- (9) Euler, Eriksson, and Brunius, Svensk. Kem. Tid., 40, 163 (1928).
- (10) Evans, Beuhler, Looker, Crawford, and Holl, J. Am. Chem. Soc., 47, 3085 (1925).
- (11) Evans, Edgar, and Hoff, Ibid., 48, 2665 (1926).
- (12) Evans and Hutchman, Ibid., 50, 1496 (1928); Evans, Chem. Rev., 6, 281 (1929).
- (13) Fager and Reynolds, IND. ENG. CHEM., 21, 357 (1929).
- (14) Fischler, Taufel, and Souci, Biochem. Z., 208, 191 (1929).
- (15) Glattfeld, Am. Chem. J., 50, 135 (1913).
- (16) Harden and Henley, Biochem. J., 16, 143 (1922).
  (17) Malaguti, Ann. chim. phys., [2] 59, 407 (1835).
- (18) Mathews, J. Biol. Chem., 6, 3 (1909).
- (19) Narian, Agr. J. India, 13, Science Congress Number, 47 (1918).

- (20) Nef, Ann., 367, 214 (1907); 376, 1 (1910); 403, 204 (1914).
- (21) Nelson and Browne, J. Am. Chem. Soc., 51, 830 (1929). (22) Nicloux, Bull. soc. chim. biol., 10, 1135 (1928); Compt. rend., 186, 1218 (1928).
- (23) Ort and Collman, J. Am. Chem. Soc., 49, 805 (1927).
- (24) Paine and Balch, Planter Sugar Mfr., 78, 127, 148 (1927); Sugar, 29, 206, 311, 416, 466 (1927).
- (25) Power and Upson, J. Am. Chem. Soc., 48, 195 (1926).
- (26) Spoehr, Ibid., 46, 1494 (1924).
- (27) Spoehr and Smith, Ibid., 48, 107, 236 (1926).
- (28) Walton, McCalip, and Hornberger, IND. ENG. CHEM., 17, 51 (1925).
- (29) Wurmser and Geloso, Compt. rend., 188, 1186 (1929).
- (30) Zerban, J. IND. ENG. CHEM., 11, 1034 (1919).

# The Chemistry of Wood II-Water-Soluble Polysaccharide of Western Larch Wood<sup>1</sup>

## Louis Elsberg Wise and Floyd C. Peterson

NEW YORK STATE COLLEGE OF FORESTRY, SYRACUSE UNIVERSITY, SYRACUSE, N. Y.

N 1916 Schorger and Smith (3) reported the presence of a water-soluble polysaccharide in western larch (Larix occidentalis, Nuttall). This interesting substance, on hydrolysis, gave extraordinarily high yields of galactose, and Schorger and Smith ventured the opinion that this was the only sugar formed.

The water-soluble substance, which was termed " $\epsilon$ galactan" by its discoverers, when distilled with 12 per cent hydrochloric acid, yielded about 6.2 per cent furfural,

while pure galactose under similar conditions gave rise to only 0.55 per cent of an aldehyde calculated as furfural. In explanation of this phenomenon, Schorger and Smith make the following comment: "It is believed that the formation of furfural is due to the peculiar structure of the galactan molecule, and not to the presence of a pentosan residue."

In a preliminary investigation on  $\epsilon$ -galactan, the present writers were able, not only to check Schörger and Smith's furfural yields in the case of the original polysaccharide, but to obtain practically the same furfural yields after the complete hydrolysis of the galactan. Theoretically such a hydrolysate, if it contained galactose as the sole sugar, should yield only negligible amounts of aldehyde when distilled with 12 per cent hydrochloric acid. This intriguing discrepancy caused the writers to repeat and to extend Schorger and Smith's work on  $\epsilon$ -galactan. The results virtually substantiated those of the previous investigators, with one important exception. Arabinose was definitely shown to be one of the products of the  $\epsilon$ -galactan hydrolysis and the percentage of arabinose (determined gravimetrically as the diphenylhydrazone) accounted quantitatively for the furfural yield obtained from the hydrolyzed galactan by two different methods.

A series of careful determinations of galactose and arabinose indicated the presence of 84 to 85 per cent anhydrogalactose

<sup>1</sup> Received January 20, 1930. Presented under the subtitle by L. E. Wise before the Division of Cellulose Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minn., September 9 to 13, 1929. The first article in this series, by Harlow and Wise, was published in IND. ENG. CHEM., 20, 720 (1928).

The water-soluble  $\epsilon$ -galactan of western larch, described by Schorger and Smith, yields 11.95 per cent arabinose and 84.6 per cent galactose on complete hydrolysis and appears to be an arabogalactan. Over 70 per cent of the galactose present, as indicated by analysis, could actually be separated in crystalline form. The arabinose was identified through its benzylphenylhydrazone and the diphenylhydrazone.

Van der Haar's modification of Tollen's mucic acid method gives a fair approximation of the galactose content in  $\epsilon$ -galactan hydrolysis mixtures. A modification of the Neuberg-Wohlgemuth method for arabinose furnishes a convenient proximate means of estimating this sugar. The excellent thiobarbituric acid method for furfural devised by Dox and Plaisance is admirably suited to the accurate determination of arabinose in the presence of galactose.

totally different samples of western larch, it is possible that the water-soluble carbohydrate is a definite chemical individual-i.e., a true arabogalactan (with a minimum molecular weight of 1104). As at this time we have no criteria of purity or homogeneity, this possibility is presented with reservations. In any event the water-soluble polysaccharide on hydrolysis yields very nearly one molecule of arabinose for every six molecules of galactose.

#### Extraction and Isolation of $\epsilon$ -Galactan<sup>2</sup>

The method used was essentially that of Schorger and Smith, with a few useful modifications. Air-dried shavings of western larch (400 to 500 grams) were placed in a linen cloth and fitted into a Büchner funnel 23 cm. in diameter, which was connected by a rubber stopper with a 5-liter roundbottom Pyrex flask. A large evaporating dish acted as cover for the funnel, and in this dish was placed another 5-liter round-bottom flask, fitted with a two-hole stopper carrying an inlet and an outlet tube for water. This second flask acted as condenser during the extraction. The lower flask was half filled with water, which was kept boiling gently. A continuous extraction was thus maintained until no further hotwater-soluble material was obtained. The extraction was usually complete at the end of 40 hours.

From this point on the directions of Schorger and Smith were closely followed, except that potassium instead of sodium carbonate was used in the neutralization, after which the

<sup>2</sup> Thanks are due to E. Wennberg for isolating and purifying over 100 grams of the polysaccharide.

and 11.95 per cent anhydroarabinose in the original polysaccharide. Rhamnose, fucose, xylose, and uronic acids were apparently not among the hydrolysis products of  $\epsilon$ -galactan, and from the analytical data, which accounted for over 96 per cent of the products of hydrolysis, it is very doubtful whether any other hexoses were present.

Since the same analytical data were obtained from  $\epsilon$ galactan isolated from two solution was rendered faintly acid with acetic acid and heated with a small amount of norite, from which it was filtered by suction and concentrated *in vacuo*. Under these conditions the final precipitate, obtained by gradually pouring the thin sirup (barely acid with acetic acid) into a large excess of 95 per cent alcohol, always separated readily, without forming a colloidal solution. The galactan was usually colorless, but in the few instances in which it showed color the material was redissolved in the minimum amount of warm water, retreated with norite, filtered, acidified with acetic acid, and reprecipitated with alcohol.

The final precipitate was always washed by repeated careful decantation with 95 per cent ethyl alcohol until it was thoroughly dehydrated. Ether then replaced the alcohol and several ether washings were made. Finally the galactan was collected on a Büchner funnel by the use of suction. The polysaccharide was dried *in vacuo* at 30° C. over sulfuric acid. In this way a colorless powder was obtained, the ash content of which varied between 0.32 and 0.56 per cent, and which always had a slight but definite reducing value. The yields usually approached 9 to 10 per cent of the weight of air-dried wood.

Note—Cuprous oxide obtained by Allihn's method from various 0.500gram samples of e-galactan: 0.0358, 0.0347, 0.0362, and 0.0370 gram. A 0.500-gram sample, which was redissolved in water, filtered, and reprecipitated, with alcohol, yielded 0.0361 gram Cu<sub>2</sub>O. Further resolution and reprecipitation, after treatment with Filtchar, gave 0.0342 gram Cu<sub>2</sub>O per 0.500 gram galactan. Another sample, twice precipitated from water with glacial acetic acid, yielded 0.0679 gram Cu<sub>2</sub>O per 1.000 gram. These values all agree closely with those of Schorger and Smith, who found that 2.500 grams galactan yielded 0.1554 gram Cu ( $\approx$  0.1750 gram Cu<sub>2</sub>O) by Allihn's method.

#### Hydrolysis of $\epsilon$ -Galactan

The oven-dried  $\epsilon$ -galactan was dissolved in 2 per cent sulfuric acid in the proportion of 1 gram of polysaccharide to 50 cc. of acid. The solution was heated in a paraffin bath, kept at 105–110° C., for 7 hours. Higher temperatures yielded discolored hydrolyzates. After completion of the hydrolysis, the solution was cooled to room temperature and nearly neutralized with hot saturated aqueous barium hydroxide, added very slowly to avoid local overheating. Prior to its addition, the volume required for complete neutralization was roughly determined by titer against 2 per cent sulfuric acid using hot barium hydroxide solution. The neutralization of the hydrolyzate was completed with carefully purified barium carbonate.

The neutralized solution was heated to  $80^{\circ}$  C. and allowed to stand overnight. Subsequently the solution was diluted to a convenient, definite volume with water and filtered. The filtrate, which was nearly colorless, always showed a pH of approximately 7.5. Measured aliquot portions of this filtrate were quantitatively concentrated *in vacuo*, for use in subsequent analyses. In several instances the solution was rendered very faintly acid with acetic acid prior to distillation.

In preparing solutions for galactose determinations, the optimum concentration was reached when each 30 cc. of solution contained the hydrolysis products corresponding to 0.600-0.900 gram of the original galactan. In the arabinose determinations the concentration was carried further, so that each 5 cc. corresponded to about 0.600 gram of the original  $\epsilon$ -galactan.

The reducing value of each solution after hydrolysis was determined (as  $Cu_2O$ ) by Allihn's method. Twelve such determinations were made, and the mean value, when arbitrarily calculated to galactose by using Browne's factor 0.898 (1), indicated a hydrolysis of 98.9 per cent. This figure checks that of Schorger and Smith, who report that 99.06 per cent of the theoretical amount of galactose was indicated by the reducing value. Later experiments showed that the hydrolytic products included about 12 per cent arabinose, and

the above figures are therefore too high. Recalculating the results on the assumption that the ash-free polysaccharide contained 88 per cent anhydrogalactose and 12 per cent anhydroarabinose, we find a mean hydrolysis figure which approaches 97.4 per cent of the theoretical.

Note-The following is a calculation based on an actual, typical analysis: 0.1000 gram e-galactan yielded 0.2174 Cu2O. Assuming that the original galactan contained 88 per cent anhydrogalactose and 12 per cent anhydroarabinose, the hydrolyzate would contain 0.09789 gram galactose and 0.01363 gram arabinose, which is equivalent to 0.0878 gram glucose (calcd. from galactose) and 0.01406 gram glucose (calcd. from arabinose), The corresponding Cu<sub>2</sub>O values are 0.1934 and 0.0293 gram, or a total of 0.2227 gram of Cu<sub>2</sub>O. This is the calculated theoretical value. The value actually found is 97.6 per cent of this figure. While the accuracy of this method of calculation is open to serious question, especially when we consider that the original e-galactan has a definite reducing action on Fehling's solution, and that a mixture of two sugars is involved, the results are presumably more accurate than those which assume complete conversion to galactose. In any case it appears that the hydrolysis approaches completion in about 7 hours.

## **Isolation and Identification of Galactose**

A typical hydrolyzate, obtained from 9.77 grams of  $\epsilon$ -galactan, was evaporated *in vacuo* to a thin sirup, treated with ethanol to precipitate a small amount of gum, and filtered. The filtrate was evaporated somewhat further, treated with a large volume of methanol containing 1 to 2 cc. of glacial acetic acid, and inoculated with a crystal of galactose. After standing in an ice chest for several days, the galactose crystals were gathered and filtered, and the filtrate was again concentrated in vacuo and treated as before. This technic was repeated until the mother liquors from previous crystallizations yielded no further crops. The total yield of crude (crystalline) galactose was 6.97 grams. Schorger and Smith obtained 37 grams of crystalline galactose from 57 grams of  $\epsilon$ -galactan. The sugar, which has already been fully identified by Schorger and Smith, yielded a crystalline p-tolylhydrazone, m. p. 167-8° C.; pure galactose p-tolylhydrazone (prepared from Pfanstiehl galactose), m. p. 166.5-167° C. The mixture melted at 167–8° C.

#### **Identification of Arabinose**

The mother liquors from the final crop of galactose crystals were treated with 25 cc. of water, evaporated under diminished pressure to remove the methanol, filtered, and divided into three parts.

(1) An aliquot portion yielded appreciable amounts of furfural, when distilled with 12 per cent hydrochloric acid, as shown by the formation of the insoluble, yellow furfuralmalonylthiourea when thiobarbituric acid in hydrochloric acid was added to the distillate (2). The absence of very appreciable amounts of methylfurfural was indicated by the percentage of nitrogen in the precipitate: found, 12.45 per cent nitrogen; calculated for  $C_9H_6O_3N_2S$ , 12.61 per cent nitrogen. Presumably rhamnose and fucose are not present in any quantity among the hydrolysis products.

(2) Another portion yielded a silky, crystalline, benzylphenylhydrazone, m. p. 174-5° C.; arabinose benzylphenyhydrazone (prepared from purified arabinose), m. p. 173-5° C. (Van der Haar (5, p. 227) gives 174° C.) The mixture melted at 174-5° C.

(3) A third portion yielded an insoluble diphenylhydrazone, which on repeated recrystallization from 75 per cent alcohol formed prismatic needles, m. p. 197° C. (uncor.); arabinose diphenylhydrazone (from Pfanstiehl arabinose), similarly crystallized, m. p. 197–197.5° C. The mixture melted at 197° C.

Note—The true melting point of arabinose diphenylhydrazone is apparently in doubt. Van der Haar (5, p. 178) gives as the melting points found,  $197^{\circ}$ ,  $197^{\circ}$ ,  $199^{\circ}$ , and  $204^{\circ}$  C., depending on conditions. We noted slight fluctuations in melting point when the rate of heating was varied. While we made no effort to determine the true, corrected melting point of the diphenylhydrazone, we standardized our procedure so that all melting points were taken under strictly comparable conditions.

## Test for Uronic Acids

One gram of  $\epsilon$ -galactan, when distilled with hydrochloric acid by Dore's<sup>3</sup> modification of the LeFevre method for uronic acids, showed a net gain in the carbon dioxide absorption tube of 0.0009 gram in 5 hours. Evidently uronic acids were absent.

## Quantitative Determination of Galactose

The writers' experiences confirm those of other investigators, who have pointed out the unreliability of the mucic acid method for galactose, in the presence of other sugars. Schorger and Smith's fluctuating results discouraged further attempts at direct oxidation of the untreated  $\epsilon$ -galactan. The present writers found, however, that the hydrolyzate (described under Hydrolysis of Galactan) could be subjected to mucic acid oxidation with fairly satisfactory results provided Van der Haar's modification of the Kent-Tollens-Creydt method (5, p. 124) was used and the following additional precautions were taken:

(1) The neutral, aliquot portion should contain the hydrolytic products corresponding to 0.6 to 0.9 gram of original polysaccharide in 30 cc. of solution.

saccharide in 30 cc. of solution. (2) If less than 0.9 gram of galactan was used, sufficient pure sucrose is added to bring the total, calculated sugar content to 1.000 gram.

to 1.000 gram. (3) The mixture is then very carefully evaporated in a beaker,  $6 \times 12$  cm., in a water bath, until the concentrated solution weighs  $20.0 \pm 0.1$  grams. Concentration below this point may lead to excessive oxidation.

(4) To the cooled, acid solution is added 0.480 to 0.500 gram (accurately weighed) of pure mucic acid.

(5) The mixture is allowed to stand in a bath maintained at  $15^{\circ} \pm 0.5^{\circ}$  C. for 48 hours or, preferably, for 42 hours at  $11-14^{\circ}$  C., and finally 6 hours at  $15^{\circ}$  C. This insures complete crystallization at a definite temperature.

(6) The mucic acid crystals are filtered off on a Gooch crucible, and washed with eight to ten 10-cc. portions of a saturated aqueous solution of mucic acid. The saturated solution should be allowed to stand for at least 48 hours at  $15^{\circ}$  C. and should be filtered just before using. The final washing is made with 5 cc. of water.

(7) The mucic acid is dried for several hours at  $100^{\circ}$  C. and weighed. Overnight drying should be avoided. The weight of the mucic acid originally added is subtracted from the final weight, and the corresponding weight of galactose found from Van der Haar's tables (5, p. 126). This is then calculated to anhydrogalactose as indicated in Table I, which includes all results obtained by this method. The mean of seven determinations was found to be 84.6 per cent of anhydrogalactose in the original ash-free  $\epsilon$ -galactan.

Table I—Per	centage	of A	nhydrogalacto	ose in Or	iginal	€-Galactan
Determined	by Van	der	Haar-Tollens	Method	after	Hydrolysis
	-		CORRESPONDING	3		

		WEIGHT OF C	ORRESPONDING	Anhydro-
ASH-FREE		GALACTOSE	WEIGHT OF	GALACTOSE
GALACTAN	MUCIC ACID	(VAN DER HAAR'S	ANHYDRO-	IN ORIGINAL
TAKEN	OBTAINED	TABLES)	GALACTOSE	e-Galactan
Gram	Gram	Gram	Gram	Per cent
0 9970	0 6651	0.8722	0.7850	78.7
0 8466	0.5886	0.7873	0.7086	83.7
0 8466	0.6018	0.8020	0.7218	85.2
0 8970	0.6392	0.8435	0.7592	84.7
0 8970	0.6481	0.8534	0.7681	85.7
0.8970	0.6692	0.8768	0.7891	87.9
0.6000	0.4222	0.5777	0.5199	86.6

#### **Furfural Determinations**

TOLLEN'S METHOD—The phloroglucinol method was applied both to the hydrolyzed and unhydrolyzed polysaccharide. The results (Table II) require no comment other than to explain a deduction of 0.47 per cent furfural, which corrects for the phloroglucinol precipitate obtained from the hydrochloric acid distillate from pure galactose.

Note---Vanselow and Wise (unpublished data) found that all commom hexoses and hexosans when distilled with hydrochloric acid yield small

\* Private communication from W. H. Dore, of the University of California, whose courtesy is gratefully acknowledged.

amounts of an aldehyde yielding a phloroglucinol precipitate. The volatile substance is probably hydroxymethylfurfural. In two instances, 2,000grams of pure galactose gave 0.0133 and 0.0127 gram of phloroglucide. This would correspond to an average of 0.0094 gram furfural, or 0.47 per cent. This is in fair agreement with the figure 0.55 per cent reported by Schorger and Smith. While it must be admitted that this method of computation is speculative, since we have no solubility data on the phloroglucide of hydroxymethylfurfural, the figure 0.47 has been used in correcting furfural values, whenever the phloroglucinol method has been employed. The results thus obtained compare favorably with those obtained by other methods.

Table II—Percentage of Furfural and Anhydroarabinose Obtained from e-Galactan by Phloroglucinol Method

e-Galactan	Phloro- Glucide	Furfural	Furfural, Minus 0.47% Correction	ANHYDRO- ARABINOSE IN ORIGINAL C-GALACTAN
Gram	Gram	Gram	Per cent	Per cent
	U	NHYDROLYZED		
0.5000	0.0582	0.0329	6.11	11.4
0.4475	0.0560 🙍	0.0318	6.64	12.4
1.0000	0.1180	0.0640	5.93	11.1
0.5000	0.0585	0.03315	6.16	11.5
	HYDROLYZ	ED PRIOR TO A	NALYSIS	
1.0000	0.1304	0.0704	6.57	12.3
0.6335	0.0757	0.0420	6.15	11.5

THIOBARBITURIC ACID METHOD OF DOX AND PLAISANCE-Here the conditions for the hydrochloric acid distillation were identical with those used in the usual phloroglucinol method. Thiobarbituric acid reagent, formed by dissolving 0.180 to 0.200 gram of pure thiobarbituric acid in 12 cc. of warm hydrochloric acid, diluting to 40 cc. with water, and filtering, was used as the precipitant, the flocculent yellow precipitate was allowed to stand overnight, and the supernatant liquid decanted through a Gooch crucible (with a rather light mat). The material was then gradually brought on the filter by means of 100 cc. of 12 per cent hydrochloric acid and washed with 400 cc. of water, care being taken never to allow the crucible to be sucked dry, so as to avoid exceedingly slow filtrations. The weight of the precipitate (furfural malonylthiourea), dried at 100° C., when multiplied by the factor 0.4324 gives the weight of furfural.

The results which can be obtained with known mixtures of galactose and arabinose are indicated in Table III. Evidently the presence of galactose has a negligible effect on the furfural determination.

Table III—Results Obtained by Thiobarbituric Acid Method for Furfural and Arabinose in Known Galactose-Arabinose Mixtures

			C	ORRESPONDIN	{G
				WEIGHT OF	
				ARABINOSE	
		FURFURAL	CORRESPOND-	RECOVERED	
GALACTOSE	ARABINOSE	MALONYL-	ING WEIGHT	(Kröber's	
TAKEN	TAKEN	THIOUREA	OF FURFURAL	TABLES)	RECOVERY
Gram	Gram	Gram	Gram	Gram	Per cent
0.0000	0.0982	0.1065	0.04605	0.0979	99.7
0,0000	0.0984	0 1062	0.04592	0.0976	99.2
0 6670	0.1000	0.1120	0.0484	0.1029	102.9
0 5670	0.1000	0.1092	0.0472	0.1003	100.3
0.5670	0.1000	0.1097	0.0474	0.1007	100.7

The results of thiobarbituric acid applied to hydrolyzed and unhydrolyzed  $\epsilon$ -galactan are given in Table IV.

Table IV-Percenta	ige of Furfura	l and Anhydro	arabino	se (Araban)
Obtained from	ϵ-Galactan by	<sup>•</sup> Thiobarbitur	ic Acid	Method

e-GALACTAN TAKEN FOR ANALYSIS	Furfural Malonyl- thiourea Found	Furfural Found	Corresponding Weight of Anhydro- arabinose	Anhydro- arabinose in Originai e-Galactan
Gram	Gram	Gram	Gram	Per cent
н	YDROLYZED WITH	2 PER CENT HY	DROCHLORIC ACID	
1.0000	0.1308	0.0566	0.1058	10.6
	HYDROLYZED WI	TH 2 PER CENT	SULFURIC ACID	
1 0000	0.1343	0.0581	0.1087	10.9
0 4256	0.0613	0.0265	0.0498	11.7
0 4256	0 0606	0.0262	0.0493	11.6
0 6080	0 0872	0.0377	0.0706	11.6
0 7000	0.0946	0.0409	0.0766	10.9
1 0000	0.1249	0.0540	0.1010	10.1
0 8494	0.1178	0.0509	0.0952	11.2
0 6267	0.0911	0.0394	0.0738	11.8
0.7862	0.1148	0.0496	0.0929	11.8
	ORIGINAL U	NHYDROLYZED	GALACTAN	
0 4980	0.0671	0.0293	0.0550	11.1
0 4983	0.0670	0.0290	0.0545	10.9

## Quantitative Determination of Arabinose as Diphenylhydrazone

The method used, after a large number of orientating experiments, was that of Neuberg and Wohlgemuth (4) slightly modified by using, in place of the free base, diphenylhydrazine hydrochloride.

Note—Diphenylhydrazine hydrochloride as obtained on the American market always contains large amounts of diphenylamine and colored impurities. The following scheme of purification was used: Five grams of the impure reagent were heated with 375 cc. of 2.5 per cent hydrochloric acid. After cooling for several hours, the solution was filtered, and to the filtrate were added 750 cc. of concentrated hydrochloric acid: The mixture was again cooled for 2 hours, and the soft needlelike crystals of the hydrochloride were filtered by suction through a Jena-glass crucible with sinteredglass filtering disk. Unless the crystals are nearly colorless, the entire operation must be repeated. The crystals are finally dried and freed from hydrochloric acid, by standing in a vacuum desiccator over fused potassium hydroxide.

In a preliminary experiment with known mixtures, 0.75 gram of diphenylhydrazine hydrochloride and 0.75 gram of crystallized sodium acetate were warmed with 5 ce. of 95 per cent ethanol. The solution was filtered from sodium chloride and washed with sufficient alcohol to bring the volume of filtrate to 5 cc. This filtrate was then added to 2.5 cc. of an aqueous solution containing 0.4204 gram of pure galactose and 0.0752 gram of pure arabinose. The alcoholic mixture was heated carefully until complete solution had been effected and then treated further with 10 cc. of a saturated 50 per cent alcoholic solution of arabinose diphenylhydrazone. The mixture was again warmed carefully so as to avoid loss of solvent and then allowed to stand overnight. The separated crystals of diphenylhydrazone were filtered off on a Gooch crucible and washed with eight 10-cc. portions of a 50 per cent alcoholic solution of arabinose diphenylhydrazone, which had been saturated at the temperature at which the filtration was carried out, and filtered just before using. The precipitate, after drying at 100° C. for 2 to 3 hours, was weighed. The weight  $\times 0.4747$  = weight of arabinose.

Weight of arabinose taken	0.0752 gram
Weight of arabinose recovered	0.0756 gram

In another experiment, in which no galactose had been added:

Weight of arabinose	taken	0.0690 gram
Weight of arabinose	recovered	0.0680 gram

Galactose alone yielded no precipitate under the conditions of the experiment. Practically the identical procedure was used in the case of the neutral hydrolyzates from  $\epsilon$ -galactan. It was generally expedient to use 5-cc. portions of the sugar mixtures corresponding to 0.6 to 0.7 gram of the original galactan (see section on Hydrolysis of Galactan) and to increase the arabinose content to about 0.150 gram by the addition of the pure sugar, the amount being gaged by making preliminary furfural determinations on aliquot portions of the same solution.

The reagent used for the precipitation of arabinose was

formed by suspending a mixture of 1.5 grams of diphenylhydrazine hydrochloride and 1.5 grams of sodium acetate in 10 cc. of hot ethanol, filtering, and washing the filter paper with sufficient alcohol to bring the volume of the filtrate to 10 cc. This reagent was then added to the 5 cc. of mixed sugar solution and the warm mixture was subsequently treated with 20 cc. of a saturated 50 per cent ethyl alcoholic solution of arabinose diphenylhydrazone. From this point on the operations were identical with those described above, except that the filtered diphenylhydrazone was washed with twelve 10-cc. portions of 50 per cent alcoholic solutions of diphenylhydrazone.

Table V gives the results of the arabinose determinations.

The mean anhydroarabinose content of  $\epsilon$ -galactan was 11.95 per cent. By the corrected phloroglucide method the calculated anhydroarabinose content was 11.7 per cent, and by the thiobarbituric acid method, 11.2 per cent.

Table	V-Percentage	Arabinose	Obtained	from	e-Galactan	by	the
	D	iphenylhyd	razone M	ethod			

			DIPHENYL-	DIPHENYL-		
			HYDRA-	HYDRAZONE		
			ZONE	CORRESPOND	-	
		TOTAL	CORRESPOND	- ING TO		ANHYDRO-
e-GALACTAN	Pure	ARABINOSI	E ING TO	ARABINOSE		ARABINOSE
TAKEN	Arabi-	DIPHENYL	- Added	Obtained	Arabi-	IN ORIGI-
FOR	NOSE	HYDRA-	Pure	FROM $\epsilon$ -	NOSE	NAL 6-
Analysis	Added	ZONE	ARABINOSE	GALACTAN	Found	GALACTAN
Gram	Gram	Gram	Gram	Gram	Gram	Per cent
0.6267	0.0706	0.3143	0.1487	0.1656	0.0786	11.0
0.6267	0.0718	0.3241	0.1512	0.1729	0.0821	11.5
0.6267	0.0757	0.3465	0.1595	0.1870	0.0888	12.5
0.6267	0.0755	0.3516	0.1590	0.1926	0.0914	12.8

These results are in fair agreement and indicate that arabinose is probably the only pentose sugar in the hydrolysis mixture.

#### Discussion

Analyses indicate that  $\epsilon$ -galactan on hydrolysis yields 84.6 per cent galactose and 11.95 per cent arabinose. If we adopt as a hypothesis that the polysaccharide is actually an arabogalactan with the condensed formula,  $[(C_5H_8O_4)-(C_6H_{10}O_5)_6]_n$ , hydrolysis should yield 88.1 per cent galactose and 11.9 per cent arabinose. These calculated figures agree fairly well with the analytical data. However, since the homogeneity of the polysaccharide has not been established, the above formulation is only tentative, and is made with due reservation.

The arabogalactan is now being subjected to fractionation, acetylation, acetolysis, and methylation, in the hope of gaining a deeper insight into its constitution. The work is also being extended to other species of larch wood.

#### Literature Cited

- (1) Browne, Handbook of Sugar Analysis, p. 421.
- (2) Dox and Plaisance, J. Am. Chem. Soc., 38, 2156 (1916).
- (3) Schorger and Smith, J. IND. ENG. CHEM., 8, 494 (1916).
- (4) Neuberg and Wohlgemuth, Z. physiol. Chem., 35, 31 (1902).
- (5) Van der Haar, "Nachweis zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren."

## French Potash Production Advances

The production of crude potash salts in the Mulhouse basin during 1929, amounting to 3,124,700 metric tons with a pure potash content of 493,000 tons, was nearly 20 per cent higher than in 1928, according to the Department of Commerce. Production figures follow:

YEAR	CRUDE SALTS	PURE POTASH
	Tons	Tons
1927	2,321,725	372,260
1928	2,618,500	410,635
1929	3,124,700	493,000

The development of the plants for refining the crude salts

has grown with the increase in potash production. This is especially true in the case of chloride production:

YEAR	Chloride 30 to 40 Per Cent K2O	Chloride 50 to 60 Per Cent K2O
	Tons	Tons
1927	60,000	296.000
1928	183,450	333,300
1929	227,250	408,600

The production of high-grade chloride, 50 to 60 per cent  $K_2O$  during December, 1929, reached the record figure of 38,900 metric tons.