

Final atomic coordinates for non-H atoms are given in Tables 2, 3, 4 and 5 for (I), (II), (III) and (IV), respectively.\* No anomalous bond distances or angles were found. Figs. 1, 2, 3 and 4 are stereoscopic drawings of compounds (I), (II), (III) and (IV), respectively.

**Related literature.** All the crystals were of similar poor diffracting quality and did not allow measurements of data with resolution good enough to perform anisotropic refinements for accurate calculation of distances and angles. Nevertheless, the main aim of the present study could still be achieved, namely the unambiguous determination of the four intermediate conformations; this knowledge is fundamental for proposing possible fragmentation reaction pathways (Sharpless, 1981;

\* Lists of structure factors, H-atom coordinates and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51654 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Snatzke & Fehlhäber, 1963; Prelog, 1965; Webster, Entenios & Silverstein, 1987).

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### Structural Studies on Abscisic-Acid-Synthesis Intermediates: (1) 5,6-Dihydro-4-methyl-6-(7,9,9-trimethyl-1,4-dioxaspiro[4.5]dec-7-en-8-yl)-2H-pyran-2-one and (2) 5,6-Dihydro-4-methyl-6-(2',2',6'-trimethylspiro[1,3-dioxolane-2,4'-[7]oxabicyclo[4.1.0]hept]-1'-yl)-2H-pyran-2-one

BY E. E. CASTELLANO AND J. ZUKERMAN-SCHPECTOR\*

*Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560 São Carlos, SP, Brazil*

AND MAURICIO G. CONSTANTINO AND PELLEGRINO LOSCO

*Departamento de Química de Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Av. Bandeirantes 3.900, 14049 Ribeirão Preto, SP, Brazil*

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**Abstract.** (1)  $C_{17}H_{24}O_4$ ,  $M_r = 292.38$ , triclinic,  $P\bar{1}$ ,  $a = 6.811$  (1),  $b = 9.564$  (2),  $c = 13.052$  (2) Å,  $\alpha = 98.66$  (1),  $\beta = 98.67$  (2),  $\gamma = 107.07$  (2)°,  $V = 786.2$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.234$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.05$  mm<sup>-1</sup>,  $F(000) = 316$ ,  $T =$

296 K, final  $R = 0.056$  for 1463 observed reflections. The pyran ring is in a half-chair conformation. (2)  $C_{17}H_{24}O_5$ ,  $M_r = 308.38$ , triclinic,  $P\bar{1}$ ,  $a = 6.401$  (3),  $b = 9.649$  (2),  $c = 13.417$  (4) Å,  $\alpha = 96.44$  (2),  $\beta = 98.73$  (3),  $\gamma = 103.77$  (2)°,  $V = 786$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.303$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.06$  mm<sup>-1</sup>,  $F(000) = 332$ ,  $T = 296$  K, final  $R = 0.055$  for 1311 observed reflections. The pyran and the epoxy O atoms are in a *cis* configuration.

\* Permanent address: Laboratório de Cristalografia e Físico-Química dos Materiais, CCEN, Universidade Federal de Alagoas, 57000 Maceió, AL, Brazil.

Table 1. Crystallographic data

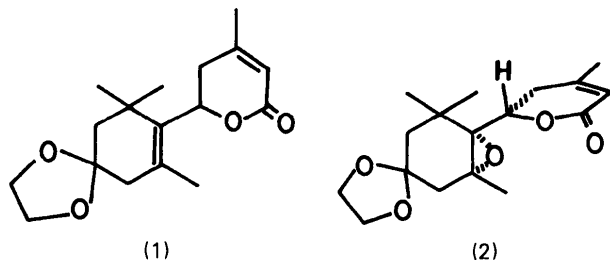
	(1)	(2)
Formula	C <sub>17</sub> H <sub>24</sub> O <sub>4</sub>	C <sub>17</sub> H <sub>24</sub> O <sub>3</sub>
M <sub>r</sub>	292.38	308.38
Crystal dimensions (mm)*	0.45 × 0.38 × 0.30	0.45 × 0.15 × 0.08
Scan type	ω-2θ	ω-2θ
Scan range (° in ω)	0.35 + 0.80tanθ	0.35 + 0.80tanθ
θ <sub>max</sub> (°)	25	24
Range of hkl	-8 < h < 8, -11 < k < 11, 0 < l < 15	-7 < h < 7, -11 < k < 11, 0 < l < 15
Total number of reflections†	3004	2722
Unique reflections	2769	2464
R <sub>int</sub>	0.02	0.02
Reflections with I > 3σ(I)	1463	1311
Number of variables refined	192	201
R	0.056	0.055
wR	0.065	0.054
w	1/σ <sup>2</sup> (F) + 0.0078F <sup>2</sup>	1/σ <sup>2</sup> (F) + 0.0005F <sup>2</sup>
Max. Δ/σ	0.03	0.03
Residual density (e Å <sup>-3</sup> )	0.27, -0.24	0.21, -0.21
S	0.87	5.40

T = 296 K, Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Function minimized  $\sum w(|F_o| - |F_c|)^2$ ,  $R = \sum |F_o| - |F_c| / \sum |F_o|$ ,  $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}$ . Values of R and wR are based on those reflections with I > 3σ(I).

\* 21 reflections were used for the orientation matrix, range of θ: 8 < θ < 20° for (1) and 6 < θ < 14° for (2).

† The intensities of two standard reflections remained essentially equal over the duration of the experiments.

**Experimental.** Data collection and refinement parameters for (1) and (2) are summarized in Table 1. The structures were solved using standard direct-methods and difference Fourier techniques. In the final cycles of full-matrix least-squares refinement, all non-H atoms were anisotropic. H atoms were included as fixed contributors to the structure.



Inspection of  $F_c$  and  $F_o$  values indicated that secondary-extinction correction was required:  $F_{corr} = F_c(1 - \chi F_c^2 / \sin\theta)$ , where  $\chi$  refined to  $7.1 \times 10^{-6}$  for (1) and  $4.2 \times 10^{-6}$  for (2). Scattering factors for non-H atoms from Cromer & Mann (1968), with corrections for anomalous dispersion from Cromer & Liberman (1970), and for H atoms from Stewart, Davidson & Simpson (1965). Programs used: *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>) for (1)
$$B_{iso} = \frac{4}{3} \sum_{i,j} B_{ij}(\mathbf{a}_i, \mathbf{a}_j).$$

	x	y	z	B <sub>iso</sub>
O(1)	0.4159 (3)	0.9729 (2)	0.3334 (2)	3.54 (6)
O(2)	0.6262 (4)	0.8741 (3)	0.4187 (2)	4.55 (7)
O(3)	0.4492 (3)	1.4224 (2)	0.1604 (2)	4.05 (6)
O(4)	0.1835 (4)	1.3805 (2)	0.0228 (2)	4.24 (6)
C(1)	0.4481 (5)	0.8737 (3)	0.3912 (2)	3.32 (9)
C(2)	0.2647 (5)	0.7643 (3)	0.4103 (3)	3.47 (9)
C(3)	0.0700 (5)	0.7407 (3)	0.3594 (2)	3.30 (8)
C(4)	-0.1148 (6)	0.6156 (3)	0.3685 (3)	4.4 (1)
C(5)	0.0349 (5)	0.8411 (3)	0.2862 (2)	3.30 (8)
C(6)	0.2079 (5)	0.9907 (3)	0.3158 (2)	2.93 (8)
C(7)	0.2041 (5)	1.0936 (3)	0.2376 (2)	2.75 (7)
C(8)	0.2627 (5)	1.0683 (3)	0.1454 (2)	3.07 (8)
C(9)	0.3311 (6)	0.9374 (4)	0.1066 (3)	4.12 (9)
C(10)	0.2700 (5)	1.1709 (3)	0.0681 (3)	3.91 (9)
C(11)	0.2484 (5)	1.3193 (3)	0.1104 (2)	3.25 (8)
C(12)	0.2659 (6)	1.5396 (4)	0.0560 (3)	5.0 (1)
C(13)	0.4426 (6)	1.5683 (4)	0.1493 (3)	4.9 (1)
C(14)	0.0929 (5)	1.3026 (3)	0.1814 (2)	3.55 (8)
C(15)	0.1393 (5)	1.2285 (3)	0.2748 (2)	3.16 (8)
C(16)	-0.0655 (6)	1.1820 (4)	0.3176 (3)	4.8 (1)
C(17)	0.3137 (6)	1.3374 (3)	0.3641 (3)	4.5 (1)

Table 3. Fractional atomic coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>) for (2)
$$B_{iso} = \frac{4}{3} \sum_{i,j} B_{ij}(\mathbf{a}_i, \mathbf{a}_j).$$

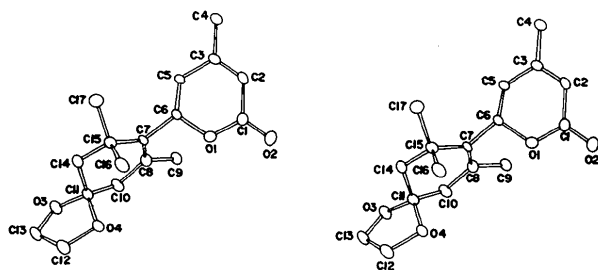
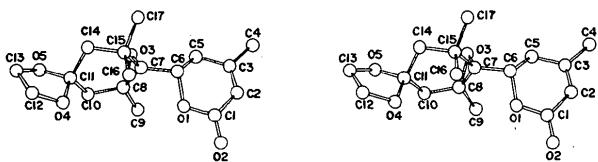
	x	y	z	B <sub>iso</sub>
O(1)	-0.3928 (4)	0.5230 (3)	0.6679 (2)	3.50 (8)
O(2)	-0.6347 (5)	0.6054 (3)	0.5738 (2)	4.7 (1)
O(3)	-0.0021 (4)	0.4807 (2)	0.8612 (2)	3.58 (7)
O(4)	-0.2028 (4)	0.1037 (2)	0.9672 (2)	4.25 (8)
O(5)	-0.4672 (4)	0.0711 (2)	0.8307 (2)	4.10 (8)
C(1)	-0.4435 (8)	0.6150 (4)	0.6050 (3)	3.4 (1)
C(2)	-0.2641 (8)	0.7271 (4)	0.5850 (3)	3.8 (1)
C(3)	-0.0617 (7)	0.7551 (4)	0.6355 (3)	3.2 (1)
C(4)	0.1172 (7)	0.8788 (4)	0.6218 (3)	4.6 (1)
C(5)	-0.0067 (6)	0.6621 (4)	0.7122 (3)	3.3 (1)
C(6)	-0.1670 (6)	0.5140 (4)	0.6860 (3)	2.9 (1)
C(7)	-0.1504 (6)	0.4141 (3)	0.7661 (2)	2.7 (1)
C(8)	-0.2369 (6)	0.4349 (4)	0.8616 (3)	3.1 (1)
C(9)	-0.3334 (7)	0.5569 (4)	0.8908 (3)	4.1 (1)
C(10)	-0.3035 (6)	0.3113 (4)	0.9194 (3)	3.7 (1)
C(11)	-0.2644 (6)	0.1674 (4)	0.8808 (3)	3.3 (1)
C(12)	-0.2740 (7)	-0.0492 (4)	0.9375 (3)	5.1 (1)
C(13)	-0.4537 (7)	-0.0706 (4)	0.8477 (3)	5.2 (1)
C(14)	-0.0900 (6)	0.1809 (4)	0.8142 (3)	3.2 (1)
C(15)	-0.1205 (6)	0.2679 (4)	0.7266 (3)	3.0 (1)
C(16)	0.0874 (7)	0.2882 (4)	0.6804 (3)	4.6 (1)
C(17)	-0.3209 (6)	0.1872 (4)	0.6431 (3)	4.0 (1)

Final coordinates for non-H atoms are given in Tables 2 and 3.\* Bond lengths and bond angles are given in Table 4. The torsion angle C5-C6-C7-C8 is -74.4 (4) and 75.8 (4)° for (1) and (2) respectively. Figs. 1 and 2 are stereoscopic drawings of compounds (1) and (2) respectively, showing crystallographic atom numbering.

\* 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 51651 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Interatomic bond distances (Å) and angles (°)*

	(1)	(2)		(1)	(2)
O(1)—C(1)	1.344 (4)	1.352 (5)	C(5)—C(6)	1.514 (4)	1.516 (5)
O(1)—C(6)	1.464 (4)	1.454 (5)	C(6)—C(7)	1.524 (4)	1.530 (5)
O(2)—C(1)	1.211 (5)	1.210 (6)	C(7)—C(8)	1.335 (4)	1.483 (5)
O(3)—C(11)	1.419 (4)	—	C(7)—C(15)	1.518 (4)	1.516 (5)
O(3)—C(7)	—	1.449 (4)	C(8)—C(9)	1.505 (5)	1.496 (5)
O(3)—C(8)	—	1.463 (5)	C(8)—C(10)	1.507 (4)	1.507 (5)
O(3)—C(13)	1.437 (4)	—	C(10)—C(11)	1.501 (4)	1.517 (5)
O(4)—C(11)	1.431 (4)	1.419 (4)	C(11)—C(14)	1.500 (5)	1.524 (5)
O(4)—C(12)	1.430 (4)	1.427 (5)	C(12)—C(13)	1.507 (6)	1.493 (7)
C(1)—C(2)	1.457 (5)	1.459 (6)	C(14)—C(15)	1.538 (4)	1.534 (5)
C(2)—C(3)	1.328 (5)	1.318 (6)	C(15)—C(16)	1.550 (5)	1.532 (6)
C(3)—C(4)	1.495 (5)	1.494 (6)	C(15)—C(17)	1.532 (5)	1.549 (5)
C(1)—O(1)—C(6)	118.4 (2)	117.2 (3)	O(3)—C(8)—C(10)	—	114.6 (3)
C(7)—O(3)—C(8)	—	61.2 (2)	C(7)—C(8)—C(9)	124.9 (3)	124.0 (3)
C(11)—O(3)—C(13)	106.8 (2)	—	C(7)—C(8)—C(10)	123.1 (3)	121.1 (3)
C(11)—O(4)—C(12)	107.0 (2)	107.4 (3)	C(9)—C(8)—C(10)	112.0 (3)	112.0 (3)
C(11)—O(5)—C(13)	—	106.4 (3)	C(8)—C(10)—C(11)	115.0 (3)	117.8 (3)
O(1)—C(1)—O(2)	118.3 (3)	118.3 (4)	O(3)—C(11)—O(4)	104.0 (2)	—
O(1)—C(1)—C(2)	117.9 (3)	117.7 (4)	O(3)—C(11)—C(10)	109.5 (3)	—
O(2)—C(1)—C(2)	123.6 (3)	123.8 (4)	O(3)—C(11)—C(14)	113.2 (3)	—
C(1)—C(2)—C(3)	123.4 (3)	123.2 (4)	O(4)—C(11)—O(5)	—	103.8 (3)
C(2)—C(3)—C(4)	123.4 (3)	123.0 (4)	O(4)—C(11)—C(10)	108.5 (2)	107.6 (3)
C(2)—C(3)—C(5)	118.3 (3)	119.3 (4)	O(4)—C(11)—C(14)	110.6 (2)	110.2 (3)
C(4)—C(3)—C(5)	118.2 (3)	117.7 (3)	O(5)—C(11)—C(10)	—	109.1 (3)
C(3)—C(5)—C(6)	111.4 (3)	109.8 (3)	O(5)—C(11)—C(14)	—	112.5 (3)
O(1)—C(6)—C(5)	111.6 (2)	111.9 (3)	C(10)—C(11)—C(14)	110.8 (3)	113.3 (3)
O(1)—C(6)—C(7)	108.0 (2)	106.4 (3)	O(4)—C(12)—C(13)	105.1 (3)	104.2 (3)
C(5)—C(6)—C(7)	115.7 (3)	115.5 (3)	O(3)—C(13)—C(12)	104.8 (3)	—
O(3)—C(7)—C(6)	—	115.1 (3)	O(5)—C(13)—C(12)	—	105.9 (3)
O(3)—C(7)—C(8)	—	59.9 (2)	C(11)—C(14)—C(15)	115.2 (3)	115.3 (3)
O(3)—C(7)—C(15)	—	112.3 (3)	C(7)—C(15)—C(14)	110.0 (3)	110.6 (3)
C(6)—C(7)—C(8)	121.5 (3)	121.2 (3)	C(7)—C(15)—C(16)	111.1 (3)	109.7 (3)
C(6)—C(7)—C(15)	115.1 (3)	115.0 (3)	C(7)—C(15)—C(17)	109.0 (3)	108.8 (3)
C(8)—C(7)—C(15)	123.3 (3)	120.2 (3)	C(14)—C(15)—C(16)	106.5 (3)	106.8 (3)
O(3)—C(8)—C(7)	—	58.9 (2)	C(14)—C(15)—C(17)	111.7 (3)	111.6 (3)
O(3)—C(8)—C(9)	—	113.6 (3)	C(16)—C(15)—C(17)	108.4 (3)	109.3 (3)

Fig. 1. ORTEP stereoscopic drawing of (1) C<sub>17</sub>H<sub>24</sub>O<sub>4</sub>.Fig. 2. ORTEP stereoscopic drawing of (2) C<sub>17</sub>H<sub>24</sub>O<sub>5</sub>.

**Related literature.** Compound (2) is one of the stereoisomers obtained by peracid oxidation of (1) and as both could be crystallized the main aim of the

present study could be achieved, namely the determination of their conformations and the unambiguous identification of the stereoisomer (2) whose identification could not be carried out by standard physicochemical methods (Constantino, Donate & Petragnani, 1986; Constantino, Losco & Castellano, 1988, and references therein).

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