Pergamon

*Tetrahedron: Asymmetry* Vol. 5, No. 12, pp. 2475-2484, 1994
Elsevier Science Ltd
Printed in Great Britain
0957-4166/94 $7.00+0.00

0957-4166(94)00325-4

# Methyl α-D-fructofuranoside: Synthesis and Conversion into Carboxylates

**Louise Johnson, Dorine L. Verraest, Jacco van Haveren, Kimmo Hakala, Joop A. Peters and Herman van Bekkum**

Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

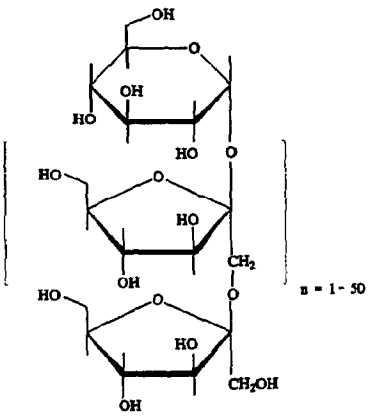
**Abstract:** Methyl α-D-fructofuranoside was synthesized by methylation of D-fructose and subsequent isolation of the α-furanoside from the anomeric mixture. This fructofuranoside was used as a starting material for the syntheses of several carboxylates, applying glycolic oxidation, selective oxidation of the primary alcohol function at the C-6 position and carboxymethylation.

## INTRODUCTION

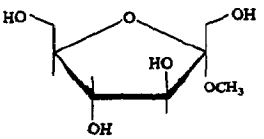
Methyl α-D-fructofuranoside is a 2-O-protected fructoside and therefore exists in a stable anomeric configuration in aqueous solution. Owing to its enantiomeric purity, this compound is an interesting starting material in the syntheses of chiral compounds, *e.g.* by selective oxidation.

In addition, methyl α-D-fructofuranoside is a useful model compound for inulin, a ß-D-(2→1)-fructan with a D-glucose unit at the reducing end (Fig. 1). Conversion of inulin into industrially relevant products such as polycarboxylates, has become of increasing interest. These polycarboxylates have many potential applications, for example as calcium sequestering agents, metal ion carriers and dispersing agents. The analysis and understanding of inulin-derived polycarboxylates are non-trivial (degree of polymerization (DP) 2-50) and therefore methyl α-D-fructofuranoside, a molecule which represents the basic unit of the inulin chain (Fig. 1), was used as a model compound. In this way it was possible to study potential reactions, characterize products and study the Ca(II)-coordination behaviour of the reaction products.

Here we report the isolation of methyl α-D-fructofuranoside from an anomeric mixture which had been synthesized by catalytic methylation of D-fructose. Conversion of methyl α-D-fructofuranoside into a carboxylate was achieved in three ways: glycolic oxidation; oxidation of the primary alcohol functions and carboxymethylation.




(a)




(b)

*Figure 1.* Inulin (a); methyl α-D-fructofuranoside (b)

## RESULTS AND DISCUSSION

### Synthesis and isolation of Methyl α-D-fructofuranoside

Silica-alumina cracking catalysts provide a facile means to obtaining 2-O-alkyl fructosides from alcohols and fructose without the formation of hydroxymethylfurfural.[1] This method served to convert D-fructose into a mixture of methyl fructoside anomers. Methyl fructofuranosides are the kinetically favoured products but an equilibrium between the furanosides and pyranosides establishes itself if the reaction is allowed to proceed for a longer period of time. In order to achieve optimal conversion it was necessary to use a large excess of the alcohol as well as to ensure the removal of water formed (to prevent deactivation of the catalyst). Less than 3% of the fructose remained unconverted and $^{13}C$ NMR measurements allowed for estimation of the anomeric mixture composition: methyl α-D-furanoside (49%), methyl ß-D-furanoside (14%) and methyl ß-D-pyranoside (34%).[2]

The ß-D-furanoside form was removed by selective hydrolysis accomplished by the addition of an enzyme, Novozym 230, an inulinase which reacts in a similar way to invertase. Residual fructose present was subsequently fermented with yeast leaving a mixture of two anomers, *i.e.* methyl α-D-fructofuranoside and methyl ß-D-fructopyranoside (1:0.85).

Separation of these anomers was carried out on a 20 g scale using anion exchange chromatography and eluting with water according to the method of Matsushima and Miyazaki.[3] Methyl α-D-fructofuranoside and methyl ß-D-fructopyranoside were obtained as syrups and their purity was confirmed by HPLC and $^{13}C$ NMR measurements.

### Oxidative glycol cleavage of methyl α-D-fructofuranoside

Conversion of inulin into 3,4-dicarboxy inulin with NaOCl/$Br^-$ as the oxidant system has been previously reported by *Besemer et al.*[4] Initial experiments using this method to oxidize methyl α-D-fructofuranoside were not promising since oxidation byproducts as well as a relatively large amount of NaCl were formed. Purification proved to be difficult and therefore other oxidation methods were

sought. The oxidative glycol cleavage of sucrose to form an open chain tetraldehyde with $NaIO_4$ had been previously studied in our laboratory[5] and in an analogous reaction, methyl α-D-fructfuranoside was converted into the dialdehyde using $NaIO_4$ (1.1 mol equiv). The pH of the reaction solution was maintained at 5 to avoid periodate-assisted hydrolysis of the furanoside and was raised to 7 at the end of the reaction in order to hydrolyse internal hemiacetals present.[6] Ionic species were removed by precipitation and by treatment with a mixed-bed ion exchange resin. The dialdehyde was obtained by lyophilization (87%).

The dialdehyde was oxidized further (Fig. 2) with sodium chlorite (2 equiv.) and hydrogen peroxide (2 equiv.). The pH during the reaction was maintained at 4.5 and raised to 9 at the end of the reaction. The dicarboxy sodium salt thus obtained, was determined by quantitative $^{13}C$ NMR to be 86% pure, the remainder being inorganic salts.[7] This compound exhibits metal ion sequestering properties which will be reported elsewhere.[8]

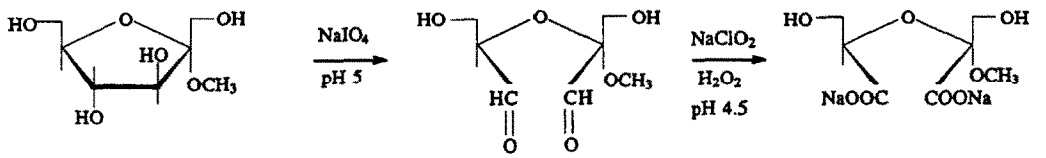



*Figure 2.* Reaction scheme for the oxidative glycol cleavage of methyl α-D-fructofuranoside.

**Pt-Catalyzed oxidation of methyl α-D-fructofuranoside**

Noble metal catalyzed oxidation using oxygen as the oxidant is a clean method for primary alcohol oxidation of carbohydrates, [9,10,11,12] and may also be applied to inulin[13]. In this study, methyl α-D-fructofuranoside was oxidized with oxygen as the oxidant and Pt on activated carbon (5%) as the catalyst at 60°C and pH = 9. A partial oxygen pressure $p(O_2)$ of 0.2 bar was applied. The oxidation was followed by monitoring the hydroxide and oxygen consumption with time. The decrease in substrate concentration and the formation of products was followed by HPLC analysis. A typical curve is presented in Fig. 3.

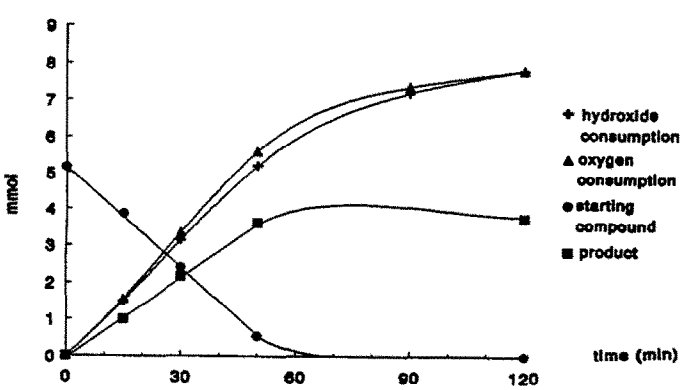



*Figure 3.* Conversion of methyl α-D-fructofuranoside into 6-oxidized methyl α-D-fructofuranoside during a Pt-catalyzed oxidation at 60°C and pH=9.

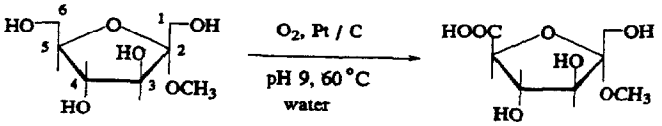



*Figure 4.* Oxidation on the C-6 position of methyl α-D-fructofuranoside.

The main oxidation product was 6-oxidized methyl α-D-fructofuranoside (Fig. 4) as established with $^{13}C$ NMR spectroscopy. The conversion of the starting compound was complete after 70 min of oxidation. At this stage the amount of 6-oxidized methyl α-D-fructofuranoside had reached a maximum (yield: 80 %). When the oxidation was continued, the oxygen and hydroxide consumption proceeded at a lower rate and the amount of 6-oxidized methyl fructoside decreased slowly. After 2 hours of reaction, the yield of 6-oxidized methyl α-D-fructofuranoside was 73 %. Using anion exchange chromatography, the product was isolated as the ammonium salt (purity: 91 %).

The oxidation is thus selective for the primary alcohol function at the C-6 position in the furanoside. Side reactions (oxidation of other positions in the furanose ring, degradation reactions) occur at a lower rate of reaction. Owing to these side reactions, the hydroxide and oxygen consumption during the oxidation was higher than predicted from the amount of 6-oxidized methyl fructoside formed (Fig. 3). A small amount of side products was detected with $^{13}C$ NMR spectroscopy, which are assumed to be a result of the oxidation of the C-1 primary alcohol function and/or oxidation of the secondary alcohol functions, possibly followed by C-C bond splitting. The main side product was carbonate ($^{13}C$ NMR: $\delta = 164$ ppm) which is formed upon decarboxylation of oxidation products and complete degradation of the fructose moiety.

When D-fructose was oxidized under the same conditions, the selectivity for C-6 oxidation was low and degradation to small organic acids such as carbonate, oxalate, glyceric acid and glycolate predominated. Apparently the 2-O-methyl group in methyl α-D-fructofuranoside plays a protecting role for the oxidation of the other alcohol functions in the furanose ring. Further enhancement in selectivity might be achieved by enlarging the 2-O-alkyl group, as was observed with the 1-O-alkyl glucosides.[10,14]

Acid hydrolysis of the 6-oxidized methyl α-D-fructofuranoside yielded D-fructuronic acid (D-*lyxo*-5-hexulosonic acid)[15,16] and methanol, as confirmed with $^{13}C$ NMR spectroscopy. In the literature[16,17], D-*lyxo*-5-hexulosonic acid was prepared by isomerisation of glucuronic acid (pH 7, 110°C), which yields a complex mixture of acids from which D-*lyxo*-5-hexulosonic acid was isolated via an ion exchange chromatography procedure. The Pt-catalyzed oxidation of methyl α-D-fructofuranoside followed by acid hydrolysis provides a new simple route for the synthesis of D-fructuronic acid.

**Carboxymethylation of methyl α-D-fructofuranoside**

The carboxymethylation of polysaccharides is a well-known derivation process, yielding polyelectrolytes which may be applied in a wide variety of fields. Inulin has been carboxymethylated in aqueous alkaline medium[18] and the product was found to exhibit excellent calcium carbonate crystallization inhibition properties.[19]

Methyl α-D-fructofuranoside was carboxymethylated by heating an aqueous solution at 75°C for 5 h with monochloroacetate and sodium hydroxide (Fig. 5). There is competition between the carboxymethylation and the hydrolysis of monochloroacetate into glycolate during carboxymethylation reactions in aqueous medium. This side reaction can be reduced by using concentrated reaction mixtures (low water content).[18]

The carboxymethylation reactions were monitored by taking samples of the reaction mixture at regular time intervals and analyzing them by HPLC. Fig. 6 illustrates the conversion with time of methyl α-D-fructofuranoside (20 mmol) reacting with monochloroacetate and sodium hydroxide (1:1:1.1) in a reaction volume of 10 ml. Under these conditions, the conversion of monochloroacetate was 94 % after 5 hours reaction time. Mono- and disubstituted methyl fructofuranosides were found as reaction products. The selectivity towards carboxymethyl fructoside was high (80 %) due to the relatively low water content.

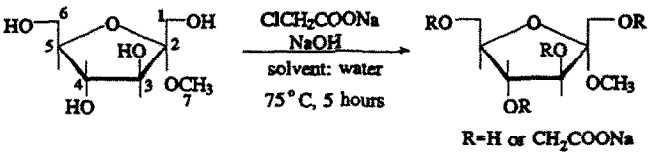



*Figure 5.* Carboxymethylation of methyl α-D-fructofuranoside.

The reaction mixture was separated by chromatography over an anion-exchange resin (in the carbonate form) in order to study the distribution of substituents in the carboxymethylated fructofuranosides. The column was first eluted with water to remove the apolar starting material and subsequently with 0.5 M ammonium carbonate. Fractions were collected and analyzed using HPLC and $^{13}C$ NMR spectroscopy. The first 50 ml of ammonium carbonate eluent contained monosubstituted methyl fructosides and glycolate. The $^{13}C$ NMR spectrum showed the presence of four different monocarboxymethylated methyl fructosides in approximately equal amounts. All four free hydroxyl groups in methyl α-D-fructofuranoside thus undergo carboxymethylation which implies that the carboxymethylation of methyl α-D-fructofuranoside is not selective with respect to position. The second fraction (50 ml) of the eluent contained a mixture of mono- and disubstituted fructosides and was not further investigated. The third fraction (50 ml) contained dicarboxymethylated methyl fructosides as was confirmed with HPLC and $^{13}C$ NMR spectroscopy. The spectrum was complicated showing six different products, this being additional confirmation for the non-selectivity of the carboxymethylation. These results are in contrast with those obtained for the carboxymethylation of inulin[13] where some selectivity (± 50 %) was found for the C-4 position in the furanose ring. We tentatively conclude that steric effects in the inulin oligosaccharides play a role in the selectivity of the carboxymethylation.

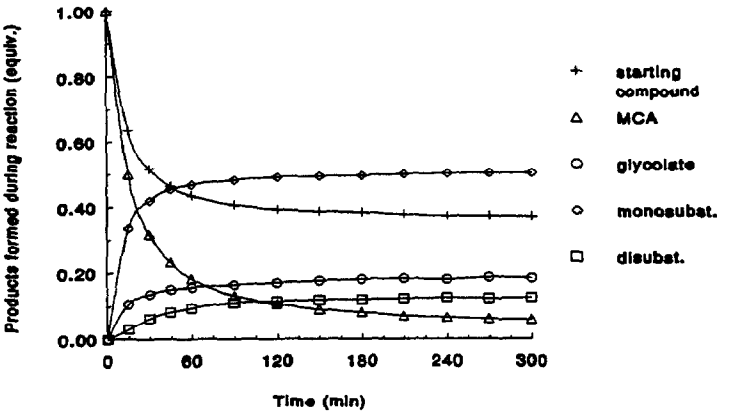



*Figure 6.* Conversion of methyl α-D-fructofuranoside (20 mmol) in a carboxymethylation reaction with monochloroacetate and NaOH (molar ratio 1:1:1.1) dissolved in 10 ml water at 75°C.

## EXPERIMENTAL SECTION

### Analytical Methods.

*HPLC Analysis.* HPLC analysis of methyl fructosides: column: Millipore-Waters, Nova-pak C18, 8 mm i.d. × 100 mm, 4 μ; eluent: water; flow rate: 1.0 ml/min; RI and $UV_{220}$ detection.
HPLC analysis of the carboxylates: Phenomenex, Rezex Organic Acid, 7.8 mm i.d. × 300 mm; eluent: 0.01 M trifluoroacetic acid; 60°C; flow rate: 0.6 ml/min; RI and $UV_{215}$ detection. The products were identified by HPLC-MS analysis using the same colunm and conditions. In this case the HPLC system was coupled to a VG 70-SE mass spectrometer.

*$^{13}C$ NMR Spectroscopy.* $^{13}C$ NMR spectra were recorded on a Nicolet NT-200 WB and a Varian VXR-400 S spectrometer using $D_2O$ as solvent and *tert*-butanol as internal standard. Quantitative $^{13}C$ NMR spectra were recorded with a 45° flip angle, an acquisition delay of 30 s, 32K datapoints and $^1H$ decoupling during the acquisition only.

Thin layer chromatography was carried out using silica gel plates (60F254 Merck) which were eluted with $CH_3OH$ or $CH_2Cl_2$:$CH_3OH$ (5:95 v/v). The plates were subsequently sprayed with a 5% ammonium molybdate/4 N $H_2SO_4$ solution and developed by charring.

### Synthesis of Methyl Fructosides

D(-)-fructose (50 g, 278 mmol) and a silica-alumina cracking catalyst (50 g, Ketjencat HA-SHPV, high alumina, super high pore volume, donated by Akzo Nobel Chemicals bv., activated at 430°C for 24 h) were refluxed with methanol (± 1200 ml, ± 100 eq)(predried with zeolite KA). The reflux was carried out for 7-8 hours with a Soxhlet attachment containing zeolite KA, typically there was >97% conversion of fructose. At the end of the reaction, the catalyst was filtered off and washed with methanol and the reaction solution evaporated *in vacuo* at 60°C (53.5g, 99%).[1]

$^{13}C$ NMR (pH = 7) measurements of the mixture revealed the composition of the reaction mixture to be as follows: methyl α-D-fructofuranoside (49%): δ (ppm) C1: 59.22, C2: 109.85, C3: 81.65, C4: 79.01, C5: 84.91, C6: 62.87, C7: 49.75; methyl ß-D-fructofuranoside (14%): δ (ppm) C1: 61.22, C2: 105.22, C3: 78.31, C4: 76.49, C5: 82.76, C6: 64.17, C7: 50.35; methyl ß-D-fructopyranoside (34%): δ (ppm) C1: 62.87, C2: 101.9, C3: 69.15, C4: 71.29, C5: 70.80, C6: 65.48, C7: 49.78; fructose (<3%): δ (ppm) C1: 65.45, C2: 99.61, C3: 69.12, C4: 71.28, C5: 70.78, C6: 64.88.[2]

Novozym 230 (1.5 ml) was added to the methyl fructoside mixture (53.5 g, 276 mmol) and after standing overnight, the enzyme was removed by filtration. As the next step, yeast (12.5 g, Sigma Bakers yeast type II) was added and the mixture allowed to stand overnight. This was then filtered with Norit over Hyflo and evaporated under reduced pressure. A yellow syrup (40g, 74%) was obtained and subjected to HPLC and $^{13}C$ NMR analysis. HPLC retention times and $^{13}C$ chemical shifts indicated the presence of two anomers *ie.* methyl α-D-fructofuranoside and methyl ß-D-fructopyranoside (1:0.85).

Separation was carried out using anion exchange column chromatography (300 ml of Dowex 1X8-200 Janssen, $OH^-$ form, column 4 cm diameter, 42 cm length) and eluting with water.[3] The course of the separation was followed using TLC and the pyranose form eluted first. Typically, a sample of the mixture of two anomers (20 g, 103 mmol) yielded 7 g (36 mmol) and 8 g (41 mmol) of methyl ß-D-fructopyranoside and methyl α-D-fructofuranoside, respectively. After evaporation of the fractions under reduced pressure, the anomeric content was checked with TLC and the purity was confirmed using HPLC and $^{13}C$ NMR spectroscopy.

**Glycolic oxidation of methyl α-fructofuranoside**

Sodium metaperiodate (4.6 g, 21.5 mmol) was slowly added to an aqueous solution (60 ml) of methyl α-D-fructofuranoside (3.8 g, 19.6 mmol) in the absence of light at room temperature. The pH was maintained at 5 by incremental additions of 1N NaOH from an automatic burette (Metrohm Dosimat 665) linked to a pH meter (Metrohm 632) and Impulsomat (Metrohm 614). At the end of the reaction the pH was raised to 7 and temperature to 50 $^{o}C$ for a period of 20 minutes. The reaction solution was cooled at 3 $^{o}C$ for 24 hours, whereupon precipitated $NaIO_3$ was filtered off and the filtrate treated with a mixed bed ion-exchange resin (45 g, Biorad AG 501-X8). After lyophilization, the dialdehyde hydrate was obtained as a sticky white precipitate (3.9 g, 17.1 mmol)(87%).[5]

An aqueous solution of sodium chlorite (technical grade, 80%) (4.04 g, 35.7 mmol) and acetic acid (1.03 g, 17.2 mmol) was added dropwise to an aqueous solution of the dialdehyde (3.9 g, 17.1 mmol), hydrogen peroxide (3.88g of a 35 % solution, 39.9 mmol) and EDTA (disodium salt) (0.084g). The oxidation was carried out over a 5 hour period at room temperature and pH 4.5 (maintained in the same way as described in the preparation of the dialdehyde). At the end of the reaction the pH was raised to 9 after which the reaction solution was evaporated under reduced pressure to approximately 50 ml. An excess of ethanol was added and the resulting viscous precipitate centrifuged. This centrifuged precipitate was washed twice with 30 ml of a water-ethanol solution (20:80, v/v) and then dissolved in water and lyophilized to yield the dicarboxy methyl α-D-fructofuranoside disodium salt (2.0 g) (38%).[5,7] This compound was determined by quantitative $^{13}C$ NMR to be 86% pure with respect to the dicarboxy

salt. The remainder is ascribed to the presence of inorganic salts formed as a result of the oxidation. $^{13}C$ NMR (pH = 7): $\delta$ (ppm) C1: 63.44, C2: 104.57, C3: 179.22; C4: 175.50, C5: 75.99, C6: 65.10; C7: 53.12.

**Oxidation with Pt on activated carbon as catalyst.**

The oxidation set-up consisted of a glass batch reactor (200 ml) equipped with a gastight stirrer (1500 rpm) and a thermostat (60°C). During the reaction the pH was kept constant automatically using a pH meter (Metrohm 654), coupled to a pH controller (Metrohm 614 Impulsomat) and a motor burette (Metrohm 655 dosimat) containing a 1 M sodium hydroxide solution. The oxygen pressure in the reactor was kept constant with an automatic oxygen supply system. The oxygen and hydroxide consumption were monitored during the reaction.

The catalyst (5% Pt on activated carbon, Janssen Chimica, 500 mg) was introduced into the reactor together with 50 ml of water. The reactor was flushed with nitrogen for 5 min to remove oxygen from the catalyst, with hydrogen for 30 min to activate the catalyst and then again with nitrogen for 5 min. The substrate, methyl α-D-fructofuranoside (1.00 g) dissolved in 30 ml water, was added to the reactor and the reaction was started by increasing the oxygen partial pressure to 0.20 bar and adjusting the pH to 9.00. Samples were withdrawn from the reaction mixture at regular time intervals. After centrifuging to remove the catalyst, 500 μl of a solution of monochloroacetic acid (10 mg/ml) was added as internal standard to 500 μl of the sample. The samples were analyzed by HPLC.

**Isolation of the 6-oxidized methyl α-D-fructofuranoside**

A column (20 x 130 mm) was packed with an anion-exchange resin (Dowex 1X8-200, 40 ml) in the carbonate form. The reaction mixture obtained from the Pt catalyzed oxidation of methyl α-D-fructofuranoside was concentrated and injected on the column. The column was eluted with 0.5 M ammonium carbonate. Fractions of 25 ml were collected and analyzed using HPLC and $^{13}C$ NMR spectroscopy. The 6-oxidized methyl α-D-fructofuranoside which eluted in the first four fractions, was isolated as the ammonium salt: $^{13}C$ NMR (pH = 7.0): $\delta$ (ppm) C1: 59.0; C2: 110.3; C3, C4, C5: 84.5, 82.2, 81.2; C6: 178.8; C7: 49.8.

**Hydrolysis of 6-oxidized methyl α-D-fructofuranoside.**

The oxidized methyl α-D-fructofuranoside (100 mg in 10 ml water) was hydrolyzed under mildly acidic conditions. The pH was adjusted to 1.5 using a 1M HCl solution and the solution was heated at 75°C for 1 hour. The product was a mixture of the α-furanose (25 %) and the ß-furanose form (75 %) of D-fructuronic acid (D-*lyxo*-5-hexulosonic acid): $^{13}C$ NMR (pH = 7.0): α-furanose form: $\delta$ (ppm) C1: 64.4; C2: 106.7; C3, C4, C5: 83.1, 82.8, 81.0; C6: 179.1; ß-furanose form: $\delta$ (ppm) C1: 64.4; C2: 103.9; C3, C4, C5: 82.0, 79.4, 77.4; C6: 179.8.

**Carboxymethylation.**

In a 50 ml round-bottom vessel methyl α-D-fructofuranoside (1.94 g, 10 mmol) was dissolved in water and sodium monochloroacetate and sodium hydroxide were added in a molar ratio of 1:1.1. The solution was heated at 75°C and stirred magnetically for 5 hours. The reaction was monitored by taking samples of the reaction mixture at regular time intervals and by analyzing them with HPLC.

**Separation of carboxymethylated methyl α-D-fructofuranosides by ion exchange chromatography.**

The reaction mixture obtained from the carboxymethylation reaction (± 3 g) was concentrated and injected onto a column (20 x 130 mm) containing 40 ml of an anion-exchange resin (Dowex 1X8-200 in the carbonate form). The column was eluted firstly with 150 ml of water and subsequently with 0.5 M ammonium carbonate. Fractions of 50 ml were collected and analyzed using HPLC and $^{13}C$ NMR spectroscopy.

## ACKNOWLEDGEMENTS

This research was financially supported by the European Commission (AIR program) and the Ministry of Agriculture, Nature Management and Fisheries (program on the oxidation of carbohydrates for agrification purposes).

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(*Received* 3 *October* 1994)