Crystal physics
Colour: colourless, transparent;
Melting point: 179–183°C.

Aldosterone: 11\beta,18-oxido-\Delta^4-pregnene-18,21-diol-3,20-dione

Crystal geometry
Laue class: monoclinic;
Space group: \( P2_1 \).

\[ a = 12.288 \pm 0.010, \quad b = 6.046 \pm 0.010, \quad c = 13.249 \pm 0.010 \text{ Å}; \]
\[ \alpha = 90, \quad \beta = 107.35 \pm 0.010, \quad \gamma = 90°; \]

\[ V = 939.4 \pm 3.0 \text{ Å}^3, \]
\[ Z = 2; \]
\[ D_x = 1.337 \pm 0.010 \text{ g.cm}^{-3}, \]
\[ D_m = 1.345 \pm 0.010 \text{ g.cm}^{-3}. \]

Crystal physics
Colour: colourless, transparent;
Melting point: 113–115°C.

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Reference
may depend on the wavelength of the radiation used or on the spacings of an internal standard (§§ 2.2 and especially 3.2). If it is a wavelength, the numerical value assumed for the wavelength should be given, together with particulars of the filter or monochromator if used. If an internal standard is used to establish the spacing scale, the standard should be named and its assumed parameter(s) given.

1.4. Temperature

The temperature of the specimen should be given. 'Room temperature' may vary by 15°C or more, depending on the laboratory and the time of the year.

1.5. Crystallographic data

It has become conventional to list the spacings (d values) and intensities, either visually estimated, densitometric, or diffractometric. The methods of determining these are considered further in sections 2 and 3 below. Certain functions of d such as \( Q = d^{-2} \) have advantages over the spacings themselves (§ 4). If a unit cell is known, either from single-crystal data or from indexing the pattern (§ 4 below) the cell should be given together with the contents of the unit cell (2) and the lines indexed. The space group should be given if known. Any lines that cannot be accounted for by the unit cell and space group should be specially designated. Observed spacings should not be replaced by spacings calculated from the unit cell. 'Reference intensities' (§§ 2.3 and especially 5.2) should be given whenever possible.

1.6. Other data

It is convenient if other data relating to the material and its identification can be given. These will include the colour of the powder, optical data (if known) for crystals of the material, density, and melting point. Any available information about polymorphism of the substance should be given, and properties that influence its handling, such as deliquescence, efflorescence, toxicity and the like.

1.7. References

In many cases not all the above data will be determined by the authors of the publication. When data (such as the unit cell, density, chemical analysis, etc.) are not derived directly from observations made by the authors, adequate literature references should be given.

2. Experimental methods

2.1. Apparatus

The usual instruments used for obtaining powder data for identification are the Debye–Scherrer camera, the focusing camera, and the powder diffractometer. All are available in a range of radii, common values being between 28 and 100 mm for cameras and 100 and 200 mm for diffractometers. The focusing principle used in focusing cameras and diffractometers admits – without loss of intensity – a much better angular resolution than a Debye–Scherrer camera of corresponding size and, when used with a focusing monochromator (as in the Guinier camera and its modifications and in some diffractometer arrangements) a great measure of achromaticity is achieved as well. The resolution of a Guinier camera or diffractometer in practice may, therefore, be of the order of three to five times as good as that of a Debye–Scherrer camera. These figures should be taken only as a rough guide, since the resolution is affected by specimen size, specimen transparency, and collimation conditions, as well as instrument radius and wavelength. The advantage is particularly evident in the low-angle region, where the lines most important for identification occur. Debye–Scherrer patterns, however, can be made with much smaller quantities of the material than normal focusing-camera or diffractometer specimens, and occasionally this may be an overriding consideration. They are ordinarily sufficient for identification, but for standard file patterns focusing-camera or diffractometer data are preferable, since it is always possible to deduce from a pattern obtained with good resolution what a pattern obtained with poorer resolution would be like, but not vice versa.

2.2. Features of pattern important for identification

The radiation used to obtain diffraction patterns is most commonly Cu Kα, but other wavelengths from Mo Kα to Cr Kα are also employed. An examination of the Powder Data File of the Joint Committee* which contains about 13000 inorganic materials indicates that the number of lines per pattern is between 10 and 100 with an average of about 35. The majority of the strongest lines of each pattern are found in a range of about 50 – 1·5 Å, corresponding to 18 – 60° in 2θ for Cu Kα radiation. About ten per cent of the lines occur at 2θ less than 18°. The 5 or 10 strongest lines are of major importance and demand the highest accuracy of measurement.

(i) These lines represent the simpler (hkl) planes and are more useful for identification than the high-order lines, which become more numerous and weaker with increasing 2θ.

(ii) If the diffraction pattern is weak, either because the phase is only a minor constituent of a mixture or because the phase does not diffract X-rays strongly, then only the strongest lines of the pattern will be observable.

(iii) A special study (Rinn & Hanawalt, 1968) of the first 14 sets of Joint Committee Powder Data File (7017 inorganic patterns) showed that if the lines of each pattern are arranged in order of intensity, it requires relatively few lines to distinguish each pattern from all others in the file. The first count was made by assuming for simplicity that two lines coincide if their d values do not differ by more than 0·03 Å, corresponding to an assumed error of ±0·015Å throughout the range of d values. Under these conditions of the 7017 patterns listed all but 275 can be identified by their five strongest lines. Most of the 275 patterns could be distinguished if the accuracy of the measurements were increased to ±0·1° 2θ. The remaining patterns included many from isostructural substances.

In the above studies intensity values were only used to determine the order of strongest lines of a pattern. If the intensity values were used as another parameter of the 'match', then the numbers of patterns identifiable by their three strongest lines would be greatly increased.

It is recommended that an internal standard be used for high-accuracy measurements of d values and intensities. For details see § 5 and Swanson, Morris & Evans (1966).

* Most users of powder data will be familiar with the card index of powder patterns compiled and now also published by the Joint Committee on Powder Diffraction Standards, Inc. (formerly published by the American Society for Testing and Materials) 1845 Walnut St., Philadelphia, Pennsylvania 19103, U.S.A. It is often, though misleadingly, referred to as the 'ASTM file'. The term 'Joint Committee Powder Data File' is preferable.
3. Derivation of spacings

3.1. Definition of spacing

It has become a convention to express powder diffraction data as a list of spacings and intensities. The spacings could be defined with reference to the crystal geometry, but they are more often regarded as a wavelength-independent measure of the observed diffraction angles 2θ through the relation

$$d = \frac{\lambda}{2 \sin \theta} \quad (1)$$

It should be emphasized that from this standpoint (1) is to be regarded as a definition of d, not as a physical law.

3.2. Standard of spacings

It is recommended that authors state explicitly (i) whether they have used an internal standard, (ii) if not, whether they have applied important corrections, such as the absorption correction for Debye–Scherrer cameras.

The accuracy of 2θ measurements may be greatly enhanced by the use of an internal standard. This means an admixed standard substance, the lines of which are measured together with those of the specimen. Final 2θ values are obtained by interpolation between the standard lines. If the pattern contains lines at low θ, two exposures with different standards may have to be made. Some suitable standards are tungsten, corundum (α-Al₂O₃) silicon and KCl at medium angles and alum and PbSO₄ at low angles.*

3.3. Listing of spacings

The range of d or 2θ covered by the camera or diffractometer should be stated. It is recommended that not only d but also the value of $Q = \frac{1}{d^2}$ be given for each line.

The list of d has the drawback of giving a distorted image of the powder pattern. Other functions of $\sin^2 \theta$ can be chosen which yield a more faithful mapping. Among these, the quantity

$$Q = 4 \sin^2 \frac{\theta}{\lambda}^2 = \frac{1}{d^2} \quad (2)$$

has the additional advantage that it allows a quick review of indexing relations, since Q, because of Bragg’s law, is equal to a homogeneous quadratic form in h, k, and l (§4). The use of $\sin^2 \theta$ (which is proportional to Q) should be avoided because it makes intercomparisons of patterns taken with different wavelengths unnecessarily difficult.

3.4. Estimates of accuracy

In Fig. 1 the errors in $d$ and $Q$, caused by an error of 0.01° in 2θ for Cu Kα radiation, as a function of θ, d or Q. easy reference. Up to $2\theta = 90^\circ$, the two errors do not deviate more than 15% from

$$\Delta d = \text{constant} \times d^2, \quad (3)$$

$$\Delta Q = \text{constant} \times Q^{1/2}. \quad (4)$$

All considerations of accuracy and of discrepancies, when referred to d values, are hampered by this distortion, because each $\Delta d$ is significant only in a very limited range of the pattern. For the same reason, the number of significant decimal places in d must be considered for each region of the pattern. Usually this number has to jump twice in the range of the d list. It is advisable to place the jumps on the safe side, so as to avoid unduly large round-off errors.

The estimated overall accuracy should, if possible, be stated as an average error in 2θ. For a rough indication, an average error in Q may also be useful, though the error in Q will usually vary more than that in 2θ. Indication of an error in d is impractical for the reasons discussed above.

3.5. Values calculated from cell parameters

Values of Q calculated from unit-cell data can be given for comparative purposes. They should be listed separately and in such a way that confusion with observed values is avoided. Partial replacement of observed values (either of d or Q) by calculated ones is undesirable, because the latter—though sometimes inherently much more accurate—depend on an indexing which is most often based largely on the lines in question (§4).

4. Indexing of patterns and derivation of cell parameters

4.1. Basis of indexing

Both indexing and unit-cell determination are based on the fact that, theoretically, $Q = \frac{1}{d^2}$ is a homogeneous...
quadratic form in \( h, k, \) and \( l \):

\[
Q = Ah^2 + Bk^2 + Ck^2 + Dkl + Eh + Fhk,
\]

with coefficients \( A \) to \( F \) depending on the reciprocal unit-cell parameters in the following way:

\[
A = (a*)^2, \quad B = (b*)^2, \quad C = (c*)^2, \quad D = 2b*c*cos \alpha*,
E = 2a*e*cos \beta*, \quad F = 2a*b*cos \gamma*.
\]

The complete relations between the reciprocal parameters \( a* \) to \( y* \) and the actual cell parameters \( a \) to \( \gamma \) are given in \textit{International Tables for X-ray Crystallography} (1959). Expressions for \( a \) to \( y \) as functions of \( A \) to \( E \) are given by Visser (1969).

### 4.2. Calculated values of \( Q \)

If the unit cell is supposedly known, the constants \( A \) to \( F \) can be calculated and the resulting list of \( Q(hk) \), ordered in a sequence of increasing \( Q \), can be compared with the observed values of \( Q \). If the majority of discrepancies is not larger than the expected error (derived from the expected error in \( \theta \), as in §3.4) both the indexing and the unit cell will be substantially correct. The cell parameters should be refined on the basis of those lines which have unambiguous indices. After one or more steps of such a least-squares refinement, a few lines may still have improbably large discrepancies. These should be marked in the list; the Powder Data File of the Joint Committee uses the indication nc (non cell).

### 4.3. Determination and confirmation of unit cell

If the unit cell is not known \textit{a priori}, an indexing may be found by trial and error or by computer methods. These have been reviewed by de Wolff (1962). The further procedure is exactly as in §4.2. In this case, however, a satisfactory agreement of calculated and observed of \( Q \) is not sufficient to make the unit cell convincing, because now the link with independent data from other sources is missing. The following quantity is recommended as an index of reliability (de Wolff, 1968):

\[
M = Q_{20}/(2dQ \cdot N_{20})
\]

where \( Q_{20} \) = value of \( Q \) for the 20th observed line (not counting 'nc' lines); \( dQ \) = discrepancy, \( |Q_{obs} - Q_{cal} | \) averaged over the first 20 observed and indexed lines; \( N_{20} \) = number of distinct \( Q \) values smaller then \( Q_{20} \), calculated according to equation (1), not including any systematic absences. If the indexing has been performed as in §4.2, \( dQ \) will be close to the average expected error in \( Q \) mentioned in §3.4. The index \( M \) is the ratio of two average discrepancies (i) the expected discrepancy \( Q_{20}/N_{20} \) for an arbitrary unit cell yielding the same density of calculated lines as the cell proposed, and (ii) the actual discrepancy \( dQ \). Material gathered so far has indicated that incorrect indexings (disproved by single-crystal methods) may have values of \( M \) up to 5, and that correct indexings have \( M \) seldom less than 10 but usually between 10 and 40.

### 4.4. Derivation of space group

If the space group is not known from single-crystal work, it is desirable to state the information derived from the indexed powder pattern.

This information is less reliable than that from single-crystal investigations. Both the relatively high background and the restricted \( \theta \) range of reliably indexed lines increase the chance that an apparently systematic absence is actually a fortuitous one. General (centring) extinctions are still quite reliable, because of the number of absent lines involved. However, glide planes and in particular screw axes often cannot be regarded as well established.

Quite apart from reliability, powders may yield less complete information than single crystals, because Laue groups such as \( 4/m \) and \( 4/mmm \) are in several cases indistinguishable. This makes it more difficult to state the findings in a compact form. For triclinic, monoclinic and orthorhombic crystals, the symbolism proposed by Donnay & Kennard (1964) may be used, since in these systems there is no fundamental difference between powder and single-crystal data.

In the systems of higher symmetry adoption of these symbols may be awkward; for example in a primitive hexagonal lattice five different symbols (\( P6/3*, P6/3, P3*1, P31*, 3P* \)) correspond to a lack of systematic absences. For powder work the older aspect symbols (\textit{International Tables for X-ray Crystallography}, 1962) are more suitable, but require the addition of the qualification ‘trigonal’, ‘tetragonal’, ‘hexagonal’, or ‘cubic’.

### 5. Intensities

#### 5.1. Indication and measurement of intensities

It is usual to give the intensities of the diffraction lines as percentages, so that the strongest one is tabulated as 100. The Joint Committee† qualifies this by the proviso that the strongest line for this purpose must be chosen from those occurring with \( \theta \) less than 90° for Cu K\( \alpha \) radiation (\( d > 1.0 \)).

Ideally it would be preferable to use integrated intensities, but because of overlapping and other reasons this is impracticable. It is recommended, therefore, that the standard method of tabulation be peak diffractometric intensities expressed as percentages of the peak intensity of the strongest lines in the front-reflexion region for copper radiation.

Ordinarily the use of a different radiation will not change the observed intensity enough to disturb identification, but care must be taken to choose the strongest line from the \( d \) range corresponding to the \( \theta \) range specified for copper. Line broadening may produce systematic variation of peak intensity with Bragg angle or with indices of reflexion, and specimens exhibiting it require special care. Noticeably broadened lines are indicated in the Joint Committee Powder Data File by the letter 'b': this normally refers to unresolved multiplets rather than diffraction broadening.

#### 5.1.1. If a diffractometer is used

The diffraction intensity is usually recorded as a function of Bragg angle and the evaluation of line intensity is a matter of interpretation of the chart. Either peak values or integrated intensities (both corrected for background) can be stated. Peak intensities will, in general, yield a satisfactory characteristic of the pattern.

Special care should be taken to avoid five errors not easily detectable in a diffractometer record.

† The Joint Committee now (1970) proposes the proviso \( d > 1.000 \) Å, as it is independent of wavelength.
(i) Statistical fluctuations due to large crystallites. These can be detected by repeating the measurement on two or more specimens. If reduction of crystallite size is difficult, rotating the specimen in its own plane will greatly help to reduce the fluctuations.

(ii) Unequal width of lines due to anisotropic particle-size broadening. If this occurs, either integrated intensities should be measured or the particularly broad lines marked ‘b’ in the list of peak values.

(iii) Preferred orientation. This can severely influence the intensities, especially for platy and for needle-shaped crystallites. Diluting the specimen, for example with flour, or embedding it in a cement (such as Canada balsam), followed by regrinding of the hardened mixture, will reduce the effect. It is also advisable to fill the specimen holder from the side.

(iv) Cold work and grain distortion can adversely affect the quality of the diffraction pattern. Annealing the material at the proper temperature can reduce this distortion.

(v) Precautions should be taken against drift of the counter or apparatus.

5.1.2. Films obtained with Guinier or Debye-Scherrer cameras can be used as such, by visual estimation or comparison of the lines with a sequence of increasing known exposures of a single line. Visual estimates are, however, often unreliable. Therefore it is strongly recommended that films be measured quantitatively by densitometer or microphotometer. The possible errors (i) – (v) mentioned above are the same. Though they are more easily detected on a film, it is no easier to suppress the effects. The Debye-Scherrer pattern has the extra difficulty of a broad sometimes irregular line shape. The absorption factor is strongly dependent on the Bragg angle and difficult to correct for, so that the Debye-Scherrer technique is likely to yield less accurate intensities.

5.1.3. The absorption factor and certain other geometrical functions of angle differ for the diffractometer and the various types of camera, so that the relative intensities of the diffraction maxima are somewhat different for the different techniques. The differences are not normally great enough to interfere with identification, but may occasionally alter the order of the strongest lines (Hughes, Lewis & Wilson, 1956). There is therefore, good reason for retaining both camera and diffractometric data in the Joint Committee Powder Data File, and for publishing new data obtained by one technique even when data obtained by another technique are already on record.

5.2. Reference intensities

It is recommended to state, in addition to relative intensities, a reference intensity which is the intensity of the strongest line as a percentage of the intensity of the $d = 2.085$ Å line of α-alumina, measured in the diffraction pattern of a mixture of equal parts by weight of the pure substance and α-alumina. The experiment can be made with another ratio, say $1:R$ parts $\text{Al}_2\text{O}_3$; in that case the observed percentage must be multiplied by $R$. α-Alumina is obtainable as a fine powder, e.g. Linde A, Union Carbide Corporation, East Chicago, Illinois, U.S.A. Other suitable substances such as carbonyl nickel, magnesium oxide or potassium chloride can also be used. In this case, the results should be converted to the above-defined value by measuring the reference intensity (with respect to alumina) of the standard line used. For further details see Swanson, McMurdie, Morris & Evans (1968).

In order to allow a rough quantitative analysis of multiphase samples, it is desirable that the intensities of at least one line of the pure components be known also on an absolute scale. Both the quantitative analysis and the derivation of such absolute figures are easy if use is made of an internal standard admixed in a known proportion. One only has to measure the ratio of the intensity of a suitable line of the compound and of the standard substance. The unknown content then follows from the fact that this intensity ratio is equal to the product of the corresponding ratio of concentrations and constants factor (determined entirely by the choice of the two lines). Hence it is sufficient to state the intensity ratio for a mixture of known proportions of pure compound plus standard. Since this does not involve any really absolute measurement, the resulting figure is called a reference intensity. In principle, the choice of standard substance and of the line pair is arbitrary. The recommended choice is the procedure followed by the National Bureau of Standards of the U.S.A.

Neither the standard substance nor the specimen preparation for this measurement need be the same as that used in measuring diffraction angles (§ 3.2.). The measures taken to suppress preferred orientation, in particular, may well make the specimen unsuitable for precise angle measurement. Hence it is better to perform the reference-intensity determination on a separate specimen.

6. Structure determination

Except for simple substances, structure determination by means of powder data alone is unusual, but must be undertaken occasionally. The most satisfactory validation of a structure determination based on powder data is probably the publication of a comparison of the directly observed intensities with those calculated from the structure, allowance being made in the calculated intensities for the trigonometric factors, temperature factors, absorption, and other such effects. Since the number of observed powder lines is small in comparison with the number of reflexions obtainable in single-crystal work, publication of this comparison does not ordinarily present the same problems as the publication of $F$ tables (III of Kennard, Speakman & Donnan, 1967). Overlapping and coincidence of lines makes a calculation of the usual $R$ factor difficult, but a modified one based on directly observed intensities:

$$R_I = \frac{\sum |I_{obs} - I_{calc}|}{\sum I_{obs}}$$

may be useful.

Since in powder work more reflexions are unobserved than in single-crystal analysis, it is essential that the summation be extended over all (including unobserved) reflexions.

References


Constructing crystal models

The usefulness of models for examining trial crystal structures and for instructional purposes is unquestioned. A new construction method is given, such that crystal models can also serve to demonstrate phase transformations involving the collinear shift of part of the unit-cell contents. Fig. 1 indicates a model of the postulated product (space group \( P\overline{3}m1-D_{3d}^{2} \)) of the high temperature phase transformation of TiNi (CsCl type) involving a shift of one third of the atoms along the [111] cubic direction (Carter, 1968). The CsCl type structure is recovered from the model as shown by supporting the appropriate rods in an elevated position by the use of paper clips above the plastic top \( P \).

Other new construction features include the base \( B \) which is made of 2 inch thick hexagonal honeycomb surrounded by an aluminum frame. The commercial honeycomb consists of aluminum foil (gauge 0-0015, alloy No. 5052) with a \( \frac{1}{4} \) inch hexagonal cell size.* The painted composition cork balls are predrilled and mounted on a sharpened drill rod (\( \frac{1}{8} \) inch diameter). These rods are positioned within the larger honeycomb cell and simultaneously made vertical by the use of a toothpick or a short section of drill rod (2\( \frac{1}{2} \) inches long), placed in the same honeycomb cell. It has been found that the honeycomb method of positioning the rods is superior to that involving perforated metal sheets separated by a spacer, adapted from Dr G. Bergman’s use, ca. 1952. (Also see Bretherton & Kennard, 1969.) Not only are perforated metal sheets with the proper hole size and spacing sometimes unavailable, but care must be exercised in their relative alignment and, further, the rods must be placed through matching holes in the two sheets. These difficulties are obviated with the use of the honeycomb construction. The false bottom \( F \) of Fig. 1 replaces the usual flat sheet and provides the extra rod length necessary to prevent the withdrawal of the rods from the base during the vertical movement of the rods involved in the transformation. The rod positions in the honeycomb are readily indicated on a sheet of paper containing projected cell dimensions, etc. (usually marked one Ångstrom to the inch). A top (as \( P \) in Fig. 1) is useful for tall constructions and is predrilled with conical shaped holes on the bottom.

A convenient template (\( T \)) for the positioning of the cork balls (usually \( \frac{1}{4} \) inch or \( \frac{3}{4} \) inch) on the rods is readily constructed of aluminum bars (\( 3 \times \frac{1}{2} \times \frac{1}{4} \) inch) drilled to slip over flexaframe rod with a tightening thumbscrew and notched (\( \frac{1}{2} \times \frac{1}{4} \) inch) to hold the drill rod. One of these bars inverted can serve as the template base (\( TB \)). For many structures only \( TB \) need be readjusted in going from one equivalent atom string to another. The small diameter of the drill rod gives a pleasant open structure, but to prevent bending, rods of this size require that the positions of the cork balls be adjusted by holding the rod with a pair of pliers and pulling the balls, rather than pushing them, into position.

References
