

due to attack by the larvae, and the number of larvae still alive was also recorded, as shown in Table I.

TABLE I  
ACTION OF BLACK CARPET BEETLE LARVAE ON DYED WOOL  
SAMPLES

| Dye   | Color of cloth | Mg. loss in wt. per 200 mg. cloth | % Larvae still alive |
|---|----------------|-----------------------------------|----------------------|
| III, R = <i>p</i> -C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na | Light yellow   | 21.2                              | 80                   |
| III, R = <i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>    | Brown          | 18.4                              | 100                  |
| III, R = <i>p</i> -C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H  | Tan            | 14.2                              | 60                   |
| III, R = β-C <sub>10</sub> H <sub>7</sub>                           | Golden-yellow  | 12.2                              | 40                   |
| Untreated sample  | White          | 67.0                              | 100                  |

### Summary

1. A convenient method for the preparation of 3,2'-nicotyrine from nicotine by means of palladium-on-asbestos catalyst is described.

2. 3,2'-Nicotyrine couples readily with diazonium salts to form azo dyes which show activity as insect-proofing agents.

3. Sodium 5'-(3,2'-nicotyrine)-azo-*p*-benzene-sulfonate has been reduced to 5'-amino-3,2'-nicotyrine.

URBANA, ILLINOIS

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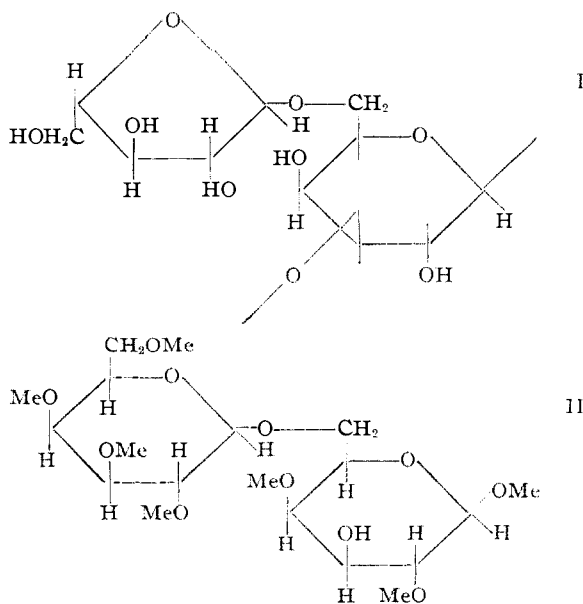
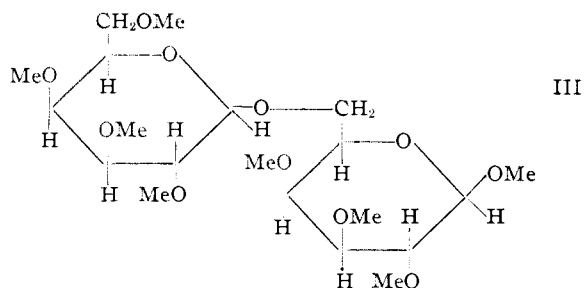
[CONTRIBUTION FROM THE WOOD CONVERSION LABORATORY OF THE UNIVERSITY OF IDAHO]

## The Constitution of Arabo-galactan. IV. The Structure of the Repeating Unit

By E. V. WHITE

In the previous papers of this series<sup>1a,b,c</sup> it has been shown that the water-soluble gum extracted from western larch, *Larix occidentalis*, yields the glycosides of 2,4-dimethyl-*d*-galactose (3 parts), 2,3,4-trimethyl-*d*-galactose (1 part), 2,3,4,6-tetramethyl-*d*-galactose (2 parts), and 2,3,5-trimethyl-*l*-arabinose (1 part) upon methanolysis of the methyl ether derivative<sup>1a</sup>. The furanopenose unit is joined by oxygen linkage through the reducing carbon to the 6-position of an adjacent galactose residue as an arabofuranosido-galactan I<sup>c</sup> and this, together with the separation of two crystalline disaccharides, heptamethyl-6-*d*-

galactosidogalactose II and octamethyl-6-*d*-galactosidogalactose III from the partial methanolysis



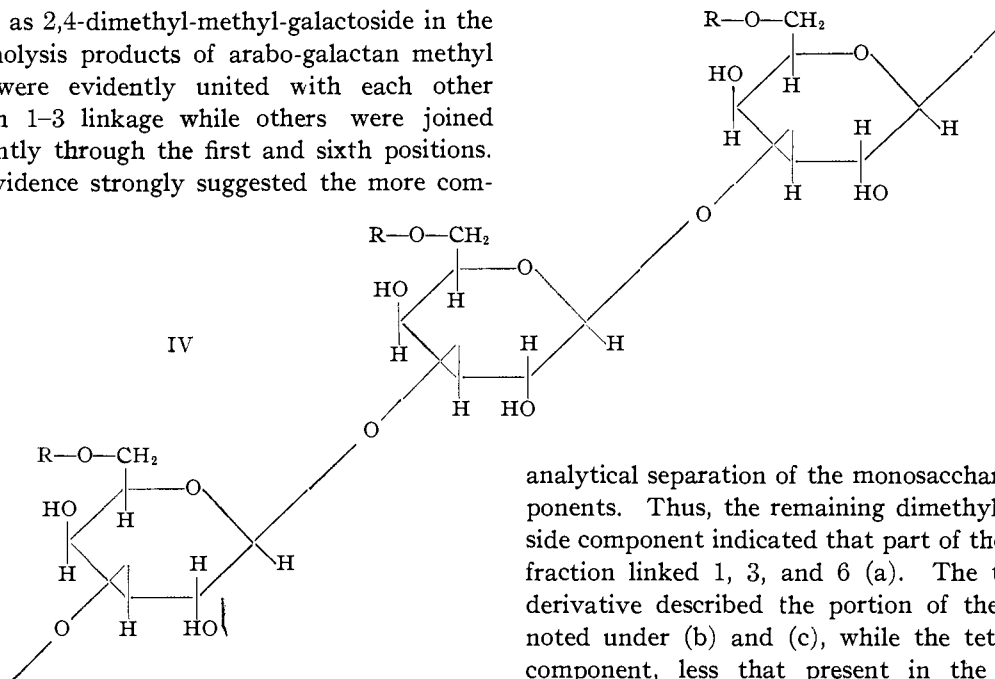
(1) (a) White, THIS JOURNAL, 63, 2871 (1941); (b) 64, 302 (1942); (c) 64, 1507 (1942).

products of methylated arabogalactan<sup>1b</sup> establishes the position of linkage of the terminal units of the polysaccharide. It is also apparent, since two of the three 2,4-dimethyl-methylgalactoside residues found in the complete methanolysis products are united through position 6 to terminal units in I and II, that these residues are joined by 1-3 linkage to dimethyl substituted units in the original methyl ether.

In the event that the third dimethylated residue is joined in a similar manner the repeating unit structure IV would be suggested wherein each unit of the 1-3 linked main chain galactose anhydrides is substituted in position 6 by the radicals R, respectively, *l*-arabinose, *d*-galactose, and 6-*d*-galactosidogalactose. However, if the above third residue is not part of the main chain but is located rather in a side-chain the radicals R become of polysaccharide character and the nature of the main chain linkage is open to question.

Preliminary experiments, reported in Part II, showed that some of the galactose residues oc-

curing as 2,4-dimethyl-methyl-galactoside in the methanolysis products of arabo-galactan methyl ether were evidently united with each other through 1-3 linkage while others were joined apparently through the first and sixth positions. This evidence strongly suggested the more com-



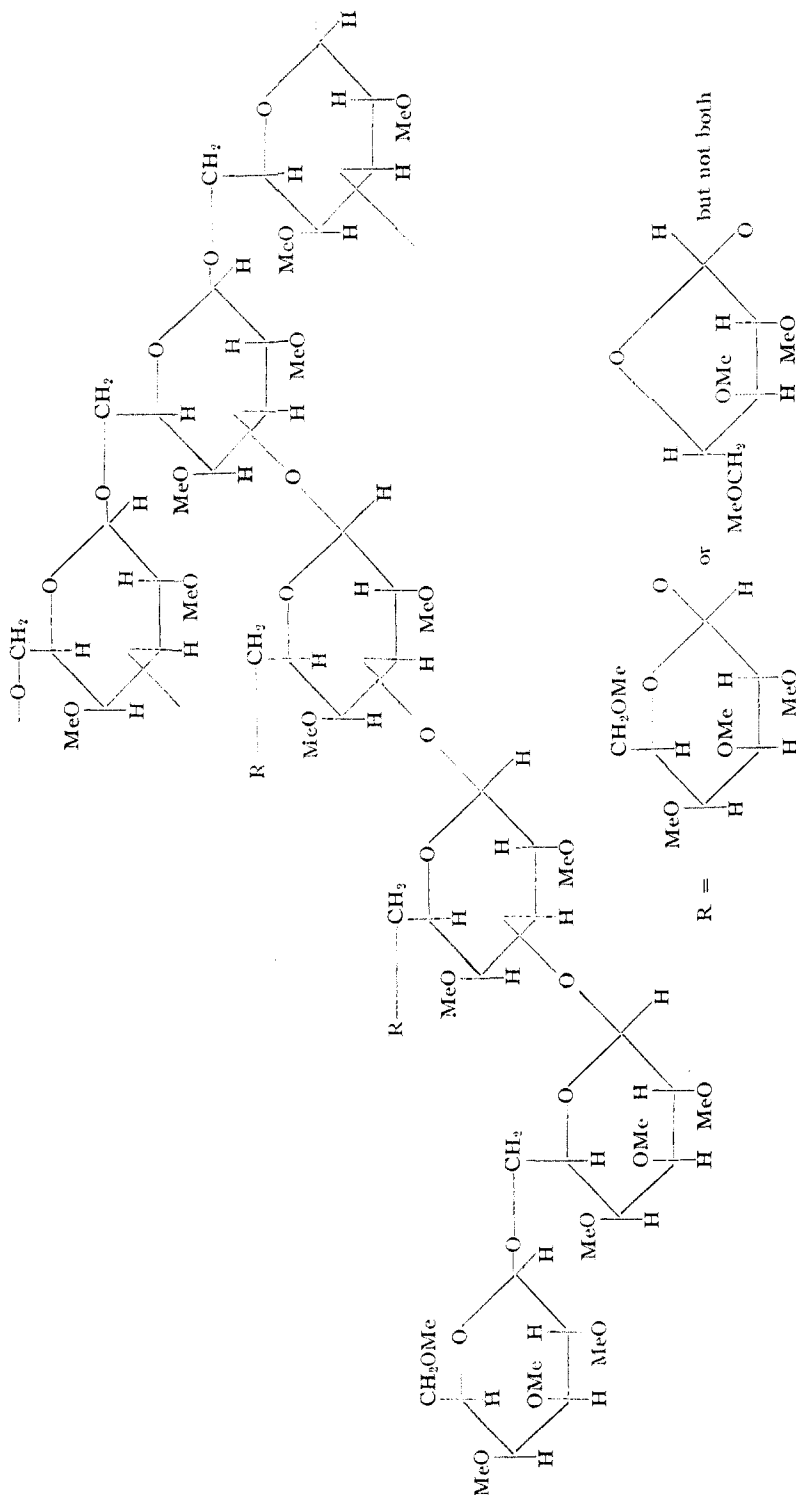
plicated structure and an extension of the problem has substantiated previous indications.

The methyl ether derivative of arabo-galactan was prepared by the previously described method<sup>1b</sup> and subjected to partial methanolysis using anhydrous methanolic hydrogen chloride. The hydrolyzing solution contained a slightly higher concentration of hydrochloric acid than was used formerly, and a similar partition of the hydrolyzate was obtained as petroleum ether-soluble and -insoluble fractions. The latter product was separated into two components by extraction with ethyl ether. The ether-soluble portion represented approximately a methylated arabo-galactan freed from the arabinose component by hydrolysis. The ether-insoluble fraction was found to consist of dimethyl galactose anhydride residues together with a small portion of terminal tetramethyl galactose.

A theoretical analysis of the ether insoluble fraction, regardless of homogeneity, reveals that the dimethyl galactose residues can be united by oxygen linkage (a) at the 1, 3, and 6 positions, (b) at the 1 and 3 positions, a hydroxyl group occupying position 6, (c) at the 1 and 6 positions with free hydroxyl at position 3, and (d) at the 1 position only, both positions 3 and 6 being hydroxylated. A differentiation among this variety of linkage was furnished upon complete methylation of the fraction followed by methanolysis and

analytical separation of the monosaccharide components. Thus, the remaining dimethyl galactoside component indicated that part of the original fraction linked 1, 3, and 6 (a). The trimethyl derivative described the portion of the original noted under (b) and (c), while the tetramethyl component, less that present in the original, allocated the proportion of dimethyl galactan hydroxylated at the 3 and 6 positions, respectively (d). A separation of the trimethyl galactoside fraction into its 2,4,6- and 2,3,4-trimethyl components furnished the ratio of 1-3 linked dimethyl galactose residues (b) to that of the 1-6 linked variety (c). On a molecular basis the decrease in dimethyl galactose anhydride resulting from etherification and, correspondingly, the sum of the tri- and corrected tetramethyl units described the over-all effect of methylation.

As a result of these experiments it was found that only a small proportion of the dimethyl galactose anhydride units present in the ether-insoluble products of partial methanolysis are united with each other through 1-3 oxygen linkage. The 1-6 linked variety, on the other hand, is relatively common and far in excess of that possibly due to the unknown character of linkage of the small tetramethylgalactose component of the fraction. Thus, since two of the three dimethyl galactose residues are known to be joined by 1-3 linkage to similar anhydrides, the conclusion is reached that the third dimethylated unit of the complete methanolysis products is joined in the original ether to other dimethyl substituted residues by 1-6 linkage. Apparently hydrolysis of arabo-galactan proceeds with removal of the labile furanopentose residue concomitant with galactan fission wherein the 1-3 linkage is somewhat more readily hydrolyzed than the 1-6 variety.



The rates of hydrolysis of the 3- and 6-galactosidogalactoses have not been evaluated for either the alpha- or beta-configurations, although the beta-methyl galactosides are known to hydrolyze more rapidly than the corresponding alpha-modifica-

tions.<sup>3</sup> During methanolysis of the methyl derivative there is progressively formed in the hydrolyzate 2,3,5-trimethyl-methylarabinoside, octamethyl- and heptamethyl-6-*d*-galactosidogalactose and apparently a chain of 1-6 linked dimethyl galactose residues together with other intermediate products eventually leading to the previously described components of complete hydrolysis.<sup>1a</sup> The process is not in any sense stepwise in character but is controlled rather by the relative rates of hydrolysis of the variety of linkage involved.

The repeating unit of arabo-galactan, which has been shown to comprise an association of six galactose residues with one unit of arabinose<sup>3</sup> must provide for the intermediate formation of the above products during methanolysis and must furnish upon complete reaction the glycosides of 2,4-dimethyl-*d*-galactose, 2,3,4-trimethyl-*d*-galactose, 2,3,4,6-tetramethyl-*d*-galactose and 2,3,5-trimethyl-*l*-arabinose in 3:1:2:1 molecular ratio. The difficulties involved in the investigation and correct representation of the complex polysaccharides are well known although in the present instance the evidence strongly supports a main chain structure of 1-6 linked galactose anhydride units as proposed by Hirst and co-workers.<sup>4</sup> Each unit of the primary chain is apparently substituted in position 3 by a secondary

chain of three 1-3 linked galactose residues each in turn substituted at the 6 position by termi-

(2) Isbell and Frush, *J. Research Natl. Bur. Standards*, **24**, 125 (1940).

(3) Wise and Peterson, *Ind. Eng. Chem.*, **22**, 362 (1930).

(4) Hirst, Jones and Campbell, *Nature*, **147**, 25 (1941).

nal units. The latter are, respectively, *d*-galactose and the radicals R, *d*-galactose and *l*-arabinose, whose relative position is, of course, not known. The tentative structure proposed for the repeating unit is represented as the methyl ether derivative V and illustrates the highly branched structure of the polysaccharide. In all phases of the problem thus far investigated no evidence has been obtained relative to heterogeneity of the repeating unit. However, the number of such units comprising arabogalactan is not known and, in common with many natural polymers, the polysaccharide may prove to be polymolecular in this respect. On the basis of viscosity studies Husemann<sup>5</sup> limits the chain length between 180 and 280 monosaccharide units.

### Experimental

**Preparation of Methylated Arabo-galactan.**—Larch sawdust was extracted with the minimum quantity of water and the extract purified, after filtering through norite and Super-Cel, by fractional precipitation using ethyl alcohol.<sup>1a</sup> The precipitate was then dissolved in water, evaporated at 50° under reduced pressure to remove residual alcohol, and methylated at 25° under nitrogen using dimethyl sulfate and 30% sodium hydroxide. After complete methylation the derivative was separated from the inorganic reaction products with chloroform. The chloroform extract, dried over magnesium sulfate and filtered, was evaporated to a sirup and extracted with petroleum ether. The residue, taken up in ethyl ether, filtered and evaporated to a sirup, was finally obtained as a light-yellow friable, glassy solid upon removal of residual solvent under reduced pressure; (Found: MeO, 44.4. Calcd. for  $(C_6H_{10}O_5)_6(C_6H_9O_4)-(CH_2)_{20}$ : MeO, 44.8). This procedure has been refined so that a relatively large quantity of uniform product can be prepared without difficulty.

**Partial Methanolysis of Arabo-galactan Methyl Ether.**—Ninety grams of methylated arabo-galactan was dissolved in anhydrous methyl alcohol and methanolic hydrogen chloride added together with fresh alcohol such that the total volume was 900 cc., 0.140 *N* in hydrochloric acid. The reacting solution was heated under reflux on a water-bath for twelve hours and cooled to room temperature. Excess acidity (0.076 *N*) was neutralized with silver carbonate and the solution treated with norite, filtered and evaporated to a sirup; yield, 93 g.

**Separation and Analysis of the Products of Partial Methanolysis.**—The sirup (93 g.) obtained upon partial methanolysis of methylated arabo-galactan was extracted thoroughly with hot ligroin. After removal of solvent by evaporation, the extract (26.0 g.) was distilled fractionally under high vacuum (0.2 mm.) yielding the portions given in Table I.

The products of Table I have been characterized previously and were not investigated further.

The residue remaining after removal of the ligroin-soluble components was extracted with ethyl ether. Upon

TABLE I

| Fraction | Temp., °C. | Yield, g. | MeO, % |
|----------|------------|-----------|--------|
| 1        | 70–90      | 16.15     | 60.5   |
| 2        | 90–180     | 3.15      | 51.1   |
| 3        | 180–200    | 3.20      | 53.1   |
| 4        | 200–250    | 1.00      | 48.9   |
| Residue  | ...        | 2.10      | 44.4   |

removal of solvent the extract gave a sirup (54.2 g.). A sample of the latter in chloroform solution was precipitated into petroleum ether, dried, and analyzed; (Found: MeO, 42.0. Calcd. for methylated arabo-galactan arabinose-free MeO, 42.6). A second sample (17.0 g.) was subjected to complete methanolysis with methanolic hydrogen chloride. The product was isolated in the usual manner, distilled fractionally, and analyzed for monosaccharide components. The results are given in Table II.

TABLE II

ANALYSIS OF METHANOLYSIS PRODUCTS FROM ETHER-SOLUBLE EXTRACT

| Fraction           | Temp., °C. | Yield, g. | MeO  | "Tetra" | "Tri" | "Di" |
|--------------------|------------|-----------|------|---------|-------|------|
| 1                  | 80–90      | 5.30      | 61.2 | 5.30    |       |      |
| 2                  | 90–105     | 1.15      | 54.7 | 0.27    | 0.88  |      |
| 3                  | 105–120    | 4.70      | 47.8 |         | 2.62  | 2.08 |
| 4                  | 120–140    | 7.35      | 41.8 |         |       | 7.35 |
| Total grams        |            |           |      | 5.57    | 3.50  | 9.43 |
| Molar ratio found  |            |           |      | 1.70    | 1.12  | 3.20 |
| Molar ratio calcd. |            |           |      | 2.00    | 1.00  | 3.00 |

The ether-soluble component of the methanolysis sirup thus appears to be a methylated arabo-galactan freed from the arabinose component by hydrolysis and having simultaneously undergone a small amount of terminal galactose fission. The fraction is obviously non-homogeneous.

The final residue remaining after extraction of the methanolysis sirup with ligroin and ethyl ether was taken up in chloroform, filtered from a small amount of inorganic material, and washed thoroughly by dropping the solution into an excess of rapidly stirred ether. The residue, taken up in acetone, was obtained as a light-yellow, friable, glassy solid upon evaporation of excess solvent under reduced pressure; yield, 13 g. (Found: MeO, 34.7). A sample (3.2 g.) subjected to complete methanolysis in the usual manner gave a sirup; yield, 3.64 g. (Found: MeO, 45.0). Fractional distillation of the sirup gave only tetramethyl-methyl-galactoside, 13.9 molar per cent., and 2,4-dimethyl-methyl-galactoside, 86.1 molar per cent.

**Methylation and Alcoholysis of the Ether-Insoluble Residue.**—The remainder of the ether-insoluble residue (9.0 g.) dissolved in 25 cc. of acetone was methylated at 30° under nitrogen using 50 cc. of methyl sulfate and 150 cc. of 30% sodium hydroxide for each methylation. The reagents were added dropwise and simultaneously over a period of three hours and the methylation was complete after three such treatments. The product was separated from the reaction mixture with chloroform, purified and isolated as a friable solid by the procedure described for the methylation of arabo-galactan; yield, 8.0 g. (Found: MeO, 44.8).

The methylated product was subjected to methanolysis in a sealed tube using 2% methanolic hydrogen chloride at

(5) Husemann, *J. prakt. Chem.*, **155**, 13 (1940).

105° for five hours. The reaction products were separated in the usual manner and distilled fractionally under high vacuum (0.2 mm.). The results are given in Table III.

TABLE III

ANALYSIS OF METHANOLYSIS PRODUCTS FROM THE ETHER-INSOLUBLE RESIDUE AFTER METHYLATION

| Fraction        | Temp., °C. | Yield, g. | MeO  | "Tetra" | "Tri" | "Di" |
|-----------------|------------|-----------|------|---------|-------|------|
| 1               | 80-90      | 3.50      | 61.5 | 3.50    |       |      |
| 2               | 90-105     | 1.25      | 52.9 | 0.05    | 1.20  |      |
| 3               | 105-115    | 1.60      | 46.5 |         | 0.94  | 0.56 |
| 4               | 115-130    | 1.85      | 41.9 |         |       | 1.85 |
| Total grams     |            |           |      | 3.55    | 2.14  | 2.41 |
| Molar per cent. |            |           |      | 41.5    | 26.5  | 31.8 |

**Analysis of Trimethyl-methyl-galactoside Sirup and Identification of the Components.**—The combined intermediate fractions (2.85 g.) from the above distillation were dissolved in 25 cc. of *N* sulfuric acid and heated on a boiling water-bath for twelve hours. The hydrolysis product was separated in the usual manner, extracted with chloroform, and fractionally distilled under high vacuum. The trimethyl-galactose portion, 1.60 g. (Found: MeO, 41.8), was dissolved in 10 cc. of pyridine and treated with 2.1 g. of trityl chloride. After two days at room temperature a small quantity of water was added to dissolve pyridine hydrochloride and the reaction poured into rapidly stirred ice water. Following two days in the ice box and occasional stirring, the flocculent precipitate was removed by filtration, washed with ice water, and dissolved in acetone. After drying and removal of solvent, a sirup was obtained from which triphenylcarbinol crystallized slowly in the presence of acetone. The non-crystallizable residue, Fraction I, (2.09 g.) comprising triphenylcarbinol and the tritylated galactose derivative, upon treatment with aniline (0.75 g.) in the usual manner gave the anilide of 2,3,4-trimethyl-6-trityl galactose after removal of solvent; m. p. 152°, recrystallized from ethyl alcohol. By calculation on the basis of yield and methoxyl content the 2,3,4-trimethyl-galactose equivalent of Fraction I was determined.

The filtrate from the tritylation reaction was neutralized with silver carbonate and filtered. Silver ion was removed as sulfide and the filtered solution, after treatment with norite, evaporated to dryness. The sirup was taken up in chloroform, filtered, and excess solvent evaporated yielding Fraction II (0.45 g.). Upon treatment with aniline in the usual manner Fraction II gave the crystalline anilide of 2,4,6-trimethyl-galactose; m. p. 178°, recrystallized from ether-ethanol.

The results of the separation are given in Table IV.

TABLE IV

ANALYSIS OF TRIMETHYL-METHYL-GALACTOSIDE SIRUP

| Fraction  | Yield | MeO  | 2,3,4-Trimethyl-galactose, g. | 2,4,6-Trimethyl-galactose, g. |
|-----------|-------|------|-------------------------------|-------------------------------|
| I         | 2.90  | 15.6 | 1.08                          |                               |
| II        | 0.45  | 41.8 |                               | 0.45                          |
| Per cent. |       |      | 70.6                          | 29.4                          |

### Summary

1. Partial hydrolysis of arabo-galactan methyl ether yields a variety of fission fragments including 2,3,5-trimethyl-methyl-*l*-arabinoside, octamethyl- and heptamethyl-6-*d*-galactosidogalactose, and a residue comprising mainly 2,4-dimethyl galactose anhydride units.

2. The individual dimethylated residues are shown to be united with each other through the first position, through the first and third positions, through the first and sixth positions, and through the first, third, and sixth positions, respectively.

3. The proportion of 2,4-dimethyl galactose anhydride linked through the first and sixth positions is considerably in excess of that joined at the first and third positions.

4. A tentative structure is presented to represent the repeating unit of arabo-galactan.

MOSCOW, IDAHO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

## Attempted Asymmetric Syntheses Involving the Grignard Reagent in Optically Active Solvents

BY D. S. TARBELL AND MARK C. PAULSON

In a recent article, it was reported<sup>1</sup> that the Grignard reaction between methylmagnesium iodide and benzaldehyde in dimethylbornylamine as solvent gave optically active methylphenylcarbinol. The same result was obtained using phenylmagnesium bromide and acetaldehyde. This reaction interested us as an example of a new type of asymmetric synthesis,<sup>2</sup> and it suggested

(1) Betti and Lucchi, *Boll. sci. facoltà chim. ind. Bologna*, No. 1-2, (1940) (*C. A.*, **34**, 2354 (1940)).

(2) Cf. Ritchie, "Asymmetric Synthesis and Asymmetric Induction," Oxford University Press, London, 1933.

the possibility of obtaining optically active secondary and tertiary alcohols by a synthetic method. We have been unable, however, to obtain optically active carbinols by this reaction under a variety of conditions, using dimethylbornylamine, *d*-methyl *s*-butyl ether, or methyl menthyl ether as solvent for the Grignard reagent.

Attempts to duplicate the preparation of methylmagnesium iodide using dimethylbornylamine as a solvent, as reported by Betti and Lucchi,<sup>1</sup> failed. In all cases the quaternary am-