

ART. XXXVII.—*On the Crystal Form of Borneol and Isoborneol*; by WM. H. HOBBS.

IN a recent paper by Bertram and Walbaum\* on an isomer of borneol ( $C_{10}H_{18}O$ ) which they have called isoborneol, Traube has described both this substance and borneol from a crystallographical standpoint. The borneol examined was obtained by reduction of camphor, had a melting point of  $206^{\circ}$ – $207^{\circ}$ , and was dextro-rotatory. The symmetry of both borneol and isoborneol as determined by Traube is hexagonal, the combination in each case being the basal pinacoid with the pyramid and prism. The chief differences between the two substances he finds to be the greater double refraction of isoborneol, and its positive optical character, borneol being optically negative. The axial ratio of borneol he determined to be exactly double that of isoborneol.

Three samples of the alcohol  $C_{10}H_{18}O$  were given me for examination to determine whether they are borneol or isoborneol. They were prepared in the School of Pharmacy of the University of Wisconsin by Mr. Carl G. Hunkel, whose study of them will be published in the *Pharmaceutische Rundschau*. The samples were prepared, one from the oil of black spruce (*Picea nigra*) in which the alcohol is contained as acetic ester, a second from the oil of the fir balsam (*Abies balsamia*), and the third from the oil of turpentine in benzene. The crystals in all these samples are larger and more highly modified than those described by Traube, and their examination has brought out new facts concerning their crystallography and physical properties. The surest basis of comparison with the crystals described by Traube has been the degree of double refraction. The crystals obtained from *Picea nigra* and *Abies balsamia* in this respect correspond exactly with the borneol of Traube's study. The crystals in the sample obtained from turpentine, on the other hand, correspond with his isoborneol so far as the degree of double refraction is concerned, *but they are always optically negative*, in this respect agreeing with borneol. It is therefore not certain that this substance is identical with the isoborneol of Bertram and Walbaum, but it seems best from all the facts to refer to it for the present as isoborneol. All the samples examined have rhombohedral symmetry. This is clearly shown by the partial occurrence of pyramids, and in the case of the crystals from *Picea nigra* by the tri-symmetric character of pittings on the basal pinacoid. Of the nine pyramidal forms which have been made out on the two substances

\* Ueber Isoborneol, Journ. f. prakt. Chemie, vol. xlix (1894), pp. 1–19.

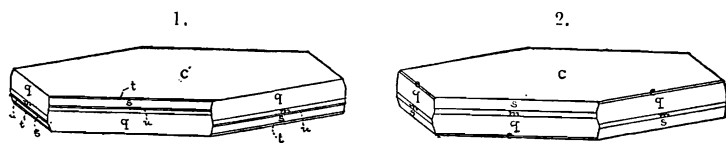
no one occurs in both positive and negative dodecants on the same crystal. The habit of both substances is broadly tabular parallel to the basal pinacoid and the plates have generally a regular hexagonal outline. One variety of isoborneol is, however, observed whose crystals take the form of rhomboidal plates owing to the disappearance of all planes from two of the opposite vertical pairs of dodecants. Although these crystals are identical with the normal variety in regard to their optical properties, they nevertheless represent an entirely different crystal combination. Crystals from all the samples have their faces more or less rounded and the measurements are as a result subject to considerable variations, but they are, nevertheless sufficiently accurate for a determination of all the forms. It is very probable that the axial ratios of borneol and isoborneol are different, since the substances differ so much in their double refraction, but they are certainly nearly identical and the difference is within the limits of error in the reading of angles on the crystals examined. I have therefore used for both substances the axial ratio determined on crystals of borneol from *Picea nigra*.

*Borneol from Picea nigra.* The crystals of this substance examined are thin, colorless, hexagonal plates having a diameter of  $\frac{1}{2}$ –1 cm. and a thickness of 0.5–1 mm. The larger plates have a wide peripheral zone which is occupied by cavities generally filled with mother liquor. The shape of these cavities is somewhat irregular, but they are oriented roughly parallel to the boundaries of the plate. Besides the basal pinacoid the prominent forms are a steep rhombohedron making nearly  $83^\circ$  with the base and a smaller rhombohedral face of opposite sign which makes nearly  $73^\circ$  with the same form. This latter form is undoubtedly the pyramid observed on the substance by Traube and it is therefore chosen for determining the axial ratio. The average of four measurements of the angle included between this face and the base (limits  $71^\circ 25'$  and  $74^\circ 6'$ ) is  $72^\circ 46'$  and if considered the fundamental rhombohedron the axial ratio would be  $\epsilon = 2.79$  (2.83, Traube). It is, however, more convenient to consider this form  $3R(30\bar{3}1)$ , which makes the axial ratio  $\epsilon = 0.93$ .

The observed forms are  $c$ , oP (0001);  $s$ ,  $3R(30\bar{3}1)$ ;  $q$ ,  $-8R(80\bar{8}1)$ ;  $m$ ,  $\infty P(10\bar{1}0)$ ;  $t$ ,  $\frac{2}{3}R(20\bar{2}3)$ ;  $u$ ,  $4R(40\bar{4}1)$ . Figure 1 represents a crystal of borneol. These forms have been determined by the following measurements:

	Measured.		Calculated.
$c \wedge s$ ,	$72^\circ 46'$	(limits $71^\circ 25'$ and $74^\circ 6'$ )	$72^\circ 46'$
$c \wedge q$ ,	82 42	(limits 81 13 and 83 47)	83 22
$c \wedge m$ ,	90 6		90 0
$c \wedge u$ ,	77 11	(limits 76 47 and 77 35)	76 54
$c \wedge t$ ,	34 38		35 37

The crystals have very perfect cleavage parallel to the base and the rhombohedron  $q$ . They are very flexible and care must be used in handling them before measurement. Pittings on the basal pinacoid are trisymmetric with the lines of symmetry meeting at angles of  $120^\circ$ .



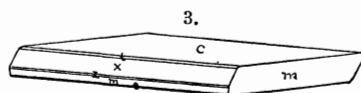
Examined under the polarizing microscope basal sections of these crystals appear isotropic and afford no interference figure. Sections parallel to the prism exhibit very weak double refraction. In sections  $2^{\text{mm}}$ . in thickness the double refraction is faintly perceptible without the use of a quartz plate. In sections  $3^{\text{mm}}$ . in thickness the double refraction is easily determined with use of the quarter undulation mica plate. A considerable number of sections were tested and all were found to be negative. In these sections the interference color only reaches the yellow of the first order when the corresponding axes of the crystal and the mica plate are parallel. These characters therefore agree well with those determined for this substance by Traube. The borneol prepared from *Abies balsamia* is optically identical with this.

*Isoborneol from Turpentine.* As already stated, the symmetry of this substance is the same as that of borneol and the axial ratio is also so nearly identical that the measurements afforded essentially the same results. The determined axial ratio  $c = 0.93$  of borneol is therefore assumed for this substance. The observed forms on the normal type of crystals are:  $c$ ,  $oP$  (0001);  $s$ ,  $3R$  ( $30\bar{3}1$ );  $q$ ,  $-8R$  ( $80\bar{8}1$ );  $m$ ,  $\infty P$  ( $10\bar{1}0$ ); and  $e$ ,  $-4R$  ( $40\bar{4}1$ ). A crystal of this type is represented in figure 2. The above forms were determined by the following measurements:

	Measured.	Average.	Calculated.
$c \wedge s$ ,	$71^\circ 52'$		
	73 24	$72^\circ 38'$	$72^\circ 46'$
$c \wedge q$ ,	81 23		
	81 58	81 41	82 42
$c \wedge m$ ,	90 32	90 32	90 08
$c \wedge e$ ,	75 16	75 10	77 11

The crystals of this substance possessing rhomboidal habit represent quite a different crystal combination from the normal type of crystals. The prominent forms on these crystals (after the base) are the rhombohedron  $\alpha$ ,  $\frac{5}{3}R$  ( $50\bar{5}3$ ) and the

prism  $m$ ,  $\infty P$  (10 $\bar{1}0$ ). Quite frequently the former appears forming two opposite sides of the rhomboid, the other two sides being formed by the prism alone (see figure 3). The form  $x$  may be the one from which Traube determined the axial ratio



of this substance. Determined from the writer's measurements of the position of this plane the axial ratio would be (considering it the fundamental rhombohedron)  $c = 1.589$ , Traube's value being  $c = 1.41$ . The observed forms comprising this combination are:  $c$ ,  $\infty P$  (0001);  $x$ ,  $\frac{5}{3}R$  (50 $\bar{5}3$ );  $m$ ,  $\infty P$  (10 $\bar{1}0$ );  $t$ ,  $\frac{2}{3}R$  (20 $\bar{2}3$ );  $z$ ,  $5R$  (50 $\bar{5}1$ ); and  $e$ ,  $-4R$  (40 $\bar{1}1$ ). The forms  $y$ ,  $\frac{1}{6}R$  and  $r$ ,  $R$  (or  $\frac{1}{11}R$ ) were also observed on one crystal but their sign was not determined. The above forms were identified by means of the following measurements:

	Measured.	Average.	Calculated.
$c \wedge m$ ,	89° 58'		
	89 59	89° 59'	90° 0'
$c \wedge x$ ,	62 31		
	60 17		
	61 26	61 25	60 49
$c \wedge e$ ,	76 44	76 44	76 54
$c \wedge y$ ,	10 30		
	10 43	10 36	10 9
$c \wedge z$ ,	79 31	79 31	79 27
$c \wedge t$ ,	36 54	36 54	35 37
$c \wedge r$ ,	49 31	49 31	$\left\{ \begin{array}{l} R, 47 3 \\ \frac{1}{11}R, 49 32 \end{array} \right.$

As regards color, enclosures, and cleavage, isoborneol seems to differ but little from borneol. The great difference between the two substances is seen when they are examined in prismatic sections in parallel polarized light. A section of borneol in which double refraction is not perceptible, would if prepared from isoborneol yield yellow of the first order. Sections of isoborneol 2<sup>mm</sup>. in thickness yield, when the interference of the crystal is added to that of the quarter undulation mica plate, violet of the second order, whereas similar sections of borneol yield under the same conditions yellow of the first order. The optical character has been tested on a considerable number of crystals and found to be always negative. The substance examined by Traube is reported to be positive.

In conclusion I would express my thanks to Professor Edward Kremers and Mr. Carl G. Hunkel of the Department of Pharmacy, University of Wisconsin, for supplying me with the material studied.

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