

acetonitriles and Derivatives," in press]. These facts are mentioned since we are still at work on similar alkylations, which, however, are probably distinct from those under way at Notre Dame.

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ISOLATION OF SPARTEINE FROM LUPINUS BARBIGER (WATSON)

Sir:

Sparteine has been found in one species of lupine, *L. luteus*, where it is accompanied by a second alkaloid, lupinine. Although a number of other species of lupines has been examined these two alkaloids have not again been found. The isolation of sparteine from *L. barbiger*, recently effected in this Laboratory is, therefore, of interest.

Leaves and stems of this plant, collected at Hilltop, ten miles north of Fairview, Utah, were obtained through the courtesy of A. B. Clawson and were identified by W. W. Eggleston. The alkaloids were extracted¹ and submitted to the action of solvents to separate them. The fraction soluble in petroleum ether contained sparteine and a second base from which it could not be separated by fractional distillation in a vacuum. The mixture yielded a picrate, platinum chloride and methiodide which had the constants of sparteine. Separation was effected through the mercuric chloride double compound, from which pure sparteine could be recovered by treatment with ammonia, shaking out with chloroform, removing the solvent and distilling under reduced pressure. The greater part came over at 185° and 7 mm. and showed n_D^{27} 1.5256 and $[\alpha]_D^{30}$ -6.07°. Willstätter and Marx² gave -5.96° at 20°. Moureu and Valeur³ give n_D^{19} 1.5293. The indices of refraction for a specimen of authentic sparteine were determined in this Laboratory as 1.5263 (24°), 1.5253 (26°), 1.5248 (28°), 1.5242 (29°). The specimen from *L. barbiger* was positive to the Jorissen⁴ H₂S-S and the modified Grant⁵ tests for sparteine. The picrate melted at 205-206° and did not depress the m. p. of sparteine picrate. The platinum chloride melted with decomposition at 248° and did not depress the melting point of sparteine platinum chloride.

The hydrobromide melted at 197° and was levorotatory $[\alpha]_D^{29}$ -18.33°. Found: H₂O, 4.40, 4.54; Br, 38.51, 38.50. C₁₅H₂₆N₂·2HBr·H₂O requires

¹ The procedure was in general that already described, THIS JOURNAL, 47, 2584 (1925).

² Willstätter and Marx, *Ber.*, 37, 2351 (1904).

³ *Bull. soc. chim. Paris*, [3] 29, 1135 (1903).

⁴ *Anal. Chim. Analyt.*, 16, 412 (1911).

⁵ *Am. J. Pharm.*, 97, 38 (1925).

H₂O, 4.35; Br, 38.63. The alkaloid regenerated from a portion of the salt showed n_D^{25} 1.5259 and yielded a picrate, m. p. 206°.

The methyl iodide was readily prepared by mixing the original fraction with excess of methyl iodide and allowing to stand in the cold. After a half-hour the whole solidified to a mass of white crystals. Sparteine usually shows no such behavior. A mixture of sparteine and methyl iodide remains liquid for weeks, unless warmed, but eventually deposits crystals. In our preparation the second alkaloid appears to catalyze the reaction.

The methyl iodide so prepared was recrystallized several times from alcohol. Dried in a desiccator the purest crop melted at 239–240°. Found: N, 7.51; I, 33.72, 33.63. C₁₅H₂₆N₂CH₃I requires N, 7.45; I, 33.75. Moureu and Valeur³ give the melting point "about 240°." Further crops of crystals obtained in the above preparation gave 6.91 and 7.19% N, indicating admixture with the second alkaloid.

These data establish the presence of sparteine in *L. barbiger*. Two or three other alkaloids are present but are not sufficiently characterized at present for identification. No evidence indicating the presence of lupinine has as yet been obtained.

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OXIDATION OF THE ALPHA AND BETA FORMS OF THE SUGARS

Sir:

In the course of studies on the oxidation of the sugars with bromine water experimental conditions have been developed by means of which it is possible to follow the oxidation of a single form of a sugar. The crystalline sugar is added to a suspension of barium carbonate in bromine water saturated with carbon dioxide, and the reaction is allowed to continue while stirring the mixture and holding the temperature constant. At intervals samples of the solution are taken and the amount of oxidation is determined by analysis. Through the buffer action of the barium carbonate and carbon dioxide the solution is maintained in a slightly acid condition (*P_H* 6). As a result the mutarotation of the sugar is relatively slow and the oxidation is relatively rapid. Equilibrium between the various forms of the sugar is not established prior to oxidation and consequently the reaction rates depend largely on the particular forms of the sugars used. There are marked differences in the rates obtained with various sugars and in the rates obtained with different forms of a given sugar.

Thus the oxidation of a sample of beta lactose is about 95% complete in three minutes, while under like conditions the reaction of alpha lactose is