

analysis the crude product was purified by dissolving 2 g. in 25 cc. of chloroform, decolorizing the solution with charcoal and reprecipitating the derivative in petroleum ether. The yellow flocculent precipitate was washed with petroleum ether, filtered and dried at 100°.

The methoxy content found was as follows. At the end of four methylations 22.8%; after eight 36.8%; after twelve 41.9%; after fourteen 44.15%; after fifteen 44.1%. Since the calculated value for a fully methylated polysaccharide of formula $[(C_6H_7O_2(OCH_3)_3)_6C_6H_6O_2(OCH_3)_2]_n$ is 44.8%, it was assumed that substitution was complete after fourteen such treatments as described above. Constancy of the methoxy value beyond this point served as further substantiation.

Completely methylated arabo-galactan is a very faintly cream-colored, amorphous solid, soluble in chloroform and acetone, slightly soluble in alcohol and water, and insoluble in petroleum ether and ethyl ether. It softens at 124° and melts at 143°; $[\alpha]^{20D}$ in chloroform, -42.03° .

Summary

1. Arabo-galactans separately isolated from

woods of Eastern, Western and European larches gave similar analyses for ash, reducing value, optical activity, anhydro-arabinose and anhydro-galactose. This similarity does not necessarily establish their chemical identity.

2. Acetyl, propionyl and benzoyl esters were made with conditions chosen to avoid degradation and to render esterification complete. On systematic fractionation from various solvent mixtures each gave fractions of similar acyl content but of variable optical activity, reducing value, specific viscosity and araban content. It was concluded that these derivatives were non-homogeneous and that in all probability the original arabo-galactans were mixtures also.

3. A fully methylated arabo-galactan from Western larch was prepared and described.

MIDLAND, MICHIGAN

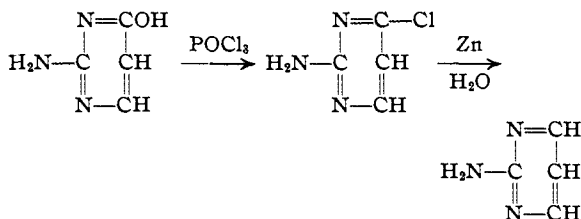
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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF TEMPLE UNIVERSITY]

A New Synthesis of Isocytosine

BY WILLIAM T. CALDWELL AND HARRY B. KIME

Consideration of certain similarities of pyridine and pyrimidine led us to begin the preparation of sulfanilamido derivatives of 2- and of 6-aminopyrimidine. However, the preparation and chemotherapeutic activity of 2-sulfanilamidopyrimidine and 4-sulfanilamidopyrimidine (6-sulfanilamidopyrimidine) having been recently described,¹ we shall report here only a preparation of isocytosine effected by reaction of guanidine hydrochloride and malic acid under conditions essentially like those used by Davidson and Baudisch² in preparing uracil. This new synthesis is of interest in that 2-aminopyrimidine may be prepared from isocytosine by the following two steps



Better yields of isocytosine were obtained from guanidine hydrochloride than from the carbonate.

(1) Roblin, Williams, Winnek and English, *THIS JOURNAL*, **62**, 2002 (1940).

(2) Davidson and Baudisch, *ibid.*, **48**, 2382 (1926).

Experimental

Guanidine hydrochloride (24 g.) was gradually added to 100 cc. of well-stirred 15% fuming sulfuric acid, the temperature being maintained below 5°. Then 24 g. of finely pulverized malic acid was added at once and the mixture heated on the steam-bath with vigorous stirring until the evolution of carbon monoxide had ceased and then for an additional half-hour. The mixture was cooled to room temperature and poured upon 300 g. of ice. A paste of barium carbonate was added in slight excess, the mixture stirred for several hours and then allowed to stand overnight. After heating the material to 50°, the barium sulfate and excess barium carbonate were removed by filtration. The filtrate was evaporated until crystallization began, cooled, and the isocytosine collected by filtration. The product was recrystallized from hot water, from which the isocytosine was obtained as white prisms; yield, 6.4 g., m. p. 276°.

Anal. Calcd. for $C_4H_5ON_3$: C, 43.22; H, 4.54. Found: C, 43.23; H, 4.70.

Conversion into 2-amino-6-chloropyrimidine with phosphorus oxychloride gave a product melting at 168–169° and at the same temperature when mixed with an authentic sample of this compound prepared by an independent method.

Summary

A new and convenient synthesis of isocytosine is described.

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