[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. LIV. Synthesis and Properties of Glycosides Related to Lignin

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In a previous communication[2] the synthesis of certain phenolic xylosides was described and their relation to the structure of lignin discussed. Additional phenolic glycosides have now been prepared and rates of hydrolysis of a number of these determined under conditions similar to those used in lignin extraction from wood, in order to ascertain the nature of the linkage (if any exists) between lignin and carbohydrate constituents. One aliphatic glycoside, β-*d*-glucoside of α-hydroxypropioveratrone, has also been prepared and included in this study.

Three methods were employed for determining the rates of hydrolysis, namely, (1) a colorimetric procedure based on a modification of the Folin–Denis colorimetric technique for estimating phenols, (2) a gravimetric method involving precipitation with mercuric acetate and (3) polarimetric determinations. The composite values are shown in Table I. Determinations of the dissociation constants of the phenols formed on hydrolysis of the above glycosides were made by measuring the *p*H of an aqueous solution of the phenol in question to which one-half an equivalent weight of sodium hydroxide had been added previously, the dissociation constant being numerically equal to the observed hydrogen ion concentration. These results are shown in Table II.

Discussion

It is evident from Table I that in the case of alkaline hydrolysis of the phenolic glycosides two distinct classes exist. In the one, characterized by the presence of a carbonyl group *para* to the phenolic hydroxyl (1, 2, 3, 4, 5 in Table I), the glycosides are seen to be much less stable toward alkalies than where the *para* carbonyl group is absent (6, 7, 8 in Table I). Also the phenols corresponding to the former group are much more acidic than those derived from the latter (Table II) and the rate of alkaline hydrolysis of the corresponding glycosides follows (in a general way)

TABLE I

HALF-LIFE PERIODS OF HYDROLYSIS OF THE GLYCOSIDES (VALUE IN MINUTES)

	Hydrolyzing agent	NaOH	NaOH	NaOH	NaOH	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2O
	Concn., %	5	5	0.1	5	5	5	0.1	1.0	
	Temperature, °C.	20	60	100	100	20	60	100	100	160
1	α-Hydroxypropiovanillone β-*d*-xyloside[a]	5520 4200[b]	46 42[b]	3.7 9.5[b]	..	6700	39	20.5	..	23
2	α-Hydroxypropiosyringone β-*d*-xyloside[c]	370	4.8	0.5	..	315	3.4	3.0	..	3.0
3	Acetovanillone β-*d*-xyloside	1200	7 8.8[b]	3 4.4[b]	..	5160	39	26	..	21
4	Acetovanillone β-*d*-glucoside[d]		...	26[b]	..	..	...	197	..	...
5	Acetovanillone β-cellobioside		...	23[b]	..	..	...	300	..	...
6	Guaiacol β-*d*-xyloside	...	1620 1950[b]	360	..	3800	25	15	..	110
7	Phenyl β-*d*-xyloside[4]	...	5160	...	60	..	57	...	..	...
8	Phenyl β-*d*-glucoside[5]	...	...	...	210	..	940	...	..	...
9	β-*d*-Glucoside of α-hydroxypropioveratrone[d]	...	...	...	258[b] 236[e]	..	...	...	137[e]	...

[a] Half life value of this xyloside with sodium cymene-2-sulfonate (96 g. per 100 cc. H_2O) at 105°, 44 hr.; at 145°, 40 min. [b] Value determined gravimetrically; other values determined colorimetrically unless otherwise indicated. [c] Gravimetric method not applicable. [d] No hydrolysis was observed on treatment with water only, aqueous phosphate buffer (*p*H 7.0 at 20°) and buffered aqueous butanol (50:50) each at 160° for 4 hr. or with an aqueous solution of sodium cymene-2-sulfonate (96 g. per 100 cc. H_2O) at 145°. [e] Value determined polarimetrically.

TABLE II

DISSOCIATION CONSTANTS OF PHENOLS

α-Hydroxypropiovanillone	$10^{-7.32}$
α-Hydroxypropiosyringone	$10^{-7.45}$
Acetovanillone	$10^{-7.50}$
Guaiacol	$10^{-9.55}$
Phenol	$10^{-9.60}$

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(2) Fisher, Hawkins and Hibbert, THIS JOURNAL, **62**, 1412 (1940).

(3) Mauthner, *J. prakt. Chem.*, **97**, 217 (1918).

(4) Helferich, *Z. physiol. Chem.*, **205**, 201 (1932).

(5) Fischer, *Ber.*, **49**, 2814 (1916).

the order of acidity of the phenol in question. In the case of acid hydrolysis the influence of the "para carbonyl group" is not apparent.

Presence of methoxyl groups *ortho* to the glycosidic linkage renders the union less stable to both alkali and acid. While, in general, aliphatic glycosides are more readily hydrolyzed by acid than by alkali, in the case of the strongly acidic phenols the rate of glycoside hydrolysis by alkali is approximately the same or greater than that by acid.

The glucosides are found to be more stable than the xylosides to both acids and alkalies and acetovanillone β-*d*-glucoside is seen to have approximately the same stability as the corresponding cellobioside.

Conclusions Concerning a Possible Lignin-Carbohydrate Complex in Wood.—Older methods of lignin extraction such as those of Klason,[6] Freudenberg[7] and Willstätter[8] involved the use of strong mineral acids. Organic acids such as formic and acetic[9] have been applied, and, in addition, a very extensive use has been made over the last fourteen years of milder techniques involving refluxing with alcohols, glycols, glycerol, etc., in presence of 2% anhydrous hydrogen chloride,[10] that is, under typical conditions for glycoside formation, involving minimum change and degradation.

More recently[11] aqueous solutions of alcohols such as butanol, propanol and ethanol have been employed either alone or in the presence of small amounts of alkali. Bailey[11b] has shown that all the lignin in aspen wood and 80% of that present in jack pine can be removed by heating under pressure at 160° for seven hours with aqueous butanol (1:1) previously buffered to a *p*H of 7 at 20°. This experiment, at first sight, would appear to indicate that any union between lignin and other plant constituents, if such exists, must be of a weak nature.

However, the fact that acids are always formed in considerable amount on heating wood with water at such a high temperature (thus producing a marked acidity (*p*H 3 or less)[12]) together with the fact, as pointed out by Corey and Maass,[12b] that in buffering a solution at 20° there is no guarantee that it will be equally well buffered at 160°, indicates the need for caution in the interpretation of Bailey's results.

The same remarks apply to the interesting results of McKee and Pelipetz,[13] who showed that 93% of the lignin in poplar could be removed by heating with a very concentrated neutral aqueous solution (approximately 1:1) of sodium cymene sulfonate at 105° for thirty hours. With maple wood a higher temperature (145°) was necessary.

The present data do not permit drawing definite conclusions regarding the existence and nature of a specific lignin union to other constituents in wood. It is known that in the early stages of plant growth certain glycosides such as coniferin are present in practically all species, and Klason's view of lignin as a condensation polymer of coniferyl alcohol, aldehyde, or both is thus seen to have a close connection with Hibbert's theory of the formation of lignin as arising from a mixture of condensation polymers formed from a series of plant respiratory catalysts of the type R—C—C—C (R = guaiacyl or syringyl).[14] The extent to which the polymerization has already taken place in the plant is unknown. However, if the presence of phenolic type lignin units is assumed and also, as seems probable, some type of union with carbohydrates takes place through the phenolic hydroxyl group, the ease of extraction of lignin, in the light of the more recent work quoted above,[11,13] would be in harmony with the present experimental results. This is the case, however, only if it be assumed that, as seems probable, a marked difference in chain length brings about no abnormal alteration in stability of such glycosidic linkages. This would apply irrespective of whether the carbohydrate were a polysaccharide or a uronic acid. There is definite evidence favoring the latter type of linkage[15] but the exact nature of the bond is not known.

The experiments both of Bailey and of McKee and Pelipetz are of great interest in this connection and it is unfortunate that no evidence is

(6) Klason, "Hauptversammlungsbericht des Vereins der Zellstoff und Papierchemiker," Berlin, 1908, p. 52.

(7) Freudenberg, *Ber.*, **62**, 1814 (1929).

(8) Willstätter, *ibid.*, **55**, 2460 (1922).

(9) Ilieff, Wright and Hibbert, THIS JOURNAL, **61**, 1477 (1939); Hunter, Wright and Hibbert, *Ber.*, **71**, 734 (1938).

(10) Cramer, Hunter and Hibbert, THIS JOURNAL, **61**, 509 (1939); Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939).

(11) (a) Aronovsky and Gortner, *Ind. Eng. Chem.*, **28**, 1270 (1936); (b) Bailey, *Paper Trade J.*, **110**, 1, 15 (1940); **111**, 63, **73**, 116 (1940).

(12) (a) Corey and Maass, *Can. J. Research*, **B13**, 289 (1935); (b) Corey and Maass, *ibid.*, **B13**, 295 (footnote) (1935).

(13) Pelipetz, Ph.D. Dissertation, Columbia University, 1937.

(14) Hibbert, THIS JOURNAL, **61**, 725 (1939); review article, *Paper Trade Journal*, **113**, No. 4, 35 (1941).

(15) Norman and Jenkins, *Biochem. J.*, **27**, 818 (1933); Norman and Shrikhande, *ibid.*, **28**, 2259 (1935); Norman, "Biochemistry of Cellulose, Polyuronides, Lignin, etc.," Clarendon Press, Oxford, 1937, pp. 59–63.

available as to the actual *p*H under the extraction conditions of the initially neutral reagents. It is not improbable that even under such conditions considerable change in the simpler lignin units may have occurred. Nevertheless the fact that by use of such mild reagents the entire lignin content can be removed and at a comparatively low temperature would again seem to indicate a relatively weak lignin–carbohydrate union. Possibly reagents such as the aromatic sulfonates may owe this property of lignin extractability to a marked extent, at least, to their power to dissolve otherwise insoluble phenols[16] and even aromatic hydrocarbons.[17]

In any event these results raise the question as to whether difficulties met with in lignin extraction may not be due in large measure to a secondary formation of difficultly soluble condensation polymers formed from simple, carbohydrate-free lignin building units such as those isolated recently by Hibbert and co-workers[10,18] and now known to be readily converted into amorphous high-molecular weight products by the action of relatively mild reagents.[19]

That the evidence so far obtained favors an aromatic rather than an aliphatic type of linkage (the latter through a hydroxyl group in the propyl side chain) is evident from the much greater stability of *β-d*-glucoside of *α*-hydroxypropioveratrone. Considerable further work is necessary to settle this problem but already it can be stated very definitely that the actual linkage of lignin to carbohydrate in wood (assuming this to be glycosidic in character) is of a relatively weak type and that its separation can be effected by mild chemical reagents at temperatures from 105–160°. Nevertheless under these conditions secondary reactions apparently occur which render the lignin more difficult to remove. The presence of an inert neutral sulfonate facilitates its removal due apparently to its specific solvent action for lignin and lignin condensation products.

Experimental

Acetovanillone Heptaacetyl *β*-Cellobioside.—This glycoside was prepared by a Helferich condensation[20] of the potassium salt of acetovanillone (14% excess) and acetobromocellobiose.[21] The cellobioside crystallized from ethanol in fine hair-like crystals; yield 53%; m. p. 208–209°.

Anal. Calcd. for $C_{35}H_{44}O_{20}$: C, 53.6; H, 5.65; OCH_3, 3.95. Found: C, 53.2; H, 5.60; OCH_3, 3.92.

Acetovanillone *β*-Cellobioside.—Deacetylation of the acetylated cellobioside was carried out at 64° by the Zemplén method.[22] As deacetylation proceeded the cellobioside crystallized from the boiling methanol in the form of fine hair-like crystals; yield 93%; m. p. 239–240° (with some decomposition).

Anal. Calcd. for $C_{21}H_{30}O_{13}$: C, 51.4; H, 6.18; OCH_3, 6.32. Found: C, 51.1; H, 6.44; OCH_3, 6.30.

Tetraacetyl *β-d*-Glucoside of *α*-Hydroxypropioveratrone.—This glucoside was prepared using the Reynolds and Evans[23] modified Königs–Knorr method. *α*-Hydropropioveratrone (1.7 g.), acetobromoglucose (3.2 g.), silver carbonate (2.8 g.) and Drierite (7.2 g.) in 32 cc. of dry purified chloroform were allowed to react for twenty-four hours at 20°, yielding an impure sirupy product, which was purified by dissolving in methanol (6 cc.), adding water (40 cc.) and crystallizing the resulting oil from 50% aqueous methanol; yield of fine hair-like crystals, 0.56 g. (13.5%); m. p. 133.6–133.8°. *Anal.* Calcd. for $C_{25}H_{32}O_{13}$: C, 55.5; H, 5.97; OCH_3, 11.5. Found: C, 55.4; H, 6.21; OCH_3, 11.3. The above yield could not be increased by carrying out the reaction at temperatures of 40 and 60°.

***β-d*-Glucoside of *α*-Hydroxypropioveratrone.**—This deacetylation was carried out by the Zemplén method[22] at 20° over a period of four hours. Neutralization of the sodium methylate by acetic acid and evaporation of the methanol solution under reduced pressure at 20° yielded a very viscous sirup, which could not be crystallized. Deacetylation at 0° also failed to produce a crystalline material.

The product could be precipitated in the form of an amorphous white powder by adding a chloroform solution of the glucoside to a tenfold volume of ligroin (30–50°) or ethyl acetate. This material contained considerable amounts of solvent even when dried at 60° under 10 mm. pressure for twelve hours. It showed no definite melting point, softening at about 85°, becoming fluid at about 135° and evolving gas throughout the heating, presumably traces of solvent. The methoxyl content of the amorphous powder was 15.5% (theor., 16.7%); that of a sample which had been heated at 135° for another twelve hours under 10 mm. pressure was 16.0%. A glassy solid resulted on cooling this melted material. Discrepancies in the analytical values are probably due to the presence of solvent in the glassy product, solution and reprecipitation in ethyl acetate failing to improve the analytical values.

Anal. Calcd. for $C_{17}H_{24}O_9$: C, 54.8; H, 6.50; OCH_3, 16.7. Found: C, 53.2; H, 6.93; OCH_3, 16.0.

Sodium Cymene-2-sulfonate.—This was prepared from barium cymene-2-sulfonate[24] by reaction with an equivalent amount of sodium sulfate. The sodium salt was crystallized twice from water.

(16) Friedländer, German Patent 181,288.

(17) McKee and Heard, *Trans. Am. Electrochem. Soc.*, **65**, 301 (1934).

(18) Brickman, Pyle, Hawkins and Hibbert, THIS JOURNAL, **62**, 986 (1940); Brickman, Hawkins and Hibbert, *ibid.*, **62**, 2149 (1940); Kulka, Hawkins and Hibbert, *ibid.*, **63**, 2371 (1941).

(19) K. A. West, Hawkins and Hibbert, unpublished results.

(20) Helferich, *Ann.*, **520**, 156 (1936).

(21) Fischer and Zemplén, *Ber.*, **43**, 2536 (1910).

(22) Zemplén, *ibid.*, **62**, 1613 (1929).

(23) Reynolds and Evans, THIS JOURNAL, **60**, 2559 (1938).

(24) Le Fèvre, *J. Chem. Soc.*, 1501 (1934).

TABLE III

HYDROLYSIS OF α-HYDROXYPROPIOVANILLONE β-*d*-XYLOSIDE BY SODIUM HYDROXIDE AT 60°

Xyloside used, mg.	Time of hydrolysis, min.	Av. values for colorimeter rdgs., mm.[a] Control	Xyloside	Control/ Xyloside	Phenol produced, mg.	Hydrolysis, %		k,[b] min.$^{-1}$
6.7	11	20.8	21.8	0.92	0.87	22		0.0226
3.35	20	19.9	27.4	.73	.57	28		.0164
3.35	40	20.2	21.6	.92	.88	44		.0145
1.68	40	20.4	31.8	.63	.45	45		.0149
1.68	73	20.7	25.2	.79	.67	67		.0152
1.68	110	20.2	22.9	.87	.78	78		.0138
1.68	199	20.7	22.5	.89	.83	83		.0089
							Av.	.0152

[a] Standard reading 20 mm. in all cases. [b] Calculated on basis of a first order reaction.

Colorimetric Determination of Rates of Hydrolyses of Phenolic Glycosides.—This method was a modification of the Folin–Denis[25] colorimetric method for estimation of phenols. It was found that intensity of the color was not directly proportional to concentration of the phenol and, furthermore, best agreement was obtained when the final solution was only slightly alkaline and the phenol concentration low. This difficulty was overcome by employing standard solutions of each phenol investigated and determining color intensity at various concentrations.

Under conditions of alkaline hydrolysis, it was found that the carbohydrate components produced substances which interacted with the Folin–Denis reagent, but this effect disappeared on prolonged treatment. For this reason, values determined with alkaline reagents varied somewhat from those obtained gravimetrically for short half-life periods.

The procedure used is illustrated in the following detailed account of the hydrolysis of α-hydroxypropiovanillone β-*d*-xyloside by 5% alkali at 60°.

After hydrolysis, the control and xyloside solutions were neutralized by addition of 1 cc. of phosphoric acid (17.5%). Then 2 cc. of water, 1 cc. of Folin–Denis reagent, 2 cc. of sodium carbonate (7.5%) and 12 cc. of warm water (35°) were added in this order and the solutions allowed to stand for fifteen minutes before color comparisons were made with a standard solution made up in the same manner and containing 1.0 mg. of α-hydroxypropiovanillone. Control solutions also contained 0.76 mg. of xyloside.

The results are shown in Table III, the values in column 5 being converted to those in column 6 by reference to Fig. 1.

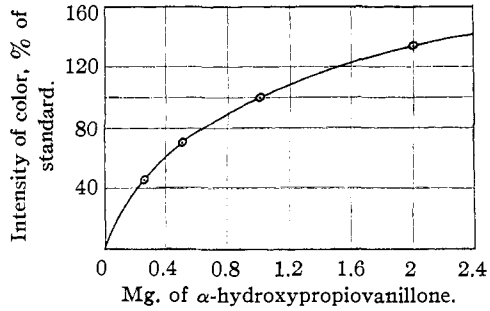

Fig. 1.—Relationship between concentration of α-hydroxypropiovanillone and intensity of color produced by it and the Folin–Denis reagent; color produced by 1.0 mg. of α-hydroxypropiovanillone chosen as 100% intensity.

(25) Folin and Denis, *J. Biol. Chem.*, **22**, 305 (1915).

In the determination of rates of hydrolysis under all other conditions, the final colored solution always contained the same amount of sodium phosphate since the quality and intensity of color is governed by the *p*H of the final solution. In each case hydrolysis curves were drawn from which the value of the half-life period was obtained. These values are listed in Table I.

Gravimetric Determination of Rates of Hydrolyses of Phenolic Glycosides.—The gravimetric determination of the rate of hydrolysis of α-hydroxypropiovanillone β-*d*-xyloside illustrates the method used.

To a solution of 10 mg. of α-hydroxypropiovanillone in 4 cc. of water, buffered with sodium acetate–acetic acid to a *p*H of 7.0, was added 1 cc. of a mercuric acetate solution (22%). The solution was allowed to stand at 20° for six hours, the precipitate filtered through an Alundum crucible, washed with water, methanol and ether and dried at 100° for six hours. The weight of mercury compound obtained was 19.9 mg., methoxyl analysis of which showed the recovery of α-hydroxypropiovanillone from solution to be 98%.

The weights of α-hydroxypropiovanillone in solutions of the partially hydrolyzed xyloside were determined by the same procedure, from which values the percentage hydrolysis was calculated.

Similar control experiments were carried out with guaiacol and acetovanillone, preliminary to the determination of the rates of hydrolysis of the glycosides of these phenols.

Determination of Rates of Hydrolysis of Glucoside of α-Hydroxypropioveratrone. Polarimetric Method.—The glucose formed from the alkaline hydrolysis of this glucoside decomposed with formation of a dark-brown solution, thus preventing observation of the rotation even after the solution had been treated with charcoal. However, on neutralization the color changed to a light yellow and observation of rotation was possible.

The rotation of glucoside solutions, partially hydrolyzed by acid, could be observed directly.

Gravimetric Method.—α-Hydroxypropioveratrone could be quantitatively separated from the carbohydrate products of alkaline hydrolysis and the unchanged glucoside by extracting the alkaline hydrolysis mixture three times with chloroform. Control experiments showed that neither the glucoside nor the products of alkaline degradation of glucose were extractable from alkaline solution by chloroform, while α-hydroxypropioveratrone was removed quantitatively by this solvent.

Summary

1. The β-cellobioside of acetovanillone and the β-*d*-glucoside of α-hydroxypropioveratrone have been prepared.

2. The rates of hydrolysis of a series of one aliphatic and several phenolic glycosides have been determined under a variety of conditions. These results, viewed in light of the knowledge of lignin extraction, indicate that a phenolic glycosidic linkage is a plausible type for the lignin-carbohydrate complex in wood (if such exists).

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Studies on Lignin and Related Compounds. LV. Synthesis and Properties of β-Hydroxypropioveratrone

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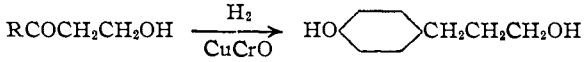
As a result of recent studies on the structure of lignin[1] it is now apparent that the fundamental lignin building units consist of an aromatic phenol nucleus with a substituted propyl side chain. Such building units, when isolated by ethanolysis and other reactions from soft woods, contain only the guaiacyl nucleus, while from hard woods a mixture of guaiacyl and syringyl components usually results. Ethanolysis of various woods has led to the isolation of α-ethoxypropiovanillone[2] and α-ethoxypropiosyringone[3] from the alkali-soluble fraction of the total ethanolysis "distillable oils."[4] It is very probable these derivatives are formed during the ethanolysis reaction from α-hydroxypropiovanillone and α-hydroxypropiosyringone, respectively, and such conversions have now been accomplished, under the usual conditions of ethanolysis.[5] From the bisulfite-soluble fraction of the ethanolysis "distillable oils," vanilloyl[6] and syringoyl methyl ketones[7] have recently been isolated, as such. Up to the present time only these four C_6–C_3 units have been identified among the ethanolysis products, and in each of them the side chain is terminated by a methyl group.

In the light of the recent theory of Hibbert[1] that lignin is a composite mixture of both low- and high-molecular weight polymers derived from a series of plant respiratory catalysts, the existence has been postulated by him of a further series of C_6–C_3 units, analogous to the Szent-Györgyi C_4 system[8] functioning in animal respiratory processes. This includes, among others, the type compound, $RCOCH_2CH_2OH$, where R may be guaiacyl or syringyl.

Hydrogenation of both isolated lignins and wood has given rise to a series of products closely related to those obtained by ethanolysis. As a result of hydrogenolysis, however, many of the functional groups, particularly those of the propyl side chain, are removed.[9] Thus 4-*n*-propylcyclohexanediol-1,2, 4-*n*-propylcyclohexanol, and 3-(4-hydroxycyclohexyl)-propanol-1 (I) have been obtained by the hydrogenation of methanol lignin (aspen)[10] and ethanol lignin (maple)[11] and the latter two compounds by the hydrogenation of maple wood.[12]

Isolation of I from the hydrogenation products of both lignin and wood suggests the presence in the latter of a "lignin building unit" such as β-hydroxypropiovanillone (II) in which the side chain terminates in a primary hydroxyl group.



II (R = Guaiacyl) I

At the present time, however, no lignin building unit having this type of side chain has been obtained by ethanolysis or other reactions. This failure may be due to its absence in older wood, to the manner in which it is united in the lignin complex, or to the fact that it may, under conditions of ethanolysis, undergo rearrangement, yielding eventually α-ethoxypropiovanillone. Such

(1) For a comprehensive review, see Hibbert, "Status of the Lignin Problem," *Paper Trade J.*, **113**, No. 4, 35 (1941).

(2) Cramer, Hunter and Hibbert, THIS JOURNAL, **61**, 509 (1939).

(3) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939).

(4) Patterson, West, Lovell, Hawkins and Hibbert, *ibid.*, **63**, 2065 (1941).

(5) West, Hawkins and Hibbert, *ibid.*, **63**, 3038 (1941).

(6) Brickman, Hawkins and Hibbert, THIS JOURNAL, **62**, 2149 (1940).

(7) Kulka, Hawkins and Hibbert, *ibid.*, **63**, 2371 (1941).

(8) For review see *Ber.*, **72**, 53 (1939).

(9) Cooke, McCarthy and Hibbert, THIS JOURNAL, **63**, 3052 (1941).

(10) Harris, D'Ianni and Adkins, THIS JOURNAL, **60**, 1467 (1938).

(11) Cooke, McCarthy and Hibbert, *ibid.*, **63**, 3056 (1941).

(12) Godard, McCarthy and Hibbert, *ibid.*, **63**, 3061 (1941).