(Cl⁻ ou Br⁻) hydraté, les écarts allant de 1 à 18° suivant les angles de torsion.

Pour le groupement guanidinium (ou guanidyle), il y a deux positions moyennes, l'une peu écartée et l'autre très écartée de la chaîne C_α à N_ε ($|\chi_4|$ voisin de 170 ou compris entre 81 et 113°).

Cohésion

L'agencement des molécules présente deux sortes de zones, l'une hydrophile où apparaissent les liaisons hydrogène, l'autre hydrophobe ne présentant que des contacts ou liaisons de van der Waals. Les proximités interatomiques les plus intéressantes sont indiquées sur la Fig. 2 et dans le Tableau 6:

– Zone hydrophile: le long des axes hélicoïdaux perpendiculaires au plan *xOy* en $(\frac{1}{4},0)$ et $(\frac{3}{4},\frac{1}{2})$, les anions Cl⁻ relient les groupements guanidinium selon un enchaînement étroit (*d* Cl···H ~ 2,4 Å) tout en formant par ailleurs des ponts latéraux avec les groupements NH peptidiques des mêmes molécules (*d* Cl···H = 2,3 Å). Le groupe N_δ–H de la chaîne Arg n'intervient pas. On relève aussi deux proximités à la limite du contact entre anion Cl⁻ et atomes H de groupements méthyle ou méthylène (*d* Cl···H = 2,9 Å).

– Zone hydrophobe: entre les cycles aromatiques, il n'apparaît aucun contact. Par contre, il y a imbrication entre groupements méthyles des deux radicaux tosyl et ester méthylique le long des axes hélicoïdaux perpendiculaires à *yOz* en $(\frac{1}{4},\frac{1}{2})$ et $(0,\frac{3}{4})$; les distances H···H (*d*=2,48 et 2,54 Å) et H···O (*d*=2,48 Å) sont proches de celles de contacts de van der Waals.

Tableau 6. *Proximités interatomiques* (Å)

Coordonnées des molécules homologues:

(I) x,y,z; (II) $\frac{1}{2}-x,\bar{y},\frac{1}{2}+z$; (III) $\frac{1}{2}+x,\frac{1}{2}-y,\bar{z}$; (IV) $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$; ($I_l$) $I+a-c$; (II_l) $II+a+b$; (III_l) $III+b+c$.

Cl······	H(31)	2,29	Cl······	N(1)	3,23
	H(41)	2,30		N(11)	3,24
	H(40, II_l)	2,46		N(11, II_l)	3,37
	H(43, II_l)	2,38		N(12, II_l)	3,27
	H(37, II + *b*)	2,92		C(8, II + *b*)	3,65
O(5)····	H(63, $III_l - a$)	2,48	O(5)····	C(23, $III_l - a$)	3,28
N(11)···	Cl($II_l - c$)	3,37	H(40)···	Cl($II_l - c$)	2,46
N(12)···	Cl($II_l - c$)	3,27	H(43)···	Cl($II_l - c$)	2,38
C(13)···	Cl(II + *b*)	3,95	H(51)···	Cl(II + *b*)	2,90
C(23)···	O(5, III_l)	3,28	H(63)···	O(5, III_l)	2,48
C(23)···	C(13, III_l)	3,74	H(63)···	H(52, III_l)	2,88
C(23)···	C(13, I_l)	3,74	H(63)···	H(52, I_l)	2,35
			H(62)···	H(52, I_l)	2,54

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Molecular Structure, Symmetry and Conformation. XVI. The Crystal and Molecular Structure of (*RS*)-Abscisic Acid*

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(*Received* 10 *November* 1975; *accepted* 16 *December* 1975)

(*RS*)-Abscisic acid crystallizes in the monoclinic space group $P2_1/c$ with $a=15\cdot30$ (1), $b=6\cdot87$ (1), $c=13\cdot97$ (1) Å, $\beta=94\cdot5$ (1)°, $Z=4$. The structure was solved by the symbolic-addition procedure with visual X-ray intensities and refined to an R of 12%. The molecules form spirals along **c**. The parallel spiral chains are held together by van der Waals foores.

Introduction

Abscisic acid is an unusual sesquiterpene showing exceptionally high optical activity. It promotes senescence and abscission of leaves and induces dormancy in buds and seeds. The X-ray analysis of (*RS*)-abscisic acid is reported here. This forms part of a programme of studies on the structure, symmetry and conformation of organic and bio-molecules.

Experimental

Single crystals of (*RS*)-abscisic acid (synthetic substance supplied by Sigma Chemical Co.) were grown by slow evaporation from aqueous solution. Photographs showed that the crystals were monoclinic, space group $P2_1/c$. The density was determined by flotation in a mixture of benzene and bromoform.

Crystal data

$C_{15}O_4H_{20}$, monoclinic, $a=15\cdot30$ (1), $b=6\cdot87$ (1), $c=13\cdot97$ (1) Å, $\beta=94\cdot5$ (1)°; systematic absences $0k0$, $k=2n+1$; $h0l$, $l=2n+1$; space group $P2_1/c$; $Z=4$,

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$M=264\cdot3, D_o=1\cdot231; D_c=1\cdot206\text{ g cm}^{-3}, \mu=7\cdot44\text{ cm}^{-1}$, $\lambda(\text{Cu }K\alpha)=1\cdot5418$ Å.

A crystal ($0\cdot2\times0\cdot3\times0\cdot2$ mm) was used to collect intensities by the multiple-film equi-inclination Weissenberg technique with Ni-filtered Cu $K\alpha$ radiation. The intensities of 1750 independent reflexions (hKl, $K=0$–5, hkL, $L=0$ and 1) were estimated visually and corrected for Lorentz and polarization factors. Spot-shape corrections were made (Phillips, 1962) and the data brought to a single scale (Rollett & Sparks, 1960). R for the common reflexions was 10%.

Structure determination and refinement

The structure was solved by the symbolic addition technique (Karle & Karle, 1963). 250 reflexions with $|E|\geq1\cdot6$ were chosen for the starting set. The phase propagation was carried out by hand with the $\sum_2$ foimula (Hauptman & Karle, 1953). An E map calculated with these 250 reflexions revealed the entire structure. A structure-factor calculation at this stage gave an R of 42%. Full-matrix least-squares refinement with unit weights and isotropic temperature factors reduced R to 18%. For further refinement Cruickshank, Bujosa, Lovell & Truter's (1961) weighting scheme $w=1/(a+F_o+b|F_o|^2)$ with $a=3\cdot8$ and $b=0\cdot02$ was used. Before anisotropic refinement the H atoms were fixed geometrically with a temperature factor of $3\cdot2$ Å^2. Two cycles of anisotropic refinement reduced R to 12%. The shifts in the parameters during the last cycle were one fifth of the estimated standard deviation in the individual parameters. The final positional and thermal parameters of all the non-hydrogen atoms are listed in Table 1.* The scattering factors were those listed in *International Tables for X-ray Crystallography* (1962).

Discussion of the structure

Molecular packing and hydrogen bonding

The packing of the molecule viewed down **b** is shown in Fig. 1. The molecular chain runs parallel to **c**. The molecules $A(1)$, $A(2)$, $A(3)$ and $A(4)$ constitute one spiral chain and the molecules $B(1)$, $B(2)$, $B(3)$ and $B(4)$

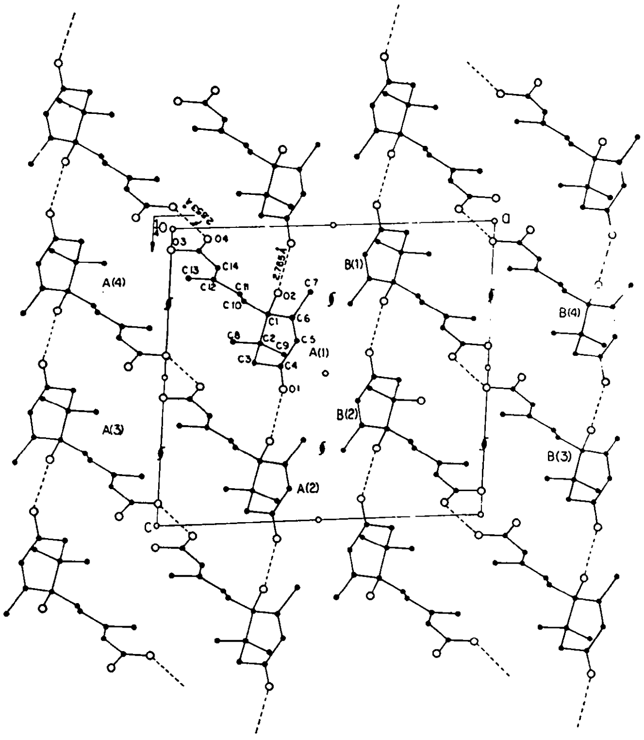

Fig. 1. Packing of the molecule viewed down **b**.

Table 1. *Fractional positional coordinates and the thermal parameters with standard deviations in parentheses*

The thermal parameter is defined by $T=\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{13}hl)]$. All values are multiplied by 10^4.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	3067 (3)	1707 (8)	2982 (3)	21 (2)	68 (15)	18 (2)	3 (8)	−6 (3)	11 (8)
C(2)	2869 (4)	837 (10)	3960 (4)	35 (2)	79 (16)	29 (3)	−15 (10)	4 (4)	9 (10)
C(3)	2722 (4)	2526 (11)	4653 (4)	34 (2)	136 (19)	36 (3)	−6 (11)	6 (5)	−26 (12)
C(4)	3517 (4)	3885 (10)	4778 (4)	44 (3)	59 (16)	26 (2)	−12 (10)	−13 (4)	4 (10)
C(5)	4011 (4)	4121 (11)	3943 (4)	31 (2)	111 (19)	34 (3)	−15 (10)	−5 (4)	10 (11)
C(6)	3833 (3)	3175 (9)	3126 (4)	23 (2)	57 (15)	29 (2)	7 (8)	−6 (3)	0 (9)
C(7)	4371 (4)	3478 (11)	2284 (5)	35 (3)	167 (21)	41 (3)	−38 (12)	12 (5)	17 (14)
C(8)	2018 (5)	−409 (14)	3883 (5)	41 (3)	282 (28)	44 (4)	−79 (15)	12 (6)	17 (16)
C(9)	3637 (5)	−450 (12)	4381 (5)	56 (4)	131 (20)	39 (3)	24 (13)	−1 (6)	61 (14)
C(10)	2259 (3)	2683 (10)	2469 (4)	22 (2)	120 (17)	27 (2)	24 (9)	−12 (4)	18 (10)
C(11)	2160 (4)	4552 (12)	2262 (4)	30 (2)	197 (22)	27 (3)	32 (11)	−15 (4)	5 (12)
C(12)	1371 (4)	5386 (11)	1744 (4)	31 (2)	132 (20)	31 (3)	51 (11)	−5 (4)	3 (12)
C(13)	529 (5)	4266 (16)	1638 (7)	35 (3)	240 (28)	106 (7)	3 (15)	−19 (7)	84 (22)
C(14)	1455 (4)	7240 (12)	1374 (5)	37 (3)	195 (24)	36 (3)	34 (12)	−2 (5)	7 (14)
C(15)	801 (4)	8371 (11)	796 (5)	29 (2)	118 (19)	44 (3)	6 (10)	−6 (5)	4 (13)
O(1)	3701 (4)	4745 (8)	5522 (3)	83 (3)	165 (17)	34 (2)	−43 (11)	−1 (4)	−10 (9)
O(2)	3306 (2)	91 (6)	2421 (3)	36 (2)	94 (12)	29 (2)	25 (6)	4 (3)	−12 (7)
O(3)	0 (3)	8026 (9)	700 (4)	36 (2)	292 (18)	88 (4)	30 (10)	−22 (4)	144 (14)
O(4)	1124 (4)	9841 (11)	403 (6)	54 (3)	321 (22)	123 (6)	0 (13)	−18 (6)	253 (18)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31570 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

a second. These parallel chains are held together by van der Waals forces, while within a group the stabilizing force is hydrogen bonding.

Intramolecular bond lengths and angles

The bond lengths and angles are given in Fig. 2, and are normal. The average standard deviations are 0·009 Å and 0·5°. The carboxyl group is un-ionized. The least-squares plane passing through the carboxyl group is given in Table 3.

Molecular conformation

The molecule exists as a *trans,trans* isomer. This is one of the possible conformations of abscisic acid (Wareing & Ryback, 1970). The six-membered ring is puckered, with C(2) out of the plane formed by the remaining five atoms. C(1), C(3), C(5), C(6), C(7) and O(1) are nearly coplanar. The torsion angles around various bonds are listed in Table 2. The convention followed is that of the IUPAC–IUB Commission on Biochemical Nomenclature (1971). The equations to the least-squares planes passing through various groups of atoms are listed in Table 3.

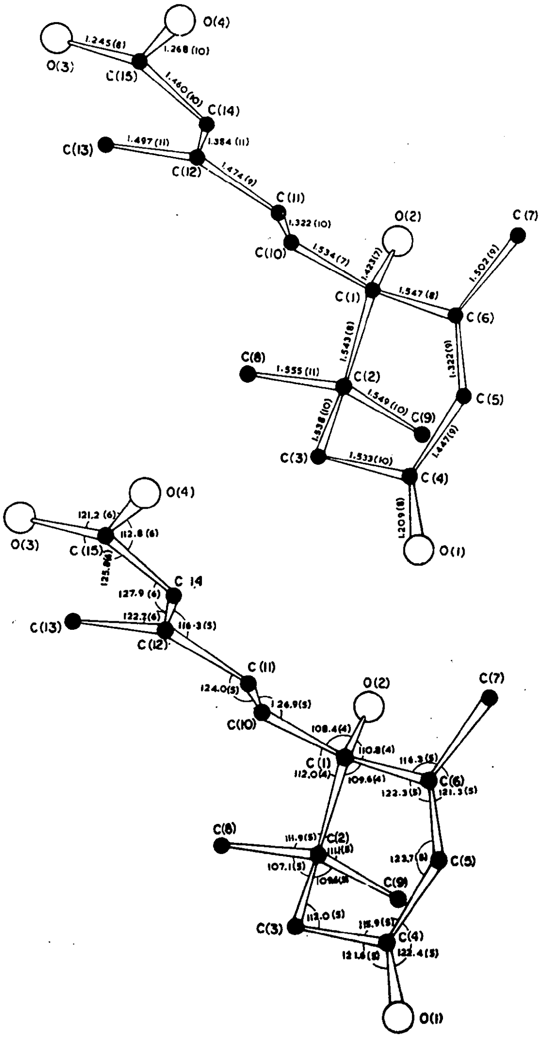

Fig. 2. Bond lengths and angles observed in the structure. ∠C(1)–C(2)–C(3) = 108·2 (5), ∠C(6)–C(1)–C(10) = 110·5 (4), ∠O(2)–C(1)–C(2) = 105·2 (4), ∠C(8)–C(2)–C(9) = 108·5 (5).

Table 2. *Torsion angles observed in abscisic acid*

Bond	Atoms	
C(1)—C(2)	C(6)C(1)C(2)C(8)	171·4 (5)°
C(1)—C(2)	C(6)C(1)C(2)C(9)	−67·0 (6)
C(2)—C(3)	C(1)C(2)C(3)C(4)	−58·2 (6)
C(3)—C(4)	C(2)C(3)C(4)C(5)	33·1 (8)
C(3)—C(4)	C(2)C(3)C(4)O(1)	−148·8 (6)
C(4)—C(5)	C(3)C(4)C(5)C(6)	−3·2 (9)
C(4)—C(5)	O(1)C(4)C(5)C(6)	178·7 (6)
C(5)—C(6)	C(4)C(5)C(6)C(7)	−179·8 (6)
C(5)—C(6)	C(4)C(5)C(6)C(1)	0·1 (9)
C(6)—C(1)	C(5)C(6)C(1)C(10)	97·6 (6)
C(6)—C(1)	C(5)C(6)C(1)O(2)	−142·1 (5)
C(6)—C(1)	C(5)C(6)C(1)C(2)	153·5 (5)
C(10)–C(11)	C(1)C(10)C(11)C(12)	178·3 (5)
C(11)–C(12)	C(10)C(11)C(12)C(13)	16·2 (1·0)
C(12)–C(14)	C(13)C(12)C(14)C(15)	−3·5 (1·2)
C(14)–C(15)	C(12)C(14)C(15)O(3)	15·7 (1·2)
C(14)–C(15)	C(12)C(14)C(15)O(4)	−166·4 (7)

Table 3. *Least-squares planes and atomic deviations* (Å)

Equation to the plane $ax+by+cz=d$ with respect to the crystallographic axes *a*, *b* and *c**, where x,y,z and d are in Å.

Plane		
I	$-0·5599x+0·7618y-0·3256z=-2·8404$	
	C(1)	−0·063†
	C(2)	−0·732†
	C(3)	0·006
	C(4)	−0·013
	C(5)	0·014
	C(6)	−0·007
II	$0·3333x-0·2644y-0·9049z=-2·5964$	
	C(10)	0·058
	C(11)	−0·062
	C(12)	0·055
	C(13)	−0·034
	C(14)	0·241†
III	$0·2093x-0·5596y-0·8018z=-3·8803$	
	C(12)	0·260†
	C(14)	0·003
	C(15)	0·010
	O(3)	−0·004
	O(4)	−0·003

† Omitted from the least-squares plane calculation.

One of us (P.S.) thanks the Council of Scientific and Industrial Research, New Delhi, India, for financial assistance.

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Acta Cryst. (1976). B**32**, 2354

The X-ray Structure of the Molecular Complex 8-Bromo-9-ethyladenine–Cyanuric Acid Monohydrate

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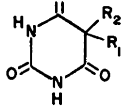
(*Received* 17 *November* 1975; *accepted* 24 *February* 1976)

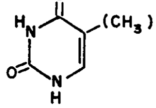
Crystals of the hydrogen-bonded complex 8-bromo-9-ethyladenine–cyanuric acid monohydrate, $C_{10}H_{13}BrN_8O_4$, have the space group $P2_1$ with unit-cell parameters $a=4{\cdot}932$ (4), $b=13{\cdot}411$ (9), $c=11{\cdot}693$ (7) Å, $\beta=108{\cdot}66$ (4)° with two complexes per unit cell. Intensity data were measured with an automated diffractometer using monochromated Mo $K\alpha$ radiation. The structure was solved with the heavy-atom technique and was refined by full-matrix least-squares procedures to a final $R=0{\cdot}042$ based on 1335 non-zero unique reflections. The adenine and cyanuric acid molecules associate through a Watson–Crick pairing and a pseudo-Hoogstein pairing in which a water molecule forms a hydrogen-bonded bridge. The hydrogen-bonding parameters in this structure are normal. In addition the structure incorporates a close $\mathrm{Br}\cdots\mathrm{O}$ contact and extensive stacking interactions.

Introduction

Despite the chemical similarity between the barbiturates (I) and uracil (or thymine) (II) the interactions between barbiturates and adenine derivatives (Voet, 1975) have been found to be quite different from those between uracil and adenine derivatives (Voet & Rich, 1970). The weak hydrogen-bond acceptor properties of the barbiturates have been described by Voet (1975) and by Gartland & Craven (1974). Parabanic acid (III), a derivative of barbituric acid, shares these weak hydrogen-bond acceptor properties (Shieh & Voet, 1975, 1976). It has been suggested that these unusual hydrogen-bonding properties are due to the electronic interactions among several closely associated carbonyl groups (Voet, 1972).



(I)



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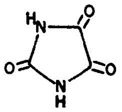

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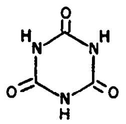

(IV)

Cyanuric acid (IV) resembles the barbiturates in that the latter's tetrahedral carbon atom has been replaced by an NH group so as to form an *s*-triazine ring. Associations between cyanuric acid and adenine derivatives can be expected from the results of Temperli, Turler & Ercegovich (1966) who found that cyanuric acid was incorporated into the RNA and DNA of a strain of thymine and uracil-requiring *E. coli* if the thymine and uracil in its growth medium were replaced by cyanuric acid.

The structural study of the crystalline complex 8-bromo-9-ethyladenine–cyanuric acid was undertaken to investigate the origin of the unusual hydrogen-bonding properties of adenine–barbiturate complexes. It will be seen below that the hydrogen-bonding properties of the above complex more nearly resemble those of adenine–uracil complexes than those of adenine–barbiturate complexes.

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