ORIGINAL

Biodegradability, Hydrolytic Degradability and Builder Performance of Starch-Based Polycarboxylates Derived from Tropical Plants

Isananto WINURSO and Shuichi MATSUMURA

Faculty of Science and Technology, Keio University

(3-14-1, Hiyoshi, Kohoku-ku, Yokohama-shi, 〒223)

Abstract : Partially dicarboxylated polysaccharides were prepared using starch from corn, sago and tapioca and comparison was made of their biodegradability, hydrolytic degradability and builder performance in detergent formulations. The biodegradability of dicarboxylated starch sodium salt (DC-starch) depended on the dicarboxylation degree. DC-starch containing more than 75~85 mol% unreacted glucopyranose groups in the polymer chain showed excellent biodegradation. DC-starch with high dicarboxylation degree was resistant to biodegradation but showed good builder performance in detergent formulation. Among DC-starches from corn, sago and tapioca starches, hydrolytic degradability and builder performance were essentially the same.

Key words : biodegradation, dicarboxylated starch, polycarboxylate, detergent builder, starch from tropical plant, water-soluble polymer.

1 Introduction

It is reported that high-molecular weight polycarboxylates showed excellent performance as dispersants and detergent builders^{1)~3)}. However, they are generally highly resistant to biodegradation. It is expected that the developments of biodegradable high-molecular weight polycarboxylates are needed in the industrial field. The introduction of biodegradable segment into the functional polymer chain is one way to design environmentally acceptable biodegradable functional polymers^{4)~6)}.

Carbohydrates may serve as an attractive raw material for the preparation of high-molecular weight poly(carboxylic acid)s because they are inexpensive, renewable and biodegradable materials^{7)~9)}. Among the carbohydrates, starch is the most abundant material, and may be one of the most promising raw material in the future. Starch is mainly composed of two types of molecules, amylose and amylopectin. The composition of amylose and amylopectin in the starch has a wide variation depending on the origin of starch, plant variety, geographical conditions, *etc.*¹⁰⁾. Particularly, corn, sago and tapioca starches, which are the most promising tropical products, attracted attention as a renewable raw material in the industrial field. In 1959, dicarboxylated starches were suggested by Hofreiter *et al.* for use with detergents to improve washing performance¹¹⁾. After this, some investigations of dicarboxylated polysaccharides were reported with respect to the synthetic methods and properties^{12)~14)}.

We previously reported some properties of polycarboxylates obtained from amylose and amylopectin individually^{15)~17)}. However, starch composed both of amylose and amylopectin has not yet been extensively studied. In this report, starches from corn, sago and tapioca

were partially dicarboxylated to retain biodegradable glycopyranose groups by the conversion of the vicinal diols of glycopyranose into dicarboxylates *via* dialdehydes and compared with respect to biodegradability, hydrolytic degradability as well as functionality.

2 Experimental

2.1 Materials and measurements

Starch samples from corn (maize, *Zea mays* L.), sago (from stems of several species of palms, principally *Metroxylon*, *Arenga* and *Mauritia* sp.) and tapioca (*Manihot utilisima* P., *Manihot esculenta*) were used in this report. The other materials were of the highest available purity and were used as purchased.

^{13}C NMR spectra were recorded with a JEOL model JNM-FX90A Fourier Transform Spectrometer operating at 22.5 MHz with complete proton decoupling (JEOL Ltd., Tokyo, Japan). Infrared (IR) spectra were measured using a JASCO Fourier Transform Spectrometer model FT/IR-5000 (JASCO Ltd., Tokyo, Japan). Number-average molecular weight ($\bar{M}_n$) and molecular weight distributions ($\bar{M}_w/\bar{M}_n$) were measured by a gel-permeation chromatographic system (GPC) with commercial GPC columns (TSK gel G5000PW+G2500PW, TOSOH Co. Ltd.) with a 0.1 M phosphate buffer containing 0.3 M NaCl, pH 6.8, as eluent. The system was calibrated with a poly(ethylene oxide) standard ($\bar{M}_n$: 3000-996000, $\bar{M}_w/\bar{M}_n$: 1.02-1.10), purchased from TOSOH Co. Ltd. (Tokyo, Japan).

2.2 Preparation of the Partially Dicarboxylated Starches

Partially dicarboxylated starch sodium salt (DC-starch) having various dicarboxylation degree was prepared by the partial conversion of the vicinal diol of the glucopyranose groups of starch into dicarboxylates *via* dialdehydes as shown in Scheme 1^{13),17)}. Preparation of dicarboxylated corn starch sodium salt (DC-corn) having a number-average molecular weight ($\bar{M}_n$) of 19300 and a dicarboxylation degree of 46 mol% [DC-corn-19300 (46)] is described as a representative.

Corn starch (5.0 g) was suspended in 0.10 M aqueous sodium periodate (145 mL) and stirred at 4°C for 6 h in the dark. After the reaction, the suspension was filtered, washed thoroughly with chilled water, dried in vacuum below 40°C to obtain diformylstarch in 92.8% yield (4.64 g). The dialdehyde content of the product, determined by the method of Nieuwenhuizen¹³⁾, was 47.5 mol%. Diformylstarch (4.0 g) was suspended in 123 mL water, nitrogen was bubbled into the solution at 0°C for 30 min, and a solution of 26 g sodium chlorite in 70 mL water was added to the aqueous diformylstarch. The pH of the solution was adjusted to 4.0 with acetic acid, and the mixture was stirred at 20°C for 24 h. The temperature was then raised to 50°C and the reaction was allowed to continue for another 1 h. Nitrogen was passed through the solution until a colorless solution was obtained. The pH of the solution was then

Scheme 1

raised to 10 with 3 M aqueous sodium hydroxide. The solution was poured slowly into a large amount of ethanol (400 mL) with stirring to precipitate the polymer. The precipitated polymer was dissolved in 50 mL of water, and the solution was then again added slowly to a large amount of ethanol (300 mL) with stirring to precipitate the polymer. The precipitated polymer was dissolved in 50 mL of water and dialyzed against distilled water for 3 d. The insoluble precipitate was removed by filtration, and the filtrate was evaporated in vacuum before freeze-dried. Further drying was carried out at 70°C in vacuum to obtain DC-corn in 96% yield (3.84 g) as a white powder. The dicarboxylate content as measured according to Neale and Springfellow¹⁸⁾ was 41 mol %. $\bar{M}_n$ =19300 and $\bar{M}_w/\bar{M}_n$ =3.6 by GPC. The following spectral data for DC-Corn-19300(46) confirm the structure. IR(KBr) : 3333(OH), 2934(CH₂), 1614, 1419 (COONa), 1153, 1024 cm⁻¹ (C-O-C). ¹³C NMR (22.5 MHz : D₂O) : 61.7-63.1(-CH₂-), 72.1-75.0 [>CH-CH(CH₂OH)-O-], 78.2-81.7 [>CH-CH(CH₂OH)-O-, -CH(OH)-], 100.9-101.8 (-O-CH-O-), 174.9-177.1 (COONa). Dicarboxylated sago starch sodium salt (DC-sago) and dicarboxylated tapioca starch sodium salt (DC-tapioca) having various degree of dicarboxylation were also obtained by a similar procedure. Typical oxidation condition and analytical data for DC-starch are shown in Table 1.

2.3 Biodegradation Test

Biochemical oxygen demand (BOD) was determined with a BOD tester (Model 200 and 100 F ; TAITEC Corp., Koshigaya-shi, Japan) by the oxygen consumption method basically according to the OECD Guidelines for Testing of Chemicals (301C, Modified MITI Test)¹⁹⁾ at 25°C, using an activated sludge freshly obtained from a municipal sewage treatment plant in

Table-1 Typical Preparation and Analytical Data of Partially Dicarboxylated Starch (DC-Starch).

Compound ^a	Oxidation of starch to dialdehyde by aqueous sodium periodate ^b			Oxidation of dialdehyde to DC-Starch by aqueous sodium chlorite ^c			
	Concentration of sodium periodate (M)	Dialdehyde		Dicarboxylate			
		Yield (%)	content (mol%)	Yield (%)	content (mol%)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
DC-Corn-11400 (7)	0.015	93	18	82	7	11400	5.1
DC-Corn-27200 (29)	0.05	93	29	80	29	27200	4.9
DC-Corn-19300 (46)	0.10	93	47	96	46	19300	3.6
DC-Corn- 9400 (77)	0.20	76	96	95	77	9400	1.7
DC-Corn- 7500 (78)	0.30	93	85	61	78	7500	1.8
DC-Sago-14300 (10)	0.015	91	18	57	10	14300	7.6
DC-Sago-18100 (23)	0.05	93	35	73	23	18100	3.8
DC-Sago- 8900 (44)	0.10	97	57	64	44	8900	2.1
DC-Sago-12300 (67)	0.20	92	89	81	67	12300	1.8
DC-Sago-11800 (81)	0.30	93	97	56	81	11800	1.8
DC-Tapioca-21100 (8)	0.015	92	18	87	8	21100	6.3
DC-Tapioca-17800 (24)	0.05	94	32	82	24	17800	2.3
DC-Tapioca-15800 (45)	0.10	95	56	70	45	15800	8.0
DC-Tapioca-15900 (73)	0.20	95	83	83	73	15900	2.3
DC-Tapioca-11400 (78)	0.30	95	96	78	78	11400	1.6

^aPolymer code indicates number average molecular weight ($\bar{M}_n$) and relative dicarboxylate content in mol % in parenthesis.

^bDialdehyde of starch was prepared by the reaction of 5.0 g starch with 145 mL aqueous NaIO₄ for 6 h at 4°C.

^cDC-Starch was prepared by the reaction of dialdehyde with aqueous sodium chlorite at pH 4 for 24 h at 20°C.

Yokohama city. The concentration of the polymer in the incubation media was 25 mg/L.

2.4 Hydrolytic Degradation

A non-enzymatic degradation test was carried out by dissolving the polymer in buffer solutions with pH values of 4, 5, 6, 8 and 10. The polymers at a concentration of 400 mg/L were incubated at 30°C in an incubator. Solutions of 0.1 M acetate buffer at pH 4.0 and 5.0, 0.1 M phosphate buffer at pH 6.0, 0.1 M tris-HCl buffer at pH 8.0, and 0.1 M glycine-NaOH buffer at pH 10.0 were used for the non-enzymatic degradation test. The degradation of the polymer was analyzed by GPC, and the hydrolytic degradability was expressed by molecular weight reduction in percent given by :

$$\text{molecular weight reduction (\%)} = [(M_0 - M_t)/M_0] \times 100$$

where M_0 is the initial molecular weight (maximum molecular weight of GPC peak) and M_t is the molecular weight (maximum molecular weight of GPC peak) after t -day incubation.

2.5 Detergency

The washing experiments were performed with water of 54 mg/L (CaCO_3) with a cloth-to-liquor ratio of 1 : 30, at a temperature of 25°C, and with a detergent concentration of 1.2 g/L. The detergency test was first conducted with a standard heavy-duty detergent formulation that contained 20% sodium dodecylbenzene sulfonate, 25% sodium tripolyphosphate (STPP) or disodium 3-oxapentanedioate (ODA), 5% sodium silicate, 3% sodium carbonate, 0.5% sodium carboxymethyl cellulose (CMC), and 46.5% sodium sulfate. The test was done to determine the detergency of the STPP and ODA formulation as a basis for comparison with the test polymers. In the experimental formulas, the STPP or ODA was replaced with an equal weight of the polymers. The washing efficiency of the polymers was determined in a Terg-O-Tometer as a device for simulation of home washers of the agitator type on a laboratory scale, using improved artificially soiled cotton cloth test pieces prepared by an aqueous dispersion method²⁰⁾. The light reflectance of the test swatches was measured by means of an automatic reflectometer equipped with a green filter. The K/S ratio (K , reflectivity coefficient; S , light scattering coefficient) was calculated using Kubelka-Munk equation²¹⁾, and the detergency was expressed according to the equation :

$$\text{detergency (\%)} = (A - B)/(A - C) \times 100$$

where, A , B and C are the K/S values of the soiled pieces, of the washed pieces and the original unsoiled pieces, respectively. The KS value was expressed according to the following equation :

$$K/S = (1 - R)^2 / 2R$$

where R is the reflectance. The relative detergency was expressed as a value of 10 for STPP and 0 for ODA.

2.6 Calcium Sequestration Capacity

A calcium ion electrode (Model 93-20, Orion Research, Inc., Boston, MA) and an ion meter (IM-20E, TOA Electronic, Ltd., Tokyo, Japan) were used to measure the equilibrium calcium ion concentrations. Ten milligrams of the polymer was dissolved in 50 mL of 1.00×10^{-3} M calcium hardness solution containing a 0.08 M KCl (ion strength, $\mu = 0.08$). The pH of the solution was adjusted to 9.0 at 30°C. The electrode was immersed in the solution, which was then stirred. After 10 min, equilibrium free calcium ion concentrations were measured, and the calcium sequestration capacity was expressed as grams of calcium ion sequestered by 100 g of polymer.

3 Results and Discussion

3.1 Preparation of Partially Dicarboxylated Starch

DC-starch having a varying amount of unreacted glucopyranose groups to provide enzymatically cleavable segments was prepared by the partial oxidation of corn, sago and tapioca starch using sodium periodate followed by sodium chlorite oxidation. Because high

molecular weight polymer is expected to show better builder performance¹⁵), oxidative-cleavage reaction of starch by sodium periodate was carried out at low temperature and for a shorter reaction time (6 h) in order to avoid molecular weight reduction by hydrolytic degradation. The dicarboxylation degree was controlled by the concentration of sodium periodate. Table 1 shows the typical oxidation conditions and analytical data for DC-starch.

3.2 Biodegradation of DC-starch

BOD values were measured to evaluate the potential biodegradability of the polymers using a BOD tester with an activated sludge and a test polymer concentration of 25 mg/L. It was found that the biodegradability of DC-starch was dependent on the amounts of the unreacted glucopyranose groups in the polymer. Figure 1 shows the relationship between 28d biodegradation (BOD_{28}/TOD), calculated from the BOD values and the theoretical oxygen demand (TOD), and the dicarboxylation degree. Biodegradability is dependent on the dicarboxylation degree, or the content of unreacted glucopyranose groups, showing that the unreacted glucopyranose groups act as a biodegradable segment even in the polycarboxylate chain. However, highly dicarboxylated DC-starch was practically resistant to biodegradation even though the unreacted glucopyranose groups remained in the polymer chain. This fact indicates that a definite block length of successive glucopyranose units is necessary to react with the hydrolyzing enzyme in the polycarboxylate polymer chain. Among the corn, sago and tapioca starches used in this test, a slight difference was observed in the biodegradation results when compared using the same dicarboxylation basis. The biodegradability was better in the order of DC-corn, DC-sago and DC-tapioca. A BOD/TOD value of greater than 60% is regarded to indicate readily biodegradability¹⁹). The dicarboxylation degrees of DC-corn, DC-sago and DC-tapioca showed that the 60% BOD-biodegradation values were 25%, 20% and 15%, respectively. The difference in biodegradability of these DC-starches is

Fig. 1 Biodegradability (BOD_{28}/TOD) of DC-Corn, DC-Sago and DC-Tapioca as Determined by the Biochemical Oxygen Demand (BOD) as a Function of the Dicarboxylation Degree after 28 d Incubation. Biodegradability was calculated from BOD, as measured by the oxygen consumption method in a BOD tester using polymer concentration of 25 mg/L with activated sludge at 25°C, and the theoretical oxygen demand (TOD).

Fig. 2 Molecular Weight Reduction of 400 mg/L DC-Tapioca with Dicarboxylation Degree of 8, 45 and 78 mol %, Respectively, in 0.1 M Acetate Buffer (pH 4.0 and 5.0), Phosphate Buffer (pH 6.0), Tris-HCl Buffer (pH 8.0) and Glycine-NaOH Buffer (pH 10.0) Solutions after 30 d Incubation at 30 °C in the Dark.

probably ascribed to the microstructure of amylopectin in the starches. When compared to the dicarboxylated amylopectin from waxy corn as reported in the previous report¹⁷⁾, the dicarboxylation degree of 17 mol% showed 60% BOD-biodegradation.

3.3 Hydrolytic Degradation

The non-enzymatic hydrolytic degradability of DC-starch was evaluated in aqueous solutions of different pH values in sterile condition. **Figure 2** shows the correlation between the dicarboxylation degree of DC-tapioca, as a typical of DC-starch, and the molecular weight reduction which is caused by the hydrolytic cleavage after 30d incubation in various pH buffer solutions. It was confirmed that DC-tapioca was quite stable against hydrolytic degradation under neutral and alkaline conditions after 10 d incubation at 30°C. However, after 30d incubation DC-tapioca tended to be degraded slightly under acidic conditions of pH below 6, and DC-tapioca with a higher dicarboxylation degree of 78% was more labile to hydrolytic degradation. These results indicate that the hydrolytic cleavage predominantly occurred at the acetal linkages of the dicarboxylated moieties other than the unreacted sugar moieties. Similar tendencies were observed for DC-corn and DC-sago, and among the DC-starches no significant difference in non-enzymatic degradation was observed. These results indicate that DC-starch is stable under washing conditions at a pH value of about 9²²⁾. We previously reported that dicarboxylated alginic acid with a dicarboxylation degree of more than 42 mol% showed significant molecular weight reduction at pH values below 8²³⁾. It was also confirmed that DC-starch was much stable than dicarboxylated alginic acid against the hydrolytic stability. The difference in hydrolytic stability of DC-starch and dicarboxylated alginic acid will be ascribed to the carboxyl groups at the C6 position of alginic acid.

3.4 Builder performance in detergent formulation

Polymeric carboxylates have been investigated as STPP substitutes and a number of polycarboxylates have been reported to give excellent builder performance in detergent formulations^{1),5),9),17)}. The builder performance of DC-starch was evaluated on an equal weight basis in a heavy-duty detergent formulation on standard soiled cotton cloth samples. The detergency, expressed as a value relative to 10 for STPP and 0 for ODA, is shown in **Fig. 3** as a

Fig. 3 Relative Detergency of DC-Starch Based on a Value of 10 for Sodium Tripolyphosphate (STPP) and 0 for Disodium 3-Oxapentanedioate (ODA).

Fig. 4 Calcium Ion Sequestration Capacity of DC-Starch as a Function of the Dicarboxylation Degree.

Calcium ion sequestration capacities of STPP and ODA were 18.2 and 13.9, respectively.

function of the dicarboxylation degree of the DC-starch. It was found that the detergency was dependent on the content of the carboxylate groups in the polymer, and a clear relationship between detergency and the carboxylate group content was seen when compared on an equal weight basis. The polymers with high carboxylate contents showed better builder performance. Among the corn, sago and tapioca starches used in this test, no significant difference was observed in the detergency test. However, a slight decrease in detergency was observed compared to that of dicarboxyamylpectin¹⁷⁾. Dicarboxyamyllose from potato showed results similar to those of DC-starches⁵⁾.

Calcium ion sequestration capacity is an indispensable property for a detergent builder. **Figure 4** shows the calcium ion sequestration capacity of DC-starch as a function of dicarboxylation degree. DC-starch with a high dicarboxylation degree showed good calcium ion sequestration capacity. A correlation between the sequestration capacity for calcium ion and the resulting detergency performance was demonstrated based on these data. DC-starches in this test and dicarboxyamyllose from potato showed similar calcium sequestration capacities⁵⁾.

4 Conclusion

Partially dicarboxylated starch sodium salt (DC-starch) from corn, sago and tapioca that contained unreacted glucopyranose groups was biodegraded according to the dicarboxylation degree or the content of the unreacted glycopyranose groups. DC-starch containing more than about 75~85 mol% unreacted glucopyranose groups in the polymer chain showed excellent biodegradation. DC-starch with a high dicarboxylation degree was resistant to biodegradation but showed good builder performance in detergent formulation. DC-starch was quite stable under neutral and slight alkaline conditions. Among DC-starches from corn, sago and tapioca starch, no significant difference in hydrolytic degradability and builder performance in detergent formulation was observed.

Acknowledgment

We wish to thank Dr. Yutaka Tokiwa, National Institute of Bioscience and Human-Technology, MITI, Japan, for the stimulating discussions and supplying corn, sago and tapioca starches.

(Received : Feb. 13, 1996, Accepted : May 24, 1996)

References

- 1) M.M. Crutchfield, *J. Am. Oil Chem. Soc.*, **55**, 58 (1978).
- 2) S. Matsumura, S. Yoshikawa, *Biodegradable Poly(carboxylic acid) Design*, ACS Symposium Series, American Chemical Society, **433**, 124 (1990).
- 3) M.B. Freeman, T.M. Bender, *Environ. Technol.*, **14**, 101 (1993).
- 4) S. Matsumura, M. Nishioka, S. Yoshikawa, *Makromol. Chem., Rapid Commun.*, **12**, 89 (1991).
- 5) S. Matsumura, M. Nishioka, H. Shigeno, T. Tanaka, S. Yoshikawa, *Angew. Makromol. Chem.*, **205**, 117 (1993).
- 6) S. Matsumura in R. Yamamoto *et al.* (Eds.), *Adv. Mat. '93, V/A : Ecomaterials, Trans. Mat. Res. Soc. Jpn.*, **18A**, 451 (1994).
- 7) S. Matsumura, *J. Synth. Org. Chem. Jpn.*, **50**, 292 (1992).
- 8) G. Swift, *J. Macromol. Sci. -Pure Appl. Chem.*, **A 32** (4), 641 (1995).
- 9) S. Matsumura, K. Amaya, S. Yoshikawa, *J. Environ. Polym. Degrad.*, **1**, 23 (1993).
- 10) J.R. Daniel, A.C.J. Voragen, W. Pilnik, *Starch and Polysaccharide*, in *Ullman's Encyclopedia of Industrial Chemistry*, **A25**, 1 (1994).
- 11) B.T. Hofreiter, I.A. Wolff, C.L. Mehlretter, *U.S. Pat.* 2 894 945 (1959).
- 12) C.A. Wilham, T.A. McGuire, A.M. Mark, C.L. Mehlretter, *J. Am. Oil Chem. Soc.*, **47**, 522 (1970).
- 13) M.S. Nieuwenhuizen, A.P.G. Kieboom, H. van Bekkum, *Starch*, **37**, 192 (1985).

- 14) M. Floor, L.P.M. Hofsteede, W.P.T. Groenland, L.A. Th. Verhaar, A.P.G. Kieboom, H. van Bakkum, *Recl. Trav. Chim. Pays-Bas*, **108**, 384 (1989).
 - 15) Y. Dannoue, S. Matsumura, *J. Jpn. Oil Chem. Soc.*, **42**, 899 (1993).
 - 16) S. Matsumura, R. Kobayashi, S. Yoshikawa, *J. Jpn. Oil Chem. Soc.*, **40**, 73 (1991).
 - 17) S. Matsumura, K. Aoki, K. Toshima, *J. Am. Oil Chem. Soc.*, **71**, 749 (1994).
 - 18) S.M. Neale, W.A. Springfellow, *Trans. Faraday Soc.*, **33**, 881 (1937).
 - 19) OECD Guidelines for Testing of Chemicals, 301C, Modified MITI Test, Organization for Economic Cooperation and Development (OECD), Paris (1981).
 - 20) O. Okumura, T. Tokuyama, T. Sakatani, Y. Tsuruta, *J. Jpn. Oil Chem. Soc.*, **30**, 432 (1981).
 - 21) P. Kubelka, *Z. Tech. Physik.*, **12**, 539 (1931).
 - 22) M.S. Nieuwenhuizen, A.P.G. Kieboom, H. van Bakkum, *J. Am. Oil Chem. Soc.*, **60**, 44 (1983).
 - 23) I. Winursito, S. Matsumura, *J. Environ. Polym. Degrad.*, **4**, 113 (1996).
-

日本油化学会誌本号掲載 論文要旨

[総説]

機能性タンパク質の配向制御

小山 行一

新技術事業団「さきがけ研究 21」

(〒300-26 つくば市東光台 5-9-4 筑波研究コンソーシアム)

機能性タンパク質の人為的配向制御は将来のバイオデバイス開発に必要な不可欠な技術である。本報告では、まずこれまで試みてこられた感光性タンパク質の一般的な配向制御技術を概観した後、バクテリオロドプシンというきわめて安定なタンパク質を BS 抗体という一分子に 2 種の異なった結合サイトを有する特殊な抗体を用いて配向を制御したわれわれの結果を紹介し、さらに免疫電顕法による配向状態を解析する手段についても述べる。

(連絡者：小山行一) Vol. 45, No. 8, 715 (1996).

[報文]

熱帯植物由来のデンプンをベースにしたポリカルボン酸塩の
生分解性、加水分解性及びビルダー性能

Isananto WINURSITO・松村 秀一

慶應義塾大学 理工学部

(〒223 横浜市港北区日吉 3-14-1)

部分的ジカルボキシル化多糖をコーン、サゴ及びタピオカデンプンより合成し、それらの生分解性、加水分解性及び洗剤配合物中でのビルダー性能について比較を行った。ジカルボキシル化デンプンナトリウム塩 (DC-starch) の生分解性はジカルボキシル化度に依存した。約 75-85 mol% 以上の未反応グルコピラノース部分をポリマー鎖中に有する DC-starch は優れた生分解性を示した。一方、ジカルボキシル化度の高い DC-starch は生分解性に劣ったが、洗剤組成物中で優れたビルダー性能を示した。コーン、サゴ及びタピオカデンプンから得られた DC-starch の中では、加水分解性及びビルダー性能に顕著な差異は認められなかった。

(連絡者：松村秀一) Vol. 45, No. 8, 723 (1996).

[報文]

ヒル, *Hirudo nipponia* における Gal α 1-6 Gal 及び
Gal β 1-6 Gal 構造を有するスフィンゴ糖脂質杉田 陸海^{*1}・森川 亜紀^{*1,*3}・John T. Dulaney^{*2}・岡田 亜希子^{*1}^{*1} 滋賀大学教育学部化学教室 (〒520 滋賀県大津市平津 2-5-1)^{*2} テネシー大学医学部腎臓学教室 (951 Court Avenue, 649 D Memphis, TN 38163, USA)^{*3} 現住所 日本医学臨床検査所バイオアッセイ事業部 (〒677 兵庫県西脇市中畑町 17-18)

チスイビル, *Hirudo nipponia* (環形動物, ヒル綱) の中性糖脂質には微量ながらグルコ及びガラクトセブロシド (NGL₁) も存在するが、主要成分は Gal α 1-6 Gal β 1-1 Cer (NGL₂), Gal α 1-6 Gal α 1-6 Gal β 1-1 Cer (NGL₃), Gal α 1-6 Gal α 1-6 Gal α 1-6 Gal β 1-1 Cer (NGL₄) の gala-6 系糖脂質である。これらの糖鎖構造は、アノマー配置において、今までに他の環形動物から見いだしている neogala 系列 (Gal β 1-6 Gal) とは異なっており, isoneogala 系列 (Gal α 1-6 Gal) と称することができよう。一方、現在のところ環形動物を特色づ