

The Crystal Structure of Ellagic Acid

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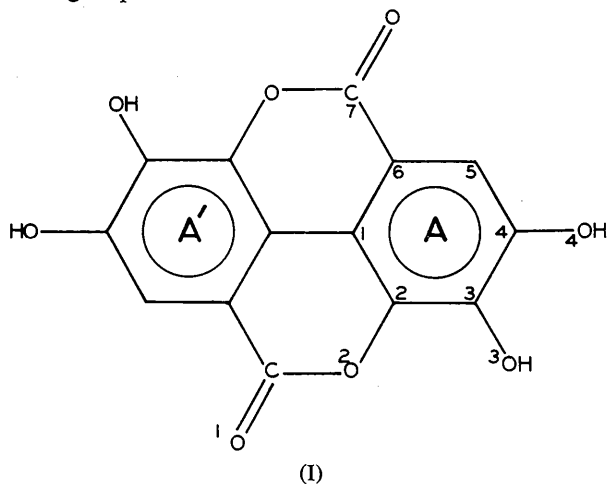
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Ellagic acid, the dilactone of 2,2'-dicarboxy-4,5,6,4',5',6'-hexahydroxybiphenyl, crystallizes in the monoclinic system, space group $P2_1/c$, with cell dimensions $a=3.745$, $b=11.442$, $c=12.528$ Å, $\beta=90.22^\circ$ and $Z=2$. The centrosymmetric molecule is essentially planar, only the lactone carbonyl groups being tilted slightly (3.6°) from the molecular plane. The crystal structure is virtually a layer type structure with all molecules lying near to the (102) plane and the molecules linked within the plane by a strong hydrogen bond between O(3) and the lactone carbonyl oxygen atom of the adjacent molecule, and a weaker hydrogen bond H(O4) to an adjacent O(3). Correlation of earlier infrared spectral results with the crystal structure of ellagic acid is indicated.

Introduction

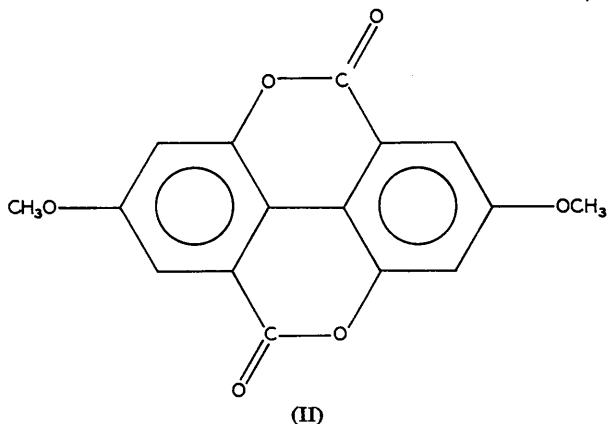
A troublesome pipe deposit, normally green in colour, produced during the neutral sulphite pulping of mature eucalyptus woods has been shown (Hillis & Carle, 1959; Baklien, 1960; Hewitt & Nelson, 1965) to comprise mainly metallic complexes of ellagic acid (I). Although referred to as an acid, the material is a dilactone, the acid function being associated with the phenolic groups.



Nelson (1965) has studied the complexing ability of ellagic acid with various cations and reported materials containing sodium, calcium, barium and magnesium. These substances are not readily obtained with definite stoichiometric composition, in contrast with the complexes of ellagic acid and certain organic compounds such as pyridine. However, it was possible to produce 2:1 ellagic acid:metal complexes and, with forcing conditions, complexes with apparently 0.9 atoms of metal per molecule of acid. On the basis of infrared

spectra, Nelson advanced hydrogen bonding schemes in both the parent compound and its magnesium complex. The suggested presence of at least two intramolecular hydrogen bonds, one to the adjacent hydroxyl group and the second to the lactone ring oxygen, does not accord with the high melting point ($>360^\circ\text{C}$) of the material. Nor does the proposed bonding provide a satisfactory basis on which to explain either the ability of monovalent cations, such as sodium, to form complexes, or the differences between the acid and its magnesium complex in respect of the intensity of the bands in the hydroxyl stretching region of their infrared spectra.

Ellagic acid is related structurally to a group of natural products isolated from such widely divergent sources as the castoreum of the Canadian beaver and the haemolymph of an Australian termite. Referred to as nasutins, the structures proposed for them are essentially methyl ethers and deoxy derivatives of ellagic acid (Moore, 1964). Each of the materials is characterized by a melting point in excess of 300°C . Of particular interest is the dimethyl ether of nasutin A (II)



which melts above 360°C indicating that intermolecular bonding must be other than by simple hydrogen bonds. For comparison the parent hydrocarbon of these materials, pyrene, melts at 150°C.

Because of their industrial significance, it was initially intended to study directly the metal complexes of ellagic acid, particularly that of sodium. However, to date, it has not been possible to obtain single-crystal specimens of these materials. Consequently the study of the structure of the acid was undertaken in anticipation that a clearer understanding of the intermolecular bonding in the parent compound would provide information capable of extrapolation to the metal complexes.

Experimental

Pure ellagic acid was obtained by refluxing with methanol a quantity of thrice-recrystallized pyridine-ellagic acid complex. Sublimation of this material under vacuum at red heat produced faint-yellow needle-like crystals, most of which proved to be twinned. Since the polarizing microscope was not fully adequate to resolve an untwinned specimen, the final selection was based on moving-film records. The specimen used was a needle of almost square cross-section, cleaved so that its final dimensions were approximately 0.2 mm × 0.2 mm × 0.2 mm. The crystal was in two almost equal fragments, slightly misaligned. Although this did not affect the intensity measurements, accurate measurements of the parameters β and c were more difficult to obtain. The parameters given below were derived from careful diffractometer measurements on four high angle reflexions (400, 0120, 0012, 306) at 21°C with Cu $K\alpha_1$ radiation ($\lambda = 1.54051 \text{ \AA}$). The density was obtained by flotation in a methyl iodide – bromobenzene mixture.

Ellagic acid $C_{14}H_6O_8$ M.W. 302.2

$a = 3.74_5 \text{ \AA}$

$b = 11.44_2 \text{ \AA}$

$c = 12.52_8 \text{ \AA}$

$\beta = 90.2_2^\circ$

$Z = 2$

$V = 536.9 \text{ \AA}^3$

$D_m = 1.87, D_x = 1.86_9 \text{ g.cm}^{-3}$.

Space group $P2_1/c$ from systematic absences: $h0l$ absent for $l = 2n + 1$; $0k0$ for $k = 2n + 1$.

Molecular symmetry $\bar{1}$.

The crystal was mounted with the (110) face perpendicular to the ϕ axis of a Picker four-cycle automatic diffractometer and intensity data collected with β -filtered Cu $K\alpha$ radiation, using the ω - 2θ scanning mode, for 908 independent reflexions for which $\sin \theta \leq 0.90$. The very intense 102 reflexion was taken as a reference standard and checked after measurement of every fifty reflexions, there being no indication of crystal deterioration during the data collection. Intensity measurements were corrected for background and Lorentz and polarization factors, but no correction

was made for absorption. The 102 reflexion, however, was excluded during refinement of the structure as it appeared to be affected by extinction.

The atomic scattering factors used for carbon, oxygen and hydrogen were those of Freeman (1959), Hoerni & Ibers (1954) and Stewart, Davidson & Simpson (1965) respectively.

Structure determination

The distribution of peaks around the origin of the three-dimensional vector distribution, together with the very intense 102 reflexion, were consistent with a planar molecule, lying in or close to the (102) plane. However, as the rings in the molecule are regular and contain no dominant atom, the correct orientation of the molecule was not readily apparent.

For the 30 innermost reflexions, structure factors were calculated for a range of orientations of the molecule in the 102 plane. On the basis of the conventional R index ($= \sum |F_o - F_c| / \sum |F_o|$) for this set of reflexions, atomic positions corresponding to the best fit were determined. These were then refined with several cycles of full-matrix least squares using the full set of reflexion data and an overall isotropic temperature factor. Over six cycles, R decreased from 0.35 to 0.16 and then with individual anisotropic temperature factors to 0.095. At this point, a three-dimensional ΔF distribution was synthesized with low-angle data ($\sin \theta / \lambda \leq 0.45$) from which the three hydrogen atoms of the asymmetric unit were located. Temperature factors for each proton were set equal to those of the atom to which they were attached and a further cycle carried out, varying only the parameters for the carbons and oxygens. After slight adjustments of hydrogen locations from a second difference map, a least-squares cycle was carried out in which parameter changes were less than 0.1 of the program-estimated standard deviation.

The assumption concerning the temperature factors of the hydrogen atoms appears to be adequate in the present analysis when the background variations of electron density of the final difference distribution are considered. The hydroxyl protons were less well-defined than the aromatic proton so that, for these atoms at least, a higher value of the temperature factor could have been introduced but with no gain in physical significance.

The final value of the reliability index, R , for all reflexions, excluding 102, was 0.070. As indicated in Table 1, R varied with $\sin \theta$ from less than 0.05 at low angles, to 0.15 at high angles. This trend most probably reflects the lower statistical precision of the high angle intensities. Individual reflexions therefore were given weights according to their counting statistics, *i.e.* $\sigma = 1 / (I - I_{\text{background}})^{1/2}$. Refinement with the weighted data yielded the weighted R for all reflexions as 0.049, comparable with the unweighted value for the low-angle data.

The resultant final atomic coordinates and thermal parameters, with their program-estimated standard deviations, are given in Table 2 while the corresponding bond lengths and angles and approach distances

are given in Table 3. Observed and calculated structure factors are compared in Table 4.

Discussion

The bond lengths and angles in ellagic acid are mostly in accord with values observed in other similar structures (*Tables of Interatomic Distances*, 1965). However, linkage of the lactone group with the biphenyl ring system AA' constrains the whole ring system to near planarity, resulting in an extended π -electron system within the molecule and hence modifying a number of bonds. Thus bonds C(6)–C(7), 1.45 Å, and C(2)–O(2), 1.37 Å, are rather shorter than the corresponding values of 1.51 and 1.47 Å respectively in aliphatic lactone and ester structures, *e.g.* Mathieson & Taylor (1961), while C(1)–C(1'), 1.42 Å, is to be compared with the value of 1.51 Å in non-planar biphenyl compounds (*Tables of Interatomic Distances*, 1965). The bond C(7)–O(2), already reduced in aliphatic lactones, does not appear to be further affected by the conjugation.

In respect of conformational detail, the two aromatic rings, A and A' , lie in a common plane through the origin and defined by (1a).

$$0.9040X + 0.0798Y + 0.4201Z = 0 \quad (1a)$$

$$0.8744X + 0.0921Y + 0.4764Z = 0.100 \quad (1b)$$

X , Y and Z refer to cartesian axes such that $X = x \sin \beta$, $Y = y$ and $Z = x \cos \beta + z$ where x, y, z are the atom coordinates in Å. All 'heavy' atoms lie within 0.01 Å of plane (1a) except for O(3), C(7) and O(1) which deviate by 0.03, 0.05 and 0.13 Å respectively. The four atoms centred on C(7) are within 0.002 Å of the plane (1b). The normals to the planes (1a) and (1b) subtend an angle of 3.6°. The molecule can therefore be described on the basis of three planes: the main plane containing the aromatic residues plus O(2) and the two secondary planes, (1b) involving C(6'), C(7), O(1) and O(2), and its centrosymmetrically related plane (1b').

Atom C(2) deviates 0.09 Å from plane (1b) so that the lactone group, C(6'), C(7), O(1), O(2) and C(2) is non-planar. In the majority of aliphatic structures, the planarity condition applies (Mathieson & Taylor, 1961) except when deviation is forced by other more dominant conformational factors, *e.g.* in β -D-glucurono- γ -lactone (Jeffrey, 1967). In ellagic acid, the reason for adopting this particular conformation must be due to the balance of several factors, some intramolecular, others intermolecular. As indicated above, there is a tendency to stabilize the molecule to full planarity by π -bond formation. It is known, however, in the case of cyclic aromatic structures (*e.g.* Harnik, Herbstein, Schmidt & Hirshfeld, 1954) that small deviations from planarity can occur and not critically modify or weaken bond character. The strain involved in matching the lactone group to the distance C(6')---C(2) may be relieved by a relaxation of one or other conformational

Table 1. *The unweighted reliability index R for different ranges of sin θ*

sin θ	R	Number of reflexions
0.00–0.10	0.035	1
0.10–0.20	0.050	6
0.20–0.30	0.036	30
0.30–0.40	0.055	42
0.40–0.50	0.049	88
0.50–0.60	0.076	109
0.60–0.70	0.056	165
0.70–0.80	0.071	207
0.80–0.90	0.148	241
0.90–1.00	0.505	1
0.00–0.33	0.046	48
0.33–0.67	0.058	333
0.67–1.00	0.091	509

Table 2. *Final atomic coordinates for ellagic acid*

Standard deviations are in brackets and refer to the last significant figure(s).

C(1)	0.9619 (11)	0.0594 (3)	0.0129 (3)
C(2)	0.0502 (10)	0.1458 (3)	0.9425 (3)
C(3)	0.9820 (11)	0.2626 (4)	0.9659 (4)
C(4)	0.8243 (11)	0.2886 (4)	0.0632 (4)
C(5)	0.7369 (11)	0.2051 (4)	0.1368 (4)
C(6)	0.8051 (11)	0.0878 (4)	0.1093 (3)
C(7)	0.7085 (11)	0.9930 (4)	0.1799 (3)
O(1)	0.5538 (9)	0.0037 (3)	0.2618 (2)
O(2)	0.2077 (8)	0.1204 (2)	0.8469 (2)
O(3)	0.0757 (9)	0.3444 (2)	0.8952 (3)
O(4)	0.7719 (9)	0.4061 (2)	0.0770 (2)
H(C5)	0.600	0.420	0.130
H(O3)	0.983	0.093	0.413
H(O4)	0.708	0.240	0.203

Table 3. *Bond lengths and angles for ellagic acid*

C(1)—C(1')	1.426 Å	C(1')—C(1)—C(2)	119.6°
C(1)—C(6)	1.383	C(1')—C(1)—C(6)	120.6
C(1)—C(2)	1.367	C(2)—C(1)—C(6)	119.8
C(2)—C(3)	1.392	C(1)—C(2)—C(3)	121.0
C(3)—C(4)	1.389	C(1)—C(2)—O(2)	121.1
C(4)—C(5)	1.369	C(3)—C(2)—O(2)	117.9
C(5)—C(6)	1.408	C(2)—C(3)—O(3)	119.0
C(6)—C(7)	1.447	C(2)—C(3)—C(4)	118.0
O(1)—C(7)	1.187	O(3)—C(3)—C(4)	123.0
O(2)—C(7)	1.376	C(3)—C(4)—C(5)	123.0
O(2)—C(2)	1.369	C(3)—C(4)—O(4)	112.5
O(3)—C(3)	1.337	C(5)—C(4)—O(4)	124.4
O(4)—C(4)	1.370	C(4)—C(5)—C(6)	117.2
H(C5)—C(5)	1.06	C(1)—C(6)—C(5)	121.0
H(O3)—O(3)	0.80	C(1)—C(6)—C(7)	117.7
H(O4)—O(4)	0.75	C(5)—C(6)—C(7)	121.3
		C(6)—C(7)—O(1)	125.1
		C(6)—C(7)—O(2)	120.0
		O(1)—C(7)—O(2)	114.9
		C(2')—O(2')—C(7)	120.9
		H(C5)—C(5)—C(4)	113
		H(C5)—C(5)—C(6)	130
		H(O3)—O(3)—C(3)	108
		H(O4)—O(4)—C(4)	112

Table 5. Oxygen–oxygen approach distances in ellagic acid

Intermolecular	
O(1)–O(4)	2.614 Å
O(1)–O(3)	3.007
O(1)–O(3')	3.100
O(3)–O(4')	2.931
Intramolecular	
O(3)–O(4)	2.646

atoms, the angle O(4)–H–O(1') being 157°. It may be noted that the angles at the carbon atoms to which these oxygen atoms are attached have apparently anomalous values, $\angle O(2')C(7)O(1)$ and $\angle C(3)C(4)O(4)$ being 114.9° and 112.5° respectively. The reasons for these deviations are not known. The second hydroxyl proton appears to form a weaker hydrogen bond between O(3) and O(4), the distance being 2.93 Å and the angle O(3)–H---O(4'), 173° (see Fig. 1). Evidently in the crystal at least, hydrogen bond formation is entirely intermolecular, in contrast with the contention (Nelson, 1965) that the weaker hydrogen bond be ascribed to an intramolecular interaction.

Correlation of the structure with certain aspects of spectroscopic evidence is of interest. Thus it has been noted that when ellagic acid is subjected to prolonged heating the infra-red absorption corresponding to the carbonyl group changes from 1705 cm⁻¹ to 1729 cm⁻¹, with reversion to the lower value on exposure to the atmosphere, apparently with uptake of water (Hewitt & Nelson, 1965). The crystals used in the present investigation were not protected from atmospheric moisture during data collection and had been stabilized for several months prior to the data collection. The final difference map contained no evidence to indicate the presence in the crystal of significant amounts of water. Variation in the carbonyl absorption of crystalline ellagic acid is therefore unlikely to be associated with change in water content. An alternative explanation is that the carbonyl group flips to the alternate dihedral angle with a corresponding change in the intermolecular bonding involved. Thus, in the room temperature stable form the carbonyl oxygen O(1) is strongly bonded to an adjacent O(4') and is out of plane by 0.13 Å. A swing to the other orientation, induced by heating, although not greatly affecting the general packing arrangement, would increase the distance O(1)–O(4) and hence lower the frequency of carbonyl absorption. Another spectroscopic effect induced by modification in this region can be correlated with the structure. Thus examination of the structure in the region of the unit cell illustrated in Fig. 2, reveals a high concentration of oxygen atoms. In particular the site marked *M* has a near-octahedral shape. It appears probable that it is this region in which cations may be accommodated and where also exchange of a cation for a proton, specifically that attached to O(3), is readily carried out. The site size would readily fit a Mg²⁺ ion in the normal octahedral coordination while

Na⁺ and other ions could probably be accommodated. That this site is associated with this function is supported by the marked change of carbonyl frequency to 1663 cm⁻¹ observed with the incorporation of Na⁺ ions. There is a corresponding decrease in the intensity of the 'so-called' weak hydrogen bonded OH ascribed to O(3).

At first sight, the rather high melting point of ellagic acid appears to correlate satisfactorily with the extensive hydrogen-bonding system linking the molecules. However, reference to the nasutins referred to above reveals that methylation of the hydroxyl groups does not modify the melting point to any marked extent (Moore, 1964). The high melting point of these compounds therefore may be a consequence of the struc-

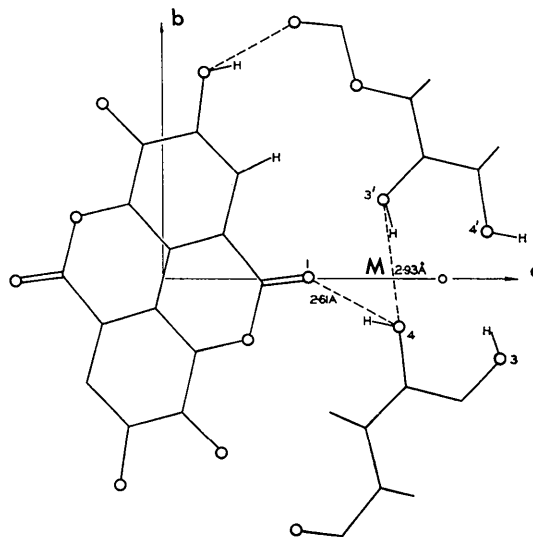


Fig. 1. Projection of the crystal structure of ellagic acid down [100]. Hydrogen bond lengths and some approach distances are shown.

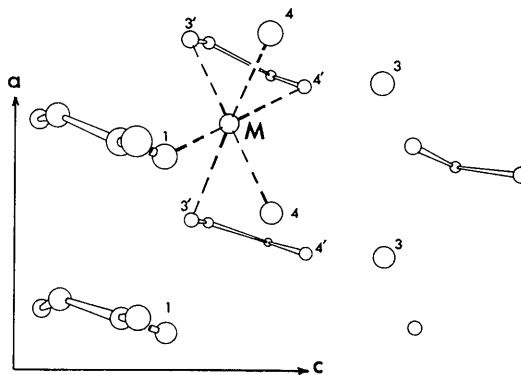


Fig. 2. View of the crystal structure of ellagic acid in the oxygen-rich region. Site *M* is indicated.

ture being composed of virtually planar molecules arrayed in planes extending throughout the crystal and stabilized by $\pi - \pi$ interactions – a graphitic type of structure perhaps further stabilized by interaction of charge separations associated with the lactone group. This possibility offers an attractive speculation concerning the intermolecular bonding and the role of lactone groups in stabilizing carbonaceous structures (see Garten & Weiss, 1957).

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The Direct Structure Determination of a Silicon Carbide Crystal of Type 120 R

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The direct method of determining polytypic structures, recently published independently by Tokonami and by Farkas-Jahnke, has been applied successfully to a SiC crystal of type 120R, whose lattice constants are $a = 3.080 \pm 0.003$, $c = 302.4 \pm 0.1$ Å when described on hexagonal axes. The Zhdanov symbol of the structure is $[32(22)_5 32.22.33]_3$. It is shown that this direct method applies whenever sufficiently accurate intensity data are available. The required accuracy has been estimated; it increases with the number of double layers in the unit cell.

Introduction

Recently, a direct method to solve the crystal structures of polytypic substances such as SiC and ZnS has been developed independently by Farkas-Jahnke (1966) and Tokonami (1966). In this paper we shall, for the most part, use the notation of the former.

In short, the method is as follows. A set of observed intensities $|F(01l)|^2$ with $l = 1, 2 \dots n$ is converted into a set of $|S(01l)|^2$ values. For the above substances the relevant equations are

$$|F(01l)|^2 = \alpha [f_{\text{I}}^2 + f_{\text{II}}^2 + 2f_{\text{I}}f_{\text{II}} \cos(3\pi l/2n)] |S(01l)|^2,$$

$$\sum_{l=1}^n |S(01l)|^2 = N^2,$$

where

- α = scaling factor,
 $f_{\text{I}}, f_{\text{II}}$ = scattering factors of the two atomic species,
 n = number of double layers in the hexagonal unit cell,
 $N = n$ for trigonal and hexagonal structures,
 $= n/3$ for rhombohedral structures.

The data are now used to compute the Patterson-like function

$$\Pi(m, p) = \frac{N}{3} + \frac{2}{3N} \sum_{l=1}^n |S(01l)|^2 \cos 2\pi \left(\frac{m}{3} + \frac{pl}{n} \right)$$

at the points $m = 0, \pm 1$; $p = 0, 1, 2 \dots N/2$ [or $(N-1)/2$ if N is odd]. It is easily shown that $\Pi(m, p)$ represents