

TABLE I
PROPERTIES OF THE ALKYL SULFONIC ACIDS

Acid	B. p. Temp., °C.	Pressure, mm.	M. p., °C.	Density ²⁴
Methyl sulfonic ²	167	10	+20	1.4844
Ethyl sulfonic ²	-17	1.3341
<i>n</i> -Propyl sulfonic	136	1	+ 7.5	1.2516
<i>n</i> -Butyl sulfonic	147	0.5	-15.2	1.1906 ^a
<i>n</i> -Amyl sulfonic	163	1	+15.9	1.1226
<i>n</i> -Hexyl sulfonic	174	1	+16.1	1.1047

^a d_4^{20} , 1.2117.

as indicator was as follows: propyl, 99.2; butyl, 100; amyl, 100; hexyl, 99.8%. Presumably the propyl acid still retained a trace of moisture.

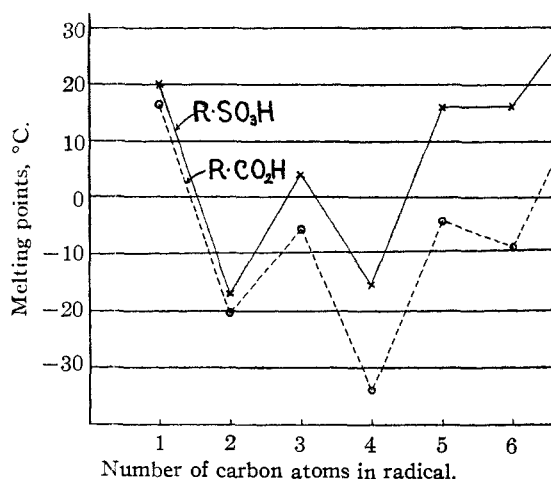


Fig. 1.—Melting points of sulfonic and carbonic acids.

The physical data obtained with these acids, together with the corresponding data for methyl and ethyl acids, are given in Table I.

These melting points are plotted along with those of the carboxy acids containing the same radicals in Fig. 1. The alternation is remarkably alike in the two series.

The acid chloride of the butyl sulfonic acid was prepared by the action of phosphorus pentachloride on the potassium salt. It boiled at 90° at 11 mm.,⁵ and had d_4^{25} , 1.2140, and d_4^{20} , 1.2404.

It was thought that butyl sulfonic acid might resemble sulfuric acid in substitution reactions, but it did not react with benzene at 80°. Aniline sulfate rearranges to sulfanilic acid, but the aniline salt of butyl sulfonic acid did not undergo any change when heated several hours at 130°. This salt is readily made by adding aniline to the acid and warming slightly. After one recrystallization it melted at 162°. Gilman and Morris⁶ give m. p. 159° for this salt obtained by the reaction of thionylaniline with butylmagnesium bromide.

Summary

n-Propyl, *n*-butyl, *n*-amyl and *n*-hexyl sulfonic acids have been prepared and characterized.

(5) Von Braun and Weissbach, *Ber.*, **63**, 2836 (1930).

(6) Gilman and Morris, *THIS JOURNAL*, **48**, 2399 (1926).

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The Isolation and Some Properties of an Alkaloid from *Crotalaria spectabilis* Roth¹

BY W. M. NEAL, L. L. RUSOFF AND C. F. AHMANN

The literature relative to the toxic species of the *Crotalariae* was reviewed in another paper,² in which the toxicity of *C. spectabilis* Roth was established. Previously known toxic species included *C. sagittalis* L., *C. juncea* L., *C. burkeana* Benth., *C. dura* Wood and Evans, and *C. globifera* E. Mey. Still other species have been suspected. Bessey and Stalker³ suspected the toxic principle of *C. sagittalis* to be an alkaloid.

(1) Presented in part before the Division of Medicinal Chemistry of the American Chemical Society at the 87th Meeting of the Society, St. Petersburg, Fla., March 25 to 30, 1934.

(2) Becker, Neal, Arnold and Shealy, *J. Agr. Research*, **50**, 911 (1935).

(3) Bessey and Stalker, *Iowa Agr. Coll. Dept. Bot. Bull.*, **111** (1884).

Timson⁴ found the seeds of *C. juncea* to give reactions suggesting the presence of an unidentified alkaloid. In no case had a specific alkaloid been isolated from any member of the genus.

This is a report of the isolation and some of the properties of an alkaloid isolated from *C. spectabilis*. Because of the large number of species (over 600) of *Crotalaria*, several of which have proven toxic, the name *monocrotaline* is suggested for this alkaloid. Succeeding alkaloids from this genus can then be named *dicrotoline*, *tricrotaline*, etc., following Couch's⁵ recommendation for the lupine alkaloids.

(4) Timson, *Rhodesia Agr. J.*, **26**, 668 (1929).

(5) Couch, *THIS JOURNAL*, **56**, 155 (1934).

Experimental

The first extracts of the seeds of *C. spectabilis* were made by soaking them in 1.25% sulfuric acid. The filtrate was shaken with Lloyd's alkaloid reagent. The basic material was liberated from the reagent with 0.1 *N* sodium hydroxide. This solution was extracted with successive portions of chloroform. Opaque crystals remained upon evaporation of the solvent.

Later extracts were made by soaking the seeds in 5% ammonium hydroxide for forty-eight hours, and extracting the filtrate with successive portions of chloroform. The crystals obtained upon evaporation of the solvent were dissolved in 1:1 hydrochloric acid, the solution thus formed was made alkaline with ammonium hydroxide, and extracted as above. Further purification was by repeated recrystallization from chloroform or absolute alcohol. Crystals from the alcohol were transparent. Crude extracts equivalent to 0.4, 0.07 and 0.015% of the dry weights of the seeds, leaves and stems, respectively, of *C. spectabilis* were prepared.

The extracted substance is soluble in chloroform and alcohol, slightly soluble in ether and very slightly soluble in water.

The compound slowly decolorizes potassium permanganate, and gives a yellowish color with Fröhde's (sulfomolybdic acid) reagent. It yields a yellowish precipitate with picric acid, a reddish-brown precipitate with Wagner's iodide reagent, a white precipitate with Mayer's reagent and a yellowish-white precipitate with Sonnenschein's phosphomolybdic acid reagent. It forms precipitates with salts of the heavy metals. All the tests were characteristic of alkaloids.

Melting point determinations of the purified compound were between 196 and 197° (uncorr.).

Anal. Calcd. for $C_{16}H_{26}O_6N$: C, 58.51; H, 7.98; N, 4.27. Found: C, 57.97; H, 7.85; N, 4.15.⁶ The molecular weight, by the above formula, is 328.3. The determination of the neutral equivalent indicated a molecular weight of 324.

Pharmacologically, it lowers the blood pressure in dogs, and decreases the rate and amplitude of terrapin heart *in situ*. This decrease was observed even when the vagus nerve was severed. The rate of contraction of isolated heart muscle strips from terrapin is stimulated immediately, followed by a decrease in rate and amplitude.

The same lesions were observed in experimental animals administered lethal doses when either the whole seeds or alkaloid *per se* was used. This would indicate that the alkaloid isolated is the toxic principle of this plant. The twenty-four-hour lethal dose for chickens is 65 mg./kg. live weight.

Summary

The initial isolation of a specific alkaloid from the genus *Crotalaria* is reported. This compound has been named *monocrotaline* and was isolated from *C. spectabilis* Roth.

The compound melts at 196–197°, and has been given the empirical formula $C_{16}H_{26}O_6N$, tentatively.

The identity of the compound as the toxic principle of *C. spectabilis* has been established.

(6) The authors are indebted to Dr. H. G. Shaw for the combustion analysis.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Energy Levels in Electrochemistry

BY WILDER D. BANCROFT AND JAMES E. MAGOFFIN

When measured against any standard electrode the changes $Cu \rightleftharpoons Cu^{++}$ and $Fe^{++} \rightleftharpoons Fe^{+++}$ are practically reversible. The change $H_2 \rightleftharpoons 2H^+$ is practically reversible at platinum black; but may show a large difference at zinc or mercury because the rate of change of atomic hydrogen to molecular hydrogen is rapid at platinum and relatively slow at zinc or mercury. To pass from hydrogen ion to molecular hydrogen, the system may have to pass through a higher energy level than molecular hydrogen. Given a substance which can be reduced at a lower energy level than that of molecular hydrogen, and it will be reduced at a platinum cathode. If the required energy level is above the molecular hydrogen level and below the atomic hydrogen level which we get with a zinc

or mercury cathode, the substance cannot be reduced at a platinum cathode but can be at a zinc or mercury cathode. If the required energy level is above that to be reached with a zinc or mercury cathode, the substance cannot be reduced electrolytically in aqueous solution. Nobody is surprised at not being able to reduce methyl alcohol to paraffin; but no explanation has ever been given why it is impossible to reduce aqueous sodium sulfate or dilute sulfuric acid to sodium sulfite or sulfurous acid. The facts were known to Faraday. We have sealed up a sodium sulfate solution with platinum and hydrogen for six months without anything being formed in that time that would decolorize potassium permanganate.