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The anomalous thermal expansion of KI at low temperatures.

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Recently Srinivasan (1955) reported that the thermal expansion coefficient of KI, determined by interferometric methods, showed two maxima (at −95 and −40 °C.) and two minima (at −60 and −25 °C.) in the low-temperature range. He found that this anomalous behaviour was exhibited by KI crystals obtained from different sources. In view of the controversy regarding the values of the thermal expansion coefficient obtained by interferometric and X-ray methods, an accurate determination of the lattice expansion of KI was undertaken to see whether these anomalies persisted when the measurements were made by X-ray methods. This work also formed a part of the wider programme in this laboratory of determining any apparent discrepancies between the thermal expansion coefficients of crystals measured by X-ray and macroscopic methods.

This investigation was carried out with the low temperature X-ray camera designed in this laboratory (Viswamitra, 1959; Viswamitra & Ramaseshan, 1960), using the Lonsdale-Smith (1941) method of cooling with liquid air. Any steady temperature between −185 and 200 °C. could be obtained by adjusting the heating currents in the two heaters below and above the crystal. The crystal chamber was surrounded by a cellophane strip which not only decreased any fluctuations in the temperature of the crystal but also prevented the deposition of ice on the specimen. Two accurately calibrated iron–constantan thermocouples measured the temperatures at the base and top of the crystal. The temperature variation was less than 0·5 °C. along the length of the specimen. The temperature itself was constant to ±1 °C. and it could be measured to an accuracy of ±0·2 °C.

The specimens were cut from large single crystals grown by the Kyropoulos technique using Merck's Analytical Reagent. These crystals were first annealed at 400 °C. for a few hours. The experimental samples were ground to about 0·2 mm. diameter and 2 mm. length and were fixed on to the X-ray camera with silico–phosphate cement. They were subjected to alternate cycles of heating and cooling to avoid any possible tilting during the course of the experiments.

The 840 reflexions using Cu $K\alpha_1$ and Cu $K\alpha_2$ radiations were obtained using a Unicam single-crystal goniometer with a specially designed back-reflexion cassette with a central collimator. The reflexions were recorded symmetrically on both sides of the collimator. On each film the reflexions obtained at two or three temperatures were recorded. The distance from the specimen to the film-holder (11·45 cm.) was accurately determined from several measurements using 99·99% pure aluminium powder as the standard. Fig. 1 gives the variation of the thermal expansion coefficient with temperature for the two specimens investigated. The range of experimental errors involved in each measurement is also indicated.

The expansion coefficients for the range 30 to 200 °C. are reproducible to within ±3%. These values agree well with those obtained by Connell & Martin (1951) using the X-ray method. They also agree well with the macroscopic values recorded by Srinivasan (1955) and Gott (1942), suggesting strongly that no significant discrepancies exist between macroscopic and lattice expansions in this region.

There is no doubt that the thermal expansion coefficient obtained by the X-ray method shows the anomalies reported by Srinivasan in his macroscopic determinations. However the actual mean values of α at the two maxima and the two minima [$\alpha_{-90}=40{\cdot}0$, $\alpha_{-60}=22{\cdot}0$, $\alpha_{-40}=38{\cdot}0$ and $\alpha_{-15}=30{\cdot}0$ $(\times 10^{-6})$] depend on the specimens and on the experimental conditions and are somewhat different from the corresponding values [38·0, 30·0, 36·0, 32·0 $(\times 10^{-6})$] obtained by Srinivasan. How far these differences are significant we cannot yet say. Repeated measurements made while the crystals were cooled from 200 to −185 °C. gave practically the same thermal expansion coefficients as those obtained when the specimens were heated from liquid–air temperature to 200 °C. The anomalies observed are not therefore due to any defects that can easily be annealed out in this range of temperature.

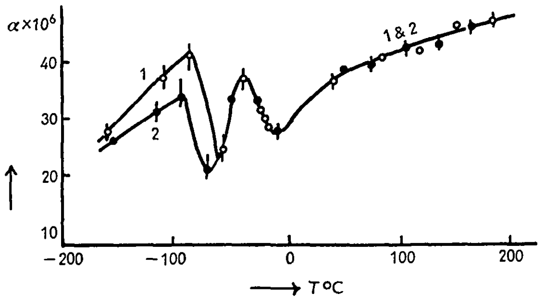

Fig. 1. The thermal expansion of KI.

There are many difficulties in attempting to present any satisfactory explanation for the observed anomalies. A model used by Schottky to explain such anomalies assumes that an atom or ion may exist in two or more energy states. With the increase of the temperature of the crystal a transfer of the atoms from a lower to a higher energy state occurs and this is accompanied by anomalies in the thermal expansion coefficient and the specific heat (Ruhemann, 1937). One could easily conceive of the iodine ion possessing two such states particularly as it is so highly polarizable. Unfortunately the experiments of Berg & Morrison (1957) do not show any such anomalies in the specific heat of KI. One is however, not very certain whether their measurements are sufficiently accurate to detect these small anomalies.

A second possible approach is to assume that electrons are trapped in the Schottky vacancies (10^{18} cm.$^{-3}$) that are known to exist in the alkali halides (Straumanis, 1953). It is now fairly well established that the number of these Schottky vacancies present in alkali halides is independent of the temperature (provided $t < 550$ °C.) and these cannot be easily annealed out (Etzel & Maurer, 1950). As the temperature is raised the electrons captured in the vacancies are released causing an outward expansion of the lattice due to the change in the electric field. This expansion would be superimposed on the regular thermal expansion and would therefore manifest itself as an anomaly. One has to postulate a rather complex process of electron capture and release if one is to explain the two maxima and minima observed in KI.

It is quite suggestive that KI exhibits thermoluminescence peaks at the same temperatures (-90 and -40 °C.) at which it exhibits thermal expansion anomalies (Sharma, 1952). However KCl which shows similar thermoluminescence does not exhibit any anomalies in lattice expansion at low temperatures. It is felt that very much more accurate experimentation, particularly on the thermal expansion of other alkali iodides as also measurements of thermoluminescence, paramagnetic resonance etc., would be necessary before any convincing explanation could be offered for the anomalies reported in this paper.

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Crystallographic data for hydroxydammarenone II.

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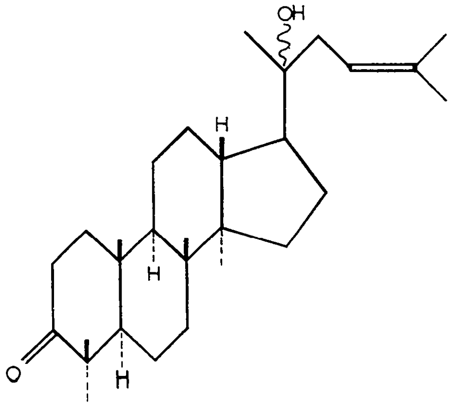
Hydroxydammarenone II, otherwise earlier known as dipterocarpol, is a triterpene constituent of dammar resin and is obtainable from several members of the dipterocarpaceae. This study was carried out to establish the proposed formula $C_{30}H_{50}O_2$; later work has shown it to have the constitution:



(See Mills & Werner, 1955, 1956; Mills, 1956; Cosserat, Ourisson & Takahashi, 1956; Godson, King & King, 1956; Biellmann, Crabbé & Ourisson, 1958).

The crystals, kindly supplied by Prof. G. Ourisson, had m.p. 134–136 °C., $[\alpha]_D = +66°$. They are colourless blocks elongated along [100], having (001) prominent, and bounded otherwise by either (010) or {011}, and {110}. The unit cell is orthorhombic with

a = 7·58 Å D_o = 1·10$_5$ g.cm.$^{-3}$
b = 11·90 Å D_c = 1·101 g.cm.$^{-3}$
c = 29·6 Å Z = 4
U = 2670 Å^3

The space group was determined uniquely from the systematic absences as $P2_12_12_1$. The calculated molecular weight is 444·2 ± 2·5, and the value of D_c given above is based on $C_{30}H_{50}O_2$ (mol.wt. = 442·7).

The axes of the indicatrix lie as follows:

$$\alpha \parallel \mathbf{b}$$
$$\beta \parallel \mathbf{a}$$
$$\gamma \parallel \mathbf{c}$$

The optic axes lie outside the field of view when viewed parallel to **c**, and the α–β birefringence is very marked. This suggests a mode of packing of the molecules approximately parallel to (010) and with their main length along **c**, and this is supported by the outstanding strength of 020 and 022.

No further work on this substance is contemplated.

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