III. *d*-Catechin.—Water of crystallization: 12.64 mg. subst. (dried 1 hour over P_2O_5 in a vacuum) H_2O, 2.56 mg.

Anal. Calcd. for $C_{15}H_{14}O_6 \cdot 4H_2O$: H_2O, 20.25. Found: H_2O, 19.89.

The melting point of the anhydrous substance rose to 171–173°.

Anal. Calcd. for $C_{15}H_{14}O_6 \cdot 4H_2O$: C, 49.72; H, 6.07. Found: C, 49.39; H, 6.20.

Absorption: λ_{max} 280 mμ, log ϵ 3.60; λ_{min} 255 mμ, log ϵ 2.70.

d-Catechin acetate was colorless prisms of m.p. 131°.

Isolation of *d*-Catechin and Prunin from the Sapwood.—Five hundred grams of the sapwood chips were boiled for 3 hours with 3 l. of methanol. The methanolic extract was concentrated to 100 ml., and the solution was extracted with ether. The ethereal layers were evaporated and the residue was recrystallized from water. After 5 recrystallizations, *d*-catechin of m.p. 97° (yield 0.95 g.) was obtained.

The mother liquor was then extracted exhaustively with ethyl acetate. After evaporation of the solvent, the residue was dissolved in 100 ml. of water and 50 ml. of ethyl acetate was added. From the solution an oily mass was gradually separated after standing several days. From the filtered solution ethyl acetate was distilled off, and the residue was dissolved in methanol. The methanolic solution was, after evaporation to a sirup, allowed to stand at room temperature. After about 3 days standing, white crystals of prunin appeared in the solution. The white mass of prunin was collected and crystallized from a small amount of methanol, added with a few drops of water. Prunin was then obtained in colorless needles of m.p. 225°. The yield of the crude substance was 0.7 g.

IV. Prunin.—Prunin is soluble in alcohol, ethyl acetate and acetone, sparingly so in methanol and insoluble in ether benzene and chloroform. A methanolic solution gave a brown-violet coloration with ferric chloride. In alcoholic solution it gave a reddish purple coloration with magnesium powder and concd. hydrochloric acid; specific rotation: 0.311 g. subst., 25 ml. acetone, 1 dm. tube; $\alpha_D = -0.52°$, $[\alpha]_D = -41.8°$.

Absorption: λ_{max} 308 mμ (inflection), log ϵ 4.12, λ_{max} 283 mμ, log ϵ 3.44.

The sample was dried over P_2O_5 in a vacuum at 110–115°; 3.084 g. subst., 6.532 g. CO_2, 1.366 g. H_2O.

Anal. Calcd. for $C_{21}H_{22}O_{10}$: C, 58.0; H, 5.0. Found: C, 57.80; H, 4.96.

Hydrolysis of Prunin.—Three-tenths gram of prunin, suspended in 20 ml. of 10% sulfuric acid, was heated 30 minutes on a water-bath. The aglycone which gradually deposited was filtered (yield 0.15 g.), m.p. 246°. This substance was identified with naringenin through a mixed melting point determination. After extracting with ether, the mother liquor was carefully neutralized with barium carbonate, filtered and evaporated on a boiling water-bath to a small volume, and then filtered again. When the filtrate was heated with phenylhydrazine hydrochloride and sodium acetate, glucosazone was formed. After recrystallization from methanol, it melted at 207°, both alone and on admixture with the authentic specimen. By the paper chromatographic method any sugar except glucose could not be detected.

A suspension of 0.31 g. of prunin in 50 ml. of 1% sulfuric acid was boiled for 1 hour. After extraction with ether, the mother liquor was neutralized with 10% sodium hydroxide. In this solution 121.5, 118.5 mg. of glucose was found according to the method of Bertrand. When postulated as naringenin: glucose = 1:1, the theoretical yield of glucose would be 128.9 mg.

Position of the Sugar in Prunin.—Fifty mg. of prunin was methylated by heating in 30 ml. of acetone with 1 mg. of dimethyl sulfate and 5 g. of potassium carbonate for 30 minutes under reflux.

After filtering, the solution was evaporated, and the residue was recrystallized from dilute methanol. A small amount of crystals thus obtained was hydrolyzed by boiling with 1% hydrochloric acid for 30 minutes and the resultant solution was shaken several times with ether. The ethereal solution was evaporated to dryness, and the residue was examined by paper chromatography, using a mixture of benzene and ligroin (1:1), saturated with water, and added with a small quantity of methanol as the mobile phase.[7] When developed with 1% methanolic ferric chloride solution, two spots, with R_f values of 0.05 and 0.00, respectively, were obtained. Authentic specimens of naringenin gave an R_f value of 0.05 and that of isosakuranetin 0.00, whereas sakuranetin gave the R_f value 0.73 in the same chromatogram.

Prunin Dimethyl Ether.—Two-tenths gram of prunin was dissolved in 30 ml. of acetone and heated after addition of 5 g. of potassium carbonate and 2 ml. of dimethyl sulfate for 6 hours. At that time, it gave no color reaction with ferric chloride. After filtering, acetone was removed by distillation, and the residue crystallized from dilute methanol in white needles of m.p. 231°; yield poor; 3.21 mg. subst., 3.345 mg. AgI.

Anal. Calcd. for $C_{21}H_{20}O_8(OCH_3)_2$: OCH_3, 13.42. Found: OCH_3, 13.31.

Hydrolysis of Prunin Dimethyl Ether.—Hydrolysis of 50 mg. of prunin dimethyl ether was effected by heating in 20 ml. of 2% hydrochloric acid on a boiling water-bath for an hour. The turbid liquor was extracted 3 times with ether. After the ethereal extract was evaporated, the residue was recrystallized from dilute methanol. White needles of naringenin dimethyl ether (m.p. 187°) were obtained. As only a small quantity was available, no analysis could be made.

Acetate of Prunin. (1).—One-tenth gram of prunin was treated with acetic anhydride (1 ml.) and pyridine (1 ml.) in the cold for one hour. Cold water was then added and the solidified mass was filtered, washed and recrystallized from methanol. Colorless needles of m.p. 187–189° were obtained. The substance gave a purplish color reaction with ferric chloride. Owing to the scarcity of pure substance, no analysis was made.

(2).—One-tenth gram of prunin was mixed with acetic anhydride (1 ml.) and pyridine (3 drops) and the mixture was heated one hour on a water-bath. The reaction mixture was poured into water and the solidified mass was filtered, washed and recrystallized from carbon tetrachloride. Colorless needles of m.p. 138–139° were obtained. This substance was not analyzed because of the lack of a pure specimen.

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Hydrolysis and Halide Complexing of Indium(III)

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In connection with other work in this Laboratory it became desirable to have a knowledge of the hydrolysis constant of In^{+3}. Hattox and DeVries,[2] from *p*H measurements in sulfate solutions at 23°, gave for the hydrolysis constant 2×10^{-4} in their most dilute (0.00631 *M*) solution. Sulfate complexing and bisulfate formation doubtless occurred in their solutions, and correction for these factors is difficult. Moeller[3] has measured the *p*H of aqueous solutions of $InCl_3$, $InBr_3$ and InI_3 over a range of concentrations at 25°. It is evident from

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[2] E. M. Hattox and T. DeVries, THIS JOURNAL, **58**, 2126 (1936).

[3] T. Moeller, *ibid.*, **63**, 1206 (1941); **64**, 953 (1942).

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.	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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[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.

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