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The lattice constants of limonin and some of its derivatives.

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As a preliminary to the crystal structure investigation of the bitter principle limonin ($C_{26}H_{30}O_8$), the unit-cell parameters and space groups of that compound and a number of its derivatives were determined.

Limonin, its acetic acid and methanol solvates all crystallise in the orthorhombic system, the first as large plates from methylene chloride, the second as prismatic needles from any solvent combination containing acetic acid, and the third as long prismatic needles from methanol–methylene chloride (but not from either pure solvent). These last crystals were unstable even in their mother-liquor and had a life-time of only a few days. *Epi*-limonol iodoacetate and chloroacetate both yield crystals in the monoclinic system from solutions in acetone-water; the former appears as plates, the latter as thin needles. For each compound precession photographs, marked with fiducial spots, taken with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) were used to obtain the crystallographic data presented in Table 1. In the case of the orthorhombic crystals the diffraction conditions in each case were that ($h00$) was present only for $h = 2n$, ($0k0$) only for $k = 2n$, and ($00l$) only for $l = 2n$; hence the space groups were each determined uniquely to be $P2_12_12_1$–D_2^4. In the case of the monoclinic crystals ($0k0$) was present only for $k = 2n$; hence their space groups were either $P2_1$–C_2^2 or $P2_1/m$–C_{2h}^2. The latter was rejected as being incompatible with the fact that both compounds were optically active.

The crystallographic data for limonin and its acetic acid solvate are similar to those reported earlier by Jones & Palmer (1949). Their unit-cell parameters were:

for limonin, 14·53, 17·75, 8·88 Å;
for the acetic acid solvate, 12·75, 16·85, 12·40 Å.

The solvate from methanol–methylene chloride was prepared under conditions previously described for the preparation of a methylene chloride solvate (Emerson, 1948). Chemical analysis of the crystals obtained in this investigation, together with the agreement between their pycnometrically determined density and that calculated on the assumption that the included molecular species was methanol, suggests a methanol-solvated limonin derivative.

The only suitable compounds for detailed structural investigation appeared to be the chloro- and iodoacetates of *epi*-limonol. Of these the former has the much smaller linear absorption coefficient for X-rays (μ), and has a smaller unit cell containing only two chemical molecules related by the screw axis. On the other hand the symmetry relationship between the two phase-determining atoms in the chloroacetate would have the disadvantage of introducing the ambiguity of a false symmetry centre in the subsequent analysis. Due consideration of the various factors led to the conclusion that the iodoacetate offered more promise of success, in spite of the fact that this structure is complicated by having four molecules in the unit cell and two in the asymmetric crystal unit, thus doubling the number of atomic positions to be determined.

A structural investigation based on three-dimensional data from the iodoacetate is now in progress.

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References

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Table 1. *Crystallographic data for limonin and its derivatives*

	Limonin	Limonin acetic acid solvate	Limonin methanol solvate	*epi*-Limonol iodoacetate	*epi*-Limonol chloroacetate
Molecular formulae	$C_{26}H_{30}O_8$	$C_{26}H_{30}O_8 . CH_3COOH$	$C_{26}H_{30}O_8 . CH_3OH$	$C_{26}H_{31}O_8(COCH_2I)$	$C_{26}H_{31}O_8(COCH_2Cl) . H_2O$
a (Å)	14·52±0·02	12·73±0·02	12·89±0·02	15·03±0·02	12·26±0·02
b (Å)	17·74±0·02	16·79±0·02	16·59±0·02	12·36±0·02	10·92±0·02
c (Å)	8·87±0·02	12·42±0·02	12·19±0·02	15·93±0·02	11·50±0·02
β	90° 0′	90° 0′	90° 0′	95° 12′±15′	93° 15′±15′
U (Å^3)	2284·8	2654·6	2606·8	2952·7	1836·4
Z	4	4	4	4	2
D_m (g.cm.$^{-3}$)	1·366	1·313	1·260	1·426	1·220
D_x (g.cm.$^{-3}$)	1·366	1·315	1·280	1·441	1·228
μ (cm.$^{-1}$) $\lambda = 0{\cdot}7107$ Å	1·2	1·2	1·2	2·0	12·3
Mol.wt.	470·5	530·6	502·5	640·5	568·0
Space group	$P2_12_12_1$–D_2^4	$P2_12_12_1$–D_2^4	$P2_12_12_1$–D_2^4	$P2_1$–C_2^2	$P2_1$–C_2^2