Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction:
ψ scans (*SHELXTL*; Sheldrick, 1985)
$T_{\min} = 0.687$, $T_{\max} = 0.775$
4048 measured reflections
2029 independent reflections
1675 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$
$\theta_{\max} = 27.48°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 21$
$l = -10 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: 4.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.071$
$S = 0.958$
2029 reflections
100 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cl3—C3	1.721 (2)	C2—C3	1.419 (2)
Cl5—C5	1.732 (2)	C3—C4	1.357 (2)
N1—C2	1.342 (2)	C4—C5	1.401 (2)
N1—C6	1.357 (2)	C5—C6	1.349 (2)
N2—C2	1.328 (2)		
C2—N1—C6	124.58 (15)	C2—C3—Cl3	117.77 (13)
N2—C2—N1	118.9 (2)	C3—C4—C5	119.2 (2)
N2—C2—C3	124.9 (2)	C6—C5—C4	120.3 (2)
N1—C2—C3	116.17 (15)	C6—C5—Cl5	119.88 (14)
C4—C3—C2	121.0 (2)	C4—C5—Cl5	119.84 (13)
C4—C3—Cl3	121.26 (13)	C5—C6—N1	118.8 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.85	2.29	3.109 (2)	161
N2—H2*B*···Cl1	0.82	2.57	3.303 (2)	150
N2—H2*A*···O1	0.86	2.02	2.856 (2)	163
O1—H1O···Cl1^{i}	0.82	2.37	3.178 (1)	170
O1—H2O···Cl1^{ii}	0.76	2.38	3.144 (2)	172

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

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1985). Software used to prepare material for publication: *SHELXTL*.

The authors thank Professor Ward T. Robinson (University of Canterbury) for the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1087). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 683–687

2,3-Bis(diphenylmethylene)succinic Anhydride, (I), 2-(2-Adamantylidene)-3-(9-fluorenylidene)succinic Anhydride, (II), and 2-(9-Fluorenylidene)-3-(3,4,5-trimethoxybenzylidene)succinic Anhydride, (III)

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Abstract

The title compounds are derivatives of dimethylenesuccinic anhydride and belong to the fulgide family of compounds. The fulgides were the first photochromic systems to be discovered. Fulgide (I) ($C_{30}H_{20}O_3$) possesses a crystallographic twofold axis. The divinylsuccinic anhydride moiety is not planar in fulgides (II) ($C_{27}H_{22}O_3$) and (III) ($C_{27}H_{20}O_6$). In both (II) and (III), the C atom bonded to the fluorenyl moiety deviates significantly from the mean plane through the five-membered ring of the fluorenyl moiety.

Comment

Among the many classes of photochromic compounds, the fulgides, first discovered by Stobbe & Eckert (1905) and Stobbe (1911), are important for their relative stability (see the scheme below). Although the first com-

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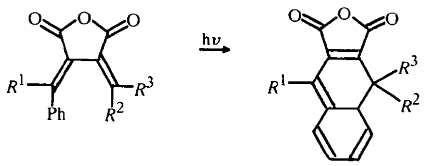
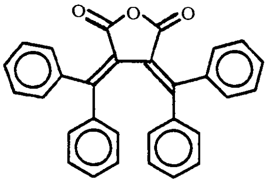
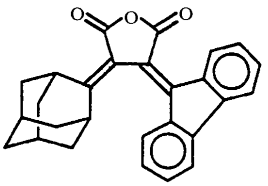
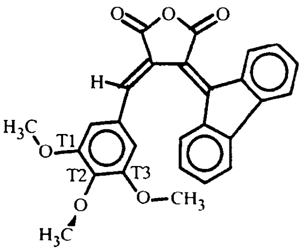


pounds of the fulgide system showed reversible photochemical properties, they were unstable during repeated irradiation. Efforts were made to improve the properties of the fulgides in order to obtain thermally stable and photochemically fatigue-resistant photochromic compounds (Darcy *et al.*, 1981; Heller & Oliver, 1981; Heller & Langan, 1981; Kaftory, 1984). We present here the crystal structures of three compounds: fulgide (I), prepared by Toda (private communication) by a procedure similar to that of Toda *et al.* (1995), and fulgides (II) and (III), prepared by Heller (1985) for testing new fatigue-resistant photochromic compounds.


(I)


(II)



(III)

As the compounds are sensitive to light, molecular changes may be occurring within the crystals; this would account for the difficulties encountered in achieving satisfactory refinement and the implausible atomic displacement parameters of some atoms [for example, C3 in (II)]. All attempts to obtain better intensity data failed.

The diene system in all three compounds is severely skewed (Otterson *et al.*, 1974). The torsion angle at the butadienyl fragment, C3—C2—C2*—C3*, is 35 (1)° in (I), but is larger in (II) and (III) [C5—C2—C3—C18 is 56 (1)° in (II) and 40 (1)° in (III)] because of the steric congestion imposed by the rigidity of the bulky fluorenyl moiety. The crystal structures of 26 fulgides were retrieved from the Cambridge Structural Database (CSD; Allen *et al.*, 1979). The torsion angle at the butadiene fragment in these compounds ranges from 2.1 to 47.9°. Where the butadiene fragment has H atoms in the 1 and 4 positions, both *cis* to the 2–3 bond, the torsion angles are significantly smaller (2.1–19.6°). For example, in the *Z*,*Z* isomer of bis(4-methoxy-3-methylbenzylidene)succinic anhydride, the torsion angle is 2.1°, but in the *E*,*E* isomer of the same molecule, it is 31.9° (Boeyens *et al.*, 1993). The steric congestion is more pronounced in (III), where the C2—C3—C18 angle opens to 136.1 (6)°. The range of the equivalent bond angles in (I) and (II) is 129.3 (7)–132.1 (4)°. It should also be noted that the C=C double bonds between the fluorenyl moieties and the succinic anhydride moieties are unusually long: 1.374 (11) Å in (II) and 1.381 (9) Å in (III). The average C=C bond length to a fluorenylidene moiety for 40 compounds from the CSD is 1.362 (4) Å.

As a result of the presence of a twofold axis passing through atom O1 and the midpoint of the C2—C2* bond in (I), the four phenyl rings adopt a propeller arrangement. The dihedral angles between the phenyl-ring planes and the plane through atoms C2, C3, C4 and C10 are 45.9 (7) and 40.3 (9)°. A similar conformation is found in the three polymorphs of 3,4-bis(diphenylmethylene)-*N*-methylsuccinimide (Toda *et al.*, 1995), the orthorhombic modification of which has crystallographic twofold symmetry. There is, however, a significant difference between the conformation of the two compounds. In (I), the inner two phenyl rings are closer to being coplanar with the succinic anhydride moiety, as shown by the dihedral angle of 40.3 (9)° compared with 64.7° in 3,4-bis(diphenylmethylene)-*N*-methylsuccinimide.

It is interesting to compare the conformation of the 3,4,5-trimethoxybenzene fragment in (III) with that in similar compounds. The torsion angles of the three methoxy groups relative to the phenyl ring were calculated for over 60 compounds from the CSD. Similar conformations were observed in 67 molecules [including (III)]. The average torsion angles (*T*1, *T*2 and *T*3 are defined in the scheme above) are *T*1 = 1.0 (9), *T*2 = 90 (1) and *T*3 = 179.1 (8)°. This conformation is shown schematically for (III). The corresponding torsion

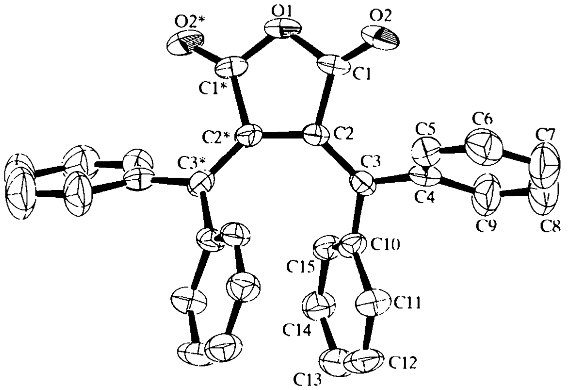


Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

angles in (III) are 16.0 (8), −74.1 (8) and 168.0 (5)°. Only three compounds adopt different conformations: in a β-pelatin derivative (Arora *et al.*, 1975), the torsion angles *T*1, *T*2, and *T*3 are −164.7, 94.7 and 175.2°, respectively; in 2,4-diamino-5-(3,4,5-trimethoxybenzyl)-pyrimidinium benzoate–benzoic acid (Giuseppetti *et al.*, 1988), they are 3.3, −67.2 and −49.5°, and similar values are found in 2,2,4,4-tetramethyl-3-(3,4,5-trimethoxyphenyl)pentan-3-ol (van Koningsveld & van Meurs, 1977).

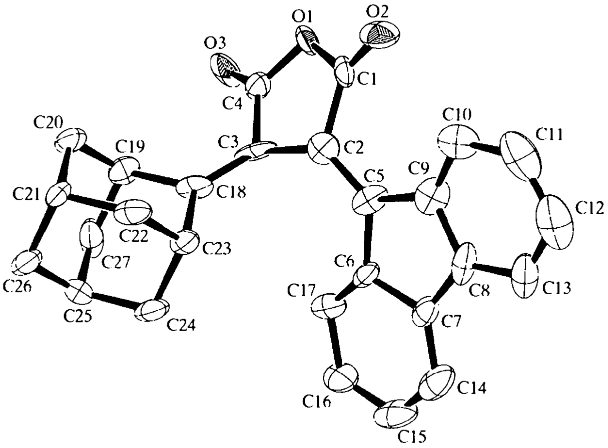


Fig. 2. The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

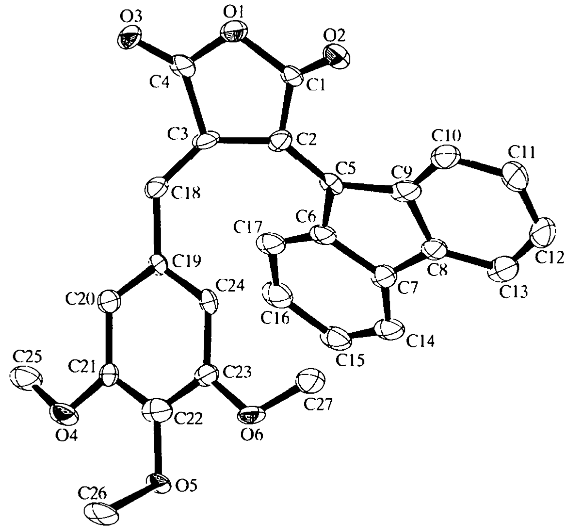


Fig. 3. The molecular structure of (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

Experimental

Dimethyl adamantylidenesuccinate and fluorenone in toluene were added to sodium hydride in toluene. The resulting half ester was hydrolyzed to a diacid and then cyclized with acetyl chloride to give (II), which crystallized from 2-butanone as orange crystals (m.p. 529 K). Dimethyl fluorenylidenesuccinate and 3,4,5-trimethoxybenzaldehyde were added to potassium *tert*-butoxide in *tert*-butanol. The resulting oily diacid was cyclized with acetyl chloride and the product, (III), was crystallized from toluene and petrol as red crystals which thermally rearranged to a yellow solid at 453 K (Whittall, 1979).

Compound (I)

Crystal data

$C_{30}H_{20}O_3$
$M_r = 428.46$
Orthorhombic
Pbcn
$a = 19.037\ (6)$ Å
$b = 9.548\ (3)$ Å
$c = 12.089\ (4)$ Å
$V = 2197.4\ (12)$ Å^3
$Z = 4$
$D_x = 1.295$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.3$–$9.6°$
$\mu = 0.083$ mm^{-1}
$T = 293\ (2)$ K
Cube
0.50 × 0.30 × 0.25 mm
Red

Data collection

Philips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1355 measured reflections
1355 independent reflections
795 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 22.01°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 5.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.087$
$wR(F^2) = 0.313$
$S = 0.970$
1306 reflections
150 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.006P)^2 + 12.5P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.075$
$\Delta\rho_{\max} = 0.342$ e Å^{-3}
$\Delta\rho_{\min} = -0.302$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

$C_{27}H_{22}O_3$
$M_r = 394.45$
Triclinic
$P\bar{1}$
$a = 11.939\ (3)$ Å
$b = 10.251\ (3)$ Å
$c = 8.731\ (2)$ Å
$\alpha = 100.45\ (2)°$
$\beta = 100.32\ (2)°$
$\gamma = 67.65\ (2)°$
$V = 964.7\ (4)$ Å^3
$Z = 2$
$D_x = 1.358$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 3.1$–$10.8°$
$\mu = 0.087$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.65 × 0.20 × 0.15 mm
Orange

Data collection

Philips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2359 measured reflections
2359 independent reflections
1252 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 22.00°$
$h = 0 \rightarrow 15$
$k = -11 \rightarrow 13$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: 2.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.078$
$wR(F^2) = 0.277$
$S = 0.238$
2359 reflections
271 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.005P)^2 + 24P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.099$
$\Delta\rho_{\max} = 0.407$ e Å^{-3}
$\Delta\rho_{\min} = -0.404$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (III)

Crystal data

$C_{27}H_{20}O_6$
$M_r = 440.43$
Triclinic
$P\overline{1}$
$a = 10.2498$ (10) Å
$b = 12.586$ (3) Å
$c = 8.189$ (4) Å
$\alpha = 96.51$ (2)°
$\beta = 87.90$ (2)°
$\gamma = 93.50$ (2)°
$V = 1047.1$ (6) Å^3
$Z = 2$
$D_x = 1.397$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71093$ Å
Cell parameters from 25 reflections
$\theta = 2.3$–$9.8°$
$\mu = 0.099$ mm^{-1}
$T = 293$ (2) K
Plate
0.35 × 0.20 × 0.08 mm
Red

Data collection

Philips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2526 measured reflections
2526 independent reflections
1638 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 22.00°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: 1.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.089$
$wR(F^2) = 0.259$
$S = 0.394$
2526 reflections
298 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.2P)^2 + 6P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.049$
$\Delta\rho_{\max} = 0.332$ e Å^{-3}
$\Delta\rho_{\min} = -0.412$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å) and angles (°)*

	(I)†	(II)	(III)
O1—C1	1.396 (7)	1.403 (9)	1.414 (8)
O1—C4	1.396 (7)	1.376 (9)	1.375 (8)
O2—C1	1.169 (7)	1.182 (9)	1.187 (8)
O3—C4	1.169 (7)	1.196 (9)	1.184 (8)
C1—C2	1.472 (8)	1.501 (11)	1.492 (10)
C2—C5	1.368 (8)	1.374 (11)	1.381 (9)
C2—C3	1.435 (12)	1.490 (12)	1.458 (9)
C3—C18	1.368 (8)	1.338 (12)	1.338 (9)
C3—C4	1.472 (8)	1.496 (11)	1.486 (9)
C1—O1—C4	113.3 (7)	111.3 (6)	111.2 (5)
O2—C1—O1	119.9 (5)	118.2 (7)	118.8 (6)
O2—C1—C2	134.7 (6)	134.6 (8)	134.7 (6)
O1—C1—C2	105.2 (6)	107.1 (6)	106.5 (6)
C5—C2—C3	132.1 (4)	132.5 (8)	130.9 (6)
C5—C2—C1	119.9 (6)	122.0 (8)	124.0 (6)
C3—C2—C1	107.3 (4)	104.3 (6)	104.9 (5)
C18—C3—C2	132.1 (4)	129.3 (7)	136.1 (6)
C18—C3—C4	119.9 (6)	122.8 (8)	116.6 (6)
C2—C3—C4	107.3 (4)	104.3 (7)	106.0 (5)
O3—C4—O1	119.9 (5)	120.3 (7)	121.3 (6)
O3—C4—C3	134.7 (6)	131.5 (8)	131.0 (7)
O1—C4—C3	105.2 (6)	108.3 (7)	107.6 (6)

† The equivalent atomic numbering in (I) is different, please refer to Fig. 1.

In each of the three compounds, the diffracted intensities decreased significantly at high diffraction angles. Attempts to obtain crystals of better quality or to collect better intensity data at low temperatures were unsuccessful. We therefore describe the crystal structures obtained from data collected up to $\theta = 22.0°$. (The poor crystal quality is probably related to the thermal/photochemical instability of the compounds.)

For all compounds, data collection: *Philips PW*110/20 *Software* (Philips, 1973); cell refinement: *Philips PW*110/20 *Software*; data reduction: *PROCN* in *Philips PW*110/20 *Software*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976) and *TEXSAN* (Molecular Structure Corporation, 1994).

The authors thank Professors H. G. Heller and F. Toda for providing samples of the title compounds.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1200). Services for accessing these data are described at the back of the journal.

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3D/2D Hydrogen-Bond Network Preferences for Five New Ryanoid Derivatives

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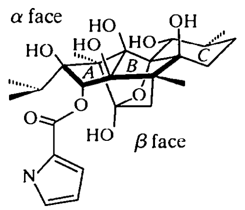
Abstract

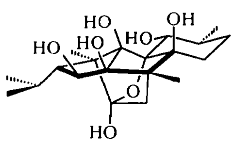
Ryanoids are a family of natural compounds that are well known for their biological activity in plants as pesticides, and in mammalian muscle tissue as calcium permeability modulators. As part of an investigation of the structure–activity relationship of ryanoids, the crystal structures of five new compounds were elucidated: 2-deoxy-3-epiryanodol ($C_{20}H_{32}O_7$), 3-deoxyryanodol hydrate (cinnzeylanol; $2C_{20}H_{32}O_7.5.15H_2O$), 2-deoxyryanodol hydrate ($2C_{20}H_{32}O_7.2.5H_2O$), 2,3-dideoxyryanodol hydrate ($C_{20}H_{32}O_6.1.5H_2O$) and 3a,4a,8,8b-tetrahydroxy-2-isopropyl-4,7-dimethyl-1-methylene-1,3a,4,4a,5,6,7,8,8a,8b-decahydro-8a,4-(epoxyethano)-benzo[*a*]pentalen-10-one ($C_{20}H_{28}O_6$). The numerous hydroxyl groups on the molecules modulate the crystal packing. Successive modifications on ring *A* induce major changes in the hydrogen-bond scheme, from a three-dimensional (3D) to a two-dimensional (2D) network.

Comment

Originally extracted from the *Ryania speciosa* Vahl plant, toxic ryanodine and its congener ryanoids show interesting properties other than their primary utility in plants as botanical pesticides (Jenden & Fairhurst, 1969; Jefferies & Casida, 1994) by modulating the calcium permeability of sarcoplasmic reticulum terminal cisternal membranes (Fairhurst & Hasselbach, 1970; Meissner, 1986; Lattanzio *et al.*, 1986). The binding of ryanodine to its corresponding receptor is complex and displays multiple affinities and cooperative binding (Lai *et al.*, 1989; Chu *et al.*, 1990; Carroll *et al.*, 1991; Pessah & Zimanyi, 1991). QSAR (quantitative structure/activity analysis) and CoMFA (comparative molecular field analysis) suggest that the binding of ryanodine to its receptor involves mainly the pyrrole and isopropyl groups buried deep inside the protein cleft (Welch *et al.*, 1994). These results are based on the study of 19 natural or synthetic ryanoids. In order to identify the structural features that are necessary to enhance biological activity and selectivity, several polyhydroxylated diterpenes were isolated from the usual source or synthesized to test their biological activity (Sutko *et al.*, 1997). The crystal structures were elucidated in order to establish their stereochemistry and conformation for further QSAR and CoMFA studies.



Ryanodine



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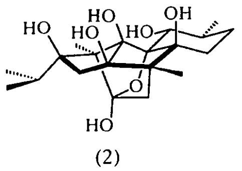

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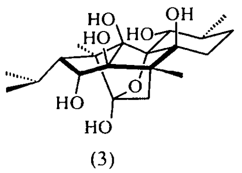

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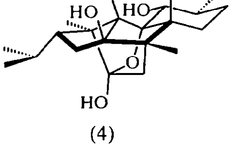

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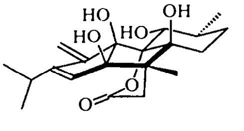

(5)

A general feature of the ryanoids is a highly polar α face opposite to a much less polar β face. The molecules tend to crystallize in the form of an optimized hydro-