

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 Judovich² 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 amine-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

* Present address: Interchemical Corp., Biochemical Div., Union, N. J.

- (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 $(\text{NH}_4)_2\text{SO}_4$: N, 21.21; S, 24.27. Found: N, 21.23; S, 23.92.

RESEARCH LABORATORIES
MERCK AND COMPANY, INC.
RAHWAY, NEW JERSEY RECEIVED SEPTEMBER 8, 1945

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, *i*-amyl and 1-methylbutyl salicylate. Cleveland, U. S. Patent 1,911,551, claimed the use of an otherwise undescribed hexyl salicylate. Roger and Dvolaitzkaya, *Recherches (Roure-Bertrand 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*-*o*-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.

TABLE I
ALKYL SALICYLATES

Alky	B. p. ^a or m. p. ^a	Yield, %	n _D ²⁰	Formula	Analyses, % ^b				De- riv. ^c	M. p., °C.	Formula	% N	
					Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found				Calcd.	Found
—C ₄ H ₉ —n	145–147 (16 mm.)	94	1.5130	C ₁₁ H ₁₄ O ₇	68.04	68.17	7.22	7.29 ^d	A	85	C ₁₁ H ₁₄ N ₂ O ₇	7.22	6.84 ^e
—C ₄ H ₉ —n	167–168 (12 mm.)	93	1.5049	C ₁₁ H ₁₄ O ₇	70.27	70.02	8.11	7.44	B ^f	59.5–60	C ₁₁ H ₁₄ N ₂ O ₇		
—C ₈ H ₁₇ —n	172–173 (6 mm.)	55	1.4983	C ₁₅ H ₂₀ O ₇	72.00	71.62	8.80	9.14	A	45	C ₁₅ H ₂₀ N ₂ O ₇	6.30	6.49 ^g
—C ₁₀ H ₂₁ —n	139–141 (0.08 mm.)	61	1.4937	C ₁₇ H ₂₄ O ₇	73.38	73.23	9.36	9.28					
—C ₁₁ H ₂₃ —n	158–163 (0.08 mm.)	70		C ₁₉ H ₂₆ O ₇	74.51	74.88	9.81	9.70	A	42	C ₁₉ H ₂₆ N ₂ O ₇	5.60	5.57 ^h
	25								B	45.5–46	C ₁₉ H ₂₆ N ₂ O ₇	7.07	7.12
—C ₁₄ H ₂₉ —n	40.5	50		C ₂₂ H ₃₂ O ₇	75.45	75.10	10.17	10.42	B	52–53	C ₂₂ H ₃₂ N ₂ O ₇	6.60	7.01
—C ₁₆ H ₃₃ —n	43–44	55		C ₂₄ H ₃₆ O ₇	76.24	76.01	10.50	9.98	B	50–51	C ₂₄ H ₃₆ N ₂ O ₇	3.27	3.44
—C ₁₈ H ₃₇ —n	53	85		C ₂₆ H ₄₀ O ₇	76.92	77.26	10.77	11.06	B	66.5–67	C ₂₆ H ₄₀ N ₂ O ₇	5.83	5.52
—CH ₂ CH(C ₂ H ₅)C ₆ H ₅ —n	189–190 (21 mm.)	67	1.5018	C ₁₈ H ₂₂ O ₇	72.00	71.45	8.80	8.41	A	95	C ₁₇ H ₁₄ N ₂ O ₇	7.18	6.97 ⁱ
—CH ₂ CH ₂ OCH ₃	145 (10 mm.)	84	1.5227	C ₁₀ H ₁₂ O ₇	61.22	60.80	6.12	6.15					
—CH ₂ CH ₂ OC ₂ H ₅	152 (10 mm.)	85	1.5157	C ₁₁ H ₁₄ O ₇	62.86	61.63	6.67	6.09					

^a All melting points and boiling points are uncorrected. ^b Microanalyses are by Misses P. Curran and A. Rainey. ^c A = 3,5-Dinitrobenzoate; B = 3,5-dinitro. ^d This is a previously reported compound; see Sah and Ma (ref. 1) and also Croxall, Sowa and Nieuwland, *J. Org. Chem.*, **2**, 253 (1937). ^e %C, calcd.: 55.67; found: 55.92; %H, calcd.: 4.12, found: 4.16. ^f Prepared and analyzed by Sah and Ma (ref. 1). ^g %C, calcd.: 59.46; found: 59.21; %H, calcd.: 5.41; found: 4.69. ^h %C, calcd.: 62.40; found: 62.34; %H, calcd.: 6.40; found: 6.08. ⁱ The mononitro derivative was obtained with this ester. ^j %C, calcd.: 52.31; found: 51.78; %H, calcd.: 3.59; found: 3.35.

homologs. The esters and derivatives prepared are listed in Table I.

The esters were all prepared by standard procedures, the actual conditions used for each one being determined by the boiling point and water-solubility of the alcohol being used.

RESEARCH LABORATORIES FREEMAN H. McMILLAN
WINTHROP CHEMICAL COMPANY, INC.
RENSSELAER, NEW YORK JOHN A. KING

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N-Furfurylmaaleamic Acid and N,N-Furfurylmethylmaleamic Acid

The following two derivatives were obtained by mixing maleic anhydride with an equivalent amount of the corresponding amine in ether. Considerable heat was evolved in both instances, with the products precipitating almost immediately.

N-Furfurylmaaleamic Acid.—Seven grams of furfurylamine gave 10 g. of white plates, m. p. 114° (uncor.), recrystallized first from an alcohol-ether mixture, and then from alcohol. The crystals are soluble in alcohol, water, ethyl acetate and acetone, insoluble in ether.

Anal. Calcd. for C₉H₈O₄N: C, 55.33; H, 4.62; neut. equiv., 195. Found: C, 55.28; H, 4.59; neut. equiv., 192.

N,N-Furfurylmethylmaleamic Acid.—Five grams of furfurylmethylamine gave 5 g. of white product, m. p. 172–173° (uncor.), recrystallized twice from a mixture of alcohol and ether, soluble in alcohol, ethyl acetate, water, acetone and methanol, insoluble in ether.

Anal. Calcd. for C₁₀H₁₁O₄N: C, 57.42; H, 5.26; neut. equiv., 209. Found: C, 57.43; H, 5.29; neut. equiv., 206.

CHEMISTRY LABORATORY
UNIVERSITY OF COLORADO
BOULDER, COLORADO

WERNER HERZ

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β',β'',β'''-Triethoxytriethylamine¹

This non-toxic compound resulted instead of trivinylamine by heating a solution of 6.24 g. (0.111 mole) of potassium hydroxide in 25 cc. 95% ethanol, under reflux, with 4.42 g. (0.0183 mole) of trichlorotriethylamine hydro-

(1) This compound is mentioned in French Patent 711,500 (1931), but no description of its preparation or properties is recorded. The compound also is incorrectly indexed in *C. A.*, **31**, 10, 274 (1937), since the reference contains no mention of it.

chloride [McCombie and Purdie, *J. Chem. Soc.* 1217 (1935)] for three hours. After filtration of the potassium chloride (theoretical quantity) the alcoholic filtrate was evaporated under 10 mm., the residue was taken up in water, thrice extracted with ether and the ether solution dried with magnesium sulfate. Distillation at 134–137° under 12 mm. yielded 2.80 g. (66%) of triethoxytriethylamine, *d*₄²⁰, 0.936. This compound could be precipitated by hydrogen chloride from ethanol solution as its hydrochloride, m. p. 193–195°. The amine was analyzed.

Anal. Calcd. for C₁₂H₂₇O₃N: C, 61.8; H, 11.6; neut. equiv., 233. Found: C, 61.7; H, 11.5; neut. equiv., 221.

When the amine was treated with one equivalent of picric acid in ethanol and crystallized from this medium, a picrate m. p. 65–66° was formed.

Anal. Calcd. for C₁₈H₃₀O₁₀N₄: C, 46.75; H, 6.54. Found: C, 47.0; H, 6.26.

When two equivalents of picric acid were used, the compound 2 picric acid: 1,β',β'',β'''-triethoxytriethylamine was formed, m. p. 229° after crystallization from alcohol.

Anal. Calcd. for C₂₄H₃₃O₁₇N₇: C, 41.7; H, 4.82. Found: C, 42.0; H, 5.09.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TORONTO
TORONTO, ONTARIO, CANADA

H. H. RICHMOND
GEORGE F. WRIGHT

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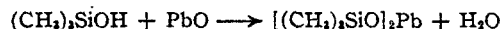
Di-(trimethylsilyl) Sulfate and Lead Trimethylsilanolate

Di-(trimethylsilyl) sulfate has been prepared by the reaction



It is a white crystalline solid, easily hydrolyzed by water to hexamethyldisiloxane and sulfuric acid. The corresponding chloride¹ and phosphate² are liquids, likewise easily hydrolyzable.

Lead trimethylsilanolate has been prepared by the reaction



It is a white crystalline solid, soluble in organic solvents, and is easily hydrolyzed by dilute sulfuric acid.

Di-(trimethylsilyl) Sulfate.—Nine and eight-tenths grams of sulfuric acid was added dropwise to 23.8 g. of (CH₃)₃SiCl with violent shaking. Hydrogen chloride was

(1) A. G. Taylor and B. V. dG. Walden, *This Journal*, **66**, 842 (1944); W. F. Gilliam and R. O. Sauer, *ibid.*, **66**, 1793 (1944).

(2) R. O. Sauer, *ibid.*, **66**, 1707 (1944).