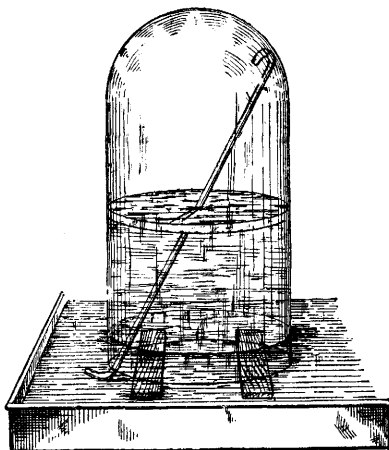


XXXVI.—*Studies of the Terpenes and allied compounds. Sobrerol, a product of the oxidation of Terebenthene (Oil of Turpentine) in Sunlight.*

By HENRY E. ARMSTRONG and W. J. POPE.

Preparation of Sobrerol.—The most convenient form of vessel in which to effect the oxidation of turpentine in sunlight is the common glass statuette shade, a suitable size being that about 6 inches in diameter and 14 inches high. A number of these shades are ranged side by side in a wooden, zinc-lined tray about 2 inches deep; they are placed across two laths three-eighths of an inch thick, so that a glass tube, bent as shown in the following figure (p. 316), may rest within the shade with the one end projecting beneath the edge of the shade into the water outside. The tray being full of water, the shade with the tube inside is placed across the laths, and an indiarubber tube having been attached to the outside end of the glass tube, air is sucked out until the water has risen within the shade and fills about one-third of it; the rubber tube is then detached, and 50–100 c.c. of turpentine delivered from a pipette underneath the edge of the shade. As the oxygen of the air is gradually absorbed, the water rises and crystals begin to collect on the interior after three or four days' exposure in bright sunshine. Oxygen, to replace that absorbed, is run in whenever necessary by attaching a rubber tube, connected with an oxygen reservoir, to the lower end of the glass tube in the shade. When a clearly defined crystalline deposit has formed over the shade down to the "nitrogen line," *i.e.*, the level to which the water rises when all

oxygen is absorbed from the air, the shade may be filled with oxygen down to the level of the water in the tray, as the formation of crystals becomes confined to the upper part of the shade. The



greatest speed of absorption noticed has been that indicated by a rise of the water 2 inches per day, but this has occurred only in abnormally bright weather with an atmosphere rich in oxygen. After six weeks' exposure or so, the oil begins to sink; the shades are then removed with the aid of a large clock glass, set aside to drain for a few hours, and the lower part cleaned with the aid of spirit; the crystalline deposit is then scraped out as far as possible by means of a flexible steel spatula, the undetached portion being removed by rinsing with hot spirit.

To purify the crude product, it is dissolved in a minimum quantity of boiling alcohol, the solution digested with animal charcoal, filtered, and rapidly cooled; by continually stirring, the crystals are caused to separate in the form of a fine meal, from which the liquor is easily expressed on a vacuum filter. If necessary, this operation is repeated, and, finally, the substance is allowed to crystallise out slowly from alcohol.

The following results, obtained on combustion of the substance so prepared, serve to verify the formula originally assigned to the product by Sobrero:—

	Experiment.		Calculated.
Carbon per cent.	70·57	70·49	70·57
Hydrogen per cent.	10·71	10·74	10·61

Dextro- and Lævo-sobrerol.

The pure substance melts at 150°. In a solution, in ordinary spirit, containing 5 grams per 100 c.c., it exhibits the specific rotatory power, $[\alpha]_D = \pm 150^\circ$. We do not claim any high degree of accuracy for this value, and propose to redetermine it when we are satisfied that we are dealing with a substance of undoubted purity.

Active sobrerol separates from its alcoholic solution in the form of long, tabular crystals attaining a length of 30 mm., and from water as stout prisms. The two isomerides, as might be expected, crystallise in enantiomorphous hemihedral forms. The crystals possess a vitreous lustre, and are colourless and transparent.

The following are the crystallographic data which establish the form of sobrerol (Fig. 1):—

Angle.	Number of observations.	Limits.	Mean.	Calculated.
<i>ac</i>	34	83° 14'—83° 58'	83° 38'	—
<i>am</i>	11	67 5—67 31	67 21	—
<i>pc</i>	7	43 5—44 14	43 41	—
<i>ap</i>	5	79 15—79 30	79 27	79° 8'
<i>cm</i>	12	87 11—87 43	87 33	87 33½'

Crystalline system. Monosymmetric.

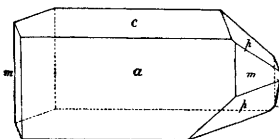
$$a : b : c = 2.4113 : 1 : 0.8531.$$

$$\beta = 83^\circ 38'.$$

Forms present.

$$\begin{aligned} a &\dots \{100\} \dots \infty P \infty \\ c &\dots \{001\} \dots 0P \\ m &\dots \{110\} \dots \infty P \\ p &\dots \{\bar{1}11\} \dots + P. \end{aligned}$$

FIG. 1.



The crystals exhibit a perfect cleavage parallel to the ortho-pinakoid (100), and an imperfect one parallel to the basal plane (001). The double refraction is negative and strong. The optic axial plane is nearly parallel to the basal plane, and the acute bisectrix is nearly perpendicular to the ortho-pinakoid; the axial angle is very large.

The crystals are flexible, and may be readily bent backwards and

forwards several times, the cleavage surfaces sliding upon each other. They are extremely soft, and may be easily rubbed into cleavage splinters between the fingers.

In very rare instances the hemihedrism is shown by the suppression of one-half of the pyramid ($\bar{1}11$) faces. The crystals nearly always consist of the forms a , c , and m alone, the hemihedral character being shown by an internal skeletal structure, which gives rise to a wedge-shaped inclusion, pointing towards opposite ends of the prism in the two oppositely active modifications (see Figs. 2 and 3). The direction of the rotation in solution may be very readily determined by means of this structure. Placing the crystal with the form (100) facing the observer, and with the obtuse axial angle in front and at the upper part of the crystal, so that the basal plane is visible as in the figures, in the case of a crystal of the *lævo*-sobrerol, the skeletal structure points from right to left, while if the crystal be one of *dextrosobrerol*, the wedge points from left to right.

FIG. 2.

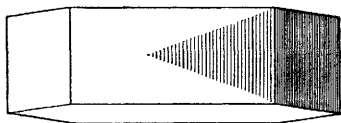
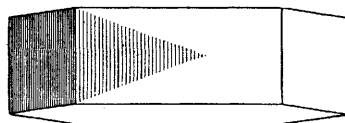


FIG. 3.



One of the ortho-pinakoid faces is very brilliant, the parallel one being more or less tessellated in character; the form (001) is very perfect, no distinction being noticeable between the parallel faces; contiguous faces of the form (110) are generally dull, while the parallel ones are almost wholly destroyed by the skeletal structure; the pyramid faces appear but seldom, and only upon crystals which do not show the above described skeletal structure, and which have all the faces of each form similar in character. The pyramid faces are large, but much rounded, and the measurements, which are obtained with difficulty, cannot be relied upon as accurate.

Twinning.—One crystal was found in which (100) was the twin plane and face of composition.

Inactive Sobrerol.

This substance is at once obtained on allowing a solution of equal weights of the two active modifications to crystallise. It melts at 130.5 – 131° . The crystals are totally different in appearance from those of the active forms, and never exhibit the peculiar internal structure which characterise the latter. The following data serve to determine the crystallographic constants:—

Angle.	Number of observations.	Limits.	Mean.	Calculated.
an	19	$66^{\circ} 16' - 68^{\circ} 53'$	$67^{\circ} 35'$	—
ad	17	$70^{\circ} 7' - 72^{\circ} 36'$	$71^{\circ} 10'$	—
dm	8	$82^{\circ} 50' - 83^{\circ} 5'$	$82^{\circ} 56'$	$82^{\circ} 55'$

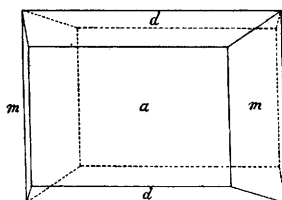
Crystalline system. Orthorhombic.

$$a : b : c = 2.4242 : 1 : 0.8268.$$

Forms present.

$$\begin{aligned} a & \dots \{100\} \dots \infty \check{P} \infty \\ m & \dots \{110\} \dots \infty P \\ d & \dots \{101\} \dots \check{P} \infty. \end{aligned}$$

FIG. 4.



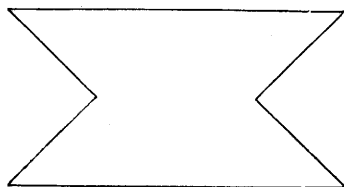
As crystallised from alcohol, the substance consists of flat, colourless, transparent tables, with bevelled edges (Fig. 4); they exhibit slight vitreous lustre, and a perfect cleavage parallel to (100), and an imperfect fibrous cleavage parallel to (001).

The optic axial plane is parallel to (001), and the axes emerge nearly normal to (110). The acute axial angle is therefore nearly $44^{\circ} 50'$.

The double refraction is strong and negative.

When a drop of the alcoholic solution is evaporated on a microscope slide, a large proportion of the small crystals so obtained present under the microscope the peculiar form shown in the figure (Fig. 5), which much resembles a skeletal structure like that possessed by the active modification, but symmetrically developed; measurable crystals do not generally show the structure, but one

FIG. 5.



crystal has been obtained showing such a double skeletal structure in a well-developed state, extending from both ends of the crystal, and meeting in an hour-glass form at the centre.

The crystals may be crushed between the fingers into long, fibrous cleavage fragments. The inactive crystals are far more brittle than those of the active modification, and the cleavage laminae do not slide over one another in so striking a manner as in the monosymmetric crystals.

Active and inactive sobrerol possess considerable crystallographic interest on account of their extraordinarily close similarity to each other, a similarity much greater than that which generally subsists between the active and inactive modification of a compound. It will be seen from the description that in their axial ratios, their habit, their optical orientation, the position of their optic axes, the sign and magnitude of double refraction, and their cleavages they are practically identical. The only differences in dimensions are that the angle β is 90° for the inactive and $83^\circ 38'$ for the active modification, and that the forms developed are different.

The resemblance even extends to the skeletal structure described above, with the important differences that this structure is unsymmetrical or wedge-shaped for the active, but symmetrical or hour-glass shaped for the inactive, modification.

The preparation of optical sections was found impossible, owing to the softness and flexibility of the crystals.

In conclusion, we desire to express our thanks to Mr. Miers, Instructor in Crystallography in the Central Institution, for the assistance and advice which he has most kindly given to one of us (W. J. P.) in carrying out the crystallographic study of sobrerol.

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