

The title molecule and the neighbouring water molecule are involved in six short intermolecular O...O contacts (< 3 Å) which are listed in Table 3. Although no detailed analysis of the hydrogen-bonding scheme is possible in view of the fact that only two of the six hydroxylic H atoms could be identified, it is clear that the crystal structure contains two-dimensional hydrogen-bonded bi-layers in the *ab* plane involving glucopyranose moieties and water molecules (Fig. 2). The hydrogen bonds which have been found [O(2')—H...O(3')(-*x*-2, $\frac{1}{2} + y$, -*z*) and O(3')—H...O(6')(-*x*-1, $\frac{1}{2} + y$, -*z*)] already form a two-dimensional network along the *ab* plane. The O(1) and O(2) atoms of the five-membered lactone are not involved in any significant short intermolecular contacts. The layers of hydrogen-bonded molecules are separated by layers with weak intermolecular interactions consisting of the lactonic groups of the title molecule (Fig. 2).

The investigation was supported in part (WJJS and ALS) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Nether-

lands Organization for Advancement of Pure Research (ZWO).

References

- CHAN, W. R., TAYLOR, D. R., WILLIS, C. R., BODDEN, R. L. & FEHLHABER, H. W. (1971). *Tetrahedron*, **27**, 5081–5091.
 CREMER, D. & POPLÉ, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 JEFFREY, G. A. & TAKAGI, S. (1977). *Acta Cryst.* **B33**, 738–742.
 MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1984). *SHELX84*. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.
 SMITH, A. B., TODER, B. H., CARROLL, P. J. & DONOHUE, J. (1982). *J. Cryst. Spectrosc. Res.* **12**, 309–319.
 SPEK, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.
 SPEK, A. L., DUISENBERG, A. J. M., LABADIE, R. P., RATNAYAKE, S., ABEYSEKERA, A. & DE SILVA, K. T. D. (1987). *Acta Cryst.* **C43**, 530–532.

Acta Cryst. (1987). **C43**, 1998–2000

Structure of 5-Hydroxy-6,7,8,3',4',5'-hexamethoxyflavone, Gardenin A*†

BY J. VIJAYALAKSHMI, S. S. RAJAN AND R. SRINIVASAN

Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India

(Received 11 September 1986; accepted 22 April 1987)

Abstract. C₂₁H₂₂O₉, *M_r* = 418.4, orthorhombic, *Pbca*, *a* = 15.873 (2), *b* = 7.241 (1), *c* = 33.715 (5) Å, *V* = 3875 (2) Å³, *Z* = 8, *D_m* = 1.42 (2), *D_x* = 1.430 (1) Mg m⁻³, λ(Co *Kα*) = 1.7903 Å, μ(Co *Kα*) = 1.493 mm⁻¹, *F*(000) = 1760, *T* = 298 K, *R* = 0.060, *wR* = 0.057 for 1715 reflections. The phenyl ring is quite planar and makes an angle of 155.2° with the *γ*-pyrone ring.

Introduction. Gardenin A is the yellow crystalline component of the *Dikamali* gum, which is the resinous exudation of the leaf bud of *Gardenia lucida* Roxb. belonging to the N.O. Rubiaceae. The structure determination was undertaken to establish the structure–activity relationship and also to confirm the

structure predicted by chemical methods (Hegnauer, 1973).

Experimental. *D_m* by flotation, yellow needles (from methanol:acetone, 1:1 mixture) 0.3 × 0.5 × 0.2 mm, Picker four-circle manual diffractometer (at the Department of Crystallography and Biophysics, University of Madras), Co *Kα* radiation, cell parameters refined from 35 strong, accurately centered reflections in the range 25 ≤ 2θ ≤ 63°, θ/2θ scan technique with a symmetric range of ±1° in 2θ and a scan rate of 2° min⁻¹, stationary background counts for 10 s at each extreme of scan width, Lp correction, absorption ignored, 2096 unique reflections with 2θ ≤ 130°, 0 ≤ *h* ≤ 16, 0 ≤ *k* ≤ 7, 0 ≤ *l* ≤ 34, 1715 observed reflections with |*F_o*| ≥ 3.0σ(|*F_o*|), solution using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), |*E*| ≥ 1.30 for phase generation, all nonhydrogens except for the six methyl carbons located from the *E* map. The methyl carbons and hydrogens subsequently located from Δρ map. Full-matrix least-squares

* 5-Hydroxy-6,7,8-trimethoxy-2-(3,4,5-trimethoxyphenyl)-4*H*-1-benzopyran-4-one (*Chemical Abstracts* name).

† Contribution No. 701 from the Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India.

refinement on F (Gantzel, Sparks & Trueblood, 1961) was carried out with anisotropic thermal parameters for nonhydrogens and isotropic for hydrogens. Final $R=0.060$, $wR=0.057$ where $w=1/F_o^2$ if $|F_o| \geq |F_o|_{\min}$ and $w=1/F_o^2_{\min}$ if $|F_o| < |F_o|_{\min}$ with $|F_o|_{\min}=15.0$.

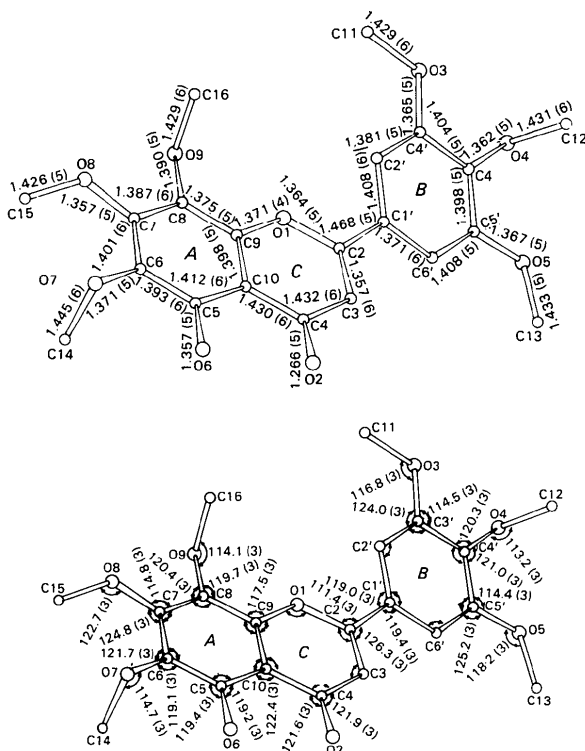


Fig. 1. Perspective views of the molecules showing bond lengths (Å) and angles (°). Additional bond angles: C(5)–C(6)–C(7) 118.9 (3), C(6)–C(7)–C(8) 120.3 (3), C(7)–C(8)–C(9) 119.9 (3), C(8)–C(9)–C(10) 122.0 (3), C(9)–C(10)–C(5) 117.4 (3), C(10)–C(5)–C(6) 121.4 (3), C(9)–O(1)–C(2) 119.9 (2), O(1)–C(2)–C(3) 122.3 (3), C(2)–C(3)–C(4) 120.6 (3), C(3)–C(4)–C(10) 116.5 (3), C(4)–C(10)–C(9) 120.2 (3), C(10)–C(9)–O(1) 120.6 (3), C(1')–C(2')–C(3') 118.4 (3), C(2')–C(3')–C(4') 121.5 (3), C(3')–C(4')–C(5') 118.7 (3), C(4')–C(5')–C(6') 120.4 (3), C(5')–C(6')–C(1') 119.3 (3), C(6')–C(1')–C(2') 121.7 (3)°.

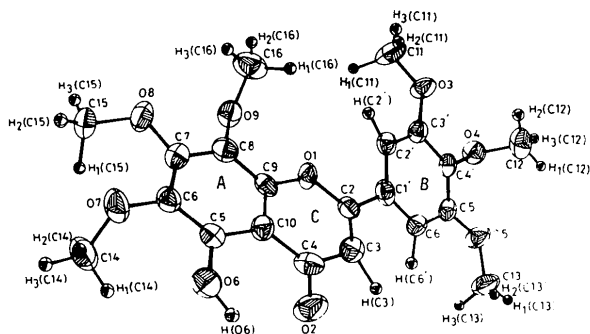


Fig. 2. ORTEP plot (Johnson, 1965) of the molecules with 50% probability.

Table 1. Fractional positional parameters ($\times 10^4$) of the non-hydrogen atoms with estimated standard deviations in parentheses and their equivalent thermal parameters

The arithmetic mean of the principal axes of the thermal ellipsoid is given by:

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

where \mathbf{a}_i and \mathbf{a}_j are lattice vectors in direct space.

| | x | y | z | $B_{eq}(\text{Å}^2)$ |
|-------|----------|----------|----------|----------------------|
| O(1) | 3025 (2) | 1335 (4) | 1239 (1) | 2.9 |
| C(2) | 3724 (2) | 1518 (5) | 1471 (1) | 2.8 |
| C(3) | 3676 (3) | 1839 (6) | 1867 (1) | 3.3 |
| C(4) | 2874 (3) | 1996 (6) | 2059 (1) | 3.4 |
| C(5) | 1319 (3) | 1882 (6) | 1964 (1) | 3.0 |
| C(6) | 620 (2) | 1695 (6) | 1717 (1) | 3.1 |
| C(7) | 747 (2) | 1436 (5) | 1310 (1) | 5.1 |
| C(8) | 1556 (3) | 1290 (6) | 1158 (1) | 3.0 |
| C(9) | 2239 (2) | 1466 (5) | 1406 (1) | 2.5 |
| C(10) | 2147 (2) | 1768 (6) | 1813 (1) | 3.0 |
| C(11) | 4495 (3) | 2583 (8) | 19 (1) | 5.1 |
| C(12) | 7234 (3) | 2436 (8) | 582 (1) | 4.6 |
| C(13) | 6850 (3) | 48 (9) | 1754 (1) | 5.2 |
| C(14) | -456 (3) | 448 (7) | 2125 (1) | 4.7 |
| O(15) | -715 (3) | 832 (7) | 1125 (1) | 4.3 |
| C(16) | 1762 (3) | 2533 (8) | 517 (1) | 5.1 |
| C(1') | 4499 (2) | 1374 (5) | 1235 (1) | 2.9 |
| C(2') | 4468 (2) | 1789 (5) | 827 (1) | 2.9 |
| C(3') | 5203 (2) | 1671 (6) | 610 (1) | 3.0 |
| C(4') | 5965 (2) | 1117 (5) | 784 (1) | 2.6 |
| C(5') | 5977 (2) | 721 (5) | 1190 (1) | 2.7 |
| C(6') | 5252 (2) | 837 (6) | 1416 (1) | 3.0 |
| O(2) | 2810 (2) | 2325 (5) | 2426 (1) | 4.7 |
| O(3) | 5261 (2) | 2095 (5) | 216 (1) | 4.1 |
| O(4) | 6669 (2) | 901 (4) | 558 (1) | 3.7 |
| O(5) | 6747 (2) | 199 (5) | 1333 (1) | 4.0 |
| O(6) | 1203 (2) | 2246 (5) | 2355 (1) | 4.2 |
| O(7) | -170 (2) | 1938 (4) | 1874 (1) | 4.0 |
| O(8) | 125 (2) | 1386 (4) | 1034 (1) | 4.1 |
| O(9) | 1682 (2) | 920 (4) | 758 (1) | 3.5 |

The final difference synthesis showed no peaks either positive or negative exceeding $0.3 e \text{ Å}^{-3}$. Atomic scattering factors for non-hydrogens from *International Tables for X-ray Crystallography* (1974), for hydrogens from Stewart, Davidson & Simpson (1965). All calculations were carried out using either an IBM 1130 computer at the University of Madras or an IBM 370 at the Indian Institute of Technology, Madras.

Discussion. The bond lengths and angles are given in Fig. 1 and an ORTEP plot (Johnson, 1965) of the molecule is given in Fig. 2.* Atomic coordinates are listed in Table 1.

In this structure the γ -pyrone (ring C) and the benzene (ring A) rings are almost planar [$\sum(\Delta/\sigma)^2 = 12.24$ and 23.54 respectively for rings C and A] the angle between the planes is $1.1(4)^\circ$. The phenyl ring (ring B) is quite planar [$\sum(\Delta/\sigma)^2 = 6.33$] and makes an angle of $155.2(4)^\circ$ with the plane of the γ -pyrone ring.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bonds and angles involving H and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43995 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The average C—C bond lengths in rings *A* and *B* are 1.39 (1) and 1.40 (1) Å respectively. These are close to the normal aromatic value, 1.395 (3) Å (*Molecular Structures and Dimensions*, 1972). The C(2)—O(1) and C(9)—O(1) bonds [1.364 (4) and 1.371 (4) Å respectively] are quite close to the values reported for similar flavonoid structures by Rossi, Cantrell, Farber, Dyott, Carrel & Glusker (1980). C(4)—C(10) and C(3)—C(4) distances [1.430 (6) and 1.432 (6) Å respectively] are close to the C—C distance in similar situations of 1.44 (1) (av) Å quoted in *Molecular structures and Dimensions* (1972) and to values found in other flavone structures (Bergstrom, Satyshur & Sundaralingam, 1981; Hayashi, Kawai, Ohno, Iitaka & Akimoto, 1974; Lee, Lu & Zee, 1974; Vijayalakshmi, Rajan, Srinivasan & Ramachandran Nair, 1986). The C(5)—O(6) bond, 1.357 (5) Å, is normal for a C_{aromatic}—O_{single} bond and a similar distance of 1.364 Å is observed in 4'-bromo-5-hydroxyflavone (Hayashi, Kawai, Ohno, Iitaka & Akimoto, 1974). The C(2)—C(1') bond linking the phenyl and γ -pyrone rings is 1.468 (5) Å, which is comparable with that observed in biphenyl where double-bond character due to resonance leads to the values of 1.489 (7) Å quoted by Bastiansen & Trætterberg (1962) and of 1.48 Å suggested by Pauling (1960). The carbonyl bond distance of 1.266 (5) Å is comparable at the 2 σ level to the value of 1.254 Å found in 4'-bromo-5-hydroxyflavone (Hayashi, Kawai, Ohno, Iitaka & Akimoto, 1974).

The methoxy groups at C(7), C(3') and C(5') lie close to the plane of ring *B*, the torsional angles C(8)—C(7)—O(8)—C(15), C(4')—C(3')—O(3)—C(11) and C(4')—C(5')—O(5)—C(13) being 156.0 (4), 177.1 (4) and 170.4 (4)° respectively. These findings may be explained as due to the overlap of the *n* electrons of the O(methoxy) with the ring π electrons. The putative ring strain is released by the opening of the angle at the C(sp², ar) atom carrying the methoxy group. The remaining methoxy groups at C(6), C(8)

and C(4') have torsions around the C(sp², ar)—O(methoxy) bond close to 90°. The angles at the C(sp², ar) atoms are close to 120° in these cases.

The mean C(sp², ar)—O(methoxy) distances and the mean O(methoxy)—C(sp³) distance in this structure are 1.369 (11) and 1.432 (6) Å respectively.

The packing of the molecules [molecular plotting program of Radhakrishnan (1982)] is shown in Fig. 3. As observed in other flavones with OH at position 5, this OH group is (intramolecularly) hydrogen bonded to the nearby carbonyl O(2), with an H(O6)···O(2) distance of 1.87 (9) and O(6)···O(2) of 2.564 (4) Å and angle O(6)—H(O6)···O(2) 123 (6)°. There are no other inter- or intramolecular hydrogen bonds in the structure. All intermolecular contacts correspond to normal van der Waals interactions and thus the crystal is a molecular crystal.

We thank Mr Thirugnanasambandam, Madras Medical College, Madras, for supplying the compound.

References

- BASTIANSEN, O. & TRÆTTEBERG, M. (1962). *Tetrahedron*, **17**, 147–154.
- BERGSTROM, R., SATYSHUR, K. & SUNDARALINGAM, M. (1981). *Acta Cryst.* **B37**, 254–258.
- GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). *UCLALS1*, Univ. of California, Los Angeles, USA.
- HAYASHI, T., KAWAI, S., OHNO, T., IITAKA, Y. & AKIMOTO, T. (1974). *Chem. Pharm. Bull.* **22**, 1219–26.
- HEGNAUER, R. (1973). *Chemotaxonomie des Pflanzen Bandlo Birkhauser*. Basel.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- LEE, T. J., LU, T. H. & ZEE, S. H. (1974). *Tetrahedron Lett.* pp. 2081–2082.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Molecular Structures and Dimensions* (1972). Vol. A1, edited by O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Patterson & W. G. Town, p. S2. Utrecht: Oosthoek.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 291. Cornell Univ. Press.
- RADHAKRISHNAN, R. (1982). *J. Appl. Cryst.* **15**, 135–136.
- ROSSI, M., CANTRELL, J. S., FARBER, A. J., DYOTT, T., CARREL, H. L. & GLUSKER, J. P. (1980). *Cancer Res.* **40**, 2774–2784.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- VIJAYALAKSHMI, J., RAJAN, S. S., SRINIVASAN, R. & RAMACHANDRAN NAIR, A. G. (1986). *Acta Cryst.* **C42**, 1752–1754.

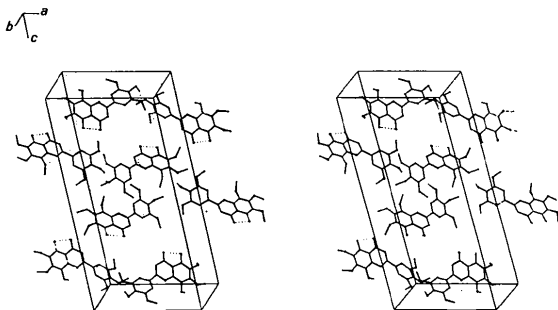


Fig. 3. Stereo packing diagram of the molecules.