[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 205]

The Unesterified Secondary Hydroxyls in Acetone Soluble Cellulose Acetate[1]

BY F. B. CRAMER, R. C. HOCKETT AND C. B. PURVES

The examination of a commercial acetone soluble cellulose acetate,[2] containing on the average 2.33 moles of acetyl and 0.67 mole of hydroxyl per glucose unit, led to the conclusion that at least 0.22 mole of the hydroxyl occupied the primary or sixth position in the anhydro-glucose residues.[3] This left not more than 0.45 mole distributed between the second and third positions in an unknown manner. If this distribution was a random one, some of the glucose units along the partly acetylated cellulose macromolecule should be devoid of acetyl in both the second and third positions. In other words, they should contain the —CHOH—CHOH— or glycol grouping. Extensive work[4] has shown that many glycols are oxidized quantitatively to two aldehyde groups by one mole of lead tetraacetate, that secondary reactions are very slow and that semi or complete acetylation thoroughly protects the glycol from the reagent. It was possible, therefore, to investigate the occurrence of 2,3 deacetylation in suitable solutions of cellulose acetates by noting their consumption of lead tetraacetate. This was followed easily by the potassium iodide–sodium thiosulfate method.[5] Both the commercial cellulose acetate and the triacetate prepared from it remained dissolved in a 50% chloroform–acetic acid mixture. The triacetate solution utilized no lead tetraacetate over a period of several days and acetylation thus protected the glycol groups of the anhydroglucose units from oxidation in a satisfactory manner. As expected, the normality of the lead tetraacetate in the acetone soluble acetate solution diminished with time but unfortunately the instability of the solvent[6] interfered with a prolonged examination. This was possible when pure glacial acetic acid was used (Fig. 1). By analogy with the similar behavior of many simple glycosides,[7] the break in the curve (Fig. 1, eighty hours) was taken to mark the end of the true glycol oxidation, and the subsequent much slower change was regarded as an oxidation of another type. With this assumption, inspection of the curve showed that each glucose residue in the acetone soluble cellulose acetate averaged $7 - 10 \times 10^{-3}$ mole of glycol grouping, or one such group was present in every 100–150 glucose residues.

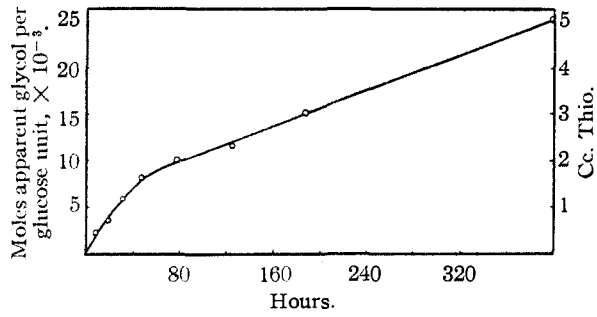

Fig. 1.—Oxidation of acetone soluble cellulose acetate with lead tetraacetate in glacial acetic acid at 25°.

If a partly acetylated cellulose averaged H moles of hydroxyl, randomly distributed along the macromolecule as x moles in the second and $H - x$ moles in the third position, the probability of the glycol grouping is $x(H - x)$ per glucose unit. This probability attains its maximum value of $H^2/4$ when $x = H/2$ or when hydroxyls in the two positions are numerically equal. In the present case, $H = 0.45$ or, at the very least, 0.35 and the probabilities of the glycol group are 0.0506 and 0.0306, respectively, or one occurs in every 20 to 32 glucose residues. The disagreement between this calculated value and the experimental one of one in 100 to 150 shows that the distribution of hydroxyl was by no means a matter of chance.

Although speculation concerning the method of distribution is premature, it seems evident that the assumption of a micellar structure for cellulose acetate in which acetyl had been lost preferentially from the surface of the micelles would lead to calculated ratios lying between 1:2 and 1:32. On the other hand, if the second positions averaged about ten times the number of unesterified hydroxyls as the third, or *vice versa*, calculation would agree approximately with experiment.

(1) Delivered at the Boston meeting of the American Chemical Society, September, 1939.

(2) Kindly given by the du Pont Company. The acetyl content was 38.6%, sulfur 0.007, ash 0.004, and the viscosity in 24% anhydrous acetone solution was 375 poises. It was a high grade sample of the most uniform commercial type.

(3) Cramer and Purves, THIS JOURNAL, **61**, 3458 (1939).

(4) Criegee, *Ber.*, **64**, 260 (1931).

(5) Dimroth and Schweitzer, *ibid.*, **56**, 1375 (1923).

(6) Eventually the thiosulfate blank titration increased and crystalline lead chloride separated owing to slight decomposition of the carefully purified chloroform.

(7) Hockett and McClenahan, THIS JOURNAL, **61**, 1667 (1939).

This would also be true if, in the partial hydrolysis from cellulose triacetate, the loss of acetyl from either one of the two positions tended to stabilize the adjacent group in the same anhydroglucose residue.

Experimental

Materials.—The acetone soluble cellulose acetate was from the batch previously studied[3] and the triacetate was made from it by careful acetylation with pyridine and acetic anhydride. Both were dried over phosphorus pentoxide in a vacuum at 55°.

The chloroform was washed with water and distilled from phosphorus pentoxide while the glacial acetic acid was distilled from chromic anhydride to free it from any aldehyde.

Oxidation with Lead Tetraacetate.—The cellulose acetate, 2.6 g. or 0.01 mole, was dissolved completely in 25 cc. of glacial acetic acid contained in a 100-cc., glass-stoppered volumetric flask. An approximately decinormal solution of lead tetraacetate in the same solvent, 25 cc., was then added at 25° and the volume made up to the mark. The viscid solution required prompt and thorough mixing, after which it was kept at 25 ± 0.5° in the dark. Samples were withdrawn at intervals in a 10-cc. pipet and discharged into 20 cc. of an aqueous solution containing 20 g. of potassium iodide and 250 g. of sodium acetate per liter. The pipet was rinsed well with 5 cc. of the acetic acid and after the addition of the rinsings the liberated iodine was titrated with $N/100$ sodium thiosulfate.[5] Vigorous shaking of the heterogeneous mixtures was necessary during the titrations, which took about five minutes each to complete. The blank on the reagents remained constant at 37.5 cc. of thiosulfate throughout the experiment. Differences from the blank are plotted as the right-hand ordinate in Fig. 1 and at the break in the curve (eighty hours) the 1 millimole sample of cellulose acetate utilized about 2 cc. of $N/100$ sodium thiosulfate. This corresponded to 10^{-5} mole of lead tetraacetate or of glycol. The results of precisely similar experiments, carried out in chloroform–acetic acid solution, are mentioned in the Introduction.

Summary

A commercial acetone soluble cellulose acetate had an average of 0.35 to 0.45 mole of unesterified hydroxyl distributed between the second and third positions of the anhydroglucose units. The unsubstituted —CHOH—CHOH— or glycol groupings it contained were estimated, by means of lead tetraacetate, to occur not more frequently than once in a hundred glucose residues. A significantly greater frequency of once in twenty to thirty was calculated by assuming a purely random distribution of hydroxyl between the two positions.

CAMBRIDGE, MASS. RECEIVED OCTOBER 17, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FISK UNIVERSITY]

Ricinus communis. I. Oxidation of Ricinoleic Acid

BY ST. ELMO BRADY

The oxidation of ricinoleic acid, its ethyl ester and its isomer, ricinelaidic acid, as well as some of their oxidation products, the trihydroxystearic acids and the *n*-aldehydo-octanoic acid has been studied and the experimental results obtained in these studies are presented in this communication.

Experimental Part

(a) Preparation and Purification of Ricinoleic Acid and Derivatives.—The castor oil was saponified with alcoholic potassium hydroxide, the excess alcohol removed, the potassium salt dissolved in water and the solution exhausted with ether to remove the unsaponifiable materials. These will be the subject of a future investigation. The free fatty acids were liberated with dilute hydrochloric acid, collected and allowed to stand for two days during which time the insoluble acids separated and were removed. The free fatty acids were mixed with an equal volume of alcohol and cooled below zero for several days, when another small portion of insoluble acids separated. The free fatty acids were again converted into the sodium salts using approximately the calculated weight of pure sodium hydroxide dissolved in alcohol. After the removal of the solvent and dilution with water a practically clear solution remained. The barium salt was precipitated from this solution, filtered, dried and refluxed with ether to remove any soluble barium salt present. Several recrystallizations of the barium ricinoleate from alcohol finally gave a white crystalline product that analyzed pure.

The dry salt was suspended in ether and carefully decomposed with dilute hydrochloric acid. After washing thoroughly and drying the ethereal solution over anhydrous sodium sulfate, the solvent was removed in a vacuum desiccator by the aid of the pump. Especial care was exercised not to heat the acid since it polymerizes very easily even at a temperature of 40°. The acid so prepared was of a very slight yellowish tinge, somewhat viscous and perfectly clear. It solidified in the refrigerator at 3–4° to a white waxy solid which melted approximately at 5°.

Anal. Calcd. for $C_{18}H_{34}O_3$: iodine no., 85.1. Found: iodine no., 85.0, 85.1.

Preparation of the Ethyl Ester of Ricinoleic Acid.—The pure ricinoleic acid was dissolved in twice the volume