etc., along their banks. Analyses of the Croton water, made at different seasons during the past five years, have shown that it is to be classed among contaminated water supplies.

On the publication of the results above stated, it was indignantly claimed by the newspaper press of Wilmington, Delaware, that an injustice had been done to their city. But subsequently, letters published in reply by citizens of the place, have affirmed the correctness of the judgment founded on the analytical data, and have enumerated the various breweries, woolen, cotton and other mills and dye-houses, as affording a sufficient explanation of the low position assigned to the water supply.

XXVI.—SOME NEW FACTS CONCERNING THYMOLE SULPHO-ACID, AND SOME OF ITS SALTS.

BY JAMES H. STEBBINS, JR.

This work was undertaken for two reasons.

First, to establish certain facts, which thus far have either been neglected or overlooked; as for example, the production of free thymole sulpho-acid, which hitherto has only been obtained in combination with other salts. It was also my intention to produce from this latter, by direct combination, the calcium, ammonium, and soda salts, all of which have thus far not been mentioned. Or starting from, say, the barium salt, to produce by indirect combination either of the previously mentioned salts.

Second, to combine these new bodies with diazo compounds, and thus ascertain whether it is possible to produce azo compounds, from phenoles of this description.

This hypothesis seems all the more probable, as only a short time since, I obtained a yellow dye-stuff, by the direct combination of diazobenzole nitrate with an alkaline solution of thymole. As this dye was insoluble in water, the usual method of rendering such compounds soluble was resorted to, namely, the introduction of the sulpho group into the benzole nucleus.

My experiments in this line will be detailed in a subsequent paper.

The first person to engage in the study of these compounds was Lallemand,* who obtained a thymole sulpho-acid, by treating thymole with hydrochlor-sulphuric acid (SO_3HCl).

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* *Jahresber.* f. 1856, 617.

In 1869, A. Engelhardt and P. Latschinoff* produced three thymole sulpho-acids, by the action of sulphuric acid upon thymole, at a temperature of about 50° C. These three sulpho acids were only obtained in combination with barium, potassium, copper, lead, etc., thus making distinct, and well characterized salts, but making no attempt to produce the free sulpho acids.

It seemed, therefore, advisable to investigate this subject, and in so doing the following experiments were made:

60 grms. of thymole were treated in an evaporating dish with 50 grms. of sulphuric acid.† The dish was placed upon a steam bath, and heated for about 15 minutes.‡

The thymole soon began to dissolve, and was constantly stirred, till suddenly nearly the whole contents of the dish solidified out into a pink, crystalline mass. This mass was then drained from a clear and colorless oily fluid which impregnated the whole crystalline body.

This oily liquid solidified into a white, crystalline mass, as soon as it came in contact with the cold sides of the glass. A few isolated crystals were examined with a magnifying glass, and showed themselves to be composed of star-shaped needles. They were then labeled and set aside for further examination.

The pink crystalline mass was then dissolved in boiling water, neutralized with carbonate of calcium, and filtered hot. The sulphate of lime thus formed, besides a small quantity of unattacked thymole, were thus gotten rid of. The filtrate so obtained is nearly colorless, and was concentrated over the steam bath, till it had assumed the consistency of a syrup. On cooling, the calcium salt of alpha thymole sulpho-acid crystallized out in rhombic plates.

The solid crystalline mass so obtained was separated from the mother liquor, and dissolved at a gentle heat in 90 per cent. alcohol. The larger part of the alcohol was distilled off, and the syrup thus formed allowed to crystallize. The salt so obtained crystallizes in long white, flexible needles, bearing a strong resemblance to asbestos filaments. If a drop of the above alcoholic solution be rapidly evaporated on a watch-glass, a large number of minute star-grouped needles are obtained. These viewed under the polariscope, show a beautiful effect of circular polarized light. The phenomenon

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* *Zeitschrift f. Chem.*, 1869, 43; and 615.

† The acid used was the common 66° acid.

‡ In this instance I used a higher temperature than Engelhardt and Latschinoff.

observed is a symmetrical black cross, when the nicols are crossed, with a series of concentric rings, dark, and light in monochromatic light; but, in white light, showing the prismatic colors in succession in each ring.

The cross becomes white when the nicols are in a parallel position, and each band of color in the white light changes to its complementary tint, thus making the uniaxial character of the crystal.*

The crystals so obtained were then redissolved in water, and allowed to crystallize. This salt crystallizes in two forms of rhombic plates.

The first, showing the planes mc: ∞ b: a; and mc: b: ∞ a; or macro and brachydomes.

The second, showing the planes mc: b: ∞ a, or brachydomes, and and ∞ a: b: ∞ c; or macropinacoids.

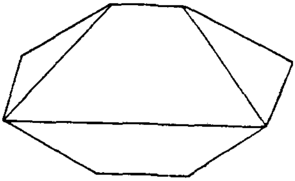

Fig. 1.

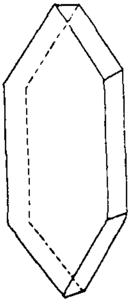

Fig. 2.

Both these crystals are the same identical compound, and constitute the calcium salt of alpha thymole sulpho-acid.

A sulphur estimation shows the correctness of this statement.

0.4246 grm. of substance yielded 0.3948 grm. $BaSO_4$, which is equivalent to :

Sulphur.............................. 12.77 per cent.

THEORY.

Sulphur.............................. 12.85 per cent.

Likewise a lime estimation gave:

Calcium .... 9.34 per cent.

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* These phenomena seem to be totally ignored by Engelhardt and Latschinoff, and I therefore look upon them as new, and worthy of a position in the literature of thymole and its substitution compounds.

THEORY.

Calcium .... 8.32 per cent.

These figures lead us, beyond doubt, to the formula:

$$[C_6H_2(CH_3)(C_3H_7)(OH)SO_3]_2Ca + 2H_2O$$

The above compound dried at 100° C., loses two molecules of water, and falls into a fine white powder. Melting point, 156 to 157° C.

It is easily soluble in water, alcohol and ether.

MOTHER LIQUOR.

The mother liquor from the first crop of crystals was poured upon a watch-glass, and after a short time crystallized in rhombic plates, showing respectively the same form, melting point and sulphur percentage, as in the previous compound. It was, therefore, considered identical

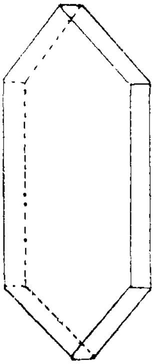
AMMONIA SALT.

A part of the Ca salt of alpha thymole sulpho-acid was next dissolved in water, heated to boiling, and decomposed by $(NH_4)_2CO_3$. The $CaCO_3$ formed was then filtered off, and the filtrate concentrated over the steam bath, to the consistency of a syrup.

The syrup so produced was then placed under the air pump, and allowed to crystallize.

After standing for a few hours, the fluid became filled with pretty, crystalline white plates. These were then drained from the mother liquor, and dried between filter paper.

The salt so obtained crystallizes in white rhombic plates, with strong vitreous lustre, and shows the planes mc: $\infty a : b$; or brachydomes; and $\infty a : b : \infty c$; or macropinacoids.



At the ordinary room temperature it loses a part of its water of crystallization, and at 100° C. all the water is driven off. while the substance crumbles into a fine white powder.

1.9748 grm. of substance, on being heated to 100° C., lost 0.3794 grm. of water, which is nearly equivalent to 2 molecules.

Therefore, the ammonium salt of thymole sulpho-acid crystallizes with 2 molecules water of crystallization.

Melting point, 172 to 172.5° C.

Therefore, this salt may be represented by the following formula:

$$C_6H_2(CH_3)(C_3H_7)(SO_3.NH_4)OH + 2\ H_2O.$$

The soda salt, as well as an attempt at producing the free alpha thymole sulpho-acid, will be described in a subsequent paper.