gas absorption stopped. The volume of hydrogen absorbed was 6.0 ml. at the above condition. This corresponds to 0.93 mole of hydrogen per mole of furcatin.

Furcatin Hexaacetate.—Two hundred mg. of furcatin was kneaded with 2 ml. of acetic anhydride and 5 drops of pyridine. When the crystals dissolved, the mixture was heated on a boiling water-bath for 5 min. and poured into ice-water with stirring. The separated acetate was recrystallized from ethanol and obtained as colorless needles which melted at 116–116.5°.

Anal. Calcd. for $C_{31}H_{38}O_{16}$: C, 55.85; H, 5.71. Found: C, 55.96; H, 5.83.

p-Vinylphenol Glucoside Tetraacetate.—Sixty five mg. of the glucoside was acetylated with 1 ml. of acetic anhydride and 5 drops of pyridine as in the case of furcatin hexaacetate. Recrystallization was repeated from ethanol and the acetate was obtained as colorless needles of m.p. 142.5°.

Anal. Calcd. for $C_{22}H_{26}O_{10}$: C, 58.66; H, 5.82. Found: C, 59.11; H; 6.44.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

Distribution of Formyl Groups in Amylose Monoformate[1]

BY ROY L. WHISTLER AND HUGH J. ROBERTS

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Amylose and starch monoformates are acetylated and the formyl groups are found to hydrolyze easily and quantitatively without appreciable loss or wandering of the acetyl groups. The monoformates, prepared by formylation in 90% formic acid, have approximately 70% of the primary hydroxyl groups formylated.

The ease with which formyl groups may be introduced and removed from starch and the suggestion that starch monoformates are extensively esterified at carbon atom C6 make the monoester interesting as an intermediate in the preparation of specific starch derivatives. The approximate monoester is easily prepared by reaction of starch at room temperature with an excess of 90% formic acid.[2–5] Wolff and co-workers[5] show that this is a reversible reaction. Browning and Sell[6] and Wolff and co-workers[5] further show that increased concentration of formic acid leads to more rapid esterification and to higher degrees of substitution, although a D. S. (average degree of substitution) above 2.3 is not obtained. By use of periodate oxidation[2,5] to determine the number of hydroxyl groups simultaneously free on carbon atoms C2 and C3 in starch monoformates evidence is obtained which suggests that the formoxy groups reside almost entirely on primary carbon atoms. However, Moe, Miller and Buckely[3] point out that if the periodate oxidation of starch monoformate is conducted in a buffered system at pH 4.2–4.3, only 0.6 mole of periodate is consumed per mole of anhydro D-glucose unit as contrasted with 1.0–1.8 moles consumed in an unbuffered system, and conclude that in the latter system hydrolysis of formate ester groups occurs. Tarkow and Stamm[7] show that starch monoformate is produced when the molar ratio of anhydrous formic acid to starch is about 2:1, and conclude that only the primary hydroxyls of starch are esterified under these conditions.

Because of the potential usefulness of a 6-*O*-formyl starch in this Laboratory, the monoformate ester is reinvestigated. As is described,[2,5,8] the monoformates are readily obtained by reaction of corn amylose or corn starch in 90% formic acid. Treatment of the formates with acetic anhydride in pyridine produces the fully esterified mixed esters.[8] It is now found, however, that the formyl groups can be removed from the acetate-formates by piperidine-catalyzed hydrolysis in aqueous acetone without significant loss of acetyl groups. It is further shown that the hydroxyl groups in the resultant acetates are those which were originally formylated since little or no acetyl wandering occurs in the deformylation. Such derivatives of amylose and starch are shown in Table I.

TABLE I

ESTERS OF AMYLOSE AND STARCH

Poly-saccharide	Formate ester Formyl groups per D-glucose unit	Mixed acetate-formate Acetyl groups per D-glucose unit	Total D. S.	Acetate ester[a] Acetyl groups per D-glucose unit
Amylose	0.83	2.16	2.99	2.21
Amylose	1.05	1.94	2.99	1.98
Amylose	1.18	1.77	2.95	1.79
Amylose	1.38	1.60	2.98	1.67
Starch	1.08	1.91	2.99	1.88

[a] Prepared by deformylation of the acetate-formate. Values given are for total acyl calculated as acetyl.

The mixed acetate-formates undergo piperidine-catalyzed hydrolysis at a rapid initial rate as shown in Fig. 1. Then as the amount of acid released becomes equivalent to the formate originally present in the ester, the rate sharply decreases to a low constant value. Extrapolation of the linear

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(1) Presented before the Division of Carbohydrate Chemistry at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959; Journal Paper No. 1393 of the Purdue Agricultural Experiment Station.

(2) D. Gottlieb, C. G. Caldwell and R. M. Hixon, THIS JOURNAL, **62**, 3342 (1940).

(3) O. H. Moe, S. E. Miller and M. I. Buckley, *ibid.*, **73**, 4185 (1951).

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(5) I. A. Wolff, D. W. Olds and G. E. Hilbert, THIS JOURNAL, **79**, 3860 (1957).

(6) B. L. Browning and L. O. Sell, *Textile Res. J.*, **23**, 939 (1953).

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(8) I. A. Wolff, D. W. Olds and G. E. Hilbert, *Ind. Eng. Chem.*, **49**, 1247 (1957).

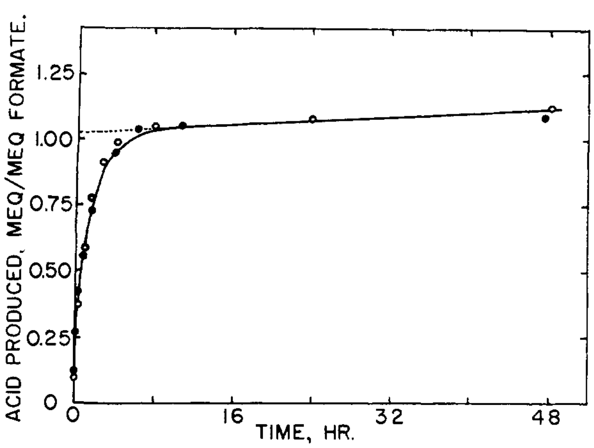

Fig. 1.—Rate of base-catalyzed hydrolysis of formate groups; amylose acetate formate (●); starch acetate formate (○).

portion of the rate curve (broken line in Fig. 1) to the ordinate yields a value very close to the expected one milliequivalent of acid per milliequivalent of formate. Furthermore, a plot of the proper functions shows that the hydrolysis of formyl groups is a second-order reaction (Fig. 2).

Primary hydroxyl groups liberated during the hydrolysis may be measured by two well established procedures. One method involves the measurement of the number of trityl (triphenylmethyl) groups introduced per D-glucose unit while the other involves the introduction of tosyl (*p*-toluenesulfonyl) groups, the replacement of primary tosyl groups with iodine and the measurement of the number of iodine atoms introduced per D-glucose unit. Both procedures have been employed satisfactorily in the measurement of free primary hydroxyl groups in partially acetylated cellulose[9] as well as in many polysaccharides and other polysaccharide derivatives. Application of both of these methods to the deformylated acetates of amylose and starch gives results which indicate that 69–78% of the polysaccharide primary hydroxyl groups are formylated in the monoformyl derivatives (Table II).

Table II

Primary Hydroxyl in Acetates of Amylose and Starch

Polysaccharide	Formyl groups removed per D glucose unit	Primary hydroxyl groups found By tritylation	By tosylation-iodination
Amylose acetate	0.78	0.60	0.68
Amylose acetate	1.02	.69	.78
Starch acetate	1.12	.72	.69
Amylose acetate	1.21	.69	.76

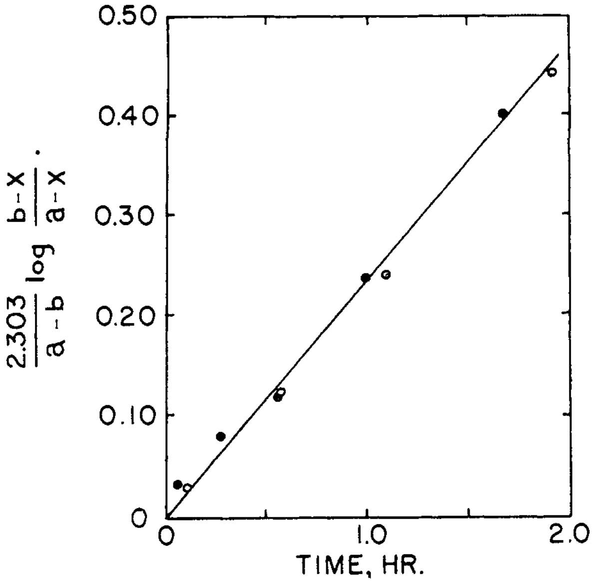

Fig. 2.—Logarithmic plot of rate of base-catalyzed hydrolysis of formate groups; amylose acetate formate (●); starch acetate formate (○).

That acetyl wandering is not appreciable during the base-catalyzed hydrolysis of formyl groups is indicated by the observation that the number of primary hydroxyl groups undergoes no detectable change when the ester is subjected to continued hydrolysis.

Duration of hydrolysis, hr.	1	3	4.5	8	24	48
Primary hydroxyl groups by tritylation, D. S.	0.38	0.65	0.68	0.72	0.71	0.72

Thus the evidence obtained here is in close agreement with the conclusions of Moe, Miller and Buckley[3] based on periodate analysis. It suggests that amylose and starch monoformates, prepared by reaction in 90% formic acid, have approximately 70% of the formyl groups on primary hydroxyls and the remaining 30% on secondary hydroxyls.

The ease of formylation of starch and the subsequent ease of acetylation and formyl removal suggest a process for producing starch acetates wherein large numbers of primary hydroxyl groups are specifically available. It further seems likely from the homogeneity of the formylation that the available primary hydroxyls are randomly distributed throughout the polysaccharide molecule.

Experimental

Amylose.—Commercial corn starch was fractionated by the butanol method of Schoch.[10] The butanol–amylose complex was recrystallized from butanol–water three times, and the amylose obtained by treatment of the purified complex first with acetone and then with absolute ethanol. Ethanol was finally removed under reduced pressure in the presence of calcium chloride. The product was a fine, white powder.

Formylation.—Formates of corn starch and amylose were prepared by the method of Wolff, Olds and Hilbert,[5] using 10 ml. of 90% formic acid per gram of polysaccharide and reaction times of 2–5 hr. at room temperature. After precipitation of the formates with methanol they were washed twice by suspension in methanol and centrifugation, allowed to stand overnight in 99.5% ethanol, filtered by suction and washed with dry ether before final drying at 50–60° under reduced pressure. The formates were analyzed by the

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(9) For examples of tritylation see (a) C. J. Malm, L. J. Tanghe and B. C. Laird, This Journal, **72**, 2674 (1950); (b) L. A. Hiller, Jr., *J. Polymer Sci.*, **10**, 385 (1953); (c) C. J. Malm, L. J. Tanghe, B. C. Laird and G. D. Smith, *Anal. Chem.*, **26**, 188 (1954); (d) H. Krässig and E. Schrott, *Makromol. Chem.*, **28**, 114 (1958). Examples of the tosylation–iodination method are found in (e) F. B. Cramer and C. B. Purves, This Journal, **61**, 3458 (1939); (f) T. S. Gardner and C. B. Purves, *ibid.*, **64**, 1539 (1942); (g) C. J. Malm, L. J. Tanghe and B. C. Laird, *ibid.*, **70**, 2740 (1948).

(10) T. J. Schoch, *ibid.*, **64**, 2957 (1942).

modified Eberstadt method recommended by Genung and Mallatt[11] for cellulose esters.

Acetylation.—The formates were dissolved in 10 volumes of anhydrous pyridine (stored over calcium hydride), an amount of freshly distilled acetic anhydride was added equivalent to twice the theoretical amount for the number of free hydroxyl groups in the formate, and the reaction mixture heated at 100° for 3.5 hours. The acetylated formates were isolated and analyzed in the same manner as the formic acid esters. The average degree of substitution of acetyl groups was calculated algebraically assuming no loss of formyl groups during acetylation.

Deformylation.—Five grams of acetylated formate was dissolved in 500 ml. of acetone. The solution was placed in a thermostat at 25 ± 0.10° and 50 ml. of an aqueous solution of redistilled piperidine (10% v./v.) added with mixing. For the rate studies, aliquots were removed periodically and 5 volumes of ice-water added. The resultant suspensions were titrated with standard hydrochloric acid using phenol red indicator, and the decrease in concentration of the base determined by comparison with a blank reaction mixture, identical except for the omission of the ester. When kinetic data were not sought, the reaction was allowed to proceed for 8 hours, whereupon the entire reaction mixture was filtered into 4–5 volumes of ice-water; the resultant precipitate was collected by suction, resuspended in water and dialyzed against deionized water. After dialysis the suspension was again filtered by suction. Drying of the filter cake in a vacuum oven resulted in products which were quite "horny," but which could be dissolved in pyridine for tritylation and tosylation. Light, finely divided diacetates were prepared by reprecipitation from pyridine solution into an excess of ethyl ether.

Tritylation.—The procedure of Malm, Tanghe, Laird and Smith[9c] was followed. Trityl contents were determined by quantitative recovery of the trityl ethers[9c] or by decomposition of the ether in sulfuric acid followed by precipitation and quantitative recovery of tritanol.[12]

Tosylation–Iodination.—The procedure of Gardner and Purves[9f] was used with slight modification. The acetates prepared by means of the deformylation reaction were dried and dissolved (overnight) in 10 parts of anhydrous pyridine. Eight to ten times the calculated theoretical amount of *p*-toluenesulfonyl chloride (recrystallized from carbon tetrachloride and stored over phosphorus pentoxide in the dark) was dissolved in the solution and the reaction mixture kept at 25° for 24 hours. The reaction products were isolated by precipitation into 80% methanol; the precipitates were washed free from chloride with the same solvent, the aqueous methanol replaced with anhydrous ether, and the products were dried in a vacuum oven. They were allowed to react with an equal weight of sodium iodide in 25 parts by volume of anhydrous diglyme (dimethyl ether of diethylene glycol) at 120° for 2 hours, and the iodo derivatives were obtained on pouring the reaction mixture into a large volume of water. These precipitates were purified by suspending in water, dialyzing the suspension against deionized water, filtering and drying. Sulfur and iodine were determined separately by the appropriate Carius method as described by Steyermark.[13]

LAFAYETTE, IND.

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[11] L. B. Genung and R. C. Mallatt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941).

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE]

Syntheses in the Terpene Series. VII.[1] A Total Synthesis of the Dinoronocerane Carbon Skeleton

BY FRANZ SONDHEIMER AND DOV ELAD

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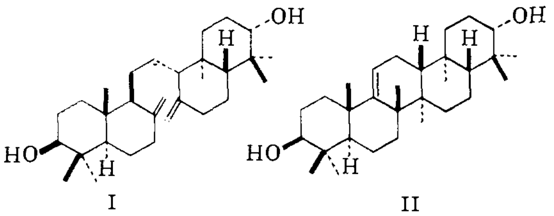
The synthesis is described of a substance which is very probably the racemate of dinoronocerane (VIII).

The triterpene alcohol α-onocerin (α-onoceradienediol) has been shown to possess the symmetrical structure I and to undergo an acid-catalyzed cyclization to the pentacyclic γ-onocerin (II).[2] The last-mentioned substance by contraction of ring E can be converted to compounds with the same carbon skeleton as the natural pentacyclic triterpenes of the hydroxyhopanone[3] and perhaps also the zeorin[4] type. We are interested in effecting total syntheses of triterpenes of the onocerin and hydroxyhopanone series since these represent an interesting class of natural products derivable from squalene by biogenetic paths not involving migration of methyl groups and also because the methods used for synthesizing these "symmetrical" compounds might be employed later for the more difficult synthesis of the pentacyclic triterpenes of the β-amyrin type.



I II

Although α-onocerin itself has not yet been obtained by synthesis, three quite distinct synthetic approaches to closely related compounds were announced, in 1957, by Corey and Sauers,[5] by Romann, *et al.*,[6] as well as by ourselves.[7] Our own work, reported as a preliminary communication, resulted in a substance which is probably the racemate of dinoronocerane (VIII). The corresponding optically active compound had previously been obtained from α-onocerin.[2] This synthetic

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[1] For part VI, see F. Sondheimer and D. Rosenthal, THIS JOURNAL, **80**, 3995 (1958).

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