2)	5525 (1)	851 (5)	980 (2)	83 (1)
F(3)	9187 (1)	-4107 (6)	3764 (2)	93 (1)
F(4)	9681 (1)	-1151 (7)	3413 (3)	111 (1)
O(1)	6779 (2)	-2523 (7)	4981 (2)	81 (1)
O(2)	7808 (1)	988 (4)	2687 (2)	54 (1)
O(3)	8818 (2)	1655 (6)	1946 (3)	80 (1)
C(1)	6220 (2)	-958 (7)	2376 (3)	50 (1)
C(2)	5613 (2)	-1923 (8)	2877 (3)	65 (1)
C(3)	5744 (2)	-2555 (9)	3858 (4)	73 (2)
C(4)	6452 (2)	-1998 (7)	4192 (3)	60 (1)
C(5)	6722 (2)	496 (6)	3316 (2)	49 (1)
C(6)	7508 (2)	755 (7)	3275 (3)	48 (1)
C(7)	7838 (2)	-2735 (6)	2821 (3)	49 (1)
C(8)	7471 (2)	-3755 (7)	1858 (3)	56 (1)
C(9)	7165 (2)	-2276 (7)	1011 (3)	59 (1)
C(10)	6402 (2)	-1865 (7)	1213 (3)	53 (1)
C(11)	8544 (2)	-1821 (7)	2541 (3)	54 (1)
C(12)	8440 (2)	427 (7)	2353 (3)	59 (1)
C(13)	9105 (2)	-2969 (9)	1927 (4)	75 (2)
C(14)	5909 (2)	-3430 (9)	734 (4)	75 (2)
C(15)	6573 (2)	1706 (7)	3745 (3)	60 (1)
C(16)	6156 (2)	277 (8)	1375 (3)	62 (1)
C(17)	9202 (2)	-2549 (9)	3031 (4)	75 (2)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

F(1)—C(16)	1.354 (5)	F(2)—C(16)	1.350 (5)
F(3)—C(17)	1.356 (6)	F(4)—C(17)	1.364 (6)
O(1)—C(4)	1.201 (5)	O(2)—C(6)	1.466 (5)
O(2)—C(12)	1.348 (5)	O(3)—C(12)	1.196 (5)
C(1)—C(2)	1.478 (5)	C(1)—C(5)	1.526 (4)
C(1)—C(10)	1.609 (5)	C(1)—C(16)	1.480 (6)
C(2)—C(3)	1.306 (6)	C(3)—C(4)	1.459 (6)
C(4)—C(5)	1.558 (5)	C(5)—C(6)	1.528 (4)
C(5)—C(15)	1.543 (6)	C(6)—C(7)	1.537 (5)
C(7)—C(8)	1.522 (5)	C(7)—C(11)	1.532 (5)
C(8)—C(9)	1.526 (6)	C(9)—C(10)	1.523 (6)
C(10)—C(14)	1.496 (6)	C(10)—C(16)	1.472 (6)
C(11)—C(12)	1.477 (6)	C(11)—C(13)	1.531 (6)
C(11)—C(17)	1.468 (5)	C(13)—C(17)	1.409 (7)
C(6)—O(2)—C(12)	108.8 (3)	C(2)—C(1)—C(5)	104.4 (3)
C(2)—C(1)—C(10)	115.1 (3)	C(5)—C(1)—C(10)	127.7 (3)
C(2)—C(1)—C(16)	122.3 (3)	C(5)—C(1)—C(16)	125.2 (3)
C(10)—C(1)—C(16)	56.7 (3)	C(1)—C(2)—C(3)	113.1 (3)
C(2)—C(3)—C(4)	110.1 (4)	O(1)—C(4)—C(3)	129.0 (4)
O(1)—C(4)—C(5)	124.7 (4)	C(3)—C(4)—C(5)	106.3 (3)
C(1)—C(5)—C(4)	101.5 (3)	C(1)—C(5)—C(6)	124.0 (3)
C(4)—C(5)—C(6)	108.0 (3)	C(1)—C(5)—C(15)	108.9 (3)
C(4)—C(5)—C(15)	104.9 (3)	C(6)—C(5)—C(15)	107.9 (3)
O(2)—C(6)—C(5)	109.8 (3)	O(2)—C(6)—C(7)	106.1 (3)
C(5)—C(6)—C(7)	121.6 (3)	C(6)—C(7)—C(8)	117.4 (3)
C(6)—C(7)—C(11)	98.4 (3)	C(8)—C(7)—C(11)	112.4 (3)
C(7)—C(8)—C(9)	115.9 (3)	C(8)—C(9)—C(10)	110.4 (3)
C(1)—C(10)—C(9)	116.7 (3)	C(1)—C(10)—C(14)	116.7 (3)
C(9)—C(10)—C(14)	115.0 (3)	C(1)—C(10)—C(16)	57.2 (3)
C(9)—C(10)—C(16)	120.1 (4)	C(14)—C(10)—C(16)	118.7 (3)
C(7)—C(11)—C(12)	107.1 (3)	C(7)—C(11)—C(13)	125.0 (4)
C(12)—C(11)—C(13)	119.1 (4)	C(7)—C(11)—C(17)	123.0 (4)
C(12)—C(11)—C(17)	119.3 (4)	C(13)—C(11)—C(17)	56.0 (3)
O(2)—C(12)—O(3)	121.4 (4)	O(2)—C(12)—C(11)	109.4 (3)
O(3)—C(12)—C(11)	129.1 (4)	C(11)—C(13)—C(17)	59.7 (3)
F(1)—C(16)—F(2)	107.6 (4)	F(1)—C(16)—C(1)	119.5 (3)
F(2)—C(16)—C(1)	120.3 (3)	F(1)—C(16)—C(10)	119.1 (3)
F(2)—C(16)—C(10)	119.7 (4)	C(1)—C(16)—C(10)	66.1 (3)
F(3)—C(17)—F(4)	106.3 (4)	F(3)—C(17)—C(11)	118.7 (4)
F(4)—C(17)—C(11)	120.2 (5)	F(3)—C(17)—C(13)	120.7 (5)
F(4)—C(17)—C(13)	122.4 (4)	C(11)—C(17)—C(13)	64.3 (3)

Final atomic coordinates are given in Table 1,* bond lengths and bond angles in Table 2. A drawing of the molecule with the numbering scheme is shown in Fig. 1 and the crystal packing is shown in Fig. 2.

Related literature. Proton (Díaz, Ontiveros, Salazar, Negrón & Joseph-Nathan, 1981) and multinuclear (Díaz, Domínguez, Mannino, Negrón & Jankowski, 1985) magnetic resonance studies. Difluorocarbene (Salazar & Díaz, 1978). Similar average bond-length asymmetry pattern in cyclopropane rings ($\delta_1 = +0.075$, $\delta_2 = -0.021$ and $\delta_3 = -0.054$) as in carbodifluoro derivatives of zaluzanin D (Díaz, Barrios, Villena & Toscano, 1991).

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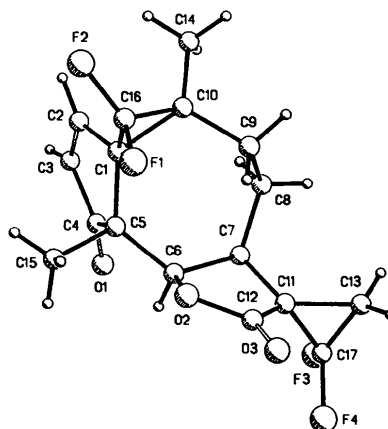


Fig. 1. Molecular structure of title compound.

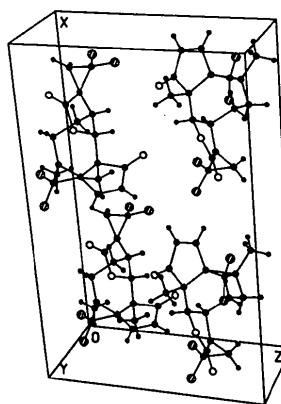


Fig. 2. Crystal packing of title compound.

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Structure of the Mosher's Ester Derivative of 5-Phenyldeltacyclene

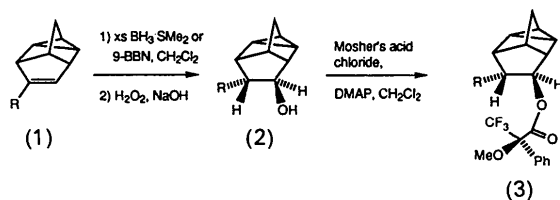
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Abstract. Octahydro-5-phenyl-1,2,4-methenopentalen-6-yl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate, $C_{25}H_{23}F_3O_3$, $M_r = 428.5$, monoclinic, $P2_1$, $a = 10.747$ (3), $b = 7.975$ (3), $c = 12.435$ (5) Å, $\beta = 92.81$ (3)°, $V = 1064.5$ (12) Å³, $Z = 2$, $D_x = 1.34$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.98$ cm⁻¹, $F(000) = 448$, room temperature, $R = 0.035$ for 1523 observed reflections. The X-ray structure determination establishes the relative stereochemistry. The $C(sp^3)$ — $C(sp^3)$ bond distances range from 1.492 (6) to 1.554 (5) Å.

Experimental. Hydroboration and oxidation of 5-phenyldeltacyclene followed by the reaction of the product alcohol with Mosher's acid chloride gave the desired compound (3).



DMAP = 4-dimethylaminopyridine;
 9-BBN = 9-borabicyclo[3.3.1]nonane; $R = C_6H_5$

Crystals from pentane. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $8 < \theta < 17^\circ$. Crystal dimensions $0.2 \times 0.2 \times 0.3$ mm; intensities of reflections with indices $h - 1$ to 12, $k 0$ to 9, $l - 14$ to 14, with $2 < 2\theta < 50^\circ$ measured, $\omega - 2\theta$ scans, ω scan width $(0.6 + 0.35 \tan \theta)^\circ$; graphite-monochromated Mo $K\alpha$ radiation; intensities of

three reflections measured every 2 h showed no evidence of crystal decay. 2316 reflections measured, 1886 unique ($R_{\text{int}} = 0.022$) and 1523 reflections with $I > 2\sigma(I)$ observed and used in the structure solution and refinement. Data corrected for Lorentz and polarization effects. The space group was assigned as $P2_1$ from the systematic absences ($0k0$ absent if $k = 2n + 1$) and confirmed by the successful structure solution and refinement. The y coordinate of one of the F atoms was fixed to define the origin along the 2_1 screw axis. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). The hand of the molecule was chosen according to the known configuration of the Mosher's ester group. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters for C, O and F atoms. A difference map showed maxima in positions consistent with the expected locations of H atoms. In the final rounds of calculations H atoms were positioned on geometric grounds ($C-H$ 0.95 Å) and included (as riding atoms) in the structure-factor calculation. The thermal parameters of these atoms were refined as a single free variable, final value $U_{\text{iso}} = 0.078$ (3) Å². Final cycles of least squares included 281 parameters, $R = 0.035$, $wR = 0.036$, goodness of fit 1.721 and $w = 1/[\sigma^2(F_o) + 0.00025(F_o)^2]$. Final value for the isotropic extinction parameter was $g = 2.8$ (6) $\times 10^{-7}$ where $F_c' = F_c(1 - gF_c^2/\sin \theta)$ (Sheldrick, 1976). Max. shift/e.s.d. in final refinement cycle 0.005; density in final difference map in range -0.14 to 0.14 e Å⁻³; there were no chemically significant features. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations carried out on a PDP 11/23 computer using *SDP* (Frenz, 1982) and an Apollo computer using *SHELX76* and *SHELXS86* (Sheldrick, 1976, 1986). Atomic

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