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(57) **Abrégé/Abstract:**

The invention relates to a chromatographic separation process of recovering mannose with high purity. The invention is based on the use of a chromatographic separation resin including a resin which is at least partly in a Ba²⁺ form resin and a resin which is in other than Ba²⁺ form.



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(54) Title: METHOD FOR THE RECOVERY OF SUGARS

(57) Abstract: The invention relates to a chromatographic separation process of recovering mannose with high purity. The invention is based on the use of a chromatographic separation resin including a resin which is at least partly in a Ba²⁺ form resin and a resin which is in other than Ba²⁺ form.



WO 03/056038 A1

METHOD FOR THE RECOVERY OF SUGARS

BACKGROUND OF THE INVENTION

The present invention relates to a chromatographic separation method of separating carbohydrates, especially sugars, from a mixture including the same. The mixture to be treated in accordance with the present invention is typically a biomass-derived solution including carbohydrates/sugars. Especially, the invention provides a chromatographic separation method of recovering mannose with high purity from biomass-derived solutions, such as spent sulphite pulping liquors. Mannose can be recovered in a crystalline form or in the form of a solution. The claimed process of recovering mannose is based on the use of a combination of a Ba^{2+} form resin and a resin in other than Ba^{2+} form as the separation resin, whereafter mannose is crystallized, if desired. In connection with the separation process of the invention, xylose and arabinose products can also be obtained as by-products, depending on the composition of the starting biomass-derived solution.

Mannose is useful e.g. for various pharmaceutical applications. It can be used as a starting material or raw material for various pharmaceutical products. Mannose is also therapeutically useful in the treatment of urine infections and intravenous inflammation conditions. In food technology, mannose is useful e.g. for so-called Positech™ applications (GMO-testing of food products).

Mannose is also useful as the raw material for the production of mannitol, which has various pharmaceutical applications.

Mannose can be recovered from wood resources, where mannose is present as a mixture with other carbohydrates and lignin components. In wood and other plant-based material, mannose typically occurs in polymeric form, such as hemicellulose, most frequently as a heteropolymer with glucose and/or galactose in glucomannans, galactoglucomannans and galactomannans. Spent liquors obtained from conifer wood-pulping processes are especially rich in mannose. Mannose has also been recovered from vegetable ivory nuts and specific seaweeds.

The recovery of mannose with high purity from plant-based material has presented a problem in the state of the art.

Jones, J.K.N & Wall, R.A. (Canadian Journal of Organic Chemistry 38 (1960), pp. 2290 to 2294) have described a process for the separation of sugars from synthetic sugar mixtures and plant extracts using ion-exchange resins. The process relates to the separation of monosaccharide mixtures, including D-mannose and D-mannitol, using neutral salt forms of sulphonic acid type ion-exchange resins. The resin Dowex™ 50W X8 in Ba²⁺ form has been used as the separation resin.

Larsson, L.I & Samuelsson, O. (Acta Chemica Scandinavica 19 (1965), pp. 1357 to 1364) describe an automatic procedure for the separation of monosaccharides present in wood hydrolysates using ion exchange resins. The separation of 16 monosaccharides, including D-mannose, has been studied by partition chromatography on strongly basic anion exchange resins in the sulphate form using ethanol as the eluant.

Furthermore, the utilization of ion exchangers for the isolation of monosaccharides has been studied with the aim to examine the behaviour of sugars on columns containing a bisulfite saturated resin. For example, an anion exchanger (Amberlite™ IRA-400) in the bisulphite form has been used to separate fructose, glucose and mannose. As a practical result of this study, an improved method for the determination of reducing sugars in sulphite waste liquor is proposed.

The interactions occurring between aluminium oxide and aqueous solutions of monosaccharides, including D-mannose have also been studied. It is suggested that by proper choice of alumina, separation of sugars can be easily and quickly achieved on a preparative as well as analytical scale.

It is also known to recover mannose from various sources through mannose derivatives. Fujita, T & Sato, T in Bull. Chem. Soc. Japan 33 (1960) 353 disclose the recovery of D-mannose through N-phenyl-D-mannopyranosylamine. It is recited that N-phenyl-D-mannopyranosylamine is so stable and insoluble in water that it was recommended for the isolation of D-mannose even from very impure raw materials.

Herrick, F.W., Casebier, R.L., Hamilton, J.K. & Wilson, J.D. ("Mannose chemicals", Applied Polymer Symposium No. 28 (1975), pp. 93 to 108) disclose a study relating to the development of an economic process for recovering mannose or its derivatives from wood resources, such as a spent sulphite liquor, where mannose is a major component of mixtures containing other carbohydrates and lignin fragments. The main achievement of this work

was the development of processes for recovering sodium mannose bisulphite and methyl mannoside from several raw materials. Processes were developed for recovering mannose from crude mixtures via two routes: (1) formation of the sodium bisulphite adducts of monomeric wood sugar mixtures, crystalliza-
5 tion and separation of sodium mannose bisulphite and regeneration of mannose from this intermediate, and (2) anhydrous methanolysis concurrent with glycosidation of crude mixed-sugar polymers or monomers, crystallization and separation of methyl α -D mannoside and regeneration of mannose from this intermediate. These procedures for recovering mannose have the drawback
10 that they are very cumbersome to carry out in practice.

Sinner, M, Simatupang, M.H. & Dietrichs, H.H. ("Automated Quantitative Analysis of Wood Carbohydrates by Borate Complex Ion Exchange Chromatography", Wood Science and Technology, 1975, pp. 307 to 322) describe a simple automated analytical method for the separation and quantita-
15 tive determination of sugars from acidic and enzymatic hydrolysates of wood polysaccharides via borate complex ion exchange chromatography. The sugars separated in this way include mannose, fructose, arabinose, galactose, xylose, glucose and disaccharides like xylobiose, cellobiose and sucrose.

GB 1 540 556 (ICI Americas, publ. 14 February 1979) relates to a
20 method of separating mannose from glucose present in aqueous solutions. The starting mixture of glucose and mannose is typically obtained by epimerization of glucose in an aqueous solution. The separation of mannose from glucose is typically carried out using a cation exchange resin in the form of an alkaline earth metal salt, such as in Ca^{2+} , Sr^{2+} or Ba^{2+} form. The cation ex-
25 change resin is preferably a strongly acid cation exchange resin, typically a resin based on styrene divinylbenzene.

The separation of sugars from lignosulphonates has been described by Hassi, R., Tikka, P. & Sjöström, E. ("Recovery of Lignosulphonates and Sugars from Spent Sulphite Liquors by Ion Exclusion Chromatography,
30 1982 International Sulfite Pulping Conference, Sheraton Centre Hotel, Toronto, Ontario, October 20-22, pp. 165 to 170). Ion exclusion chromatography on a strongly acid cation exchange resin has been applied to the fractionation of lignosulphonates and sugars, including mannose, present in a spent sulphite liquor. The resin used in the tests was a strongly acid gel-type polysty-
35 rene cation exchange resin (Amberlite™ IR-120, Ca^{2+} form). It is proposed that the sugar fraction might be used as a raw material source for mannitol produc-

tion.

Finnish Patent 78734 (Suomen Sokeri Oy, publ. 5 April 1987) relates to a multi-step process of separating sugars and lignosulphonates from a spent sulphite pulping liquor. This process comprises introducing a spent sulphite pulping liquor into a chromatographic column including a separation resin in a metal salt form, typically a strongly acid cation exchange resin in a Ca^{2+} form, eluting the column with water to recover a fraction rich in lignosulphonates and a fraction rich in sugars, introducing the fraction rich in sugars thus obtained into another chromatographic column including a separation resin in a monovalent metal salt form, typically in Na^+ form. A sugar fraction free from lignosulphonates is obtained.

WO 96/27029 (Xyrofin Oy, publ. 6 September 1996) relates to a method of recovering an organic compound, such as sugars, from solutions by crystallizing the compound substantially by way of nucleation. It is proposed that mannose can be recovered by the nucleation crystallization process, for example.

Finnish Patent 97 625 (Xyrofin Oy, publ. 5 March 1996) discloses a process for crystallizing xylose. In this process, xylose is recovered by crystallization from solutions in which the xylose purity is relatively low. Especially, this process concerns recovering xylose from biomass-derived solutions.

WO 99/10542 (Cultor Corporation, publ. 4 March 1999) discloses a process of recovering L-arabinose from sugar beet pulp by a chromatographic separation method using a cation exchanger in a monovalent metal form as the separation resin. The L-arabinose solution thus obtained is purified by means of cation and anion exchangers and adsorbent resins.

WO 01/21271 A1 (Sohkar Oy, publ. 29 March 2001) discloses a method of recovering pectin, arabinose and salts from vegetable material using a cation exchange resin, which is preferably in the form of a multivalent metal.

Biomass-derived raw materials used for the recovery of mannose are typically complex multicomponent mixtures. Separation of mannose with sufficient purity from these complex mixtures has presented a problem. One of the problems associated with the above-described known processes is that they provide mannose as a mixture with other closely-related sugars or that they do not provide mannose with a sufficient degree of purity. On the other hand, the production of mannose from mannans and other mannose deriva-

tives is technically very cumbersome. Furthermore, it has been problematical to prepare suitable starting mannose solutions for the crystallization of mannose to obtain a crystalline mannose product.

It has now been found that mannose with high purity can be effectively recovered from biomass-derived carbohydrate-containing solutions using a novel chromatographic separation method. With the chromatographic method of the invention, a mannose fraction having a purity of 45 to 80% or more can be obtained. The mannose fraction obtained from the chromatographic separation can then be further purified by crystallization. The crystallization provides a crystalline mannose product having a purity of up to 99% or more. In connection with the method of the invention, various other sugars, such as xylose and arabinose can be recovered as by-products, depending on the composition of the starting biomass-derived raw material.

BRIEF DESCRIPTION OF THE INVENTION

It is thus an object of the present invention to provide a method of recovering a mannose product with high purity from carbohydrate mixtures containing the same. As by-products, various other sugars, such as xylose and arabinose can be recovered.

In accordance with one aspect of the present invention, there is provided a method of recovering mannose from a solution derived from biomass, comprising subjecting said solution to a chromatographic separation process using at least one chromatographic separation resin bed which is substantially in a Ba^{2+} form and at least one chromatographic separation resin bed, where the resin is a cation exchange resin in other than Ba^{2+} form; and recovering at least one mannose fraction.

In an embodiment of the invention the chromatographic separation process of the method comprises at least two chromatographic separation steps, whereby at least one of these steps is carried out with a chromatographic separation resin bed which is substantially in a Ba^{2+} form and at least one of these steps is carried out with a chromatographic separation resin bed, where the resin is a cation exchange resin in other than Ba^{2+} form.

In another embodiment of the invention, the method comprises feeding a solution derived from biomass into a first chromatographic column including a chromatographic separation resin bed which is substantially in a Ba^{2+} form, eluting said column with an eluant, recovering a first mannose fraction, and

then feeding said first mannose fraction into a second chromatographic column including a chromatographic separation resin bed, where the resin is a cation exchange resin in other than Ba^{2+} form, eluting said column with an eluant, and recovering a second mannose fraction.

5 In a further embodiment of the invention, the chromatographic separation process comprises two separation steps with a chromatographic separation resin bed which is substantially in a Ba^{2+} form and one separation step with a chromatographic separation resin bed, where the resin is a cation exchange resin in other than Ba^{2+} form.

10 In another embodiment of the invention, the method comprises feeding a solution derived from biomass into a first chromatographic column including a chromatographic separation resin bed which is substantially in a Ba^{2+} form, eluting said column with an eluant, recovering a first mannose fraction, feeding said first mannose fraction into a second chromatographic column including a
15 chromatographic separation resin bed which is substantially in a Ba^{2+} form, eluting said column with an eluant, recovering a second mannose fraction, and then feeding said second mannose fraction into a third chromatographic column including a chromatographic separation resin bed, where the resin is a cation exchange resin in other than Ba^{2+} form, eluting said column with an
20 eluant, and recovering a third mannose fraction.

 In another embodiment of the invention, the cation exchange resin in other than Ba^{2+} form is in the form of a cation selected from hydrogen, NH_4^+ , alkali metal cations and alkaline earth metal cations.

 In another embodiment of the invention, the cation is selected from
25 NH_4^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} .

 In another embodiment of the invention, the chromatographic separation process is carried out with a strongly acid cation exchange resin.

 In another embodiment of the invention, the purity of the at least one mannose fraction is 45 to 80% mannose on RDS.

30 In another embodiment of the invention, the purity of the second mannose fraction is 45 to 80% mannose on RDS.

 In another embodiment of the invention, the purity of the third mannose fraction is 45 to 80% mannose on RDS.

 In another embodiment of the invention, the chromatographic separation
35 process provides a mannose fraction having a purity of more than 80% on RDS.

In another embodiment of the invention, the purity of the second mannose fraction is more than 80% on RDS.

In another embodiment of the invention, the purity of the third mannose fraction is more than 80% on RDS.

5 In another embodiment of the invention, the method further comprises one or more purification steps selected from membrane filtration, ion exchange, evaporation, filtration and derivatization carried out before, after or between said chromatographic separation step or steps.

10 In another embodiment of the invention, the derivatization comprises forming N-phenyl-D-mannopyranosylamine as a mannose derivative.

In another embodiment of the invention, the method further comprises crystallization of mannose to obtain a crystalline mannose product.

In another embodiment of the invention, the crystallization is carried out with a solvent selected from water, alcohol and a mixture of alcohol with water.

15 In another embodiment of the invention, the crystallization is carried out with a mixture of ethanol and water.

In another embodiment of the invention, the crystallization is carried out with water.

20 In another embodiment of the invention, the crystallization provides crystalline mannose having a purity of more than 90% on RDS.

In another embodiment of the invention, the crystallization provides crystalline mannose having a purity of more than 95% on RDS.

In another embodiment of the invention, the crystallization provides crystalline mannose having a purity of more than 99% on RDS.

25 In another embodiment of the invention, the method further comprises separation of other sugars.

In another embodiment of the invention, the method comprises separation of xylose as a pre-treatment step.

30 In another embodiment of the invention, the separation of xylose is carried out through crystallization.

In another embodiment of the invention, the method further comprises separation of arabinose.

35 In another embodiment of the invention, the method further comprises separation of xylose by precipitation crystallization as a pre-treatment step and the separation of arabinose is carried out before the precipitation crystallization of xylose.

In another embodiment of the invention, the separation of arabinose is carried out by a chromatographic separation process to recover an arabinose fraction.

5 In another embodiment of the invention, the chromatographic separation is carried out using a chromatographic separation resin bed in the form of a monovalent cation.

In another embodiment of the invention, the monovalent cation is selected from hydrogen, ammonium and alkali metal cations.

10 In another embodiment of the invention, the cation is selected from H^+ , NH_4^+ , Na^+ and K^+ .

In another embodiment of the invention, the method further comprises chromatographic purification of said arabinose fraction.

15 In another embodiment of the invention, the chromatographic purification of said arabinose fraction comprises at least one step using a chromatographic separation resin bed in the form of an alkaline earth metal cation.

In another embodiment of the invention, the alkaline earth metal is Ca^{2+} .

In another embodiment of the invention, the separation of arabinose is carried out with a strongly acid cation exchange resin.

20 In another embodiment of the invention, the method further comprises separation of rhamnose as a pretreatment step.

In another embodiment of the invention, the separation of rhamnose is carried out before the separation of arabinose.

25 In another embodiment of the invention, the solution derived from biomass is a biomass hydrolysate containing mannose and further sugars selected from xylose, arabinose, rhamnose, galactose, glucose and fructose.

In another embodiment of the invention, the solution derived from biomass is a biomass hydrolysate containing mannose and further sugars selected from xylose, arabinose and rhamnose.

30 In another embodiment of the invention, the solution derived from biomass is a hydrolysate derived from mannose-containing vegetable material.

In another embodiment of the invention, the solution derived from biomass is a hydrolysate derived from lignocellulosic material.

In another embodiment of the invention, the solution derived from biomass is a hydrolysate derived from softwood or hardwood.

35 In another embodiment of the invention, the solution derived from biomass is a spent sulphite pulping liquor.

In another embodiment of the invention, the spent sulphite pulping liquor is a spent sulphite pulping liquor recovered after the separation of rhamnose.

5 In another embodiment of the invention, the spent sulphite pulping liquor is a spent sulphite pulping liquor recovered after the separation of xylose.

In another embodiment of the invention, the mannose is D-mannose.

10 The invention is based on the idea of purifying the mannose-containing carbohydrate mixture chromatographically using at least two separation resins, one of which is Ba^{2+} -based resin.

With the method of the invention, a mannose product with high purity can be obtained.

DEFINITIONS RELATING TO THE INVENTION

15

In the specification and throughout the examples and the claims, the following definitions have been used:

SAC refers to a strongly acid cation exchange resin.

20 DS refers to a dry substance content measured by Karl Fischer titration, expressed as % by weight.

RDS refers to a refractometric dry substance content, expressed as % by weight.

BRIEF DESCRIPTION OF THE DRAWINGS

25

The following drawings are illustrative embodiments of the invention and are not meant to limit the scope of the invention as defined in the claims in any way.

30 Figure 1 is a graphical presentation of the concentration profile of the mannose-arabinose separation with Na^+ form SAC resin (separation A) of Example 1.

Figure 2 is a graphical presentation of the concentration profile of the mannose separation with Ba^{2+} form SAC resin (separation C.1) of Example 1.

35 Figure 3 is a graphical presentation of the concentration profile of the repeated mannose separation with Ba^{2+} form SAC resin (separation C.2)

of Example 1.

Figure 4 is a graphical presentation of the concentration profile of the mannose separation with Ca^{2+} form SAC resin (separation C.3) of Example 1.

5 Figure 5 is a graphical presentation of the concentration profile of the arabinose separation with Ca^{2+} form SAC resin (separation E.1) of Example 1.

10 Figure 6 is a graphical presentation of the concentration profile of the repeated arabinose separation with Ca^{2+} form SAC resin (separation E.2) of Example 1.

Figure 7 is a process scheme describing one embodiment of the invention for recovering mannose and xylose. The process also includes separation of arabinose as a pre-treatment step.

DETAILED DESCRIPTION OF THE INVENTION

15 The invention relates to a method of recovering mannose from a solution containing the same. The method of the invention is characterized in that said mixture is subjected to a chromatographic separation process using at least one chromatographic separation resin bed which is at least partly in a Ba^{2+} form and at least one chromatographic separation resin bed which is in
20 other than Ba^{2+} form and recovering at least one mannose fraction.

The chromatographic separation process of the invention typically comprises at least two chromatographic separation steps, whereby at least one of these steps is carried out with a chromatographic separation resin bed which is at least partly in a Ba^{2+} form and at least one of these steps is carried
25 out with a chromatographic separation resin bed which is in other than Ba^{2+} form.

One embodiment of the invention is typically carried out by feeding a solution containing mannose into a first chromatographic column including a chromatographic separation resin bed which is at least partly in a Ba^{2+} form,
30 eluting said column with an eluant, recovering a first mannose fraction, and then feeding said first mannose fraction into a second chromatographic column including a chromatographic separation resin bed in other than Ba^{2+} form, eluting said column with an eluant, and recovering a second mannose fraction.

In another embodiment of the invention, said chromatographic
35 separation process comprises two separation steps with a chromatographic

separation resin bed which is at least partly in a Ba^{2+} form and one separation step with a chromatographic separation resin bed in other than Ba^{2+} form.

This embodiment of the invention is typically carried out by feeding a solution containing mannose into a first chromatographic column including a chromatographic separation resin bed which is at least partly in a Ba^{2+} form, eluting said column with an eluant, recovering a first mannose fraction, feeding said first mannose fraction into a second chromatographic column including a chromatographic separation resin bed which is at least partly in a Ba^{2+} form, eluting said column with an eluant, recovering a second mannose fraction, and then feeding said second mannose fraction into a third chromatographic column including a chromatographic separation resin bed in other than Ba^{2+} form, eluting said column with an eluant, and recovering a third mannose fraction.

In the above-mentioned embodiment of the invention, some other separation may be carried out before the Ba^{2+} separation. In the same way, some other separation may be carried out between the Ba^{2+} separations. Furthermore, between two ion exchange operations, equilibration of the ions or the ion composition is typically carried out, for example by ion exchange.

In one embodiment of the invention, said resin (resin bed) which is at least partly in a Ba^{2+} form is substantially in a Ba^{2+} form. During the chromatographic separation process, balancing of the chromatographic column occurs, whereby said resin bed which is at least partly in a Ba^{2+} form may even contain other ions, such as H^+ , alkali metal cations, such as Na^+ and K^+ , and alkaline earth metal cations, such as Ca^{2+} and Mg^{2+} .

Said resin which is at least partly in a Ba^{2+} form refers to a cation exchange resin.

Said resin (resin bed) in other than Ba^{2+} form refers to a resin, which is in the form of a cation other than Ba^{2+} . Said resin is typically a cation exchange resin, where the cation is in the hydrogen form (H^+), in NH_4^+ form or in the form of a metal selected from alkaline metals and alkaline earth metals, such as Na^+ , K^+ , Mg^{2+} and Ca^{2+} . An especially preferred metal is Ca^{2+} .

The chromatographic separation for obtaining mannose in accordance with the present invention is typically carried out with a strongly acid cation exchange resin. A preferred resin is a cross-linked styrene-divinylbenzene based resin. A suitable cross-linking degree of the resin is 1 to 20% by weight, preferably 3 to 8% by weight. The average particle size of the resin is normally 10 to 2000 μm , preferably 100 to 400 μm . Zeolite-based mo-

lecular sieves can also be used.

The eluant used in the chromatographic separation according to the present invention is either water, a solvent, e.g. an alcohol, or a mixture thereof. A preferred eluant is water.

5 The elution is preferably carried out at a temperature from 10 to 95°C, more preferably from 30 to 95 °C, most preferably from 55 to 85°C.

The chromatographic separation method of the invention provides a mannose fraction where mannose is in a solution form. The mannose product obtained from the chromatographic separation has a typical purity of 45 to
10 80% mannose on RDS.

To improve the yield of the chromatographic separation, recycle fractions of the chromatographic separation can also be used.

The chromatographic separation method of the invention may further comprise one of more purification steps selected from membrane filtration, ion exchange, evaporation, filtration and derivatization. These purification
15 steps may be carried out before, after or between said chromatographic separation step/steps.

Ion exchange is typically carried out to purify the mannose-containing solution from SO_4^- ions, for example.

20 In the derivatization method, a mannose derivative is formed, whereafter mannose is regenerated from the derivative thus obtained. One example of useful mannose derivatives is N-phenyl-D-mannopyranosylamine.

The mannose solution obtained from the chromatographic separation can be further purified by crystallization to obtain a crystalline mannose
25 product. The crystallization is typically carried out using a solvent selected from water, alcohol and a mixture of water and alcohol. In a preferred embodiment of the invention, the crystallization is carried out with a mixture of ethanol and water.

The crystallization is carried out by evaporating the mannose solution or mannose syrup obtained from the chromatographic separation to an
30 appropriate dry substance content (e.g. to RDS of about 85%). The boiling syrup may be seeded with mannose seed crystals. The seeds, if used, are suspended in a crystallization solvent, which may be either water, a solvent, e.g. an alcohol, or a mixture thereof. A typical crystallization solvent is ethanol.
35 After cooling the crystallization mass to room temperature, the crystallization solvent is added. The crystallization mass may then be allowed to stand for a

period of time, preferably for 3 to 6 days, typically at room temperature, whereafter the crystals are filtered off. The filtration cake is washed with the crystallization solvent. Mannose crystals with a high purity are obtained.

5 The crystallization provides crystalline mannose having a purity of over 90%, preferably over 95% and most preferably over 99% on RDS.

 The method of the invention may also comprise separation of other sugars, such as xylose, rhamnose and arabinose, depending on the composition of the starting mannose-containing solution. The separation of other sugars is typically carried out before the separation of mannose.

10 The method of the invention may thus comprise separation of xylose as a pretreatment step. The recovery of xylose may be carried out by various methods, e.g. through precipitation crystallization.

 The xylose precipitation crystallization is preferably carried out immediately before the chromatographic separation of mannose.

15 In the xylose precipitation crystallization, the solution containing mannose and some xylose is subjected to a crystallization step. The precipitation crystallization of xylose is typically carried out by evaporating the solution to a desired dry substance content, seeding the solution with xylose seed crystals, and then cooling the crystallization mass according to a desired cooling
20 program. The crystallization mass is filtered to obtain a xylose cake and mannose-containing crystallization run-off. Xylose is recovered from the crystallization cake and the run-off containing mannose is subjected to the chromatographic purification described above for obtaining mannose with high purity in accordance with the present invention.

25 The method of the invention may also comprise separation of arabinose, preferably as a pretreatment step. The separation of arabinose may be carried out before the precipitation crystallization of xylose. Chromatographic separation is typically used for the recovery of arabinose. The chromatographic separation of arabinose is preferably carried out using a chromatographic separation resin bed in the form of a monovalent cation, which is
30 selected from hydrogen, ammonium and alkali metal cations. Said monovalent cation is typically selected from H^+ , Na^+ , K^+ and NH_4^+ . An arabinose fraction is recovered. The chromatographic separation resin is preferably a strongly acid cation exchange resin.

35 The arabinose fraction may be subjected to further chromatographic purification. The chromatographic purification of the arabinose fraction typically

comprises at least one step using a chromatographic separation resin bed in the form of an alkaline earth metal, preferably Ca^{2+} . The arabinose fraction thus obtained may also be crystallized.

5 The method of the invention may also comprise separation of rhamnose as a pretreatment step. The separation of rhamnose is typically carried out before the separation of arabinose.

For xylose-rich raw materials, the method of the invention may also comprise separation of xylose as a pretreatment step. The separation of xylose is typically carried out before the separation of arabinose.

10 The method of the invention may also include further purification steps, such as membrane filtration, e.g. ultrafiltration and nanofiltration, ion exchange, evaporation and filtration to remove e.g. lignosulphonates, acids (organic acids and inorganic acids) and salts.

15 The starting solution containing mannose is typically a mixture containing carbohydrates, such as sugars. The solution may contain, in addition to mannose, e.g. xylose, galactose, glucose, rhamnose, arabinose and fructose. The mixture may also contain disaccharides and higher saccharides.

20 The material containing a mixture of carbohydrates is typically derived from a biomass, typically mannose-containing vegetable material, such as softwood or hardwood, straw, corn husks, corn cobs, corn fibers and sugar beet. The starting material is as a rule used in the form of a hydrolysate obtained e.g. by prehydrolysis, total hydrolysis, steam hydrolysis, enzymatic hydrolysis or acid hydrolysis.

25 The biomass hydrolysate used for the recovery of mannose in accordance with the present invention is typically a spent liquor obtained from a pulping process. The spent liquor is especially a spent sulphite pulping liquor, which may be obtained by acid, basic or neutral sulphite pulping. If the biomass hydrolysate, e.g. the spent liquor contains mannose in polymeric form, the polymeric mannose can be hydrolysed by acids or enzymes before the
30 chromatographic separation steps.

A typical spent liquor useful in the present invention is a mannose-containing spent liquor, which is preferably obtained from acid sulphite pulping. The spent liquor may be obtained directly from sulphite pulping. It may also be a concentrated sulphite pulping liquor or a side-relief obtained from sulphite
35 cooking. It may also be a mannose-containing fraction chromatographically obtained from a sulphite pulping liquor.

In the present invention, the liquor to be treated may also be any other liquor obtained from the digestion or hydrolysis of biomass, typically a hydrolysate obtained from acid hydrolysis of lignocellulosic material. Such a hydrolysate may be obtained from lignocellulosic material for example by
5 treatment with an inorganic acid, such as hydrochloric acid, sulphuric acid or sulphur dioxide, or by treatment with an organic acid, such as formic acid or acetic acid. A spent liquor obtained from solvent-based pulping, such as phenol-based pulping and ethanol-based pulping may also be used.

The starting solution containing mannose may be e.g. a spent sulphite pulping liquor recovered after the separation of rhamnose. The starting
10 solution may also be a spent sulphite pulping liquor recovered after the separation of xylose.

The mannose product obtained in accordance with the present invention typically comprises D-mannose.

15 The following examples illustrate the invention. The examples are not be construed to limit the claims in any manner.

In the following examples, the following definitions are used:

DS refers to the dry substance content measured by Karl Fischer titration, expressed as % by weight, unless otherwise indicated.

20 The contents (expressed in % on DS) of various components of the fractions obtained from the chromatographic and other separations have been measured using the HPLC method.

Example 1

25 A process scheme describing the multistep separation process of Example 1 is presented in Figure 7.

The starting liquor used in the first step of the process was a mannose-containing side stream separated from Ca^{2+} based sulphite spent liquor after the recovery of xylose and rhamnose. Birch had been used as raw material for the sulphite pulping.
30

The mannose-containing side stream recovered after the separation of rhamnose was subjected to chromatographic separation to obtain a mannose fraction and an arabinose fraction (chromatographic separation A). The mannose fraction was subjected to separation B (xylose precipitation crystallization) to obtain a xylose cake and a crystallization run-off containing mannose.
35 The mannose-containing run-off from the crystallization of xylose was

subjected to three successive chromatographic separations (C.1), (C.2) and (C.3). The mannose fraction from the last chromatographic separation was subjected to mannose crystallization.

5 The arabinose fraction from separation (A) was subjected to two successive chromatographic separations (E.1) and (E.2) for recovering purified arabinose.

The starting mannose-containing liquor obtained after the separation of rhamnose had the following composition:

Component	Content (% on DS)
Xylose	36
Mannose	15
Galactose	13
Glucose	4.8
Rhamnose	0.6
Arabinose	4.9
Fructose	1.4
Others	24.6

10

(A) Separation of arabinose using Na⁺-form SAC resin

A strongly acid cation exchange resin in Na⁺ form was used to remove the salts from the feed and to collect arabinose from the end of the elution profile. The separation was done using the following separation conditions:

15

Column diameter	0.6 m
Bed height	5.3 m
Feed size	108.5 l
Feed RSD	35 g/100 g
Temperature	65 °C
Flow rate	170 l/h
Resin	Finex CS 11 GC, 5.5% DVB, average particle size 0.35 mm

The composition of the mannose and arabinose fractions collected from separation (A) are set forth in Table 1.

Table 1.

Composition of the mannose and arabinose fractions in % on DS

Component	Mannose fraction	Arabinose fraction
Xylose	43	34
Mannose	19	13
Galactose	16	10
Glucose	6.3	0.2
Rhamnose	1.1	0.1
Arabinose	1.8	17
Fructose	1.2	2.2
Others	8.9	23.5

5

The mannose yield was 38% for mannose purity of 19 % on DS and xylose purity of 43 % on DS.

The concentration profile of separation (A) is presented in Figure 1.

10

(B) Xylose precipitation crystallization

The mannose fraction obtained from separation (A) and having a xylose content of about 43 % on DS was subjected to precipitation crystallization to separate xylose.

15

The precipitation crystallization of xylose was carried out in pilot scale with one crystallizer of about 200 liters. The feed liquor was evaporated to a final DS of 87.5%. The batch was seeded in a boiling pan with xylose seed crystals. The mass was cooled down from 60°C to 31°C in 48 hours and then the mass was held at 31°C for 24 hours. No dilutions were made. The mass was dropped down to a mingler and then filtrated.

20

The results of the xylose precipitation crystallization are set forth in Table 2. The table shows the contents of various components in the crystallization feed, cake and run-off in % on DS.

Table 2.

25

Analysis results of the xylose precipitation crystallization

Component	Feed	Cake	Run-off
-----------	------	------	---------

Glucose	5.9	2.9	7.0
Xylose	42.7	73.8	29.8
Arabinose	3.5	1.0	2.9
Mannose	19.5	7.2	23.7

The mannose purity of the crystallization run-off increased to about 24 % on DS and the xylose purity decreased to about 30%.

5

(C) Mannose separations

(C.1.) Mannose separation with Ba²⁺ form SAC resin

The run-off fraction obtained from the xylose precipitation crystallization was subjected to chromatographic separation using a Ba²⁺ form SAC resin. The separation was done using the following separation conditions:

10

Column diameter	0.225 m
Bed height	5.3 m
Feed size	11.9 l
Feed RSD	32 g/100 g
Temperature	65 °C
Flow rate	25 l/h
Resin	Finex CS 08 GC, 4 % DVB, average particle size 0.38 mm

The mannose fraction was collected with a mannose yield of 70% and the total purity of 49 % on DS was obtained. The composition of the mannose and xylose fractions is presented in Table 3.

15

Table 3.

Composition of the mannose and xylose fractions from the first separation with Ba²⁺ form SAC resin in % on DS

Component	Xylose fraction	Mannose fraction
Xylose	47	9.2
Mannose	9.6	49
Galactose	23	13
Glucose	12	0.2

Rhamnose	1.8	0.8
Fructose	0.1	4.0
Others	6.5	24.2

The concentration profile of separation (C.1) is presented in Figure 2.

5 (C.2.) Ba²⁺ form SAC resin separation

A second Ba²⁺ form SAC resin separation was used to purify the mannose fraction obtained from the previous step (separation C.1). The same separation conditions were used as in separation (C.1) above.

10 The mannose fraction obtained from the separation had a purity of 63 % on DS with a mannose yield of 68%. The compositions of the mannose and xylose fractions in % on DS are set forth in Table 4.

Table 4.

15 Composition of the mannose and xylose fractions from the second separation with Ba²⁺ form SAC resin

Component	Xylose fraction	Mannose fraction
Xylose	19	1.1
Mannose	41	63
Galactose	24	3.5
Glucose	0.5	-
Rhamnose	1.4	0.2
Fructose	0.7	7.8
Others	13.9	24.3

The xylose fraction still contained 40% mannose.

20 The concentration profile of separation (C.2) is presented in Figure 3.

(C.3.) Separation with Ca²⁺ form SAC resin

25 The mannose fraction obtained from separation (C.2) was subjected to a further chromatographic separation using Ca²⁺ form SAC resin. The separation was done using the following separation conditions:

Column diameter	0.225 m
Bed height	4.8 m
Feed size	11 l
Feed RSD	30.7 g/100 g
Temperature	65 °C
Flow rate	30 l/h
Resin	Finex CS 11 GC, 5.5 % DVB, average particle size 0.35 mm

The composition of the mannose fraction in % on DS is set forth in Table 5.

5

Table 5.

Composition of the mannose fraction obtained from the separation with a Ca^{2+} form SAC resin

Component	Mannose fraction
Xylose	1.8
Mannose	80
Galactose	5.1
Glucose	-
Rhamnose	0.2
Fructose	2.6
Others	10.3

10

Mannose fraction purity of 80 % on DS was obtained with a mannose yield of 70%. The concentration profile of separation (C.3) is presented in Figure 4.

15

D. Mannose crystallization

(D.1.) Mannose crystallization using water-ethanol solvent (batch 1)

2924 g of mannose syrup having a DS of 51% and a mannose content of 78%, based on the refractometric dry solids content of pure mannose, was evaporated to RDS of 86.2% and moved to a 2-liter reaction vessel at a temperature of 30°C. Seeding (30°C, RDS 86.2%) was made to the boiling

20

syrup with 0.03% seeds on DS. The seeds were suspended with 10 ml ethanol.

The mass was cooled down from a temperature of 30°C to a temperature of 25°C. 800 g ethanol was added slowly to the mass.

5 After 5 days from seeding, the crystals were filtrated with a pressure filter. The filtration gave a cake purity of 93.0% (including solvent ethanol as impurity) and a mother liquor purity of 52.5% (including solvent ethanol as impurity). This corresponds to a mannose yield of 41%. The crystal size was in the range of 10 to 20 µm.

10 The filtration cake was washed twice with ethanol. The crystals were centrifuged and dried at 40°C for 24 hours. The crystals had a crystal water content of 0.3% and a mannose content of 99.9%.

(D.2). Mannose crystallization using water-ethanol solvent (batch 2)

15 1230 g of a mannose syrup having a DS of 50% and a mannose content of 93%, based on the refractometric dry solids content of pure mannose, was evaporated to an RDS of 84.1% and moved to a 2-liter reaction vessel at a temperature of 30°C. Seeding (30°C, RDS 84.1%) was made to the boiling syrup with 0.03% seeds on DS. The seeds were suspended with 10 ml
20 ethanol.

The mass was cooled down from a temperature of 30°C to a temperature of 20°C. 300 g ethanol was added slowly to the mass.

After 3 days from seeding, the crystals were centrifuged. The centrifuging gave a cake purity of 96.0% (including solvent ethanol as impurity). The
25 centrifuging result corresponds to a 50% mannose yield. The crystal size was in the range of 30 to 50 µm.

The centrifuging cake was washed twice with ethanol. The crystals were centrifuged and dried at 40°C for 24 hours. The crystal water content was analyzed to be 0.2%, and the crystal mannose content to be 99.7%.

30

(D.3.) Mannose crystallization using water as the solvent

1552 g of a mannose syrup having a DS of 50% and a mannose content of 80%, based on the refractometric dry solids content of pure mannose, was evaporated to an RDS of 86.7% and moved to a 1-liter reaction
35 vessel at a temperature of 60°C. Seeding (60°C, RDS 86.7%) was made to the boiling syrup with 0.07% seeds on DS.

The mass was cooled down from a temperature of 60°C to a temperature of 25°C. After 6 days from seeding, the centrifuging cake gave a purity of 99.5%. The centrifuging result corresponds to a mannose yield of 30%. The crystal size was in the range of 30 to 50 µm.

5

(E) Purification of the arabinose fraction

The arabinose fraction obtained from separation (A) had a purity of 10 % on DS. This fraction was further purified with a Ca²⁺ form SAC resin.

10

(E.1.) Purification of the arabinose fraction with a Ca²⁺ form SAC resin.

The separation was done under the following separation conditions:

Column diameter	0.225 m
Bed height	4.9 m
Feed size	18.8 l
Feed RSD	30.2 g/100g
Temperature	65°C
Flow rate	30 l/h
Resin	Finex CS 11 GC, 5.5% DVB, average particle size 0.40mm

15

The compositions of the feed, xylose and arabinose fractions in % on DS are set forth in Table 6.

Table 6.

Composition of the feed, xylose and arabinose fractions from the first separation with Ca²⁺ resin

20

Component	Feed	Xylose fraction	Arabinose fraction
Xylose	39	50	21
Mannose	16	16	14
Galactose	13	15	9.2
Glucose	1.1	1.5	0.3
Rhamnose	0.3	0.3	0.3

Arabinose	9.7	3.5	19
Fructose	0.1	0.6	1.3
Others	20.8	13	35.4

The concentration profile of separation (E.1) is presented in Figure 5.

5 (E.2.) Repeated purification of the arabinose fraction with a Ca^{2+} form SAC resin

The arabinose fraction obtained from separation (E.1) was subjected to another purification with a Ca^{2+} form resin. The separation was done using the following separation conditions:

10

Column diameter	0.225 m
Bed height	4.9 m
Feed size	20 l
Feed RSD	30.6 g/100g
Temperature	65°C
Flow rate	30 l/h
Resin	Finex CS 11 GC, 5.5% DVB, average particle size 0.40mm

The composition of the feed, xylose and arabinose fractions in % on DS is set forth in Table 7.

15

Table 7.

Composition of the feed and xylose and arabinose fractions from the second separation with a Ca^{2+} form resin

Component	Feed	Xylose fraction	Arabinose fraction
Xylose	27	43	14
Mannose	16	20	13
Galactose	11	15	7
Glucose	0.2	0.6	0.0
Rhamnose	0.4	0.4	0.3

Arabinose	18	6.2	26
Fructose	3.8	1.5	5.3
Others	23.6	13.6	34.7

The arabinose was collected with an 85% yield.

The concentration profile of separation (E.2) is presented in Figure 6.

5 It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described above but may vary within the scope of the claims.

CLAIMS

1. A method of recovering mannose from a solution derived from biomass, comprising subjecting said solution to a chromatographic separation process using at least one chromatographic separation resin bed which is substantially in a Ba^{2+} form and at least one chromatographic separation resin bed, where the resin is a cation exchange resin in a Ca^{2+} form, and recovering at least one mannose fraction.

2. The method as claimed in claim 1, wherein said chromatographic separation process comprises at least two chromatographic separation steps, whereby at least one of these steps is carried out with a chromatographic separation resin bed which is substantially in a Ba^{2+} form and at least one of these steps is carried out with a chromatographic separation resin bed, where the resin is a cation exchange resin in a Ca^{2+} form.

3. The method as claimed in claim 2, comprising feeding a solution derived from biomass into a first chromatographic column including a chromatographic separation resin bed which is substantially in a Ba^{2+} form, eluting said column with an eluant, recovering a first mannose fraction, and then feeding said first mannose fraction into a second chromatographic column including a chromatographic separation resin bed, where the resin is a cation exchange resin in a Ca^{2+} form, eluting said column with an eluant, and recovering a second mannose fraction.

4. The method as claimed in claim 2, wherein said chromatographic separation process comprises two separation steps with a chromatographic separation resin bed which is substantially in a Ba^{2+} form and one separation step with a chromatographic separation resin bed, where the resin is a cation exchange resin in a Ca^{2+} form.

5. The method as claimed in claim 4, comprising feeding a solution derived from biomass into a first chromatographic column including a chromatographic separation resin bed which is substantially in a Ba^{2+} form, eluting said column with an eluant, recovering a first mannose fraction, feeding said first mannose fraction into a second chromatographic column including a chromatographic separation resin bed which is substantially in a Ba^{2+} form, eluting said column with an eluant, recovering a second mannose fraction, and then feeding said second mannose fraction into a third chromatographic column including a chromatographic separation resin bed, where the resin is a

cation exchange resin in a Ca^{2+} form, eluting said column with an eluant, and recovering a third mannose fraction.

5 6. The method as claimed in any one of claims 1 through 5, wherein said chromatographic separation process is carried out with a strongly acid cation exchange resin.

7. The method as claimed in claim 1, wherein the purity of said at least one mannose fraction is 45 to 80% mannose on RDS.

8. The method as claimed in claim 3, wherein the purity of said second mannose fraction is 45 to 80% mannose on RDS.

10 9. The method as claimed in claim 5, wherein the purity of said third mannose fraction is 45 to 80% mannose on RDS.

10. The method as claimed in claim 3, wherein the purity of said second mannose fraction is more than 80% on RDS.

15 11. The method as claimed in claim 5, wherein the purity of said third mannose fraction is more than 80% on RDS.

20 12. The method as claimed in any one of claims 1 through 11, wherein the method further comprises one or more purification steps selected from membrane filtration, ion exchange, evaporation, filtration and derivatization carried out before, after or between said chromatographic separation step/steps.

13. The method as claimed in claim 12, wherein said derivatization comprises forming N-phenyl-D-mannopyranosylamine as a mannose derivative.

25 14. The method as claimed in any one of claims 1 through 13, wherein the method further comprises crystallization of mannose to obtain a crystalline mannose product.

15. The method as claimed in claim 14, wherein said crystallization is carried out with a solvent selected from water, alcohol and a mixture of alcohol with water.

30 16. The method as claimed in claim 15, wherein said crystallization is carried out with a mixture of ethanol and water.

17. The method as claimed in claim 15, wherein said crystallization is carried out with water.

35 18. The method as claimed in any one of claims 14 through 17, wherein said crystallization provides crystalline mannose having a purity of more than 90% on RDS.

19. The method as claimed in any one of claims 14 through 18, wherein said crystallization provides crystalline mannose having a purity of more than 95% on RDS.

20. The method as claimed in any one of claims 14 through 19,
5 wherein said crystallization provides crystalline mannose having a purity of more than 99% on RDS.

21. The method as claimed in any one of claims 1 through 20, wherein the method further comprises separation of other sugars.

22. The method as claimed in claim 21, wherein the method com-
10 prises separation of xylose as a pre-treatment step.

23. The method as claimed in claim 22, wherein the separation of xylose is carried out through crystallization.

24. The method as claimed in any one of claims 21 through 23, wherein the method further comprises separation of arabinose.

25. The method as claimed in claim 24, wherein the method further
15 comprises separation of xylose by precipitation crystallization as a pre-treatment step and the separation of arabinose is carried out before the precipitation crystallization of xylose.

26. The method as claimed in claim 24 or 25, wherein said separation
20 tion of arabinose is carried out by a chromatographic separation process to recover an arabinose fraction.

27. The method as claimed in claim 26, wherein said chromatographic separation is carried out using a chromatographic separation resin bed in the form of a monovalent cation.

28. The method as claimed in claim 27, wherein said monovalent
25 cation is selected from hydrogen, ammonium and alkali metal cations.

29. The method as claimed in claim 28, wherein said cation is selected from H^+ , NH_4^+ , Na^+ and K^+ .

30. The method as claimed in any one of claims 26 through 29,
30 wherein the method further comprises chromatographic purification of said arabinose fraction.

31. The method as claimed in claim 30, wherein the chromatographic purification of said arabinose fraction comprises at least one step using a chromatographic separation resin bed in the form of an alkaline earth
35 metal cation.

32. The method as claimed in claim 31, wherein said alkaline earth

metal is Ca^{2+} .

33. The method as claimed in any one of claims 26 through 32, wherein said separation of arabinose is carried out with a strongly acid cation exchange resin.

5 34. The method as claimed in any one of claims 21 through 33, wherein the method further comprises separation of rhamnose as a pretreatment step.

35. The method as claimed in claim 34, wherein the separation of rhamnose is carried out before the separation of arabinose.

10 36. The method as claimed in any one of claims 1 through 35, wherein said solution derived from biomass is a biomass hydrolysate containing mannose and further sugars selected from xylose, arabinose, rhamnose, galactose, glucose and fructose.

15 37. The method as claimed in any one of claims 1 through 36, wherein said solution derived from biomass is a biomass hydrolysate containing mannose and further sugars selected from xylose, arabinose and rhamnose.

20 38. The method as claimed in any one of claims 1 through 37, wherein said solution derived from biomass is a hydrolysate derived from mannose-containing vegetable material.

39. The method as claimed in any one of claims 1 through 38, wherein said solution derived from biomass is a hydrolysate derived from lignocellulosic material.

25 40. The method as claimed in any one of claims 1 through 39, wherein said solution derived from biomass is a hydrolysate derived from softwood or hardwood.

41. The method as claimed in any one of claims 36 through 40, wherein said solution derived from biomass is a spent sulphite pulping liquor.

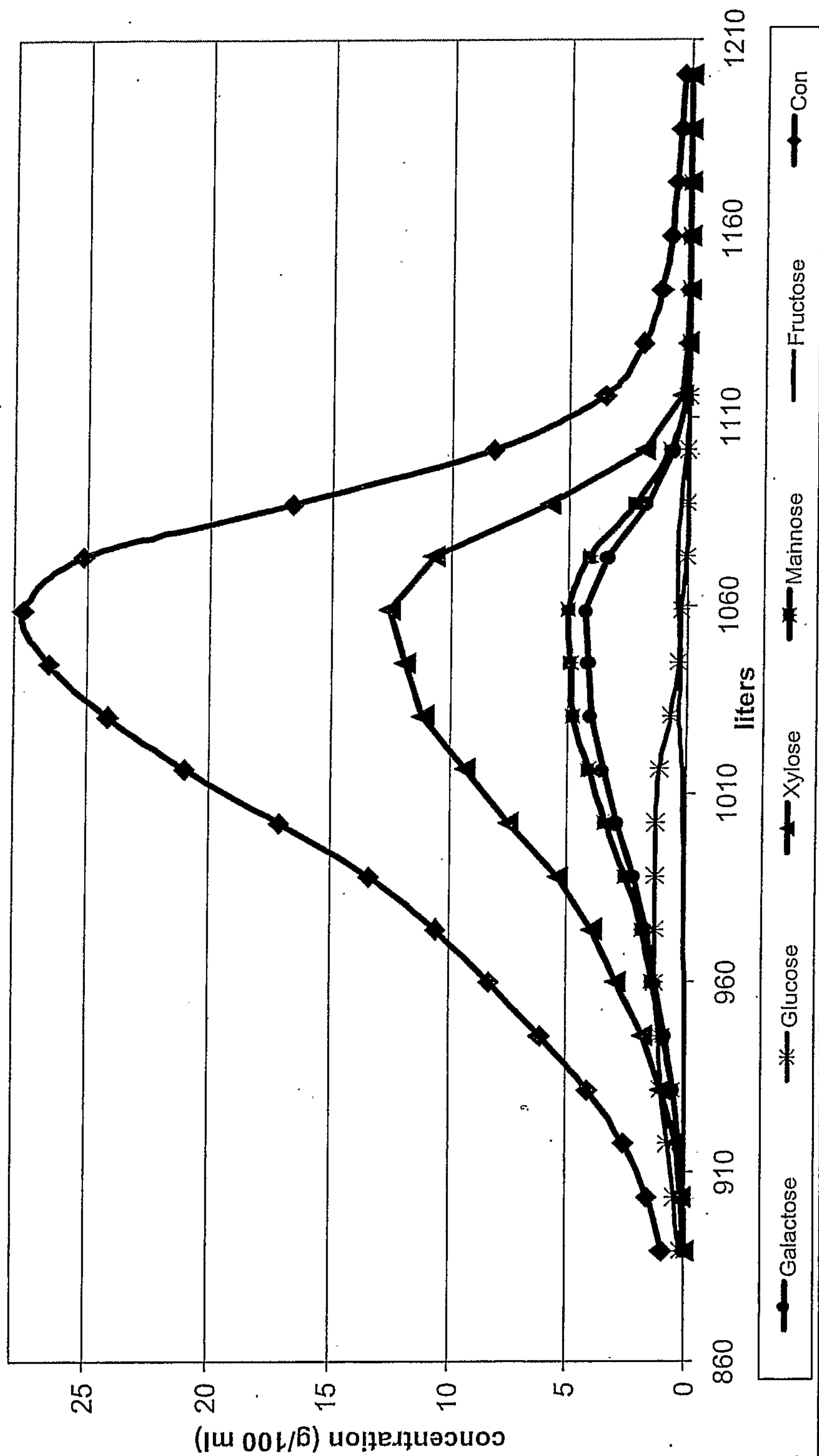
30 42. The method as claimed in claim 41, wherein said spent sulphite pulping liquor is a spent sulphite pulping liquor recovered after the separation of rhamnose.

43. The method as claimed in claim 42, wherein said spent sulphite pulping liquor is a spent sulphite pulping liquor recovered after the separation of xylose.

35 44. The method as claimed in any one of claims 1 through 43, wherein said mannose is D-mannose.

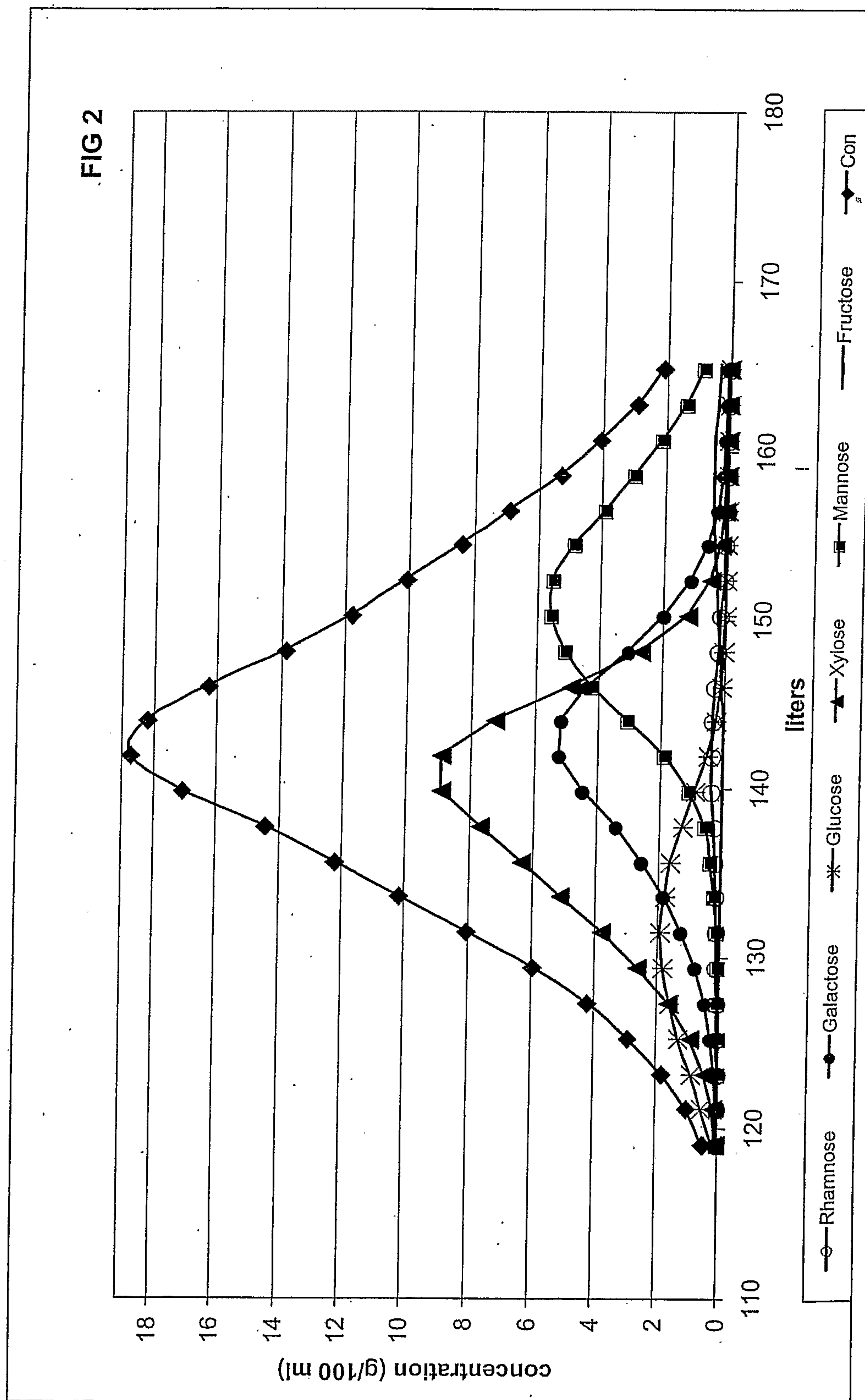
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FIG 1



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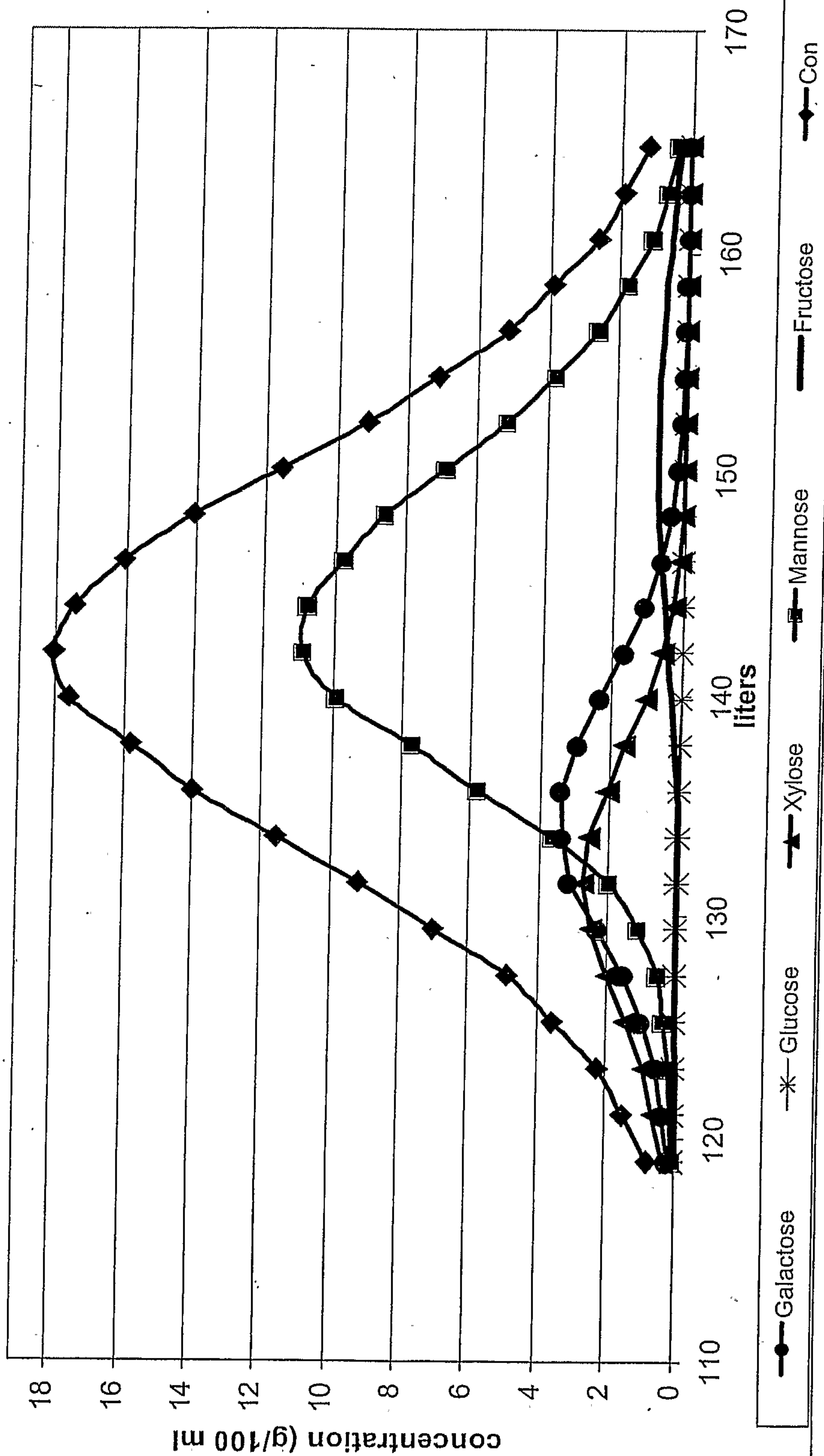
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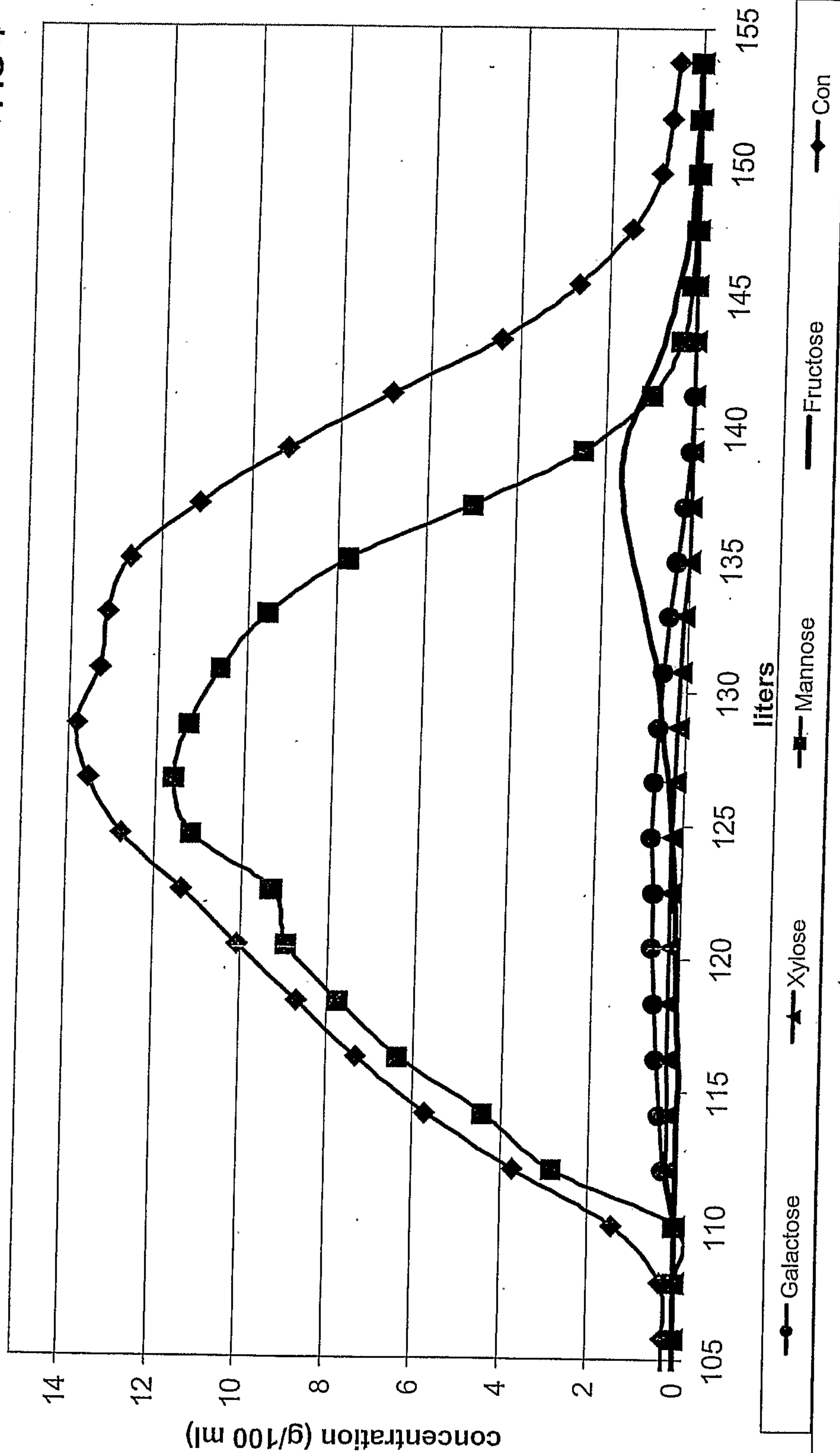
FIG 3



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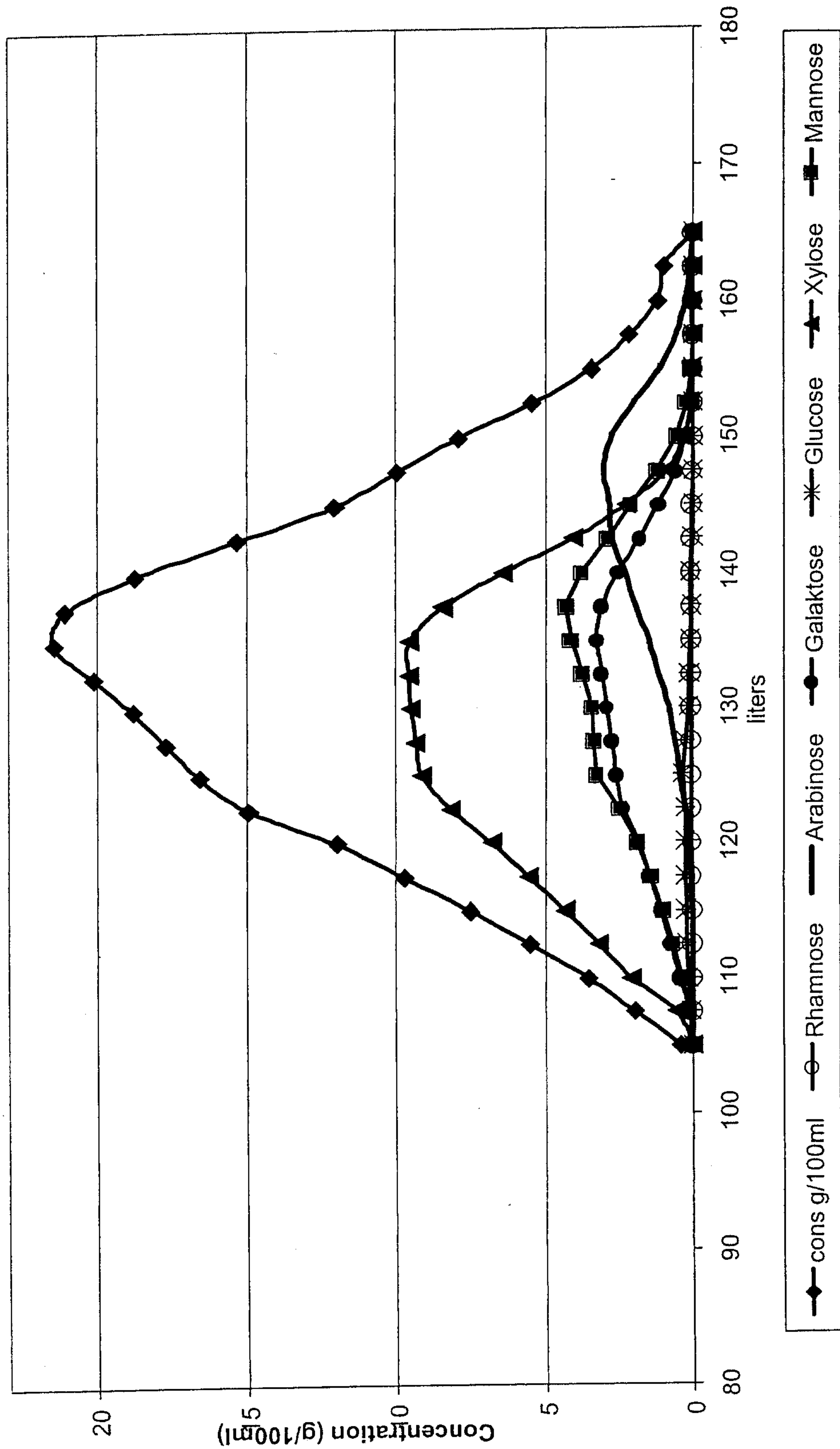
FIG 4



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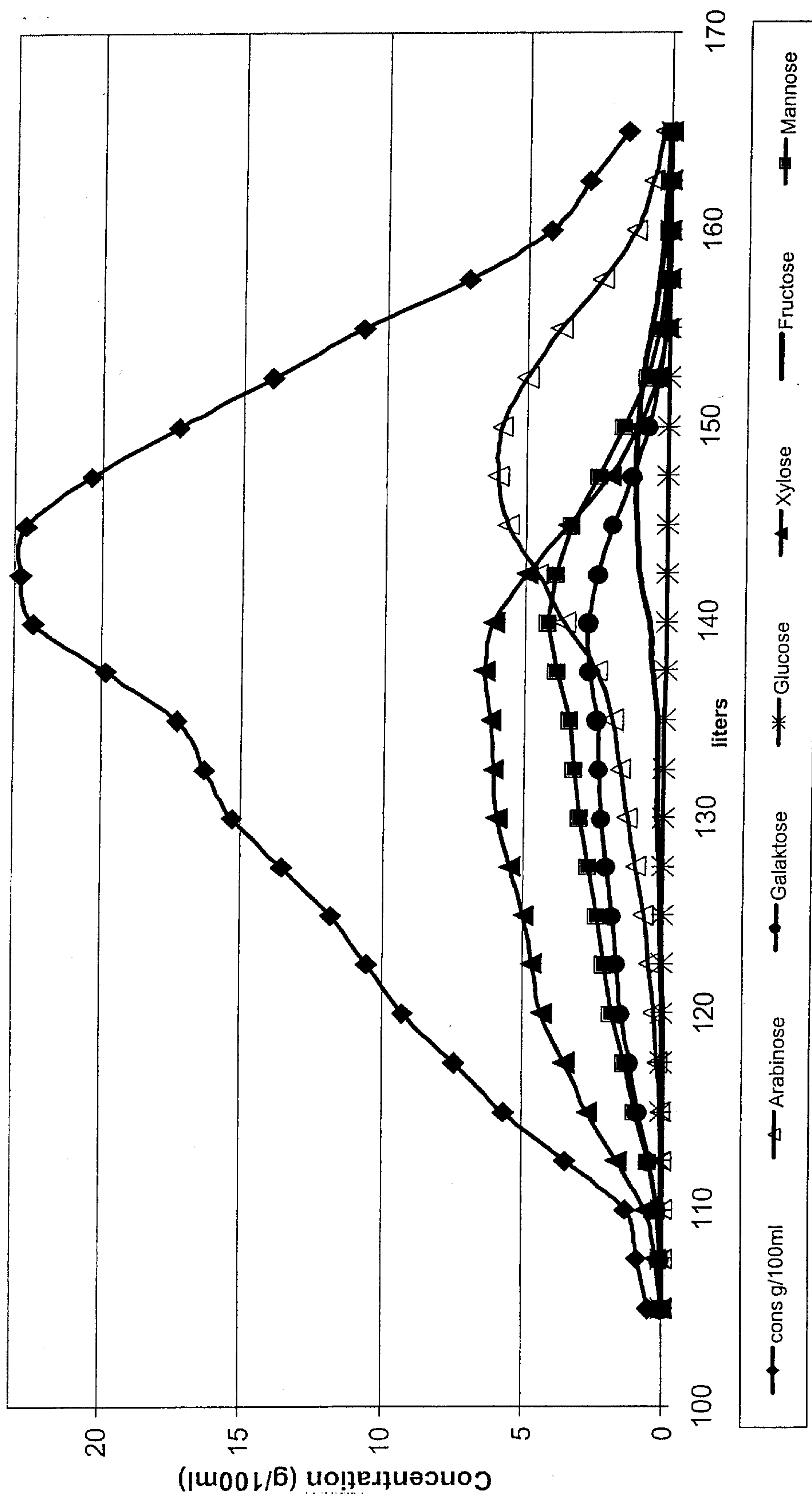
FIG 5



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FIG 6



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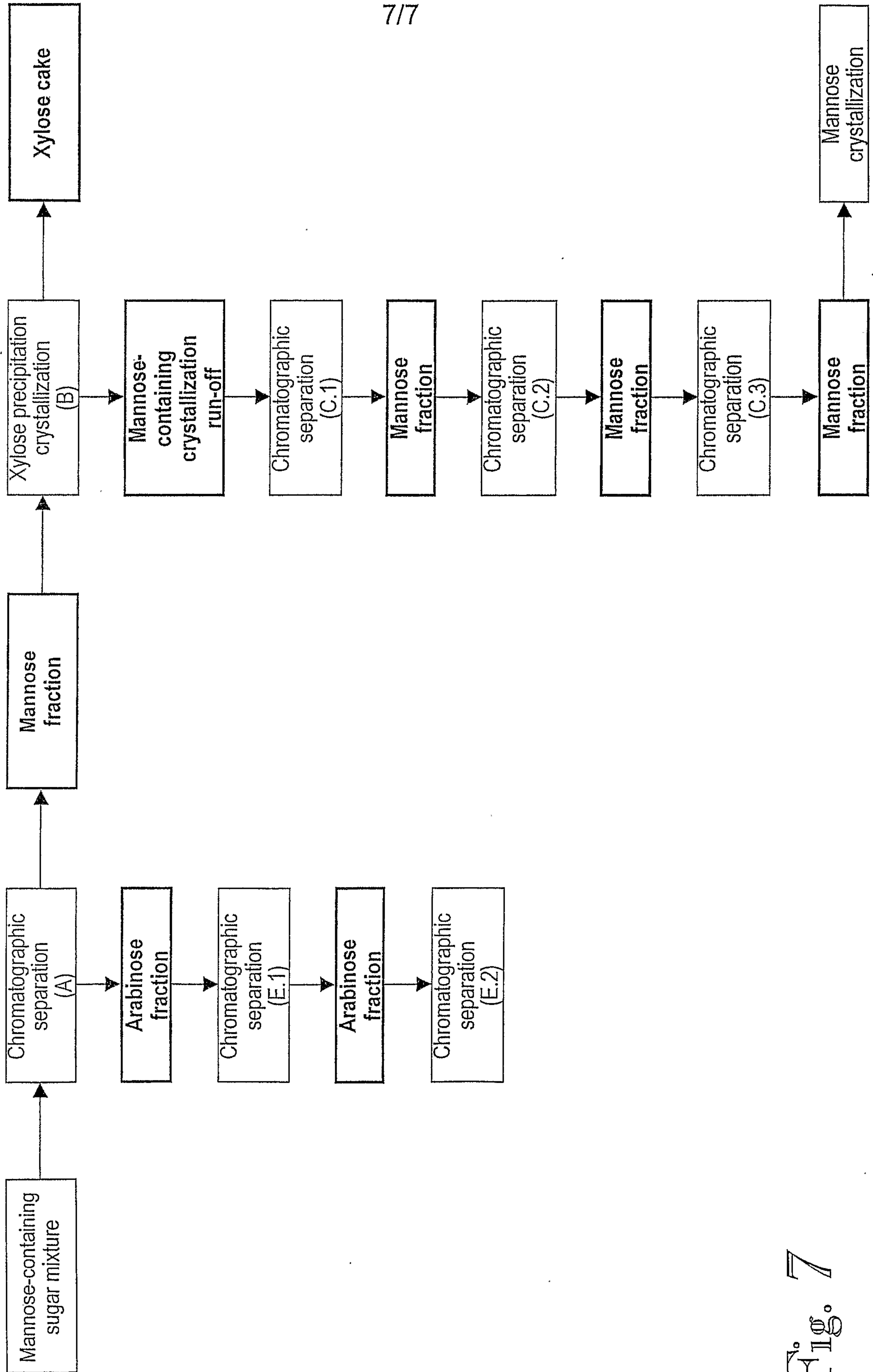


Fig. 7