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ON THE OPTICAL ROTATION OF PINEN HYDRO- CHLORIDE.

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THE data found in the handbooks concerning the optical properties of this well-known compound, commonly called artificial camphor, are far from being in accord with each other or in accord with the actual facts. The earliest published results making pretense to accuracy are apparently those of Berthelot.¹ The conditions favoring the production of the compound from *l*-pinen or purified French turpentine oil and the physical properties of the finished substance are clearly stated. Some of the succeeding observers seem to have overlooked this earlier work and have published much less carefully controlled data.

I have elsewhere called attention to the production of this body from purified American turpentine,² but consider it necessary to add something to the data there presented, inasmuch as the somewhat misleading statement of Pesci³ and Wallach, and Conrady⁴ as to the inactivity of the product, have passed into the literature. See, for example, Landolt's "Optisches Drehungsvermögen," 2d ed., p. 556.

¹ *Ann. chim. phys.* [3], 40, 5 and later.

² *J. Anal. Appl. Chem.*, February, 1893.

³ *J. B.* (1888), 900.

⁴ *Ann. Chem.* (Liebig), 252, 156; *J. B.* (1889), 737.

The product is easily made by passing dry hydrochloric acid gas into turpentine oil, but to obtain it in pure condition it is necessary to employ a turpentine which has been purified by treatment with alkali and subsequent fractionation. The direction is usually given to cool the turpentine by immersing the container in a freezing-mixture, but this is not necessary. The maximum amount of product is not obtained at a low temperature, but at a temperature much above the freezing-point, possibly about 30° C. Inasmuch, however, as the turpentine becomes very warm during the reaction it is necessary to cool somewhat to maintain this temperature in the liquid. Marsh and Gardner¹ state that a high temperature is even better than a low temperature for production of the compound.

To determine the effect of temperature at the time of passing the gas through the turpentine the following experiment was made. Some commercial oil was allowed to stand several days over well-dried potassium carbonate, with frequent shaking, and was then poured off and treated with metallic sodium during a week in the same manner, and practically until all action ceased. The clear liquid remaining was then distilled, the higher boiling portions being rejected. From fresh American oil it is easy to obtain in this way the major portion boiling from 156° to 158°. A liter of the product so obtained which showed the specific rotation,

$$[\alpha]_D = +14.65^\circ$$

was divided into two portions. One was poured into a flask kept cool by ice and salt, while the other was poured into a similar flask, connected with the first but allowed to stand in the air. A rapid current of dry hydrochloric acid gas was bubbled through both flasks during several hours on two days. The separation of the crystalline solid began first in the cold flask, which finally had to be disconnected to allow the gas to pass. In the second flask, which became quite warm during the reaction, 40° or above, crystallization was slow, but in the end fully as much product was obtained here as in the other. Both masses of crystals were collected on filters and allowed to drain thoroughly. They were then dissolved in hot pure alcohol and

¹ *J. Chem. Soc.*, 59, 725 (1891).

recrystallized by cooling. The new crystals were dissolved and crystallized again from alcohol, and the products now obtained were drained thoroughly and dried between porous plates. For polarization tests benzene solutions were made containing exactly five grams in twenty-five cc. The same specific rotation was found for the two products; *viz.*,

$$[\alpha]_D^{20} = +7.17^\circ.$$

The absolute agreement in the rotation values is probably accidental, but it is at least evident that the temperature effect cannot be important, as was indeed pointed out by Berthelot.¹ It may also be noticed that the specific rotation is about half of that of the original pinen, but this fact is without importance, as very different values are found from different oils. Some chemists give much higher values for the specific rotation. Flawitzky, for example², gives values between $+24^\circ$ and $+30^\circ$ for different samples. Marsh and Gardner³ state that the specific rotation is from $+3^\circ$ to $+5^\circ$. Wallach and Conrady⁴ in giving the substance as inactive state that *d*-pinen is much more readily made inactive by hydrochloric acid than is *l*-pinen, but offer no evidence to explain this view. If this were true it is likely that this effect of the acid would be heightened by increase of temperature, but observations, such as given above, show that this is not the case.

In investigations on the pinen from American oil it must be remembered that the commercial turpentine is distilled from the oleoresin from a number of distinct species of pine, and the product, as it appears in commerce, is always, and unavoidably, a mixture. The oil from any one tree undoubtedly contains both *d*- and *l*-pinen,⁵ but from the long-leaf yellow pine and most other common varieties the oil obtained contains *d*-pinen in greatest abundance, while the so-called *spruce* pines of the region around Mobile, and elsewhere, yield an oil richest in *l*-pinen. As the separation of the optical antipodes by fractional distillation is

¹ *Loc. cit.*

² *Ber. d. chem. Ges.*, 15, 5, and Landolt's "Optisches Drehungsvermögen."

³ *Loc. cit.*

⁴ *Loc. cit.*

⁵ This is not the view generally held, it being sometimes assumed that the antipodes are not present in the same plant. See Landolt's "Optisches Drehungsvermögen," Second Edition, page 116.

impossible, it will be recognized that the usual methods of obtaining dextro pinen from commercial American turpentine are entirely fallacious. It may be added here that the separation of the right and left hydrochloride by fractional crystallization appears to be equally impossible. I mixed in one trial fifty grams of a *d*-product, showing $\alpha = +1.25^\circ$ with fifty grams of an *l*-product, showing $\alpha = -7.01^\circ$, dissolving and crystallizing from strong alcohol in two fractions. For the first fraction I found $\alpha = -2.84^\circ$ and for the second $\alpha = -2.85^\circ$, while the mean calculated value of the mixture is $\alpha = -2.88^\circ$. Practically the same result is obtained by precipitating partially by water instead of crystallizing from alcohol. These results are in accord with the observed behavior of antipodes in general, as regards solubility.

Some years ago I distilled six samples of perfectly fresh "spruce" dip, each from a single tree, and found that the oils differed in specific rotation, running from -36.6° to -40.8° . Carefully made fractions from these oils, boiling between 156° and 156.7° , gave specific rotations between -40.1° and -42.5° . These differences cannot be traced to oxidation or other changes due to keeping, because the liquid oleoresins distilled were fresh, were "dip" or first-year products, were sent immediately in sealed tin cans, and were distilled with steam without delay. The differences I believe to be due here and in all other cases to the presence of both *d*- and *l*-pinen in the oil of each tree. That the low rotation of many dextro oils is not due to oxidation-products is easily shown by the fact that these oils suffer but little change through treatment with alkali carbonates or the metals themselves; and further, by the fact that the old and partially dried oleoresins, known as "scrape" products, often yield oils showing as high a rotation as those from the fresh dip products.

Supposing now that the most carefully separated low-boiling fractions of American oil contain both *d*- and *l*-pinens the following experiment may suggest a reason for the low rotation of the hydrochloride from the common oil. A sample of left rotating oil treated with alkali and fractionated furnished a principal portion boiling from 156° to 157° . This showed a specific rotation :

$$[\alpha]_D^{20} = -17.11^\circ.$$

The hydrochloride was made in the usual manner and purified by crystallization from strong alcohol. The dried fractions were dissolved in pure benzene to produce solutions containing twenty grams in 100 cc. Three fractions gave specific rotations :

$$1 \quad [\alpha]_D^{20} = -18.29^\circ$$

$$2 \quad [\alpha]_D^{20} = -18.46^\circ$$

$$3 \quad [\alpha]_D^{20} = -18.21^\circ$$

Essentially the same results were found from alcoholic solutions, and from a solution in benzene containing forty grams to 100 cc., a slightly lower value was found. While the data are insufficient to determine the true specific rotation of the pure substance it is evident that the effect of the acid was not to lessen the activity of the pinen, but to increase it. The best comparison is made by introducing the molecular rotations. For the original this is

$$[M] = -17.11^\circ \times 136 = -2326.9,$$

and for the hydrochloride it is

$$[M] = -18.32 \times 172.5 = -3160.2,$$

from which it appears that on comparing equal molecules the rotation is much increased.

Assuming now that the action of hydrochloric acid on *l*-pinen is to increase rather than to decrease the rotating power while the action on the *d*-pinen is to produce a hydrochloride with nearly the same or probably a somewhat decreased rotation, it is apparent that from a common dextro oil the hydrochloride obtained must necessarily show a lower rotation. It could even follow that a change of sign would result, but I have not yet observed this possible case in any one of the many samples which I have converted into hydrochloride. I have found a specific rotation of less than 1° in several instances. The inactivity of the preparations from dextro American oil described by Pesci¹ and by Wallach and Conrady² may doubtless be accounted for in this manner. If, as Wallach assumes, the *d*-pinen becomes readily inactive under treatment with hydrochloric acid, it would

¹ *Loc. cit.*

² *Loc. cit.*

certainly follow that the hydrochloride from much of the dextro American oil must show a negative rotation. But this is not in agreement with the facts.

Pesci appears to be in error, with others, in giving the melting-point of the hydrochloride as 125° . A careful determination of three preparations from rather large amounts of purified and fractionated oil gives me 131° as the true melting-point, and this agrees with the value given by Riban.¹

My thanks are due Mr. Frank Wright for valuable help in preparing samples of the hydrochloride and in determination of the optical constants.

CHICAGO, April, 1890.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
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SEPARATIONS OF METALLIC SULPHIDES BY MEANS OF HYDROCHLORIC ACID GAS.

BY J. BIRD MOYER.

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A NUMBER of quantitative separations have been made in the last few years through the agency of the haloid acids in gas form. With a few exceptions the experiments made in this laboratory and elsewhere required the use of metallic oxides or the salts of oxygen acids. The analogy of sulphur to oxygen in its derivatives led to the conclusion that similar behavior might be expected from the metallic sulphides. Smith and Keeley¹ found that arsenic sulphide, antimony sulphide, and stannic sulphide were completely volatilized in a stream of hydrochloric acid gas and that stannous sulphide, though not volatilized, was changed to stannous chloride. An attempt was made by them to effect a separation of stannic sulphide from stannous sulphide in this manner but it proved unsuccessful. Smith and Field² separated arsenic sulphide from vanadium sulphide quantitatively by this method.

The acid sulphides being volatile in hydrochloric acid gas it was natural to suppose that they might be separated quantitatively from the more basic metallic sulphides. It was hardly

¹ Wurtz's Dictionary, Vol. V, 306 and 312.

² This Journal, 18, 1096.

³ *Ibid.*, 18, 1051.