equal parts of ether and benzene and 2 g. of phenylhydrazine in 10 cc. of ether added. After three hours, 1.6 g. of a voluminous solid, melting at 130–140°, was filtered off. Concentration of the mother liquor yielded 0.85 g. of a yellow compound, which after recrystallization from alcohol was identified as cinnamic aldehyde phenylhydrazone, by a mixed m. p. with an authentic sample. The lower melting compound was white, and after one recrystallization from alcohol melted at 138–140°. It was not investigated further and was probably the phenylhydrazide of cinnamalmalonic acid.

Synthesis of Cinnamylidene Cinnamalmalonate.—Two grams of cinnamalmalonic acid was suspended in a mixture of 4 g. each of acetic acid and acetic anhydride and 1.2 g. of cinnamic aldehyde, and two drops of sulfuric acid was added. The mixture warmed and became purple, slowly turning to green. On standing overnight a solid crystallized out. The solution was diluted with ether and filtered. The solid weighed 1.7 g. and an additional 0.5 g. was obtained from the mother liquor. After recrystallization from benzene–petroleum ether, the compound proved to be identical with the previously obtained cinnamylidene cinnamalmalonate.

Thermal Decomposition of β-Lactonic Acids.—Ten grams of β-phenyl-β-propiolactone-α-carboxylic acid (III) was heated at 160° in a distilling flask until the evolution of gas ceased. The volatile decomposition product was collected, the residue heated under reduced pressure and the two distillates united. The 3.3 g. of liquid distillate was fractionated at atmospheric pressure. It gave 0.5 g. of acetic acid, identified as acetanilide, and an oil, which was shown to be benzaldehyde by conversion to the semicarbazone.

Ten grams of α-methyl-β-phenyl-β-propiolactone-α-carboxylic acid (IV) was likewise decomposed at 190° and yielded 4 g. of liquid. Fractionation gave 0.6 g. of propionic acid, identified as propiotoluidide, and 3.3 g. of benzaldehyde.

Alkaline Cleavage of the Propiolactonic Acids.—The above two β-propiolactone-α-carboxylic acids, (III) and (IV), α,β,β-trimethylpropiolactonic acid (II) and β,β-pentamethylene-β-propiolactone-α-carboxylic acid were treated with alkali as follows: $^1/_{40}$ of one mole was dissolved in a solution of 4.2 g. of potassium hydroxide in 40 cc. of water and heated on the steam-bath for an hour. One equivalent of semicarbazide hydrochloride was then added and the solutions heated for four hours. With the two first acids, the precipitation of benzaldehyde semicarbazone was immediate, but with the two following the respective semicarbazones separated only upon cooling. The yield of benzaldehyde semicarbazone in each case was about 60%, that of cyclohexanone semicarbazone was quantitative, while acetone semicarbazone was obtained in only 25% yield. Acidification of the aqueous filtrates, repeated extraction of the solutions with ether and concentration of the extracts yielded practically the theoretical yields of malonic and methylmalonic acids.

Summary

1. It has been shown that benzaldehyde may replace acetone in the Ott synthesis of β-lactonic acids from malonic acid. Salicylic aldehyde does not thus lead to the formation of a tetracyclic β-lactonic acid, but to the more stable, hexacyclic *o*-lactonic derivative, carboxycoumarin. On the other hand, cinnamic aldehyde reacts with malonic acid by the Meldrum method to form cinnamalmalonic acid, which partially condenses, at the carboxyl groups, with the aldehyde to give the corresponding acetal derivative.

2. The thermal and chemical properties of β-lactonic acids and their alkali salts have been further examined, and it has been shown that all the compounds are cleaved by heat, and by alkali, through the first-formed β-hydroxy malonates, by rupture at the α,β-carbon linkage. The contradicting statements of Khandiah, and assumption of Salkowski[5] have been disproved.

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[CONTRIBUTION FROM THE PATHOLOGICAL DIVISION, BUREAU OF ANIMAL INDUSTRY]

Deltaline, A New Alkaloid from *Delphinium Occidentale* S. Wats

BY JAMES FITTON COUCH

The larkspurs form a genus of important stock-poisoning plants on the western ranges and in the southern Appalachian mountains. *Delphinium occidentale* is less toxic than the more important *D. barbeyi* which it closely resembles and with which it grows over a wide area of the western mountains. The toxic properties of *D. scopulorum* have been ascribed by Heyl[1] to an amorphous alkaloid melting at 184–185° which he named delphocurarine and assigned the formula $C_{23}H_{33}O_7N$. It was of interest to determine whether the less toxic *D. occidentale* contains the same substance in smaller amounts or some other less poisonous base.

Examination of a quantity of the whole plant of *D. occidentale* collected in Utah has resulted in the isolation of a crystalline alkaloid to which the name deltaline has been assigned in accordance with the system first used by Markwood.[2] This substance has the empirical formula $C_{21}H_{33}O_6N$ and is therefore isomeric with one of the alkaloids,

(1) G. Heyl, *Süddeut. Apoth.-Ztg.*, **43**, 249–51 (1903).

(2) Markwood, *J. Am. Pharm. Assoc.*, **13**, 696–702 (1924).

delcosine, isolated by Markwood[2] from *D. consolida*. No specimen of the latter has been available for direct comparison but the difference in melting points (180–181° as against 198–199°) and behavior toward solvents indicates that they are not identical.

Deltaline contains two methoxyl groups and three hydroxyls capable of being acetylated. It may therefore be formulated: $C_{19}H_{24}ON(OCH_3)_2(OH)_3$. The products of acid and alkaline hydrolysis are complex and have not yet been identified.

Experimental

Material Used.—The plant was collected by A. B. Clawson during July and August, 1932, at the Salina Experiment Station, Salina, Utah, and was identified by Ivar Tidestrom, then botanist at the Bureau of Plant Industry. It had not yet bloomed. The plant was dried in the shade and shipped to Washington, D. C., where it was ground to a coarse powder for use. The ground plant contained 7.97% of moisture.

Extraction of the Alkaloids.—19.22 kg. of plant was extracted with alcohol in a percolator, the alcohol was distilled from the percolate and the residue was extracted with boiling water in portions so long as soluble material was removed. The insoluble fatty material weighed 704 g.

The water extracts were concentrated to convenient volume, one-fourth was reserved for other tests and the remainder was made alkaline with sodium hydroxide, which precipitated a thick resinous mass. The whole was extracted with chloroform, which dissolved the precipitate. After four extractions the aqueous layer no longer responded to tests for alkaloids. No phenolic alkaloid is present in the plant. The chloroform was distilled from the extract and left a brownish sirup of nauseating odor, insoluble in alcohol. This was dissolved in dilute hydrochloric acid, filtered from some resinous matter, made alkaline with sodium hydroxide, and again shaken out with ether, and then with chloroform. On distilling off the ether there was left 109 g. of yellowish crystals. The chloroform solution yielded 21.6 g. of a brownish alkaloidal oil, which has not been crystallized. The total alkaloids represent 0.98% of the dry plant.

The ether-soluble alkaloid was recrystallized from alcohol and then from 25% alcohol from which it separated in long silky needles. Dried over calcium chloride they melted at 180–181°. They contained no water of crystallization.

Anal. Calcd. for $C_{21}H_{33}O_6N$: C, 63.76; H, 8.40; N, 3.54. Found: C, 63.67, 63.71, 63.56; H, 8.45, 8.41, 8.41; N, 3.62, 3.64. In alcohol $(\alpha)^{24}_{\mathrm{D}}$ −27.86°, $c = 1.432$, $l = 2$, $a = 0.798°$. Calcd. for $2CH_3O$: 15.70. Found: 15.68.

Deltaline is soluble in methanol, ethanol, chloroform, ether and acetone. It did not form a picrate and did not react with methyl iodide. Attempts to prepare crystalline salts were unsuccessful.

The Gold Chloride.—This is precipitated by gold chloride from a solution of deltaline in dilute hydrochloric acid as a light yellow flocculent precipitate. On attempting to recrystallize it from dilute hydrochloric acid the substance is precipitated as oily drops that gradually solidify to minute crystals. Washed and dried these melted at 120–125°. The substance decomposed when attempts were made to determine the crystal water.

Anal. Calcd. for $B \cdot HAuCl_4 \cdot 3H_2O$: Au, 24.69. Found: Au, 24.69, 24.62.

The Acetyl Compound.—The alkaloid was warmed with acetyl chloride and after twenty-four hours the product was diluted with water, made alkaline with sodium hydroxide and shaken out with chloroform. The latter removed a gummy substance which was purified by solution in alcohol. On evaporation of the solvent there remained an amorphous residue that melted at 270–272°.

Anal. Calcd. for $C_{21}H_{30}O_6N \cdot 3C_2H_3O$: C, 62.15; H, 7.54. Found: C, 62.10; H, 7.43.

Summary

Delphinium occidentale S. Wats contains 0.98% of alkaloids, the largest proportion of which is a new alkaloid, deltaline, isomeric but not identical with delcosine isolated from *D. consolida* by Markwood.

WASHINGTON, D. C.

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