

THE PREPARATION, PROPERTIES, AND USES OF SILICO-  
DUODECITUNGSTIC ACID.\*

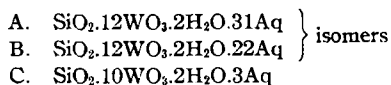
I. THE PREPARATION OF THE ACID AND ITS SALTS.<sup>1</sup>

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HISTORICAL.

Silicoduodecitungstic<sup>3</sup> acid was discovered by Marignac (1) in 1863 while preparing ammonium tungstate. The acid was formed during extraction of tungsten from the ore, which contained silica, and, being extremely soluble, was found in the mother liquors. He then prepared the acid by boiling a mixture of tungstic acid with gelatinous silicic acid, obtaining the solid acid by evaporation of the filtered liquid. The sodium, potassium, and ammonium salts were described, and the empirical formula  $8MO.20WO_3.2SiO_3$  suggested for the salts. In a second paper (2) in 1864 two other acids were described: tungstosilicic acid, an isomer of the first, to which the formula  $12WO_3.SiO_2.4HO + Aq$  was given, and silicoduodecitungstic acid of the formula  $SiO_2.10WO_3.4HO.3Aq$ . These acids were separated as mercurous salts, which were quite insoluble but easily decomposed by hydrochloric acid.

Wyrouboff (3) in 1896 followed essentially the procedure of Marignac in preparing the acid, substituting nitric acid for hydrochloric in generating the tungstic acid. Copaux (4) in 1908 made one of the most valuable contributions to the knowledge of these compounds. There were then three acids known, which, in modern nomenclature, had the formulas



Copaux prepared "A" in three ways.

1. By reaction in a boiling solution of sodium tungstate,  $Na_2WO_4$ , and sodium silicate,  $Na_2SiO_3$  (water glass), the solution being kept neutral with nitric acid. The compound was extracted by ether in the presence of sulfuric acid.

2. By reaction between sodium tungstate and sodium orthosilicate,  $Na_4SiO_4$ , in a sealed tube at  $150^\circ C$ . The compound was isolated by means of ether and sulfuric acid.

3. By reaction between boiling solutions of sodium tungstate and water glass made acid with acetic acid. The compound was extracted as before.

Acid "B" was made by Procedure 3 under Acid "A," with the substitution of sulphuric acid for the acetic acid. Acid "C" was formed by boiling "A" with a large excess of ammonia. Silica at first precipitated but almost completely redissolved and the ammonium salt of "C" crystallized from the filtrate.

\* Contribution from the Department of Chemistry of the University of Illinois.

<sup>1</sup> Read at the 72nd Meeting of the American Pharmaceutical Association, Buffalo, New York, August 25-29, 1924.

<sup>2</sup> From a thesis presented by Edward Oscar North in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

<sup>3</sup> Throughout this paper the term silicotungstic acid will be understood to refer to silicoduodecitungstic acid.

Goddefroy (5), 1876, found that the alkaloidal salts of this acid were very insoluble, and also called attention to the low solubility of the rubidium and caesium salts. Bertrand (6, 7), 1899, published the first detailed study of the alkaloidal salts of the acid. He maintained that the paper of Goddefroy had not been available and was unknown to him, and that his study was entirely independent. He determined the sensitiveness of the reaction with eighteen or more alkaloids and, with Javillier (8, 9), used the acid in the quantitative determination of nicotine as a means of separating the pure alkaloid. Javillier (10) continued the work, studying the compounds of antipyrine (11), atropine, conine, pyramidone and spar-teine.

Guillemard (12) in 1903 described the use of the acid in determining the animal bases in the urine, which he referred to as alkaloidal nitrogen. Chapin (13), in 1911, published a direct method for the determination of nicotine in tobacco extracts, precipitating nicotine silicotungstate which was filtered and ignited, the determination being based on the weight of silicotungstic anhydride obtained.

Ferenz and David (14) used the acid for the separation of alkaloids from impure solutions; recovering the alkaloids by decomposition of their salts with sodium hydroxide and ether. Rasmusson (15), 1917, outlined a procedure for the analysis of belladonna, using a correction factor because of the solubility of atropine silicotungstate. Taigner (16), 1919, in studying the salts of atropine, strychnine and cocaine, found that when dried at  $120^{\circ}$  they all had the same type formula, *viz.*,  $12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot 4$  alkaloid. This permitted a gravimetric determination of these alkaloids without ignition. Heiduschka and Wolff (17) have studied the ratio of alkaloid to silicotungstic acid in a number of salts, determining the conditions under which these salts are formed. Sindlinger and Mach (18), 1924, have described the determination of pyridine and nicotine. By making allowance for the solubility of the pyridine salt in dilute hydrochloric acid it has been possible to determine this base quantitatively, and by the use of selective solvents for the two salts to determine the percentage of each of the two bases in a mixture.

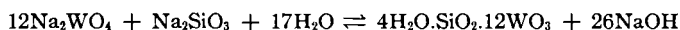
#### THEORETICAL.

Of the three methods suggested by Copaux (*loc. cit.*) for the preparation of "A" the first yields the best results. The sealed tube method is cumbersome and not applicable to large amounts, and the acetic acid used in the third method at times causes some reduction of the silicotungstic acid. In the first method, there are at least several sources of difficulties. The sodium tungstate solution must be continuously stirred during the neutralization with nitric acid, since a local excess produces a precipitate of tungstic anhydride which dissolves with difficulty. The water glass, if not neutralized cautiously, yields a troublesome gel. During the heating the reaction of the solution must be frequently determined and nitric acid cautiously added to maintain neutrality.

Sulphuric acid is added in this method to finally liberate the acid, which is extracted by shaking the solution with ether. The ether solution is apparently similar to a hydrate, and is a heavy oily liquid, miscible neither with water nor ether. The sulphuric acid has a tendency to cause a precipitation of tungstic anhydride which is carried down with the ether and promotes the formation of emul-

sions. Sulphuric acid is carried down by the ether complex, cannot be volatilized with the ether, and tends to initiate a spontaneous decomposition on standing.

In the procedure which we have adopted, hydrochloric acid is substituted for the nitric, sulphuric and acetic acids made use of by Copaux. The formation of the acid from sodium tungstate and sodium silicate may be represented by the following reaction:



If the reaction is to proceed from left to right it is only necessary to heat the acid to favor hydrolysis of the salts and to neutralize the alkali as it is set free. A slight theoretical excess of sodium silicate over sodium tungstate is used, and upon the slow addition of hydrochloric acid no tungstic anhydride is precipitated. The only turbidity results from the liberation of the excess of silicic acid after the combination has taken place, and this gel is readily removed by filtration. Addition of a large excess of hydrochloric acid does not produce a precipitate. After the reaction is complete, the silicotungstic acid is readily extracted by ether without emulsification forming a distinct bottom layer, and the hydrochloric acid carried down with the complex volatilizes with the ether.

Previous investigators have been well agreed upon all of the properties of this acid except its basicity. Silicotungstic acid is quite stable. It will decompose chlorides and nitrates and is very resistant towards boiling sulphuric and perchloric acids. It is readily reduced by free metals such as copper, iron, aluminum and zinc, blue compounds being formed.

Silicotungstic acid forms salts with mono-, di- and trivalent metals, but not with metals forming the oxide  $\text{RO}_2$ , according to Wyruboff (*loc. cit.*). The salts may contain four or eight equivalents of the base. Those which are of the nature of acid salts are very soluble in ether, alcohol and water, the neutral salts much less readily so.

The most interesting property of the acid is that of forming sparingly soluble compounds with many organic bases. These include the secondary and tertiary aliphatic and aromatic amines and quaternary ammonium derivatives. Insoluble salts are not formed by the primary amines. Salts of the secondary bases are usually soluble in hot water, those of the tertiary bases being least soluble. An exception to the last statement is found in the effect of adjacent groups, such as the hydroxyl or carboxyl, which tend to neutralize the basicity of the compound or to render its salts more soluble.

Marignac (2) believed that the acid was octabasic. He found that a solution of a salt containing four equivalents of a base would decompose carbonates and turn blue litmus red. The addition of more base turned the litmus blue, but on standing the red color returned. He also found that the acid was slowly decomposed by an excess of alkali with the formation of normal tungstate and silicate.

When silicotungstic acid is titrated with standard alkali, using methyl orange as indicator, an end-point is obtained when the equivalent of four acid hydrogens have been neutralized. When the acid is titrated in hot solution with standard alkali and phenolphthalein indicator, the equivalent of twenty-six hydrogens are neutralized. Copaux (19) claimed that a sharp, though not permanent, end-point, was obtained with phenolphthalein at a point corresponding to the neutralization

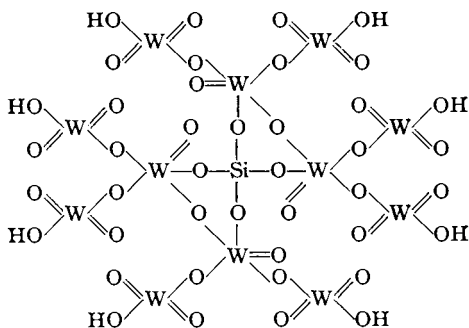
of four hydrogens. This is entirely contrary to results obtained in this laboratory.

While the acid has been found to contain eight replaceable hydrogens, as shown by the formation of normal potassium and ammonium salts, the salts which are formed with tertiary organic bases represent the neutralization of but four equivalents of hydrogen. The empirical formulas obtained upon analysis of these salts, however, do not support the theory of the octabasicity of the acid. In the usual manner of formation of such salts, there is a direct addition of the ions of the acid to the nitrogen of the base. Such an addition would mean that the number of molecules of water which must be eliminated to form the anhydride of the acid would be the same, regardless of whether the acid or the alkaloidal salt was heated. Actual experiments show that only one-half as much water can be eliminated from the alkaloidal salt as from the free acid, forming the same anhydride in each case.

The neutral metallic salts were formed by the addition of an actual excess of alkali to the acid, the alkaloidal salts were precipitated in solutions acid with a strong mineral acid. It would thus appear that there is a condition of equilibrium existing in the acid solution, in which system there are both tetra- and octabasic acids present as members. The presence of a strong acid may repress the ionization of four hydrogens, permitting, at the same time, a dehydration with the formation of a partial anhydride. The condition is thus exactly the same as the state of equilibrium between chromic and dichromic acids, or between a dichromate and a true acid chromate in solution.

The octapotassium salt, prepared in this laboratory, is acidic towards phenolphthalein, neutral towards litmus, and alkaline towards methyl orange and methyl red.

The following is suggested as a structural formula for silicoduodecitungstic acid, showing it as a derivative of orthosilicic acid:



One would predict that in an acid of this type, four hydrogens would have practically equal value and would be replaced simultaneously by a base in the neutralization of the acid. The ionization of the four remaining hydrogens would be of a much lesser degree. Copaux states that the remaining hydroxyl groups are alcoholic. However, neutral metallic salts are formed by the replacement of the eight hydrogens by bases, and a titration with a base using phenolphthalein as indicator shows a gradual endpoint which would be suggestive of a formula of this type.

Rosenheim and Jaenicke (20) reported that the acid formed quadratic crystals with twenty-eight molecules of water and rhombohedral crystals with twenty-two molecules of water. By the use of a dilatometer, they found the transition point at 28.5°.

Copaux (4) claimed that his acids had, respectively, thirty-one and twenty-two molecules of water of crystallization.

Another compound with fifteen molecules of water of crystallization was obtained. All of these forms effloresce rapidly and are therefore indefinite in composition as kept in the laboratory.

The product described in this paper is a white crystalline powder having the formula  $4\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ . It is completely and rapidly soluble in water, ether, ethyl and other alcohols, acetone, ethyl acetate, and amyl acetate. The water of crystallization is very constant. A sample kept for a period of one year shows the same amount of water of crystallization. The solutions of the acid are very stable. The solid acid is very easy to handle, does not effloresce nor deliquesce during weighing and is not reduced by contact with metals.

#### EXPERIMENTAL.

*Preparation of Silicotungstic Acid.*—One thousand grams of sodium tungstate were dissolved in 2000 cc. of water. To the solution were added 75 grams of a 40° Bé. solution of sodium silicate (water glass). The mixture was stirred briskly with a motor stirrer and heated to boiling, while 600 cc. of hydrochloric acid, d. 1.18, were added dropwise from a separatory funnel. The entire time consumed was about ninety minutes. The slight precipitate of gelatinous silicic acid was filtered off and the mixture cooled. Four hundred cc. of the concentrated hydrochloric acid were added and the solution cooled again. This solution in 500-cc. portions was shaken with ether and the bottom oily layer of the ether complex was drawn off. This was gently heated on the steam-bath to remove most of the ether, and the product finally dried in a vacuum oven at 70°. The mixture was stirred repeatedly during the drying on the steam-bath to break up lumps, and was not placed in the oven until it could be ground in a mortar. An 85% yield was obtained.

*Analysis of the Acid.*—Separation of the tungsten and silica was effected by the method of Perillon (22), wherein the  $\text{WO}_3$  was volatilized in a current of gaseous hydrochloric acid. The silica was then volatilized by means of hydrofluoric and sulfuric acids. The weight of silicotungstic anhydride was determined by ignition of the acid. The tungsten as volatilized could not be readily collected, and its weight was therefore determined by difference.

	Found.		Theory for $4\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ .
$\text{H}_2\text{O}$	5.49%	5.55%	5.389%
$\text{SiO}_2$	2.04%	2.05%	1.996%
$\text{WO}_3$	92.46%	92.37%	92.615%
	$\text{SiO}_2 \cdot \text{WO}_3 :: 1 : 11.76$		1:12

#### *Titration of Acid. Methyl Orange Indicator.*

Weight of sample	0.5024 gram	0.5217 gram
Cc. N/1 KOH consumed	0.6699	0.6976
Wt. equivalent to 1000 cc. N/1 KOH	750.0 grams	747.4 grams
Equivalents per mole	4.008	4.02
Equivalent weight of anhydride, ave.		708.4
Theory		711.07

*Titration of Acid. Phenolphthalein Indicator.*—This titration was carried out in a boiling solution, by adding standard potassium hydroxide solution until a permanent red color was obtained, then cooling the solution and titrating the excess of alkali with standard acid.

Weight of acid	0.5188 gram	0.5174 gram
Cc. <i>N</i> /1 KOH	4.391	4.483
Wt. equivalent to 1000 cc. <i>N</i> /1 KOH	118.1 grams	115.4 grams
Equivalents per mole	25.5	26.0
Theory	26.0	26.0

The reaction in this titration is the exact reverse of that previously given for the formation of the acid and is a substantiation of that reaction. The silicotungstic acid has been completely decomposed into potassium tungstate and potassium silicate, since the solution now gives a heavy precipitate with concentrated hydrochloric acid. If, however, the hydrochloric acid is titrated gradually into the hot alkaline solution mentioned above, the silicotungstic acid is reformed.

*Preparation and Analysis of Potassium Silicotungstate.*—This salt was prepared by adding a slight excess of potassium carbonate to a solution of the acid. The salt was recrystallized twice from hot water. The water of crystallization was determined by igniting the salt. The silicotungstic anhydride was determined by adding a solution of cinchonine hydrochloride to a solution of the salt in dilute hydrochloric acid with ignition of the cinchonine silicotungstate precipitated. The filtrate from this precipitate was evaporated with sulfuric acid and the residue of potassium sulfate gently ignited. The oxides of silicon and tungsten were separated by the method of Perillon as in the analysis of the acid.

Analysis.	Obtained.	Theory for $4K_2O \cdot SiO_2 \cdot 12WO_3 \cdot 14H_2O$ .
H <sub>2</sub> O	7.10%	6.91% 7.26%
SiO <sub>2</sub>	1.86%	1.80% 1.73%
WO <sub>3</sub>	80.19%	80.38% 80.16%
K <sub>2</sub> O	10.85%	10.91% 10.85%

*Titration of Potassium Salt in Hot Solution.*—The potassium salt, in boiling aqueous solution, was titrated with standard potassium hydroxide, using phenolphthalein as indicator, in the same fashion as the free acid. The solution after the titration was found to yield a dense precipitate when strongly acidified with hydrochloric acid.

Weight of salt	0.7386 gram	0.7420 gram
Cc. of <i>N</i> /1 KOH consumed	3.695	3.75
Salt titrated by 1000 cc. <i>N</i> /1 KOH	199.98	197.8
Equivalents	17.4	17.6
Theory	18.0	

This is regarded as further proof of the octabasic character of the acid.

*Preparation and Analysis of the Ammonium Salt.*—The ammonium salt was prepared by adding a slight excess of ammonium hydroxide to a solution of the acid. The ammonium salt was a dense microcrystalline substance, only slightly soluble in water. On ignition of the salt the water of crystallization and the ammonia were driven off, leaving silicotungstic anhydride. The silica and tungstic anhydride were determined as in the acid. Ammonia was determined by distilling the salt with an excess of alkali, receiving the ammonia in standard acid.

Analysis.	Obtained.	Theory for $4(NH_4)_2O \cdot SiO_2 \cdot 12WO_3 \cdot H_2O$ .
H <sub>2</sub> O	0.80%	0.93% 0.58%
(NH <sub>4</sub> ) <sub>2</sub> O	6.69%	6.61% 6.78%
SiO <sub>2</sub>	2.00%	1.96% 1.95%
WO <sub>3</sub>	90.46%	90.62% 90.68%
SiO <sub>2</sub> :WO <sub>3</sub>	1:11.71	1:11.96 1:12

*Preparation and Analysis of the Alkaloidal Salts.*—All of the salts, unless otherwise specified, were precipitated by addition of a solution of silicotungstic acid to a solution of the alkaloidal hydrochloride in hydrochloric acid about 0.6 *N*. After

filtration the salts were washed with approximately 1% hydrochloric acid and dried at a temperature between 100° and 120°.

To determine the amount of anhydride present a weighed amount of the salt was ignited in an electric muffle. The loss in weight represented alkaloid and water of crystallization. In some cases, the composition was further checked by determining nitrogen according to Kjeldahl.

*Pyridine Silicotungstate.*—This is a white microcrystalline powder which is quite soluble in hot dilute hydrochloric acid.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_5\text{H}_5\text{N}$  (m. wt. 3196.6):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 88.99%;  $\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O}$ , 11.01%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 89.02%, 89.00%;  $\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O}$ , 10.98%, 11.00%.

*Quinoline Silicotungstate.*—This was a white pulverulent substance, apparently less soluble than pyridine silicotungstate.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_9\text{H}_7\text{N}$  (m. wt. 3396.7);  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 83.75%;  $\text{C}_9\text{H}_7\text{N} + \text{H}_2\text{O}$ , 16.25%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 83.65%, 83.68%.  $\text{C}_9\text{H}_7\text{N} + \text{H}_2\text{O}$ , 16.35%, 16.32%.

*Nicotine Silicotungstate.*—Freshly distilled water-white nicotine was quickly dissolved in dilute hydrochloric acid and precipitated with an excess of silicotungstic acid. The liquid containing the amorphous precipitate was heated to boiling and allowed to cool, obtaining a white crystalline product, not salmon colored as described by Bertrand (7).

The product was dried at 60°.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 5\text{H}_2\text{O}$  (m. wt. 3294):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 86.34%;  $\text{C}_{10}\text{H}_{14}\text{N}_2 + \text{H}_2\text{O}$ , 13.66%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 86.22%, 86.24%;  $\text{C}_{10}\text{H}_{14}\text{N}_2 + \text{H}_2\text{O}$ , 13.78%, 13.76%.

Another specimen was prepared and dried at 100°. The nicotine used was not water-white and the salt had a yellow tint.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$  (m. wt. 3204):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 88.75%;  $\text{C}_{10}\text{H}_{14}\text{N}_2 + \text{H}_2\text{O}$ , 11.25%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 88.25%, 88.05%;  $\text{C}_{10}\text{H}_{14}\text{N}_2 + \text{H}_2\text{O}$ , 11.75%, 11.95%.

*Quinine Silicotungstate.*—This was a white pulverulent compound extremely insoluble in water and dilute acids.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 2\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$  (m. wt. 3528.9):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 80.60%;  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 + \text{H}_2\text{O}$ , 19.40%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 80.47%, 80.51%;  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 + \text{H}_2\text{O}$ , 19.53%, 19.49%.

*Cinchonine Silicotungstate.*—This was a white microcrystalline product extremely insoluble in water and dilute acids. The last traces of water of crystallization are removed with difficulty. This compound was heated for six hours at 120° without appreciable change.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 2\text{C}_{19}\text{H}_{22}\text{N}_2\text{O} \cdot 2\text{H}_2\text{O}$  (m. wt. 3504.9):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 81.15%;  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O} + \text{H}_2\text{O}$ , 18.85%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 81.15%, 81.35%.  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O} + \text{H}_2\text{O}$ , 18.85%, 18.65%.

*Morphine Silicotungstate.*—A buff-colored compound which is moderately soluble in alcohol and dilute acids.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{17}\text{H}_{19}\text{NO}_3$  (m. wt. 4021.3):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 70.73%;  $\text{C}_{17}\text{H}_{19}\text{NO}_3 + \text{H}_2\text{O}$ , 29.27%, N, 1.37%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 70.39%, 70.56%;  $\text{C}_{17}\text{H}_{19}\text{NO}_3 + \text{H}_2\text{O}$ , 29.61%, 29.44%; N, 1.44%.

*Codeine Silicotungstate.*—A buff-colored precipitate slightly soluble in alcohol and dilute acids.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{18}\text{H}_{21}\text{NO}_3$  (m. wt. 4077.3):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 69.74%;  $\text{C}_{18}\text{H}_{21}\text{NO}_3 + \text{H}_2\text{O}$ , 30.26%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 69.51%, 69.65%;  $\text{C}_{18}\text{H}_{21}\text{NO}_3 + \text{H}_2\text{O}$ , 30.49%, 30.35%.

*Apomorphine Silicotungstate.*—This compound resembled in color and solubility the salts of morphine and codeine.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{17}\text{H}_{17}\text{NO}_2$  (m. wt. 3949.2):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 72.02%;  $\text{C}_{17}\text{H}_{17}\text{NO}_2 + \text{H}_2\text{O}$ , 27.98%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 72.15%, 71.94%;  $\text{C}_{17}\text{H}_{17}\text{NO}_2$ , 27.85%, 28.06%.

*Narceine Silicotungstate.*—This compound was buff colored when first precipitated. It dissolved in hot dilute hydrochloric acid and on cooling was deposited in reddish crystals.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{23}\text{H}_{27}\text{NO}_8$  (m. wt. 4661.8):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 61.01%;  $\text{C}_{23}\text{H}_{27}\text{NO}_8 + \text{H}_2\text{O}$ , 38.99%; N, 1.20%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 61.14%, 60.97%;  $\text{C}_{23}\text{H}_{27}\text{NO}_8 + \text{H}_2\text{O}$ , 38.86%, 39.03%; N, 1.22%.

*Narcotine Silicotungstate.*—This was a yellowish pulverulent compound, very insoluble in water and dilute acid.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{22}\text{H}_{23}\text{NO}_7$  (m. wt. 4533.5):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 62.74%;  $\text{C}_{22}\text{H}_{23}\text{NO}_7 + \text{H}_2\text{O}$ , 37.26%; N, 1.24%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 62.55%, 62.50%;  $\text{C}_{22}\text{H}_{23}\text{NO}_7 + \text{H}_2\text{O}$ , 37.45%, 37.50%; N, 1.31%.

*Strychnine Silicotungstate.*—This salt was previously prepared by Taigner (*loc. cit.*). The product obtained in this laboratory agrees with the one which he has described. The compound was extremely insoluble and required long washing with dilute hydrochloric acid to remove the excess of silicotungstic acid. The color was faintly yellow.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$  (m. wt. 4217.5):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 67.45%;  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2 + \text{H}_2\text{O}$ , 32.55%; N, 2.64%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 67.68%, 67.46%;  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2 + \text{H}_2\text{O}$ , 32.32%, 32.54%; N, 2.46%.

*Brucine Silicotungstate.*—It had a slight bluish tint and was very insoluble in water and dilute acids. Like the strychnine salt long washing was required to remove the excess of silicotungstic acid.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$  (m. wt. 4457.9):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 63.82%;  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4 + \text{H}_2\text{O}$ , 36.18%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 63.56%, 63.57%;  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4 + \text{H}_2\text{O}$ , 36.44%, 36.33%.

*Cocaine Silicotungstate.*—A white microcrystalline salt, already mentioned by Taigner (*loc. cit.*).

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{17}\text{H}_{21}\text{NO}_4$  (m. wt. 4093.5).  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 69.60%;  $\text{C}_{17}\text{H}_{21}\text{NO}_4 + \text{H}_2\text{O}$ , 30.40%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 69.80%, 69.70%;  $\text{C}_{17}\text{H}_{21}\text{NO}_4 + \text{H}_2\text{O}$ , 30.20%, 30.30%.

*Caffeine Silicotungstate.*—This first precipitated as a white amorphous compound but changed to pale yellow crystals on standing.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$  (m. wt. 3657):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 77.78%;  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2 + \text{H}_2\text{O}$ , 22.22%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 77.60%, 77.50%;  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2 + \text{H}_2\text{O}$ , 22.40%, 22.50%.

*Theobromine Silicotungstate.*—This formed as a faint yellow powder.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_7\text{H}_8\text{N}_4\text{O}_2$  (m. wt. 3600.8):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 78.99%;  $\text{C}_7\text{H}_8\text{N}_4\text{O}_2 + \text{H}_2\text{O}$ , 21.01%; N, 6.23%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 78.77%, 78.84%;  $\text{C}_7\text{H}_8\text{N}_4\text{O}_2 + \text{H}_2\text{O}$ , 21.23%, 21.16%; N, 6.10%.

*Veratrine Silicotungstate.*—The compound had a slight purple color, which was deepened by heating in dilute sulphuric acid. A discrepancy existed between the composition as determined by theory and analysis. The salt was prepared from several different lots of alkaloid with invariably the same composition. Heiduschka and Wolff (17) state that the 1 : 4 compound could only be obtained by precipitation in alcoholic solution.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{32}\text{H}_{49}\text{NO}_9$  (m. wt. 5246.5):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 54.22%;  $\text{C}_{32}\text{H}_{49}\text{NO}_9 + \text{H}_2\text{O}$ , 45.78%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 55.55%, 55.51%;  $\text{C}_{32}\text{H}_{49}\text{NO}_9 + \text{H}_2\text{O}$ , 44.45%, 44.49%.

*Colchicine Silicotungstate.*—This was a bright yellow amorphous salt.

*Analysis.* Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{22}\text{H}_{26}\text{NO}_6$  (m. wt. 4477.3):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 63.53%;  $\text{C}_{22}\text{H}_{26}\text{NO}_6 + \text{H}_2\text{O}$ , 36.47%; N, 1.25%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 63.55%, 63.45%;  $\text{C}_{22}\text{H}_{26}\text{NO}_6 + \text{H}_2\text{O}$ , 36.45%, 36.55%; N, 1.21%.



Jensen (23) claims to have prepared a salt in which the ratio of acid to base was 1:5.

*Atropine Silicotungstate*.—This salt was also prepared by Taigner (*loc. cit.*). It is a white crystalline compound, slightly soluble in hot dilute hydrochloric acid. The solubility, however, is slight enough to permit of quantitative precipitation from a concentrated solution.

*Analysis*. Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{17}\text{H}_{23}\text{NO}_3$  (m. wt. 4037.4):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 70.45%;  $\text{C}_{17}\text{H}_{23}\text{NO}_3 + \text{H}_2\text{O}$ , 29.55%; N, 1.39%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 70.05%, 70.23%;  $\text{C}_{17}\text{H}_{23}\text{NO}_3 + \text{H}_2\text{O}$ , 29.95%, 29.77%; N, 1.46%.

*Hyoscyamine Silicotungstate*.—Like the atropine salt, this compound was white, crystalline and moderately soluble.

*Analysis*. Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{17}\text{H}_{23}\text{NO}_3$  (m. wt. 4037.4):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 70.45%;  $\text{C}_{17}\text{H}_{23}\text{NO}_3 + \text{H}_2\text{O}$ , 29.55%; N, 1.39%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 70.34%, 70.47%;  $\text{C}_{17}\text{H}_{23}\text{NO}_3 + \text{H}_2\text{O}$ , 29.66%, 29.53%; N, 1.30%.

*Berberine Silicotungstate*.—This was a saffron-colored compound. Pictet (24) gives  $\text{C}_{20}\text{H}_{17}\text{NO}_4$  as the composition of berberine; Schmidt (25),  $\text{C}_{20}\text{H}_{19}\text{NO}_5$ . Schmidt's formula was used in the following calculations.

*Analysis*. Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{20}\text{H}_{19}\text{NO}_5$  (m. wt. 4293):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 66.25%;  $\text{C}_{20}\text{H}_{19}\text{NO}_5 + \text{H}_2\text{O}$ , 33.75%; N, 1.31%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 66.00%, 66.06%;  $\text{C}_{20}\text{H}_{19}\text{NO}_5 + \text{H}_2\text{O}$ , 34.00%, 33.94%; N, 1.27%.

*Hydrastine Silicotungstate*.—This was a pale yellow amorphous compound.

*Analysis*. Calculated for  $2\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{C}_{21}\text{H}_{21}\text{NO}_6$  (m. wt. 4413.4):  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 64.45%;  $\text{C}_{21}\text{H}_{21}\text{NO}_6 + \text{H}_2\text{O}$ , 35.55%; N, 1.27%. Found:  $\text{SiO}_2 \cdot 12\text{WO}_3$ , 64.27%, 64.20%;  $\text{C}_{21}\text{H}_{21}\text{NO}_6 + \text{H}_2\text{O}$ , 35.73%, 35.80%; N, 1.25%.

#### SUMMARY.

1. Silicoduodecitungstic acid has been prepared in a much more stable form than previously known by a simplification of a method devised by Copaux.
2. The acid was found to have the empirical formula  $4\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ . The acid formed normal salts with potassium and ammonium in which eight atoms of hydrogen were replaced by a base.
3. A difference in the degree of ionization of the acid hydrogens was observed. In that titrations of the acid by means of a base with methyl orange or methyl red as indicator show a sharp endpoint when four of these hydrogens have been replaced.
4. The acid forms stable salts with tertiary organic bases. The salts of a large number of alkaloids have been prepared, the majority of which are so insoluble as to indicate the possibility of employing them in a quantitative procedure.
5. The salts of the tertiary bases, precipitated from acid solution, show a partial dehydration of the same order as that existing in a dichromate.
6. All of the phases of this investigation are being continued.

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URBANA, ILLINOIS,  
AUGUST, 1924.

(Part II will appear in a succeeding issue.)

### PHYTOCHEMICAL NOTES.\*

#### No. 94. Oil of *Echinacea angustifolia*.<sup>1</sup>

BY FRITZ BISCHOFF.

Two samples of a volatile oil, recently discovered by Professor Lloyd in the root of *Echinacea angustifolia*, were submitted by him to this laboratory. He had observed that the yield from the fresh roots was somewhat greater, *viz.*, 1.5 p. c., than that from the dry roots, *viz.*, 1.25 p. c. However, the physical constants of both oils were found to be very nearly identical, the most characteristic being the remarkably low density of 0.80. The results of this preliminary study indicate that the oils consist for the most part of a single constituent, which is very probably a tetrahydrosesquiterpene with two double bonds. Over 80% of the oil, either from the fresh or dried roots, boils within a range of 8°. By fractionation it was possible to obtain 40% of the total oil boiling within 2°. The analysis for carbon and hydrogen, the boiling point range (at 260° C.) and the fact that the substance adds on an amount of bromine equivalent to two double bonds pointed to the empirical formula

\* From the laboratory of Edward Kremers.

<sup>1</sup> History of the Discovery of the Volatile Oil of *Echinacea* Root.

In the working of *Echinacea* on a large scale by means of the extracting apparatus employed in my laboratory, the content of the concentrator gradually changes from a highly alcoholic menstruum to one which, if the drug be fresh, and not fully dried, becomes practically an aqueous liquid.

It was noticed in the manipulation that when this liquid was withdrawn from the concentrator and allowed to stand, an oily substance separated and floated on the surface, this being in considerable amount when large batches (1000 lbs. each) were manipulated.

In the finishing of the preparation for use of physicians, alcohol was employed as a diluent of the mixture as a whole, the amount being established by another constituent of *Echinacea* quite different from this oily separate, which, but without any recognition whatever of its presence, became a part of the final product.

On further examination and separation of the oil, it was found that on standing it separated an extraneous coloring material, the greater part of it becoming an overlying, practically transparent oil. This, decanted and filtered, but without further manipulation, constitutes the oil you have received, and which so excited my interest as to lead me to feel assured it was worthy of scientific examination.

Very truly yours,

JOHN URI LLOYD, May 17, 1924.