Anal. Calcd. for $C_{39}H_{54}O_3N_8$: N, 14.69. Found: N, 15.24.

Cholestenone from III.—III (50 mg.), refluxed for one hour in 4% methanolic potassium hydroxide (15 ml.), gave a neutral fraction (42 mg.), which crystallized to yield cholestenone, m.p. 78–80°.

Cholestenone-4-C^{14}.—$C^{14}H_3I$ (originally 1.8 millicuries in 266 mg.), which had been stored in the dark for four years but which was deeply pigmented, was distilled through drierite (clear distillate). The system was then flushed with an equal weight of carrier methyl iodide. The Grignard reagent prepared from the combined alkyl halide (3.74 millimoles) reacted, as described above, with 1.2 g. (3.1 millimoles) of the enol-lactone I to furnish, on direct crystallization, 650 mg. (52%) of the hemiacetal II, m.p. 160–175°, count 6.12×10^8. The mother liquors yielded 270 mg. of 3,5-seco-5-keto-cholestan-3-oic acid, m.p. and admixture m.p. 151–154°. This recovery of starting material, not encountered in C^{12} runs with the same molar proportion of methyl iodide, may be due to (a) impurities in the small sample of $C^{14}H_3I$, (b) loss of appreciable total alkyl halide through decomposition on long storage, (c) difference in reaction rate between C^{12} and C^{14}, or a combination of the three factors.

II (650 mg.) was converted by procedure A above to 526 mg. (1.37 millimoles, 45%) of cholestenone-4-C^{14}, m.p. 76–78°, count 6.12×10^8.

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Preparation of Acetic-2-C^{14} Acid[1]

BY DANIEL N. HESS

A method has been developed for the preparation of high specific activity acetic-2-C^{14} acid from methanol-C^{14}. The method, which involves the intermediate formation of methyl hydrogen sulfate and acetonitrile, is simpler and is better suited to the synthesis of a product with high specific activity than the conventional method involving carbonation of methyl-C^{14}-magnesium iodide.[2] Yields averaging 87% have been obtained on a 10-millimole scale.

Experimental

A 10.5-millimole portion of crystalline sulfur trioxide was introduced into the reaction flask[3] equipped with a magnetic stirring bar. The flask was quickly attached to a vacuum line, and the 10-ml. bulb was immersed in liquid nitrogen. A 10.06-millimole aliquot of methanol vapor (39.2 millicuries), measured manometrically, was added to the reaction flask. The liquid nitrogen bath was replaced by an ice-bath, and the reaction mixture was stirred. After the initial reaction had subsided, an additional one-half hour at room temperature was allowed for completion of the reaction. Complete reaction was demonstrated by the absence of methanol vapor pressure as determined with a McLeod gage.

The flask was removed from the vacuum line, the bulb was immersed in liquid nitrogen, and 10 ml. of 7.5 *M* potassium cyanide was added dropwise. After the flask was allowed to warm slowly to room temperature with stirring for one-half hour, the acetonitrile solution was distilled into a calibrated 40-ml. flask. Three successive 10-ml. portions of water were added to the reaction flask and distilled to ensure complete transfer of the acetonitrile. Radioactivity assay showed a 96% yield to acetonitrile-2-C^{14}.

The acetonitrile was hydrolyzed by refluxing with 50 millimoles of potassium hydroxide for 24 hours. The radiochemical yield to potassium acetate-2-C^{14}, based on methanol, was 91%.

The alkaline solution of potassium acetate was acidified with 85% phosphoric acid and titrated with a solution of potassium permanganate.[4] The solution was distilled to dryness after the addition of three successive small portions of water. The distillate was titrated with potassium hydroxide, and the water evaporated. The potassium acetate was dried at high vacuum until no pressure greater than 10^{-4} mm. was observed after standing one-half hour under static vacuum at 120°.

The dried salt was covered with phosphoric acid thoroughly saturated with phosphorus pentoxide, the flask was attached to the vacuum line, and the acetic acid was collected in a liquid nitrogen cooled receiver. When the rate of evolution subsided, the flask was gradually heated to 120°, and the temperature maintained until there was no further evolution of acetic-2-C^{14} acid. Thirty-five and two-tenths millicuries of acetic-2-C^{14} acid was obtained, or a yield of 90% based on methanol-C^{14}. In order to determine the purity of the acetic acid prepared by this procedure, the product from a typical run and a purified derivative were analyzed using dilution technique. The radioactivity of the diluted acetic acid was 2.49 μc. per mmole, and the radioactivity of the derivative was 2.52 μc. per mmole. Thus, the product is pure within the limits of the analytical method which has an estimated error of ±1%.

Carbon-14 analyses of the methanol, acetonitrile and acetic acid were made on the methyl-3,5-dinitrobenzoate, phloroacetophenone and *p*-nitrobenzyl acetate derivatives, respectively. These derivatives prepared from appropriately diluted samples were converted to carbon dioxide by wet-combustion and assayed for radioactivity by determination of the ion current with a dynamic condenser electrometer. The isotopic dilution method of determining yields[5] and the carbon-14 analysis procedure[6] have been published.

Acknowledgment.—The author wishes to express his indebtedness to Dr. O. K. Neville for his advice and interest in the execution of this project.

(4) This destroyed any cyanide and formate that might be present.

(5) G. A. Ropp, THIS JOURNAL, **72**, 4459 (1950).

(6) O. K. Neville, *ibid.*, **70**, 3499 (1948).

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Improvements in the Preparation of L-Arabinose from Mesquite Gum[1]

BY C. S. HUDSON

Directions for the preparation of L-arabinose from mesquite gum have been published by Anderson and Sands,[2] by Isbell[3] and recently by White,[4] who has made radical improvements on the older directions. Present knowledge of the structure of mesquite gum, recently reviewed by Jones and Smith,[5] indicates that its graded acid hydrolysis can be expected to liberate principally the L-arabinose moiety as the first step. However, in the earlier methods[2,3] experience showed that it was necessary to continue the acid hydrolysis considerably beyond this first stage in order to be able to control the foaming during subsequent operations. Our experience with the earlier methods[2,3] was not encour-

(1) This document is based upon work performed under Contract Number W-7405, eng. 26 for the Atomic Energy Project at Oak Ridge National Laboratory.

(2) B. M. Tolbert, *J. Biol. Chem.*, **173**, 205 (1948).

(3) The reaction flask consisted of a 25-ml. flask with a 10-ml. bulb sealed onto the bottom. The purpose of the bulb was to contain the small quantities of reagents in the sulfonation phase of the experiment. The larger bulb provided ample volume for subsequent reactions.

(1) Presented at the Portland, Oregon, Meeting of the American Chemical Society in September, 1948.

(2) E. Anderson and Lila Sands, (a) THIS JOURNAL, **48**, 3172 (1926); (b) *Org. Syntheses*, **8**, 18 (1928).

(3) H. S. Isbell in "Polarimetry, Saccharimetry and the Sugars," Circular C440, Natl. Bur. Standards, p. 457 (1942).

(4) E. V. White, THIS JOURNAL, **69**, 622, 715 (1947).

(5) J. K. N. Jones and F. Smith, *Advances in Carbohydrate Chem.*, **4**, 243 (1949).