

Table 3. *Torsion angles in ring B* (°)

The maximum value of the e.s.d.'s is 2°.

	(Ia)	(Ib)	(IIa)	(III)	(IV)
C(13)—C(16)—C(15)—C(14)	-53	-53	-55	-53	-57
C(16)—C(15)—C(14)—C(7)	-5	-5	-3	-6	-4
C(15)—C(14)—C(7)—C(6)	79	81	82	78	79
C(14)—C(7)—C(6)—C(5)	-48	-49	-50	-44	-46
C(7)—C(6)—C(5)—C(13)	-43	-42	-39	-44	-42
C(6)—C(5)—C(13)—C(16)	73	70	68	68	67
C(5)—C(13)—C(16)—C(15)	4	5	7	7	9

References: (Ia) colchicine (Lessinger & Margulis, 1978a); (Ib) thiocolchicine.6H₂O (Koerntgen & Margulis, 1977); (IIa) isocolchicine (Lessinger & Margulis, 1978b); (III) pseudothiocolchicine (present work); (IV) demethylisothiocolchicine (Margulis, 1977).

in the plane of the troponoid ring C [the angle being 7.6 (2)°]. The value of the S—C(11) bond length [1.757 (5) Å] is close to the one corresponding to a conjugated system (Koerntgen & Margulis, 1977; Clark & Margulis, 1980). This fact suggests that the free-electron pairs of the S atom could conjugate with the troponone π system, in contrast to the hypothesis of Danieli *et al.* (1985) based on the absence of bathochromic effect in the electronic absorption spectra of (III).

The A and C rings are considerably twisted: the angle between them, 50.7 (1)°, is necessary to accommodate the fused seven-membered ring B. The conformation of ring B is similar to that found in other

colchicine derivatives (see Table 3); the difference between corresponding torsion angles is within 7°.

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Structures of Two Hydrated Cage Diketones

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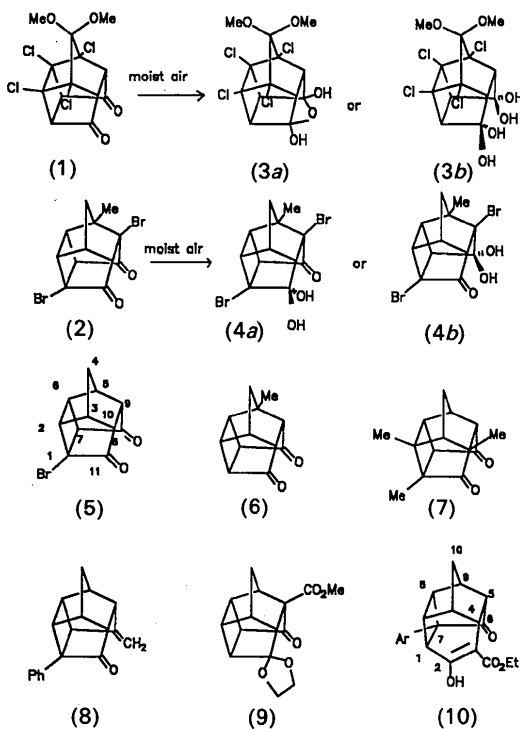
Abstract. 2,3,5,6-Tetrachloro-8,11-dihydroxy-4,4-dimethoxy-8,11-epoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane, (3a), C₁₃H₁₂Cl₄O₅, $M_r = 390.05$, monoclinic, $P2_1/n$, $a = 7.392$ (1), $b = 12.726$ (3), $c = 16.107$ (2) Å, $\beta = 95.64$ (1)°, $V = 1507.8$ (5) Å³, $Z = 4$, $D_x = 1.718$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 8.06$ cm⁻¹, $F(000) = 792$, $T = 298$ K, $R = 0.0395$ for 2783 reflections. 1,9-Dibromo-11,11-dihydroxy-5-methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane-8-one,

(4a), C₁₂H₁₂Br₂O₃, $M_r = 364.05$, triclinic, $P\bar{1}$, $a = 6.713$ (1), $b = 14.013$ (2), $c = 14.579$ (2) Å, $\alpha = 113.29$ (1), $\beta = 99.58$ (1), $\gamma = 99.31$ (1)°, $V = 1202.3$ (4) Å³, $Z = 4$, $D_x = 2.011$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 66.68$ cm⁻¹, $F(000) = 712$, $T = 295$ K, $R = 0.0640$ for 3888 reflections. The two open-ended cage compounds are composed of four five-membered rings and a four-membered ring. The diketone moieties in the parent compounds have added water to form a dihydrate, (3a), and a monohydrate, (4a). The parent diketone usually contains

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two long bonds, C(1)—C(7) and C(9)—C(10), owing to through-bond coupling of the keto π systems; however, hydration removes these interactions, and the corresponding bond lengths are significantly shorter.

Introduction. As part of a program concerned with the synthesis and chemistry of novel substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones (PCUD-8,11-diones) (Marchand, 1989), cage diketones (1) (McBee, Dively & Burch, 1955; Marchand & Chou, 1973) and (2) were prepared. It was readily apparent from NMR spectral evidence that these materials had been obtained (after exposure to moist air) in the hydrated form. Like the parent diketone (1), analysis of the ¹³C NMR spectrum of the hydrate obtained indicated that this compound contains a mirror plane. Hence, both ketone functionalities must be involved in hydrate formation, and the hydrated form of (1) must possess either structure (3a) or (3b). By way of contrast, only one ketone functionality in (2) takes part in hydrate formation; hence, the hydrated form of (2) must possess either structure (4a) or (4b). The question of the structures of both hydrates has been resolved by single-crystal X-ray structural analysis.



Experimental. All data were collected on a Nicolet R3m/ μ update of a P2₁ diffractometer using the ω -scan mode with a variable scan rate of 4 to 29.3° min⁻¹ and graphite-monochromated Mo K α

Table 1. Data collection and refinement parameters

	(3a)	(4a)
Color	Colorless	Colorless
Crystal dimensions (mm)	0.43 × 0.33 × 0.30	0.40 × 0.28 × 0.10
Lattice parameter 2 θ range (°)	23.38–29.90	24.07–28.80
Systematic absences	$h0l, h + l = 2n + 1$ $0k0, k = 2n + 1$	None
Space group	P2 ₁ /n	P $\bar{1}$
2 θ range (°)	3–55	3–55
hkl range	–9, 9; 0, 16; 0, 20	–8, 8; –18, 18; 0, 18
Check reflections	(244) (136)	(200) (071)
Transmission factors	0.630–0.663	0.342–0.892
Reflections measured	3892	5965
Unique reflections	3459	5494
R _{int}	0.006	0.008
Reflections $\geq 3\sigma(I)$	2783	3888
R (R _{all})	0.0395 (0.0527)	0.0640 (0.0972)
wR (wR _{all})	0.0414 (0.0427)	0.0336 (0.0347)
S	1.506	1.969
(Δ/σ) _{max}	0.03	0.02
Residual peaks (e Å ⁻³)	–0.25, 0.41	–1.01, 1.06*
g (weighting scheme)	0.00018	0.00035
x (extinction correction)†	0.00061 (5)	0.0004 (3)

* Adjacent to a Br atom.

† $F = F_c/[1.0 + 0.002xF_c^{2.0} \cdot 25]$.

radiation. The data were corrected for Lorentz-polarization effects, and a ψ -scan-based empirical absorption correction was applied. Lattice parameters were obtained from a least-squares refinement of 25 reflections. The structures were solved by direct methods and refined by a block-cascade least-squares technique. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. All computer programs supplied by Nicolet for Desktop 30 Micro-eclipse and Nova 4/C configuration (Sheldrick, 1985); atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Data collection and refinement parameters are given in Table 1.*

In compound (3a), the methyl H atoms were allowed to ride at a fixed distance on the attached C atom with a single isotropic thermal parameter while the remaining H-atom positions were refined with isotropic thermal parameters. Atomic positional parameters are given in Table 2 while selected bond distances and angles are given in Table 4. In compound (4a) there are two independent molecules per asymmetric unit. All H atoms except H(O1') and H(O2') were located in difference maps. Methyl H atoms were allowed to ride on the attached C atom with isotropic thermal parameters refined. The remaining H-atom positional parameters were refined with isotropic thermal parameters. Atomic

* Lists of structure factors for (3a) and (4a), anisotropic thermal parameters, H-atom parameters, and all bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52889 (63 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates and equivalent isotropic factors

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>	$U_{eq}(\text{\AA}^2)$
C(1)	0.3102 (3)	0.0887 (2)	0.8282 (2)	0.033 (1)
C(2)	0.3243 (3)	0.2087 (2)	0.8171 (1)	0.027 (1)
Cl(2)	0.4704 (1)	0.2525 (1)	0.7449 (1)	0.042 (1)
C(3)	0.1293 (3)	0.2553 (2)	0.8105 (1)	0.025 (1)
Cl(3)	0.0433 (1)	0.2888 (1)	0.7081 (1)	0.042 (1)
O(1)	0.1394 (3)	0.3443 (2)	0.8769 (1)	0.024 (1)
O(2)	-0.0247 (2)	0.3801 (1)	0.9003 (1)	0.030 (1)
C(4)	0.2516 (2)	0.4238 (1)	0.8512 (1)	0.030 (1)
C(5)	0.2218 (3)	0.2706 (2)	0.9477 (1)	0.026 (1)
Cl(5)	0.2618 (1)	0.3245 (1)	1.0485 (1)	0.042 (1)
C(6)	0.3882 (3)	0.2198 (2)	0.9127 (2)	0.028 (1)
Cl(6)	0.5995 (1)	0.2782 (1)	0.9417 (1)	0.044 (1)
C(7)	0.3741 (3)	0.0999 (2)	0.9215 (2)	0.033 (1)
C(8)	0.2003 (3)	0.0764 (2)	0.9621 (2)	0.032 (1)
O(3)	0.2297 (2)	0.0401 (2)	1.0417 (1)	0.044 (1)
O(4)	0.1058 (2)	0.0010 (1)	0.9057 (1)	0.037 (1)
C(9)	0.0889 (3)	0.1786 (2)	0.9448 (1)	0.025 (1)
C(10)	0.0250 (3)	0.1678 (2)	0.8507 (1)	0.026 (1)
C(11)	0.1078 (3)	0.0616 (2)	0.8300 (2)	0.032 (1)
O(5)	0.0146 (3)	0.0126 (1)	0.7628 (1)	0.046 (1)
C(12)	-0.1352 (4)	0.4438 (2)	0.8411 (2)	0.044 (1)
C(13)	0.2837 (4)	0.5123 (2)	0.9074 (2)	0.047 (1)

Table 3. Fractional atomic coordinates and equivalent isotropic temperature factors

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>	$U_{eq}(\text{\AA}^2)$
C(1)	1.1463 (10)	0.8239 (4)	0.4310 (4)	0.022 (3)
Br(1)	1.1363 (1)	0.8505 (1)	0.5705 (1)	0.037 (1)
C(2)	1.1845 (11)	0.9212 (4)	0.4049 (5)	0.035 (3)
C(3)	1.3397 (11)	0.9058 (5)	0.3375 (5)	0.037 (3)
C(4)	1.2252 (13)	0.9185 (5)	0.2450 (6)	0.050 (4)
C(5)	1.0246 (11)	0.8362 (5)	0.2194 (5)	0.040 (3)
C(6)	0.9716 (11)	0.8749 (5)	0.3271 (5)	0.034 (3)
C(7)	0.9308 (10)	0.7758 (5)	0.3521 (5)	0.028 (3)
C(8)	0.9322 (10)	0.6845 (5)	0.2548 (5)	0.030 (3)
O(3)	0.8071 (7)	0.5999 (3)	0.2081 (3)	0.043 (2)
C(9)	1.0975 (10)	0.7348 (4)	0.2164 (5)	0.031 (3)
Br(9)	1.1170 (2)	0.6388 (1)	0.0832 (1)	0.064 (1)
C(10)	1.3136 (10)	0.7836 (5)	0.2970 (5)	0.032 (3)
C(11)	1.3089 (10)	0.7637 (4)	0.3939 (5)	0.029 (3)
O(1)	1.5076 (7)	0.8101 (3)	0.4589 (4)	0.038 (2)
O(2)	1.2331 (8)	0.6554 (3)	0.3729 (4)	0.035 (2)
C(12)	0.8495 (13)	0.8190 (6)	0.1315 (6)	0.063 (5)
C(1')	0.6604 (9)	0.4357 (4)	0.3334 (5)	0.023 (3)
Br(1')	0.7694 (1)	0.5715 (1)	0.4530 (1)	0.040 (1)
C(2')	0.7946 (10)	0.3965 (4)	0.2549 (5)	0.026 (3)
C(3')	0.6435 (10)	0.3482 (5)	0.1456 (5)	0.030 (3)
C(4')	0.6763 (11)	0.2357 (5)	0.0915 (5)	0.038 (3)
C(5')	0.6406 (10)	0.2011 (4)	0.1763 (5)	0.027 (3)
C(6')	0.7889 (9)	0.2957 (5)	0.2762 (5)	0.026 (3)
C(7')	0.6605 (10)	0.3360 (5)	0.3556 (5)	0.024 (3)
C(8')	0.4536 (10)	0.2534 (4)	0.3065 (5)	0.023 (3)
O(3')	0.3516 (7)	0.2096 (3)	0.3453 (3)	0.038 (2)
C(9')	0.4310 (10)	0.2256 (4)	0.1921 (4)	0.025 (3)
Br(9')	0.1868 (1)	0.1094 (1)	0.1051 (1)	0.043 (1)
C(10')	0.4310 (11)	0.3277 (5)	0.1718 (5)	0.027 (3)
C(11')	0.4499 (10)	0.4279 (4)	0.2694 (5)	0.023 (3)
O(1')	0.2888 (7)	0.4152 (4)	0.3154 (4)	0.047 (3)
O(2')	0.4439 (8)	0.5168 (4)	0.2509 (4)	0.053 (3)
C(12')	0.6593 (12)	0.0900 (5)	0.1617 (5)	0.039 (4)

positional parameters are given in Table 3 while selected bond distances and angles are listed in Table 4.

Table 4. Selected bond lengths (\AA) and bond angles ($^\circ$)

	(3a)	(4a)	(4a)
C(1)—C(2)	1.542 (3)	1.547 (10)	1.558 (10)
C(1)—C(7)	1.537 (3)	1.545 (8)	1.553 (10)
C(1)—C(11)	1.539 (3)	1.526 (10)	1.520 (9)
C(2)—C(3)	1.552 (3)	1.531 (11)	1.553 (9)
C(2)—C(6)	1.573 (3)	1.525 (9)	1.558 (11)
C(3)—C(4)	1.554 (3)	1.527 (12)	1.530 (9)
C(4)—C(5)	1.554 (3)	1.507 (10)	1.535 (12)
C(5)—C(6)	1.545 (2)	1.570 (11)	1.560 (7)
C(6)—C(7)	1.538 (3)	1.564 (11)	1.541 (10)
C(7)—C(8)	1.527 (3)	1.490 (8)	1.508 (8)
C(8)—C(9)	1.550 (3)	1.519 (11)	1.530 (10)
C(9)—C(10)	1.548 (3)	1.558 (8)	1.572 (11)
C(10)—C(11)	1.535 (3)	1.548 (11)	1.522 (8)
C(8)—O(3)	1.361 (3)	1.193 (6)	1.196 (9)
C(8)—O(4)	1.451 (3)	—	—
C(11)—O(5,1)	1.373 (3)	1.382 (7)	1.387 (9)
C(11)—O(4,2)	1.445 (3)	1.410 (8)	1.380 (9)
C(2)—C(1)—C(7)	90.2 (2)	90.7 (5)	90.2 (5)
C(2)—C(1)—C(11)	107.5 (2)	105.0 (6)	105.6 (5)
C(7)—C(1)—C(11)	102.0 (2)	112.8 (4)	112.3 (5)
C(1)—C(2)—C(3)	108.3 (2)	108.0 (6)	106.4 (5)
C(1)—C(2)—C(6)	89.6 (2)	89.9 (5)	89.1 (5)
C(2)—C(3)—C(4)	104.5 (2)	102.1 (6)	104.3 (6)
C(3)—C(4)—C(5)	93.1 (2)	97.2 (7)	95.7 (6)
C(4)—C(5)—C(6)	104.7 (2)	100.8 (5)	102.9 (5)
C(2)—C(6)—C(7)	89.1 (2)	90.9 (6)	90.7 (5)
C(5)—C(6)—C(7)	108.5 (2)	107.5 (5)	108.3 (5)
C(1)—C(7)—C(6)	91.1 (2)	88.6 (5)	89.9 (6)
C(6)—C(7)—C(8)	107.6 (2)	103.5 (6)	103.3 (4)
C(7)—C(8)—C(9)	102.3 (2)	102.9 (5)	101.6 (6)
C(8)—C(9)—C(10)	102.0 (2)	112.0 (6)	111.0 (5)
C(9)—C(10)—C(11)	101.6 (2)	112.0 (6)	112.7 (6)
C(1)—C(11)—C(10)	102.5 (2)	98.9 (6)	100.0 (5)
C(7)—C(8)—O(4)	103.6 (2)	—	—
C(8)—O(4)—C(11)	97.6 (2)	—	—
C(1)—C(11)—O(4)	103.1 (2)	—	—
O(1)—C(11)—O(2)	—	113.5 (6)	106.3 (5)

Discussion. Drawings of compounds (3a) and (4a) are shown in Figs. 1 and 2. The parent diketone is composed of a norbornane moiety (two fused five-membered rings) fused along the sides to two five-membered rings and at one end to a four-membered ring. The side five-membered rings and the end four-membered ring are fused forming an open-ended cage. The formation of hydrates of diketone compounds in the presence of moisture is not unexpected (Watson, Nagl, Steglich & Ebert, 1988), and the formation of a monohydrate of (5) has been reported (Marchand & Reddy, 1985).

The structures of several derivatives of the parent diketones have been determined. The 3-methyl derivative (6) (Marchand, Suri, Earlywine, Powell & van der Helm, 1984), the 1,2,10-trimethyl derivative (7) (Watson, Nagl, Kashyap, Marchand & Zhao, 1989), and the 8-methylene-1-phenyl derivative (8) (Watson, Kashyap, Marchand & Vidyasagar, 1989) can be used for structural comparisons. In the above three compounds the C(1)—C(7) and C(9)—C(10) bonds average 1.590 (5) and 1.589 (1) \AA in length. This has been interpreted to be a result of the delocalization of the oxygen lone pairs by a 1,3 interaction *via* the σ framework (Ōsawa &

Kanematsu, 1986; Marchand, Huang, Kaya, Baker, Jemmis & Dixon, 1987). If one of the keto functionalities is converted into an ethylene ketal as in (9), C(1)—C(7) and C(9)—C(10) are shortened to 1.560 (3) and 1.577 (2) Å, respectively (Watson, Nagl, Marchand, Reddy & Reddy, 1989). This result suggests that participation of the ketone functionalities must occur with concomitant lengthening of the C(1)—C(7) and C(9)—C(10) bonds. In a series of 7-substituted pentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodecanes [*i.e.* (10), Marchand, Annapurna, Reddy, Watson & Nagl (1989)], in which one five-membered

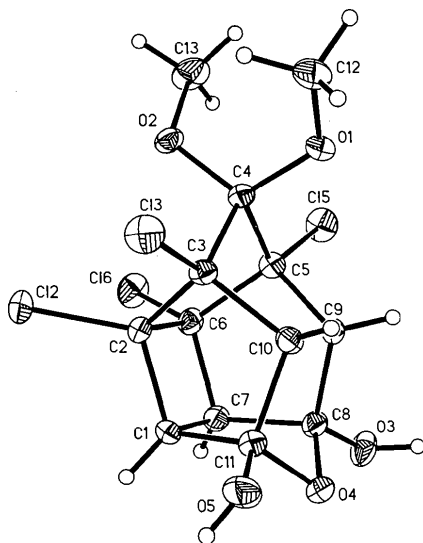


Fig. 1. Drawing of (3a) with thermal ellipsoids at the 30% probability level. H atoms are represented by spheres of arbitrary size.

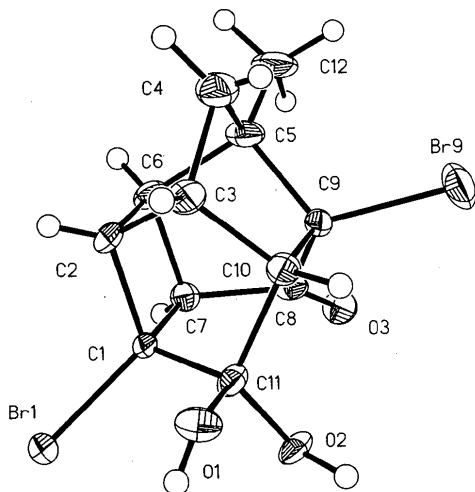


Fig. 2. Drawing of (4a) with thermal ellipsoids at the 30% probability level. H atoms are represented by spheres of arbitrary size.

ring is replaced by a six-membered ring and the π system of one keto function is replaced by an internal enol double bond in the six-membered ring, a similar lengthening is observed [1.587 (5) and 1.580 (1) Å for the two similar bonds, *i.e.* C(1)—C(7) and C(4)—C(5), respectively]. Upon complete reduction of the π system these bonds become 1.547 (3) and 1.567 (3) Å, respectively (Marchand, Watson & Kashyap, 1989). In (3a) and (4a) we should observe a shortening of the C(1)—C(7) and C(9)—C(10) bonds owing to the loss of the keto π system; however, bond lengthening may occur around the cage owing to the presence of electron-withdrawing substituents.

In (3a), both keto functions have been hydrated, and the C(1)—C(7) and C(9)—C(10) bonds are shortened to 1.537 (3) and 1.548 (3) Å. The influence of the methoxy groups and Cl atoms is more subtle. While the C(2)—C(6), C(3)—C(4) and C(4)—C(5) bonds of 1.573 (3), 1.554 (3) and 1.554 (3) Å are considerably longer than the average values for (6), (7) and (8) [1.548 (5), 1.521 (4) and 1.518 (10) Å, respectively], the C(2)—C(3) and C(5)—C(6) distances are not significantly different [1.552 (3) and 1.545 (3) Å compared with 1.550 (6) and 1.547 (10) Å, respectively].

Monohydrate (4a) more closely resembles monoketal (9) (Watson, Nagl, Marchand, Reddy & Reddy, 1989) except for the bromine substitution. There are two independent molecules of (4a) in the unit cell, and the average values for C(1)—C(7) and C(9)—C(10) are 1.549 (4) and 1.565 (7) Å, respectively. These are shorter than the values reported for the corresponding C—C bonds in the ketal but longer than those in (3a); however, larger standard deviations render more detailed comparisons of limited value. The distances and angles in (3a) and (4a) differ for several reasons. In (3a) the bridging oxygen O(4) leads to a C(8)···C(11) distance of 2.178 (3) Å while the same distance in (4a) is 2.709 (10) Å. The increase in the C(8)···C(11) distance leads to significant differences in angles, *e.g.* C(7)—C(1)—C(11) and C(8)—C(9)—C(10) are 102.0 (2) and 102.0 (2)° in (3a), and 112.8 (4), 112.3 (5)° and 112.0 (6), 111.0 (5)° in (4a). In (3a) the more electronegative Cl atom drains electron density from the adjacent bonds leading to increased distances while the less-electronegative bromine is less perturbing in (4a). Differences in hydrogen bonding lead to differences in some chemically equivalent bonds in (3a), and to differences between the two independent molecules in (4a).

Two intermolecular hydrogen bonds are formed by (3a): H(O5)···O(2) (0.5 - x, 0.5 + y, 1.5 - z) = 2.20 (4), O(5)···O(2) = 2.874 (3), O(5)—H(5) = 0.76 (4) Å, O(5)—H(O5)···O(2) = 147 (1)°; O(4)···H(O3) (-x, -y, 2 - z) = 1.90 (3), O(4)···O(3) =

2.750 (3), O(3)—H(O3) = 0.86 (3) Å, O(3)—H(O3)⋯O(4) = 170 (1)°. In (4a), hydroxyl H atoms for one molecule were located in difference maps, but those for the second molecule were not found. Two hydrogen bonds and one short O⋯O distance are noted: O(2')⋯O(3) = 2.801 (6); O(2')⋯H(O2)(-1 + x, y, z) = 1.97 (8), O(2')⋯O(2) = 2.817 (6), O(2)—H(O2) = 0.99 (8) Å, O(2')⋯H(O2)—O(2) = 143 (2)°; O(3')⋯H(O1)(2 - x, 1 - y, 1 - z) = 2.26 (8), O(3')⋯O(1) = 2.989 (6), O(1)—H(O1) = 0.75 (7) Å, O(3')⋯H(O1)—O(1) = 165 (2)°.

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Structure of Synthetic Bromobeckerelide. A Case of Diastereomeric Selection in the Solid State

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Abstract. 4-Bromo-5-hydroxy-3-(1-hydroxybutyl)-5-methyl-5H-furan-2-one, C₉H₁₃BrO₄, recrystallized from CH₂Cl₂/hexane, m.p. 359–360 K, *M_r* = 265.1, triclinic, *P* $\bar{1}$, *a* = 5.9067 (4), *b* = 9.4807 (9), *c* = 11.0895 (11) Å, α = 74.16 (1), β = 79.96 (1), γ = 71.87 (1)°, *V* = 565.1 (1) Å³, *Z* = 2, *F*(000) = 268, *D_x* = 1.56 Mg m⁻³, λ (Mo *K* α) = 0.71069 Å, μ = 3.59 mm⁻¹, room temperature, *R* = 0.044 [*wR* = 0.043, *w* = 1/ σ^2 (*F_o*)] for 1273 observed reflections [*|F_o*| > 4 σ (*F_o*)]. In the solid state, which is different from the situation in solution, only the diastereomer having the like configuration is observed. Molecules of the same configuration are linked by hydrogen

bonds involving both hydroxyl groups of the same molecule.

Introduction. Bromo- and chlorobeckerelide [(1) and (2)] were isolated as an inseparable 10:1 mixture from the red marine alga *Beckerella subcostatum* collected near Kozu island, Japan. The unusual structure and potent antimicrobial activity of (1) and (2), which were reported some 12 years ago (Ohta, 1977), have generated considerable interest. Despite various approaches, the synthesis of the major constituent (1) has only been recently accomplished (Jefford, Jaggi & Boukouvalas, 1989), thereby