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PHOTOCHEMICAL REACTIONS—XXIII†

MOLECULAR AND CRYSTAL STRUCTURE OF 3-DEHYDRO GIBBERELLIN A_3

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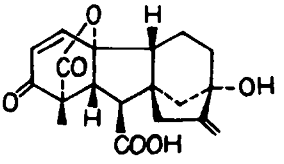
Abstract—In connection with topophotochemical studies, the structure of 3-dehydro gibberellin A_3 1 has been established by X-ray analysis, and the molecular packing determined. The final discrepancy factor R was 0·078.

For photochemical studies in the gibberellin field in solution[1] as well as in the crystalline state[2,3] the 3-dehydro gibberellin A_3-system was found to be quite suitable. The free acid 1 upon $n\rightarrow\pi^*$-excitation of the enone chromophore is transformed in good yield to the corresponding ring A phenolic acid.[2] The corresponding methyl ester under the same UV-irradiation conditions, however, undergoes intermolecular cycloaddition leading to two dimerisation products in 39% and 12% yield, respectively.[3] For explanation of this divergent crystal-controlled photoreactivity an X-ray analysis of 3-dehydro gibberellin A_3 was performed.



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A single crystal of compound 1 ($C_{19}H_{20}O_6$) crystallized from acetone/hexane as needles, m.p. 227–229° (acetone-hexane) and $[\alpha]_D^{22}+60{\cdot}7°$ (EtOH)[4] with the monoclinic space group $P2_1$; $a = 9{\cdot}344$, $b = 10{\cdot}07$, $c = 9{\cdot}301$ Å, $\beta = 101{\cdot}71°$; $D_x = 1{\cdot}334\ g{\cdot}cm^{-1}$, $Z = 2$. Weissenberg photographs were taken with CuK_α-radiation from which 791 independent reflexions were measured photometrically.

The structure was determined by the Cordal system derived from the convolution molecule method by Hoppe and Paulus.[5] All atomic parameters (including hydrogen atoms) were refined by least-squares methods to a final discrepancy factor $R = 0{\cdot}078$. The final atomic positional parameters are listed in Table 1. The resulting molecular structure including bond lengths and angles is shown in Figs. 1 and 2.

The bond length C(19)–O(10)[6] adjacent to the ketone group is 1·34 Å, the bond length C(10)–O(10) of the ether linkage in the lactone ring is 1·51 Å. Similar values for corresponding bond lengths were found by Huber[7] and ascribed to a small contribution of the resonance form $R-\underset{\underset{O^-}{|}}{C}=O^+-R$. In the structure of 16α,17-dibromo gibberellic acid[8] similar differences between the two C–O bonds in the lactone ring were observed. As expected the difference between the bond lengths C(7)–O(7,0) = 1·20 Å and C(7)–O(7,0 H) = 1·30 Å in the carboxyl group is diminished by resonance. The torsional angle between ring B and the carboxyl group defined by the angle between the plane

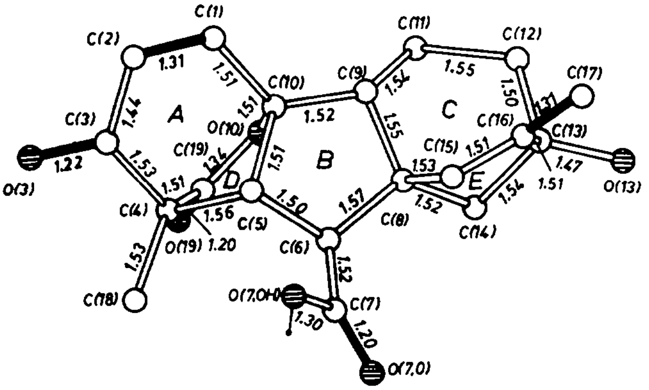

Fig. 1. Bond lengths in the structure of 3-dehydro gibberellin A_3 in Å. The standard deviations are 0·019 Å.

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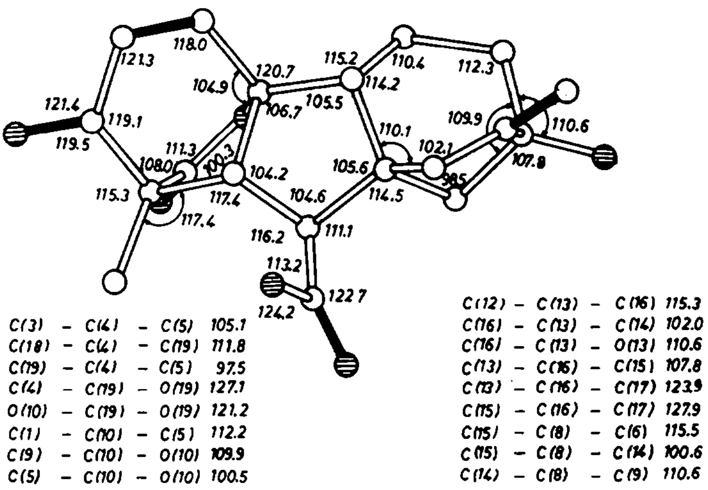
†Part XXII: B. Voigt, G. Adam, N. S. Kobrina and E. P. Serebryakov, *Z. Chem.* **15**, 103 (1975); Gibberellins—XXXVII, Part XXXVI: M. Lischewski and G. Adam, *Tetrahedron Letters*, in press.



C(3) –	C(4) –	C(5)	105.1
C(18) –	C(4) –	C(19)	111.8
C(19) –	C(4) –	C(5)	97.5
C(4) –	C(19) –	O(19)	127.1
O(10) –	C(19) –	O(19)	121.2
C(1) –	C(10) –	C(5)	112.2
C(9) –	C(10) –	O(10)	109.9
C(5) –	C(10) –	O(10)	100.5

C(12) –	C(13) –	C(16)	115.3
C(16) –	C(13) –	C(14)	102.0
C(16) –	C(13) –	O(13)	110.6
C(13) –	C(16) –	C(15)	107.8
C(13) –	C(16) –	C(17)	123.9
C(15) –	C(16) –	C(17)	127.9
C(15) –	C(8) –	C(6)	115.5
C(15) –	C(8) –	C(14)	100.6
C(14) –	C(8) –	C(9)	110.6

Fig. 2. Bond angles in the structure of 3-dehydro gibberellin A_3 in degrees. The standard deviations are 1·4 Å.

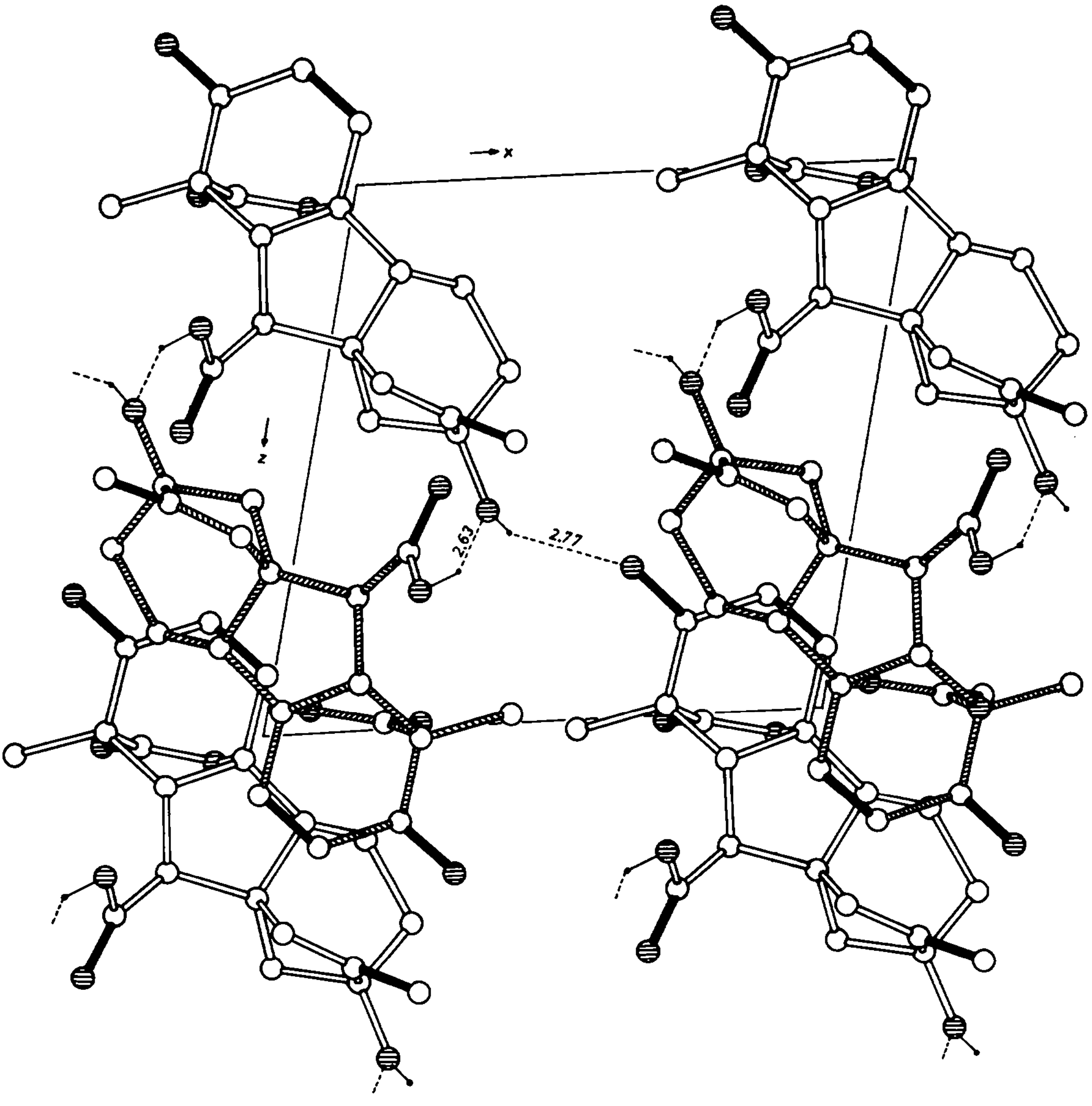


Fig. 3. Arrangement of molecules in the xz projection.

Table 1. Positional parameters (ESD in parentheses)

Atom		X		Y		Z	
C	(1)	1·0183	(14)	0·1085	(17)	1·1189	(13)
C	(2)	1·1396	(13)	0·1241	(16)	1·2179	(13)
C	(3)	1·2803	(12)	0·1128	(16)	1·1799	(13)
C	(4)	1·2876	(12)	0·0787	(15)	1·0219	(12)
C	(5)	1·1594	(11)	0·1572	(13)	0·9237	(12)
C	(6)	1·1380	(11)	0·1417	(16)	0·7604	(12)
C	(7)	1·2143	(13)	0·2442	(16)	0·6831	(12)
C	(8)	0·9675	(11)	0·1467	(14)	0·7021	(11)
C	(9)	0·9008	(12)	0·1115	(15)	0·8361	(13)
C	(10)	1·0300	(12)	0·0845	(13)	0·9617	(12)
C	(11)	0·7862	(14)	−0·0004	(16)	0·8064	(17)
C	(12)	0·6758	(13)	0·0249	(21)	0·6587	(16)
C	(13)	0·7463	(13)	0·0929	(16)	0·5475	(14)
C	(14)	0·9098	(13)	0·0531	(17)	0·5738	(14)
C	(15)	0·9062	(14)	0·2795	(15)	0·6361	(15)
C	(16)	0·7532	(15)	0·2400	(18)	0·5562	(18)
C	(17)	0·6388	(20)	0·3183	(23)	0·5177	(27)
C	(18)	1·4396	(12)	0·0920	(19)	0·9856	(15)
C	(19)	1·2257	(13)	−0·0590	(18)	0·9883	(13)
O	(3)	1·3939	(10)	0·1303	(14)	1·2720	(10)
O	(7,0)	1·2437	(11)	0·2235	(13)	0·5650	(11)
O	(7,OH)	1·2394	(10)	0·3555	(10)	0·7534	(9)
O	(10)	1·0787	(8)	−0·0564	(8)	0·9568	(9)
O	(13)	0·6762	(10)	0·0497	(12)	0·3978	(10)
O	(19)	1·2926	(10)	−0·1640	(12)	1·0002	(11)
H	(1)	0·9221	(143)	0·1114	(177)	1·1455	(147)
H	(2)	1·1479	(172)	0·1405	(212)	1·3310	(166)
H	(5)	1·1698	(136)	0·2700	(168)	0·9591	(136)
H	(6)	1·1846	(134)	0·0371	(167)	0·7498	(131)
H	(9)	0·8637	(149)	0·2114	(172)	0·8594	(148)
H	(13,OH)	0·6494	(145)	0·1371	(177)	0·3672	(146)
H	(7,OH)	0·2933	(143)	0·4268	(180)	0·7236	(139)
H	(11·1)	0·7324	(136)	−0·0026	(162)	0·8830	(139)
H	(11·2)	0·8322	(175)	−0·1159	(214)	0·8231	(174)
H	(12·1)	0·6009	(187)	0·1044	(223)	0·6799	(177)
H	(12·2)	0·6313	(143)	−0·0967	(172)	0·6183	(141)
H	(14·1)	0·9287	(151)	−0·0449	(192)	0·5980	(148)
H	(14·2)	0·9448	(112)	0·0861	(137)	0·4700	(121)
H	(15·1)	0·8955	(172)	0·3405	(203)	0·7177	(172)
H	(15·2)	0·9722	(188)	0·3362	(225)	0·5848	(179)
H	(17·1)	0·6491	(168)	0·4415	(211)	0·5364	(168)
H	(17·2)	0·5614	(142)	0·2868	(176)	0·4130	(141)
H	(18·1)	1·4312	(138)	0·0492	(177)	0·8808	(136)
H	(18·2)	0·4696	(152)	0·1914	(164)	0·0070	(166)
H	(18·3)	1·5006	(135)	0·0331	(173)	1·0841	(130)

C(5), C(6), C(7) and the least squares plane C(6), C(7), O(7,0), O(7,OH) is $\psi = 25{\cdot}0°$.

The molecules form sheets parallel to the b, c plane (Fig. 3). In the b direction the molecules are linked in spirals around a screw axis by the intermolecular hydrogen bonds O(7,OH)... O′(13) of 2·63 Å but in the c direction by van der Waals bonds only. A similar arrangement of molecules in sheets was observed in the structure 16α,17-dibromo gibberellic acid[8] also caused by such a O(7,OH)... O′(13) hydrogen bond. The sheets in the 3-dehydro gibberellin A_3 structure are linked by a second intermolecular hydrogen bond O(13)... O′(3) of 2·77 Å.

The distance between the O(1)–C(2) double bond and the terminal C(16)–C(17) olefinic group of the neighbouring molecule was found to be 4·5 Å. Furthermore the two double-bond systems are not parallel but at an angle of 28°, and the planes of their π-orbitals are nearly orthogonal. From these reasons interaction between the groups is not possible and, therefore, upon UV-irradiation in the $n \rightarrow \pi^*$ absorption region crystalline 1 is transformed by intramolecular decarboxylation to the corresponding ring A phenolic acid.[2] In contrast to this behaviour irradiation of the corresponding methylester in the crystalline state leads to an intermolecular photocycloaddition of the excited enone double bond C(1)–C(2) to the terminal olefin part C(16)–C(17) of a second molecule forming a cyclobutane dimer as a main product.[3] The differing photochemical reactivity of the two compounds can be explained by the different geometrical arrangement of molecules in the crystals. This appears to be due to the fact that the hydrogen bond O(7,OH)... O′(13) found in the free enone acid cannot exist in the corresponding methylate, which crystallizes in the tetragonal space group $P4_12_12$ with the lattice parameters $a = b = 9{\cdot}85$, $c = 36{\cdot}09$ Å indicating the different mode of molecule packing.

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