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# Hyperolactone C

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**Key indicators**

Single-crystal X-ray study
*T* = 95 K
Mean σ(C–C) = 0.009 Å
*R* factor = 0.068
*wR* factor = 0.154
Data-to-parameter ratio = 7.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.



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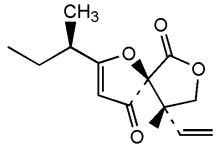
The crystal structure of a known spirolactone, hyperolactone C [systematic name: (5*S*,9*S*)-9-methyl-2-phenyl-9-vinyl-1,7-dioxaspiro[4.4]non-2-ene-4,6-dione], isolated from *Hypericum lloydii* (Svenson) P. Adams (Sandhill St John's Wort, Clusiaceae), native to the southeastern USA, is presented.

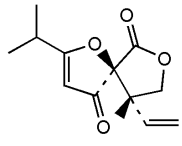
## Comment

*Hypericum lloydii*, (Svenson) P. Adams, section Myriandra (Sandhill St John's Wort, Clusiaceae) is one of 57 species of *Hypericum* that occur in the USA (USDA–NCRS, 2002). This native low shrub frequently occurs on sandy or eroding granitic soils in dry woods and pinelands, particularly in the Appalachian Mountain region of the southeastern USA (Radford *et al.*, 1968; Robson, 1996). Fractionation of the dichloromethane extract of the aerial parts of *H. lloydii* has led to the isolation of the known spirolactone, (−)-hyperolactone C.

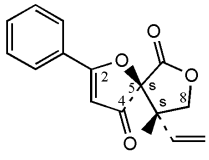
This compound was previously isolated (Aramaki *et al.*, 1995) from *H. monogynum* (published as *H. chinense*, section Ascyreia) along with three related structures, hyperolactones A (Tada *et al.*, 1989), B and D (see scheme). The hyperolactones A, B and C have also been reported from synthesis (Ueki *et al.*, 1998, 2000). This paper represents the first report of this type of spirolactone from a species of *Hypericum* section *Myriandra* and the first X-ray crystallographic report for hyperolactone C (Fig. 1). The furan-3-one ring is planar and is inclined at an angle of 9.9 (3)° to the plane of the benzene ring. The furan-2-one ring adopts a conformation intermediate between an envelope and a half-chair.



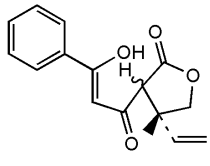
Hyperolactone A



Hyperolactone B



Hyperolactone C



Hyperolactone D

## Experimental

The aerial portions of *H. lloydii* were collected while in flower, and a voucher specimen was stored with the University of Georgia

Herbarium in Athens, GA. The dried ground aerial parts of *H. lloydii* were extracted with dichloromethane, yielding a crude extract that was subjected to vacuum liquid chromatography. Fractions of 25 ml each were eluted from the column using a gradient from 100% hexane to 100% ethyl acetate, with a final column wash of methanol, and were combined on the basis of similarity of TLC profiles to give 16 fractions. Fraction 12 (eluted at 20% ethyl acetate) displayed a prominent violet spot in TLC. Upon standing, this fraction yielded a flaky green–gold mica-like precipitate, which was then filtered and further purified by preparative TLC. Recrystallization from ethyl acetate of the purified material gave 120 mg of crystals, which were subsequently identified using spectroscopic measurements as hyperolactone C. Crystals suitable for X-ray diffraction were obtained from chloroform. Hyperolactone C was isolated as long clear prismatic crystals (m.p. 370 K). Optical rotation $[\alpha]_D$ (295 K) −270.7° ($CHCl_3$, *c* 0.11). This value differs from that (−356.0°, EtOH, *c* 0.02) reported by Aramaki *et al.* (1995), but this difference may be attributed to the use of different solvents. EIMS indicated a molecular formula of $C_{16}H_{14}O_4$ (*m*/*z* 270.09). UV $\lambda_{max}$ absorptions at 304 and 254 nm indicated the presence of a chromophore with extended conjugation. The IR spectrum showed two strong bands indicating carbonyl groups at 1782 and 1705 $cm^{-1}$. Hyperolactone C was poorly soluble in hexane and ethanol, but fully soluble in ethyl acetate, acetone, chloroform and chloroform/methanol (1:1).

*Crystal data*

$C_{16}H_{14}O_4$
$M_r$ = 270.27
Monoclinic, $P2_1$
*a* = 6.215 (7) Å
*b* = 7.491 (7) Å
*c* = 14.461 (15) Å
β = 98.68 (8)°
*V* = 665.5 (12) $Å^3$
*Z* = 2
$D_x$ = 1.349 Mg $m^{-3}$
Mo *Kα* radiation
Cell parameters from 35 reflections
θ = 4.4–10.6°
μ = 0.10 $mm^{-1}$
*T* = 95 (2) K
Prism, colorless
0.42 × 0.25 × 0.12 mm

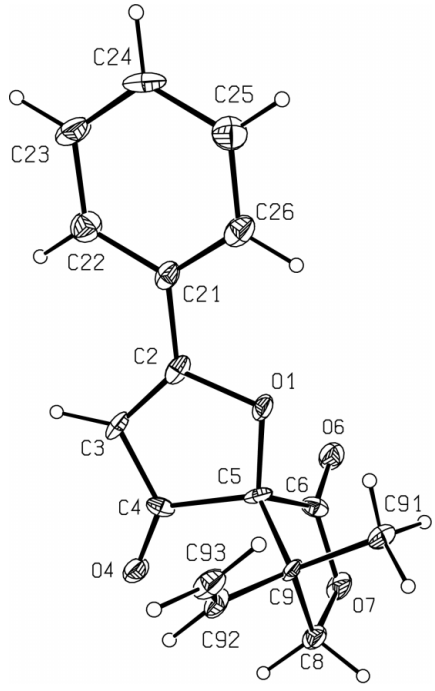



**Figure 1**
Stereoscopic *ORTEP* (Johnson, 1965) plot of hyperolactone C. Displacement ellipsoids are drawn at the 50% probability level.

*Data collection*

Stoe four-circle diffractometer
ω scans
Absorption correction: none
1612 measured reflections
1270 independent reflections
943 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.087
$\theta_{max}$ = 25.0°
*h* = −7 → 7
*k* = −3 → 8
*l* = −1 → 17
3 standard reflections
every 100 reflections
intensity decay: 0.1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.154
*S* = 1.08
1270 reflections
175 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.1091P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.28 e $Å^{-3}$

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

| | | | |
|---|---|---|---|
| O1—C2 | 1.383 (7) | C5—C9 | 1.551 (9) |
| O1—C5 | 1.424 (7) | C6—O6 | 1.193 (8) |
| C2—C3 | 1.348 (9) | C6—O7 | 1.331 (8) |
| C2—C21 | 1.462 (7) | O7—C8 | 1.482 (9) |
| C3—C4 | 1.439 (8) | C8—C9 | 1.530 (9) |
| C4—O4 | 1.225 (7) | C9—C91 | 1.550 (8) |
| C4—C5 | 1.576 (8) | C9—C92 | 1.513 (9) |
| C5—C6 | 1.521 (9) | C92—C93 | 1.347 (10) |
| | | | |
| C2—O1—C5 | 108.2 (5) | C9—C5—C4 | 113.3 (5) |
| C3—C2—O1 | 114.0 (5) | O6—C6—O7 | 123.9 (6) |
| C3—C2—C21 | 130.6 (5) | O6—C6—C5 | 126.9 (6) |
| O1—C2—C21 | 115.2 (5) | O7—C6—C5 | 109.1 (5) |
| C2—C3—C4 | 108.8 (5) | C6—O7—C8 | 110.2 (5) |
| O4—C4—C3 | 132.7 (6) | O7—C8—C9 | 105.7 (5) |
| O4—C4—C5 | 123.0 (5) | C92—C9—C8 | 112.7 (5) |
| C3—C4—C5 | 104.2 (5) | C92—C9—C91 | 114.4 (6) |
| O1—C5—C6 | 112.4 (5) | C8—C9—C91 | 109.8 (5) |
| O1—C5—C9 | 114.3 (6) | C92—C9—C5 | 111.3 (5) |
| C6—C5—C9 | 102.6 (5) | C8—C9—C5 | 99.3 (5) |
| O1—C5—C4 | 104.7 (4) | C91—C9—C5 | 108.2 (5) |
| C6—C5—C4 | 109.6 (6) | C93—C92—C9 | 124.7 (6) |

C atoms of the phenyl ring were fitted to a regular hexagon with C—C = 1.39 Å. The rotational orientation of the methyl group was refined. All H atoms were placed at idealized positions, with C—H = 0.95–0.99 Å. $U_{iso}$(H) values of the phenyl ring were refined with a common parameter. $U_{iso}$(H) of the methyl and methylene groups and of H atoms attached to C93 were refined in the same manner. Other $U_{iso}$(H) values were refined independently. The absolute configuration could not be determined from the diffraction data due to the absence of heavy atoms, but was assigned as *SS* according to the configuration attributed by Tada *et al.* (1989) to hyperolactone A; the Friedel pairs were merged.

Data collection: local software; cell refinement: local software; data reduction: local software; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: (Johnson, 1965); software used to prepare material for publication: *SHELXL*97.

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