room temperature the crystalline product which formed was filtered, washed with water and dried; wt. 15 g. The solid was treated with boiling water and 6 g. of the thiosulfonate separated as an oil. Crystals of β-(*p*-tolylsulfonyl)-propionic acid separated on cooling the aqueous solution; wt. 9 g. (26%), m.p. 106–107°. The melting point of a mixture with acid prepared above was not depressed.

A number of β-(arylsulfonyl)-propionic acids were prepared using the same procedures as are described for β-(*p*-tolylsulfonyl)-propionic acid.

β-(Phenylsulfonyl)-propionic Acid (VIII). From Sodium Benzenesulfinate.—Wt. 3.7 g. (17.5%); m.p. 119–120°.[16]

Anal. Calcd. for $C_9H_{10}O_4S$: C, 50.49; H, 4.67; S, 14.94; neut. equiv., 214. Found: C, 50.55; H, 4.72; S, 14.89; neut. equiv., 215.

Sodium benzenesulfinate and sodium β-chloropropionate in water gave, on warming, followed by acidification, a 28% yield of β-(phenylsulfonyl)-propionic acid; m.p. 121–123°. The melting point of a mixture with the above sample was not depressed.

β-(*p*-Chlorophenylsulfonyl)-propionic Acid (a) From Sodium Chlorobenzenesulfinate.—Wt. 13 g. (3.5%), m.p. 142–143°.

Anal. Calcd. for $C_9H_9ClO_4S$: C, 43.47; H, 3.65; S, 12.89; Cl, 14.26; neut. equiv., 248.7. Found: C, 43.51; H, 3.68; S, 12.87; Cl, 14.35; neut. equiv., 250.4.

(b) **From *p*-Chlorobenzenesulfinic Acid.**—Wt. 6.5 g. (17.4%), m.p. 138–140°. The melting point of a mixture with the above sample was not depressed.

β-(2,5-Dichlorophenylsulfonyl)-propionic Acid (a) From Sodium 2,5-Dichlorobenzenesulfinate.—Wt. 12.2 g. (29%), m.p. 149–150°.

Anal. Calcd. for $C_9H_8Cl_2O_4S$: C, 38.18; H, 2.85; S, 11.32; Cl, 25.05; neut. equiv., 283.1. Found: C, 38.27; H, 3.15; S, 11.43; Cl, 25.03; neut. equiv., 288.6.

(b) **From 2,5-Dichlorobenzenesulfinic Acid.**—Wt. 9 g. (21.2%), m.p. 149–151°. The melting point of a mixture with the above sample was not depressed.

(c) **From β-(2,5-Dichlorothiophenoxy)-propionic Acid.**—β-(2,5-Dichlorothiophenoxy)-propionic acid (IX) was prepared from β-propiolactone and 2,5-dichlorothiophenol[8] and oxidized with aqueous potassium permanganate.[16] The resulting β-(2,5-dichlorophenylsulfonyl)-propionic acid melted at 150–151° after recrystallization from water. Melting points of mixtures with the above samples were not depressed.

β-Succinimidopropionic Acid (X).—One mole (72 g.) of β-propiolactone was added during one hour to a solution of one mole (99 g.) of succinimide and one mole (40 g.) of sodium hydroxide in 250 ml. of water. The reaction mixture was stirred and held at 25° with external cooling. After an additional 15 minutes the solution was neutralized with concd. hydrochloric acid and concentrated by vacuum evaporation to 200 ml. Addition of 50 ml. of concd. hydrochloric acid and cooling to 5° gave a crystalline precipitate of β-succinimidopropionic acid which was separated by filtration. The filtrate was concentrated, treated with 75 ml. of ethanol and filtered from salt. Cooling the filtrate gave more product. The combined crude β-succinimidopropionic acid, m.p. 119–123°, weighed 105 g. (61%); m.p. 129–130°[17] after three recrystallizations from ethanol.[18]

Anal. Calcd. for $C_7H_9NO_4$: C, 49.12; H, 5.26; N, 8.19; mol. wt., 171. Found: C, 49.25; H, 5.38; N, 8.1; mol. wt., 174.

Acknowledgment.—The authors wish to take this opportunity to acknowledge with thanks the analytical data furnished by W. P. Tyler, J. R. Kubik, D. W. Beesing, A. K. Kuder and D. M. Kurtz.

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[16] E. Schjanberg, *Ber.*, **76B**, 287 (1933).

[17] O. A. Moe and D. T. Warner, THIS JOURNAL, **71**, 1251 (1949).

[18] We are indebted to T. H. Shelley for this experiment.

BRECKSVILLE, OHIO RECEIVED AUGUST 24, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, GENERAL MILLS, INC.]

Investigation of the Reserve Carbohydrates of Leguminous Seeds. II. Derivatives[1]

BY OWEN A. MOE, SIDNEY E. MILLER AND MARJORIE IWEN BUCKLEY

The preparation of the 2-cyanoethyl ethers of galactomannan and glucomannan polysaccharides is disclosed. The hydrolysis of the resultant ethers is discussed, and the gelation phenomena of the resultant products are reported. The carboxymethyl ether of polysaccharide from guar has been prepared and the properties have been noted.

A previous communication[2] discussed some preliminary studies relevant to the periodate oxidation of reserve carbohydrates from leguminous seeds. The preliminary results were interpreted as indicating the presence of 1,4-linkages in these polymeric galactomannans with the possibility of branching at the C_6-position. Since that time, extensive work involving methylation studies and X-ray diffraction studies has elucidated the structure of these carbohydrates. The results have shown that in the polymeric galactomannans from guar[3-7] and carob bean[8,9] the mannose units form the main chain and are linked in a 1,4-fashion, whereas the galactose units are present as branches (one unit) at the C_6-position. Extensive methylation data[7] may elucidate still finer points of structure. The present publication relates to the preparation and some properties of diverse derivatives of these polysaccharides.

The 2-cyanoethyl ethers of these polysaccharides were prepared by the reaction between the polymeric carbohydrates and acrylonitrile in the presence of an alkaline catalyst. The degree of substitution of the resulting 2-cyanoethyl ethers could be readily controlled by variations in the quantity of acrylonitrile employed. When one mole of acrylonitrile was used per anhydropyranose unit, the resulting 2-cyanoethyl ethers had values of 0.4–0.5 for the degree of substitution, and these values increased to 1.6–1.8 when six moles of acrylonitrile per sugar unit were used. These results were obtained when the reactions were carried out at room temperature for a two–four hour period. The progress of the cyanoethylation reaction could be observed visually since the derivatives separated from the reaction mixtures as nearly white products.

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[1] Paper No. 120, Journal Series, General Mills, Inc., Research Dept.

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

[3] J. F. Carson and W. D. Maclay, *ibid.*, **70**, 2220 (1948).

[4] J. Swanson, *ibid.*, **71**, 1510 (1949).

[5] K. J. Palmer and M. Ballantyne, *ibid.*, **72**, 736 (1950).

[6] Z. F. Ahmed and R. L. Whistler, *ibid.*, **72**, 2524 (1950).

[7] C. M. Rafique and F. Smith, *ibid.*, **72**, 4634 (1950).

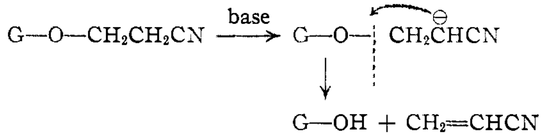
[8] F. Smith, *ibid.*, **70**, 3249 (1948).

[9] E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1278 (1948).

In this connection, the cyanoethylation of a polymeric glucomannan was studied. The glucomannans are reserve carbohydrates usually found in the corms of plants of the *Araceae* family, such as *Amorphophallus oncophyllus* (found principally in Java) from which the product known as iles mannan is obtained, and *Amorphophallus rivieri* from which konnyaku flour is obtained. These glucomannans are composed principally of mannose and glucose in a ratio of 2:1[10] and a great similarity in composition and properties has been found.[10] The glucomannan from *Amorphophallus rivieri* is an effective agent for the creaming of latex.[11]

It was observed that iles mannan exhibited the characteristic gel formation with borax as noted with the galactomannan products. The cyanoethylation reaction also proceeded smoothly with iles mannan and the progress of the reaction could be observed visually.

Hydrolyses of the 2-cyanoethyl ethers were carried out in alkaline media and proceeded readily with the evolution of copious quantities of ammonia. The resulting 2-carboxyethyl ethers obtained had very low values (0.1–0.2) for the degree of substitution. It was apparent that cleavage of the cyanoethyl ether linkages had occurred.



$$\mathrm{G{-}O{-}CH_2CH_2CN} \xrightarrow{\text{base}} \mathrm{G{-}O{-}\,\overset{\ominus}{CH_2CHCN}} \longrightarrow \mathrm{G{-}OH + CH_2{=}CHCN}$$

This would be the expected reaction when the case of removal of a proton, by a base, from the carbon atom alpha to the cyano group is considered.

The 2-cyanoethyl ethers from guar gum, of varying degrees of substitution, were subjected to oxidation by periodate, and the drop in periodate consumption with increased substitution is indicated in Table I. The results from periodate studies are indicative of random distribution on the basis of present structure concepts.

Table I

Periodate Oxidations (Buffered Media, 17-18°) of the 2-Cyanoethyl Ethers from Guar

Degree of substitution	Moles of periodate consumed per substituted sugar unit 24 hr.	48 hr.	144 hr.
0.96	0.62	0.63	0.68
1.13	.56	.58	.60
1.45	.41	.42	.42
2.00	.20	.22	.22

It has been previously reported[2] that these reserve carbohydrates are very sensitive to the action of borates[12,13] with which clear firm gels are formed. The sensitivity to the activity of borates was postulated to be the result of vicinal hydroxyl groups which possess the *cis* configuration. It was also shown that these *cis* glycol systems could be found at the C_2- and C_3-positions of the mannose units if a 1,4-linkage system were present. The 2-carboxyethyl ethers (D.S. 0.1–0.2) also display this same property with borax and, in addition, these latter derivatives are sensitive to the action of metallic salts, such as ferrous sulfate, aluminum sulfate and aluminum chloride forming gels. The original carbohydrates employed in the present study did not exhibit this behavior.

In view of these gel forming characteristics, it was desirable to test the carboxymethyl derivatives in a similar manner. Accordingly, the carboxymethyl ether of the guar polysaccharide was prepared by reaction with sodium chloroacetate in the presence of alkali. The resultant derivatives (D.S. 0.3–0.5) formed very firm stable gels when aqueous sols were treated with the previously mentioned metallic salts.

Experimental

Cyanoethylation of the Galactomannan Carbohydrates.—A typical cyanoethylation experiment may be detailed in the following manner. The galactomannan from carob seed (8.1 g. dry basis, 0.05 mole) was mixed thoroughly with water (150 cc.) and permitted to stand at room temperature for 24 hours. An aqueous sodium hydroxide solution (10 g. of 20%) was added with thorough mixing. Acrylonitrile (10.6 g., 0.2 mole) was added (care being taken to assure complete mixing). The reaction mixture was permitted to stand at room temperature for a period of four hours. As the reaction progressed, the 2-cyanoethyl ether derivative began to separate as a white product. After four hours, the liquid layer was removed by decantation, and the derivative was washed repeatedly with absolute methanol, mixed with methanol in a Waring Blendor, washed with ether, collected by filtration and dried *in vacuo*.

Anal. (dry basis): Calcd. for mono-2-cyanoethyl ether ($C_9H_8O_5N$): N, 6.66. Found: N, 8.86 (degree of substitution about 1.5).

The above described separation phenomena were always noted visually when the molar ratio of acrylonitrile to polysaccharide was at least 3:1. In order to achieve the preparation of a cyanoethylation product with D.S. of 2.0, it was frequently necessary to use up to 15 molar quantities of acrylonitrile when the above reaction conditions were employed. In a similar manner, it was possible to prepare the 2-cyanoethyl ether of a polymeric glucomannan such as iles mannan. Again, the separation of the reaction product was served.

The results obtained employing a variety of these carbohydrate gums are summarized in Table II, and the following experimental conditions were imposed: The carbohydrate gum (18 g., dry basis) was completely dispersed in water (200 cc.). The sodium hydroxide solution (10 g. of 20%) was added with vigorous stirring. Acrylonitrile (30 g.) was added and the resultant reaction mixture was mixed vigorously. After two hours, the reaction products were collected essentially as previously noted.

Table II

Name of seed	Composition of mucilage, % Mannose	Galactose	N of cyanoethyl derivative, %
Flame tree (*Delonix regia*)	79.2[14]	18.5[13]	7.18
Tara (*Caesalpinia spinosa*)	70.9[14]	26.3[13]	8.77
Guar (*Cyamopsis tetragonolobus*)	64[4]	36[4]	9.00
Carob Bean (*Ceretonia siliqua*)	80[6]	20[6]	9.26
Honey locust (*Gleditschia tricanthos*)	70.5[14]	26.0[13]	9.28

Hydrolyses of 2-Cyanoethyl Ethers.—The general hydrolytic procedure may be described as follows: The derivative (20 g.) was mixed with an aqueous solution of sodium hydroxide (200 g. of 10%). The resultant reaction mixture was heated in a boiling water-bath. The copious evolution of

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[10] J. E. DeGroot, C. J. Van Hulssen and D. R. Koolhoos, *Chem. Weekblad.*, **36**, 69 (1939).

[11] "Advances in Colloid Science," Interscience Publishers, Inc., New York, N. Y., 1942, p. 248.

[12] R. Hart, *Ind. Eng. Chem., Anal. Ed.*, **2**, 329 (1930).

[13] A. L. Williams, *Analyst*, **53**, 411 (1928).

[14] E. Anderson, *Ind. Eng. Chem.*, **41**, 2887 (1949).

ammonia was soon noted, and after the mixture was heated for 30 minutes, water (150 cc.) was added. The excess base was neutralized with 5 N acetic acid. The hydrolysis product was precipitated by the addition of methanol, washed repeatedly with absolute methanol, ground to a fine white product and dried in a vacuum desiccator. Analysis showed only 0.2% nitrogen.

In order to determine the degree of substitution of the resultant 2-carboxethyl ether derivative, the above crude product was treated as follows: A portion of the hydrolysis product (4 g.) was dissolved in water (75 cc.), and acetic acid was added gradually with stirring. The continuous addition of the acid caused a white fibrous product to precipitate. This product was collected, washed with methanol, and dissolved in water (50 cc.). The treatment with acetic acid (mineral acids could also be used) was repeated in a Waring Blendor. The precipitated product was collected, washed repeatedly with absolute methanol, ground, washed with ether and dried in a vacuum desiccator. The dry product was dissolved in an excess of 0.1 N sodium hydroxide and after complete solution, the excess alkali was titrated with 0.1 N hydrochloric acid. The degree of substitution was 0.17 (the usual range was 0.1–0.2).

Oxidation by Periodate of 2-Cyanoethyl Ethers.—The ether derivative (0.5 g., dry basis) was mixed with 0.05 M buffered periodate[1] (350 cc.), and reaction temperature was maintained at 17°. The consumption of oxidant at 24-, 48- and 144-hour intervals was determined by removing aliquots as previously detailed.[2] The experimental results are given in Table I.

Preparation of Carboxymethyl Ethers of Galactomannans.—A typical procedure for the preparation of the carboxymethyl ethers is as follows: The carbohydrate from guar seed (30 g.) was mixed with aqueous sodium hydroxide solution (60 g. of 20%) until a completely smooth and homogeneous mass resulted. Sodium chloroacetate (30 g. in 50 cc. water) was added with thorough mixing. The temperature of the reaction mixture was gradually increased to 80° and water (100 cc.) was added. Heating at 80° was continued for approximately two hours and water (100 cc.) was added. The reaction mixture was cooled to room temperature, and the excess alkali was neutralized with 5 N acetic acid. The reaction product was precipitated by the addition of alcohol, washed with alcohol, ground and dried *in vacuo*. The degree of substitution (0.53), which may be varied at will, was determined as previously described.

Gel Formation with Certain Polyvalent Metallic Salts.—All of the 2-carboxyethyl and carboxymethyl ethers prepared in the current study displayed the characteristic gel formation with certain water-soluble metallic salts. Accordingly, the addition with stirring of 1–5 cc. of 20% aqueous solutions of aluminum sulfate, ferrous sulfate, aluminum chloride and ferric chloride to aqueous sols (1–4%) of the carbohydrate ethers resulted in gels. The addition of either aluminum sulfate or ferrous sulfate to a 3% aqueous sol of the above-described carboxymethyl ether resulted in extremely firm gels which showed no tendency to undergo syneresis over a 72-hour period.

MINNEAPOLIS, MINNESOTA RECEIVED JULY 30, 1951

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

1-(2′,3′-Dimethoxyphenyl)-1-cyclohexen-6-one

BY RODERICK A. BARNES AND DONALD F. REINHOLD[1]

2,3-Dimethoxyphenyllithium was treated with 1,2-cyclohexanedione to produce a ketol. Although the free ketol could not be dehydrated, its 2,4-dinitrophenylhydrazone lost the elements of water readily. By this procedure 1-(2′,3′-dimethoxyphenyl)-1-cyclohexen-6-one was prepared in an over-all yield of 28%. The Michael addition of ethyl malonate to this ketone has been carried out.

2-Arylcyclohexanones have been used for the preparation of substituted phenanthrenes[2] and compounds related to morphine.[3,4] Similarly in recent publications which appeared while our work was in progress it has been suggested that 2-arylcyclohexenones also might be used to construct compounds having the morphine ring system.[5,6,7]

The present work was independently initiated to develop a convenient procedure for the preparation of the 2-arylcyclohexenone VII.[8] This has been accomplished by using a three-step process starting from 1,2-cyclohexanedione. An alternative procedure for the synthesis of VII has recently been reported by Pappo and Ginsberg.[6]

The reaction of 2,3-dimethoxyphenyllithium with 1,2-cyclohexanedione was carried out by adding the diketone to two equivalents of the lithium compound. The first equivalent apparently reacted to form the lithium enolate of one carbonyl group. The second carbonyl group then reacted in the normal manner. No higher molecular weight products were formed, indicating that there was little tendency to form a glycol by addition of the aryllithium to both carbonyl groups.

Attempts to dehydrate ketol I with a mixture of acetic anhydride and acetyl chloride were unsuccessful. With acetyl chloride alone some of the unsaturated ketone VII was formed but the major product was a chloroketone (II). Dehydrohalogenation of II could not be effected by heating with pyridine, lutidine or quinoline.[9]

When ketol I was treated with 2,4-dinitrophenylhydrazine and sulfuric acid in the cold the corresponding 2,4-dinitrophenylhydrazone was obtained as a yellow crystalline solid (m.p. 172–173°). However if the reaction mixture was refluxed for an hour a red 2,4-dinitrophenylhydrazone (m.p. 142–143°) separated in 90% yield. This product proved to be the derivative (IV) of the desired unsaturated ketone VII.

An alternate synthesis of VII was realized by selenium dioxide oxidation of 1-(2′,3′-dimethoxy-

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[1] Abstracted from a thesis presented by D. R. Reinhold to the graduate faculty in partial fulfillment of the requirements for the Ph.D. degree, June, 1951.

[2] M. S. Newman and M. D. Farbman, THIS JOURNAL, **66**, 1550 (1944).

[3] V. Boekelheide, *ibid.*, **69**, 790 (1947).

[4] E. C. Horning, M. G. Horning and E. J. Platt, *ibid.*, **69**, 2929 (1947).

[5] W. E. Bachmann and E. J. Fornefeld, *ibid.*, **72**, 5529 (1950).

[6] R. Pappo and D. Ginsberg, *J. Chem. Soc.*, 516 (1951).

[7] C. F. Koelsch, THIS JOURNAL, **73**, 2951 (1951).

[8] The procedure reported here was devised after early experiments involving the addition of nitrosyl chloride to 1-(2′,3′-dimethoxyphenyl)-1-cyclohexene were found to give poor and variable yields. R. Pappo and D. Ginsberg, ref. 6, have since reported satisfactory results from the nitrosyl chloride reaction.

[9] W. E. Bachmann and L. Wick, THIS JOURNAL, **72**, 3388 (1950), were able to eliminate hydrogen bromide from 2-bromo-2-phenylcyclohexanone by reaction with 2,6-lutidine.