Crystal and Molecular Structures of Methyl 2α,3α;4α,5α-Diepoxy-*cis*-(1α*H*,2α*H*)-bicyclo[4.1.0]heptane-7α-carboxylate and Methyl 2,5-Dihydroxybicyclo[4.1.0]heptane-7-carboxylate

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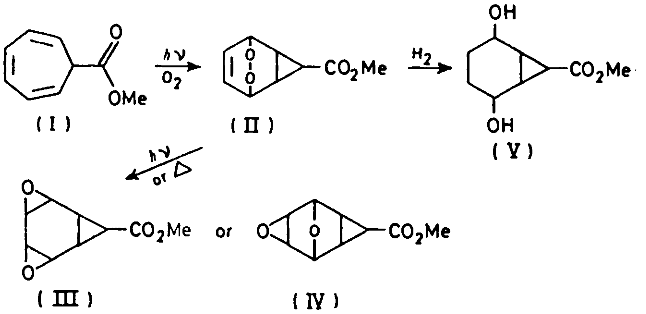
X-Ray crystal analysis has been used to identify one isomer (III) of the two products $C_9H_{10}O_4$ {methyl 2,5-epidioxybicyclo[4.1.0]hept-3-ene-7-carboxylate (II) and methyl 2α,3α; 4α,5α-diepoxy-*cis*(1α*H*,2α*H*)-bicyclo-[4.1.0]heptane-7α-carboxylate (III)} produced by the photosensitized oxygenation of methyl cyclohepta-2,4,6-trienecarboxylate (I). Crystals of (III) are orthorhombic, space group $P2_12_12_1$, with a = 19.548(1), b = 6.0101(5), and c = 7.3944(4) Å and Z = 4. By hydrogenation of (II), methyl 2,5-dihydroxybicyclo[4.1.0]heptane-7-carboxylate (V) is formed which also crystallizes in space group $P2_12_12_1$ with Z = 4, and cell dimensions a = 18.192(1), b = 7.7284(5), and c = 6.7139(3) Å. The structures were solved by the tangent formula phasing method and refined by full-matrix least-squares to R 0.055 (962 observed reflections) and 0.044 (1 028 observed reflections) respectively.

Compound (III) contains a six-membered ring consisting of two planar fragments oriented at 3.4° to each other. The epoxide groups are tilted 108.0 and 105.6° from the plane through the four carbon atoms they include. In compound (V), two C–O bonds are broken, allowing the six-membered ring to assume the half-chair conformation. The cyclopropyl ring is inclined at 107.1 (III) and 109.0° (V) to the best plane through the two included and two adjacent carbon atoms. In both compounds, the carbonyl oxygen is located directly behind the cyclopropyl ring.

PHOTOSENSITIZED oxygenation of methyl cyclohepta-2,4,6-trienecarboxylate (I) produces methyl 2,5-epidioxybicyclo[4.1.0]hept-3-ene-7-carboxylate (II) which, by further photolysis or thermolysis, isomerizes to give compound (III) or (IV) whose structure could not be identified by n.m.r. spectroscopy.[1] We report the crystal structure analysis of (III) as well as of the hydrogenation product of (II), methyl 2,5-dihydroxybicyclo-[4.1.0]heptane-7-carboxylate (V). The correct structure of (V) has been previously suggested by Ziegler.[2] ‡



EXPERIMENTAL

Unit-cell dimensions and space group were determined by photographic methods. Crystal data are given in Table 1. Cell parameters were subsequently refined by least-squares analysis of θ values measured on a Siemens AED diffractometer with Cu-K_α radiation (λ = 1.5418 Å). During data collection, the diffractometer was operated in the θ—2θ scan mode by use of the five-value technique.[4] The standard deviation of an intensity was calculated from counting statistics using $\sigma^2(I) = S + B + (dS)^2$ where S = scan count, B = background, corrected to scan time, $I = S - B$, and d = an empirical constant to allow for instrumental errors, taken as 0.02. Lorentz and polarization factors were applied and structure amplitudes and normalized structure amplitudes (E values) calculated. The structures were solved by an adaptation[5] of the weighted multisolution tangent formula.[6] In both cases, the most probable solution based on R_α[5] consisted of essentially correct phases and produced E maps which clearly revealed the positions of the non-hydrogen atoms.

TABLE 1

Crystal data for the two compounds

	(III) $C_9H_{10}O_4$	(V) $C_9H_{14}O_4$
M	182.2	186.2
Lattice system	Orthorhombic	Orthorhombic
a/Å	19.54 8(1)	18.192(1)
b/Å	6.010 1(5)	7.728 4(5)
c/Å	7.394 4(4)	6.713 9(3)
U/Å^3	868.7	943.9
D_m/g cm^{-3}	1.39	1.31
Z	4	4
F(000)	384	400
Space group	$P2_12_12_1$ (D_2^4, No. 19)	$P2_12_12_1$ (D_2^4, No. 19)
μ(Cu-K_α)/cm^{-1}	9.45	8.71
No. of θ values used in cell parameter refinement	45	37
Independent reflections	1 012	1 089
Unobs. reflections ($I/\sigma(I) \leqslant 1.0$), systematic absences, and reflections omitted for extinction	50	61
Obs. reflections	962	1 028
No. of reflections and $E_{\min.}$ used for tangent formula refinement	196, 1.3	141, 1.5

Refinement was begun with the full-matrix least-squares approach, minimizing $\Sigma w\Delta^2$. Scattering factors were

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‡ The reported melting point of 115 °C (acetone), however could not be confirmed. M.p. 96 °C (methyl acetate) was found on repeating Ziegler's hydrogenation procedure with highly pure (II).[3]

[1] A. Ritter, P. Bayer, J. Leitich, and G. Schomburg, *Liebigs Ann. Chem.*, 1974, 835.

[2] H. Ziegler, Thesis, Göttingen University, 1952, p. 49.

[3] A. Ritter and P. Bayer, unpublished results.

[4] D. J. Brauer and C. Krüger, *Acta Cryst.*, 1973, **B29**, 1684.

[5] P. J. Roberts, R. C. Pettersen, G. M. Sheldrick, N. W. Isaacs, and O. Kennard, *J.C.S. Perkin II*, 1973, 1978.

[6] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1970, **B26**, 274.

taken from ref. 7 for the carbon and oxygen atoms and from ref. 8 for hydrogen. The weighting scheme used was $w = [\sigma(F)\cdot\{2F_{\text{min.}} + F_o + 2F_o^2/F_{\text{max.}}\}]^{-1}$. After several cycles of refinement using anisotropic temperature factors, hydrogen atoms were located as residual electron density on difference Fourier maps. These were given isotropic temperature factors and included in the next cycles of refinement. The ethyl hydrogen atoms did not refine well and were subsequently held fixed in the positions found from the difference maps. However, their temperature factors were allowed to refine. Refinement was considered to have converged when all parameter shifts were small fractions of their standard deviations. An analysis of variance computed after convergence is given in Table 2. Final values of R and R' $[=\{\Sigma w|F_o - F_c|^2/\Sigma w F_o^2\}^{\frac{1}{2}}]$ were 0.055 and 0.074 (III), and 0.044 and 0.055 (V).

TABLE 2

Analysis of variance

(*a*) As a function of $\sin\theta$

(i) For (III)											
	$\sin\theta$	0.0—0.42	—0.53	—0.61	—0.68	—0.74	—0.79	—0.83	—0.87	—0.91	—0.94
	N *	104	92	96	106	97	103	83	96	106	79
	V *	24	24	25	18	15	18	16	18	16	16
(ii) For (V)											
	$\sin\theta$	0.0—0.42	—0.53	—0.62	—0.69	—0.74	—0.79	—0.83	—0.87	—0.91	—0.94
	N	107	99	112	108	98	105	96	103	105	95
	V	35	30	29	27	26	26	22	26	27	30

(*b*) As a function of $\sqrt{(F/F_{\text{max.}})}$

(i) For (III)											
	$\sqrt{(F/F_{\text{max.}})}$	0.0—0.11	—0.13	—0.15	—0.17	—0.20	—0.23	—0.28	—0.33	—0.41	—1.00
	N	130	94	81	84	109	84	105	99	83	93
	V	16	19	18	20	18	20	25	26	16	11
(ii) For (V)											
	$\sqrt{(F/F_{\text{max.}})}$	0.0—0.19	—0.23	—0.26	—0.28	—0.31	—0.34	—0.39	—0.45	—0.55	—1.00
	N	120	111	107	82	106	105	94	108	100	95
	V	26	28	29	26	32	32	29	25	24	26

* N = The number of reflections in the group, $V = 10^2 \times M\Sigma w\Delta^2/N\Sigma w$ where N is the total number of reflections.

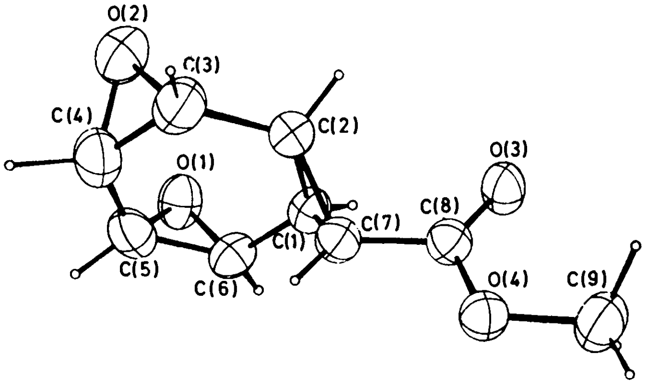

FIGURE 1 The molecular structure and numbering scheme for (III)

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21495 (8 pp., 1 microfiche).* Final positional and thermal parameters are given in Table 3 together with their standard deviations calculated from the inverse matrix of the last refinement cycle. In Tables 4 and 5, bond lengths and valency angles are tabulated with their standard deviations calculated from the full correlation matrix.

DISCUSSION

Molecular Structure.—The numbering scheme and molecular structures are given in Figures 1 and 2 for (III) and (V) respectively. These structures lend themselves to comparison with the four compounds (VI),[9] (VII),[10] (VIII),[11] and (IX).[12]

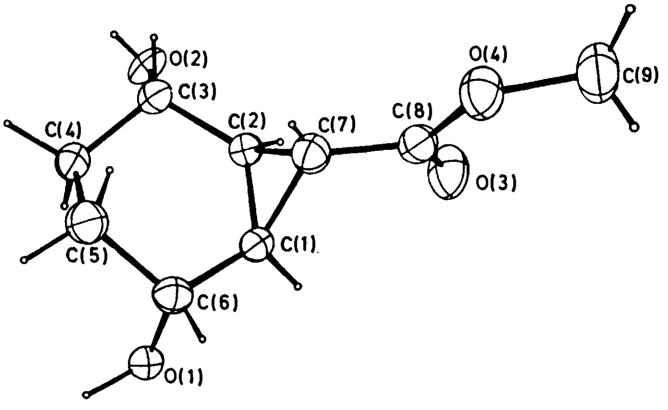

FIGURE 2 The molecular structure and numbering scheme for (V)

Our X-ray analysis determined isomer (III) of the products $C_9H_{10}O_4$ of the photosensitized oxygenation of methylcyclohepta-2,4,6-trienecarboxylate (I) to be the diepoxide of the hypothetical methyl norcaradiene-7-carboxylate. The compound has the same fundamental

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[7] D. T. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, 3175.

[9] C. Kabuto, M. Yagihara, T. Asao, and Y. Kitahara, *Angew Chem.*, 1973, **85**, 860.

[10] C. Krüger and P. J. Roberts, *Cryst. Struct. Comm.*, 1974, **3**, 459.

[11] C. J. Fritchie, *Acta Cryst.*, 1966, **20**, 27.

[12] W. Littke and U. Druck, *Angew. Chem.*, 1974, **86**, 557.

ring structure as (VI) and bears some resemblance to (VII).

Hydrogenation of (II) produces the 2,5-diol (V). C(4) and C(5) both obtain an extra hydrogen atom and the six-membered ring assumes the half-chair configuration.

In (III), the bond lengths C(1)–C(6), C(2)–C(3), and C(4)–C(5) average 1.488 Å. This value represents a severe shortening from the usual sp^3–sp^3 distance (1.533 Å),[13] and can be attributed to the conjugative effect of the unsaturated character of three-membered rings. Structures (VI), (VII), and (IX) have this feature in common, with eight bond lengths ranging from 1.475

TABLE 3

(*a*) Final fractional co-ordinates (× 10^3 for hydrogen, × 10^4 for others) and their standard deviations. Isotropic *U* values (× 10^3) are given for the hydrogen atoms

(i) For (III)

	x	*y*	*z*	*U*
C(1)	4 153(2)	−327(5)	8 212(4)	
C(2)	3 536(2)	−362(6)	9 335(4)	
C(3)	3 598(2)	−533(7)	11 333(5)	
C(4)	4 261(2)	−806(7)	12 145(5)	
C(5)	4 892(2)	−759(7)	11 019(5)	
C(6)	4 842(2)	− 476(7)	9 067(6)	
C(7)	3 758(1)	1 801(5)	8 448(4)	
C(8)	3 348(1)	2 539(5)	6 876(4)	
C(9)	2 850(3)	5 594(7)	5 396(6)	
O(1)	5 023(2)	−2 590(5)	9 831(3)	
O(2)	3 838(2)	−2 677(5)	11 979(4)	
O(3)	3 088(1)	1 313(4)	5 768(4)	
O(4)	3 278(1)	4 732(4)	6 824(3)	
H(1)	417(3)	−4(12)	726(12)	195(26)
H(2)	314(1)	−108(6)	881(4)	66(8)
H(3)	324(3)	67(11)	1 206(11)	159(22)
H(4A)	425(2)	−120(9)	1 341(8)	110(13)
H(5A)	523(3)	−36(10)	1 175(8)	130(17)
H(6)	514(3)	−1(10)	857(7)	122(17)
H(7)	391(2)	284(9)	928(6)	103(12)
H(9A)	295	512	422	129(17)
H(9B)	236	491	545	410(44)
H(9C)	276	712	563	205(26)

(ii) For (V)

	x	*y*	*z*	*U*
C(1)	1 203(1)	6 332(3)	1 285(3)	
C(2)	1 131(1)	6 908(3)	3 396(3)	
C(3)	877(1)	5 667(3)	5 017(3)	
C(4)	490(2)	4 092(3)	4 145(4)	
C(5)	945(2)	3 290(3)	2 498(4)	
C(6)	1 010(1)	4 498(3)	705(4)	
C(7)	1 893(1)	6 687(3)	2 500(4)	
C(8)	2 305(1)	8 281(3)	2 051(3)	
C(9)	3 489(1)	9 530(4)	1 945(5)	
O(1)	309(1)	4 656(2)	−308(3)	
O(2)	400(1)	6 633(2)	6 305(2)	
O(3)	2 031(1)	9 633(3)	1 584(4)	
O(4)	3 029(1)	8 034(2)	2 241(3)	
H(1)	108(2)	721(4)	9(5)	50(8)
H(2)	94(2)	818(3)	359(5)	50(8)
H(3)	132(2)	527(4)	583(5)	44(7)
H(4A)	0(2)	452(4)	359(5)	67(10)
H(4B)	35(2)	326(6)	521(7)	92(12)
H(5A)	77(2)	211(4)	210(5)	57(9)
H(5B)	147(2)	289(5)	284(6)	86(12)
H(6)	139(2)	402(5)	−45(6)	79(11)
H(7)	222(1)	578(4)	284(5)	46(7)
H(9A)	341	1 001	58	219(27)
H(9B)	335	1 045	295	210(26)
H(9C)	401	922	213	81(11)
H(10)	14(2)	350(5)	−54(6)	84(12)
H(11)	23(2)	604(5)	751(7)	72(10)

TABLE 3 (*Continued*)

(*b*) Anisotropic temperature factors * (Å^2 × 10^3) with their standard deviations; values for (V) follow those for (III)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	88(2)	68(1)	63(2)	1(1)	4(1)	7(2)
	39(1)	37(1)	31(1)	1(1)	1(1)	−1(1)
C(2)	76(2)	73(2)	67(2)	5(1)	−4(1)	−9(1)
	36(1)	35(1)	30(1)	1(1)	−1(1)	−1(1)
C(3)	104(2)	96(2)	68(2)	10(2)	9(2)	−1(2)
	40(1)	39(1)	29(1)	3(1)	1(1)	2(1)
C(4)	121(3)	91(2)	60(2)	−6(2)	−1(2)	6(2)
	57(1)	37(1)	36(1)	7(1)	2(1)	−7(1)
C(5)	94(2)	81(2)	97(2)	−5(2)	−27(2)	2(2)
	61(1)	36(1)	42(1)	0(1)	−4(1)	3(1)
C(6)	83(2)	86(2)	91(2)	14(2)	11(2)	11(2)
	47(1)	41(1)	32(1)	−4(1)	3(1)	−1(1)
C(7)	74(1)	61(1)	65(1)	−4(1)	−2(1)	−3(1)
	36(1)	40(1)	40(1)	4(1)	0(1)	0(1)
C(8)	73(1)	60(1)	66(1)	−2(1)	−2(1)	−5(1)
	38(1)	45(1)	37(1)	5(1)	0(1)	0(1)
C(9)	130(3)	76(2)	88(2)	13(2)	−23(2)	7(2)
	45(1)	61(2)	69(2)	3(2)	7(1)	−14(1)
O(1)	120(2)	93(2)	83(2)	2(1)	−6(1)	32(2)
	54(1)	44(1)	33(1)	1(1)	−5(1)	−9(1)
O(2)	121(2)	105(2)	84(2)	29(2)	−3(1)	−10(2)
	54(1)	47(1)	31(1)	5(1)	8(1)	9(1)
O(3)	111(2)	69(1)	85(1)	−5(1)	−27(1)	−5(1)
	49(1)	47(1)	78(1)	18(1)	−4(1)	0(1)
O(4)	91(1)	60(1)	76(1)	−1(1)	−8(1)	−1(1)
	34(1)	53(1)	59(1)	6(1)	1(1)	−4(1)

* Coefficients in the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

TABLE 4

(*a*) Bond lengths (Å), with standard deviations in parentheses

	(III)	(V)
C(1)–C(2)	1.465(5)	1.491(3)
C(1)–C(6)	1.490(5)	1.511(3)
C(1)–C(7)	1.504(4)	1.522(3)
C(2)–C(3)	1.486(4)	1.522(3)
C(2)–C(7)	1.520(4)	1.520(3)
C(3)–C(4)	1.438(6)	1.523(3)
C(3)–O(2)	1.452(5)	1.435(3)
C(4)–C(5)	1.489(6)	1.515(4)
C(4)–O(2)	1.401(5)	
C(5)–C(6)	1.457(6)	1.528(3)
C(5)–O(1)	1.431(5)	
C(6)–O(1)	1.435(5)	1.449(3)
C(7)–C(8)	1.480(4)	1.473(3)
C(8)–O(3)	1.214(4)	1.199(3)
C(8)–O(4)	1.326(4)	1.338(3)
O(4)–C(9)	1.444(5)	1.441(3)

(*b*) Bond lengths involving hydrogen atoms

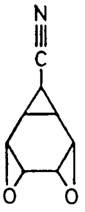
	(III)	(V)
C(1)–H(1)	0.73(9)	1.08(3)
C(2)–H(2)	0.97(3)	1.05(3)
C(3)–H(3)	1.14(7)	1.03(3)
C(4)–H(4A)	0.96(6)	1.02(3)
C(4)–H(4B)		1.00(4)
C(5)–H(5A)	0.89(6)	1.00(3)
C(5)–H(5B)		1.03(4)
C(6)–H(6)	0.74(5)	1.11(4)
C(7)–H(7)	0.93(5)	0.95(3)
C(9)–H(9A)	0.94	1.00
C(9)–H(9B)	1.04	1.01
C(9)–H(9C)	0.95	0.99
O(1)–H(10)		0.96(4)
O(2)–H(11)		0.98(4)

to 1.489, mean 1.483 Å. Structure (VIII) shows a related phenomenon. In this case, the interaction of the cyclopropyl ring and the double bonds causes a shortening to 1.475 and 1.485 Å of the two bond lengths involved. As previously observed,[10] the C–C distance (1.513 Å) between the two *cisoid* cyclopropyl rings in (VII) is thought to be influenced by such conjugative effects but counterbalanced by the repulsive steric interaction of the methyl groups.

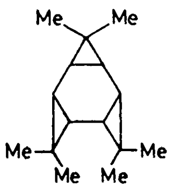
TABLE 5

Valency angles (°), with standard deviations in parentheses

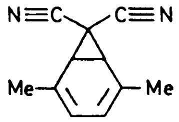
	(III)	(V)
C(2)–C(1)–C(6)	120.2(3)	120.3(2)
C(2)–C(1)–C(7)	61.6(2)	60.6(1)
C(6)–C(1)–C(7)	117.8(3)	120.0(2)
C(1)–C(2)–C(3)	119.8(3)	121.2(2)
C(1)–C(2)–C(7)	60.5(2)	60.7(1)
C(3)–C(2)–C(7)	117.7(3)	119.3(2)
C(2)–C(3)–C(4)	119.7(3)	111.7(2)
C(2)–C(3)–O(2)	114.5(3)	106.7(2)
C(4)–C(3)–O(2)	58.0(3)	111.5(2)
C(3)–O(2)–C(4)	60.5(3)	
C(3)–C(4)–C(5)	120.8(3)	110.7(2)
C(3)–C(4)–O(2)	61.5(3)	
C(5)–C(4)–O(2)	117.1(3)	
C(4)–C(5)–C(6)	120.0(3)	111.5(2)
C(4)–C(5)–O(1)	118.4(3)	
C(6)–O(1)–C(5)	61.1(3)	
C(6)–C(5)–O(1)	59.6(2)	
C(5)–C(6)–C(1)	119.2(4)	112.8(2)
C(5)–C(6)–O(1)	59.3(2)	110.7(2)
C(1)–C(6)–O(1)	116.3(4)	104.3(2)
C(1)–C(7)–C(2)	58.0(2)	58.7(1)
C(1)–C(7)–C(8)	116.2(2)	117.4(2)
C(2)–C(7)–C(8)	116.1(2)	116.8(2)
C(7)–C(8)–O(3)	125.1(3)	124.9(2)
C(7)–C(8)–O(4)	112.1(2)	111.3(2)
O(3)–C(8)–O(4)	122.7(3)	123.9(2)
C(8)–O(4)–C(9)	115.9(3)	116.4(2)



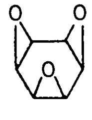
(VI)



(VII)



(VIII)



(IX)

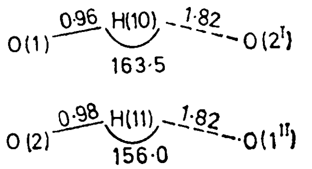


FIGURE 3 Hydrogen bonding parameters in (V): O(2^{I}) is at $-x, -\frac{1}{2}+y, \frac{1}{2}-z$, and O($1^{II}$) is at $x, y, -1+z$

The half-chair conformation in (V) prevents a delocalization of electron density around the six-membered ring and the distances C(1)–C(6), C(2)–C(3), and C(4)–C(5) increase to 1.511, 1.522, and 1.515 Å respectively.

The mean of the C(3)–C(4) and C(5)–C(6) bond lengths in (III) (1.448 Å) is considerably shorter than that (1.470 Å) of comparable distances in (IX). These values are to be compared with the distance (1.472 Å) in ethylene oxide.[14] In (V) the C(3)–C(4) and C(5)–C(6) distances (1.523 and 1.528 Å) reflect the general relaxation of the six-membered ring upon opening of the epoxide rings.

The mean C–O distance in (III) (1.430 Å) is to be compared with 1.448 and 1.437 Å, the means in (VI) and (IX), and with 1.436 Å in ethylene oxide.[14]

The six-membered ring in (III) consists of the two planar fragments C(6), C(1)–(3) and C(3)—(6) (root-mean-square deviations 0.001 and 0.004 Å) which deviate by 3.4° from being coplanar. In (V), the four atoms C(6), C(1)—(3) are coplanar (root-mean-square deviation 0.004 Å) with C(4) and C(5) displaced −0.427 and 0.344 Å respectively from this plane. The plane of the cyclopropyl ring in (III) is inclined at 107.1° to the plane of C(6), C(1)—(3) compared with 104.2, 110.1, and 108.1° in (VI), (VII), and (VIII) and with 109.0° in (V).

The epoxide rings in (III) are tipped 108.0 and 105.6° to the plane of C(3)—(6). These are comparable to values ranging from 104.8 to 106.9° for (VI) and (IX).

In both (III) and (V) the carboxylate groups C(7), C(8), O(3), and O(4) are planar (root-mean-square deviations 0.004 and 0.001) and in both cases the carbonyl oxygen is located directly behind the cyclopropyl ring. The angles between the plane of the carboxylate group and that of the cyclopropyl ring are 88.8 (III) and 92.0° (V). The torsion angles C(1)–C(7)–C(8)–O(3) and C(2)–C(7)–C(8)–O(3) are −35.1 and 30.3° for (III), and 36.1 and −30.7° for (V). This orientation of the C=O double bond again manifests the unsaturated nature of the cyclopropyl ring. We suggest a partially delocalized system between the cyclopropyl ring, C(8) and O(3). This would of course require the C(7)–C(8) bond length to be shorter than the expected 1.505 Å[13] for sp^3–sp^2, and observed values are 1.480 (III) and 1.473 Å (V).

The hydroxy-groups in (V) allow an intermolecular hydrogen-bonding network in which each hydroxy-group acts as both donor and acceptor. The parameters of this system are given in Figure 3.

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