Stereochemistry of an Intermediate in a Synthetic Route to Gibberellic Acid. A Structure with a Short Carbon–Oxygen Intermolecular Contact[1]

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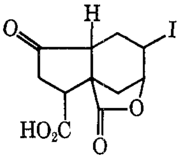
Received September 15, 1970

Dolby and associates[3] have prepared **1** as a possible intermediate in the synthesis of gibberellic acid (**2**).[4] While most of the stereochemical details of **1** have been established,[3] the question as to whether the hydrindanone system is *cis*-**3** or *trans*-**4** was unanswered. A crystal structure analysis of **1** was undertaken to resolve this stereochemical uncertainty in a short period of time.



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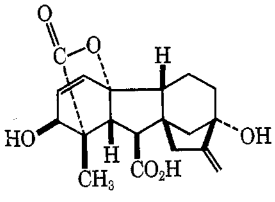

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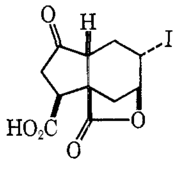

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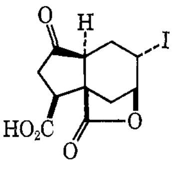

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Experimental Section

A crystalline sample of **1** was kindly supplied by Professor Lloyd Dolby of the University of Oregon. The crystals are colorless platelets with mp 166° dec. Crystal data for $C_{11}H_{11}O_5I$ are M = 350.10, monoclinic; a = 6.07 (2), b = 21.94 (5), c = 8.89 (2) Å, β = 102° 35′ (20′), $V = 1155 \times 10^{-24}$ cm^3, ρ_{measd} = 1.98 g cm^{-3}, Z = 4, ρ_{calcd} = 2.01 g cm^{-3}; systematic absences: $h0l$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$; space group $P2_1/a$. The cell dimensions were determined from precession photographs using Mo Kα radiation (λ 0.7107 Å). The density was determined by flotation in a mixture of bromoform and n-hexane. A total of 879 nonzero structure amplitudes was obtained from visual measurements on equiinclination Weissenberg photographs (Cu Kα radiation) taken on a crystal mounted about the a axis.

The structure was solved by the heavy atom method and has been refined to an R factor[5] of 0.14 on all observed data[6] by least-squares methods. Anisotropic temperature factors were introduced for the iodine atom; positional and isotropic thermal parameters were refined for all other nonhydrogen atoms. Hydrogen atoms were not included in any calculations. The scattering factor curves used were those for neutral iodine, carbon, and oxygen from the compilation in "International Tables for X-Ray Crystallography,"[7] the curve for iodine being corrected for the real component of anomalous dispersion.[8] The final atomic coordinates and thermal parameters are listed in Table I.

TABLE I
FINAL ATOMIC COORDINATES
AND FINAL TEMPERATURE PARAMETERS[a,b]

	x	y	z	B_θ (Å^2)
C(1)	0.748 (7)	0.175 (1)	0.457 (3)	0.8 (6)
C(2)	0.627 (7)	0.189 (1)	0.596 (3)	0.6 (6)
C(3)	0.695 (7)	0.139 (1)	0.711 (3)	1.2 (6)
C(4)	0.693 (7)	0.077 (1)	0.646 (3)	0.9 (6)
C(5)	0.835 (8)	0.071 (2)	0.519 (4)	1.6 (7)
C(6)	0.703 (7)	0.112 (1)	0.402 (3)	0.1 (5)
C(7)	0.753 (7)	0.117 (1)	0.236 (3)	1.2 (6)
C(8)	0.617 (7)	0.178 (2)	0.168 (3)	1.2 (6)
C(9)	0.671 (8)	0.214 (2)	0.320 (4)	2.0 (8)
C(10)	0.460 (9)	0.093 (2)	0.396 (4)	2.3 (8)
C(11)	0.636 (8)	0.066 (2)	0.127 (4)	1.7 (7)
O(1)	0.678 (6)	0.011 (1)	0.191 (3)	2.9 (6)
O(2)	0.534 (4)	0.073 (1)	−0.004 (2)	0.6 (4)
O(3)	0.625 (6)	0.272 (1)	0.317 (3)	2.3 (5)
O(4)	0.288 (5)	0.091 (1)	0.301 (3)	2.2 (5)
O(5)	0.466 (5)	0.072 (1)	0.549 (3)	1.7 (5)
I	1.0326 (7)	0.1506 (1)	0.8584 (3)	c

[a] Coordinates are given as fractions of the unit cell edge with estimated standard deviations in parentheses. The origin is in "International Tables for X-Ray Crystallography." [b] Isotropic thermal parameters (B_θ) are expressed as $\exp[-(B_\theta \sin^2 \theta/\lambda^2)]$. Anisotropic thermal parameters are expressed as $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. [c] b_{11}, 0.033 (2); b_{22}, 0.00260 (8); b_{33}, 0.0053 (3); b_{12}, −0.0014 (6); b_{13}, 0.0182 (10); b_{23}, −0.0010 (3).

Results and Discussion

A view of the structure is shown in Figure 1, from which it is apparent that the stereochemistry is trans as in **4**. Bond lengths and angles[6] agree within the accuracy of the analysis (C–C length ± 0.04 Å) with accepted values.[9]

The six-membered ring [C(1)–C(6)] is in the chair conformation with the iodine atom in an axial orientation. The five-membered lactone ring [C(4), C(5), C(6), C(10) and O(5)] is in an "envelope" conformation with C(5) lying 0.71 Å out of the best plane through the five atoms of the lactone group. The cyclopentanone ring [C(1), C(6), C(7), C(8), and C(9)] is in the "half-chair" conformation with C(6) and C(7) lying −0.37 and 0.39 Å (*i.e.*, on opposite sides) from the best plane through C(1), C(9), C(8), and O(3).

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(1) This structure determination was carried out as part of formal lecture and laboratory courses in X-ray crystallography taught at the University of Illinois in the fall of 1968. The preliminary crystal examination, collection of the X-ray data, and solution of the structure were carried out during normal class hours. The principal aim of the investiation was to demonstrate the relative ease and rapidity of an X-ray structural solution, based on film methods, to a chemical problem. While no special effort was made to obtain highly accurate intensity measurements, or the maximum amount of data, or to refine fully the structure, the chemical problem was unquestionably resolved. We acknowledge the assistance, interest, and enthusiasm of Ramsey Gitany, Gary Hougen, Rich Klobuchar, Nicholas J. Loy, and Celeste Stepien.

(2) Alfred P. Sloan Research Fellow.

(3) L. J. Dolby, S. Esfandiari, C. A. Elliger, and K. S. Marshall, *J. Org. Chem.*, **36**, 1277 (1971).

(4) The stereochemistry of gibberellic acid was established as a result of two X-ray studies: F. McCapra, A. I. Scott, G. A. Sim, and D. W. Young, *Proc. Chem. Soc.*, 185 (1962); *J. Chem. Soc. C*, 1577 (1966); and J. A. Hartsuck and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **85**, 3414 (1963).

(5) $R = \Sigma||F_{\text{obsd}}| - |F_{\text{calcd}}||/\Sigma|F_{\text{obsd}}|$.

(6) The final list of h, k, l, $|F_{\text{obsd}}|$, and F_{calcd} and the detailed values of bond lengths, angles, and intermolecular contacts will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit $3.00 for photocopy or $2.00 for microfiche.

(7) "International Tables for X-Ray Crystallography," Vol. III, C. H. MacGillavry and G. D. Rieck, Ed., Kynoch Press, Brimingham, England, 1962, pp 201–209.

(8) Reference 7, pp 213–216.

(9) O. Kennard in ref 7, pp 275–276.

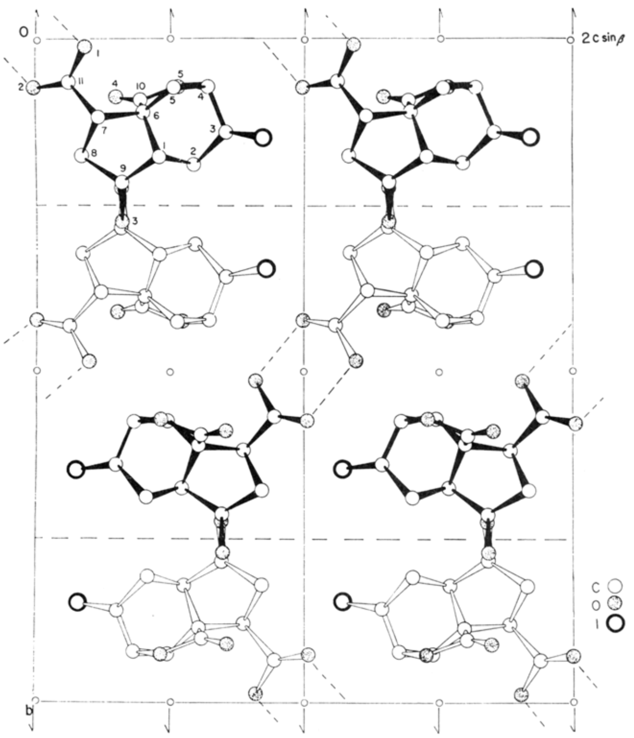

Figure 1.—View of the molecular packing down the *a* axis.

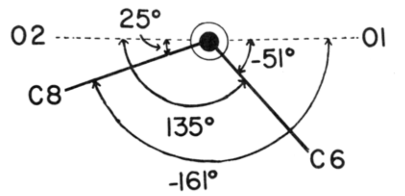

Figure 2.—The torsion angles around the C(7)–C(11) bond. The angle ABCD is considered positive, if, when looking from B to C, atom A has to be rotated clockwise to eclipse atom D.

The torsion angles involving the carboxyl group are shown in Figure 2. Both the C–O bond lengths [C(11)–O(2), 1.20 (4); C(11)–O(1), 1.34 (4) Å] and the torsion angles around the C–C (carboxyl) bond, according to Dunitz and Strickler,[10] suggest that C(11)–O(2) is the double bond in the carboxyl group. The O(1)···O(2) distance involved in an intermolecular hydrogen bond is 2.63 (3) Å. Of particular note is the C(9)···O(3) ($^1/_2 + x$, $^1/_2 - y$, z) contact of 2.79 (5) Å (Figure 3). This rather short distance between a carbon atom of a carbonyl group and the oxygen atoms of a symmetry-related carbonyl group is similar in length to those observed in chloranil[11] and in alloxan,[12,13] although the geometric disposition of groups resembles rather that found in perdeuterated violuric acid monohydrate.[14] There may also be a C–H···O hydrogen bond (length 3.23 Å) between C(7) and O(4) (at $1 + x$, y, z) although the existence of such interactions is still a matter of lively debate.[15,16]

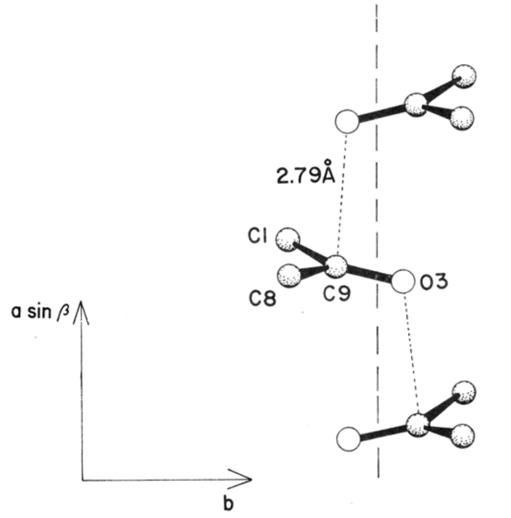

Figure 3.—The arrangement of carbonyl groups looking along the *z* direction.

Registry No.—4, 28128-99-6.

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[11] S. S. C. Chu, G. A. Jeffrey, and T. Sakurai, *Acta Crystallogr.*, **15**, 661 (1962).

[12] W. Bolton, *ibid.*, **17**, 147 (1964).

[13] C. K. Prout and S. C. Wallwork, *ibid.*, **21**, 449 (1966).

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[15] J. Donohue in ref 10, pp 443–465.

[16] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, pp 182–183.

The Effect of Alkyl Substitution on the Boron-11 Chemical Shifts in Aminoboranes and Borates[1a]

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Received September 14, 1970

There is considerable evidence[2] that ^{11}B chemical shifts are controlled by the degree of electron occupancy of the vacant p_z orbital on boron. Thus, compounds containing trivalent boron absorb at much lower field than do quadrivalent boron complexes, and the shift to low field is greatest for compounds in which trivalent boron is attached to groups lacking p or π electrons. Trimethylborane, for example, has the lowest known chemical shift (-86.4 ppm[3]) relative to boron trifluoride etherate (EBT),[4] while compounds with groups capable of donating electrons to boron appear at much higher field (*e.g.*, -18.1 ppm for trimethyl borate).[3]

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[1] (a) Reported in part at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970; (b) National Science Foundation Undergraduate Research Participant, 1969.

[2] (a) G. R. Eaton, *J. Chem. Educ.*, **46**, 547 (1969); (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, New York, N. Y., 1968, p 970; (c) P. C. Lauterbur in "Determination of Organic Structure by Physical Methods," Vol. II, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, p 476.

[3] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **81**, 4496 (1959).

[4] All chemical shifts reported in this paper are relative to EBT.