demonstrate very plainly the changes which go on in nature, under a certain environment, in particular types of petroleum. The environment is a governing condition. Under a different one true asphalt would be formed, such as is widely distributed in nature. The question arises as to what these conditions are, especially in view of the fact that both forms of solid bitumen must be looked upon as originating in petroleum and are sharply differentiated from each other. The asphalts consist, to a very considerable extent,

Source	Flow ° F.	Specific Gravity	Per cent Soluble in Naphtha	Per cent Residual Coke
RESIDUAL:				
Texas Residual Petroleum		0.9524	88.0	6.5
GILSONITES:				
1 Utah (softest)	285	1.011	55.5	10.0
2 Utah		1.037	46.9	12.3
3 Utah	260		47.2	12.8
4 Utah	345	1.037	46.1	13.9
5 Utah (hardest)	Intumesces	1.057	24.5	16.7
GRAHAMITES:				
Cuba, Bahia	Intumesces	1.157	38.8	40.0
Trinidad	Intumesces	1.156	14.8	40.0
West Va	Intumesces	1.130	9.4	36.8
Colorado	Intumesces	1.160	0.8	47.4
Oklahoma	Intumesces	1.184	0.4	51.4

of hydrocarbons not acted upon by sulfuric acid; *i. e.*, of saturated hydrocarbons. Gilsonite, on the other hand, contains but a very small amount of such components. They may both have a common origin in petroleum but the environment to which this has been subjected has been so dissimilar in each case as to result in quite a different product. In the case of the gilsonite, the bitumen in which it has originated has been confined in relatively narrow veins. In that of the asphalts it has been spread out horizontally and subjected to quite different conditions, with a resulting product of entirely different character, the one consisting of more than 20 per cent of saturated hydrocarbons and the gilsonites and grahamites containing but a relatively small amount, as appears from the following data:

	Specific Gravity	Per cent Soluble in Naphtha	Per cent Saturated Hydrocarbons
Petroleum Flux (Texas)	0.956	97.5	72.8
Residual Pitch	1.089	65.0	33.1
Bermudez Asphalt	1.082	62.2	24.4
Gilsonite (Utah)	1.044	47.7	5.5
Grahamite (Okla.)	1.171	0.4	0.3

These differences in character may be accounted for by the fact that gilsonite and grahamite originate in veins which are vertical or nearly so while the asphalts occur under entirely different conditions.

A material intermediate between an asphalt and gilsonite is found in shales of Tertiary age in the Central Valley of California at Asphalto, in vertical fissures, which confirms the idea that the character of a solid bitumen originating in petroleum is dependent on the environment to which it is exposed.

It is of interest to observe that the veins of gilsonite and grahamite end rather abruptly at certain depths and do not thin out gradually, and also that the material near the vein walls and also the surface consists of a harder form of bitumen than the mass of the deposit.

Grahamite is the result of metamorphic changes in gilsonite and gilsonite of similar changes in petroleum brought about by its environment. That they are of considerable geological age as to origin can be seen from the fact that in one instance in the strata in which gilsonite occurs there is a fault extending a quarter of a mile without any disturbance of the enclosed bitumen, showing that the gilsonite must have been introduced into the vein before the displacement.

WOOLWORTH BUILDING
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THE GALACTAN OF LARIX OCCIDENTALIS

By A. W. SCHORGER AND D. F. SMITH

Received March 1, 1916

The western larch (*Larix occidentalis*, Nuttall) is found in extensive stand in the Pacific Northwest. It is a magnificent tree sometimes reaching a height of 200 feet and a diameter of 5 to 8 ft. In the course of some experiments it was found that a considerable portion of the wood was soluble in water. Further investigations led to the interesting discovery that the soluble matter consisted almost entirely of a galactan $(C_6H_{10}O_5)_n$ (specific rotation $[\alpha]_D^{20°} + 12.11°$) yielding only galactose on hydrolysis. The water-soluble content of the wood varied from 8 to 17 per cent in the individual trees examined.

A large number of galactans have been found in nature but only a few have been well characterized. Many of the galactans yield other sugars than galactose on hydrolysis so that the terms galacto-mannan, galacto-araban, etc., are applied, depending upon the sugars obtained. The galactan from western larch has been called ϵ-galactan. The δ-galactan isolated by Müntz[1] from the seeds of lucerne, by Maxwell[2] from beans, and by Lindet[3] from barley has the rotative $a_j + 84.6°$ and is precipitated from aqueous solution with lead acetate: ϵ-galactan has the rotation $[\alpha]_D^{20°} + 12.11°$ and it is not precipitated from aqueous solution with lead acetate.

The β-galactan of Winter[4] and Prinsen-Geerligs[5] has a yellow color and when dried is insoluble in water: ϵ-galactan is white and is readily soluble in water after drying.

The γ-galactan of Lippman[6] and others is *originally* insoluble in cold water and is precipitated from concentrated solutions by lead acetate: γ-galactan differs also from ϵ-galactan in having a very high rotation, $[\alpha]_D = +238°$. The δ-galactan of Payen[7] and Bauer[8] obtained from agar-agar and other sources is insoluble in cold water and when dissolved in 500 parts of boiling water a gelatinous mass is formed on cooling: ϵ-galactan shows no inclination to gelatinize.

The unusual occurrence of ϵ-galactan was of such interest as to warrant a careful examination of the literature with respect to the occurrence in woods of carbohydrates yielding galactose. It was found that Trimble[9] had examined an *excrescence* of *Larix occidentalis* that contained 19.4 per cent of reducing sugar and

[1] *Compt. rend.*, **94**, 453.
[2] *Am. Chem. J.*, **12**, 26.
[3] *Bull. de l'assoc. Chem.*, **20**, 1223.
[4] *Deut. Zuckerind.*, **15**, 538.
[5] *Chem.-Ztg.*, **21**, Rep. 150.
[6] *Ber.*, **20** (1887), 1001; *Z. Ver. Zuckerind.*, **36**, 259; **37**, 468; **38**, 1252.
[7] *Compt. rend.*, **49**, 521.
[8] *Jour. prakt. Chem.*, **30**, II, 283.
[9] *Am. J. Pharm.*, **70** (1898), 152.

68.7 per cent of non-reducing sugar. The reducing sugar was stated to resemble dextrose but none of the carbohydrates were actually identified. In the specimens of wood examined no indication of exudations was observed. We have found that galactan itself has a slight reducing action on Fehling's solution. In the purification of the galactan all the alcoholic solutions were saved and examined for the occurrence of free sugar. The concentrated extract deposited a small amount of impure crystals having a sweetish taste. The phenylosazone was prepared but the amount was too small to be sufficiently freed from impurities to give a melting point of value. Apparently the only authentic occurrence of galactose in nature is that found by Lippman.[1] Ivy berries after a frost were found to have a crystalline efflorescence of galactose. It is possible that the free sugar in the larch is galactose that has been formed in a similar manner.

Galactans have been indirectly found in small amounts in wood by oxidation to mucic acid, but in no case apparently has the source of the mucic acid been actually isolated or determined. Tollens,[2] Krause[3] and recently Hägglund[4] have detected galactose in sulfite liquor. The galactose found by Hägglund amounted to only 0.27 per cent of the weight of the wood of *Pinus sylvestris*. Klason[5] also obtained traces of mucic acid from *P. sylvestris* and Fromherz[6] from the lignocellulose of the aspen (*Populus tremula*).

We have found galactans to be characteristic of the coniferae, using the mucic acid method of identification.

EXPERIMENTAL

ISOLATION OF ϵ-GALACTAN—The following method of isolation was adopted, after considerable experimentation:

Approximately 500 g. of sawdust are placed in a flask with 2 liters of water and allowed to digest on the steam bath for 24 hours, with frequent shaking. The amber-colored extract is filtered off and the extraction repeated with additional quantities of water. The extract is decolorized by addition of 15 to 20 cc. of a saturated solution of tannic acid followed by a slight excess of a solution of lead acetate. The tannic acid-lead acetate compound that occludes all the coloring matter is allowed to settle and the supernatant solution decanted and filtered. The excess of lead acetate is removed by treating the filtrate with hydrogen sulfide and filtering. After neutralizing the free acetic acid with sodium carbonate and evaporating the extract to a thin syrup under reduced pressure to minimize charring, the galactan is precipitated by allowing the syrup to flow slowly into a large excess of 95 per cent alcohol with constant stirring.

Under proper conditions the galactan precipitates as a white gummy mass that becomes hard and granular as dehydration proceeds. In some cases the galactan forms a milky colloidal solution when poured into alcohol. Under these conditions precipitation can be effected by the addition of a small amount of an electrolyte such as hydrochloric acid. Products of hydrolysis, if formed, will be removed in the subsequent purification. The galactan is then filtered. In order to obtain a pure product it is necessary to resort to fractional precipitation with the aid of a centrifuge. The galactan is dissolved in sufficient water to form a thin syrup and then 50 per cent alcohol is added with rapid stirring until permanent turbidity is produced. The solution is then quickly placed in the centrifuge and whirled until the supernatant liquid is perfectly clear. The solution is then decanted and the same operation repeated as often as necessary. The galactan is finally purified by repeated solution in water and precipitation with alcohol. It is finally triturated with absolute alcohol, washed with ether and dried at 105° C.

PROPERTIES OF ϵ-GALACTAN—The purified galactan forms a white, amorphous, granular powder, readily forming a clear solution in cold and hot water without gelatinization, and is slightly soluble in acetic acid and 95 per cent alcohol. It had no definite melting point but decomposes around 250°. One gram of a very pure preparation gave only a trace of ash. A 10 per cent solution of the galactan in water had the specific rotation $[\alpha]_D^{20°} + 12.11°$.

Twenty-five cc. of a solution containing 2.5 g. of galactan reduced 0.1554 g. of Cu by Allihn's method. When distilled with 12 per cent hydrochloric acid the galactan gave 6.18 per cent of furfural equivalent to 10.54 per cent of pentosan. Pure galactose under similar conditions gave a precipitate with phloroglucine equivalent to 0.55 per cent furfural. The furfural phloroglucide from the galactan was only slightly soluble in 95 per cent alcohol showing the absence of methyl furfural in the distillate. Analysis of the galactan gave the following results:

	Found	$C_6H_{10}O_5$	Calculated for 89.5 $C_6H_{10}O_5$ + 10.5 $C_5H_8O_4$
C	44.63	44.44	44.53
H	6.20	6.17	6.16
O	49.17	49.39	50.31

The yield of furfural indicates the presence of 10.5 per cent pentosan but no pentose could be isolated from the sugars formed by hydrolysis of the galactan. The differences between the figures found by analysis and those calculated are insufficient to establish the presence of a pentosan. The mother liquor remaining after the removal of the greater portion of the galactose by crystallization gave on acetylation only galactose pentacetate; the osazone obtained was that of galactose; and on oxidation with nitric acid, mucic and oxalic acids were formed but no trihydroxyglutaric acid. 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. A parallel case is found in the celluloses isolated from various woods. The cellulose from western larch gave 5.5 per cent of furfural and that from yellow birch about 17.0 per cent of furfural on distillation with 12 per cent hydrochloric acid.

[1] *Ber.*, **43** (1910), 3611.
[2] *Ber.*, **23** (1890), 2990.
[3] *Chem. Ind.*, **29** (1906), 217.
[4] *Biochem. Z.*, **70** (1915), 416.
[5] *Arkiv. Kemi, Min. Geol.*, [6] **3** (1908), 1.
[6] *Z. physiol. Chem.*, **50** (1906), 238.

The difficulty of purifying the galactan is due to its colloidal nature. When examined in an ultramicroscope of the Zsigmondy-Siedentopf type a fine Tyndall effect was obtained. In determining the molecular weight by the freezing point method 3.875 g. of galactan dissolved in 39.88 g. of water lowered the freezing point 0.055°. These data indicate a molecular weight of 3286 or an empirical formula $(C_6H_{10}O_5)_{20}$. Since the galactan was of questionable purity the lowering of the freezing point observed may have been due to the presence of foreign matter.

HYDROLYSIS OF THE GALACTAN—The galactan was hydrolyzed by dissolving in 2.5 per cent sulfuric acid in a round bottom flask, provided with a reflux condenser, and boiling in an oil bath maintained at 105–110°. The time necessary for complete hydrolysis varied considerably with the concentration of the solution in galactan. In one experiment 57 g. of galactan dissolved in 1.5 liters of 2.5 per cent H_2SO_4 required 40 hrs. boiling for complete hydrolysis. During this period the contents had charred somewhat. The sulfuric acid was then neutralized with $BaCO_3$, filtered, the filtrate decolorized by boiling with blood charcoal and again filtered. Concentration of the filtrate under diminished pressure gave a syrup only slightly colored. The syrup was then taken up in hot 95 per cent ethyl alcohol and allowed to stand over night for the precipitation of a small amount of gummy matter invariably present. The clear alcoholic solution was decanted, evaporated to a syrup and the syrup treated with a small amount of absolute methyl alcohol. On cooling in a freezing mixture and stirring with a glass rod crystallization of the sugar takes place at once. The crystals were then filtered off, washed with methyl alcohol, redissolved in a small amount of water, and again crystallized with methyl alcohol as before.

This method gives excellent results, perfectly white crystals being readily obtained. Glacial acetic acid and hot methyl alcohol containing about 0.25 per cent of HCl gas were also employed. The syrup obtained from the 57 g. of galactan hydrolyzed as outlined above was then taken up in about 200 cc. of hot methyl alcohol containing hydrochloric acid. By seeding with galactose crystals and scratching with a rod, 35 g. of sugar crystallized out after standing in the ice box over night. The mother liquor from these crystals gave an additional 2 g. of sugar after 24 hours, making a total yield of 65 per cent crystalline sugar. On concentrating the mother liquor to a syrup, adding phenylhydrazine and glacial acetic acid and heating on the water bath, only a small amount of osazone was obtained.

Another experiment was carried out in which the course of the hydrolysis was followed by Fehling's solution. Galactan amounting to 9.4278 g. was dissolved in one liter of 2.5 per cent sulfuric acid and hydrolyzed in the manner previously mentioned. By means of a syphon through the stopper of the flask portions of the solution were removed at regular intervals. After cooling, 25 cc. of the solution were transferred to a 100 cc. flask, the acid being neutralized with sodium carbonate and the solution made up to the mark. Twenty-five cc. of the solution so prepared were used for determining the reducing power by Allihn's method. The copper was obtained electrolytically. The factor 0.898 given by Brown[1] was used in reducing to galactose the percentages of sugar obtained in terms of dextrose. Theoretically, 9.4278 g. of galactan should yield on hydrolysis 10.475 g. of galactose and the 25 cc. sample employed would contain 0.06547 g. of galactose. The following results were obtained:

No. hours Boiled	Mg. of Cu Obtained	Mg. Galactose Found	Theoretical Amount of Galactose	Per cent of Theoretical
2	77.1	43.82	65.47 g.	66.93
3	110.2	62.47	65.47 g.	95.42
5	111.1	62.97	65.47 g.	96.19
8	114.4	64.85	65.47 g.	99.06
12	110.4	62.58	65.47 g.	95.59
15	106.5	60.41	65.47 g.	92.17
20	105.6	59.91	65.47 g.	91.51
28	105.1	59.63	65.47 g.	91.08

The results obtained show that under the conditions of the experiment, maximum hydrolysis, that is 99 per cent, is obtained by eight hours' heating.

The ease with which the galactose can be obtained and the high yields recommend ϵ-galactan as a source of galactose. Ordinarily galactose is obtained by hydrolysis of lactose and elimination of the glucose by fermentation. This is but a troublesome method and the yields obtained are not good.

EXAMINATION OF SUGAR

GALACTOSE—The repeatedly crystallized sugar melted at 155–157°, by rapid heating at 159–160°. The melting point of galactose is ordinarily 163–165°. The sugar in aqueous solution had an initial rotation $[\alpha]_D^{20°} = +124°$, changing to $[\alpha]_D^{20°} = +83.54°$, where it remained constant. The sugar is accordingly mutarotatory. The following results were obtained on ultimate analysis:

	C	H	O
Found	39.93	6.65	53.42
Calculated for $C_6H_{12}O_6$	40.00	6.66	53.34

GALACTOSE HYDRAZONE—Five grams of the sugar in 10 cc. of water were added to a solution of 20 cc. of water containing 5 g. of freshly distilled phenylhydrazine and 5 g. of glacial acetic acid. By rubbing the side of the beaker with a glass rod, the hydrazone began to form in 10 min. and after about 15 min. almost a solid mass was obtained. The yield was 3.5 g. After three crystallizations from 95 per cent alcohol by addition of water, the snow-white hydrazone obtained melted at 155–156°. When mixed with the hydrazone of galactose obtained from lactose the melting point was not changed.

GALACTOSE PHENYLOSAZONE—Osazones were prepared from the galactose from ϵ-galactan and from lactose. The galactose phenylosazone from western larch melted at 189°. The galactose phenylosazone prepared from lactose melted at 189–190°. When mixed with the first preparation the melting point was not changed.

[1] *J. Am. Chem. Soc.*, **28** (1906), 442.

GALACTOSE PENTACETATE—The pentacetate[1] prepared by the method of Erwig and Konig[2] melted at 141°. Ten grams of the sugar yielded 4.5 g. of the pentacetate.

FERMENTATION—Attempts to ferment the hydrolyzed sugar with *Saccharomyces cerevisiae* gave negative results, but with *S. Carlsberg* I about 40 per cent of alcohol was obtained. The fermentation experiments are being continued.

OXIDATION OF THE SUGAR

The sugar as oxidized with nitric acid (sp. gr. 1.15) by the method of Tollens and about 75 per cent of its weight of mucic acid was obtained. Using the factor 1.33 the yields of mucic acid obtained showed the sugar to consist of 98.61 to 99.98 per cent galactose.

OXIDATION OF THE GALACTAN

The galactan as well as the crystalline sugar yields considerable quantities of mucic acid on oxidation with nitric acid. The mucic acid after solution in a large volume of hot water deposited, on cooling, fine crystals that melted at 215° after washing with alcohol and ether. The ammonium salt decomposed at 222–223° and gave the pyrrol reaction.

The mucic acid was further oxidized to tartaric and oxalic acid by Fischer's[3] method using alkaline potassium permanganate. After removal of MnO_2, acidification with HCl and addition of NH_4Cl and $CaCl_2$ at boiling temperature, a precipitate of calcium oxalate was obtained which was decomposed with sulfuric acid. The filtrate from the $CaSO_4$ yielded crystals of oxalic acid. These crystals were identified by heating with *p*-toluidine, the oxal-*p*-toluidine obtained melting at 268°.

The tartaric acid remaining in the filtrate from the calcium oxalate was obtained as the calcium salt by concentration of the solution. On digestion with K_2CO_3, $CaCO_3$ was formed and filtered off. Acidification of the filtrate with acetic acid yielded the insoluble acid potassium tartrate. After recrystallization from water and drying the potassium was determined as K_2SO_4.

0.2898 g. of $KH.C_4H_4O_6$ gave 0.1324 g. K_2SO_4
0.1324 g. K_2SO_4 = 0.05941 g. K_2 = 20.50 per cent found
K_2 calculated for $KH.C_4H_4O_6$ = 20.74 per cent

QUANTITATIVE DETERMINATION OF GALACTAN BY OXIDATION TO MUCIC ACID

A method for the quantitative determination of galactose and galactans, depending on oxidation by means of nitric acid to the difficultly soluble mucic acid, has been employed for a long time, especially by agricultural chemists. Even pure galactose seldom yields more than 75 per cent of its weight of mucic acid so that it is necessary to employ a factor according to the material oxidized. The method first developed by Tollens is essentially as follows:[4]

Place in a beaker 5.5 cm. in diameter and 7 cm. deep, 1 to 5 g. of galactose (or galactan) together with 60 cc. of nitric acid (sp. gr. 1.15) and evaporate the solution to exactly one-third of its volume in a water bath at 94–96° C. After standing 24 hrs., add 10 cc. of water, and allow to stand an additional 24 hrs. The mucic acid is then filtered off, washed with water, alcohol, and ether in succession, dried and weighed. The weight of mucic acid multiplied by 1.33 gives galactose while multiplying the weight of mucic acid by 1.20 gives galactan. If the galactan occurs in plant or similar material, extraction with ether is made previous to oxidation. The mucic acid obtained is dissolved out with ammonium carbonate and subsequently liberated with nitric acid.

Since but 65 per cent of crystalline galactose was obtained from the galactan, proof was lacking that the galactan as isolated consisted entirely of the anhydride of galactose. It was hoped that this point could be settled by oxidation to mucic acid but curiously conflicting results were obtained. In the majority of our experiments direct oxidation could be employed since we were using the isolated galactan.

The first case of the unreliability of the method was found in oxidizing the extract from the wood. Only 6 to 9 per cent of the galactan could be accounted for in this way while by precipitation of the galactan from the clarified solution with alcohol and weighing the galactan directly a yield of 17 per cent of galactan was obtained from one sample of wood.

Samples of galactan were prepared by repeated precipitation from the aqueous solution with alcohol, washing with ether, and drying finally at 105°. A large number of oxidations were carried out by the usual method. Some of the results obtained are given in the following table:

TABLE I

Sample	Exp. No.	Grams Galactan Employed	Grams Mucic Acid Obtained	Per cent Galactan By factor 1.20
A	1	3.7419	1.6615	53.28
	2	2.7647	1.2532	54.39
B	3	1.3324	0.4869	43.85
	4	0.9038	0.6120	81.26
	5	1.3075	0.8914	81.81
C	7	0.3603	0.2815	93.77
	8	0.3306	0.1400	50.82
	9	3.8350	1.4242	44.56
	12	0.8886	0.5835	78.80

The above data show clearly that the method does not yield accurate or consistent results regardless of the weight of sample employed.

The method was then tried for galactose. A carefully purified sugar prepared from lactose and melting at 162–163° was oxidized with the following results:

TABLE II

Gram Galactose	Gram Mucic Acid Obtained	Per cent Galactose By Factor 1.33
0.5285	0.3968	99.86
0.3538	0.2606	97.96
0.5732	0.4194	97.31

Oxidation of galactose from the galactan in the same manner gave results equivalent to 99.98 to 98.61 per cent galactose. Considering the character of

[1] Acknowledgment is made to Mr. H. C. Howard for preparation of the galactose pentacetate.

[2] *Ber.*, **22** (1889), 2207.

[3] *Ibid.*, **27** (1894), 1, 397.

[4] Bureau of Chemistry, *Bull.* **107**, 55; see also Miyake, *J. Coll. Agr. Japan*, **4**, Pt. 8.

the method the results obtained with galactose are very satisfactory.[1]

It was thought that better results might be obtained if the galactan were hydrolyzed previous to oxidation. Accordingly known amounts of galactan were hydrolyzed with 3 per cent H_2SO_4, the acid was removed with $BaCO_3$ and the sugar in the form of a thick syrup oxidized with 60 cc. of the nitric acid.

TABLE III

Grams Galactan	Gram Mucic Acid	Per cent Galactan By Factor 1.20
1.2925	0.7074	65.68
1.6925	0.3938	27.92
1.0393	0.4775	55.13
1.1775	0.6135	62.52

The results are no more satisfactory than those obtained by direct oxidation of the galactan.

A series of experiments were conducted in which the strength of the nitric acid was varied while other conditions remained the same. A series of eight acids were employed in which the sp. gr. at 18° as determined by a Westphal balance ranged from 1.124 to 1.356. The per cent of galactan as determined from the weights of mucic acid using nitric acid of sp. gr. 1.124, 1.130 and 1.174 were 87.57, 80.95 and 89.52 per cent, respectively. When the sp. gr. of the acid exceeded 1.174 there was a marked decrease in the yield of mucic acid.

A considerable number of additional experiments were carried out employing nitric acids of sp. gr. 1.124, 1.150, and 1.174, in which the evaporation temperature and amount of acid were varied. However, no conditions were found by which consistent results could be obtained. Since in some cases (experiment No. 7, Table I) at least 94 per cent of the galactan could be accounted for as galactose anhydride, it is not probable that any sugar other than galactose is formed on hydrolysis; at least, if an additional sugar is formed, it is present in small amount.

Our experiments have shown that the method of determining galactans by oxidation to mucic acid is entirely unreliable even when the isolated galactan is used. If the method is unreliable for apparently pure galactans it must be even less reliable where the plant material containing the galactan is oxidized directly. It is well known that the presence of foreign organic bodies[2] hinder and in some cases entirely prevent the separation of the mucic acid. The unreliability of the method has recently been pointed out also by Dore.[3]

[1] The work on the oxidation of galactose and galactan was completed before the note by Dore, THIS JOURNAL, 7 (1915), 721, on the determination of galactan appeared. According to Dore when 2 g. of galactose were oxidized 90 per cent was recovered as mucic acid while when 0.2 g. was used the recovery was 54 to 74 per cent. The oxidations were accordingly repeated on small samples of galactose from western larch. The beakers were immersed in a water bath, the temperature of which did not exceed 87°. The following results were obtained:

Galactose Gram	Mucic Acid Obtained Gram	Galactose By Factor 1.33 Per cent
0.2843	0.2036	95.25
0.3658	0.2760	100.30
0.2290	0.1578	91.65
0.4642	0.3489	99.97

[2] Lippman, "Chemie der Zuckerarten," 3rd Ed., Vol. I, p. 274.

[3] *Loc. cit.*

ACETYL DERIVATIVES OF ε-GALACTAN

An attempt to prepare an acetyl derivative of the galactan with acetic anhydride using zinc chloride as a catalyzer was unsuccessful. The material charred badly during heating and no acetyl derivative separated on pouring the solution into water. It was found, however, that acetyl derivatives could be prepared using acetic anhydride with sodium acetate crystals or anhydrous sodium acetate. The derivatives obtained by means of anhydrous and crystalline sodium acetate were found to be entirely different in melting point and ease of hydrolysis with mineral acids.

The anhydrous sodium acetate gave an acetyl derivative that melted between 165 and 173°. This derivative was extremely hard to hydrolyze, using sulfuric acid of approximately $N/4$ strength.

The *crystalline sodium acetate* gave a derivative that melted between 185 and 192°, and hydrolyzed readily with the sulfuric acid employed.

The acetyl derivatives were prepared as follows: (*a*) *Derivative with Anhydrous Sodium Acetate*—Four grams of anhydrous sodium acetate were added to 50 g. of acetic anhydride and heated to boiling; 7 g. of finely powdered galactan were then added in small amounts at first and the remainder after a lapse of 10 min. The boiling was continued for 20 min. after the last of the galactan had been added. All of the galactan did not go into solution. After cooling to about 50°, the whole was poured into 600 cc. of cold distilled water from which the acetyl derivative separated at first as a heavy viscous oil that became hard and granular after several minutes standing. The acetyl derivative was then filtered off and washed with a large amount of cold water. It was then dissolved in a very small amount of glacial acetic acid solution, being assisted by gentle heating. The solution is poured into a liter of cold water, the precipitated derivative filtered off and well washed with water. This procedure was repeated an additional three times. The derivative was finally dissolved in a small amount of 95 per cent alcohol and poured into a liter of cold water. In this case a milky solution was obtained and it was necessary to add a small amount of an electrolyte (NaCl) in order to produce coagulation and precipitation. The derivative was finally well washed with water and dried for 3 hrs. at 105°. The yield was 3 g.

The acetyl derivative was very resistant to hydrolysis. When 0.1912 g. of the material was boiled with 87 cc. of approximately $N/4$ H_2SO_4 for 28 hrs., hydrolysis was still incomplete and considerable charring had resulted. When 0.2614 g. of the derivative was boiled with $N/4$ KOH for 19 hrs., approximately 20 per cent of the material remained unattacked.

It was found that hydrolysis could be effected under pressure with $N/4$ H_2SO_4. About 0.5 g. of the derivative was placed in a pressure bottle with 70 cc. of standard acid. The bottle was then placed in an autoclave for $1^1/_4$ hours under a pressure of 40 lbs. per sq. in. The resulting solution was then titrated with standard alkali, using phenolphthalein as the indicator.

0.6788 g. acetyl derivative gave 0.4002 g. acetic acid
0.3441 g. acetyl derivative gave 0.2061 g. acetic acid

Per cent Acetic Acid Found	Per cent Calculated for $C_6H_8O_5(OC.CH_3)_2$	$C_6H_7O_5(OC.CH_3)_3$
58.96	48.78	62.5
59.90	.....	....

The results indicate a mixture of triacetyl derivative with a lower derivative.

(*b*) *Derivative with Hydrated Sodium Acetate*—The procedure followed in this case was identical with that described above except that 4 g. of crystalline sodium acetate and 10 g. of galactan to 50 g. of acetic anhydride were employed. A yield of 3.5 g. of the purified acetyl derivative was obtained.

Approximately 0.3 g. of the derivative was hydrolyzed by boiling with 100 cc. of $N/4$ H_2SO_4 under a reflux condenser for about 4 hrs., complete solution being obtained. The solution was then titrated with standard alkali in the usual manner.

0.2625 g. acetyl derivative gave 0.1297 g. acetic acid
0.3530 g. acetyl derivative gave 0.1722 g. acetic acid

Per cent Acetic Acid Found			Calculated for $C_6H_8O_5(OC.CH_3)_2$
Duplicates		Mean	
49.40	49.78	49.09	48.78

The results show that in this case an approximately pure diacetyl derivative of the galactan was obtained.

OCCURRENCE OF GALACTANS IN OTHER CONIFERS

A number of species of conifers were examined to determine if galactans were a normal constituent. Approximately 100 g. of the wood in the form of fine sawdust were extracted several times by digestion with hot water on the steam bath, the aqueous extract evaporated nearly to dryness and the residue treated with 60 cc. of nitric acid in the manner previously described. The crystalline residues obtained were filtered off, washed with water, and dissolved in a minimum amount of boiling water. The solution was filtered hot and the filtrate allowed to stand in the cold for 24 hrs. The mucic acid was then filtered off, washed with water, alcohol, and ether and the melting point determined. Owing to the unreliability of the method of determining galactans quantitative results were not attempted and for the same reason a failure to obtain mucic acid in certain samples is not a positive indication of their absence. The results obtained are given in the following table in which the signs + and — indicate the presence or absence of mucic acid:

Sample No.	Species	Mucic Acid Present	Melting Point Mucic Acid
a	Longleaf Pine (*Pinus palustris*)	+	214–215°
314–11	Longleaf Pine (*Pinus palustris*)	+	215
314–12	Longleaf Pine (*Pinus palustris*)	+	215
314–13	Longleaf Pine (*Pinus palustris*)	+	210
314–41	Pond Pine (*Pinus serotina*)	+	210–211
314–31	Cuban Pine (*Pinus heterophylla*)	+	211
314–35	Cuban Pine (*Pinus heterophylla*)	+	212
314–21	Loblolly Pine (*Pinus taeda*)	—	
314–22	Loblolly Pine (*Pinus taeda*)	+	212
314–30	Loblolly Pine (*Pinus taeda*)	—	
1	Douglas Fir (*Pseudotsuga taxifolia*)	+	215

The longleaf and Cuban pines gave apparently the largest amounts of mucic acid.

SUMMARY

I—The wood of the western larch (*Larix occidentalis*) has been found to contain approximately 10 per cent of a galactan not previously described and which has been named ϵ-galactan.

II—The only sugar obtained on hydrolysis of ϵ-galactan is galactose.

III—The determination of galactans by oxidation to mucic acid by the method of Tollens has been shown to be unreliable.

IV—Galactans have been shown to be characteristic of several of the common conifers.

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A MODIFICATION OF WHIPPLE'S METHOD FOR ORGANIC NITROGEN IN SEWAGES

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Received November 8, 1915

The direct process for total nitrogen in sewages consists in the digestion of a known quantity of sewage in acid solution with or without $CuSO_4$, making decidedly alkaline with NaOH, allowing to settle until clear, and nesslerizing an aliquot portion made up to 50 cc. volume. Several methods embodying these principles have been proposed. Their chief point of difference consists in the reagents used to remove such substances as calcium and magnesium, which cause a turbidity upon nesslerization. They are best adapted to that particular sewage for which they were designed. That another factor of equal importance needs some emphasis was forcibly brought home to us upon trying to apply one of the already proposed methods to Kansas sewages; namely, the effect of time the digestates are alkaline before nesslerized, upon the quantity of nitrogen obtained.

HISTORICAL

Rideal[1] was the first to propose a method whereby organic nitrogen could be determined by direct nesslerization. His method is as follows: 10 cc. of a sewage, or 100 cc. of an effluent plus 4 cc. of pure sulfuric acid, are heated in a pear-shaped hard glass flask in a slanting position until the liquid becomes colorless. When about 2 or 3 cc. remain, the flask is cooled and is washed out with small quantities of ammonia-free water into a 100 cc. measuring flask until the volume reaches about 40 cc. An excess, *i. e.*, about 25 cc. of soda solution (25 per cent) free from ammonia is now added, when a flocculent precipitate is thrown down. After cooling, the liquid is made up to 100 cc., transferred to a clean, dry, stoppered bottle, and shaken at intervals until the flocculi subside. A suitable fraction of the clear liquid is then pipetted off into a Nessler glass, diluted to 50 cc., and nesslerized.

McGowan[2] used a similar method, the chief difference being the addition of potassium oxalate to the alkaline solution to precipitate the calcium, and a proviso that the solution be "rendered just alkaline with purified potash."

Phelps[3] used the following method with some success: The sewage is digested with 5 cc. of concentrated H_2SO_4 until colorless, cooled, and diluted to 250 cc. A 2 cc. portion is neutralized with NaOH

[1] *Sewage*, 2nd Ed., **1907**, 39.
[2] *4th Rep. Royal Com. of Sew. Disp.*, **4**, 35, Part 2.
[3] *J. Infect. Dis.*, **1** (1904), 327.