exposed even to dry air for more than about 10 hr. began to lose their orienting power on crystals grown from the vapor, but in growth from solution oriented overgrowths were obtained on films several weeks old. The induced polymorphism (Schulz, 1951*b*) of RbBr (which depends on good atomic matching) indicates that also in growth from solution the deposit probably contacts the silver.

It might be objected that during the growth from solution the orientation was induced not by the silver but by the substrate for the silver (the mica or NaCl) acting through imperfections in the silver film. Against such objections are these cases: (1) NaCl on (Ag–NaCl). The orientation (Fig. 2(*b*)) is different from NaCl directly on NaCl (Fig. 2(*a*)). (2) CsCl and CsBr on (Ag–mica). The orienting forces were sufficiently strong to induce the abnormal structure. Directly on mica these salts have the normal structure and a [100] fiber orientation. (3) CsCl and CsBr on (Ag–NaCl). The orientation (Fig. 2(*a*)) is different from that of the direct deposit on NaCl which gives either the abnormal structure with the orientation of Fig. 2(*a*) or the normal structure with the orientation in Fig. 2(*d*). These examples indicate that the silver films are the effective orienting agents.

Conclusion

In addition to showing the actual orientation in a large number of particular cases (Tables 2 and 3) the experiments lead to the following more general conclusions: (1) Although an oriented silver substrate may have a very irregular microscopic geometric surface, it can, nevertheless, induce a definite orientation in a deposit. This indicates that the orienting influence of the substrate is propagated to the deposit across any crystallographic plane as interface. As a consequence it is rather artificial (even if convenient) to speak of matching onto the particular crystallographic plane which happens to be parallel to the macroscopic substrate surface. (2) Factors determining the orientation of a deposit would include (*a*) the relation of its lattice constants to those of the substrate, (*b*) the method of its growth (vapor or solution) and (*c*) electrical conditions at the interface. These results are of importance in the study of corrosion since a typical case is that of an ionic layer forming over a metal substrate (Cabrera & Mott, 1948–49).

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X-ray Studies of the Terpenes. I. Crystallographic Data for α-*l*-Menthol

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The α form of *l*-menthol has been found to be trigonal with space group $C3_1$, $a = 21{\cdot}60 \pm 6$, $c = 6{\cdot}11 \pm 1$ Å and with three molecules in the asymmetric unit. Previous powder work is thus shown to have been interpreted wrongly and is here corrected.

1. Introduction

Menthol has played a prominent part in the development of the study of optical activity in organic materials and, therefore, its chemical constitution and the relations between its isomers have received considerable attention (for a summary see Simonsen, 1947, vol. 1, p. 230). As a result, the number of possible molecular models has been reduced, but an investigation of the stereochemistry, especially at the three asymmetric carbon atoms, is desirable.

Comparatively little, however, has been recorded

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of the physical properties, but enough, nevertheless, to emphasize the need for an investigation of the crystal structure. Wright (1917) has drawn attention to the fact that while the melt is laevo-rotatory, $[\alpha_D] = -0{\cdot}5$ deg.mm.$^{-1}$, yet the normal, stable (α) form is strongly dextro-rotatory, $[\alpha_D] = +2{\cdot}5$ deg.mm.$^{-1}$, for propagation along the optic axis. Such a difference is clearly associated with the crystal structure. Wright (1917) has also described three monotropic modifications, β, γ, δ, formed by abrupt chilling of the melt. So far, owing to their mode of production and short life of but a few minutes, they have been studied only with the polarizing microscope. Their optical properties differ and one of the transitions ($\gamma \rightarrow \alpha$) involves a marked, but unknown, increase of density.

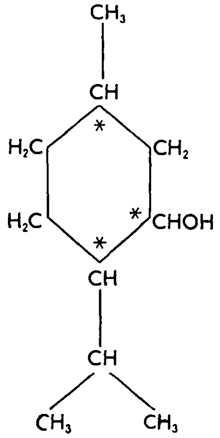

Fig. 1. The asymmetric carbon atoms in menthol are marked with asterisks.

The present X-ray investigation was begun with the hope of establishing directly the molecular and crystal structure of α-*l*-menthol and also in order to examine the polymorphous forms. The structure has, however, proved to be unexpectedly complicated and no conclusions as to either of these objectives can be regarded as satisfactorily established until further studies at low temperatures are completed. Accordingly no attempt is made in this preliminary note to discuss the crystal structure. The only previous X-ray work known to us is a powder investigation by Sidhu (1939), but as a result of our studies with single crystals the powder lines have had to be reindexed. This is discussed in § 3.

2. Single-crystal results

The bulk of the work described was carried out on a commercial sample of natural *l*-menthol of Chinese origin, but concordant results were obtained with a natural specimen from Brazil and also a synthetic menthol (method of synthesis unknown). All three were commercially available pharmaceutical preparations (B.P. standard). In form all the crystals appeared, as reported previously (Wright, 1917; Groth, 1906–19, vol. 3, p. 650), to consist of fragments of hexagonal prisms without regular ends. These proved to be the trigonal prisms $\{11\bar{2}0\}$ and $\{2\bar{1}\bar{1}0\}$. Crystals of a size suitable for X-ray examination evaporated completely in about 48 hr. (m.p. 42° C.); those used were preserved by enclosure in a thin-walled Lindemann glass tube plugged with 'plasticine' or wax.

Photographs taken for oscillations about the *c* axis proved rather difficult to index for the following reasons:

(1) The sheets of the reciprocal lattice perpendicular to [00.1] had the form of a fine-mesh trigonal lattice so that even 5° oscillations often led to ambiguity in the indexing. (Cu $K\alpha$ radiation was used throughout.)

(2) The unusual uniformity of the intensities made identification of the reflexions less obvious.

(3) Frequent twinning (with $\{11\bar{2}0\}$ or $\{2\bar{1}\bar{1}0\}$ as composition plane) gave rise to pseudo-planes of symmetry.

Most specimens consisted of bundles of long laths cemented parallel to [00.1], but a few single crystals were found. The use of Weissenberg photographs was not attended by the first two difficulties and they were, therefore, preferred for the investigation of the reciprocal lattice. The Laue symmetry was thus confirmed to be $\bar{3}$, and among the (00.*l*) reflexions only (00.3) and (00.6) were observed. The latter, at $\sin\theta \doteqdot 0{\cdot}75$, was quite strong although, apart from $(10\bar{1}6)$, all other reflected intensities were negligible beyond $\sin\theta = 0{\cdot}55$. There were no other systematic absences. It is considered, therefore, that the space group is $C3_1$ (or $C3_2$).

The curious uniformity of the observed intensities and the rarity of accidental absences (see Fig. 2) has been accounted for by an application of the distribution method of intensity statistics to the (*hki*0) zone. The results are in satisfactory agreement with the low-dispersion acentric distribution (Rogers, 1950; Howells, Phillips & Rogers, 1950) which is indicative of a non-centrosymmetric projection. This is in agreement with the above space-group and with the optical activity.

The lattice constants were found to be

$$a = 21{\cdot}60 \pm 6,\quad c = 6{\cdot}11 \pm 1\ \text{Å}\,.$$

The limited precision achieved is due to the absence of reflexions with $\sin\theta \geq 0{\cdot}55$.

The literature contains a number of determinations of the density of the liquid which are in satisfactory agreement. The values recorded for temperatures below 42° C. are, however, most discordant and, with the exception of that of Moriya (1881) ($d_{15}^{15} = 0{\cdot}890$ g.cm.$^{-3}$; m.p. 39° C.), probably relate to the supercooled substance (thus Zeitschel & Schmidt (1926) $d_{15}^{15} = 0{\cdot}9035$ g.cm.$^{-3}$) or are extrapolations from the liquid data (Kenyon & Pickard (1915) $d_4^{20} = 0{\cdot}9007$ g.cm.$^{-3}$). If the value is taken as 0·904 g.cm.$^{-3}$, the unit cell contains 8·65 molecules. In view of the large de-

Table 1. *Revised indexing of the powder photographs of α-l-menthol*

		Ramsay & Rogers (Lewis)				Sidhu	
*hk.l**	d_c (Å)	d_o (Å)†		*I*		d_o (Å)	*I*
10.0	18·70	Cut off		—		Cut off	—
11.0	10·80	§				10·25	*vs*
20.0	9·35						
21.0	7·07	7·07		0·5			
30.0	6·23	6·29	*A*	1·0		5·92	*m*
10.1	5·84	5·83		0·2			
22.0	5·40	5·28		0·9	*bb*	5·11	*vs*
11.1	5·32						
31.0	5·19						
20.1	5·12						
40.0	4·68	4·63	*B*	0·7	*b*		
21.1	4·62						
30.1	4·36	4·35	*C*	0·9	*b*	4·36	*s*
32.0	4·29						
41.0	4·08	4·10	*D*	1·0	*b*	4·00	*s*
22·1	4·05						
31.1	3·95	3·95		0·2			
50.0	3·74	3·74		0·2			
40,1	3·71						
33.0	3·60	3·52		0·3			
42.0	3·54						
32.1	3·51						
41.1	3·41	3·37		0·3		3·40	*w*
51.0	3·36						

* Reflexions from the planes *hk.l*, $hk.\bar{l}$, *kh.l* and $kh.\bar{l}$ are not equal in this space group. The intensities listed are, therefore, the visually estimated sums of the four.

† The spacings recorded here are the mean values obtained from the three specimens: Chinese, Brazilian and synthetic menthol. Many more lines with lower spacings were observed. All were weak and each could be due to a number of different crystallographic planes.

§ This line appears only on photographs taken with a 9 cm. camera and is very strong (see Fig. 3 (*a*)). All the above spacings are derived from photographs taken with a 19 cm. camera.

b = broad, *bb* = very broad.

parture from the integer 9, the density was redetermined with a small density bottle holding about 10 mg. of menthol. Many of the larger crystals appeared to contain cavities so a number of the smaller and apparently flawless specimens were selected for this purpose. The results of four determinations on different sets of crystals gave a value for the density of $0{\cdot}917 \pm 0{\cdot}005$ g.cm.$^{-3}$. The calculated density, if 9 molecules per cell is assumed, is $0{\cdot}94_3$ g.cm.$^{-3}$, so that the experimental value, although higher than any hitherto recorded, is still about 3% below the calculated value. Although Wright (1917) found very little difference between the densities of α-menthol and the melt, Bridgman (1915) found a volume change of 0·0612 cm.^{3}g.$^{-1}$ at 75 atmospheres pressure on fusion of α-menthol. The latent heat, calculated from this value and measurements of the variation of the melting point with pressure by Hulett (1899), was 19·0 cal.g.$^{-1}$ in good agreement with the experimental value of 18·9 cal.g.$^{-1}$ (Brunner, 1894). From the density–temperature graph the density of the melt at the fusion point (42.5° C.) is 0·8828 g.cm.$^{-3}$ and so from Bridgman's volume change the density of the solid at 42·5° C. is $0{\cdot}933_2$ g.cm.$^{-3}$. This is in considerably better agreement with $0{\cdot}94_3$, the X-ray value for room temperature.

It is concluded, therefore, that all previous menthol specimens as well as the present contained cavities. One specimen, apparently perfect from the exterior, was found to contain a tubular cavity of irregular cross-section almost the full length of the crystal. All attempts at recrystallization from solvents have failed to give crystals with a better texture; the fine laths formed by slow sublimation appear to be satisfactory, but are very thin and fragile.

The asymmetric unit consists, therefore, of three unrelated molecules (i.e. 33 atoms, considering carbon and oxygen only). A direct attack on the structure is complicated by the number of possible structural and configurational isomerides and also by the absence of even one centrosymmetric projection. Nevertheless, it has been possible to make some headway, especially with the aid of a parallel determination of the isomorphous structures of menthylamine hydrochloride and hydrobromide.

3. Powder results

The cell dimensions published by Sidhu (1939) are incompatible with the single-crystal results quoted in the preceding section, but all his observed lines can be reindexed (see Table 1). His conclusions that there are 8 molecules per unit cell, and that the structure is close-packed hexagonal, must also be rejected. These erroneous conclusions were partly the result of using a small-diameter camera (5·73 cm.) and a

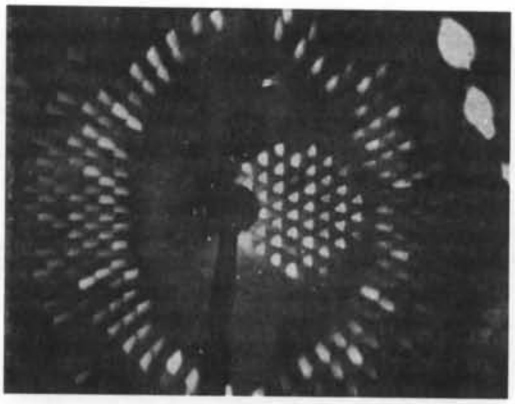

Fig. 2. An end-on photograph with the X-ray beam nearly parallel to the *c* axis.

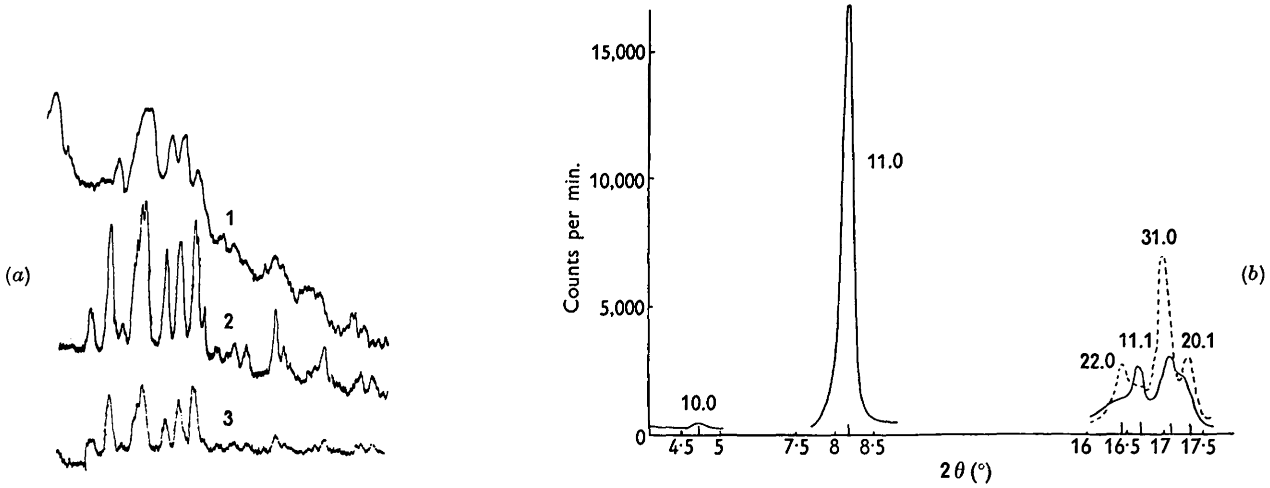

Fig. 3(*a*). The low-angle end of the powder patterns of α-*l*-menthol: (1) 9 cm. camera, specimen rolled on to glass fibre; (2) 19 cm. camera, specimen = powder + canada balsam; (3) 19 cm. camera, powder + gum tragacanth. The horizontal scales of the 9 cm. and 19 cm. patterns are not quite equal: the patterns are reproduced with the 5·28 Å 'line' in register. (*b*) Geiger-counter-spectrometer measurements of some low-angle lines. Note the horizontal axis is not continuous. The two records for the quadruplet were obtained from specimens differently prepared.

specimen of wide diameter (0·7 mm.), and partly due to the use of a Hull–Davey chart, which presumably did not extend to a ratio $c/a = 0{\cdot}283$. The majority of the lines he observed are unresolved clusters and after the first few the number of possible planes increases greatly. The $\{10\bar{1}0\}$ line was not recorded, as it was cut off by the knife edge.

The composite character of many of the lines, which is predicted from the single-crystal data (see Table 1), was partly evident on microphotometer traces of photographs taken with a 19 cm. camera (see Fig. 3(*a*)). This was adequately confirmed by an examination of powdered menthol using the Geiger-counter spectrometer recently constructed at Cardiff. Fig. 3(*b*) indicates the number of counts per minute (uncorrected for dead time) observed on scanning some of the low-angle lines. The peaks are in all cases in good agreement with the calculated position of the line. They are very narrow (width at half-height $\doteqdot 10'$), so that it has been possible to identify the four components of the photographic 'line' at 5·28 Å. It was also possible to record a very weak peak for the $\{10\bar{1}0\}$ reflexion at a Bragg angle of 2° 22′ (18·7 Å). This reflexion was cut off on photographs taken with both the 9 and the 19 cm. cameras and only doubtfully recorded on single-crystal photographs.

The relative strengths of the lines were found by both photography and the spectrometer to vary considerably according to the method of preparing the specimen (see Fig. 3(*a*) and (*b*)). The crystals do not readily powder, but crush into flakes. Rolling of the cylindrical specimen or similar treatment to compress the block of powder for the spectrometer resulted in a marked degree of preferred orientation. This variation of the relative strengths of the powder lines unfortunately affects some of those used for cataloguing menthol in the A.S.T.M. index. They are marked *A*, *B*, *C*, *D* in Table 1.

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