

a jacketed copper Grignard reactor (20 liters capacity) developed at Penn State was used. To 608 g. (25 moles) of magnesium and 12,500 ml. of ether was added 2662 g. (25 moles) *t*-amyl chloride; from the product mixture was decanted 20 moles (12,200 ml.) of a clear ether solution of *t*-amylmagnesium chloride. This solution was then added dropwise at the rate of 450 cc. per hour to a mixture of 2150 g. (20 moles) of freshly prepared isobutyryl chloride in 4000 ml. of dry ether, at 16–18° and stirring continued for five days, also at 16–18°. After decomposing the product by pouring onto 10 kg. of ice, the ether layer and water layer were separately distilled. The combined ether layer distillates upon fractionation gave cuts 1–5, 88 g., b. p. 50–76° at 80 mm.,  $n_D^{20}$  1.3840–1.4092, containing isobutyraldehyde and isobutyl alcohol; cut 6, 22 g., b. p. 76–82° at 80 mm.,  $n_D^{20}$  1.4111; cuts 7–10, 89 g., b. p. 84–87.5° at 90 mm.,  $n_D^{20}$  1.4070–1.4081, containing isobutyl isobutyrate; cuts 11–14, 108 g., b. p. 88–94° at 100 mm.,  $n_D^{20}$  1.4091–1.4136, containing isobutyl isobutyrate and 2,4,4-trimethyl-3-pentanone; cuts 15–18, 2021 g., b. p. 94° at 100 mm. to 87° at 35 mm.,  $n_D^{20}$  1.4214, 2,4,4-trimethyl-3-pentanone; and cut 20, 41 g., residue. Based on isobutyryl chloride, yields were estimated as 73% 2,4,4-trimethyl-3-pentanone, 10% isobutyl isobutyrate, 2% isobutyraldehyde and 1% isobutyl alcohol.

In a second preparation, also on 20-mole scale, in which the rate of addition of Grignard solution (625 cc. per mole) was constant at about 600 cc. per hour, and the temperature was 14–17°, there were obtained yields of 87% 2,4,4-trimethyl-3-pentanone, 5% isobutyl isobutyrate, 0.1% isobutyraldehyde, and 2% isobutyl alcohol.

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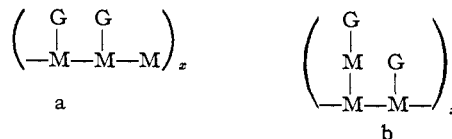
## Methylation of Guar Polysaccharide<sup>1</sup>

By JOHN W. SWANSON

Purified guar polysaccharide, a mannogalactan consisting of 60% mannan and 37% galactan units, has been methylated, subjected to methanolysis, and the resulting glycosides separated into three principal fractions by means of high vacuum fractional distillation. Fraction 1 has been hydrolyzed to the corresponding sugar and identified as 2,3,4,6-tetramethylgalactose, through its crystalline anilide. This derivative was obtained in a yield sufficient to account for 90% of the galactose present in the original polysaccharide. A sample of the unfractionated glycoside mixture was also hydrolyzed and converted to the anilides; only one crystalline anilide has been recovered. This anilide, which was identical with the above, was obtained in sufficient yield to account for 87% of the galactose present. The other two principal fractions (3 and 4 in Table I) correspond to trimethyl and dimethyl sugar units, respectively. These fractions have not been conclusively identified, but they appear to be largely methylated mannose derivatives.

Although insufficient data have been obtained to make any conclusive statements, it is interesting to note that at least 90% of the galactose units appear to be present in the polymer chain as

side units and, therefore, possess four free hydroxyl groups. If the other two main fractions are principally trimethyl and dimethyl mannose, respectively, then the following types of units may be present in guar polysaccharide



G = anhydrogalactose unit  
M = anhydromannose unit

Moe, Iwen and Miller<sup>2</sup> have reported that guar mannogalactan in buffered medium consumes one mole of periodic acid per hexose unit. Structures (a) and (b) might also consume an *average* of one mole of periodic acid per hexose unit because each of the side galactose units would presumably consume two moles of periodate and the units located at the branching points would consume no periodic acid, whereas the units from which branching does not occur would consume one mole of periodic acid. Such a reaction with the galactose units would be expected to lead to the formation of a considerable quantity of formic acid. Whistler and co-workers<sup>3</sup> have recently published formic acid data which support the proposed structure as indicated by methylation.

## Experimental

**Methylation of Guar.**—Ten grams of purified guar polysaccharide was dissolved in 500 ml. of water and methylated under nitrogen by the simultaneous dropwise addition during five hours of 100 ml. of dimethyl sulfate and 280 ml. of 30% sodium hydroxide. After complete reaction of the dimethyl sulfate, the excess alkali was carefully neutralized with dilute sulfuric acid and the partially methylated product was salted out with sodium sulfate. The supernatant salt solution was dialyzed, evaporated under vacuum, and the residue combined with the precipitated gum product. The polysaccharide content of this residue was so small after two methylations that this procedure was not deemed necessary for later methylations. The product from the first methylation was then redispersed in water and the methylation repeated. The final product (or part thereof for methoxyl determination) was dissolved in chloroform, dried over anhydrous sodium sulfate, and precipitated with an excess of light petroleum ether. After five to six methylations and reprecipitation to remove ash, the methoxyl content was 45.4% and the ash content 0.8%; yield 11.5 g., 91.2%;  $[\alpha]_D^{25} + 46.4$  (CHCl<sub>3</sub>, *c* 0.67.)

**Methanolysis of Methylated Guar.**—Five and one-half grams of the methylated guar was dissolved in 80.5 ml. of anhydrous methanol and 46.5 ml. of methanol-hydrogen chloride was added (final concentration of hydrogen chloride, 3.0%). The high viscosity decreased very rapidly. The mixture was centrifuged to remove 0.02 g. of a dark solid, giving a clear light yellow solution. The optical rotation was followed to a constant value ( $[\alpha]_D^{25} + 66.5^\circ$ ) at room temperature and then to a constant value of  $[\alpha]_D^{25} + 74.8^\circ$  after refluxing on a steam-bath for six and one-fourth hours. The hydrochloric acid was neutralized with silver carbonate and, after filtration, the solution was evaporated under vacuum to a sirup. The

(1) Presented before the Division of Sugar Chemistry and Technology at the 112th meeting of the American Chemical Society, New York, N. Y., 1947.

(2) O. A. Moe, S. E. Miller and M. H. Iwen, *THIS JOURNAL*, **69**, 2621 (1947).

(3) R. L. Whistler, *et al.*, *ibid.*, **70**, 3144 (1948).

small amount of ash was removed by addition of ethyl ether and filtration. The remainder of the glycosidic sirup (5.7 g.) was distilled at 0.04 mm. and 120–142° (bath temperature). The product, a water-white viscous sirup, weighed 5.6 g.; the methoxyl content was 51.9%.

**Fractionation of the Distilled Glycosides.**—The distilled mixture of glycosides (4.44 g.) was placed in a 25-ml. pear-shaped flask containing glass wool and attached to a high-vacuum fractionating apparatus similar to that described by Hibbert.<sup>4</sup> The mixture was slowly fractionated during twelve hours under a vacuum of 0.006 mm. and a bath temperature range of 110–160°. The last fraction was not distilled through the column because of its high boiling point and extremely viscous nature. The data for the various fractions are presented in Table I.

TABLE I

DATA CONCERNING THE METHYLATED GLYCOSIDE FRACTIONS OF METHYLATED GUAR POLYSACCHARIDE

Fraction	Weight obtained, g.	Methoxyl, %	Yield, %	Molar ratio	$[\alpha]_{25}^D$	$n_{20}^{D^a}$
1	1.2873	60.8	39.1	1.7	37.6	1.4493
2	0.4155	60.1				
3	0.9486	52.1	21.9	1.0	20.7	1.4599
4	1.6890	43.5	38.9	1.9		
Total	4.3314					

<sup>a</sup> Refractive index of mixed glycosides 1.4597.

**Preparation of the Anilide of Fraction One.**—Fraction one (0.28 g.) was hydrolyzed under reflux at 85° in 10 ml. of *N* sulfuric acid for fifteen hours and then converted to the anilide by the method described by White.<sup>5</sup> The product, after five recrystallizations from absolute ethanol, melted at 193–194°. Calcd. for 2,3,4,6-tetramethylgalactose anilide, m. p. 193.5°, C<sub>18</sub>H<sub>25</sub>O<sub>5</sub>N: C, 61.7; H, 8.1; N, 4.5; OCH<sub>3</sub>, 39.8. Found: C, 61.7; H, 8.2; N, 4.4; OCH<sub>3</sub>, 39.8. A 90% yield of the galactose was obtained in the form of this crystalline anilide.

A sample of the mixed glycosides was also hydrolyzed and similarly converted to the anilides. Only one crystalline anilide was recovered in 85% yield; this was identical with that obtained from fraction one.

(4) I. Levi, W. L. Hawkins and H. Hibbert, *ibid.*, **64**, 1957 (1942).

(5) E. V. White, *ibid.*, **63**, 2871 (1941).

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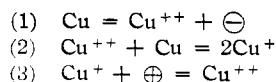
APPLETON, WISCONSIN

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## Mechanism of the Copper and Halogen-Ion Catalysis of Dissolution of Copper

BY ZOLTÁN SZABÓ

The rate of solution of Cu in acid, in the presence of oxygen at saturation, is known to increase with the concentration of H<sup>+</sup> and Cl<sup>-</sup> ions, and to increase linearly with the concentration of the Cu<sup>++</sup> ions produced, except at high [Cu<sup>++</sup>] where it lags behind the first-order rate with respect to [Cu<sup>++</sup>]. The observed independence of the rate of stirring indicates that the rate of dissolution is not controlled by diffusion to and from the metal surface. These facts can be accounted for by the three-step mechanism



where (1) includes reactions between Cu and O<sub>2</sub> or OH, and (3) is representative, in particular, of the reaction (3')  $2\text{Cu}^+ + 2\text{H}^+ + 1/2\text{O}_2 = 2\text{Cu}^{++} + \text{H}_2\text{O}$ .

Since the activity of Cu<sup>+</sup> in the solution is low at all times, and these ions are steadily removed through (3'), the oxidation-reduction potential Cu<sup>+</sup>/Cu<sup>++</sup> is very much higher than Cu/Cu<sup>+</sup>, and reaction (2) proceeds from left to right. Absence of an effect of the rate of stirring indicates that (2) is a fast reaction. Consequently, the rate determining step is (3), specifically (3'). The activity of Cu<sup>+</sup> is still further lowered, and (2) still further shifted to the right, by formation of complex ions [CuCl<sub>*n*</sub>(*n*-1)<sup>-</sup>]. This accounts for the accelerating effect of Cl<sup>-</sup> ions.

From (3'), the rate of solution of the metal is

$$-d[\text{Cu}^+]/dt = k'[\text{Cu}^+]^2[\text{O}][\text{H}^+]^2$$

or, if Cu<sup>+</sup> is mainly present as complex ion

$$-\frac{d[\text{CuCl}_n^{(n-1)-}]}{dt} = k''[\text{CuCl}_n^{(n-1)-}]^2[\text{O}][\text{H}^+]^2$$

With the equilibrium constants  $[\text{Cu}^+][\text{Cl}^-]^n / [\text{CuCl}_n^{(n-1)-}] = K_2$ , and

$$\frac{\sum_1 [\text{Cu}^{++}][\text{Cl}^-]^{2n}}{[\text{CuCl}_n^{(n-1)-}]^2} = K_2^2$$

and noting  $k'K_1 = k_1$ , and  $k''K_1 = k_2$ , these equations become, respectively

$$-d[\text{Cu}^+]/dt = k_1[\text{Cu}^{++}][\text{H}^+]^2[\text{O}] \quad (A)$$

and

$$-\frac{d[\text{Cu}^+]}{dt} = k_2[\text{Cu}^{++}][\text{H}^+]^2[\text{O}] \frac{[\text{Cl}^-]^{2n}}{K_2^2} \quad (B)$$

Either A or B accounts for the first-order rate law in [Cu<sup>++</sup>]. With regard to the effect of Cl<sup>-</sup> ions, if one assumes *n* = 3 and [Cl<sup>-</sup>] = 10<sup>-2</sup>, the ratio [Cl<sup>-</sup>]<sup>6</sup>/K<sub>2</sub><sup>2</sup> becomes ~1.<sup>1</sup> The concentration [Cl<sup>-</sup>] ≈ 10<sup>-2</sup> actually divides the ranges of applicability of equations A and B, the former being valid at [Cl<sup>-</sup>] < 10<sup>-2</sup>, the latter at [Cl<sup>-</sup>] > 10<sup>-2</sup>. There are not enough data to test the second order with respect to [H<sup>+</sup>]; in an experiment of Glauner,<sup>2</sup> the ratio of the amounts of Cu dissolved in 0.27 *N* and in 0.135 *N* acid was 32:5, that is higher than proportional to [H<sup>+</sup>].<sup>2</sup>

The corrosion is predominantly brought about by (2), the role of (1) being primarily to initiate the autocatalytic process, whereas the rate is determined by (3').

By analogous considerations, autocatalysis can be expected in the dissolution of iron but not in the case of lead. This is in agreement with observations.

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(1) St. v. Náráy-Szabó and Szabó, *Z. physik. Chem.*, **A166**, 228 (1933).

(2) R. Glauner, *ibid.*, **A142**, 67 (1929).