his calculated hydrolysis constants that complexing of In^{+3} by halide ions occurs in such solutions. We have systematically interpreted his data on the assumption of equilibria (1) and (2)

$$In^{+3} + H_2O = InOH^{+2} + H^+ \qquad (1)$$

$$In^{+3} + X^- = InX^{+2} \qquad (2)$$

X^- stands for Cl^-, Br^- or I^- in the appropriate cases. We may write the equilibrium constants for these reactions in terms of concentrations (moles/liter) of the various species $K_1 = (InOH^+)(H^+)/(In^{+3})$; $K_2 = (InX^{+2})/(In^{+3})(X^-)$.

If we denote the total concentration of indium (III) by m, it follows that

$$m = (In^{+3}) + (InOH^{+2}) + (InX^{+2}),\ (InX^{+2}) = 3m - (X^-),\ \text{and}\ (InOH^{+2}) = (H^+)$$

Combining these relations we obtain equation (3)

$$\frac{m - (H^+)}{(H^+)^2} = \frac{3m\, K_2/K_1}{1 + (K_2(H^+)^2/K_1)} + \frac{1}{K_1} \qquad (3)$$

Assuming that $K_2(H^+)^2/K_1$ is small compared to unity equation (4) results.

$$\frac{m - (H^+)}{(H^+)^2} = 3m\frac{K_2}{K_1} + \frac{1}{K_1} \qquad (4)$$

From the experimental data,[3] the quantity $m - (H^+)/(H^+)^2$ was calculated for various values of m, in the range 5.10^{-4} M to 4.10^{-2} M, and plotted as a function of m. In accordance with equation (4) this plot was linear in dilute solutions. From the slope and intercept of this line values of K_1 and K_2 were calculated. An analytical treatment of the data using the interpolation formula of Lagrange[4] was also made. The values of K_1 and K_2 thus obtained agreed quite well with those found by the graphical method. Actually the graphical extrapolation is, to a certain extent, subjective and the agreement with the analytical procedure provides some justification for the graphical values. Although corrections involving the activity coefficients of the several species might be expected to affect the values of K_1 and K_2 by as much as 20%, we have not incorporated such corrections in our treatment since the graphical values (presumably pertaining to infinite dilution) and the analytical values (which are, in a sense, averages over a range of concentrations) are in accord.

Table I gives the values of K_1 and K_2 obtained by the analytical method. These values bear out the validity of the assumption that $K_2(H^+)^2/K_1$ is small compared to unity since (H^+) is of the order of 10^{-4} M in the solutions upon which the above calculations are based. K_1 is independent of the anion, and the halide complexing constants decrease with increasing anion radius as might be expected for electrostatically bonded complexes.

TABLE I

Solution	$K_1 \times 10^4$	K_2
$InCl_3$	1.36	225
$InBr_3$	1.38	159
InI_3	1.46	95.5

Equation (3) may be solved for (H^+) in terms of m, K_1 and K_2. Inserting the above values for these constants we have calculated (H^+) for various values of m. These calculated values of (H^+) together with the experimental values of Moeller are presented in Table II for several dilute solutions of each of the indium halides.

TABLE II

Solution	$m \times 10^3$	$(H^+) \times 10^4$ Calcd.	$(H^+) \times 10^4$ Exptl.
$InCl_3$	0.5	1.8	1.8
	5	4.1	4.0
	10	4.7	4.8
	20	5.0	5.7
$InBr_3$	2.5	3.8	3.8
	5	4.8	4.7
	20	6.0	6.6
	40	7.0	7.9
InI_3	2.5	4.3	4.3
	5	5.4	5.3
	10	6.5	6.6
	20	7.5	8.1

The agreement of the experimental and calculated values of (H^+) provides substantiation of the original assumption of equilibria (1) and (2) and also of the tabulated values of K_1 and K_2.

From the magnitude of the values given in Table I for K_1 and K_2 it may be seen that in concentrated solutions the hydrolysis reaction becomes

$$InX^{+2} + H_2O = InOH^{+2} + H^+ + X^- \qquad (5)$$

since reaction (2) is virtually complete. Designating the equilibrium constant of reaction (5) as K_5 and using our previous notation

$$K_5 = \frac{(2m + (H^+))(H^+)^2}{m - (H^+)}$$

The values of K_5, calculated for solutions in which m is greater than 0.04 M, increase with m as would be qualitatively expected from the decrease in the activity coefficients of ionic species with increasing ionic strength. Quantitatively, however, the increase in K_5 is so great that the quotient of the activity coefficients must fall below the limiting Debye–Hückel values. While further halide complexing of InX^{+2} to form InX_2^+ doubtless occurs, the trend in K_5 can only be interpreted by assuming that the species $In(OH)X^+$ is also formed, and that it is more important than InX_2^+ in these solutions.

Since activity coefficient corrections are so important in these concentrated solutions (greater than 0.04 M) any quantitative calculation involving the complexes InX_2^+ and $In(OH)X^+$ is not possible with the present data.

We have selected an unweighted average of the values of K_1 given in Table I, $K_1 = 1.40 \times 10^{-4}$, as the "best" value for the hydrolysis constant of In^{+3}.

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Acetylation of Amylaceous Polysaccharides

BY ALLENE JEANES AND R. W. JONES

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The frequent use of acetates of amylaceous substances in investigations on particle weight and

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(4) See for example, H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943.

structure has motivated a long-continued search for practical methods for obtaining fully acetylated, undegraded products with favorable solubility characteristics. One of the most recently described procedures for acetylation is cumbersome and time-consuming, apparently because the polysaccharides were in an unfavorable physical state.[1] Recently, variable molecular weight data have been reported on materials acetylated by various, non-standardized procedures[2,3]; the poor solubility of the acetates has been a matter of much concern; and physical measurements have been reported on incompletely acetylated products.[4] These same inadequacies in application of methods have characterized the literature on starch acetates for many years. Most of them can be corrected easily, as is shown here.

The data reported here show that if the polysaccharide is in a suitable physical condition, complete acetylation can be accomplished directly, rapidly, and without degradation by any one of three different methods. These employed acetic anhydride catalyzed by either pyridine or by sodium acetate at 100°, or acetic anhydride catalyzed by pyridine in the presence of formamide at room temperature. As is shown later, the products from each of the methods had desirable solubility characteristics. Contrary to recently expressed opinion,[1] no evidence of degradation was obtained for the products acetylated at 100°. However, under certain conditions recommended by others, variable results were obtained by acetylation in formamide (Table I).

TABLE I

COMPARISON OF AMYLOSE TRIACETATES PREPARED BY DIFFERENT METHODS

Corn amylose sample[a]	Method of acetylation	Acetyl content ±0.2 %[b]	[η], trichloroethane, 25°
A	Pyridine, 100°	44.8	2.08
B	Pyridine, 100°	45.1	2.15
A	Sodium acetate, 100°	44.7	1.97
A (complex)[c]	Formamide	44.9	2.01
A	Formamide	44.6	2.00
A (treated)[d]	Formamide. two steps[e]	45.1	1.88
B (treated)	Formamide, two steps	44.8	2.02
A (treated)	Formamide, heated[f]	45.2	1.60
	Repeated	45.2	1.66
	Repeated	44.6	1.90[g]

[a] Amylose samples from two different corn starch preparations were used. [b] For method of analysis see Allene Jeanes and C. A. Wilham, THIS JOURNAL, **74**, 5339 (1952). [c] The butanol complex was acetylated. [d] Pretreated as described in reference (1) except that treatment in potassium hydroxide was at 0° and some of the excess ether was removed *in vacuo*. [e] Acetylation carried out in two steps.[1] [f] The pretreated amylose was dissolved in formamide by heating to 85°.[3] [g] The variation in values for duplicate acetylations by other procedures did not exceed ±0.12. The measurement of intrinsic viscosity of samples was reproducible to ±0.04.

Acetylations by pyridine or sodium acetate catalysis at 100° were carried out on amylose isolated from the butanol complex[5] in an exceptionally reactive, dry state in which all particles reacted uniformly. Further treatment before acetylation was not necessary. Our acetylations in formamide were successful on the same amylose preparations without recourse to pretreatment,[1] two-step acetylation,[1,3,6] and filtration[1] deemed necessary by others. Still more direct was the acetylation in formamide of the amylose–butanol complex without isolation of the amylose in the dry state. Each of these procedures is applicable to large- or small-scale operations.

Equally successful acetylations catalyzed by pyridine at 100° or at room temperature in the presence of formamide have been obtained on suitably prepared waxy corn starch, corn starch and corn amylopectin, and could, without doubt, be obtained similarly on any amylaceous polysaccharide.

Heating our polysaccharide preparations in formamide to obtain solution, as recommended by some investigators[3,6] was unnecessary, it appeared to cause variable results (Table I), and seems questionable in view of the fact that formyl derivatives have been obtained under similar conditions.[7]

From our experimentation and results we conclude that the formamide method has two distinct advantages. Polysaccharides which are separated originally from aqueous solutions need not be isolated in the dry state before acetylation. Furthermore, the triacetates produced show the superior property of dissolving in certain solvents in which the products from other methods are insoluble.

Experimental

Materials and Methods.—The starches and starch fractions[5] used met high standards for homogeneity of composition and freedom from extraneous non-carbohydrate substances.

Formamide was a neutral fraction obtained from a commercial product by distillation *in vacuo*.

Viscosity measurements were made in Ostwald–Cannon–Fenske tubes No. 100 at concentrations of 0.2 to 0.4%.

Preparation of Dry, Reactive Polysaccharides for Acetylation.—Recrystallized corn amylose–butanol complex was collected in the bowl of a continuous supercentrifuge, and thence added to a large volume of absolute ethanol which was agitated in a Waring Blendor. The precipitated amylose was washed thrice by resuspension in absolute ethanol with care to protect it from atmospheric moisture. It was collected on a filter and freed from ethanol *in vacuo* at room temperature over anhydrous calcium chloride. It was then equilibrated with atmospheric moisture and sieved.

A concentrated aqueous solution of corn amylopectin (one volume) was added slowly to five volumes of absolute ethanol which was agitated in a Waring Blendor. The precipitate was washed and dried as described for amylose.

In order to obtain starches in a physical state in which all particles reacted readily and uniformly, they were gelatinized in water at 100° and dehydrated to fluffy, amorphous products. The swollen granules were either left intact or disintegrated by vigorous mechanical agitation for about 5 minutes, and the cooled paste then was treated as described for amylopectin.

Acetylation.—Acetylation in formamide was by an adaptation of the method of Carson and Maclay,[6] and for the purposes of comparison, the proportion of reagents reported by Potter and Hassid[1] was used. Five grams of air-dried, homogeneously reactive polysaccharide (60 mesh), or 5 g. of amylose in the form of its butanol complex, was mixed uniformly with 70 ml. of cold formamide, and then 125 ml. of

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(1) A. L. Potter and W. Z. Hassid, THIS JOURNAL, **70**, 3774 (1948).

(2) F. C. Cleveland and R. W. Kerr, *ibid.*, **71**, 16 (1949).

(3) R. W. Kerr and F. C. Cleveland, *ibid.*, **71**, 3455 (1949).

(4) B. A. Dombrow and C. O. Beckmann, *J. Phys. Colloid Chem.*, **51**, 107 (1947).

(5) T. J. Schoch, THIS JOURNAL, **64**, 2957 (1942).

(6) J. F. Carson and W. D. Maclay, *ibid.*, **68**, 1015 (1946).

(7) K. M. Gaver, E. P. Lasure and L. M. Thomas, U. S. Patent 2,538,903 (January 23, 1951).

pyridine and 100 ml. of acetic anhydride were added slowly, with stirring and slight cooling.

After several hours a clear solution, free of undissolved particles, resulted. After 20 hours at room temperature, the solution was added to a large volume of vigorously stirred ice and water and the dingy-looking precipitate was washed free of acid with water. A second acetylation treatment[1,3] resulted in no change in acetyl content or in intrinsic viscosity. To provide comparison with the results of others, several variations of this procedure are indicated in Table I.

For acetylation with pyridine as catalyst at 100°, 5 g. of oven-dried polysaccharide (60 mesh) was stirred for 3 hours with 20 ml. of pyridine and 17 ml. of acetic anhydride. The homogeneous solution was cooled, poured into vigorously agitated ethanol, and the colorless precipitate was washed free of acid and dried in the air.

For acetylation with fused sodium acetate as catalyst at 100°, 5 g. of air-dried corn amylose (60 mesh) was soaked in 75 ml. of acetic anhydride overnight, then 1.5 g. of fused sodium acetate was added and the mixture stirred at 100° for 6 hours. The homogeneous solution was cooled, poured into vigorously stirred ice-water, and the colorless product was washed free of acid with water.

Solubility of the Triacetates.—Corn amylose triacetates prepared by the formamide or sodium acetate methods were soluble in acetone; that prepared by the pyridine method at 100° was not. All corn amylose triacetate preparations, as well as the triacetates from corn starch, were soluble in chloroform and 1,1,2-trichloroethane. Preparations of waxy corn starch triacetate from both the pyridine method at 100° and the formamide method were soluble in acetone as well as in the chlorinated solvents. Corn amylopectin triacetate prepared by the pyridine method at 100° was insoluble in the chlorinated solvents, but that prepared by the formamide method was readily soluble.

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(8) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

Alkylation of 2-Naphthol by Esters of Aliphatic Acids

BY SAUL PATAI AND M. BENTOV

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In the course of a study on the preparation of aromatic methacrylates[1] the transesterification of methyl methacrylate with 2-naphthol in the presence of sulfuric acid was investigated. Instead of the expected ester, 2-methoxynaphthalene was formed. In order to elucidate this reaction, the transesterification of other aliphatic esters with other phenolic compounds was tried, using sulfuric acid, orthophosphoric acid or metallic sodium as the catalyst. Phenol, 1-naphthol, 4-hydroxybiphenyl and 4-nitrophenol did not react with methyl methacrylate or ethyl acetate. 2-Naphthol, on the other hand, reacted readily in the presence of sulfuric acid, but not of phosphoric acid or sodium, with methyl methacrylate, methyl acetate, ethyl acetate and ethyl butyrate, yielding 2-methoxynaphthalene with the methyl esters and 2-ethoxynaphthalene with the ethyl esters, but failed to react with ethyl formate or dimethyl oxalate. With methyl benzoate the normal product of transesterification, 2-naphthyl benzoate, was obtained.[2]

2-Naphthol is known to be one of the very few phenols which can be alkylated by alcohols in the presence of acids.[3] This fact may be related to the tautomerizability of 2-naphthol.[4]

As, however, our experiments were carried out under strictly anhydrous conditions, no alcohol could be formed as an intermediate in the reaction. It must, therefore, be assumed, that the alkylation is caused in both cases by the hydrogen alkyl sulfate, formed in the conditions of our experiments from the ester and sulfuric acid. The dissociation constant of formic acid is about ten times, and that of oxalic acid about a thousand times greater than that of either acetic, butyric or methacrylic acid: the failure of the reaction with the esters of formic and oxalic acid could then be due to the strength of these acids, which prevents the formation of the alkylsulfuric acids by interaction of the esters with sulfuric acid.

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Experimental

A mixture of 0.04 mole of 2-naphthol, 0.1 ml. of concencentrated sulfuric acid and 0.08 mole of the ester was refluxed for four hours with the exclusion of moisture. (In the case of methyl methacrylate, some hydroquinone was added to the reaction mixture.) The product was poured into an excess of 5% aqueous sodium hydroxide solution and cooled for one hour in an ice-bath, and the resulting precipitate filtered and recrystallized from ethanol. 2-Methoxy- and 2-ethoxynaphthalene were identified by melting point (72 and 37°, respectively) and mixed melting point with authentic samples. Yield of 2-methoxynaphthalene from methyl acetate 20–25%; from methyl methacrylate 45–50%; of 2-ethoxynaphthalene from ethyl acetate 40–45%; from ethyl butyrate 20–25%.

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(1) S. Patai, M. Bentov and M. E. Reichmann, THIS JOURNAL, **74**, 845 (1952).

(2) C. A. Bischoff and A. Hedenstrom (*Ber.*, **35**, 3449 (1902)) obtained di-2-naphthyl oxalate from diphenyl oxalate and 2-naphthol, and report the failure of the reaction with diethyl oxalate.

(3) C. Liebermann and A. Hagen, *ibid.*, **15**, 1427 (1882); L. Gattermann, *Ann.*, **244**, 72 (1888); W. A. Davis, *J. Chem. Soc.*, **77**, 33 (1900); L. F. Fieser and W. C. Lothrop, THIS JOURNAL, **57**, 1459 (1935).

(4) N. N. Voroshcov, *Bull. Inst. Polyt. Ivanovo-Voznesensk*, **6**, 125 (1922); *C. A.*, **17**, 1637 (1923); J. C. Salfeld, *Ber.*, **73**, 376 (1940).

Cohumulone, a New Hop Constituent

BY F. L. RIGBY AND J. L. BETHUNE

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In the course of an investigation to develop a quantitative method for the estimation of the isohumulone content of beer, petroleum ether extracts of several beers were distributed in a 100-tube all-glass countercurrent apparatus using a solvent system of 2,2,4-trimethylpentane and a phosphate-citrate buffer *p*H 4.9. The concentration in each