Abstract: The dicarboxylic acids of isomannide and isosorbide are disclosed, with processes for making the same.
ISOSORBIDE AND ISOMANN1DE DERIVATIVES AND PROCESSES FOR MAKING THE SAME

[0001] The present application is in the field of art relating to cyclic bifunctional carboxylic acid monomers derived from renewable materials, to the methods by which such monomers are made, and to polymer compositions incorporating these monomers.

[0002] Terephthalic acid (benzene-1,4-dicarboxylic acid) is a cyclic bifunctional carboxylic acid monomer which finds widespread commercial application as a primary precursor of polyethylene terephthalate (PET), a thermoplastic resin with widespread use in textiles and containers for food, beverages, and other liquids. Terephthalic acid is polymerized, usually with ethylene glycol monomers in an equimolar ratio with terephthalic acid, to yield the polycondensate PET. Terephthalic acid can also be copolymerized with other diacid monomers or esters thereof to obtain polymers with specific desired properties.

[0003] Terephthalic acid is commonly produced by oxidation of p-xylene originating from non-renewable petroleum derivatives. However, such petroleum-derived materials are frequently expensive to produce and use because of fluctuations in the pricing and availability of petroleum, and are increasingly likely to remain so as petroleum reserves are reduced and new supplies prove more costly and difficult to secure. Further, PET polymers have raised concerns for their potential to disrupt human endocrine activity, as it has been suggested that PET polymers may release yield endocrine disrupters under commonly used conditions. In addition, PET may under certain conditions break down to yield acetaldehyde, causing the development of off-taste in bottled water. Detectable levels of antimony catalyst are present both inside PEC polymers and on the surface, and can migrate into food and beverages in contact with PET, especially fruit juices in PET bottles.

[0004] In view of the dependence of conventional PET polymers on increasingly scarce and costly petroleum resources and further in view of the additional concerns just described, renewable source-based alternatives have been earnestly sought. The most abundant type of biobased or renewable
source alternative feedstock for producing such materials, namely carbohydrates, are however generally unsuited to current high temperature industrial processes. Compared to petroleum-based, hydrophobic aliphatic or aromatic feedstocks with a low degree of functionalization, carbohydrates such as polysaccharides are complex, overfunctionalized hydrophilic materials.

Consequently, researchers have sought to produce biobased materials that derive from carbohydrates but which are less highly functionalized, including more stable bifunctional materials more or less analogous to terephthalic acid, such as 2,5-furandicarboxylic acid (FDCA), levulinic acid and isosorbide. For the present invention, isosorbide and the related isohexides isomannide and isoidide are especially of interest. Recently, in Wu et al., "Isohexide Derivatives from Renewable Resources as Chiral Building Blocks", *ChemSusChem*, vol. 4, pp. 599-603 (2011), several C2/C5 carbon-extended bifunctional derivatives were synthesized from isomannide to provide greater reactivity in common melt polycondensation conditions for forming polyester polymers using the isohexides (or derivatives based thereon). The initial strategy was to make the dinitrile by a nucleophilic substitution of activated hydroxyl groups by cyanide. Unexpectedly for the authors, however, neither the bistosylate nor bismesylate of isomannide showed any reactivity towards cyanide, even though a broad range of reaction conditions were tried. Finally, a successful combination was tried, and the authors were able to obtain the desired dinitrile (in an exo-exo stereochemistry compared to the original endo-endo stereochemistry of the isomannide starting material) through the bistriflate of isomannide, formed by reacting isomannide with trifluorosulfonic anhydride and pyridine in dichloromethane.

Since the diacid was expected to be a possible biobased alternative to terephthalic acid, initial efforts from the dinitrile then focused on hydrolysis to the diacid. Various aqueous routes were explored but also proved unsatisfactory; finally it was determined that by making the dinitrile into a dimethyl ester, then purifying the same, the purified dimethyl ester could undergo hydrolysis to provide isoidide dикаrboxylic acid. The diacid is
described as having been obtained as "a white solid in high isolated yield (84%) and high purity (99.0%)." Other bifunctional derivatives were then also prepared from the isoidide dimethyl ester, in particular, a diol and a diamine.

[0007] While the isoidide diacid and other bifunctional derivatives of isoidide were thus eventually successfully made starting from isomannide, the article does also mention the possibility of the like bifunctional derivatives being made starting from the isosorbide and isoidide stereoisomers; but in contemplating this possibility, the authors noted that $S_{n2}$ reactions on isohexide endo-hydroxyl groups were strongly favored over exo-substitution for steric reasons, and so the authors selected the endo-endo isomannide isomer as a starting material for trying to make the novel bifunctional derivatives in question. The exo-endo isosorbide and exo-exo isoidide derivatives were carried over in the meanwhile for further "investigations."

SUMMARY OF THE INVENTION

[0008] The present invention in a first aspect concerns isomannide-3,6-dicarboxylic acid. In a second aspect, the invention relates to isosorbide-3,6-dicarboxylic acid.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0009] Isomannide-3,6-dicarboxylic acid was successfully prepared from isoidide through isoidide ditriflate and through cyanide displacement to the dinitrile of isomannide (including a Walden inversion from an exo-exo stereochemistry to an endo-endo configuration), followed by hydrolysis of the cyanide to the dicarboxylic acid [IUPAC (3S, 3aS, 6S, 6aS)-hexahydrofuro[3,2-b]furan-3,6-dicarboxylic acid]. Details of the synthesis and isolation are reported below in Example 1.

[0010] The starting isoidide material can be obtained by any known method for making isoidide. According to one embodiment, the isoidide starting material can be prepared by epimerization from isosorbide. In L. W. Wright, J. D. Brandner, J. Org. Chem., 1964, 29 (10), pp 2979-2982, for example, epimerization is induced by means of Ni catalysis, using nickel supported on diatomaceous earth. The reaction is conducted under relatively
severe conditions, such as a temperature of 220°C to 240 °C at a pressure of 150 atmosphere. The reaction reaches a steady state after two hours, with an equilibrium mixture containing isoidide (57%), isosorbide (36%) and isomannide (7%). Comparable results were obtained when starting from isoidide or isomannide. Increasing the pH to 10-11 was found to have an accelerating effect, as well as increasing the temperature and nickel catalyst concentration. A similar disclosure is to be found in US Patent No. 3,023,223.

[0011] In EP 1 647 540, L-iditol is prepared starting from sorbitol. In a first step sorbitol is converted by fermentation into L-sorbose, which is subsequently hydrogenated into a mixture of D-sorbitol and L-iditol. This mixture is then converted into a mixture of L-iditol and L-sorbose. After separation from the L-sorbose, the L-iditol can be converted into isoidide. Thus, sorbitol is converted into isoidide in a four-step reaction, in a yield of about 50%.

[0012] A preferred method for preparing isoidide by the epimerization of isosorbide is described in European Patent Application No. 12156170.8, filed Feb. 20, 2012 for "Method of Making Isoidide". wherein a supported ruthenium catalyst is used at a starting pH of above 7, preferably of from 8 to 10, with the starting pH referring to the pH of the aqueous solution of isosorbide.

[0013] The epimerization of isosorbide into isoidide is conducted according to this process under relatively mild conditions, such that an equilibrium production of isoidide can be attained while avoiding mass losses through hydrodeoxygenation and providing a better overall yield compared to the results of Wright and Brandner.

[0014] The support can vary widely, including silica, alumina, titania, zirconia, and carbon. A carbon support is preferred, inter alia since it can be operated at a wider pH range than other supports. As well, a carbon supported ruthenium catalyst was observed to act more favorably in the epimerization of isosorbide, than other supports, e.g., Al2O3. The catalytically active metal preferably consists essentially of ruthenium, and the support preferably consists essentially of carbon. A suitable ruthenium content is described as from 1% to 10% by weight of ruthenium, based on the total weight of the catalyst, preferably being about 5% by weight of the catalyst.
In order to conduct the epimerization, isosorbide is provided in the form of an aqueous solution. The concentration of isosorbide therein may widely vary. However, for the sake of process economics as well as results in terms of yield, it is preferred for the isosorbide concentration to be in a range of from 25% by weight to 75% by weight. More preferably, the isosorbide concentration is 30% to 60% by weight. The optimum concentration is believed to approximately 50% by weight.

The aqueous solution is subjected to an atmosphere comprising hydrogen. The hydrogen pressure can widely vary, for example, from 20 to 200 bars. However, it was found particularly effective to employ a relatively low pressure in the range of from to 55 bars, and preferably about 40 bars.

Calculated on the basis of a water paste comprising 50% of a 5% ruthenium on carbon catalyst, the catalyst concentration in the reactor, calculated as a weight percentage based on the aqueous solution of isosorbide, can range from as low as, e.g., 1% to as high as, e.g. 50%. However, for the sake of process economics as well as results in terms of yield and specificity, it is preferred for a 5% ruthenium catalyst to be employed in a concentration of from 2 to 20%, and more preferably about 4%. It will be understood that these percentages will hold, mutatis mutandis, for other water paste concentrations than 50%, and other catalyst loadings than 5%.

The skilled person will be aware of how to generally conduct the ruthenium catalyzed reaction. Background references in this respect include US 6,177,598 and US 6,570,043.

The ruthenium catalyst as mentioned preferably comprises a carbon support. Different types of carbon support are contemplated and may be used, e.g., activated carbon or carbon nanotubes. The activated carbon can be, e.g., 50-70% wetted powder. Typically preferred catalysts include commercial ruthenium on carbon catalysts e.g. BASF or Evonik (Strem Chemicals). A background reference on Ru/C catalysts is Sifontes Herrera et al., J. Chem Technol Biotechnol (2011), "Sugar hydrogenation over a Ru/C catalyst."

The epimerization reaction is conducted preferably at an elevated temperature, i.e. above 20°C, and preferably below 250°C. A preferred
The temperature range is 200° to 240°, most preferably about 220°C. The duration of the reaction will generally be shorter at higher temperatures. The residence time in the reactor where the isosorbide solution is subjected to hydrogen under the influence of the catalyst, will generally range from 0.1 to 10 hours, preferably 0.25 to 4 hours, and more preferably 1-2 hours.

It is preferred to adjust the pH of the aqueous solution of isosorbide. Although, for the sake of conducting the epimerization per se, the pH may widely vary, it has been found that unwanted side reactions, which lead to loss of matter as a result of the formation of volatiles, can be reduced considerably by adjusting the pH to a value of 8 to 10.

From the equilibrium mixture, the isoidide starting material can be recovered by separation methods known to the skilled person, such as by chromatographic techniques, selective crystallization or distillation. The latter can be conducted, e.g. as disclosed by Wright et al., J. Org. Chem., 1964, 29 (10), pp 2979-2982, mentioned above.

In like manner, isosorbide-3,6-di-carboxylic acid was also successfully prepared from isosorbide, according to the procedure described in Example 2 below. The isosorbide starting material can be obtained by any known method for making isosorbide, for example, as described in US 7,420,067 to Sanborn or as described in US 6,849,748 or 7,439,352, both to Sanborn et al.

The present invention is further illustrated by the examples which follow:
Example 1

For preparing the isomannide 3,6-di carboxylic acid, initially (3S,3aS,6S,6aS)-hexahydrofuro[3,2-b]furan-3,6-diyl bis(trifluoromethanesulfonate) was prepared:

\[
\begin{align*}
\text{HO} & \quad + \quad \text{F}_3\text{SO}_3\text{SO}_2\text{CF}_3 & \quad \text{+} \quad \text{N} & \quad \rightarrow \quad \text{HO} & \quad + \quad \text{C}_6\text{H}_4\text{SO}_3\text{SOF}_3\text{CF}_3 \\
\text{catalytic} & \quad \text{CH}_2\text{Cl}_2 & \quad 0^\circ\text{C}
\end{align*}
\]

in a procedure adapted from ChemSusChem 2011, 4, pp. 599-603, a 50 mL oven dried boiling flask was charged with 2 g of isoidide, 85 mg of 4-dimethylaminopyridine, 2.44 mL of dry pyridine, and 25 mL of dry dichloromethane. The homogeneous solution was chilled to about 0 deg. C in a brine/ice bath, and while vigorously stirring under a N2 blanket, 4.5 mL of trifluoromethanesulfonic anhydride was added dropwise via syringe. After complete addition, a gelatinous, stationary mass was observed, which dissolved upon attaining room temperature. The reaction proceeded overnight at room temperature, after which the solution was poured over a Celite pad, the filtrate washed with 100 mL of 1M HCl, and the methylene chloride phase dried over anhydrous magnesium sulfate, furnishing 5.22 g of a loose, white precipitate after concentration in vacuo (93%).


From the isomannide ditriflate prepared as described, the dinitrile (IUPAC (3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-dicarbonitrile) was then prepared.

In doing so, an oven-dried 250 mL round bottomed flask was charged with 1.54 g of potassium cyanide (23.6 mmol), 6.24 g of 18-crown-6 (23.6 mmol) and 75 mL of anhydrous THF; the mixture was chilled to about 0 deg. C in a saline/ice bath and purged with argon. A separate, oven-dried 100 mL round bottomed flask was charged with 4.4 g of 3S,3aS,6S,6aS-hexahydrofuro[3,2-b]furan-3,6-diyl bis(trifluoromethanesulfonate (isoidide ditriflate) and 25 mL of anhydrous THF. This mixture was then added dropwise to the cyanide/18-crown-6 solution (over a period of about 10 min).
After addition, the heterogeneous solution was allowed to warm to room temperature and stirred for 5 hours.

[0030] After this allotted time, the slightly darkened solution was poured over 50 mL of ice water, 50 mL of methylene chloride was added, and the resultant Diphasic solution was transferred to a 250 mL separatory funnel. Here, the bottom organic phase was removed, washed twice with 50 mL of water, and concentrated in vacuo to produce 8.10 g of a dark, seemingly insoluble precipitate. Approximately 2 g of this material was triturated with 100 mL of dichloromethane for 1 hour, the solids were filtered off, and the solution concentrated in vacuo, producing about 1.600 g of a crude, light-yellow semisolid. This material was then dissolved in a minimum amount of methylene chloride, adsorbed to about 20 g of silica gel (60A, 40-63 μM, 230 x 400 mesh), dried under vacuum, and added to a prefabricated silica gel column.

[0031] Flash chromatography ensued using a gradient 1:1 to 1:3 Hexane (Hex)/Ethyl Acetate (EtOAc) mobile phase proportion, monitoring the elution of products by GC/MS (CI) and TLC (cerium molybdate stain). The initial products (diastereomers) eluted as 20 cc fractions at 1:1 Hex/EtOAc with a rf of -0.6 (1:1 Hex/EtOAc). After concentration, 130 mg of a clear semi-solid was obtained. High resolution (HR) GC/MS revealed signals at 14.00 min and 15.28 min and manifested the same mass spectra fragmentation pattern for each with a molecular ion of 138.0573 m/z. 1H NMR of diastereomer A; (400 MHz, CDCl3), δ 5.30 (d, J = 4.6 Hz, 1H), 4.99 (t, J = 4.2 Hz, 1H), 4.76 (d, J = 5.0 Hz, 1H), 4.18-4.16 (m, 2H), 4.10-4.09 (m, 1H), 3.25 (m, 1H). 1H NMR of diastereomer B; (400 MHz, CDCl3), δ 5.28 (d, J = 4.6 Hz, 1H), 5.08 (t, J = 4.2 Hz, 1H), 4.84 (d, J = 5.0 Hz, 1H), 4.16-4.14 (m, 2H), 4.06-4.04 (m, 1H), 3.91 (t, J = 4.2 Hz, 1H). The spectral data is consistent with the following structures (3R,3aR,6aR)-2,3,3a,6a-tetrahydrofuro [3,2-b]furan-3-carbonitrile and (R) or (S)-2,3,5,6-tetrahydrofuro [3,2-b]furan-3-carbonitrile:
Further structural elucidation as well as absolute stereochemical assignments will follow for the proposed compounds is in progress.

The penultimate molecular entity to elute did so in 20 cc fractions 33-46 at 1:2 Hexane/EtOAc composition, with a rf of 0.1 (1:1 Hex/EtOAc) and 0.3 (1:2 Hex/EtOAc). Inspissations under vacuum afforded approximately 100 mg of a white semi-solid. HR GC/MS disclosed a single peak at 15.72 min with a molecular ion of 165.0674 m/z. 1H NMR (400 MHz, CDCl3), δ 5.00-4.96 (dd, J = 5.6, J = 2.2 Hz, 1H), 4.88 (t, J = 4.2 Hz, 1H), 4.23 (t, J = 5.0 Hz, 1H), 4.14-4.10 (m, 2H), 4.07 (t, J = 5.8 Hz, 1H), 3.22-3.20 (m, 2H). The spectral data is consistent with the following structures (3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-dicarbonitrile - enantiomer:

The last molecular entity to elute occurred in 20 cc fractions 62-67 at a eluent ratio of 1:3 Hexane/EtOAc, and manifested an rf of 0.1 (1:2 Hex/EtOAc). Concentration of this material under vacuum afforded approximately 120 mg of a translucent semi-solid. HR GC/MS conveyed a single peak at 17.04 min with a molecular ion of 165.0509. The fragmentation pattern was congruent with the aforementioned dinitrile. This was confirmed with GC/MS (EI) which revealed a peak at 35.638 min and a salient fragment at 137.0. 1H NMR (400 MHz, CDCl3). δ 4.88 (d, J = 4.4, 2H), 4.29 (t, J = 4.0 Hz, 2H), 4.11 (t, J = 4.2 Hz, 2H), 3.27 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 115.13, 83.11, 70.87, 36.66. The spectral data is consistent with (3R,3aR,6R,6aR)-hexahydrofuro[2-b]furan-3,6-dicarbonitrile.
Approximately 6 grams of black precipitate remains crude. The total crude recovered was about 8 grams, so it can be assumed that similar yields of the aforementioned molecular entities would be observed upon serial flash chromatographic sequestration. Hence, the overall quantities of (3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-dicarbonitrile and enantiomer is calculated to be about 400 mg (23%) and that of the 3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-dicarbonitrile to be about 480 mg (27%). Collectively, the actual yield of isomannide dinitrile is 50%.

Following preparation of the dinitrile, the isomannide 3,6-dicarboxylic ((3S,3aS,6S,6aS)-hexahydrofuro[3,2-b]furan-3,6-dicarboxylic acid) was prepared from the dinitrile:

A 10 mL round bottomed flask was charged with 100 mg of the (3S,3aS,6S,6aS)-hexahydrofuro[3,2-b]furan-3,6-dicarbonitrile 1 (0.6 mmol) and 3 mL of concentrated hydrochloric acid (~12 M). The resulting suspension was then stirred at 75 deg. C under argon for 6 hours. After this time, the light yellow solution was cooled to room temperature, then with a short path condenser under reduced pressure (10 torr) and with gentle heating (50 deg. C) was concentrated. A beige colored precipitate was observed after 2 hours, weighing 115 mg, and was determined to be (3S,3aS,6S,6aS)-hexahydrofuro[3,2-b]furan-3,6-dicarboxylic acid 2 (95%) by spectroscopic analysis. 1H NMR (d6-DMSO, 400 MHz) δ (ppm) 12.45 (s, 2H), 4.75 (d, J = 6.2 Hz, 2H), 3.83 (t, J = 4.2 Hz, 2H), 3.79 (t, J = 4.4 Hz, 2H).
3.23-3.21 (m, 2H); 13C NMR (d6-DMSO, 100 MHz) δ (ppm) 170.10, 83.92, 68.98, 50.49.

[0038] Example 2

[0039] The isosorbide-3,6-dicarboxylic acid (IUPAC (3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-dicarboxylic acid) was synthesized, corresponding to structure 4 in the formula, in a series of steps:

![Chemical diagram]

[0040] Initially, isosorbide-3,6-ditriflate (IUPAC (3R,3aS,6S,6aS)-hexahydrofuro[3,2-b]furan-3,6-diyl-bis(trifluoromethanesulfonate), corresponding to structure 2) was prepared from isosorbide (structure 1).

[0041] A 100 ml two neck boiling flask containing a magnetic stir bar was charged with 1.00 g of isosorbide (6.84 mmol), 4.25 g of triflic anhydride (15.05 mmol), and 30 mL of anhydrous THF. An argon inlet adapter and rubber septum were then fitted to the flask ports, and the mixture was chilled to about 0 deg. C in an ice/brine bath. While stirring and under an argon blanket, 1.65 mL of pyridine (20.5 mmol) was injected dropwise via a syringe over a 5 minute period. Once added, the brine bath was removed and the reaction continued at room temperature for 2 hours, by which time TLC (4:1 EtOAc/MeOH) indicated that all isosorbide had been consumed. Excess solvent and pyridine was evaporated under vacuum and the syrupy residue dissolved in about 2 mL CH2Cl2 before being directly charged to a prefabricated silica gel flash column (Hex/EtOAc). The target, (3R,3aS,6S,6aS)-hexahydrofuro[3,2-b]furan-3,6-diyl
bis(trifluoromethanesulfonate) 2, was observed to elute with a 4:1 Hex/EtOAc mobile phase (cerium molybdate stain), rf 0.7 (1:1 Hex/EtOAc) producing 2.25 g of a white precipitate after drying (81%). 1H NMR (d6-DMSO, 400 MHz) δ 5.52 (m, 2H), 4.26 (m, 2H), 3.99 (m, 2H), 3.55 (m, 2H); Elemental Analysis: Predicted C (23.42%) H (1.97%); Found C (23.48%) H (1.99%).

[0042] The isosorbide 3,6-dinitrile (IUPAC (3R,3aR,6S,6aR)-hexahydrofuro[3.2-b]furan-3,6-dicarbonitrile, corresponding to structure 3) was then prepared.

![Chemical Structure Diagram]

[0043] An oven dried. 100 mL boiling flask was charged with 349 mg of potassium cyanide (5.36 mmol), 1.42 g of 18 crown 6 (5.36 mmol), and 10 mL of anhydrous THF. The heterogeneous mixture was then chilled to 0 deg. C in an ice/brine bath. In a separate 50 mL boiling flask, 1.00 g of the isosorbide ditriflate (2.44 mmol) was dissolved in 10 mL of THF, then the solution was poured into a 50 mL addition funnel and added to the cyanide solution at a rate of ~2 mL/min. Once the entire volume had been added, the mixture was removed from the ice/brine bath and the reaction continued at room temperature for another 2 hours. At this time, a deep red solution was observed, and multiple spots developed on a silica gel TLC plate. The solvent was evaporated under vacuum, the remainder dissolved in a minimum amount of CH2Cl2 and charged to a prefabricated silica gel column. Carefully monitored flash chromatography was then conducted with gradient CH2Cl2 to EtOAc eluents. Three distinct fraction sets were collected; those corresponding to isosorbide dinitrile transpired with an eluent ratio of 6:1 EtOAc/CH2Cl2, and after drying, produced 333 mg of a deep-yellow semi-solid (81%). 1H NMR (d6-DMSO, 400 MHz) δ 5.26 (m, 2H), 4.09 (m, 2H), 4.02 (m, 2H), 3.37 (m, 2H); HRMS (M+H) Predicted for C8H9N2O2: 165.0664; Found 165.0662.
[0044] Following preparation of the isosorbide dinitrile as described, the isosorbide 3,6-diacid was made (IUPAC (3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-dicarboxylic acid, corresponding to structure 4).

![Diagram]

[0046] A 10 mL round bottomed flask was charged with 100 mg of the isosorbide-3,6-dinitrile (0.6 mmol) and 3 mL of concentrated hydrochloric acid (about 12 M). The resulting suspension was then stirred at 75 deg.C under argon for 6 hours. After this time, the reddish solution was cooled to room temperature, then concentrated with a short path condenser under reduced pressure (about 10 torr) and with gentle heating (50oC). A dark brown precipitate was observed after overnight drying, weighing 111 mg (90%), and this was determined to be isosorbide-3,6-dicarboxylic acid spectroscopically. 

$^1$H NMR (D2O, 400 MHz) $\delta$ 4.89 (m, 2H), 4.01 (m, 2H), 3.89 (m, 2H), 3.22 (m, 2H); HRMS (M+) Predicted for C8H10O6: 202.0477; Found. 202.0466.
CLAIMS

1. \((3S, 3aS, 6S, 6aS)\)-hexahydrofuro\([3,2-b]\)furan-3,6-di-carboxylic acid.
2. \((3R, 3aR, 6S, 6aR)\)-hexahydrofuro\([3,2-b]\)furan-3,6-di-carboxylic acid.
3. The dicarboxylic acid of isomannide.
4. The dicarboxylic acid of isosorbide.
A. CLASSIFICATION OF SUBJECT MATTER
C07D 493/04(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D 493/04; C09D 5/08; C08G 63/12; C09K 3/00; C08G 63/91

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: isohexide, dicarboxylic acid, isomannide, isosorbide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Form PCT/ISA/210 (second sheet) (July 2009)
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