The Crystal and Molecular Structure of *dl*-2-*cis*-4-*trans*-Abscisic Acid

Hideo UEDA* and Jiro TANAKA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

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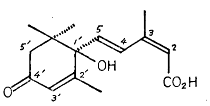
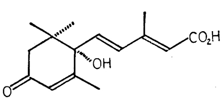
The crystal and molecular structure of *dl*-2-*cis*-4-*trans*-abscisic acid has been determined by the X-ray method. The crystal is monoclinic, $P2_1/c$, with lattice parameters $a=6.316(1)$, $b=33.575(3)$, $c=7.607(1)$ Å, and $\beta=118.42(1)°$. The molecule has two independent conjugated systems forming respective planes which are orthogonal to each other. The molecules form a dimer by the hydrogen bonding and are connected by the other hydrogen bonding along the c-axis.

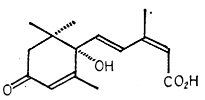
Abscisic acid is an important plant hormone which promotes abscission of leaves and dormancy in buds and seeds. Ohkuma, Lyon, and Adicott[1] isolated abscisic acid and determined its chemical structure. Cornforth and his co-workers[2,3] synthesized and determined the absolute configuration of natural (+) abscisic acid as (I) by applying Mill's empirical rule to the diols obtained through the reduction of optically active abscisic acid.



I



II



III

Burden and Taylor[4] reported that $(+)_{589}$-2-*trans*-4-*trans*-abscisic acid(II) obtained from violaxanthine shows a positive Cotton effect, which is in contradiction with the result of Cornforth and his co-workers. Oritani and Yamashita,[5–7] Ryback,[8] Mori,[9] and Weiss, Koreda, and Nakanishi[10] showed that the natural $(+)_{589}$-abscisic acid has *S*-configuration(III) at C_1'.

The crystal structure of *dl*-2-*trans*-4-*trans*-abscisic acid has been determined recently by Swaminathan, Vijayalakshmi, and Srinivasan;[11] the acid has only 1% activity as compared to the natural (*S*)-2-*cis*-4-*trans*-abscisic acid.[2,12]

In this paper we report on the crystal and molecular structure of *dl*-2-*cis*-4-*trans*-abscisic acid, which has the most efficient hormonal activity.

Experimental

The crystals were obtained as transparent thin plates from ethanol solution in the dark in a refrigerator.

The space group was determined as $P2_1/c$ from the oscillation and Weissenberg photographs. The density was measured by the floatation method in KI aqueous solution. The unit-cell parameters were determined by the least-squares method, using twelve reflections carefully measured on Hilger & Watts four circle diffractometer with Ni-filtered Cu*K*α radiation ($\lambda=1.5418$ Å). The intensity data were collected on the diffractometer with the 2θ-ω scanning mode ($2\theta \leqq 57$ °). The size of the crystal used was 0.2×0.1×0.3 mm. The crystal used for the X-ray measurement was mounted in a glass capillary. In order to confirm the stability of the crystal and the counting system, the intensities of three standard reflections were measured every 50 reflections. The fluctuation and decay of standard reflections were within 5%. No absorption nor extinction correction was made. The crystal data are given in Table 1.

TABLE 1. CRYSTAL DATA

$C_{15}H_{20}O_4$
Mol wt: 264.32
Crystal system: $P2_1/c$; $Z=4$
$a=6.316(1)$, $b=33.575(3)$, $c=7.607(1)$ Å;
$\beta=118.42(1)°$
$D_m=1.232$, $D_c=1.237$ g cm^{-3}
$\mu=7.37$ cm^{-1} (for Cu*K*α radiation)

Determination and Refinement of the Structure

The structure was determined by the direct method with the program MULTAN[13] using 162 reflections with $|E| \geqq 1.70$. An *E* map computed from the phase set with the highest figures of merit ($FOM=1.16$) revealed the positons of 16 atoms. Other atoms were found by the successive Fourier synthesis. Refinement of the structure was performed by the block-diagonal least-squares method with 1315 independent reflections of $|F^{\circ}| \geqq 3\sigma$. The final refinement was carried out with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal factors for hydrogen atoms. The *R*-index converged to 0.071 with an equal weight for each reflection. The atomic scattering factors were

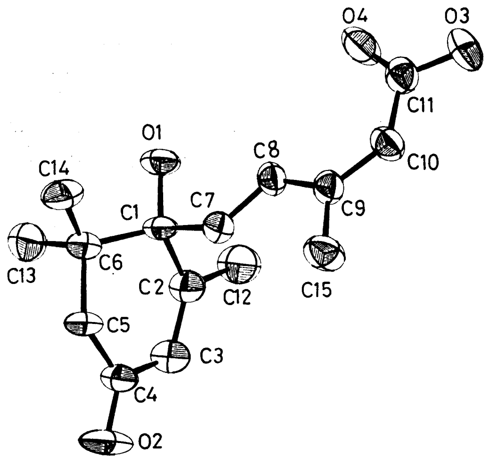


Fig. 1. The atomic labelings of abscisic acid. Carbon and oxygen atoms are represented as thermal ellipsoids of a size such that the vibrating atoms have a 50% probability of being found within them.

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* Present address: Central Research Laboratory, Ube Industries Ltd., Nishihon-machi, Ube, Yamaguchi 755.

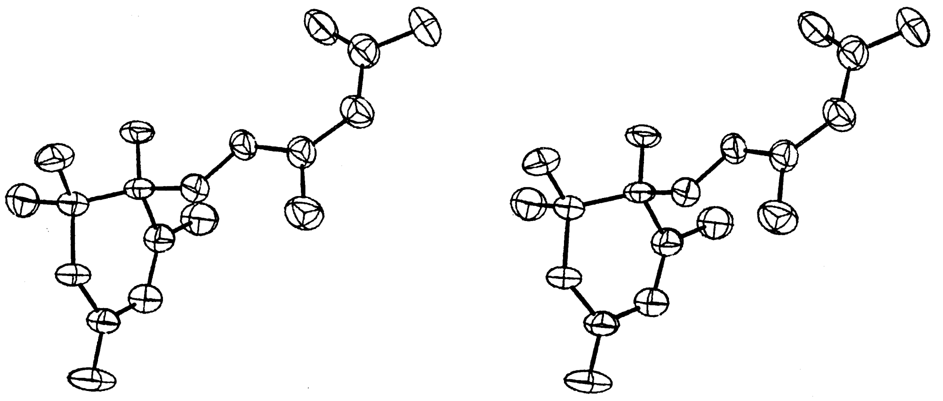

Fig. 2. A stereoscopic view of abscisic acid. The criterion to the themal ellipsoids of carbon and oxygen atoms are the same as in Fig. 1.

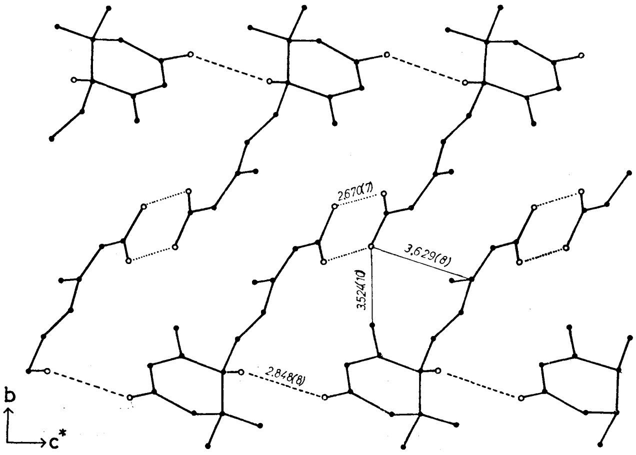

Fig. 3. Hydrogen bond network viewed along the a-axis. Carbon atoms are depicted as filled circles and oxygen atoms as open circles. Hydrogen bonds are represented with both dotted and broken lines.

taken from the International Tables for X-Ray Crystallography.[14] The program HBLS-IV coded by Ashida in UNICS was utilized for the refinement. The program ORTEP coded by Johnson was used for drawing of Figs. 1 and 3. A part of the computation was performed at the Nagoya University Computation Center. The observed and calculated structure factors are given in Table 2.[20]

Results and Discussion

The molecular structure, atomic labelings, and thermal ellipsoids are shown in Fig. 1. It can be seen that the conformation around C–C double bonds is *cis-trans*. The positional and thermal parameters of non-hydrogen atoms with their standard deviations are given in Tables 3 and 4, respectively. The coordinates and isotropic thermal parameters of hydrogen atoms are given in Table 5.

Molecular Structure. The bond lengths and bond angles with their standard deviations are given in Tables 6 and 7, respectively. The bond distances are normal. The C=O bond of the carboxylic group takes the *cis*-conformation with respect to the diene group. The angles, C(1)C(7)C(8), C(7)C(8)C(9), C(8)C(9)-C(10), and C(9)C(10)C(11), are larger than 120°, having values 128, 123, 126, and 128°, respectively. The conjugated double bond of the diene group forms plane A. Deviations of atoms from the plane and equations of the planes are given in Table 8. The carboxylic group forms plane B, at 9° to plane A.

The six-membered ring is puckered, C(1) and C(6) being out of plane C formed by the remaining atoms, C(2), C(3), C(4), C(5), C(12), and O(2). The planarity of plane C is fairly good, the largest deviation being 0.016 Å of C(3).

Planes A and C are orthogonal; the dihedral angle is 91°. A stereoscopic projection of the (*S*)-isomer is shown in Fig. 2. Two independent chromophores take a chiral configuration, the strong optical rotatory power of the $(+)_{589}$-abscisic acid thus being explained.

Crystal Structure. The crystal structure projected along the a-axis is shown in Fig. 3. The molecule is connected with neighboring ones by the hydrogen bonds; two molecules related by a center of symmetry form a dimer through the hydrogen bonds of carboxylic groups.

Table 3. Atomic coordinates and their standard deviations of heavy-atoms

	x	*y*	*z*
O(1)	0.7982(8)	0.1463(1)	0.0594(6)
O(2)	0.5798(10)	0.1750(2)	0.6589(7)
O(3)	0.3078(9)	−0.0211(1)	−0.4123(6)
O(4)	0.5107(8)	0.0363(1)	−0.3416(6)
C(1)	0.6629(11)	0.1460(2)	0.1663(8)
C(2)	0.8387(11)	0.1314(2)	0.3769(8)
C(3)	0.8011(12)	0.1408(2)	0.5332(9)
C(4)	0.6163(14)	0.1678(2)	0.5158(8)
C(5)	0.4581(12)	0.1874(2)	0.3191(8)
C(6)	0.5644(12)	0.1878(2)	0.1716(8)
C(7)	0.4714(11)	0.1143(2)	0.0868(8)
C(8)	0.4473(10)	0.0849(2)	−0.0385(8)
C(9)	0.2706(10)	0.0535(2)	−0.0896(8)
C(10)	0.2421(11)	0.0222(2)	−0.2077(9)
C(11)	0.3681(11)	0.0139(2)	−0.3252(8)
C(12)	1.0300(13)	0.1034(2)	0.3986(10)
C(13)	0.7673(14)	0.2189(2)	0.2437(10)
C(14)	0.3582(14)	0.2002(2)	−0.0331(10)
C(15)	0.1037(11)	0.0554(2)	0.0032(9)

TABLE 4. ANISOTROPIC THERMAL FACTORS[a] (× 10⁴) AND THEIR STANDARD DEVIATIONS OF HEAVY-ATOMS

	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
O(1)	424(18)	9(1)	163(10)	−8(5)	−2(4)	382(23)
O(2)	898(32)	19(1)	220(12)	26(8)	−4(5)	747(35)
O(3)	560(22)	9(1)	274(13)	−24(5)	−42(4)	462(29)
O(4)	472(20)	10(1)	276(12)	−30(5)	−47(4)	455(28)
C(1)	390(25)	7(1)	126(13)	−20(6)	−9(5)	323(31)
C(2)	378(27)	7(1)	187(15)	−5(6)	−1(5)	249(35)
C(3)	521(32)	9(1)	159(15)	3(8)	6(5)	343(37)
C(4)	580(33)	9(1)	177(15)	−26(8)	−14(5)	432(39)
C(5)	508(24)	8(1)	188(15)	−6(7)	−7(5)	444(38)
C(6)	512(31)	7(1)	166(15)	9(7)	4(5)	409(36)
C(7)	335(24)	7(1)	161(14)	7(6)	3(5)	282(31)
C(8)	336(24)	6(1)	141(13)	17(6)	1(4)	224(30)
C(9)	299(23)	6(1)	158(14)	6(6)	−2(5)	173(31)
C(10)	301(24)	6(1)	216(16)	3(6)	−7(5)	240(33)
C(11)	310(25)	7(1)	172(15)	15(6)	−7(5)	128(32)
C(12)	445(32)	13(1)	222(18)	38(9)	24(7)	299(40)
C(13)	691(39)	8(1)	308(20)	−36(8)	−14(6)	620(49)
C(14)	655(39)	10(1)	222(18)	17(8)	16(6)	496(45)
C(15)	312(26)	10(1)	248(17)	−18(7)	−24(6)	304(36)

[a] The anisotropic thermal factors are of the form $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{31}+klB_{23})\}$.

TABLE 5. HYDROGEN ATOM PARAMETERS AND THEIR STANDARD DEVIATIONS

	x	y	z	B/Å²
H(O1)	0.375(12)	−0.026(2)	−0.473(10)	4.8(1.8)
H(O3)	0.699(11)	0.159(2)	−0.039(9)	3.3(1.5)
H(C3)	0.905(12)	0.125(2)	0.662(10)	3.3(1.9)
H(C5a)	0.420(10)	0.219(2)	0.338(8)	1.8(1.3)
H(C5b)	0.296(11)	0.176(2)	0.257(9)	3.5(1.6)
H(C7)	0.372(10)	0.113(2)	0.662(9)	3.3(1.6)
H(C8)	0.546(10)	0.083(2)	−0.093(8)	1.5(1.3)
H(C10)	0.125(9)	0.000(2)	−0.234(7)	0.6(1.1)
H(C12a)	0.957(11)	0.077(2)	0.342(11)	7.3(2.1)
H(C12b)	1.135(11)	0.112(2)	0.349(11)	7.2(2.1)
H(C12c)	1.122(11)	0.095(2)	0.508(9)	4.1(1.7)
H(C13a)	0.832(11)	0.224(2)	0.134(9)	3.8(1.6)
H(C13b)	0.705(11)	0.250(2)	0.241(10)	3.2(1.6)
H(C13c)	0.924(12)	0.211(2)	0.380(10)	4.3(1.7)
H(C14a)	0.324(10)	0.233(2)	−0.019(8)	2.6(1.4)
H(C14b)	0.254(10)	0.178(2)	−0.077(8)	1.9(1.3)
H(C14c)	0.427(11)	0.206(2)	−0.109(9)	3.6(1.6)
H(C15a)	0.204(11)	0.054(2)	0.134(9)	4.1(1.6)
H(C15b)	−0.024(10)	0.038(2)	−0.058(8)	2.3(1.4)
H(C15c)	0.014(10)	0.083(2)	−0.025(8)	2.2(1.3)

TABLE 6. BOND LENGTHS AND THEIR STANDARD DEVIATIONS

O(1)–C(1)	1.433(8) Å	O(2)–C(4)	1.239(10)Å
O(3)–C(11)	1.312(9)	O(4)–C(11)	1.224(9)
C(1)–C(2)	1.532(10)	C(1)–C(6)	1.545(10)
C(1)–C(7)	1.503(10)	C(2)–C(3)	1.356(11)
C(2)–C(12)	1.476(11)	C(3)–C(4)	1.433(11)
C(4)–C(5)	1.499(11)	C(5)–C(6)	1.558(11)
C(6)–C(13)	1.538(12)	C(6)–C(14)	1.537(12)
C(7)–C(8)	1.330(9)	C(8)–C(9)	1.449(9)
C(9)–C(10)	1.337(9)	C(9)–C(15)	1.524(10)
C(10)–C(11)	1.479(9)		
C(*i*)–H(*i*)			
Average	0.99		
Range	0.81—1.15		

TABLE 7. BOND ANGLES AND THEIR STANDARD DEVIATIONS

O(1)–C(1)–C(2)	105.8(5)°	O(1)–C(1)–C(6)	111.3(6)°
O(1)–C(1)–C(7)	110.9(5)	C(2)–C(1)–C(6)	111.1(6)
C(2)–C(1)–C(7)	103.9(6)	C(6)–C(1)–C(7)	113.4(6)
C(1)–C(2)–C(3)	120.4(7)	C(1)–C(2)–C(12)	117.6(6)
C(3)–C(2)–C(12)	121.6(7)	O(2)–C(3)–C(4)	121.6(8)
C(2)–C(3)–C(4)	122.7(7)	O(2)–C(4)–C(5)	119.0(7)
C(3)–C(4)–C(5)	119.4(7)	C(4)–C(5)–C(6)	114.8(6)
C(1)–C(6)–C(5)	109.1(6)	C(1)–C(6)–C(13)	110.5(6)
C(1)–C(6)–C(14)	111.9(6)	C(5)–C(6)–C(13)	108.5(6)
C(5)–C(6)–C(14)	107.0(6)	C(13)–C(6)–C(14)	109.7(7)
C(1)–C(7)–C(8)	127.5(6)	C(7)–C(8)–C(9)	123.0(6)
C(8)–C(9)–C(10)	126.3(6)	C(8)–C(9)–C(15)	117.1(6)
C(10)–C(9)–C(15)	116.6(6)	C(9)–C(10)–C(11)	128.2(6)
O(3)–C(11)–O(4)	123.1(6)	O(3)–C(11)–C(10)	111.5(6)
O(4)–C(11)–C(10)	125.4(6)		

TABLE 8. DEVIATIONS OF NONHYDROGEN ATOMS FROM LEAST-SQUARES PLANES CONTAINING THE CONJUGATED DOUBLE BONDS

Plane A[a]		Plane B[b]		Plane C[c]	
C(7)	0.008Å	O(3)	0.000Å	C(2)	−0.008Å
C(8)	−0.006	O(4)	0.000	C(3)	0.016
C(9)	−0.003	C(10)	0.000	C(4)	0.010
C(10)	0.036	C(11)	0.000	C(5)	0.000
C(11)	−0.020	C(9)[d]	0.088	C(12)	−0.004
C(15)	−0.015			O(2)	−0.014
C(1)[d]	0.147			C(1)[d]	−0.205
O(1)[d]	−0.005			C(6)[d]	0.484
O(3)[d]	0.144				
O(4)[d]	−0.197				

[a] The equation of the plane is: $0.3286X-0.5420Y+0.5238Z-3.220=0$. [b] The equation of the plane is: $0.4212X-0.4217Y+0.5057Z-3.378=0$. [c] The equation of the plane is: $0.6007X+0.7577Y-0.0618Z-5.885=0$. [d] Omitted from the least-squares plane calculation.

TABLE 9. HYDROGEN BONDS AND SHORT VAN DER WAALS CONTACTS

The Roman numerals represent the symmetry operators relevant to the atoms listed second.

Hydrogen bonds

Donor	Aceptor	Distance D···A	H···A	Angle D–H···A
O(1)—H(O1)···	O(2)$^{\text{i}}$	2.848(8)Å	2.14(7)Å	147(6)°
O(3)—H(O3)···	O(4)$^{\text{ii}}$	2.670(7)	1.91(8)	171(8)

Short van der Waals contacts

O(2)–C(14)$^{\text{iii}}$	3.360(11)Å	O(3)–C(9)$^{\text{iv}}$	3.629(8)Å
O(3)–C(10)$^{\text{v}}$	3.296(9)	O(3)–C(11)$^{\text{ii}}$	3.482(9)
O(3)–C(12)$^{\text{iv}}$	3.524(10)	O(4)–C(11)$^{\text{ii}}$	3.421(9)
O(4)–C(12)$^{\text{vi}}$	3.534(10)	O(4)–C(15)$^{\text{vii}}$	3.459(9)
C(9)–C(11)$^{\text{iv}}$	3.664(9)	C(10)–C(10)$^{\text{iix}}$	3.608(9)
C(12)–C(15)$^{\text{vii}}$	3.632(11)		

Symmetry code

Superscript	Symmetry operator		
i)	x	y	$1+z$
ii)	$1-x$	$-y$	$-1-z$
iii)	x	y	$-1+z$
iv)	$1-x$	$-y$	$-z$
v)	$-x$	$-y$	$-1-z$
vi)	$1+x$	y	$1+z$
vii)	$-1+x$	y	z
iix)	$-1-x$	$-y$	$-z$

The O(3)-H···O(4) distance is 2.67 Å, the angle O(3)-H···O(4) is 171°, and the H atom is nearly on the line O(3)···O(4). Another hydrogen bond exists between the hydroxyl group attached to the cyclohexenone ring and the carbonyl group of the ring of the adjacent molecule. The O(1)-H···O(2) distance is 2.85 Å and the angle O(1)-H···O(2) is 147°. The hydrogen bond is not linear, but the distance is within the range of the O-H···O hydrogen bond.[15]

Other short contacts are given in Table 9. Most of them are in the range of van der Waals contact, but O(3)···C(10) 3.30 Å is slightly shorter than the sum of van der Waals radii (3.40 Å). Close C···O contacts have been reported and several types of molecular interaction have been recognized.[16-19] In one type the C-H group is attached to the electronegative oxygen atom. In another type the C=O group interacts with aromatic rings or C=C groups. In the present crystal the oxygen atom of the carboxylic group is close to the carbon atom of the diene group and situated antiparallel.

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