other hand, methyllithium gave a product with zirconium tetrachloride in ether at low temperature which decomposed at room temperature to give not ethane, but exclusively methane. In like manner, the product from the reaction of ethylmagnesium bromide on zirconium tetrachloride underwent thermal decomposition to give ethane exclusively, and no butane. In short, the aryl compound gave, in the zirconium tetrachloride studies, an RR product whereas the alkyl compounds gave RH products. This suggested an examination of the thermolysis of ethylsilver prepared from ethylmagnesium bromide and silver bromide in ether. The chief hydrocarbon obtained was butane.

A suspension of 20.0 g. (0.106 mole) of dry silver bromide (freshly prepared from silver nitrate and sodium bromide) in 25 cc. of dry ether was cooled in an ice-bath and stirred rapidly while 65 cc. of a 1.54 *M* solution of ethylmagnesium bromide in ether was added dropwise over a twenty-five minute period. After all the Grignard solution had been added the ice-bath was removed but stirring was continued. Within several minutes a vigorous evolution of gas took place and sufficient heat was evolved to boil the ether. The gas was collected over water and analyzed by absorption and combustion methods. The yield of butane was 42% and the yield of ethylene was 4.7%. From a duplicate experiment the yield of butane was 48% and the yield of ethylene 3.5%. The formation of olefins from reactions of silver halides and alkylmagnesium halides has apparently not been reported hitherto. The weight of metallic silver was 11.0 g. or 95% of the silver in the original silver bromide.

These results indicate that the thermal decomposition of organometallic compounds in the presence of a solvent is not a simple reaction, and may or may not involve free radicals.

Summary

Evidence is presented for the formation of phenylthallium by pyrolysis of triphenylthallium in xylene. This thermally unstable organometallic "radical" is readily converted to triphenylthallium and metallic thallium, probably by way of diphenylthallium

$$C_6H_5Tl \longrightarrow Tl + (C_6H_5)_2Tl \longrightarrow Tl + (C_6H_5)_3Tl$$

When triphenylthallium is pyrolyzed in the presence of organic functional groups, the phenylthallium formed shows reactions of a typical moderately reactive organometallic compound.

The order of decreasing reactivity of some phenyl-metallic compounds is: RMgX, RTl, R_3In, R_3Ga, R_3Tl.

AMES, IOWA

RECEIVED JULY 15, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE NEW YORK STATE COLLEGE OF FORESTRY AND SYRACUSE UNIVERSITY]

The Chemistry of Wood. VII. The Esters and Ethers of the Water Soluble Polysaccharides of Larch Wood[1]

BY F. C. PETERSON, A. J. BARRY, H. UNKAUF AND L. E. WISE[1]

The so-called ϵ-galactan isolated by means of water extraction from western larch wood[2] was later shown to be an arabo-galactan.[3] Very similar polysaccharides were also obtained from Eastern, European[4,5] and Siberian larches.[6] Investigators at Syracuse[3,4,5,7] noted that on hydrolysis these substances gave arabinose and galactose in an approximate ratio of 1 mole to 6 moles. It was assumed, with reservations, that these substances were homogeneous polysaccharides with the empirical formula $[(C_5H_8O_4)(C_6H_{10}O_5)_6]_n$. Although Wise and Unkauf found that the fractions obtained by the gradual addition of alcohol to a water solution of the polysaccharide appeared to be identical, the possibility remained that at the instant of precipitation the concentration of alcohol in the localized region of addition might be high. An aliquot of the polysaccharide might thus be precipitated instead of a less soluble fraction. Derivatives of the water-soluble polysaccharide fraction from three species of larch wood (Western, Eastern, and European) have now been prepared and studied by methods of fractionation in an effort to establish their homogeneity or non-homogeneity and thus that of the original polysaccharide preparations.

Preparation of Arabo-galactan.—The cold water extract prepared as formerly[3] was concentrated at 65° (40 mm.) to a sirup, containing about 9.3% solids, corresponding to a refractive index of about 1.3470. After an electrodialysis[5] to remove inorganic matter, the concentrate was poured into 10 volumes of 95% ethyl alcohol and the resulting precipitate was washed twice by decantation with alcohol. As the preparations reacted poorly with

---

(1) Presented before the Division of Sugar Chemistry at the Baltimore meeting of the American Chemical Society, April 3–7, 1939. Paper VI, ref. 5.

(2) Schorger and Smith, *Ind. Eng. Chem.*, **8**, 494 (1916).

(3) Wise and Peterson, *ibid.*, **22**, 362 (1930).

(4) Wise, Hamer and Peterson, *ibid.*, **25**, 184 (1933).

(5) Peterson, Maughan and Wise, *Cellulosechem.*, **15**, 109 (1934).

(6) Nikitin and Soloviev, *J. Applied Chem.* (U. S. S. R.), **8**, 1016 (1935).

(7) Wise and Unkauf, *Cellulosechem.*, **14**, 20 (1933).

TABLE I

PROPERTIES OF ESTERS OF LARCH ARABO-GALACTAN

Analysis of esters	Calcd.	Acetate from Western Found	Calcd.	Propionates from			Calcd.	Benzoates from	
				Western Found	Eastern Found	European Found		Western Found	Eastern Found
Carbon, %	49.95	49.73	54.47	.....	.....	54.46	68.25	68.26	68.37
Hydrogen, %	5.60	5.67	6.71	.....	.....	6.68	4.68	4.85	4.83
Acyl value, %[a]	44.66	43.74	51.6	51.5	51.3	51.2	66.2	67.5	66.5
Araban, %[b]	6.72	6.45	...	6.71	6.21	6.18	...	4.34	4.09
Sp. rotn., $[\alpha]^{20}\text{D}$ in *m*-cresol	...	−35.10	...	−33.67	−32.07	−39.06	...	−37.57	−29.52
Sp. viscosity[c]	...	2.63	...	2.42	3.34	3.51	...	3.56	4.89
Melting point, °C.	...	200	...	160	160	160	...	222	222
PROPERTIES OF THE ARABO-GALACTAN REGENERATED BY SAPONIFICATION OF THE ESTER									
Reducing value (mg. $Cu_2O/{}^1/_2$ g.)	...	25.6	...	36.5	22.4	24.4	...	39.8	23.5
Sp. rotn., $[\alpha]^{20}\text{D}$ in H_2O	...	14.16	...	.....	16.80	12.23	...	17.58	20.57

[a] Method of Barnett.[9] [b] Method of Dox and Plaisance, ref. 8. [c] Method of Staudinger[10] using prime molar solutions in *m*-cresol at 20 ± 0.03°.

acylating mixtures after drying in a desiccator, the material was left suspended in ether until needed. Small aliquots were removed, filtered and dried, first by concentrated sulfuric acid for one day at room temperature to constant weight and then *in vacuo* over phosphorus pentoxide at 70°. Yields varied up to 10% of the weight of wood extracted. Except for their lower ash contents, 0.02 to 0.16%, the properties of the arabo-galactans from all three species of larch did not differ significantly from those reported earlier. Found $[\alpha]^{20}\text{D}$ in water, +11.2 to +15.4°; anhydro-arabinose, 13.1–14.3%; anhydro-galactose[4] 81.4–85.5%; degree of hydrolysis[4] 93.5–99.6%; samples, 0.5 g., had reducing values of 27.8 to 38.3 mg. of cuprous oxide. Thiobarbituric acid[8] was used as a precipitant for furfural and the anhydro-arabinose values are corrected by the factor $(0.9486)^{-1}$ for the presence of galactose. This factor was obtained by analyzing several appropriate known mixtures of the two sugars.

Preparation of Arabo-galactan Esters.—The uniform ether suspension containing a known weight of arabo-galactan (found from the dry weight of an aliquot) was centrifuged and ten times the weight of pyridine added to the residue, which was estimated to contain approximately 8% of water. After the expulsion of traces of ether by warming to 80°, the material remained in the pyridine in a highly peptized state. The appropriate acylating agent (acetic or propionic anhydride, or benzoyl chloride, 0.5–0.95 mole per mole of pyridine) was added dropwise at 80–85° during a period of four hours with constant stirring. After standing for twelve to fifteen hours, acetate and propionates were isolated by diluting the reaction mixtures with pyridine containing enough water to decompose the excess acylating agent and by pouring the diluted mixture into ten volumes of ice water. In the case of the benzoates, the excess reagent was eliminated as alcohol-soluble ethyl benzoate by using ethyl alcohol instead of water in the above decomposition and precipitation. The insoluble esters were isolated by standard methods and purified by pouring 10% solutions in chloroform into ten volumes of petroleum ether. It was noted that incompletely esterified products were obtained when less than one-half mole of acylating agent per mole of pyridine was used. The latter was always in excess to avoid hydrolysis of the polysaccharide.

Properties of the Esters.—The esters in the crude form were obtained as nearly colorless amorphous powders.

When purified by reprecipitation of 10% chloroform solutions of the derivative into ten volumes of petroleum ether, white granular products were obtained which possessed similar solubility properties. All were soluble in chloroform, acetone, dioxane, nitrobenzene, ethyl benzoate, and *m*-cresol; sparingly soluble in ethanol, butyl cellosolve, and water; and insoluble in ethyl ether and petroleum ether.

The physical properties and analytical data of the esters are summarized in Table I.

Deacylation of the Esters.—While there are no direct criticisms which would preclude the application of the general methods of saponification in alcoholic base, a modification was developed for the arabo-galactan esters which depended on solution of a sample in dioxane followed by addition of alcoholic alkali to yield, at first, a clear solution from which the polysaccharide shortly settled out. In this way a homogeneous deacylation was accomplished which could not well be effected in alcohol in which the esters are insoluble.

The procedure consisted in dissolving two grams of the acetate or propionate in 50 cc. of dioxane and 70 cc. of ethanol or 3 g. of the benzoate in 100 cc. of dioxane and adding 125 cc. of 0.4 *N* ethanolic potassium hydroxide. Standing at 22°, the clear solution became turbid shortly after the alkali addition (seventeen seconds sharply, in the case of the propionate). In fifteen minutes, the regenerated polysaccharide settled out and a test of the supernatant liquor showed it to be devoid of unsaponified ester. After thirty minutes, the mixture was centrifuged and the precipitate washed successively with 1% ethanolic acetic acid, ethanol, and then ethyl ether which was finally removed by warming at 35°. The conversion was quantitative.

Fractionation of the Propionyl and Benzoyl Derivatives.—Since neither of the esters exhibited crystalline tend-

---

(8) Dox and Plaisance, THIS JOURNAL, **38**, 2156 (1916); *cf.* Wise and Peterson, ref. 3.

(9) Barnett, *J. Soc. Chem. Ind.*, **40**, 9T (1921).

(10) Staudinger "Die hochmolekularen organischen Verbindungen, Kautschuk, und Cellulose," J. Springer, Berlin, 1932.

TABLE II

FRACTIONATION OF ARABO-GALACTAN PROPIONATE OF WESTERN LARCH

					In *m*-cresol		Saponified material in aqueous solution	
Petroleum ether added, cc.	Yield, g.	Fraction	Propionyl content, %	Araban content, %	Sp. rotn.	Sp. viscosity, $N_{sp.}/c$	Reducing value, mg. Cu_2O/$^1/_2$ g. sample	Sp. rotn.
969	2.89	A	50.93	5.61	−42.46	3.09	...	...
81	7.03	B	51.56	5.76	−40.81	2.57	30.1	13.50
144	8.94	C	51.46	6.36	−37.12	2.35	33.3	14.14
208	6.36	D	51.44	7.32	−30.35	2.26	37.6	15.00
Excess	4.94	E	51.45	9.66	−23.38	2.12	48.6	18.18
Residues	0.52	Non-fract. sample	51.54	6.71	−33.67	2.42	36.5	...
Total yield		30.68	Recovery = 30.68/31.46 = 97.5%					
Initial wt.		31.46						

encies, the sharp separation generally characteristic of crystalline substances when fractionally crystallized could not be expected. Further, advantage could be taken of no great differences in solubilities of the various polysaccharide combinations which conceivably might make up the arabo-galactan ester, due to the similarity in properties of such closely related bodies. It is evident that while partial precipitation might be resorted to, caution must be exercised in using any method involving the addition, to a solution of the ester, of a liquid in which the ester is insoluble. If such an addition caused an immediate precipitation, it might be due to local concentration of the precipitant in the region of the solution with which it first came into contact. In that region, complete precipitation of the solution rather than fractional separation would result.

Method of Fractionation.—A quantity of arabo-galactan propionate was dissolved in chloroform in the proportion of one gram of the ester to 10 cc. of the solvent. Petroleum ether (b. p. 35–60°) was then added in sufficient quantity barely to produce turbidity at 35°. The solution was warmed until a clear homogeneous solution resulted which on cooling slowly to room temperature became cloudy. On further slow cooling to 0° the turbidity became progressively greater until finally, after standing at 0° overnight, a gum settled out, leaving the supernatant liquid perfectly clear. While the fractionation probably did not simulate precipitation by crystalline nucleation, a separation of the least soluble constituent must have been effected uniformly throughout the solution. Following decantation of the mother liquor, the gum which conveniently adhered to the bottom of the flask was dissolved to a thin solution in chloroform and poured into ten volumes of petroleum ether. The precipitate was filtered off, washed with fresh petroleum ether, and placed in a vacuum desiccator to remove the ether. The powder was left in the open air for a day to allow the strongly adsorbed chloroform to vaporize and then dried to constant weight in the oven at 105° (two to three hours).

Starting with the mother liquor from the first precipitation the process was repeated to obtain a second fraction. In the same manner several fractions were progressively collected and designated as A, B, C, etc., in the order of their precipitation. In some cases a number of successive small gum deposits were dissolved together in chloroform and recovered as one fraction. When, after several precipitations, the amount of ester left in the mother liquor was equivalent to a workable fraction, it was recovered by pouring the solution into an excess of petroleum ether and collecting the precipitate in the usual fashion. In this way, the propionate of arabo-galactan from Western larch, for example, was resolved into five fractions as shown in Table II.

The analytical data on the several fractions are also tabulated along with the data on a sample of the original non-fractionated ester. The residues noted in the tables represent the combined rinsings of equipment used. These are added along with the weights of the fractions to determine the total yield of precipitates from which the recovery is computed. The data of Table II are representative also of the fractionation of the arabo-galactan propionates from Eastern and European larches.

The arabo-galactan benzoate was found to be less soluble in warm than in cold mixtures of chloroform and petroleum ether. So, following each addition of ether, the resulting suspension was shaken several times while kept at 0°, then allowed to settle at room temperature and the gum taken off in the usual manner. Further, to ensure good fractional separation, each fraction was made up of several successive small amounts of gum precipitated separately by small additions of the ether. In Table III are compiled the fractionation and analytical data pertaining to the benzoyl derivative of arabo-galactan from Western larch. That from Eastern larch showed similar results.

With reference to the data shown in the tables, it is to be noted that while the acyl values of the fractions remain practically constant, their araban contents increase with the order of their isolation. Since acylation in pyridine is recognized as a mild treatment and since the reducing values of the regenerated arabo-galactans are nearly the same as those determined prior to acylation, it is evident from the foregoing that arabo-galactan is not a distinct chemical entity but may be comprised of two or more molecular species. The progressive change in physical properties of the fractions with the order of their isolation is indicative of the resolution of a mixture. The variation in viscosities is interpreted to signify differences in average molecular weights. The reducing values found are also consistent with this view.

Fractionation of the Acetyl Derivative.—A method somewhat similar to that described by Hirst, Plant and Wilkinson[11] was followed in fractionating the acetate. A mixture

---

(11) Hirst, Plant and Wilkinson, *J. Chem. Soc.*, 2375–2383 (1932).

TABLE III

FRACTIONATION OF ARABO-GALACTAN BENZOATE FROM WESTERN LARCH

					In *m*-cresol		Saponified material in aqueous solution	
Petroleum ether added, cc.	Yield, g.	Fraction	Benzoyl content, %	Araban content, %	Sp. rotn.	Sp. viscosity, $N_{sp.}/c$	Reducing value, mg. Cu_2O/ 1/2 g. sample	Sp. rotn.
1692	29.62	A	66.7	3.76	−40.60	4.02	29.8	17.05
105	32.70	B	66.8	3.97	−38.42	3.53	31.8	17.48
180	25.54	C	67.0	4.28	−37.79	3.45	36.7	17.79
300	21.51	D	67.8	4.72	−35.18	3.27	39.8	18.11
Excess	10.68	E	68.2	6.15	−20.09	3.18	57.5	19.70
		Non-fract. sample	67.5	4.34	−37.57	3.56	39.8	17.58
Total yield	120.05	Recovery = 120.05/122.04 = 98.37%						
Initial wt.	122.04							

of two solvents was employed, each of which possessed widely divergent solvent properties.

The procedure adopted is briefly described as follows: The purified acetate was treated with a solvent mixture composed of 21% (by vol.) dioxane and 79% butyl cellosolve. Of this mixture, 75 cc. was taken for each gram of acetate. Complete solution of the ester was effected by warming to about 55° on a water-bath, after which it was permitted to cool to 20° and allowed to stand for twenty-four hours at this temperature. Ordinarily, at the end of this period, a mixture of gum and granular particles formed on the bottom and sides of the flask. The mother liquor was separated by centrifuging, concentrated *in vacuo* at 80° to 10–15 cc. and the ester recovered by precipitation into petroleum ether. In this manner the first fraction was obtained.

Treatment of the residual gum with petroleum ether caused the material to harden, whereupon the supernatant liquor was decanted and the ester obtained as a dry granular powder. This residue was then subjected to further fractionation by repeating the procedure with a fresh mixture of dioxane–butyl cellosolve. Since the soluble fractions became progressively smaller on successive extractions using the above solvent mixture, it was necessary to increase the dioxane content of the mixture to 27% for the last three extractions. In some cases where the individual fractions were not of sufficient amount for complete analysis, two or more successive fractions were combined and homogenized by reprecipitation. In this way four successive main fractions were resolved and designated by the subscript letter "S" (see Table IV). Fractions designated by the subscript letter "R" represent aliquots segregated from the insoluble gums of the successive fraction steps prior to their further fractionation. These are indicated by D, E, F.

Table IV represents the fractionation and analytical data pertaining to the acetyl derivative of Western larch arabo-galactan. The extreme differences indicated in the table are significant of the resolution of a mixture.

Methylation of Arabo-galactan.—The methyl ether of arabo-galactan was prepared by a method involving simultaneous de-acetylation and methylation of the acetate similar to that employed by Haworth and others in the cases of cellulose and starch. This was carried out in the following manner.

A solution of 40 g. of the acetate in 300 cc. of boiling acetone was treated with 480 cc. of 30% sodium hydroxide and 160 cc. of methyl sulfate both added in small portions over a period of three hours while stirring vigorously. A slight alkalinity was maintained throughout the reaction. At the end, the acetone was distilled off and the temperature raised to 100° for one hour to destroy excess methyl sulfate and the solution neutralized with 10% sulfuric acid. The solution was evaporated under reduced pressure and the residuum extracted with chloroform. The extract was dried over calcium chloride and then evaporated to dryness. The yellow glassy solid so obtained was subjected to further methylation under similar conditions except that the amounts of reagents were reduced in proportion to the amount of product re-treated.

The progress of methylation was followed by the Zeisel method for determining methoxy content. For this

TABLE IV

FRACTIONATION OF ARABO-GALACTAN ACETATE FROM WESTERN LARCH

				In *m*-cresol		Saponified material in aqueous solution	
Yield, g.	Fraction	Acetyl content, %	Araban content, %	Sp. rotn.	Sp. viscosity, $N_{sp.}/c$	Reducing value, mg. Cu_2O/ 1/2 g. sample	Sp. rotn.
10.219	A_S	43.52	7.74	−24.80	2.05	36.00	15.55
10.283	$(BCD)_S$	43.77	6.45	−31.36	2.38	30.20	14.59
9.088	E_S	43.37	5.97	−36.71	2.56	25.40	13.63
5.373	$(FG)_S$	43.35	6.38	−32.43	2.54	23.32	Dark
8.885	D_R	43.62	5.58	−35.63	2.93	21.20	Dark
8.163	E_R	43.15	5.25	−37.42	2.92	21.35	Dark
9.134	G_R	42.99	5.50	−35.10	3.36	18.85	Dark
	Non-fractionated	43.74	6.45	−35.10	2.63	25.57	14.16
Total	61.145	Recovery = 61.145/66.091 = 92.5%					

analysis the crude product was purified by dissolving 2 g. in 25 cc. of chloroform, decolorizing the solution with charcoal and reprecipitating the derivative in petroleum ether. The yellow flocculent precipitate was washed with petroleum ether, filtered and dried at 100°.

The methoxy content found was as follows. At the end of four methylations 22.8%; after eight 36.8%; after twelve 41.9%; after fourteen 44.15%; after fifteen 44.1%. Since the calculated value for a fully methylated polysaccharide of formula $[(C_6H_7O_2(OCH_3)_3)_6C_5H_6O_2(OCH_3)_2]_n$ is 44.8%, it was assumed that substitution was complete after fourteen such treatments as described above. Constancy of the methoxy value beyond this point served as further substantiation.

Completely methylated arabo-galactan is a very faintly cream-colored, amorphous solid, soluble in chloroform and acetone, slightly soluble in alcohol and water, and insoluble in petroleum ether and ethyl ether. It softens at 124° and melts at 143°; $[\alpha]^{20}D$ in chloroform, −42.03°.

Summary

1. Arabo-galactans separately isolated from woods of Eastern, Western and European larches gave similar analyses for ash, reducing value, optical activity, anhydro-arabinose and anhydrogalactose. This similarity does not necessarily establish their chemical identity.

2. Acetyl, propionyl and benzoyl esters were made with conditions chosen to avoid degradation and to render esterification complete. On systematic fractionation from various solvent mixtures each gave fractions of similar acyl content but of variable optical activity, reducing value, specific viscosity and araban content. It was concluded that these derivatives were non-homogeneous and that in all probability the original arabo-galactans were mixtures also.

3. A fully methylated arabo-galactan from Western larch was prepared and described.

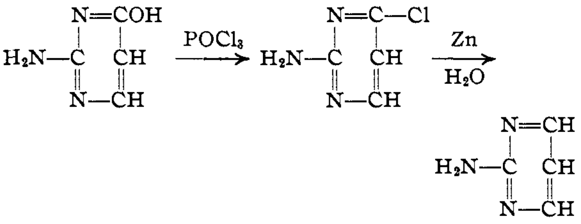
MIDLAND, MICHIGAN RECEIVED JANUARY 20, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF TEMPLE UNIVERSITY]

A New Synthesis of Isocytosine

BY WILLIAM T. CALDWELL AND HARRY B. KIME

Consideration of certain similarities of pyridine and pyrimidine led us to begin the preparation of sulfanilamido derivatives of 2- and of 6-aminopyrimidine. However, the preparation and chemotherapeutic activity of 2-sulfanilamidopyrimidine and 4-sulfanilamidopyrimidine (6-sulfanilamidopyrimidine) having been recently described,[1] we shall report here only a preparation of isocytosine effected by reaction of guanidine hydrochloride and malic acid under conditions essentially like those used by Davidson and Baudisch[2] in preparing uracil. This new synthesis is of interest in that 2-aminopyrimidine may be prepared from isocytosine by the following two steps



Better yields of isocytosine were obtained from guanidine hydrochloride than from the carbonate.

Experimental

Guanidine hydrochloride (24 g.) was gradually added to 100 cc. of well-stirred 15% fuming sulfuric acid, the temperature being maintained below 5°. Then 24 g. of finely pulverized malic acid was added at once and the mixture heated on the steam-bath with vigorous stirring until the evolution of carbon monoxide had ceased and then for an additional half-hour. The mixture was cooled to room temperature and poured upon 300 g. of ice. A paste of barium carbonate was added in slight excess, the mixture stirred for several hours and then allowed to stand overnight. After heating the material to 50°, the barium sulfate and excess barium carbonate were removed by filtration. The filtrate was evaporated until crystallization began, cooled, and the isocytosine collected by filtration. The product was recrystallized from hot water, from which the isocytosine was obtained as white prisms; yield, 6.4 g., m. p. 276°.

Anal. Calcd. for $C_4H_5ON_3$: C, 43.22; H, 4.54. Found: C, 43.23; H, 4.70.

Conversion into 2-amino-6-chloropyrimidine with phosphorus oxychloride gave a product melting at 168–169° and at the same temperature when mixed with an authentic sample of this compound prepared by an independent method.

Summary

A new and convenient synthesis of isocytosine is described.

PHILADELPHIA, PA. RECEIVED JUNE 17, 1940

---

[1] Roblin, Williams, Winnek and English, THIS JOURNAL, **62**, 2002 (1940).

[2] Davidson and Baudisch, *ibid.*, **48**, 2382 (1926).