Table V, fractions 1 and 2 (130 cc.) contained only 0.004 g. of valeronitrile. The original nitrile solution contained 3.172 g. of valeronitrile in 130 cc. Therefore, 16.5 g. of silica gel adsorbed 3.168 g. of nitrile before adsorption ceased to be complete. This amount is equivalent to 19% of the weight of the silica gel. The nitrile can be displaced from the silica gel by means of hot water. By use of the data in Table VI it can be shown that silica gel will adsorb 18% of its weight of lauronitrile from a hydrocarbon solution before small amounts of nitrile appear in the effluent liquid. In the last of the adsorption experiments it is shown possible to remove practically all of the nitriles from a cracked fraction and to recover it after adsorption by heating the silica gel. The original 25 cc. of cracked material contained 0.942 g. of nitrogen, of which 0.861 g. was accounted for in the material removed from the silica gel by heating. Less than 1% of the nitriles was not adsorbed.

Summary

1. The decomposition of high molecular weight amides by heat has been shown to cause a simultaneous hydration and dehydration which leads to the formation of almost equal amounts of acids and nitriles.

2. A non-catalytic method has been developed for preparation of high molecular weight nitriles from fatty acids and ammonia.

3. High molecular weight nitriles have been cracked in the liquid and vapor phases to yield straight chain hydrocarbons and nitriles.

4. Methods have been described which permit the separation of nitriles from hydrocarbons.

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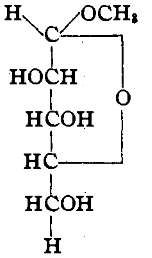
[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Crystalline Alpha-Methyl-*d*-arabinofuranoside[1]

BY EDNA M. MONTGOMERY AND C. S. HUDSON

A new crystalline methyl *d*-arabinoside, which is shown in the accompanying article by Jackson and Hudson to be the alpha form of *d*-arabinofuranoside,[2] has been isolated from the mixture of substances that is obtained by the reaction of *d*-arabinose and methyl alcohol containing hydrochloric acid under mild conditions of glycoside formation. This reaction is accompanied by a double reversal of the sign of optical rotation, as has been reported by previous investigators.[3] The authors were able to crystallize the new furanoside, the rotation[4] of which (+123 in water) is opposite in sign to that of the sugar itself (−105) and to those of its alpha (−17) and beta (−245) methyl pyranosides, by stopping the reaction at its point of highest positive rotation. The substance crystallizes in well formed, clear prisms and the yield is about 9%. Its fast rate of hydrolysis in aqueous acid conforms with the behavior of known furanosides of aldoses. From the present knowledge of the rotation of this alpha form it appears safe to conclude that the rotation of beta-methyl-*d*-arabinofuranoside, a substance now unknown, will be found to be strongly in the levo direction.



Alpha-methyl-*d*-arabinofuranoside, $[\alpha]^{20}_{D}$ +123

Experimental

The removal of solvents and the drying of sirups and crystals were carried out at 25–27° in desiccators supplied with calcium chloride and soda lime and evacuated by a pump. When constant weights were desired the higher vacuum of an oil pump was used for final dryings. The hygroscopic character of the furanoside crystals and the high humidity of the summer atmosphere during the work made it advisable to perform many of the manipulations in dry air. We used a cabinet of 55 × 39 × 43 cm. dimen-

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Report of the isolation of this compound was included in a paper entitled "The Oxidation of Alpha and Beta Forms of Methyl *d*-Arabinoside and Methyl *d*-Xyloside," presented by E. L. Jackson and C. S. Hudson at the Pittsburgh meeting of the American Chemical Society, Sept. 7–11, 1936.

(3) Baker and Haworth, *J. Chem. Soc.*, **127**, 365 (1925); Levene, Raymond and Dillon, *J. Biol. Chem.*, **95**, 699 (1932).

(4) Throughout this article the rotations are specific rotations at 20° for sodium light.

sions constructed of copper with a glass top and a removable end with strip felt closure, the other end being provided with two openings of 13 cm. diameter into which long rubber gloves[5] were fitted with adhesive tape.

Crystallization of α-Methyl-*d*-arabinofuranoside.—One hundred grams of finely powdered and sieved *d*-arabinose, rotation −105 in water, was agitated at 20° with 4 liters of anhydrous methyl alcohol containing 29.2 g. of hydrochloric acid (0.2 normal). Complete solution was obtained after thirty minutes and the observed rotation was strongly to the left, −65. On standing at 20° the solution became non-reducing after four and one-half hours and its specific rotation was then +24. On further standing the rotation increased in the dextro direction, reached a maximum of +45 after seventeen hours, and then receded until after forty-two hours it had reversed its sign and become −17. The new furanoside was obtained in greatest yield if the reaction was stopped when the rotation reached its maximum positive value. The acid was removed with silver oxide, the excess silver with hydrogen sulfide, the solution was concentrated *in vacuo* to 200 cc. (bath at 40°), transferred to a liter bottle, further concentrated to a thick sirup and finally dried overnight in an evacuated desiccator. The sirup was extracted six times at room temperature (25°) with 400-cc. portions of anhydrous ether, using a shaking machine for forty-five minutes for each extraction. At this point extraction with warm ether dissolved a relatively small amount of material, the rotation of which was much lower than that of the readily soluble portion. The ether was removed at the pump from the combined cold extractions (bath at 35°) leaving a sirup weighing about 23 g. of specific rotation +100 to +105, as tested on samples dried to constant weight. An ethyl acetate solution of this sirup which was kept at 5° crystallized spontaneously after two months. In later preparations the seeded sirup crystallized to a cake in two days. It was stirred with 25 cc. of ethyl acetate and filtered to remove sirupy material. The crystalline glycoside, dried under reduced pressure for several hours, weighed 11.5 g. and rotated +118 in water. It was recrystallized from 50 cc. of warm ethyl acetate by slowly cooling to 5° over a period of four to five hours. After three recrystallizations a crop of well formed, transparent prisms was obtained which was dried to a constant weight of 6.1 g., rotation +123 in water ($c = 1.20$). Recrystallization did not change this value. An additional 3.8 g. of pure material was obtained from the mother liquors; total yield, 9%. It did not reduce Fehling's solution but was readily hydrolyzed by acids to give a reducing solution. It melted at 65–67° in a closed tube, solidifying to colorless crystals on cooling. By warming 1.0 g. of the furanoside in 200 cc. of ether, which had been dried with sodium, a solution of about 0.80 g. was obtained which deposited crystals after two days at 5°. These were dried to a constant weight of 0.35 g. and showed a rotation of +123 ($c = 1.24$) in water, m. p. 65–67°. The glycoside was not difficult to prepare in pure anhydrous condition in small quantities, *i. e.*, 0.5 to 1.0 g. It is quite hygroscopic and is extremely soluble in water, methyl, ethyl, propyl and amyl alcohols, soluble in ethyl acetate and slightly soluble in ether.

Anal. Calcd. for $C_5H_9O_4(OCH_3)$: C, 43.88; H, 7.38; OCH_3, 18.91. Found: C, 44.08; H, 7.50; OCH_3, 18.63.

Rates of Hydrolysis of the Three Methyl-*d*-arabinosides.—The rates were measured on 2% solutions of the glycosides at 98° by polarimetric observations after rapid cooling to 20°, using 0.05 N aqueous hydrochloric acid with each pyranoside, and 0.01 N acid with the furanoside, which is more readily hydrolyzed. The reactions follow the unimolecular course and the coefficient $k = 1/t \log ((r_0 - r_\infty)/(r - r_\infty))$, expressed in minutes and decimal logarithms, has the following values: α-methyl-*d*-arabinopyranoside, 0.0032; β-methyl-*d*-arabinopyranoside, 0.0032; α-methyl-*d*-arabinofuranoside, 0.0068. Assuming the rate to be proportional to the acidity, the coefficient is about 0.00064 for the pyranosides in 0.01 N acid and it is seen that the furanoside is hydrolyzed about ten times faster than the pyranosides.

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Summary

A new crystalline arabinoside, alpha-methyl-*d*-arabinofuranoside, specific rotation in water +123, m. p. 65–67°, has been isolated. Its rate of hydrolysis in aqueous acid is about ten times that of either alpha- or beta-methyl-*d*-arabinopyranoside.

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[5] Obstetrical gloves, furnished by dealers in medical supplies, are very satisfactory.