

SHIKIMIC ACID AND DERIVATIVES.*

I. SALTS OF SHIKIMIC ACID.

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A. Salts of Metals.—The following salts of metals have been described thus far, *viz.*, those of sodium, potassium, magnesium, calcium, strontium, barium and lead. Apparently the three hydroxy groups in shikimic acid interfere with the isolation of simple salts in crystalline form. Previous work has been repeated and attempts to prepare new salts were made.

Lithium Shikimate.—This was made by the action of shikimic acid on lithium carbonate in the presence of water. The product was amorphous. Being difficultly soluble in organic solvents, recrystallization did not prove satisfactory. When heated with xylene to remove moisture (3.4 p. c.), it was obtained in slightly colored scales. Analyses yielded the following results:

1. 0.2001 Gm. gave 0.059 Gm. Li_2SO_4 , corresponding to 3.72 p. c. Li.
 2. 0.2045 Gm. gave 0.061 Gm. Li_2SO_4 , corresponding to 3.76 p. c. Li.
- The theoretical percentage is 3.86 p. c.

Sodium Shikimate.—This is one of the few salts previously described. It was obtained by Eykman (1) in 1891 as "large rhombic sphenoids." It was again prepared by S. Y. Chen (2) in 1929. No difficulty was experienced in its preparation. When analyzed, the following results were obtained:

1. 0.2675 Gm. yielded 0.0830 Gm. Na_2SO_4 = 10.05 p. c. Na.
 2. 0.3220 Gm. yielded 0.1005 Gm. Na_2SO_4 = 10.11 p. c. Na.
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| Calculated for $\text{C}_6\text{H}_8(\text{OH})_3\text{COONa}$ | 11.74 p. c. |
| $\text{C}_6\text{H}_8(\text{OH})_3\text{COONa} \cdot 2\text{H}_2\text{O}$ | 9.91 p. c. |
| $\text{C}_6\text{H}_8(\text{OH})_3\text{COONa} \cdot \text{H}_2\text{O}$ | 10.75 p. c. |

Potassium Shikimate.—This salt was obtained in an amorphous condition by S. Y. Chen (3) in 1929. Repetition of the experiment yielded crystals as large as those of the sodium salt. However, when prepared from an alcoholic medium needle-shaped crystals resulted.

When analyzed, the following results were obtained:

1. 0.3172 Gm. yielded 0.1332 Gm. K_2SO_4 = 18.84 p. c. K.
 2. 0.2035 Gm. yielded 0.0835 Gm. K_2SO_4 = 18.41 p. c. K.
- Computed for $\text{C}_6\text{H}_8(\text{OH})_3\text{COOK}$ 18.43 p. c. K.

Silver Shikimate.—This salt was obtained by heating the acid with freshly precipitated silver oxide in the presence of water. Recrystallized from water, it was obtained in prisms.

Upon analysis the following results were obtained:

1. 0.2327 Gm. yielded 0.0892 Gm. Ag corresponding to 38.33 p. c. Ag.
 2. 0.2270 Gm. yielded 0.1020 Gm. Ag corresponding to 38.24 p. c. Ag.
- Computed for $\text{C}_6\text{H}_8(\text{OH})_3\text{COOAg}$ = 38.41 p. c.

Copper Shikimate was obtained by heating the acid with freshly precipitated

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cupric hydroxide suspended in water. A brownish green crystalline product resulted upon evaporation of the filtrate (from the excess $\text{Cu}(\text{OH})_2$). It is insoluble in organic solvents, but dissolves in concentrated alkali (without precipitation of cupric hydroxide).

Distilled with xylene it yielded 7.4 p. c. of water, corresponding to a dihydrate. The dehydrated salt was red in color. When analyzed, the following results were obtained:

1. 0.1910 Gm. yielded 0.0320 Gm. CuO corresponding to 13.38 p. c. Cu .
 2. 0.1447 Gm. yielded 0.0247 Gm. CuO corresponding to 13.63 p. c. Cu .
- Computed for $(\text{C}_6\text{H}_6(\text{OH})_3\text{COO})_2\text{Cu} = 15.52$ p. c.
 Computed for $(\text{C}_6\text{H}_6(\text{OH})_3\text{COO})_2\text{Cu}\cdot 3\text{H}_2\text{O} = 13.71$ p. c.

Chen in 1929 called attention to the fact that a strongly alkaline solution of shikimic acid mixed with a solution of copper sulfate yields a solution similar to Fehling's solution (8). Like tartaric acid, shikimic acid is a hydroxy acid.

Magnesium Shikimate.—This was reported by S. Y. Chen in 1929 (4). The salt was obtained in an amorphous condition from magnesium carbonate and shikimic acid in the presence of water. The amorphous mass is very hygroscopic and difficultly soluble in organic solvents. When heated with xylene to remove moisture (15 p. c.) slightly colored microscales were obtained which are no longer hygroscopic.

Analysis yielded the following results:

1. 0.1792-Gm. sample gave 0.0190 Gm. MgO corresponding to 6.63 p. c. Mg .
 2. 0.1870-Gm. sample gave 0.0201 Gm. MgO corresponding to 6.48 p. c. Mg .
- Computed for $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Mg} = 6.57$ p. c.

Calcium Shikimate.—It was prepared by Oswald in 1891 (5); also by S. Y. Chen in 1929 (6). The salt was made by neutralizing shikimic acid with milk of lime. A crystalline compound was obtained. It can be precipitated from its aqueous solution by methyl alcohol and can be crystallized from dilute alcohol.

Analysis yielded the following results:

1. 0.2040-Gm. sample gave 0.0627 Gm. CaSO_4 corresponding to 9.05 p. c. Ca .
 2. 0.2493-Gm. sample gave 0.0765 Gm. CaSO_4 corresponding to 9.04 p. c. Ca .
- Computed for $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Ca} = 10.37$ p. c.
 Computed for $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Ca}\cdot 3\text{H}_2\text{O} = 9.11$ p. c.

The salt may be crystallized with three molecules of water.

Oswald reported with $6\text{H}_2\text{O}$.

Strontium Shikimate.—It also was prepared by Oswald in 1891 (7); again by S. Y. Chen in 1929 (8). Repetition of their experiments yielded a powder. It is slightly soluble in acetone and very difficultly soluble in other organic solvents.

Analysis yielded the following results:

1. 0.2492-Gm. sample gave 0.0982 Gm. SrSO_4 corresponding to 18.37 p. c. Sr .
 2. 0.2524-Gm. sample gave 0.0997 Gm. SrSO_4 corresponding to 18.84 p. c. Sr .
- Computed for $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Sr} = 20.21$ p. c.
 Computed for $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Sr}\cdot 2\text{H}_2\text{O} = 18.66$ p. c.

Oswald also reported $2\text{H}_2\text{O}$ of crystallization.

Barium Shikimate.—This was likewise prepared by Oswald in 1891 (9); also by S. Y. Chen in 1929 (10). An amorphous brittle mass was obtained by heating barium carbonate and shikimic acid with water. Like the lithium salt it is very difficultly soluble in organic solvents.

Analysis yielded the following results:

1. 0.2102-Gm. sample gave 0.0877 Gm. BaSO_4 corresponding to 24.56 p. c. Ba.
 2. 0.2672-Gm. sample gave 0.1120 Gm. BaSO_4 corresponding to 24.67 p. c. Ba.
- Computed for $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Ba} = 28.42$ p. c.
Computed for $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Ba} \cdot 4\text{H}_2\text{O} = 24.74$ p. c.

Oswald reported no water of crystallization.

Lead Shikimate.—This was made by the action of shikimic acid on lead carbonate in the presence of water. An amorphous brittle mass was obtained as Chen reported in 1929. Attempts to recrystallize it from organic solvents were not successful. When heated with xylene to remove moisture (5.5 p. c.), it was obtained in yellowish brown scales.

Analysis yielded the following results:

1. 0.321-Gm. sample gave 0.169 Gm. PbSO_4 corresponding to 35.97 p. c. Pb.
 2. 0.3085-Gm. sample gave 0.162 Gm. PbSO_4 corresponding to 35.87 p. c. Pb.
- Computed for $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Pb} = 37.45$ p. c.
Computed for $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Pb} \cdot 2\text{H}_2\text{O} = 35.98$ p. c.

Zinc Shikimate.—This salt was obtained from zinc carbonate and shikimic acid in aqueous solution. It can be purified by recrystallizing from water or by dissolving in water and then precipitated with alcohol. It was obtained in crystalline form. Upon analysis the following results were obtained:

1. 0.1988 Gm. yielded 0.0395 Gm. ZnO corresponding to 15.96 p. c. Zn.
 2. 0.1484 Gm. yielded 0.03 Gm. ZnO corresponding to 16.23 p. c. Zn.
 3. 0.1059 Gm. yielded 0.0211 Gm. ZnO corresponding to 15.96 p. c. Zn.
- The theoretical percentage is 15.89.

REFERENCES.

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Dr. William E. Weiss gave the address of welcome to the convention of the National Wholesale Druggists at White Sulphur Springs, West Virginia, on October 4th. He made the following timely statement:

"Any new plan, law or proposal which fails to consider the wholesaler, the manufacturer, the retailer, the employees of our industry and the general public—which favors one or more at the expense of another—no matter how bright and promising it may appear when first examined, it must eventually fail to accomplish any permanent good purpose."