Molecular Modeling Studies on the Reduction of Inososes and Deoxy-inososes.
A Synthetic and Historical Overview of the Cyclitols.

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(Abstract)

The inososes are a group of compounds, containing six-membered rings that have five hydroxyls (four for the deoxyinososes) and a carbonyl. Due to the relative ease of their reduction to inositols, a study aimed at the potential preparation of these useful natural products was undertaken. The constitution of the hydroxyls shows that either the $\alpha$ or $\beta$ face can react with an appropriate reducing agent, such as Raney Ni/H$_2$, to yield the expected inositol. It has been shown by others that, by using Raney Ni/H$_2$ as the reducing agent equilibrium between the two chair conformations can be established and the carbonyl can be reduced stereoselectively. This is shown in the example below for *allo*-1-inosose:

Molecular modeling with PCMODEL© which invokes MMX calculations was performed to permit a distinct prediction of the course and the stereochemical outcome of the reduction of the inososes.

Several inososes and deoxyinososes were modeled to demonstrate the ability of MMX calculations to predict the stereochemical outcome of the reduction. Based on the results of molecular modeling, which include the heats of formation, and the strain energies, the lowest energy form was determined for each inosose and deoxyinosose. With the lowest energy form predicted, stereochemistry of the inositol or deoxyinositol product was predicted. In one case, a comparison with known experimental results was made.
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Table of Contents

I. Introduction

II. Historical
   1. Cyclitols
   2. Review of Cyclitol Syntheses
   3. Hydrogen Bonding

III. Discussion
   1. Introduction
   2. MMX-Energy Calculations of Inososes and their Reduction Products.
   3. Summary

IV. Conclusion

V. Tables and calculations

VI. References

VII. Vita
I. Introduction

The cyclitols, or oxygenated cyclohexanes, are of interest from a synthetic viewpoint in that they exhibit important biological functions and have four to six stereocenters. These natural products possess, within their structures, hydroxyls around a cyclohexane ring. The inositolts (cyclohexanehexols (A)), quercitolts

\[ \text{(cyclohexanepentols (B))}, \text{ dihydroconduritolts (cyclohexanetetrols (C))}, \text{ and conduritolts (cyclohexenetetrols (D)) (Figure 1) have described as well as theorized biological activities:} \]

1. *Myo*-inositol triphosphate acts as a cellular secondary messenger by binding to a specific receptor on the receiver cell's surface and converting the incoming signal to a response inside the target cell. \(^1\)

2. Pinitol, a methyl ether derivative of *D-chiro*-inositol, is a known growth inhibitor of *Heliothis zeae* via reduction of ingestion. \(^2\)

3. Conduritolts, as well as dihydroconduritolts, exhibit a potential use as glycosidase inhibitors. \(^3\)

4. Quercitolts (or deoxy-inositolts) have been found to be readily oxidized by *Acetobacter suboxydans*. \(^4\)

In order to increase an understanding of the chemistry of the inositolts, a study in the energetics of their formation from the corresponding inosose (I) (Figure 2) was undertaken. The focus of this study is to determine the stereochemical outcome of reduction of a known inosose by using molecular modeling/MMX calculations.

In addition to molecular modeling, a tabular survey of past syntheses of the cyclitols, is presented, due to the abundance of these compounds reported in the literature.
Figure 2. Reduction of inosose
II. Historical

1. Cyclitols

In 1850, an optically inactive cyclohexane polyol was isolated. The compound was given the name inositol and the suffix -ol was added later. After subsequent isolation of other inositols, prefixes were added to the names of the nine different inositol isomers which exist as seven meso forms (epi, neo, muco, myo, scylo, allo, and cis) and one D, L pair (D- and L-chiro -inositol), (Fig.3).n.b.* (see page 7)

![Chemical structures of inositol isomers](image)

**Figure 3.** The nine isomers of hexahydroxycyclohexane

The first identified inositol was myo - inositol, which is also the most common and one found either free or in a combined form as a methyl ether or phosphate derivative.7
myo -inositol is found in nearly all living tissues. It has even been detected in the mammalian central nervous system.\(^8\) The next most abundant inositols are D- and L-chiro -inositol, the optically active forms. These inositols are isolated predominantly in the form of their methyl ether derivatives, D-(+)-pinitol and L-(−)-quebrachitol.\(^7\) D-chiro-Inositol is a structural component of the antibiotic kasugamycin.\(^28\) It also has been detected in human hepatic tissue.\(^8\) The last inositol which is readily available from natural sources is scyllo -inositol, and has been isolated not only from plant \(^9\) and fish sources \(^9\) but has also been detected in small amounts in mammalian tissue.\(^10\)

The first report of neo and muco inositol was from synthetic means eventhough they have since been isolated form natural sources. \(^5\) Allo-, cis-, and epi- were also first synthesized and later detected in nature. \(^6\) Neo -inositol has been isolated from soil phytate \(^14\) whereas muco -inositol has been found in many plant sources as a methyl ether derivative.\(^6\)

Many of the naturally occurring methyl ether derivatives of the inositols are found to be related to myo -inositol. These include D- and L-bornesitol, D- and L-ononitol, sequoyitol, dambonitol, and (-)-liriodendritol.\(^16\) Other methyl ethers of inositol such as D-(+)-pinitol and L-(−)-quebrachitol are derived from D and L-chiro -inositol respectively.\(^11\)

The pentahydroxycyclohexanes, previously referred to in the literature as quercitols, were isolated as long ago as 1849 \(^12\), from the acorns of an oak tree of the species Quercus, hence the name quercitol. \(^13\) This original quercitol, dextro -quercitol, has since been found in vegetable matter \(^7\) following its constitutional determination some eighty years after its isolation. \(^14\) Stereochemical theory predicts there to be ten deoxyninositols or quercitols (Fig.4), four of which are meso compounds and the remaining six are pairs of enantiomers. These compounds are best prepared by hydrogenation of a corresponding anhydroinositol\(^15\), which has the general structure:

![Structure](image)

Hydrogenation of a chloro- \(^16\), bromo- \(^14\), iodo- \(^16\) deoxyninositol, may also be employed. Still other means have been utilized which do not yield clean results. \(^18\) One of these methods is acidic hydrogenolysis of an inosose but side reactions can occur especially if there is an axial hydroxyl a to the carbonyl.\(^17\)
Figure 4. Ten isomers of pentahydroxycyclohexane

The tetrahydroxycyclohexanes, most common of which are the dihydroconduritols, are a subclass of the inositolts in which the number of hydroxyls is four instead of six. There are three families of cyclohexane-tetrols, with substitution patterns: 1,2,3,4-; 1,2,4,5-; and 1,2,3,5- (Fig. 5). The numbers refer to the positions at which hydroxyls are located. Most of these compounds are not found in nature, but nearly all possible stereo and positional isomers have been synthesized, mostly by reduction of a conduritol to give the corresponding dihydroconduritol. Hydroxylation of an unsaturated precursor has been utilized to synthesize the tetrols as have enzymatic, asymmetric, and other synthetic methods.
Figure 5. Three forms of tetrahydroxycyclohexanes

The cyclohexenetetrols, commonly referred to as conduritols, were first isolated in 1908 by Kubler. Upon determination of configuration, it was determined that six diastereomers were possible (Fig. 6). All the conduritols have been synthesized and a review by Balci gives an overview of the preparation of these compounds.

Figure 6. Six Diastereomers of Conduritols

The known biological activities of the cyclitols make for challenging and interesting synthetic work. Inositol phosphates are known as cellular secondary messengers which act to regulate intracellular calcium by not only mobilizing calcium from internal stores but possibly also indirectly stimulating calcium entry. The deoxyinositols have been tested but so far have not revealed any important function. 2-Deoxy-D-chiro-inositol was tested for action on human cancer cells but no support or inhibition was revealed. Some conduritols derivatives are active site directed inhibitors of glycohydrolases as well as β-galactosidase inactivators. A few epoxide derivatives of the conduritols exhibit such biological activity as tumor inhibition, antileukemic activity, and antibiotic activity.
has even been determined that some species of bacteria, e.g. *Klebsiella aerogenes* use myo-inositol and other cyclitols as carbon and energy source.\(^8\)

The ubiquitous utility of these compounds and their biological importance prompted an investigation of methods that would aid in predicting the stereochemistry of reduction of inososes as the means of their stereocontrolled production. The discussion section describes the molecular modeling utilized to predict stereochemical outcome of inosose reduction.

The following section lists the available data concerning the cyclitols and their structure and synthesis.

\*n.b. -The numbering system used follows the index guide of Chemical Abstracts and is represented in Figure 3 in the text. A somewhat different numbering system was published by Reitz\(^{44}\) and is represented below.

\[ \text{scyllo} \quad \text{myo} \quad \text{neo} \quad \text{epi} \quad \text{D-chiro} \quad \text{L-chiro} \quad \text{cis} \quad \text{muco} \quad \text{allo} \]

The inositol stereoisomers with hydroxyls omitted
II. Historical

2. Review of Cyclitol Syntheses

The cyclitols are interesting because they are natural products which exhibit important biological activity. They contain four or more chiral centers but are not necessarily chiral compounds; the chirality of these compounds makes their synthesis challenging. Many of the cyclitols have been synthesized and the literature was extensively reviewed. Some of the more common synthetic methods are summarized below. These are subdivided into three general areas according to the methods by which the compounds are synthesized; i, cyclitol/cyclitol interconversions, which were the first methods used to prepare the inositol not found in nature; ii, biocatalysis, or the conversion of achiral starting materials to chiral products via biological transformations; and iii, de novo synthesis using such methods as chiral auxiliaries as exemplified by the approach of by Vogel.

Comprehensive listing of all known syntheses is found at the end of this section (Table 1).

i, Cyclitol Interconversions

a. Acid hydrolysis of an anhydro-inositol (prepared from L-chiro-inositol) yields neo-inositol (see fig. 7).

\[
\begin{align*}
\text{O} & \quad \text{H}_2\text{O} \\
\text{O} & \quad \text{OH} \\
\text{O} & \quad \text{OH} \\
\text{O} & \quad \text{OH} \\
\text{O} & \quad \text{OH} \\
\end{align*}
\]

Figure 7

b. Methylation of myo-inositol yields L-bornesitol (see fig. 8).

\[
\begin{align*}
\text{HO} & \quad \text{BaOH} \quad \text{H}_2\text{O} \\
\text{HO} & \quad \text{OH} \quad \text{DMS} \\
\text{HO} & \quad \text{OH} \\
\text{HO} & \quad \text{OH} \\
\text{HO} & \quad \text{OH} \\
\end{align*}
\]

Figure 8
c. Elimination of vicinal sulfonyloxy-groups in an epi-inositol derivative by iodide ion gives conduritol-D (see fig. 9)\textsuperscript{31}

\[
\text{RO} \quad \overset{\text{NaI}}{\text{acetone}} \quad \text{OH} \quad \text{OH} \\
\text{RO} \quad \text{R} = p - \text{NO}_2\text{C}_6\text{H}_4\text{SO}_2
\]

**Figure 9**

d. *tao*-Quercitol (or 1-deoxy-*neo*-inositol) has been prepared by hydrogenolysis from the corresponding halo-derivative (see fig. 10)\textsuperscript{15}

\[
\text{Br} \quad \overset{\text{Amberlite IR-45}}{\text{H}_2} \quad \text{Raney Ni} \quad \text{OH} \quad \text{OH} \\
\text{HO} \quad \text{HO} \quad \text{HO} \quad \text{HO}
\]

**Figure 10**

ii. Biocatalysis

a. (+) and (-)-pinitol have been synthesized from benzene via microbial oxidation followed by epoxide opening with a chiral nucleophile (see fig. 11)\textsuperscript{32,38}

\[
\overset{P. \text{ putida}}{\text{CH}_2} \quad \text{OH} \quad \text{OH} \quad \text{MeO} \\
\text{HO} \quad \text{HO} \quad \text{OH} \quad \text{OH}
\]

**Figure 11**
b. Dihydroconduritol C has been prepared from chlorobenzene with the key step being the microbial oxidation of the aromatic ring with *Pseudomonas putida* (see fig. 12). 19

![Figure 12]

iii. De novo Syntheses

a. (-)-Conduritol B was prepared from bicyclic ether 26 in Vogel's "naked sugar" approach (see fig. 13). 34

![Figure 13]

b. Hetero Diels-Alder cycloadduct 27 gave Conduramine-A1 upon further elaboration (see fig. 14). 35

![Figure 14]
c. Catalytic reduction of an epoxy endoperoxide and epoxide opening of the resultant oxirane yields dihydroconduritol F (see fig. 15). 20
These and many other methods have been performed often using naturally occurring compounds as chiral starting reagents, e.g. inositols and sugars. Other methods exist that use achiral compounds as starting materials which are converted to chiral compounds, e.g. microbial oxidations and asymmetric oxidations of alkenyl or dienyl compounds. 39

The phosphate derivatives, not included here, are abundant in the literature 36 and deserve a review dedicated to their syntheses. The following tabular survey summarizes the structures of cyclitols, their various syntheses, and the natural sources from which they were isolated.
II. Historical

3. Hydrogen Bonding

A hydrogen bond, by definition, is a bond between a hydrogen atom (that is covalently bonded to an electronegative atom) and a second atom that is greater in electronegativity than a hydrogen atom. The first report of such a bond was by Latimer and Rodebush in 1920.

The concept of hydrogen bonding gained wider acceptance when Pauling discussed its properties in "The Nature of the Chemical Bond." Previous to this publication is the report by Pauling of the dependence on hydrogen bonding in infrared spectral absorbances of hydroxyl and imino functional groups. It was stated that in compounds like catechol and o-chlorophenol the electronegative atom is attracted to the hydroxyl proton so as to stabilize the configuration so that the atoms are cisoid (I) as opposed to being transoid (II) (figure 16). This interaction between hydroxyl hydrogen or imino hydrogens and X has also been detected in many biological structures.

\[
\begin{align*}
\text{Figure 16} \\
\text{X = Electronegative Atom}
\end{align*}
\]

The Watson-Crick model of DNA was defined by the hydrogen bonds between the hetero base pairs, adenine-uracil, or thymine and guanosine-cytosine, in the double helical structure of this essential biological compound. There are four different base pair interactions of adenine and uracil combinations, two defined by Watson and Crick and two defined by Hoogsten as determined from crystal structure studies. These base pair interactions are shown in figures 17 and 18.

Crystal structures provide an excellent method for studying hydrogen bonds. This is exemplified in the crystal structures of cyclodextrins which give excellent quality crystals for study. Their hydrogen bonds are between water molecules and the hydroxyls which act as both donors and acceptors. Cyclodextrins, which crystallize as polyhydrates, contain large chains of OH---HO type hydrogen bonds. These hydrated
Figure 17

The guanosine-cytosine bases form the Watson-Crick GC\(^2\) and reversed Watson-Crick GC\(^3\), (figure 19) due to the complimentary donor-acceptor interactions of these molecules.

Figure 18

compounds display what is termed as 'flip-flop hydrogen bonds' which is the positional and rotational disorder between the water molecules and hydroxyl groups. 58 In this
system, the bonding serves to determine the cleft formed by the intramolecular hydrogen bonds.

In addition to studies of purine and pyrimidine, hydrogen bonds playing a key role in conformational analysis. NMR studies by Kishi 57 have shown that anomeric rotamers of α-(axial)-C-glycosides (of the type IV) have the preferred conformation (III), Figure 20

![Figure 20](image)

where β-(equatorial)-C-glycosides (of the type VI), analogous to the axial compound have the preferred conformation (V). Solvent effect studies, with particular attention paid to hydrogen bonding, showed that polarity does not play a large role in this conformational determination. The protection of the free hydroxyls did little to alter the conformation of the compounds. 57

![Figure 21](image)

In determinations of conformation of diamides 59 and triamides 60, intramolecular hydrogen bonding was found to be a key factor contributing to the stability of the molecule. In the triamide the preferred conformation displays a nine-membered ring hydrogen bond (figure 22) whereas the diamide is more flexible and little intramolecular hydrogen bonding occurs at room temperature yet at lower temperatures, where rotations may be frozen out, intramolecular hydrogen bonding existed 59

![Figure 22](image)
The secondary structure of peptides was studied by Kemp using conformational analysis.\textsuperscript{61} Conjugates of short peptides were prepared because they were believed to exhibit hydrogen bonding similar to that in $\alpha$-helices. These $\alpha$-helices may act as a mold (or template) for the folding of the linked peptide chains. The $\beta$ turns of the peptide sheet were assigned by $^1$H NMR studies.\textsuperscript{62} Epindolinidione derived peptides (Figure 23) link so as to give a characteristic $\beta$-sheet structure due to intramolecular hydrogen bonding.\textsuperscript{62}

![Chemical structure](image)

**Figure 23**

The work of Cram\textsuperscript{63} and Rebek\textsuperscript{64} on guest-host chemistry (or molecular recognition) invokes, as an important factor in determining the structure in molecular complexes, hydrogen bonding, as well as ion pairing, acid/base interactions, and van der Waals attractive forces. Hosts are analogous to receptor sites on cells in biological chemistry and guests are analogous to hormones, substrates, inhibitors, and cofactors. For a guest to complex to a host binding site hydrogen bonds must contact and attract so as to have as little nonbonded repulsions as possible. Guests complex with hosts when stereoelectronic factors are complimentary over a large surface area of each host and guest.\textsuperscript{65} Some of the hosts studies by Cram\textsuperscript{63} are of the spherand family. The "receptor site" (or host) of these compounds is defined by the intramolecular hydrogen bonds.

Molecular recognition studies by Rebek\textsuperscript{64} involve not only modifying of hydrogen bonds so as to increase selectivity for nucleoside attachment (see below) but also studying the shape of the host for recognition by the guest. For example, molecules with both imide and lactam functionalities act as host by complexing asymmetric diketopiperazine in a U-shaped cleft configuration (Figure 25).
The diketopiperazine is able to complex via hydrogen bonds without producing steric interaction problems.

Water forms many hydrogen bonds to other water molecules or hydrogen bonds between itself and other species in aqueous solutions, yet nonpolar species aggregate when placed in aqueous solutions. Bonds between water molecules are more favorable than water molecules bonded to hydrocarbons. The hydrophobic effect \(^{66}\) is the key factor in these interactions. With water as a solvent Diels-Alder reactions with added LiCl show an increased rate of reaction. \(^{67}\) This can be explained in that Li\(^+\) may be solvating electron pairs and thereby freeing up hydrogen bond donor sites to bond to Cl\(^-\).
which solvates the molecules involved in the Diels-Alder reaction. By adding the salt large cavity formation (which the hydrocarbon fits into) is more difficult 67, so this salt may simply solvate the hydrocarbon more easily.

Seeing how hydrogen bonds play an important part in biological systems, reaction rates and molecular recognition, how can one know if a hydrogen bond will form between a donor and an acceptor. According to Etter, 68 there are three rules for hydrogen bonding in organic compounds:

1. "All good proton donors and acceptors are used in hydrogen bonding."
2. "Six-membered ring intramolecular hydrogen bonds form in preference to intermolecular hydrogen bonds.
3. "The best proton donors and acceptors remaining after intramolecular hydrogen bond formation form intermolecular hydrogen bonds to one another."

By use of graph sets, 68 Etter was able to characterize a hydrogen according to one of five types, C (chain), R (ring) two types, D (dimer), S (intramolecular), and Ni (network). In examining crystal structures, graph sets can be assigned and patterns of hydrogen bonds can be determined. This recognition of hydrogen bonding patterns has been used as a method for determining aggregation patterns in crystal structures. 68

The volume of literature on hydrogen bonding is vast and has been widely reviewed. For recent reviews on various topics of hydrogen bonding see the work of Saenger 58, Joesten, Kachur, and the others mentioned in this section.
Table 1. Cyclitols and their derivatives arranged from least substituted to most substituted.
Cyclohexanetetrols and their Derivatives


Physical Constants: mp = 193 °C; Anal. calc'd for C₆H₁₂O₄: C 48.6, H 8.16; Found: C 48.4, H 8.20.

Spectral Properties: ^1H NMR (D₂O) δ 2.22 (q, 4H (CH₂)); 4.43-4.67 (m, 4H (O-C-H)).

Synthesis:


Physical Constants: mp = 198-203 °C; Anal. calc'd for C₆H₁₂O₄: C, 48.64; H, 8.16; Found: C, 48.94; H, 8.29.

Synthesis:
Isolation and/or Identification:

Physical Constants: mp = 200°C ; [α]D20 = - 8.3° (c 0.5{mg/100mL}, water);
Anal calcd for C6H12O4: C 48. H 8.2; Found: C 48. H 3.05

Synthesis:

Isolation and/or Identification: Le Drian, C.; Vionnet, J.P.; Vogel, P., Helv.

Physical Constants: mp = 144-145 °C ; [α]D17 = - 27.2° (c 1.1{mg/100mL},
H2O); IR (KBr) ʋ 3400, 3280, 3060, 3020, 2960, 1680, 1500, 1440, 1330, 1270,
1200, 1140, 1090, 1060, 1020, 990, 900 cm⁻1; Anal calcd for C6H12O4: C 48.6 H
8.18; Found: C 48.5 H 8.20

Spectral Properties: Spectral Properties: 1H NMR (250 MHz, CD3OD) δ 3.42
(m, H-C(1), H-C(4)); 3.15 (part of AA'X', 3J (H-C(1), H-C(2)) = 3J (H-C(2), H-
C(3)) = 9, 4J (H-C(1), H-C(3)) = 5J (H-C(1), H-C(4)) = 0, H-C(2), H-C(3)); 1.92 (m,
2H, Heq-C(5), Heq-C(6)); 1.38 (m, 2H, Haax-C(5), Haax-C(6)); 13C NMR (62.9 MHz,
CD3OD) δ 79.1, 73.9 (2d, 1J (C,H) = 140 Hz); 30.0 (t, 1J (C,H) = 129 Hz); MS (70
eV) m/z 112 (19, [M-36]+), 86 (94), 83(19), 73 (100), 71 (32), 70 (21), 60 (56), 57
(61).
Synthesis:

![Dihydroconduritol-C](image)


Physical Constants: Rf = 0.29 (Butanone; glacial AcOH: 2% Boric Acid, 9:1:1); mp = 157-158°C; [α]_{D}^{20} = -35.8° (c 4.7 {mg/100mL}, water); Anal calcd for C_{6}H_{12}O_{4}: C 48.6 H 8.16; Found: C 48.6 H 8.20.

Spectral Properties: \textsuperscript{1}H NMR (360 MHz, CD_{3}OD) δ 3.9 (td, J = 3, 3 Hz, H-C(2)); 3.67 (ddd, J = 10, 9, 4.5 Hz, H-C(4)); 3.58 (ddd, J = 10, 4.5, 3 Hz, H-C(1)); 3.23 (dd, J = 9, 3 Hz, H-C(3)); 1.83 (dq, J = 13 Hz, 4.5 Hz, Heq-C(5)); 1.70 (td, J = 13 Hz, J = 13, 10, 4.5 Hz, Hax-C(6)); 1.59 (dq, J = 13 Hz, J = 4.5 Hz, J = 1 Hz, Heq-C(6)); 1.19 (tdd, J = 13 Hz, J = 13, 10, 4.5 Hz, Hax-C(5))

Synthesis:
1,2,3,4-Cyclohexanetetrol
or Dihydroconduritol D


Physical Constants: mp = 222 °C.

Synthesis:

(+)-cyclohexane-1,2/3,4-
tetrol or
Dihydroconduritol-E


Physical Constants: mp = 215°C; [α]D^26 = +72° (c1.7{mg/100mL}, H2O); Anal calcd for C6H12O4: C 48.6, H 8.15; Found: C 48, H 8.2

Synthesis:

Physical Constants: mp = 135-136 °C; $[\alpha]_D^{20} = +31^\circ$ (c .07{mg/100mL}, H$_2$O); IR (KBr) v 3400, 3300, 2960, 2940, 2860, 1580, 1440, 1350, 1300, 1250, 1210, 1180, 1130, 1110, 1050, 1030, 990, 930, 880, 850 cm$^{-1}$; Anal. calcd for C$_6$H$_{12}$O$_4$: C 48.6 H 8.18; Found: C 48.5 H 8.20

Spectral Properties: $^1$H NMR (250 MHz, CD$_3$OD) $\delta$ 3.98 (q, $^3$J = 3 Hz, H-C(1)); 3.58 (t, $^3$J = 9 Hz, H-C(3)); 3.41 (td, $^3$J = 9, 9, 5.5 Hz, H-C(4)); 3.35 (dd, $^3$J = 9, 3 Hz, H-C(2)); 1.85 (dq, $^2$J = 14 Hz, $^3$J = 3.5 Hz, H$_{eq}$-C(6)); 1.85-1.71 (m, H$_{ax}$-C(5), H$_{eq}$-C(5)); 1.54 (dddd, $^2$J = 14 Hz, $^3$J = 12, 3, 2.5 Hz, H$_{ax}$-C(6)) $^{13}$C NMR (62.9 MHz, CD$_3$OD) $\delta$ 76.5, 76.1 (2d, $^1$J (C,H) = 145 Hz); 74.2 (d, $^1$J (C,H) = 140 Hz); 70.6 (d, $^1$J (C,H) = 145 Hz); 28.1 (t, $^1$J (C,H) = 125 Hz); 27.7 (t, $^1$J (C,H) = 130 Hz); MS (70 eV) m/z 112 (13,[M-36]$^+$), 86 (100), 83 (17), 73 (88), 71 (26), 70 (20), 60 (41), 57 (52).

Synthesis:

![Chemical Structure](image)


Physical Constants: Colorless oil; Purified by column chromatography on silica gel (Lobar, AcOEt/ petroleum ether 1:2) $[\alpha]_D^{25} = +33.5^\circ$ (c 1.05{mg/100mL}, CHCl$_3$); IR (KBr) v 2980, 2940, 1750, 1440, 1240, 1100, 1050, 1040, 940, 920, 830 cm$^{-1}$; Anal. calcd for C$_{14}$H$_{20}$O$_8$: C 53.1 H 6.37; Found: C 53.1 H 6.35
Spectral Properties: $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 5.4 (m, 2H); 2.14, 2.04, 2.03, 2.00 (4s, CH$_3$CO); 1.5-2.1 (m, 4H); $^{13}$C NMR (62.9, CDCl$_3$) $\delta$ 169.9 (s, COCH$_3$), 72.1, 71.9, 70.9 (3d, $^1$J (C,H) = 150 Hz); 68.4 (d, $^1$J (C,H) = 145 Hz); 24.5 (t, $^1$J (C,H) = 135 Hz); 20.9, 20.8, 20.6, 20.5 (4q, $^1$J (C,H) = 130 Hz, CH$_3$CO); MS (70 eV) $m/z$ 214 (2.5), 196 (14), 172 (3), 171 (16), 170 (6), 155 (13), 154 (83), 136 (18), 129 (14), 128 (16), 113 (14), 112 (100), 111 (19), 103 (19), 95 (13), 94 (42), 84 (13), 83(22).

Synthesis:


Physical Constants: mp = 259-260°C ;

Synthesis:


Physical Constants: mp = 142-143 °C; Anal calcd for C$_6$H$_{10}$O$_4$: C, 49.31; H, 6.89; Found: C, 49.38; H, 7.06.
Spectral Properties: $^1$H NMR (D$_2$O) $\delta$ 6.02 (doublet, $J = 1$ Hz, 2H) 4.40 (quartet, $J = 3.5$, 1 Hz, m 2H) 4.02 (doublet, $J = 3.5$ Hz, 2H)

Synthesis:

\[ \text{(-)-1L-Cyclohex-5-ene-1,3/2,4-tetrol or Conundrol-B} \]


Physical Constants: mp = 174-175 °C; $[\alpha]_D^{20} = -179^o$ (c 1.2 [mg/100mL], MeOH); IR (KBr) $\nu$ 3260, 3080, 2900, 2440, 1420, 1380, 1270, 1200, 1130, 1080, 1030, 1000, 950, 790 cm$^{-1}$; Anal calcd for C$_6$H$_{10}$O$_4$: C 49.3 H 6.89; Found: C 49.4 H 6.93

Spectral Properties: $^1$H NMR (250 MHz, CD$_3$OD) $\delta$ 5.62 (s, H-C(5), H-C(6)); 4.12, 3.42 (AA'XX', 4H, J (H-C(1), H-C(2)) = 7.5 Hz), J (H-C(1), H-C(4))=3, J (H-C(2),H-C(3))=10, J (H-C(12), H-C(3))=0; $^{13}$C NMR (62.9 MHz,CD$_3$OD) $\delta$ 130.7(d, $^1J$ (C,H) =161); 77.5 (d, $^1J$ (C,H) = 142); 73.6 (d, $^1J$ (C,H) = 141); MS (70 eV) m/z 128(0.3, [M-18]$^+$), 110 (3), 99 (24), 86 (100), 82 (11), 81 (9), 71 (12), 60 (11), 58 (8), 57 (77).
Synthesis:

Synthesis References (Racemic Conduritol-B):

![Structural formula of (+)-Cyclohex-5-ene-1,2,3,4-tetrol or Conduritol-E](image)


Physical Constants: mp = 193°C; [α]D^28 = +332° (c 1.9 mg/100mL), H_2O); Anal calcd for C_6H_10O_4: C 49.0 H 6.9; Found: C 49.1 H 6.8.

Synthesis:

![Structural formula of (+)-1D-Cyclohex-5-ene-1,2,4/3-tetrol or (+)-Conduritol F](image)


Physical Constants: mp = 129-130°C; [α]_D^{25} = +97.4° (c 0.7 mg/100mL), H_2O); IR (KBr) v 3400, 2920, 1640, 1400, 1100, 1060, 1010, 950, 870, 800 cm^{-1}; Anal calcd for C_6H_10O_4: C 49.3 H 6.89; Found: C 49.2 H 6.95
Spectral Properties: $^1$H NMR (250 MHz, CD$_3$OD) $\delta$ 5.85 (ddd, $^2$J = 10 Hz, $^3$J = 4.7, 2 Hz, H-(C(5))); 5.76 (dd, $^2$J = 10 Hz, $^3$J = 2 Hz, H-C(6)); 4.21 (ddd, $^3$J = 4.7, 4.2 Hz, $^5$J = 1 Hz, H-C(4)); 3.98 (dt, $^3$J = 7.6, 2 Hz, $^4$J = 2 Hz, $^5$J = 1 Hz, H-C(1)); 3.67 (dd, $^3$J = 10.4, 7.6 Hz, H-C(2)); 3.46 (dd, $^3$J = 10.4, 4.2 Hz, H-C(3)); $^{13}$C NMR (62.9 MHz, CD$_3$OD) $\delta$ 133.9 (dt, $^1$J (C,H) = 161 Hz, $^9$J (C,H) = 6 Hz); 128.1 (dt, $^1$J (C,H) = 162 Hz, $^9$J (C,H) = 4 Hz); 74.0, 73.9 (2dm, $^1$J (C,H) = 140 Hz); 72.7 (dm, $^1$J (C,H) = 142 Hz); 68.1 (dd, $^1$J (C,H) = 145 Hz, $^9$J (C,H) = 10 Hz); MS (70 eV) m/z 110 (2.5,[M-36]+), 99 (17), 86 (100), 82 (8), 60 (10), 57 (76).

Synthesis:

\[
\begin{align*}
\text{OMe} \\
\text{HO} \\
\text{HO} \\
\text{OMe} \\
\end{align*}
\]

$3\beta, 6\beta$-Dimethoxy-4-ene-1\alpha,2\alpha$\text{-dil}$ or 1,4-di-
O-methyl-Conduritol-A

Isolation and/or Identification: Cambie, R.C.; Renner, N.D.; Rutledge, P.S.; Woodgate, P.D., Synthetic Communications, 1989, 19, 537.

Physical Constants: IR (neat) $\nu$ 3650-3150 (OH), 1095 (OMe), 740 cm$^{-1}$ (C=C); Anal calcd for C$_8$H$_{14}$O$_4$: C, 55.2; H, 8.1; Found: C, 54.9; H, 8.1.

Spectral Properties: $^1$H NMR $\delta$ 3.45 (s, 6H), 3.70 (br. s, 2H exchanged with D$_2$O), 3.86 (d, $^3$J = 5Hz, 2H), 4.01 (d, 2H), 5.90 (s, 2H); $^{13}$C NMR $\delta$ 56.8 (C), 70.2 (CH), 78.2 (CH$_3$), 127.3 (CH$_3$); MS (Cl, EI, 70 eV) m/z (rel. intensity) 114 (C$_6$H$_{10}$O$_2$), 60 (C$_2$H$_4$O$_2$).

Synthesis:

Physical Constants: mp = 105 °C Anal calcd for C_{10}H_{14}O_6: C, 52.3; H, 6.1; Found: C, 52.2; H, 6.0.

Synthesis:


Physical Constants: mp = 100-101 °C; IR (KBr) v 3400, 2990, 1390, 1080 cm^{-1}; Anal calcd for C_{9}H_{14}O_4: C, 58.0; H, 7.6; Found: C, 57.9; H 7.8. Optically inactive.

Spectral Properties: ^1H NMR (CDCl_3) δ 1.35 (s, 3H), 1.46 (s, 3H), 3.12 (br. s, 4H), 4.27 (br. s, 4H), 5.85 (s, 2H); ^13C NMR (CDCl_3) δ 24.52, 26.77, 69.96, 79.28, 109.42, 131.07.

Synthesis:
Isolation and/or Identification: Cambie, R.C.; Renner, N.D.; Rutledge, P.S.; Woodgate, P.D., Synthetic Communications, 1989, 19, 537.

Physical Constants: IR (neat) ν 1110 (OMe), 735 cm⁻¹ (C=C); Anal calcd for C₁₀H₁₈O₄: C, 59.4; H, 9.0; Found: C, 59.2; H, 9.1

Spectral Properties: ¹H NMR δ 3.45 (s, 6H), 3.53 (s, 6H), 3.60 (d, J=1.2 Hz, 5H), 3.93 (dd, 2H), 5.87 (d, J= 1.2 Hz, 2H); ¹³C NMR δ 127.9 (C), 76.3, 78.6 (CH), 57.1, 58.4 (CH₃); MS m/z (rel. intensity) 114 (C₆H₁₀O₂), 88 (C₄H₈O₂).

Synthesis:


Physical Constants: bp = 130 °C (0.05 mm Hg); IR (neat) ν 2950, 1750, 1375, 1225, 1060, 1030 cm⁻¹; Anal calcd for C₁₄H₁₈O₈: C, 53.50; H, 5.77; Found: C, 53.44, H, 5.97.
Spectral Properties: ¹H NMR (CDCl₃) δ 2.03 (s, 3H), 2.06 (s, 3H), 5.31 (d, 2H), 5.40 (dd, 2H), 5.85 (s, 2H); ¹³C NMR (CDCl₃) δ 20.61, 20.91, 69.17, 69.31, 127.68, 169.67, 170.03; MS (70 eV m/z rel. intensity)) 255, 254, 212, 183, 170, 152, 141, 128, 111, 110, 99, 86, 82.

Synthesis:

![Tetra-O-benzoate conduritol-A](image)

Isolation and/or Identification: Cambie, R.C.; Renner, N.D.; Rutledge, P.S.; Woodgate, P.D., Synthetic Communications, 1989, 19, 537.

Physical Constants: mp = 127.5-130 °C; Found: C, 72.5; H, 4.5.

Spectral Properties: MS m/z 562 (M, < 1%), 441 (M-OBz, 2), 105 (C₇H₅O, 100), 77 (Ph,15).

Synthesis:
(1) Fricke, W.; Kern, W.; Steger, H., Arch. Pharm., 1940, 278, 145,

![(-)-Tetra-O-acetylcyclohex-5-en-1,3/2,4-tetrol or(-)-Tetra-O-acetyconduritol-B](image)

Physical Constants: mp = 120-121 °C; [α]D25 = -172.4° (c 1.1{mg/100mL},
CHCl3); IR (KBr) ν 3250ν 3080, 2960, 1760, 1440, 1380, 1220, 1140, 1070, 1050,
1030, 970, 930, 800 cm-1; Anal calcd for C14H18O8: C 53.5 H 5.77; Found: C
53.4 H 5.73

Spectral Properties: 1H NMR (250 MHz, CDCl3) δ 5.70 (s, H-C(5), H-C(6));
5.59, 5.33 (A'AXX', 4 H, J (H-C(1), H-C(2)) = 8 Hz, J (H-C(1), H-C(4)) = 2.5 Hz, J
(H-C(2), H-C(3)) = 11, J (H-C(1), H-C(3)) = 0); 2.06, 2.04 (2s, 2 Ac); 13C NMR
(62.9 MHz, CDCl3) δ 170.3 (s, CO); 127.4 (d, 1J (C,H) = 168); 71.4, 71.2 (2d, 1J
(C,H) = 155); 20.8, 20.6 (2q, 1J (C,H) = 130); MS (70 eV) m/z 212 (3), 194 (1), 183
(2), 170 (3), 153 (5), 152 (35), 141 (10), 128 (8), 111 (17), 119 (100), 99 (10), 82 (8),
81 (6).

Synthesis:

1958, 375.

Physical Constants: mp = 102-104° C; Anal calcd for C14H18O8: C 53 H 5.7;
Found: C 53. H 5.75

Synthesis:

Physical Constants: Colorless oil, purified by column chromatography on silica gel (Lobar; AcOEt/Petroleum ether, 1:2); \([\alpha]_D^{25} = +45.6^\circ\) (c 1.12, mg/100mL, CHCl₃); IR (film) \(\nu\) 3250, 3060, 2980, 2940, 2860, 1750, 1460, 1370, 1220, 1050, 970, 930, 790 cm\(^{-1}\); Anal calc'd for C₁₄H₁₈O₈: C 53.5 H 5.77; Found: C 53.5 H 5.74

Spectral Properties: \(^1\text{H}\) NMR (360 MHz, CDCl₃) \(\delta\) 5.91 (ddd, \(^3\)J = 10, 5 Hz, \(^4\)J = 1 Hz, H-C(6)); 5.84 (dd, \(^3\)J = 10, 2 Hz, H-C(5)); 5.62 (dd, \(^3\)J = 5, 4 Hz, H-C(1)); 5.56 (dd, \(^3\)J = 10, 7.5 Hz, H-C(3)); 5.52 (ddd, \(^3\)J = 7.5, 2 Hz, \(^4\)J = 1 Hz, H-C(4)); 5.14 (dd, \(^3\)J = 10, 4 Hz, H-C(2)); 2.11, 2.08, 2.05, 2.02 (4s, 4 CH₃CO); \(^1\text{C}\) NMR (62.9 MHz, CDCl₃) \(\delta\) 170.3, 170.1, 169.8 (3s, 3 CO); 130.7, 125.2 (2dm, \(^1\)J (C,H) = 169 Hz); 71.7 (dm, \(^1\)J (C,H) = 150 Hz); 69.0 (dm, \(^1\)J (C,H) = 148 Hz); 65.7 (dm, \(^1\)J (C,H) = 158 Hz); 20.85, 20.8, 20.7, 20.5 (4q, \(^1\)J (C,H) = 130 Hz); MS (70 eV) m/z 255 (1, [M-59]+), 212 (7), 183 (5), 170 (5), 153 (6), 152 (32), 141 (19), 128 (13), 111 (22), 110(100), 99(15), 82 (11), 81 (12).

Synthesis:

\[
\begin{align*}
\text{OAc} & \quad \text{Me} \\
\text{OAc} & \quad 1,4-di-O-acetyl-O- \\
\text{Me} & \quad \text{isopropylidene conduritol A} \\
\text{OAc} & \quad \text{or (1,4/2,3)-1,4-di-O-acetyl-} \\
\text{Me} & \quad 2,3-O-isopropylidene-5- \\
\text{Me} & \quad \text{cyclohexene-1,2,3,4-tetrol}
\end{align*}
\]


Physical Constants: mp = 79 °C; IR (KBr) \(\nu\) 3400, 2945, 1755, 1375, 1220, 1060 cm\(^{-1}\); Anal calc'd for C₁₃H₁₈O₆: C, 57.8; H, 6.7; Found: C, 57.7; H, 6.7

Spectral Properties: \(^1\text{H}\) NMR (CDCl₃) \(\delta\) 1.35 (s, 3H), 1.47 (s, 3H), 2.09 (s, 6), 4.25 (m, 2), 5.25 (m, 2), 5.70 (s, 2H); \(^1\text{C}\) NMR (CDCl₃) \(\delta\) 21.08, 25.09, 27.09, 71.63, 105.65, 128.22, 170.18.
Synthesis:

\[
\begin{align*}
\text{1,2:3,4-Di-O-} \\
\text{isopropylidenecyclohex-5-} \\
\text{ene-1,2,3,4-tetrol}
\end{align*}
\]


Physical Constants: mp = 60-61°C; Anal. calc'd for C\textsubscript{12}H\textsubscript{18}O\textsubscript{4}: C 63. H 8.0; Found: C 63.6 H 7.95

Synthesis:

\[
\begin{align*}
\text{all-cis-1,2:3,4-Di-O-} \\
\text{isopropylidenecyclohex-5-} \\
\text{ene-1,2,3,4-tetrol}
\end{align*}
\]


Physical Constants: mp = 67-68°C; Anal. calc'd for C\textsubscript{12}H\textsubscript{18}O\textsubscript{4}: C 63. H 8.0; Found: C 61. H 7.65.

Synthesis:

**Physical Constants:** mp = 44-48 °C; [α]D25 = -65° (c 2.5 mg/100 mL), CHCl3; IR (film) ν 3260, 3060, 2960, 2930, 2890, 2860, 1705, 1420, 1390, 1360, 1250, 1155, 1090, 1060, 1000, 990, 960, 935, 910, 880, 830, 770 cm⁻¹; Anal. calcd for C24H50O4Si3; C 59.2 H 10.3 Si 17.3; Found: C 59.2 H 10.4 Si 17.25

**Spectral Properties:**  
1H NMR (360 MHz, CDCl3) δ 6.68 (dd, 3 J = 10.5, 2.5 Hz, H-C(3)); 5.98 (dd, 3 J = 10.5 Hz, 4f = 2 Hz, H-C(2)); 4.33 (ddd, 3 J = 6, 2.5 Hz, 4f = 2 Hz, H-C(4)); 3.9 (d, 3 J = 8.5 Hz, H-C(6)); 3.8 (dd, 3 J = 8.5, 6 Hz, H-C(5)); 0.95, 0.94, 0.91 (3s, 3 t-BuSi); 0.16, 0.10, 0.06, 0.02, (4s, 3Me2Si) 13C NMR (90.55 MHz, CDCl3) δ 197.4 (s, C(1)); 148.8 (d, 1J (C,H) = 162 Hz, C(3)); 126.8 (d, 1J (C,H) = 165 Hz, C(2)); 77.6 (d, 1J (C,H) = 140 Hz); 77.5 (d, 1J (C,H) = 145 Hz); 72.9 (d, 1J (C,H) = 140 Hz); 26.3, 26.2, 26.0, (3q, 1J (C,H) = 125 Hz, 3t-BuSi); 18.6, 18.2, 17.9 (3t-BuSi); -3.7, -3.9, -4.6, -4.7 (4q, 1J (C,H) = 120 Hz, 3Me2Si); MS (70 eV) m/z 430 (12), 429 (29, [M-57]+), 401 (7), 147 (9), 133 (6), 75 (20), 74 (9), 73 (100), 57 (28).

**Synthesis:**  


**Physical Constants:** mp = 39-42°C; [α]D25 = -24° (c 2.5 mg/100 mL), CHCl3; IR (film) ν 3206, 2960, 2940, 2890, 2860, 1470, 1360, 1250, 1170, 1120, 1080, 1000, 970, 940, 890, 870, 830, 780 cm⁻¹; Anal. calcd for C24H52O4Si3; C 58.9 H 10.7 Si 17.23; Found: C 59.0 H 10.6 Si 17.20

34
Spectral Properties: $^1$H NMR (360 MHz, CDCl$_3$) δ 5.62 (s, H-C(5), H-C(6)); 4.23 (br. dd, $^3$J = 10, 4.5 Hz, H-C(1)); 3.94 (br. s, H-C(4)); 3.90 (m, $^3$J = 5, 25 Hz, H-C(3)); 3.81 (dd, $^3$J = 5, 4.5 Hz, H-C(2)); 2.30 (d, $^3$J = 10, OH); 0.92, 0.91, 0.89 (3s, 3t -BuSi); 0.14, 0.10, 0.09 (3s, 3Me$_2$Si); $^{13}$C NMR (90.55 MHz, CDCl$_3$) δ 129.1, 128.4 (2d, $^1$J (C,H) = 160 Hz, C(5), C(6)); 73.9 (d, $^1$J (C,H) = 145 Hz); 71.2 (dm, $^1$J (C,H) = 143 Hz); 71.0 (d, $^1$J (C,H) = 147 Hz); 66.0 (d, $^1$J (C,H) = 148 Hz); 26.1, 26.05, 25.9 (3q, $^1$J (C,H) = 126 Hz, 3t -BuSi); 18.3, 17.9 (2s, 3t -BuSi); -3.8, -4.2, -4.3, -4.4, -4.9 (5q, $^1$J (C,H) = 118 Hz, 3Me$_2$Si); MS (70 eV) m/z 431 (1.6, [M-57$^+$]), 299 (18), 288 (16), 225 (9), 200 (17), 147 (20), 133 (8), 75 (35), 73 (100).

Synthesis:


Physical Constants: colorless oil, purified by prep HPLC(Zorbax-sil., 250 x 21 mm, 8 ml/min, Et$_2$O:petroleum ether 1:20); [α]$_D^{25}$ = -8.3° (c 2.9{mg/100mL}, CHCl$_3$); IR (film) ν 3260, 2950, 2930, 2860, 1470, 1250, 1170, 1120, 1080, 900, 870, 830, 770 cm$^{-1}$; Anal. calcd for C$_{24}$H$_{52}$O$_4$Si$_3$: C 58.9 H 10.7 Si 17.23; Found: C 59.0 H 10.7 Si 17.18.

Spectral Properties: $^1$H NMR (360 MHz, CDCl$_3$) δ 5.98 (dd, $^3$J = 10.3, 5 Hz, H-C(5)); 5.79 (br.dd, $^3$J = 110.3, 4 Hz, H-C(6)); 3.98 (br. t, $^3$J = 3.5, 3 Hz, H-C(3)); 3.93-3.96 (m, H-C(1), H-C(2)); 3.81 (br. ddd, $^3$J = 11.5,3 Hz, H-C(4)); 2.76 (d, $^3$J = 11Hz, OH); 0.90, 0.89 (2s, 3t -BuSi); 0.15, 0.14, 0.10, 0.09 (4s, 3Me$_2$Si); $^{13}$C NMR (62.9 MHz, CDCl$_3$) δ 129.0 (d, $^1$J (C,H) = 162 Hz); 128.4 (d, $^1$J (C,H) = 164 Hz); 73.8 (d, $^1$J (C,H) = 147 Hz); 71.2. (dm, $^1$J (C,H) = 145 Hz); 71.0, 66.0 (2d, $^1$J (C,H) = 145 Hz); 26.1, 26.0, 25.8 (6q, $^1$J (C,H) = 125 Hz, 3t -BuSi); 18.3, 18.2, 17.9, (3s, 3t -BuSi); -3.8, -4.26, -4.32, -4.35, -4.4, -4.9 (6q, $^1$J (C,H) = 119 Hz, 3Me$_2$Si); MS (70 eV) m/z 432 (1), 431 (3, [M-57$^+$]), 299 (14), 288 (7), 225 (22), 200 (9), 197 (15), 167 (8), 149 (14), 147 (27), 133 (12), 115 (6), 75 (46), 73 (100), 57 (51).

Synthesis:
Cyclohexanepentols and their Derivatives

(-)-vibo-Quercitol or 1-deoxy-myoinositol


Physical Constants: mp = 161-163 °C; \([\alpha]_D^{20} = +55^o\) (c 0.5{mg/100mL}, water);

Synthesis:

Synthesis of Enantiomorph:

sacyllo-Quercitol or 1-deoxy-scylo-inositol


Physical Constants: mp = 233.5-234.5 °C
Synthesis:

\[
\begin{align*}
\text{OH} & \\
\text{HO} & \\
\text{OH} & \\
\text{OH} & \\
\text{OH} & \\
\end{align*}
\]

Cis-quercitol or 1-deoxy-cis-inositol


Physical Constants: $R_f = 0.39$ (acetone/water, 4:1); mp = 235-240 °C (decomp.);
Anal calc for $C_6H_{12}O_5$: C 44.0 H 7.5; Found: C 43. H 7.35.

Synthesis:
(-)-gala-Quercitol or 2-deoxy-allo-inositol


Physical Constants: \( mp = 257-258 \, ^\circ\text{C} \); \([\alpha]_D^{22} = -48.6^\circ \) (c 0.5\{mg/100mL\}, H\(_2\)O); IR (KBr) \( \nu \) 3400 (O-H), 1030 (C-O), 1060 (C-O), 1450 (methylene C-H bending) \( \text{cm}^{-1} \); Anal calc'd for C\(_6\)H\(_{12}\)O\(_5\): C 43.9 H 7.37; Found: C 43.7 H 7.32

Synthesis:

(+-)-talo-Quercitol or 1-deoxy-neo-inositol


Physical Constants: \( R_f = 0.36 \) (acetone/water, 4:1); \( mp = 246-248 \, ^\circ\text{C} \); \([\alpha]_D^{21} = +62^\circ \) (c 0.5 \{mg/100mL\}, H\(_2\)O); IR (KBr) \( \nu \) 3400 (O-H), 1030 (C-O), 1060 (C-O), 1450 (methylene C-H bending) \( \text{cm}^{-1} \); Anal calc'd for C\(_6\)H\(_{12}\)O\(_5\): C 43.9 H 7.37; Found: C 43.8 H 7.22

Synthesis:

Physical Constants: mp = 261-262 °C; IR (KBr) v 3300 (O-H), 1030 and 1080 (C-O) cm⁻¹; Anal calcd for C₆H₁₂O₅: C 43.9 H 7.37; Found: C 43.4 H 7.31

Synthesis:


Physical Constants: mp = 159 °C; [α]D²⁰ = +73.7° (c 1.2{mg/100mL}, EtOH); Anal calcd for C₉H₁₆O₅: C 52.9 H 7.9; Found: C 52. H 7.95

Synthesis:

(-)-talo-Quercitol Pentaacetate

Physical Constants: mp = 182-183 °C ; [a]D$^27$ = + 28° (c {mg/100mL}, solvent); IR (KBr) u 1750 (C=O), 1360 (methyl C-H bending), 1230 (ester C-O) cm$^{-1}$; Anal calcd for C$_{16}$H$_{22}$O$_{10}$: C 51.3 H 5.92; Found: C 51.6 H 6.05

Synthesis:

\[
\text{(-)-gala-Quercitol Pentaacetate}
\]


Physical Constants: mp = 117-118 °C ; [a]D$^27$ = - 240° (c 0.5 {mg/100mL}, CHCl$_3$); IR (KBr) u 1750 (C=O), 1360 (methyl C-H bending), 1230 (ester C-O) cm$^{-1}$; Anal calcd for C$_{16}$H$_{22}$O$_{10}$: C 51.3 H 5.92; Found: C 51.4 H 5.73

Synthesis:

\[
\text{DL-allo-Quercitol-pentaacetate}
\]


Physical Constants: mp = 92-94 °C ; IR (KBr) u 1750 (C=O) cm$^{-1}$; Anal calcd for C$_{16}$H$_{22}$O$_{10}$: C 51.3 H 5.93; Found: C 51.3 H 5.89.
Synthesis:

$$\text{(-)-1,2,4,3/5-Penta-O-acetate-cyclohexane pentaol}$$


Physical Constants: $mp = 122-124 \, ^\circ C$

Synthesis:

$$D,L-(1,2,4,6\text{-R}-6\text{-Bromo quercitol})$$


Physical Constants: $mp = 169.5-171 \, ^\circ C$

Synthesis:

$$\text{meso-(1,3,5)-A-6-Bromo quercitol}$$

Physical Constants: $\text{mp} = 223-224 \degree C$; Anal calcd for $\text{C}_6\text{H}_{11}\text{BrO}_2$: C 29.6 H 4.5 Br 32.88; Found: C 30.0 H 5.0 Br 33.12

Synthesis:

![Structure of 6-Bromoquercitol](image)


Physical Constants: $\text{mp} = 227-229 \degree C$; $[\alpha]_{D}^{18} = -137^\circ$ (c 0.1{ mg/100mL}, H$_2$O); IR (KBr) $\nu$ 3400 (O-H), 1150 (C-O) cm$^{-1}$; Anal calcd for $\text{C}_6\text{H}_{11}\text{O}_5\text{Br}$: C 29.6 H 4.5 Br..32.88; Found: C 29.6 H 4.6 Br..33.33

Synthesis:

![Structure of 3-Bromo-3-deoxy-L-inositol](image)


Physical Constants: $\text{mp} = 201-203 \degree C$; $[\alpha]_{D}^{14} = -44^\circ$ (c 5 {mg/100mL}, H$_2$O); IR (KBr) $\nu$ 3400 (O-H), 1150 (C-O) cm$^{-1}$; Anal calcd for $\text{C}_6\text{H}_{11}\text{O}_5\text{Br}$: C 29.6 H 4.5 Br..32.88; Found: C 29.7 H 4.6 Br..33.04

Synthesis:

Synthesis:


Physical Constants: mp = 106-108 °C; Anal calcd for C_{16}H_{11}BrO_{10}: C 42.4 H 4.6 Br 17.63; Found: C 42.6 H 4.9 Br 18.50.

Synthesis:

**Cyclohexanehexols and their Derivatives**

Physical Constants: \( \text{Rf} = 0.30 \) (acetone/water, 4:1); \( \text{mp} = 270-275^\circ\text{C} \); Anal. calcd for: \( \text{C}_6\text{H}_{12}\text{O}_6 \). C 40. H 6.7; Found: C 40. H 6.6.

**Synthesis:**


Physical Constants: mp = 286 °C; Anal calcd for: C₆H₁₂O₆: C 40.0  H 6.7
Found: C 39.8  H 6.7

Synthesis:


Physical Constants: mp = 315 °C; Anal calcd for C₆H₁₂O₆: C 40. H 6.7; Found: C 40.3  H 7.2

Synthesis:


Physical Constants: mp =240-243°C; [a]D₁₈ = -71+/− 5(c .07{mg/100mL}, H₂O);
Synthesis:

![Allo-inositol hexa-acetate](image)


Physical Constants: mp = 143-144°C; Anal. calcd for C_{18}H_{24}O_{12}: C 50. H 5.6; Found: C 50.0 H 5.7

Synthesis:

![Myo-inositol-hexa-acetate](image)


Physical Constants: mp = 216-217°C

Synthesis:

![Neo-inositol hexa-acetate](image)

Physical Constants: \( mp = 253 \; ^\circ C \); Anal. calcd for \( \text{C}_{18}\text{H}_{24}\text{O}_{12} \): C 50.0 H 5.6; Found: C 50.3 H 5.65

**Synthesis:**

![Hexa-O-acetyl-muco-inositol](image)


Physical Constants: \( mp = 179-180 \; ^\circ C \); Anal. calcd for \( \text{C}_{18}\text{H}_{24}\text{O}_{12} \): C 50.0 H 5.6; Found: C 50.1 H 5.6

**Synthesis:**

![Hexa-O-benzoyl-muco-inositol](image)


Physical Constants: \( mp = 248 \; ^\circ C \); Anal. calcd for \( \text{C}_{48}\text{H}_{36}\text{O}_{12} \): C 71.6 H 41.5; Found: C 71.6 H 4.5.
Synthesis:

![image of allo-inositol hexabenzoate](image)


**Physical Constants:** mp = 188 °C; Anal calcd for C₄₈H₃₆O₁₂: C 71.6; H 4.5; Found: C 71.3; H 4.5

Synthesis:

![image of Penta-O-acetyl-1-O-methyl-(-)-inositol](image)


**Physical Constants:** mp = 111°C; [a]D₁₅ = -31° (c 3.8{mg/100mL}, EtOH); Anal calcd for C₁₇H₂₄O₁₁: C 50. H 6.0; Found: C 50. H 6.0

Synthesis:

![image of (+)-Finitol](image)
Isolation and Identification:

Physical Constants: mp = 186-187 °C ; [α]D^20 = +61.5° (c 0.27{mg/100mL}, H_2O)

Spectral Properties: ^1H NMR (500 MHz, D_2O, HOD = 4.74) d 3.96-3.94 (2H m, 1-H and 6-H); 3.76 (1H dd, J = 10.0 and 2.8 Hz, 2-H or 5-H); 3.71 (1H dd, J = 10.0 and 2.8 Hz, 5-H or 2-H); 3.60 (1H t, J = 9.7 Hz, 4-H); 3.54 (3H s, MeO); 3.29 (1H t, J = 9.7 Hz, 3-H);
^13C NMR (Varian 220-Mcps, D_2O, dioxane-internal reference) d 110.0 (c-3); 120.4 (C-4); 120.8 (C-1 or C-6); 121.1 (C-1 or C-6); 121.9 (C-5); 122.7 (C-2); 133.1 (CH_3).

Synthesis:

(-)-Pinitol


Physical Constants: mp = 186 °C ; [α]D^20 = -61.4° (c 0.21{mg/100mL}, H_2O)

Spectral Properties: ^1H NMR (500 MHz, D_2O, HOD = 4.74) d 3.96-3.94 (2H m, 1-H and 6-H); 3.76 (1H dd, J = 10.0 and 2.8 Hz, 2-H or 5-H); 3.71 (1H dd, J = 10.0 and 2.8 Hz, 5-H or 2-H); 3.60 (1H t, J = 9.7 Hz, 4-H); 3.54 (3H s, MeO); 3.29 (1H t, J = 9.7 Hz, 3-H)

Synthesis:

Physical Constants: mp =212°C ; Anal calcd for C_7H_14O_6; C 43. H 7.25; Found: C 43. H 7.1

Synthesis:


Physical Constants: mp = 199-200°C ; Anal calcd for C_7H_14O_6; Found: C 43. H 7.2


Physical Constants: mp = 207°C ; [α]_D^{18} =-58° (c 1.5{mg/100mL}, H_2O); Anal calcd for C_7H_14O_6; C 43. H 7.25; Found: C 43.1 H 7.2
Synthesis:

\[
\begin{align*}
&\text{OMe} \\
&\text{HO} \\
&\text{OMe} \\
&\text{OH} \\
&\text{OH} \\
&\text{1,2-Di-O-methyl-myoinositol}
\end{align*}
\]


Physical Constants: mp = 162-163°C; Anal calcd for C₈H₁₆O₆: C 46.1 H 7.75; Found: C 46. H 7.7

Synthesis:

\[
\begin{align*}
&\text{OMe} \\
&\text{MeO} \\
&\text{OMe} \\
&\text{OH} \\
&\text{OH} \\
&\text{1,4,5,6-Tetra-O-methyl-myoinositol}
\end{align*}
\]


Physical Constants: mp = 105-106 °C; Anal calcd for C₁₀H₂₀O₆: C 50.8 H 8.55; Found: C 51. H 8.3

Synthesis:
2-O-acetyl-3,4,5,6-tetra-O-methyl-myoinositol


Physical Constants: mp = 109-111 ºC; Anal calcd for C₁₂H₂₂O₇: C 51. H 7.95; Found: C 51. H 7.8

Spectral Properties:¹H NMR (CHCl₃) δ 5.58 (t, J = 2.5 Hz, H-2); 3.42 (s); 3.60 (Me); 3.64 (2Me); 2.16 (Ac)

Synthesis:

1-O-Acetyl-3,4,5,6-tetra-O-methyl-myoinositol

Isolation and Identification: mp = 87-89 ºC; Anal calcd for C₁₂H₂₂O₇: C 51. H 7.95; Found: C 51. H 7.9

Physical Constants: mp = 87-89 ºC; Anal calcd for C₁₂H₂₂O₇: C 51. H 7.95; Found: C 51. H 7.9

Spectral Properties:¹H NMR (CDCl₃) δ 4.70 (dd, J = 10.5, 2.5 Hz, H-1); 4.21 (t, J = 2.5 Hz, H-2); 3.49 (s); 3.56 (s); 3.61 (s); 3.63 (Me); 2.16 (Ac).

Synthesis:

Physical Constants: mp = 194 °C ; Anal calcd for C_{14}H_{22}O_9: C 50. H 6.6; Found: C 50. H 6.6

Spectral Properties: \textsuperscript{1}H NMR (CHCl\textsubscript{3}) d 3.25 (dd, J = 2.75, 9.5 Hz, H-1,3); 4.45 (t, J = 2.75 Hz, H-2); 5.48 (t, J = 9.5 Hz, H-4,6); 5.01 (t, J = 9.5 Hz, H-5); 3.46 (2Me); 1.99 (Ac); 2.03 (2Ac);

Synthesis:


Physical Constants: mp = 202°C ; Anal calcd for C_{16}H_{24}O_{10}: C 51.0 H 6.45; Found: C 51.2 H 6.3

Synthesis:

Physical Constants: mp \(=193^\circ\text{C} \); \([a]D^{25} = -1^\circ\) (c 3.7{mg/100mL}, pyridine); Anal. calc'd for C\(_{14}H_2O_{8}S\) \(\text{C} 48.2\) \(\text{H} 5.5\) \(\text{S} 8.9\); Found: C 48.5, 48. H 5.5, 5, S 8.9, 9.1

Synthesis:

![Oxonol-penta-acetate](image)


Physical Constants: \(mp = 127-130^\circ\text{C} \); \([a]D = -11^\circ\) (c 0.7{mg/100mL}, chloroform)

Synthesis:

![(-)-Bromositol-penta-acetate](image)


Physical Constants: \(mp = 141-143^\circ\text{C} \); \([a]D = -10^\circ\) (c 1.6{mg/100mL}, acetone)

Synthesis:

Physical Constants: \( \text{mp} = 152-153^\circ \text{C} \)

Synthesis:


Physical Constants: \( \text{mp} = 235-236^\circ \text{C} \); IR (6\% sol'n in chloroform) Perkin-Elmer Model 12C with rock salt prism u 911(w), 930(m), 946(w), 979(m), 1040(s), 1122(m), 1172(w) cm\(^{-1}\); Anal calcd for \( \text{C}_{17}\text{H}_{24}\text{O}_{11}\) C .50. H 5.95; Found: C 50. H 6.0

Synthesis:

Physical Constants: mp = 152°C; [α]D19 = -18.2° (c 4.3{mg/100mL}, CHCl3); Anal. calc'd for C22H28O12S: C 51.1 H 5.4 S ..6.2; Found: C 51.0, 51. H 5.5, 5. S ..6.2, 6.3

Synthesis:

\[
\text{HO}_{\text{in}} \quad \text{OH} \\
\text{THPO} \\
\text{OH} \\
\text{5-O-(2-Tetrahydropyranyl)-myo-inositol} \\
\text{OH}
\]


Physical Constants: mp = 213-215°C; Anal. calc'd for C11H20O7: C 50. H 7.6; Found: C 49. H 7.65

Synthesis:

\[
\text{HO}_{\text{in}} \quad \text{OH} \\
\text{HO} \\
\text{4-O-Tosyl-myo-inositol} \\
\text{OH} \quad \text{OTs}
\]


Physical Constants: mp = 173-174°C (decomp. in a capillary); Anal. calc'd for C13H18O8S: C 64. H 6.4; Found: C 64. H 6.4

Synthesis:
1-O-Tosyl-\textit{myo}-inositol


**Physical Constants:** mp = 223-224°C (decomp.); Anal. calcd for C\textsubscript{13}H\textsubscript{18}O\textsubscript{8}S: C 46. H 5.4; Found: C 46.4 H 5.5

**Synthesis:**

1,2-Anhydro-(+)-inositol


**Physical Constants:** mp = 129-130°C; Anal. calcd for C\textsubscript{6}H\textsubscript{10}O\textsubscript{5}: C 44. H 6.2; Found: C 44. H 6.1

**Synthesis:**

1,2-Anhydro-neo-inositol


**Physical Constants:** mp = 205-206°C

**Synthesis:**
1,2-O-Isopropylidene-
muco-inositol


**Physical Constants:** \( mp = 162 \, ^\circ C \); **Anal calcd for** \( C_9H_{16}O_6 \): C 49.1; H 7.3; **Found:** C 49.0; H 7.5

**Synthesis:**

5,6-O-Isopropylidene-allo-
inositol


**Physical Constants:** \( mp = 144-145 \, ^\circ C \); **Anal calcd for** \( C_9H_{16}O_6 \): C 49.1; H 7.3; **Found:** C 49.1; H 7.3.

**Synthesis:**
1,2-isopropylidene (−)
inositol


Physical Constants: mp = 157.5-158 °C; Anal. calcd for C₉H₁₆O₆: C 49. H 7.35; Found: C 49. H 7.4

Synthesis:

1,2-O-Cyclohexylidene-
myo-inositol


Physical Constants: mp = 179 °C; Anal. calcd for C₁₂H₂₀O₆: C 55. H 7.75; Found: C 55. H 7.8

Synthesis:

1,2-O-Benzylidene-myo-
inositol

Physical Constants: mp = 140-142°C; Anal calcd for C_{13}H_{16}O_{6}: C 58. H 6.0; Found: C 58. H 6.2

Synthesis:

\[
\begin{align*}
\text{OME} & \\
\text{AcO} & \\
\text{AcO} & \\
\text{OAc} & \\
(-)-4,5,6-\text{Tri-O-acetyl-1-O-methyl-2,3-anhydro-allo-inositol}
\end{align*}
\]


Physical Constants: mp = 76 °C; [α]_{D}^{16} = -63.8° (c 4.2 mg/100 mL, CHCl_{3}); Anal calcd for C_{13}H_{18}O_{8}: C 51.6 H 6.0; Found: C 51. H 6.1

Synthesis:

\[
\begin{align*}
\text{OTHP} & \\
\text{HO} & \\
\text{HO} & \\
\text{OH} & \\
\text{1,2-Di-O-(2-}
\text{tetrahydropyran)-myo-}
\text{inositol}
\end{align*}
\]


Physical Constants: mp = 183-185 °C; Anal calcd for C_{16}H_{28}O_{8}: C 55.1 H 8.1; Found: C 54. H 8.0

Synthesis:
1,2-O-Cyclopentylidene-
myo-inositol


Physical Constants: mp = 164-166°C; Anal calcd for C₁₁H₁₈O₆: C 53.6  H 7.4; Found: C 53.7  H 7.5

Synthesis:

3,4-Di-tosyl-(-)-inositol


Physical Constants: mp = 185-186°C; [α]D²⁷ = -28° (c 4.3{mg/100mL}, pyridine); Anal calcd for C₂₀H₂₄O₁₀S₂: C 49. H 4.9  S 13.1; Found: C 49. H 4. S 12.7

Synthesis:

2-Methyl-5,6-
isopropylidene
(-) inositol

Physical Constants: mp = 134-135.5°C; Anal calcd for C_{10}H_{18}O_{6}; C 51. H 7.75; Found: C 51. H 7.65


\[
\begin{align*}
\text{OH} & \\
\text{O} & \\
\text{O} & \\
\text{O} & \\
\text{O} & \\
\text{O} & \\
\text{OH} & \\
1,2,4,5-	ext{Di-O-methylene-} \\
\mu \text{c-o-inositol}
\end{align*}
\]


Physical Constants: mp = 162°C; Anal calcd for C_{8}H_{12}O_{6}; C 47.0; H 5.9; Found: C 47.3; H 5.9


\[
\begin{align*}
\text{OH} & \\
\text{O} & \\
\text{O} & \\
\text{O} & \\
\text{O} & \\
\text{O} & \\
\text{OH} & \\
1,2,5,6-	ext{diisopropylidene} \\
(-)\text{inositol}
\end{align*}
\]


Physical Constants: mp = 153°C; [\alpha]_{D}^{20} = -4.7^\circ (c 1.2\text{ mg/100mL}, \text{ EtOH});
Anal calcd for C_{12}H_{20}O_{6}; C 55.3 H 7.75; Found: C 55.2 H 7.85

1,2:3,4-diisopropylidene-
epi-inositol


Physical Constants: mp = 181°C; Anal calcd for C_{12}H_{20}O_6: C 55.3 H 7.75; Found: C 55.1 H 7.95

Synthesis:

1,2:4,5-Diisopropylidene-
epi-inositol


Physical Constants: mp = 181°C; Anal calcd for C_{12}H_{20}O_6: C 55.3 H 7.75; Found: C 54.9, 55.7 H 7.8, 7.9

Synthesis:

Physical Constants: mp = 166-168 °C; Anal calcd for C_{13}H_{20}O_8: C 51.3; H 6.6; Found: C 51.5; H 6.7

Synthesis:


Physical Constants: mp = 142-143°C; Anal calcd for C_{14}H_{20}O_{10}: C 48. H 5.8; Found: C 48. H 5.9.

Synthesis:

Physical Constants: mp = 138-140°C; Anal calcd for C₁₄H₂₀O₁₀·¹/₂H₂O: C 47.0 H 5.9; Found: C 47.1 H 5.75

Synthesis:

\[
\begin{align*}
\text{OAc} & \\
\text{OAc} & \\
\text{OH} & \\
\text{H₂O} & \\
\text{OAc} & \\
1,4,5,6-Tetra-O-acetyl-2,3- & \\
\text{O-cyclohexylidene-\textit{myo-}} & \\
\text{inositol, monohydrate} & \\
\end{align*}
\]


Physical Constants: mp = 100°C; Anal calcd for C₁₄H₂₀O₁₀·H₂O: C 45. H 6.05; Found: C 46.2 H 6.0

Synthesis References:

\[
\begin{align*}
\text{OAc} & \\
\text{OAc} & \\
\text{OH} & \\
\text{1,2:5,6-Di-O-} & \\
\text{cyclohexylidene-\textit{myo-}} & \\
\text{inositol} & \\
\end{align*}
\]


Physical Constants: mp = 133°C; Anal calcd for C₁₈H₂₈O₆: C 63. H 8.3; Found: C 63.2 H 8.3

Synthesis:

Physical Constants: mp = 174°C; Anal. calcd for C_{18}H_{28}O_{6}: C 63. H 8.3;
Found: C 63.1 H 8.0

Synthesis:

Physical Constants: mp = 158°C; Anal. calcd for C_{18}H_{28}O_{6}: C 63.5 H 8.3; Found: C 63.7 H 8.4

Synthesis:


Physical Constants: mp = 118-119 °C; [α]_{D}^{20} = -18.2° (c 1{mg/100mL}, CHCl_{3}); Anal. calcd for C_{19}H_{36}O_{6}: C 64.4 H 8.55; Found: C 64.7 H 8.55.

Synthesis:
1,2:5,6-Di-O-
cyclohexylidene-(-)-inositol


Physical Constants: mp = 209-210 °C; \([\alpha]_D^{27} = -16^\circ\) (c 1.4{mg/100mL}, CHCl₃); \([\alpha]_D^{27} = +4.5^\circ\) (c {mg/100ml}, dioxane) Anal. calc'd for C₁₈H₂₈O₆: C 63.5 H 8.3; Found: C 63.3 H 8.3

Synthesis:

3-Methyl-1,2:5,6-
diisopropylidene (+) inositol


Physical Constants: mp = 103-104°C; \([\alpha]_D^{23} = -22.0^\circ\) (c 3.4{mg/100mL}, H₂O); Anal. calc'd for C₁₃H₂₂O₆: C 56.85 H 8.05; Found: C 56.95 H 8.0.

Synthesis:

1,3,4,5,6-Penta-O-acetyl-
myo-inositol

Physical Constants: mp = 159-162 °C

Spectral Properties: $^1$H NMR (CHCl$_3$) d 4.35 (t, J = 2.5 Hz, H-2); 2.02 (3Ac); 2.11 (2Ac);

Synthesis:


Physical Constants: mp = 85-86 °C

Spectral Properties: $^1$H NMR (CHCl$_3$) d 5.58 (t, J = 2.75 Hz, H-2); 4.02 (t, J = 9.5 Hz, H-6); 1.99 (s); 2.03 (s); 2.07 (s); 2.10 (s); 2.17 (Ac)

Synthesis:


Physical Constants: mp = 178 °C

Spectral Properties: $^1$H NMR (CHCl$_3$) d 5.04 (dd, J = 2.6, 10.5 Hz, H-1,H-3); 5.58 (t, J = 2.6 Hz, H-2); 2.01 (2Ac); 2.11 (Ac); 2.21 (2Ac)

Synthesis:

Physical Constants: mp = 163-166 °C

Spectral Properties: $^1$H NMR (CHCl$_3$) δ 5.60 (t, J = 2.5 Hz, H-2); 1.99 (Ac); 2.02 (2Ac); 2.08 (s); 2.22 (Ac)

Synthesis:


Physical Constants: mp = 109-110 °C; $[\alpha]_D^{20} = -302^0$ (c 1.1{mg/100mL}, CHCl$_3$); Anal. calcd for C$_{19}$H$_{30}$O$_6$: C 64.4 H 8.55; Found: C 64.5 8.5.

Synthesis:

Physical Constants: mp = 195-197°C; Anal. calc'd for C_{21}H_{26}O_{12}S: C 50.2 H 5.2; Found: C 50.35 H 5.4

Synthesis:


Physical Constants: mp = 173°C; Anal. calc'd for C_{25}H_{32}O_{7}: C 67.55 H 7.25; Found: C 67.25 H 7.05

Synthesis:

**Physical Constants:** mp = 185 °C; Anal. calcd for C\(_{25}\)H\(_{32}\)O\(_7\): C 67.55 H 7.25; Found: C 67.5 H 7.1

**Synthesis:**

![1,2:4,5-Di-O-acetate-muco-inositol](image)

**Isolation and Identification:** Dangschat, G.; Fischer, H.O.L., *Carbohydrate Research* 1987, 164, 343.

**Physical Constants:** mp = 176 °C

**Synthesis:**

![(-)-3,4:5,6-Di-O-isopropylidene-1,2-anhydro-allo-inositol](image)


**Physical Constants:** mp = 108-109 °C; [\(\alpha\)]\(_D\)\(_{15}^{15}\) = + 13.5° (c 1.6{mg/100mL}, MeOH); Anal. calcd for C\(_{12}\)H\(_{18}\)O\(_5\): C 59.5 H 7.5; Found: C 60.2, 59.75 H 7.5, 7.65

**Synthesis:**
\[
\begin{align*}
R &= \text{Me-SO}_2 \\
(1R)-1,2:5,6-\text{Di-isopropylidene-3,4-di-O-methanesulfonylinositol}
\end{align*}
\]


**Physical Constants:** \( \text{mp} = 260^\circ \text{C} \); \([\alpha]_D^{17} = -120^\circ \) (c 1.0{mg/100mL}), CHCl\(_3\)); Anal. calcd for C\(_{14}\)H\(_{24}\)O\(_{10}\)S\(_2\) . . C 40.25 H 5.7; Found: C 40.35 H 5.8

**Synthesis:**

\[
\begin{align*}
\begin{align*}
1,2:3,4:5,6-\text{Triisopropylidene} \\
(-)-\text{jinositol}
\end{align*}
\end{align*}
\]


**Physical Constants:** \( \text{mp} = 213-214^\circ \text{C} \); \([\alpha]_D^{25} = +38.1^\circ \) (c 1.0{mg/100mL}), CHCl\(_3\)); Anal. calcd for C\(_{15}\)H\(_{24}\)O\(_6\): C 60.0 H 8.05; Found: C 59.85 H 8.2

**Synthesis:**

Physical Constants: mp = 127-128°C; Anal. calcd for C_{15}H_{24}O_{6}: C 60.0 H 8.05; Found: C 59.55 H 8.1

Synthesis:


Physical Constants: mp = 218-219 °C; Anal. calcd for C_{16}H_{24}O_{8}: C 55.8 H 7.0; Found: C 55.9 H 7.0.

The isomer was obtained from the mother liquor. mp = 138 °C Anal. Found: C 55.9; H 7.0.

Synthesis:
3,6-Diacetyl-1,2:4,5-diisopropyldiene-\textit{epi}-inositol


\textbf{Physical Constants:} mp $= 201-203^\circ \text{C}$; Anal. calcd for C$_{16}$H$_{24}$O$_8$: C 55.8 H 7.0; Found: C 55.65 H 6.95

\textbf{Synthesis:}

3,4-Diacetyl-1,2:5,6-diisopropyldiene (-) inositol


\textbf{Physical Constants:} mp $= 129^\circ \text{C}$; [\(\alpha\)]$_D^{22}$ $= -116.5^\circ$ (c 2.1{mg/100mL}, CHCl$_3$); Anal. calcd for C$_{16}$H$_{24}$O$_8$: C 55.8 H 7.0; Found: C 55.55 H 7.05.

\textbf{Synthesis:}
5,6-Diacetyl-1,2:5,6-diisopropylidene-epi-inositol


Physical Constants: mp = 138°C; Anal. calc for C_{16}H_{24}O_{8}: C 55.8 H 7.0; Found: C 55.45 H 7.2

Synthesis:

1,2,3,6-Tetra-O-acetyl-4,5-O-isopropylidene-muco-inositol


Physical Constants: bp = 175-180°C (0.6 mm Hg); Anal. calc for C_{17}H_{24}O_{10}: C 52.6; H 6.2; Found: C 52.2 H 6.5.

Synthesis:
(+/-)-3,4,5,6-tetra-O-acetyl-1,2-O-isopropylidene-myoinositol


Physical Constants: $\text{mp} = 122-123^\circ\text{C}$

Synthesis:

1,2,3,4-Tetra-O-acetyl-5,6-O-isopropylidene-allo-inositol


Physical Constants: $\text{mp} = 125^\circ\text{C}$; Anal. calcd for $\text{C}_{17}\text{H}_{24}\text{O}_{10}$: C 52.6 H 6.2; Found: C 52.7 H 6.3

Synthesis:

1,3,4,5,6-Penta-O-acetyl-2-O-propionyl-myoinositol

Physical Constants: mp = 175-177°C; Anal. calcd for C_{19}H_{26}O_{12}: C 51.1 H 5.85; Found: C 51.0 H 6.15

Synthesis:  

![Diagram of chemical structure]

1,4,5,6-Tetra-O-acetyl-2,3-O-cyclopentylidene-myoinositol


Physical Constants: mp = 132°C; Anal. calcd for C_{19}H_{26}O_{10}: C 55.05 H 6.3; Found: C 55.1 H 6.2

Synthesis:  

![Diagram of chemical structure]

1,2,3,4,6-Penta-O-acetyl-5-O-propionyl-myoinositol


Physical Constants: mp = 171-172 °C; Anal. calcd for C_{19}H_{26}O_{12}: C 51.1 H 5.85; Found: C 50.8 H 5.85

Synthesis:  

Physical Constants: mp = 90°C; [α]D 24° = +53.4° (c 4.4 mg/100 mL), EtOH; Anal. calcd for C20H28O8S: C 56.1 H 6.6 S 7.5; Found: C 56.2, 55.8 H 6.5, 6.5 S 7.6, 7.8

Synthesis:


Physical Constants: mp = 118°C; Anal. calcd for C20H28O10: C 56.05 H 6.6; Found: C 55.85 H 6.5

Synthesis:

Physical Constants: mp = 143-145 °C; Anal. calcd for C_{20}H_{28}O_{12}: C 52.15 H 6.15; Found: C 52.25 H 6.15

Synthesis:

\[ \text{Ph} \]
\[ \text{AcO} \]
\[ \text{AcO} \]
\[ \text{OAc} \]
\[ \text{OAc} \]
1,2-O-benzylidene-3,4,5,6-tetra-O-acetyl-myo-inositol


Physical Constants: mp = 156-158°C; Anal. calcd for C_{21}H_{24}O_{10}: C 57.8 H 5.5; Found: C 57.8 H 5.5

Synthesis:

\[ \text{O}
\[ \text{O}
\[ \text{O}
\[ \text{O}
\[ \text{OAc}
\[ \text{OAc}
\[ \text{OTs}
1,2:5,6-Di-O-isopropyldiene-3-O-acetyl-4-O-tosyl-(-)-inositol


Physical Constants: mp = 144°C; \([\alpha]_D^{19} = 114^\circ (c 2.3\text{ mg/100 mL}, \text{ CHCl}_3); \)
Anal. calcd for C_{21}H_{28}O_{9}S: C 55.25 H 6.2 S..13.1; Found: C 49.4 H 4.9 S..12.7

Synthesis:

Physical Constants: $mp = 183-185 \, ^\circ C$; Anal. calcd for $C_{21}H_{30}O_{12}$: C 53.15 H 6.35; Found: C 52.9 H 6.25

Synthesis:


Physical Constants: $mp = 225-226 \, ^\circ C$; Anal. calcd for $C_{21}H_{30}O_{12}$: C 53.15 H 6.35; Found: C 53.5 H 6.4

Synthesis:

Physical Constants: mp = 179 °C; Anal. calcd for C$_{22}$H$_{32}$O$_8$: C 62.25 H 7.6; Found: C 62.0 H 7.45

Synthesis:


Physical Constants: mp = 120°C; Anal. calcd for C$_{22}$H$_{32}$O$_8$: C 62.25 H 7.6; Found: C 62.7 H 7.7

Synthesis:
1,3,4,5,6-Penta-O-acetyl-2-O-tosyl-myoinositol


Physical Constants: mp = 219-220°C; Anal. calcd for C_{23}H_{28}O_{13}S: C 50.75 H 5.2; Found: C 50.9 H 5.3

Synthesis:

1,2,4,5,6-Penta-O-acetyl-3-O-tosyl-myoinositol


Physical Constants: mp = 149-150°C; Anal. calcd for C_{23}H_{28}O_{13}S: C 50.75 H 5.2; Found: C 50.65 H 5.2

Synthesis:

R=p-NO_2C_6H_4SO_2
(1R)-1,2,5,6-Diisopropylidene-3,4-di-O-p-nitrobenzenesulfonylmyo-inositol

83

Physical Constants: $mp = 171-172^\circ$C; $[\alpha]D^{17} = -62^\circ$ (c 1.0{mg/100mL})CHCl$_3$; Anal. calcd for C$_{24}$H$_{26}$O$_{14}$N$_2$S$_2$: C 45.7 H 4.15; Found: C 45.55 H 4.05

Synthesis:


Physical Constants: $mp = 161-162^\circ$C; $[\alpha]D^{14} = -79.6^\circ$ (c 2.6{mg/100mL}), CHCl$_3$; Anal. calcd for C$_{26}$H$_{32}$O$_{10}$S$_2$: C 54.95 H 5.65 S..11.3; Found: C 54.9, 55.0 H 5.4, 5.1 S..11.6, 11.6

Synthesis:


Physical Constants: $mp = 191-192$°C; $[\alpha]D^{25} = +13.1^\circ$ (c 2.1{mg/100mL}), dioxane); Anal. calcd for C$_{24}$H$_{36}$O$_6$: C 68.55 H 8.6; Found: C 68.8 H 8.9
Synthesis:

\[
(+/-)\text{-1,2;3,4:5,6-Tri-O-cyclohexylidene-} \text{myo-} \text{inositol}
\]


Physical Constants: \( mp = 154-156 \, ^\circ C \); Anal. calcd for \( C_{24}H_{36}O_{6} \): C 68.55 H 8.6; Found: C 68.7 H 8.55

Synthesis:

\[
\text{1,4,5,6-Tetra-O-acetyl-2,3-di-O-(2-tetrahydropyrany)l-} \text{myo-} \text{inositol}
\]


Physical Constants: \( mp = 204-206 \, ^\circ C \); Anal. calcd for \( C_{24}H_{36}O_{12} \): C 55.8 H 7.05; Found: C 55.9 H 7.0

Synthesis:
1,4,5,6-Tetra-O-acetyl-2-O-
(2-tetrahydropyranyl)-3-O-
tosyl-myoinositol


**Physical Constants:** mp = 169-170 °C; Anal. calc'd for C\textsubscript{26}H\textsubscript{34}O\textsubscript{13}S: C 53.2 H 5.8; Found: C 53.3 H 5.7

**Synthesis:**

R=p-NO\textsubscript{2}C\textsubscript{6}H\textsubscript{4}SO\textsubscript{2}
(+/-)-1,2,3,4-Tetra-O-
acetyl-5,6-di-O-p-
nitrobenzenesulfonyl-epi-
inositol


**Physical Constants:** mp = 190°C; Anal. calc'd for C\textsubscript{26}H\textsubscript{26}O\textsubscript{18}N\textsubscript{2}S\textsubscript{2}: C 43.45 H 3.65; Found: C 43.4 H 3.6

**Synthesis:**

(1R)-1,2,5,6-Tetra-O-
acetyl-3,4-di-O-tosylinositol

Physical Constants: mp = 158°C; [α]D17 = +17.4° (c 1.3{mg/100mL}, CHCl3); Anal. calcd for: C28H32O14S2: C 51.2 H 4.9 S 9.7; Found: C 51.15 H 4.9 S 9.8

Synthesis:

\[
\begin{align*}
&\text{AcO} \quad \text{OAc} \\
&\text{AcO} \quad \text{OTs} \\
&\text{1,4,5,6-tetra-O-acetyl-2,3-di-O-tosyl-myco-inositol} \\
&\text{AcO} \quad \text{OAc} \\
&\text{AcO} \quad \text{OTs}
\end{align*}
\]


Physical Constants: mp = 173°C; Anal. calcd for: C28H32O14S2: C 51.2 H 4.9; Found: C 51.5 H 5.1

Synthesis:

\[
\begin{align*}
&\text{AcO} \quad \text{OAc} \\
&\text{AcO} \quad \text{OTs} \\
&\text{2,4,5,6-Tetra-O-acetyl-1,3-O-tosyl-myco-inositol} \\
&\text{AcO} \quad \text{OAc} \\
&\text{AcO} \quad \text{OTs}
\end{align*}
\]


Physical Constants: mp = 220-222°C; Anal. calcd for: C28H32O14S: C 51.2 H 4.9; Found: C 50.9 H 4.9

Synthesis:

Physical Constants: mp = 145 °C; Anal. calcd for C_{30}H_{26}O_{14}N_{2}S_{2}: Found: C 45.8  H 4.3

Synthesis:


Physical Constants: mp = 262°C; Anal. calcd for C_{32}H_{36}O_{8}: C 70.05  H 6.6; Found: C 70.5  H 6.75

Synthesis:

**Physical Constants:** $mp = 136-137$ and $158^\circ$C two allotropic forms; *Anal. calcd* for C$_{32}$H$_{36}$O$_8$: C 70.05 H 6.6; *Found:* C 70.2 H 6.5

**Synthesis:**

---


**Physical Constants:** $mp = 205^\circ$C *Anal. calcd* for C$_{32}$H$_{36}$O$_8$: C 70.05 H 6.6; *Found:* C 69.9 H 6.45

**Synthesis:**
4-O-Benzoyl-1,2,5,6-di-O-cyclohexyldiene-3-O-tosyl-
myo-inositol


Physical Constants: $\text{mp} = 204-207^\circ \text{C}$; *Anal. calcd* for $\text{C}_{32}\text{H}_{38}\text{O}_{9}\text{S}$: C 64.2 H 6.4; *Found*: C 64.65 H 6.5

Synthesis:

3-O-Benzoyl-1,2,5,6-di-O-cyclohexyldiene-4-O-tosyl-
myo-inositol


Physical Constants: $\text{mp} = 146-147^\circ \text{C}$; *Anal. calcd* for $\text{C}_{32}\text{H}_{38}\text{O}_{9}\text{S}$: C 64.2 H 6.4; *Found*: C 64.0 H 6.4

Synthesis:
1,2-O-Benzylidene-3,4,5,6-tetra-O-acetyl-my-o-inositol


Physical Constants: mp = 280°C (decomp.); Anal. calc'd for C_{41}H_{32}O_{10}: C 71.9  H 4.7; Found: C 71.8  H 4.8

Synthesis:
III. Discussion

1. Introduction

The field of computational chemistry has grown enormously since the basic theories were brought about by D.H. Andrews in 1930. The present-day calculation methods provide for accurate structures and energies for molecules of great complexity. The concept that brought about this computational analysis holds that bonds have "natural" lengths and angles, and molecules adjust their geometries so that they may be as close to the ideal values as possible.

Molecular mechanics methods have become an important research tool for theoretical and experimental chemists. The program utilized in these calculations is PCMODEL®, which invokes a MMX type of calculation. MMX is a calculational method that runs on personal computers or VAX systems and is used to perform molecular mechanics operations on 296 different atoms and lone pairs. The MMX calculations are similar to MM2 but vary in that MMX calculations can give reasonable geometries for more complex structures than MM2. MMX also provides heats of formation for conjugated p systems including radicals, cations, and anions. MM2 has been updated frequently by Allinger to include parameters for various functional groups.

The MM2 (molecular mechanics, program 2), calculation method developed by Allinger, treats molecules as a collection of deformable balls (atoms) whose size is related to the van der Waals radius. It uses the premise that these atoms are held together by bonds whose lengths, angles and harmonic stretching and bending force constants are chosen to reproduce the structure and strain energy of organic molecules. A review discussing the development of MMX was published in 1990 by Gajewski et al.

The reduction of the inososes and the deoxy-inososes are of interest because they would be readily converted to the corresponding inositols (cyclohexanehexols) and deoxy-inositols (cyclohexanepentols). These compounds can yield one of two inositols or deoxyinositols by either an exo or endo attack of the reducing agent.

Reduction of the carbonyl in the inosose shown in Figure 15 to a hydroxyl can occur to yield either an equitorial or an axial -OH. The use of molecular modeling and energy calculations can help predict the outcome of such reductions provided equilibrium conditions are involved. As an example, reduction of myo-1-inosose (see figure 15) could yield either myo-inositol (6) or D-chiro-inositol (2). One of the properties that molecular
energy calculations give is the heat of formation of each product and serves to estimate relative stabilities.

Figure 15. Reduction of Myo-1-inosose

The procedure used for determining accurate molecular structures and energies for these compounds involves the modeling of each compound in its chair conformation with the majority of the hydroxyls equatorial and again in its ring flipped conformation with the majority of the hydroxyls axial. Those compounds with three axial hydroxyl groups can undergo chair-chair interconversions. The inositosls and deoxyinositosls with less than three axial hydroxyls interconvert less readily. The energy is then calculated and a comparison of the structures determines the lowest energy form.

The discussion revolves around these ideas and includes molecular modeling and energy calculations of the lowest energy form inososes and their reduction products in an attempt to predict the outcome of the experiment and, where possible, compare such prediction with experimental evidence for validity.
III. Discussion

2. MMX-Energy Calculations of the Inososes and Deoxy-inososes and their Reduction Products.

In evaluating the results from molecular modeling studies, one must examine the following:

1. Conformation of cyclitol.

The preferred conformation of these compounds was assumed to be the chair conformation. In an unsubstituted cyclohexane ring, the chair is the most stable conformation as we know from general organic chemistry principles. This conformation may be free of angle strain and torsional strain, but there does exist interactions between gauche atoms.

The chair conformation lies at an energy minimum whereas the boat conformation is an at energy maximum. The boat conformation is 7.1 kcal/mole higher in energy than the chair and the twist boat, albeit better than the boat, is nonetheless 5.5 kcal/mole higher than the chair conformation. Structural representations of these cyclitols in the literature show not only the inositols in the chair conformation but also the inososes. The above mentioned assumption has been validated by modeling myo-inositol, the most common inositol, in both the boat and chair forms. In the example of myo-inositol, the boat conformation has 7.81 kcal/mole of strain energy more than the chair conformation. Even with a deoxy inosose the preferred conformation is also the chair as observed in the example of 1-deoxy-cis-inosose where the chair conformation has only 1.59 kcal/mole of strain energy less than the boat conformation.

Quantifying strain energy has been made possible by using the concept that simple strainless molecules do exist, and large molecules are said to be strainless if their heats of formation can be predicted as summations of the bond energies and other increments from the small strainless molecules. When the experimentally determined heat of formation is found to be greater than the calculated, the molecule has strain associated with it. In the above case, the conformation is a contributing factor of the molecule gives rise to the strain in the molecule. The boat conformation allows for interactions between the pseudo-axial
hydroxyls, whereas the chair conformation is staggered so as to allow for relief of most strain except inherent strain which exists as a result of the gauche interactions within the ring itself.

\[
\text{Strain Energy} \quad -8.76 \\
\text{1-deoxy-cis-2-inosose}
\]

\[
\text{Strain Energy} \quad -7.17
\]

\[
\text{Strain Energy} \quad -23.12 \\
\text{myo-inositol}
\]

\[
\text{Strain Energy} \quad -15.31
\]

Table 2 Chair vs. Boat Conformation

Due to the large number of hydroxyls present in the cyclitols, hydrogen bonding is a factor that needs to be taken into account. The program PCMODEL© allows one to hydrogen bond selected or all acidic hydrogens. This factor was accounted for by selecting all acidic hydrogens to be hydrogen bonded. By correcting for this factor, energy of hydrogen bonded compounds was found to be lower than that of those compounds whose intramolecular distances forbade hydrogen bonding. The only source of hydrogen bonding recognized by MMX is electrostatic attraction, where all hydrogen bond acceptor atoms require lone pairs. In the early versions of MM2 hydrogen bonds were longer and weaker than what was known about the hydrogen bond experimentally. Much of the attraction between the hydrogen atom forming the hydrogen bond and the electronegative atom is due to electrostatics but dipole-dipole interactions are also taken into account. This excludes hydrogen bonding to double bonds and halogens even though in theory this can occur. The ability of the hydrogen atoms to bond depends on the basicity of the donor lone pair and the acidity of the hydrogen atom. When using PCMODEL© with the option to hydrogen bond atoms, an acidic hydrogen can be selected for hydrogen bonding and if the intranuclear distance is equal to less than 2.25 Å then the acidic hydrogen and the basic lone pair will hydrogen bond.
With the favored conformation determined, the modeling of the individual inositol, deoxy-inositol, deoxyinososes and inososes was undertaken. The MMX energy calculations were performed utilizing the chair conformation of the aforementioned compounds.

It is possible that in compounds of the structure (A), where hydrogen bonding is likely, the boat conformation may be the preferred conformation. Yet when modeled in this conformation, the iterative manipulations performed by PCMODEL© showed a stable chair-like structure to be the more stable conformer.

The other aspect of the modeling that deals with the question of conformation is the axial and equitorial positioning of hydroxyl groups. Each compound has two chair conformations, these conformations being those that have the majority of the groups axial and those that have the majority of the hydroxyls equitorial. The heat of formation is determined by an MMX calculation and this contributes to the conformation of each compound. In examining each chair, as shown in the example in Figure 27,

![Figure 27](image)

the lowest energy form is determined, in this case the structure with the OH group axial at C1 has a heat of formation of -276.97 kcal/mole whereas the equitorial OH has a heat of formation of -278.98 kcal/mole. This difference in heat of formation permits one to
theorize the most stable conformation of the compound. Knowing heats of formation and strain energies allow for a comparison of relative energetics of isomers.

In molecular mechanics, hydrogen bonding contributions result from dipole-dipole interactions, charge-charge interactions where the charges are derived from the dipoles of a molecule which include the atom-lone pair bond where an attraction between the lone pair and the hydrogen atom exists and has a van der Waals radii of 0.2 Å. This means that for hydrogen bonding to exist any atom that accepts hydrogen bonds must have a donor pair of electrons. These lone pair electrons reduce marked dipole moments and can then hydrogen bond. Hydrogen bonding has been used to determine the most stable conformation of a molecule. In the case of the inositol and deoxy-inositols, the conformation of these compounds with acidic protons is dependent upon which of the atoms are actually hydrogen bonded. In the first example the non-bonded molecule is lower in energy. This lower energy can be accounted for by the fact that the singly hydrogen bonded molecule has 1,3-diaxial interactions between the hydrogens at those positions (marked by a star,*). These interactions do not exist in the non-hydrogen bonded allo-inositol example (entry 1) because it can easily twist out of the rigid chair conformation. It is a fundamental principle of organic chemistry that acidic protons do hydrogen bond when possible, which demonstrates that even though the non-hydrogen bonded molecule may be lower in energy it is not a reality. All the acidic hydrogens are selected for hydrogen bonding but the program, through manipulations of the respective structures, either allows or forbades this bonding to occur. For the program to recognize intramolecular hydrogen bonds the donor and acceptor can be no further than 2.25 Å. In the second entry, there also exists 1,3-diaxial interactions which in the doubly hydrogen-bonded example are able to twist out of the plane so as to not have as severe steric interactions as the non-hydrogen bonded example has due to geometrical constraints without any hydrogen bonding. The hydrogen bonded conformers are locked into their respective chair formations as shown in Figure 28 (ΔHf in kcal/mole). Both ring flipped conformations of allo-inositol have hydrogen bonded atoms. Hydrogen bonding provides very little, if any, stabilization to the molecule as shown in the slight difference in heats of formation in Figure 28. It is possible that where hydroxyls are 1,3-diaxial the conformation would favor hydrogen bonding in the case of chiro-3-inosose (allo-2-inosose, compound 77 section V). The intramolecular distance in this case is 2.90 Å and this would be a hydrogen bonded species under experimental conditions but PCMODEL© recognizes 2.25 Å or less as an intramolecular distance for hydrogen bonding. Where possible, 1,3-diaxial hydrogens do hydrogen bond as in the case of the g-alkoxy alcohols. The hydrogen bonded conformation (see Figure 27b) (C) is preferred over the non-
hydrogen bonded structure (C'). These interactions contribute to the conformation as do hydrogen bonds between gauche atoms. When the preferred conformation is a distorted chair hydroxyls that are gauche can hydrogen bond to one another. This would tend to flatten out the cyclohexane ring. The crystal structure of muco-inositol gives a distorted chair, an overall flattening of the cyclohexane ring results. The two axial O atoms are further apart than any of the vicinal gauche O atoms. In the crystal structure of this compound (see below), no intramolecular hydrogen bonding occurs even though

\[\text{muco-Inositol}\]

interatomic distances favor the formation of such bonds. These heats of formation vary so slightly that the difference may well be within experimental error.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Hydrogen Bonded $\Delta H_f$</th>
<th>Non-hydrogen Bonded $\Delta H_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-276.88</td>
<td>-277.33</td>
</tr>
<tr>
<td>2</td>
<td>-279.73</td>
<td>-279.61</td>
</tr>
</tbody>
</table>

In the case of some of the inososes, hydrogen bonding occurs with the acidic protons a to the carbonyl. As in the example of *epi*-5-inosose, the hydrogen bonded compound is slightly lower in energy as seen in Figure 29.

The hydrogen bonding between the hydroxyls at C3 and C4 and those between the hydroxyls at C5 and C6 along with the hydrogen bonding of the acidic proton a to the carbonyl allow the conformation of this compound to be locked in place. Opposite of this is the free movement of the hydroxyls of the non-hydrogen bonded *epi*-5-inosose, which introduces interactions between the hydroxyls at C5 and C6. Even with these interactions, the preferred conformations for both conformers is the chair formation (section V. Tables).
For this work to be validated, α-D-mannose, β-D-glucose, α-D-glucose and α-D-galactose were modeled to determine their calculated ΔH_f and compare that to their known experimental ΔH_f values. 46

![α-D-Mannose](image)

![α-D-Glucose](image)

\[\Delta H_f \text{ exp't'1} = -302.70 \text{ kcal/mol} \quad \Delta H_f \text{ exp't'1} = -304.26 \text{ kcal/mol}\]
\[\Delta H_f \text{ cald'd} = -265.02 \text{ kcal/mol} \quad \Delta H_f \text{ cald'd} = -271.75 \text{ kcal/mol}\]

![β-D-Glucose](image)

![α-D-Galactose](image)

\[\Delta H_f \text{ exp't'1} = -302.78 \text{ kcal/mol} \quad \Delta H_f \text{ exp't'1} = -304.09 \text{ kcal/mol}\]
\[\Delta H_f \text{ cald'd} = -264.36 \text{ kcal/mol} \quad \Delta H_f \text{ cald'd} = -269.07 \text{ kcal/mol}\]

The differences represent a 8% error in calculations. This can be accounted for by conditions at which each set of heats of formation were measured. This being that the literature values are reported as solids and the calculated numbers are determined in the gas phase. The molecular modeling program uses parameters that do not correspond to actual experimental facts. These include calculations being performed in the gas phase, whereas most reported heats of formation are solid phase and intramolecular hydrogen bonds where most molecules with acidic hydrogens are able to inter- as well as intramolecular hydrogen bond.

These literature heats of formation follow the general trend α-D-glucose > α-D-galactose > β-D-glucose > α-D-mannose whereas the calculated H_f are α-D-glucose > α-D-galactose > α-D-mannose > β-D-glucose. The numbers calculated are not absolute, they are applicable only to other calculated numbers because of the parameters within the
program. In the graphical representation of the general trend, deviation from the experimental value occurs with α-D-glucose being higher in energy than α-D-mannose.

The final aspect that needs to be addressed is the selectivity of the reducing agent. In utilizing a reducing agent like NaBH₄, stereoselective reduction would not be realized unless an extremely bulky group were used to protect a hydroxyl that is α to the carbonyl. In a NaBH₄ reduction, equilibrating conditions do not exist and therefore delivery of the hydride anion can occur on either the α or β face of the inosose. Conformational analysis is unnecessary considering that this reduction method would produce two isomers regardless of preferred conformation. Experimental results 48 of a NaBH₄ (Figure 30) reduction on allo-2-inosose (chiro-3-inosose) show that products are formed in a 75:25 ratio of allo-inositol to D-chiro-inositol.

Figure 30

If a reduction method were employed where equilibrating conditions could exist, preference of a lower energy conformation would be a factor in the ratio of products
formed. Using the strain energies of each conformer shown in Fig.31, analysis of this data would predict the chair conformation B to be the more favored structure.

\[
\begin{align*}
\text{allo-2-inosose} & \quad \Delta H^\circ_f = 3.3 \text{ kcal/mol} \\
\text{B} & \\
\text{allo-2-inosose}
\end{align*}
\]

**Figure 31**

Reduction of B could yield one of two compounds, \textit{allo}-inositol or \textit{D-chiro}-inositol, calculational methods show that formation of \textit{allo}-inositol is favored by 0.75 kcal/mol.

\[
\begin{align*}
\text{allo-2-inosose} & \quad \text{H}_2/\text{Raney Ni} \\
\text{B} & \\
\text{D-chiro-inositol} & \quad \Delta H^\circ_f = -0.75 \text{ kcal/mol} \\
\text{allo-inositol}
\end{align*}
\]

The products formed would be in equilibrium with one another if this reduction were radical and hydrogen atom abstraction was occurring.\textsuperscript{50} By determining the \(\Delta H_f\) (assuming \(\Delta S = 0\)) of these two products, \(K\) (the equilibrium constant) was determined to be 0.28 which corresponds to a ratio of 80:20 of allo-inositol to \textit{D-chiro}-inositol. Actual experimental results showed that \(\text{H}_2/\text{Raney Ni}\) reduction of \textit{allo}-2-inosose gave \textit{allo}-inositol in a crude yield of 90%.

Upon examination of NMR data \textsuperscript{48} for \textit{allo}-2-inosose (\textit{chiro}-3-inosose) it was revealed that in reality the molecule probably does not exist in a rigid chair conformation. Coupling constants (see figure below) suggest that the true conformation should be more boat-like in character so as to attain long range coupling of the protons \(\alpha\) to the carbonyl which suggests planarity of carbons 2, 3, and 4 in the molecule and therefore disproves our original conformational analysis.
*Chiro-3-inosose chair*

\[ J_{\text{Calc'd}} (C4(H)-C5(H)) = 8.56 \text{ Hz}; \]
Dihedral angle (C4(H)-C5(H)) = -167.39°

\[ J_{\text{Calc'd}} (C1(H)-C2(H)) = 2.3 \text{ Hz}; \]
Dihedral angle (C1(H)-C2(H)) = 54.06°

*Chiro-3-inosose boat*

\[ J_{\text{Calc'd}} (C4(H)-C5(H)) = 2.47 \text{ Hz} \]
Dihedral angle (C4(H)-C5(H)) = -123.21°

\[ J_{\text{Calc'd}} (C1(H)-C2(H)) = 7.85 \text{ Hz} \]
Dihedral angle (C1(H)-C2(H)) = 7.39°

\[ J_{\text{Expt'1}} (C4(H)-C5(H)) = 9.7 \text{ Hz (D}_2\text{O)} \]
\[ J_{\text{Expt'1}} (C1(H)-C2(H)) = 3.0 \text{ Hz (D}_2\text{O)} \]
\[ J_{\text{Expt'1}} (C4(H)-C5(H)) = 9.3 \text{ Hz (DMSO)} \]
\[ J_{\text{Expt'1}} (C1(H)-C2(H)) = 3.3 \text{ Hz (DMSO)} \]

In examining calculated dihedral angles, corresponding coupling constants determined from the Karplus equation: \( J = A + B \cos \Phi + C \cos 2\Phi \), where \( A = 4 \text{ Hz, } B = -0.5 \text{ Hz, } C = 4.5 \text{ Hz and } \Phi \) is the dihedral angle. The calculated dihedral angles for the minimized boat structure are less in agreement than the dihedral angles of the chair conformation shown above.

It can be shown by crystal structure that the sugars studied do not have intramolecular hydrogen bonds.\(^{72-74,76}\) Each sugar is represented below (Figure 32) and has been shown to intermolecular hydrogen bond only apparently due to the crystal packing of the molecules shown. Myo-\(^{75}\), epi-\(^{77}\), and muco-inositol (as seen previously) have published crystal structures which show no intramolecular hydrogen bonds (Figure 33).
\( \alpha \)-D-Galactose

\( \alpha \)-D-Glucose

\( \beta \)-D-glucose

\( \alpha \)-D-mannose gauche/gauche

\( \alpha \)-D-mannose gauche/trans

Figure 32. Crystal Structures of Sugars
Figure 33. Crystal Structures of Inositols

With this information, a more accurate prediction of conformation can be achieved. Each of these compounds as modeled revealed no intramolecular hydrogen bonding. Of course, each of these compounds in solution would be able to intra- and intermolecular hydrogen bond with itself as well as the substance that is solvating it.
III. Discussion

3. Summary

The intent of these modeling studies was to utilize the calculated heats of formation and strain energies to predict the stereochemical outcome of a reduction of inososes and deoxyinososes. By inputting the individual structures into PCMODEL© and performing the iterative calculations on each compound, the desired information obtained. With this data attained, conclusions were drawn as to favored conformation of each inosose and deoxyinosose as well as predominant product formed. Calculated data revealed that hydrogen bonded compounds are lower in energy than their non hydrogen bonded counterparts. Hydrogen bonded compounds should be lower in energy than non hydrogen bonded compounds because of the energy contribution from that bond. Comparing these result with experimental data is a bit disappointing due to the fact that they are not in accord with one another. According to Allinger 49 six-membered rings containing other kinds of functional groups (cyclohexene and cyclohexanone included) consistently have calculated heats of formation that do not agree with experimental data.
IV. Conclusion

It has been shown that this modeling system can predict the outcome of a catalytic hydrogenation reduction reaction. This is accounted for by the known experimental data for the reduction reaction of allo-2-inosose being in accord with the calculated data. This single result does not validate the entire molecular modeling studies because the conformation of the starting inosose is taken to be a chair conformation where the actual conformation exists somewhere closer the boat conformation according to NMR data. The validity of this work comes into question when comparing the results from modeling α-D-mannose, α-D-glucose, β-D-glucose, and α-D-galactose with the known experimental heats of formation. The experimental stability trend follows α-D-glucose > α-D-galactose > β-D-glucose > α-D-mannose, whereas the calculated trend follows α-D-glucose > α-D-galactose > α-D-mannose > β-D-glucose. The program PCMODEL© takes into account factors that are assumptions for calculational purposes that are not assumptions experimentally. This allows for a certain degree of error, the experimentally measured heats of formation vary by a small degree, 1.56 kcal/mol difference between the four isomeric sugars. Another factor to consider that does not seem to be accounted for by PCMODEL© is that these compounds have nonbonded resonance (anomeric effect) which should make their energies less than that calculated for the inositosls and deoxyinositosls, but what is brought to light is that all of these compounds (the sugars and inositosls and deoxyinositosls) have calculated heats of formation and strain energies along the same magnitude.

A factor that is not taken into account by PCMODEL© is that hydrogen bonding occurs intermolecularly as well as intramolecularly. By modeling a single molecule of the inositosls or deoxyinositosls intermolecular hydrogen bonding cannot be taken into account.

Use of this program does seem to have some synthetic utility by at least one example. However the wide applicability of this program to more complex systems/reactions with many external factors may not be a reality.
V. Tables

ΔH°\text{r}'s are calculated at the bottom of each page for the two ring conformations.
- * denotes the predicted favored conformation of chair conformations
- * denotes the predicted favored product for each reduction reaction
| Compound | MMX-ENERGY | $H_f$ (kcal/mole) | SE (kcal/mole) |
|----------|------------|-------------------|----------------|---|
| 1-deoxy-cis-2-inosose (26) | 1.98 | -220.29 | -9.14 |
| 1-deoxy-cis-2-inosose (27) | 2.36 | -219.91 | -8.76 |
| 5-deoxy-allo-inositol | 1.49 | -236.22 | -12.37 |
| 5-deoxy-allo-inositol | 1.96 | -235.75 | -11.90 |
| 1-deoxy-cis-inositol | 0.02 | -237.68 | -13.84 |
| 1-deoxy-cis-inositol | -1.79 | -239.50 | -15.65 |

$\Delta H^\circ_f (26 \rightarrow 27) = 0.38$ kcal/mol

109
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY $H_f$ (kcal/mole)</th>
<th>SE (kcal/mole)</th>
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$\Delta H^o_r (28 \rightarrow 29) = 2.78$ kcal/mol
<table>
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<th>$H_f$ (kcal/mole)</th>
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$\Delta H^\circ (\text{TH}) \rightarrow 31 \approx 2.59$ kcal/mol
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$\Delta H^\circ_f (32 \rightarrow 33) = -0.85$ kcal/mol
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Same structure
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<td>-13.62</td>
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$\Delta H^\circ_f (35 \rightarrow 36) = -4.38 \text{ kcal/mol}$
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<td>-13.62</td>
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$\Delta H_f^{\circ} (37 \rightarrow 38) = -3.37$ kcal/mol
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$\Delta H_f^{\circ} (39 \rightarrow 40) = 2.62 \text{ kcal/mol}$
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</tr>
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<td>-237.47</td>
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<td>-234.39</td>
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<td>-238.11</td>
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<tr>
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<td>-14.26</td>
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$\Delta H_f^{\circ} (41 \rightarrow 42) = -2.56 \text{ kcal/mol}$
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<th>SE (kcal/mole)</th>
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<td>2-deoxy-alo-inositol</td>
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<td>238.80</td>
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<tr>
<td>1-deoxy-neo-inositol</td>
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$\Delta H^o_f$ (43 $\rightarrow$ 44) = 6.42 kcal/mol
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</tr>
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<td>2-deoxy-allo-inositol</td>
<td>-1.60</td>
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<td>-12.26</td>
</tr>
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<td>2-deoxy-allo-inositol</td>
<td>-1.10</td>
<td>-238.80</td>
<td>-14.96</td>
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<tr>
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<td>-14.26</td>
</tr>
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$\Delta H^o_f (45 \rightarrow 46) = -2.41$ kcal/mol
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<th>SE (kcal/mole)</th>
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$\Delta H^o_t (47 \rightleftharpoons 48) = -0.52 \text{ kcal/mol}$
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<td>-13.62</td>
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$\Delta H^\circ_f (49 \rightarrow 50) = 1.60$ kcal/mol
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Same structures
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<th>SE (kcal/mole)</th>
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<td>-11.97</td>
</tr>
<tr>
<td>1-deoxy-neo-inositol</td>
<td>-1.88</td>
<td>-239.58</td>
<td>-15.74</td>
</tr>
</tbody>
</table>

$\Delta H_f^0 (56 \rightarrow 57) = -1.19$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MNX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$S_f$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-deoxy-epi-5-lanosose (58)</td>
<td></td>
<td>-0.95</td>
<td>-11.07</td>
</tr>
<tr>
<td>2-deoxy-epi-5-lanosose (59)</td>
<td></td>
<td>0.05</td>
<td>-10.07</td>
</tr>
<tr>
<td>2-deoxy-allo-inositol</td>
<td></td>
<td>1.60</td>
<td>-17.26</td>
</tr>
<tr>
<td>2-deoxy-allo-inositol</td>
<td></td>
<td>-1.10</td>
<td>-14.96</td>
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<td>2-deoxy-allo-inositol</td>
<td></td>
<td>3.11</td>
<td>-10.55</td>
</tr>
<tr>
<td>2-deoxy-epi-inositol</td>
<td></td>
<td>-0.40</td>
<td>-14.26</td>
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</table>

$\Delta H_f^{\circ} (58 \rightarrow 59) = 1.00$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY $H_f$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-deoxy-neo-3-inosose (60)</td>
<td>4.59</td>
<td>-217.67</td>
</tr>
<tr>
<td>2-deoxy-neo-3-inosose (61)</td>
<td>-0.65</td>
<td>-223.91</td>
</tr>
<tr>
<td>2-deoxy-neo-inositol</td>
<td>1.86</td>
<td>-235.85</td>
</tr>
<tr>
<td>2-deoxy-neo-inositol</td>
<td>1.06</td>
<td>-236.64</td>
</tr>
<tr>
<td>5-deoxy-alle-inositol</td>
<td>1.49</td>
<td>-236.22</td>
</tr>
<tr>
<td>5-deoxy-alle-inositol</td>
<td>1.96</td>
<td>-235.75</td>
</tr>
</tbody>
</table>

$\Delta H^\circ_f (60 \rightarrow 61) = -5.24$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-deoxy-neo-4-inosose (62)</td>
<td></td>
<td>-0.74</td>
<td>-224.52</td>
</tr>
<tr>
<td>2-deoxy-neo-4-inosose (63)</td>
<td></td>
<td>-1.78</td>
<td>-225.56</td>
</tr>
<tr>
<td>2-deoxy-neo-inositol</td>
<td></td>
<td>1.86</td>
<td>-235.85</td>
</tr>
<tr>
<td>2-deoxy-neo-inositol</td>
<td></td>
<td>1.06</td>
<td>-236.64</td>
</tr>
<tr>
<td>2-deoxy-allo-inositol</td>
<td></td>
<td>1.60</td>
<td>-236.10</td>
</tr>
<tr>
<td>2-deoxy-allo-inositol</td>
<td></td>
<td>-1.10</td>
<td>-238.80</td>
</tr>
</tbody>
</table>

$\Delta H^\circ_f (62 \rightleftharpoons 63) = -1.04$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY $\Delta H_f$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-deoxy-neo-5-imosose (64)</td>
<td>0.01</td>
<td>-223.77</td>
</tr>
<tr>
<td>2-deoxy-neo-5-imosose (65)</td>
<td>-2.44</td>
<td>-226.22</td>
</tr>
<tr>
<td>2-deoxy-neo-inositol</td>
<td>1.86</td>
<td>-235.85</td>
</tr>
<tr>
<td>2-deoxy-neo-inositol</td>
<td>1.96</td>
<td>-236.64</td>
</tr>
<tr>
<td>1-deoxy-scyllo-inositol</td>
<td>-1.57</td>
<td>-239.27</td>
</tr>
<tr>
<td>1-deoxy-scyllo-inositol</td>
<td>0.78</td>
<td>-238.49</td>
</tr>
</tbody>
</table>

$\Delta H_f^o (64 \rightarrow 65) = -2.45$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MNX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$S_E$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-deoxy-muco-4-inosose (66)</td>
<td>1.31</td>
<td>-220.95</td>
<td>-9.81</td>
</tr>
<tr>
<td>3-deoxy-muco-4-inosose (67)</td>
<td>2.58</td>
<td>-219.69</td>
<td>-8.54</td>
</tr>
<tr>
<td>3-deoxy-muco-inositol</td>
<td>1.05</td>
<td>-236.65</td>
<td>-12.81</td>
</tr>
<tr>
<td>3-deoxy-muco-inositol</td>
<td>0.83</td>
<td>-236.87</td>
<td>-13.03</td>
</tr>
<tr>
<td>1-deoxy-myo-inositol</td>
<td>0.37</td>
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<td>-14.23</td>
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<tr>
<td>1-deoxy-myo-inositol</td>
<td>0.24</td>
<td>-237.47</td>
<td>-13.62</td>
</tr>
</tbody>
</table>

$\Delta H^o_f (66 \rightleftharpoons 67) = 1.26$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-deoxy-muco-5-inosose (68)</td>
<td></td>
<td>2.12</td>
<td>-221.66</td>
</tr>
<tr>
<td>3-deoxy-muco-5-inosose (69)</td>
<td></td>
<td>-1.68</td>
<td>-225.46</td>
</tr>
<tr>
<td>3-deoxy-muco-inositol</td>
<td></td>
<td>1.05</td>
<td>-236.65</td>
</tr>
<tr>
<td>3-deoxy-muco-inositol</td>
<td></td>
<td>0.83</td>
<td>-236.87</td>
</tr>
<tr>
<td>3-deoxy-muco-inositol</td>
<td></td>
<td>1.60</td>
<td>-236.10</td>
</tr>
<tr>
<td>2-deoxy-allo-inositol</td>
<td></td>
<td>1.10</td>
<td>-238.80</td>
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</table>

$\Delta H_f^{\circ} (68 \rightleftharpoons 69) = -3.8$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-deoxy- allo-1-inosose (70)</td>
<td></td>
<td>3.14</td>
<td>-220.65</td>
</tr>
<tr>
<td>5-deoxy- allo-1-inosose (71)</td>
<td></td>
<td>-0.85</td>
<td>-224.63</td>
</tr>
<tr>
<td>1-deoxy-meso-inositol</td>
<td></td>
<td>1.89</td>
<td>-235.82</td>
</tr>
<tr>
<td>1-deoxy-meso-inositol</td>
<td></td>
<td>-1.88</td>
<td>-239.58</td>
</tr>
<tr>
<td>5-deoxy- allo-inositol</td>
<td></td>
<td>1.49</td>
<td>-236.22</td>
</tr>
<tr>
<td>5-deoxy- allo-inositol</td>
<td></td>
<td>1.96</td>
<td>-235.75</td>
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</tbody>
</table>

$\Delta H^o_f (70 \rightarrow 71) = -3.98$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$S_E$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-deoxy-1-allo-3-inosose (72)</td>
<td>.90</td>
<td>-222.88</td>
<td>-9.22</td>
</tr>
<tr>
<td>5-deoxy-1-allo-3-inosose (73)</td>
<td>-1.89</td>
<td>-225.67</td>
<td>-12.01</td>
</tr>
<tr>
<td>5-deoxy-1-allo-inositol</td>
<td>1.49</td>
<td>-236.22</td>
<td>-12.37</td>
</tr>
<tr>
<td>5-deoxy-1-allo-inositol</td>
<td>1.96</td>
<td>-235.75</td>
<td>-11.90</td>
</tr>
<tr>
<td>2-deoxy-D-chiro-inositol</td>
<td>2.78</td>
<td>-234.93</td>
<td>-11.08</td>
</tr>
<tr>
<td>2-deoxy-D-chiro-inositol</td>
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<td>-239.05</td>
<td>-15.21</td>
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$\Delta H_f (72 \rightarrow 73) = -2.79$ kcal/mol
<table>
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<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allo-1-Inosose (74)</td>
<td>-4.52</td>
<td>-266.30</td>
<td>-17.82</td>
</tr>
<tr>
<td>Allo-1-Inosose (75)</td>
<td>-5.79</td>
<td>-268.07</td>
<td>-19.09</td>
</tr>
<tr>
<td>neo-Inositol</td>
<td>-3.31</td>
<td>-279.52</td>
<td>-20.35</td>
</tr>
<tr>
<td>neo-Inositol</td>
<td>-3.23</td>
<td>-279.44</td>
<td>-20.27</td>
</tr>
<tr>
<td>allo-Inositol</td>
<td>-3.52</td>
<td>-279.73</td>
<td>-20.56</td>
</tr>
<tr>
<td>allo-Inositol</td>
<td>-5.31</td>
<td>-276.88</td>
<td>-17.71</td>
</tr>
</tbody>
</table>

Δ$H^\circ_f (74 \rightarrow 75) = -1.27$ kcal/mol
<table>
<thead>
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<th>MMX-ENERGY</th>
<th>$H_i$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allo-2-inosose</td>
<td>-8.41</td>
<td>-270.76</td>
<td>-21.71</td>
</tr>
<tr>
<td>Allo-2-inosose</td>
<td>-5.11</td>
<td>-267.40</td>
<td>-18.41</td>
</tr>
<tr>
<td>(77)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-chiro-inositol</td>
<td>-2.77</td>
<td>-278.98</td>
<td>-19.81</td>
</tr>
<tr>
<td></td>
<td>-0.76</td>
<td>-276.97</td>
<td>-17.80</td>
</tr>
<tr>
<td></td>
<td>-3.52</td>
<td>-279.73</td>
<td>-20.56</td>
</tr>
<tr>
<td>Allo-inositol</td>
<td>-5.31</td>
<td>-276.88</td>
<td>-17.71</td>
</tr>
<tr>
<td></td>
<td>3.30 kcal/mol</td>
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<td></td>
</tr>
</tbody>
</table>

$\Delta H^\circ_f (76 \rightarrow 77) = 3.30$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>SE (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allo-3-inosose (78)</td>
<td>-4.20</td>
<td>-266.48</td>
<td>-17.50</td>
</tr>
<tr>
<td>Allo-3-inosose (79)</td>
<td>-5.11</td>
<td>-267.40</td>
<td>-18.41</td>
</tr>
<tr>
<td>L-chiro-inositol</td>
<td>-6.38</td>
<td>-282.59</td>
<td>-23.42</td>
</tr>
<tr>
<td>L-chiro-inositol</td>
<td>-3.87</td>
<td>-276.58</td>
<td>-17.41</td>
</tr>
<tr>
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<td>-5.52</td>
<td>-279.73</td>
<td>-20.56</td>
</tr>
<tr>
<td>allo-inositol</td>
<td>-5.31</td>
<td>-276.88</td>
<td>-17.71</td>
</tr>
</tbody>
</table>

$\Delta H_f (78 \rightarrow 79) = -0.92$ kcal/mol
<table>
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<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>SE (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1-l-icosose (80)</td>
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<td>-266.38</td>
<td>-17.39</td>
</tr>
<tr>
<td></td>
<td>-5.63</td>
<td>-267.92</td>
<td>-18.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-281.84</td>
<td>-22.67</td>
</tr>
<tr>
<td></td>
<td>-5.63</td>
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<td>-22.67</td>
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<td>-5.31</td>
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</tr>
<tr>
<td></td>
<td>-2.77</td>
<td>-278.98</td>
<td>-19.81</td>
</tr>
<tr>
<td>epi-l-inositol</td>
<td>-.76</td>
<td>-276.97</td>
<td>-17.80</td>
</tr>
</tbody>
</table>

$\Delta H_f^{\circ} (80 \rightarrow 81) = -1.54$ kcal/mol
<table>
<thead>
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<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-4.15</td>
<td>-266.44</td>
</tr>
<tr>
<td>D-chiro-1-inosose (82)</td>
<td></td>
<td>-2.93</td>
<td>-265.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-6.08</td>
<td>-282.29</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>-2.50</td>
<td>-278.71</td>
</tr>
<tr>
<td>myo-inositol</td>
<td></td>
<td>-2.77</td>
<td>-278.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-2.76</td>
<td>-276.97</td>
</tr>
</tbody>
</table>

$\Delta H_f^o (82 \rightarrow 83) = 1.22$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$S_E$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ep1-1-inosose (84)</td>
<td>-2.97</td>
<td>-265.25</td>
<td>-16.27</td>
</tr>
<tr>
<td>Ep1-1-inosose (85)</td>
<td>-6.08</td>
<td>-268.36</td>
<td>-19.38</td>
</tr>
<tr>
<td>allo-inositol</td>
<td>-3.52</td>
<td>-279.73</td>
<td>-20.56</td>
</tr>
<tr>
<td>allo-inositol</td>
<td>-5.31</td>
<td>-276.88</td>
<td>-17.71</td>
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<tr>
<td>epi-inositol</td>
<td>-2.77</td>
<td>-278.98</td>
<td>-19.81</td>
</tr>
<tr>
<td>epi-inositol</td>
<td>.76</td>
<td>-276.97</td>
<td>-17.80</td>
</tr>
</tbody>
</table>

$\Delta H_f^{\circ} \ (84 \rightarrow 85) = -3.11 \ \text{kcal/mol}$
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>SE (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epi-2-inosose (86)</td>
<td>-3.72</td>
<td>-258.57</td>
<td>-19.02</td>
</tr>
<tr>
<td>Epi-2-inosose (87)</td>
<td>-2.19</td>
<td>-264.47</td>
<td>-15.49</td>
</tr>
<tr>
<td>myo-inositol</td>
<td>-6.08</td>
<td>-282.29</td>
<td>-23.12</td>
</tr>
<tr>
<td>myo-inositol</td>
<td>-2.50</td>
<td>-278.71</td>
<td>-19.54</td>
</tr>
<tr>
<td>epi-inositol</td>
<td>-2.77</td>
<td>-278.98</td>
<td>-19.81</td>
</tr>
<tr>
<td>epi-inositol</td>
<td>-7.76</td>
<td>-276.97</td>
<td>-17.80</td>
</tr>
</tbody>
</table>

$\Delta H^\circ$ (86 $\rightarrow$ 87) = -5.90 kcal/mol
<table>
<thead>
<tr>
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<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epl-3-Inosose (88)</td>
<td>-4.00</td>
<td>-266.29</td>
<td>-17.30</td>
</tr>
<tr>
<td>Epl-3-Inosose (89)</td>
<td>0.02</td>
<td>-262.26</td>
<td>-13.28</td>
</tr>
<tr>
<td>MucO-Inositol</td>
<td>5.30</td>
<td>-270.91</td>
<td>-11.74</td>
</tr>
<tr>
<td>MucO-Inositol</td>
<td>1.58</td>
<td>-274.63</td>
<td>-15.46</td>
</tr>
<tr>
<td>MucO-Inositol</td>
<td>-2.77</td>
<td>-278.98</td>
<td>-19.81</td>
</tr>
<tr>
<td>Epl-Inositol</td>
<td>.76</td>
<td>-276.97</td>
<td>-17.80</td>
</tr>
<tr>
<td>Epl-Inositol</td>
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<td></td>
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</tr>
</tbody>
</table>

$\Delta H_f^\circ (88 \rightarrow 89) = 4.03$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epl-4-lanos (90)</td>
<td>-4.38</td>
<td>-266.67</td>
<td>-17.68</td>
</tr>
<tr>
<td>Epl-4-lanos (91)</td>
<td>-1.72</td>
<td>-264.00</td>
<td>-15.02</td>
</tr>
<tr>
<td>myo-inositol</td>
<td>-6.08</td>
<td>-282.29</td>
<td>-23.12</td>
</tr>
<tr>
<td>myo-inositol</td>
<td>-2.50</td>
<td>-278.71</td>
<td>-19.54</td>
</tr>
<tr>
<td>epl-inositol</td>
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</tr>
<tr>
<td>epl-inositol</td>
<td>-7.76</td>
<td>-276.97</td>
<td>-17.80</td>
</tr>
</tbody>
</table>

$\Delta H^\circ_f (90 \leftrightarrow 91) = 2.67$ kcal/mol
<table>
<thead>
<tr>
<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>SR (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epi-5-inosose (92)</td>
<td>-5.72</td>
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<td>-20.56</td>
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<tr>
<td>Allo-inositol</td>
<td>-5.31</td>
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<td>-17.71</td>
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<tr>
<td>Allo-inositol</td>
<td>-2.77</td>
<td>-278.98</td>
<td>-19.81</td>
</tr>
<tr>
<td>Epi-inositol</td>
<td>-0.76</td>
<td>-276.97</td>
<td>-17.80</td>
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</table>

$\Delta H^\circ_f (92 \rightarrow 93) = 1.30 \text{ kcal/mol}$
<table>
<thead>
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<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>$S_E$ (kcal/mole)</th>
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<tbody>
<tr>
<td>L-cho-1-inosose (94)</td>
<td>-6.43</td>
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<td>-19.73</td>
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<td>-16.48</td>
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<td>L-cho-ino-sitol</td>
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<td>278.71</td>
<td>-19.54</td>
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$\Delta H_f^{\circ}$ (94 → 95) = 3.24 kcal/mol
<table>
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<th>Compound</th>
<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
<th>SE (kcal/mole)</th>
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</thead>
<tbody>
<tr>
<td>Muco-1-inosose (96)</td>
<td>3.34</td>
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<td>-16.64</td>
</tr>
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<td>-18.52</td>
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<td>-11.74</td>
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<tr>
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<td>1.58</td>
<td>-274.63</td>
<td>-15.46</td>
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<td>D-chiro-inositol</td>
<td>2.77</td>
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<td>-19.81</td>
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<td>D-chiro-inositol</td>
<td>.76</td>
<td>-276.97</td>
<td>-17.80</td>
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$\Delta H_f^\circ (96 \rightarrow 97) = -1.89 \text{ kcal/mol}$
<table>
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<th>$H_f$ (kcal/mole)</th>
<th>$S_E$ (kcal/mole)</th>
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</thead>
<tbody>
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<td>Muco-2-Inosose (98)</td>
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<td>-15.46</td>
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$\Delta H_f^{\circ} (98 \rightarrow 99) = 4.95$ kcal/mol
<table>
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<th>MMX-ENERGY</th>
<th>$H_t$ (kcal/mole)</th>
<th>$SE$ (kcal/mole)</th>
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</thead>
<tbody>
<tr>
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<td>-17.80</td>
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$\Delta H^\circ_r (100 \rightarrow 101) = -1.90$ kcal/mol
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<th>$H_f$ (kcal/mole)</th>
<th>$S_E$ (kcal/mole)</th>
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</thead>
<tbody>
<tr>
<td>Myo-1-inosose (102)</td>
<td>-3.84</td>
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<td>-19.54</td>
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<td>L-chiro-inositol</td>
<td>-3.75</td>
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$\Delta H^*_f (102 \rightarrow 103) = -2.62$ kcal/mol
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<th>MMX-ENERGY</th>
<th>$H_f$ (kcal/mole)</th>
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<tbody>
<tr>
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$\Delta H_f^{(104 \rightarrow 105)} = -6.76$ kcal/mol
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<tr>
<td>Myo-3-inosose (106)</td>
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<td>-19.54</td>
</tr>
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<td>D-chiro-inositol</td>
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<td>-19.81</td>
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<td>D-chiro-inositol</td>
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$\Delta H^*_f$ (106 $\rightarrow$ 107) = 0.11 kcal/mol
<table>
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<th>SE (kcal/mole)</th>
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<tbody>
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<td>Myo-5-inosose (108)</td>
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<td>-279.44</td>
<td>-20.27</td>
</tr>
</tbody>
</table>

$\Delta H^*_f(108 \rightarrow 109) = -3.25$ kcal/mol
VI. References


More literature for biological activity of cyclitols see:

VII. VITA

Mary Catherine Cebulak was born in New Kensington, Pennsylvania on June 1, 1968. She graduated from Valley High School (New Kensington, Pa.) in 1986. The fall of that same year she entered Gannon University and graduated with a Bachelor of Science degree in chemistry in spring of 1990. In fall of 1990, Mary continued her study of chemistry at Virginia Tech under the direction of Dr. Tomas Hudlicky in pursuit of a Master’s degree in organic chemistry.

Mary C. Cebulak