The acetate of m. p. 123° is so readily hydrolyzed that it is difficult to free it completely from acetic acid. Aqueous solutions become acid to test paper after standing a few minutes at room temperature. When this acetate is heated in a bath at 200° for twenty minutes, it rearranges with the formation of 1-acetyl-5,5-dimethylhydantoin and unidentified products.

We may formulate the acetate of m. p. 123° either as 3-acetyl-5,5-dimethylhydantoin or as 5,5-dimethylhydantoin-2-enolacetate. We prefer the latter because the structure of an enol acetate seems more consistent with the ease of hydrolysis and rearrangement.

THE RESEARCH LABORATORIES
WALLACE & TIERNAN PRODUCTS CO.
BELLEVILLE, NEW JERSEY RECEIVED OCTOBER 10, 1945

Determination of the Nature of the Volatile Base from the Rhizome of the Pitcher Plant *Sarracenia Purpurea*

BY A. WALTI*

Medicinal properties have repeatedly been ascribed to the rhizome of the pitcher plant, *Sarracenia purpurea*.[1] More recently Judovich[2] has prepared an aqueous distillate from the rhizome of the pitcher plant which has been used for the relief of spinal root pain.[3] The effect of the distillate of the pitcher plant rhizome on the isolated saphenous nerve of the cat has been investigated by Stewart and Hughes by the cathode ray oscillograph method. They found that it obliterated the potentials of the pain-carrying C fibers of the nerve but not those of the motor carrying fibers at the concentrations used.[4]

We have investigated the distillate of this plant rhizome which was obtained on steam fractionation of the powdered rhizome in the presence of caustic alkali and found it to yield a volatile base with an amino-like odor as previously mentioned by Bjorklund and Dragendorff.[5] On neutralization with hydrochloric or sulfuric acid, salts were formed which on crystallization were found to be identical with those of ammonium chloride and ammonium sulfate, respectively. The effects of ammonium chloride on the saphenous nerve when tested by the cathode ray oscillograph as well as the clinical results with ammonium chloride and ammonium sulfate on intractable pain reported by Bates and Judovich were in agreement with those previously obtained with the neutralized distillate of the pitcher plant rhizome.[6]

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(1) For review see J. S. Hepburn, *Am. J. Pharm.*, **100**, 675 (1928).

(2) B. D. Judovich, *Med. Rec.*, **141**, 583–585 (1935).

(3) Bates, Wand, B. D. Judovich, *Clin. Med. Surg.*, **46**, 205–207 (1939).

(4) W. B. Stewart, B. D. Judovich, T. Hughes and A. Walti, *Am. J. Physiol.*, **129**, 474 (1940).

(5) Bjorklund and Dragendorff, *Arch. Pharm.*, **169**, 93 (1864).

(6) W. Bates and B. D. Judovich, *Anesthesiology*, **3**, 663 (1942); B. D. Judovich, *ibid.*, **4**, 313 (1943).

Experimental

A suspension was made of 500 g. of powdered pitcher plant rhizome, *Sarracenia purpurea*, in 1200 ml. of distilled water and 400 ml. of 30% sodium hydroxide. Steam was passed through the mixture until the last runnings of the distillate no longer gave a positive test for volatile base with litmus. The distillate was slightly turbid and had a distinct amine-like odor. It was neutralized with hydrochloric acid and concentrated at reduced pressure. The colored solution was treated with a little charcoal, filtered and concentrated further until crystallization occurred. The crystals were dissolved in little water, again treated with charcoal, filtered and alcohol was added until crystallization occurred. This crystallization was repeated. Recrystallization gave material which did not melt up to 320° and sublimed when heated in a small test-tube over a free flame.

Elementary analysis of the substance gave the following values. *Anal.* Calcd. for NH_4Cl: N, 26.2; Cl, 66.3. Found: N, 25.6; Cl, 64.6.

The crystalline substance yielded a flavianate, m. p. 289°, and that prepared from reagent ammonium chloride melted at 291°. A 5% solution of the isolated substance and one prepared from laboratory reagent ammonium chloride gave identical orange precipitates on treatment with an equal amount of Nessler reagent, and white precipitates with 10% phosphotungstic acid. It was evident, therefore, that the crystalline compound isolated from the neutralized distillate was ammonium chloride.

In another experiment, the alkaline distillate was neutralized with dilute sulfuric acid. The concentrated solution was clarified with little charcoal and concentrated till crystallization occurred. The perfectly white crystals gave the following analysis. *Anal.* Calcd. for $(NH_4)_2SO_4$: N, 21.21; S, 24.27. Found: N, 21.23; S, 23.92.

RESEARCH LABORATORIES
MERCK AND COMPANY, INC.
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NEW COMPOUNDS

Some Higher Alkyl Salicylates

Although a great many derivatives of salicylic acid have been prepared, there is scant mention in the chemical literature of the simple saturated alkyl salicylates in which the alkyl group contains more than five carbon atoms.[1] In order to study possible uses of these compounds we have prepared all of the straight-chain even-numbered alkyl salicylates from butyl to octadecyl, 2-ethylhexyl salicylate and the salicylic acid esters of 2-methoxyethanol (Methyl Cellosolve) and 2-ethoxyethanol (Cellosolve). Some of these esters were characterized as their 3,5-dinitrobenzoates and others as their 3,5-dinitro derivatives; neither derivative is very suitable for characterization because of the difficulty of crystallization, the low melting points, and the close proximity of the melting points of the

(1) Sah and Ma, *Science Repts. Natl. Tsing Hua Univ., Ser. A*, **1**, 201 (1932); *Chem. Zentr.*, **103**, II, 3389 (1932); *C. A.*, **26**, 5929 (1932), have reported physical constants for carefully purified samples of methyl, ethyl, propyl, isopropyl, butyl, isobutyl and isoamyl salicylate. Freeman and Haller, THIS JOURNAL, **60**, 2274 (1938), have done the same for *n*-amyl, *t*-amyl and 1-methylbutyl salicylate. Cleveland, U. S. Patent 1,911,551, claimed the use of an otherwise undescribed hexyl salicylate. Roger and Dvolaitskaya, *Recherches (Roure-Betrand fils)*, **1**, 79 (1937); *C. A.*, **32**, 1241 (1938), prepared and characterized *n*-heptyl salicylate. Rule, Miles and MacGillivray, *J. Chem. Soc.*, **132**, 2274 (1929), prepared *d-s-β*-octyl salicylate. Segessemann, U. S. Patent 2,093,576, described the sulfonation of the otherwise undescribed 2-ethylhexyl salicylate Thomas, U. S. Patent 2,062,950, described dodecyl salicylate, characterized only by its saponification number.