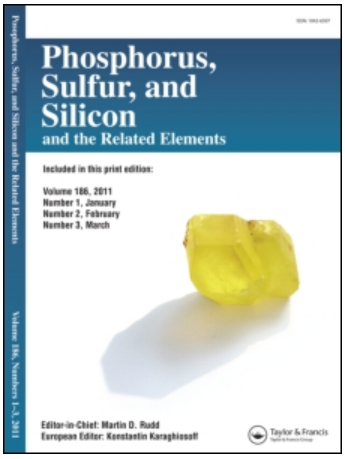


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE SYNTHESIS AND CHARACTERIZATION OF THIO SUGAR ESTERS OF DIORGANYLARSINOUS ACIDS

Maria V. Rosenthal[a]; Ralph A. Zingaro[a]
[a] Department of Chemistry, Texas A&M University, College Station, Texas, U.S.A.

To cite this Article Rosenthal, Maria V. and Zingaro, Ralph A.(1980) 'THE SYNTHESIS AND CHARACTERIZATION OF THIO SUGAR ESTERS OF DIORGANYLARSINOUS ACIDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 9: 1, 107 — 115
To link to this Article: DOI: 10.1080/03086648008078226
URL: http://dx.doi.org/10.1080/03086648008078226

Phosphorus and Sulfur, 1980, Vol. 9, pp. 107–116
0308-664X/80/0901-0107$06.50/0

THE SYNTHESIS AND CHARACTERIZATION OF THIO SUGAR ESTERS OF DIORGANYLARSINOUS ACIDS

MARIA V. ROSENTHAL† and RALPH A. ZINGARO

Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

(*Received November 30, 1979*)

The synthesis of diorganylarsino derivatives of 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranose and 1,2,3,4-tetra-O-acetyl-6-thio-β-D-glucopyranose is described. The diorganyl groups used are: dihexadecyl, didodecyl, di-*n*-octyl, dicyclohexyl, dibutyl, dipropyl, diethyl, methyl-*n*-propyl and 2-hydroxyethylmethyl.

The compounds have been characterized by proton and carbon-13 nuclear magnetic resonance spectroscopy, mass spectroscopy, and elemental analysis. All spectral data are consistent with the proposed structures.

The compounds prepared have been screened to determine whether they display carcinostatic activity. *In vivo* tests in mice with lymphocytic leukemia (PS 388) have afforded preliminary results which indicate that the diethylarsino derivative of 1-thioglucose tetraacetate may have a high level of activity. Results obtained with the dihexadecylarsino derivatives are also promising.

INTRODUCTION

A large number of potential carcinostatic compounds have been synthesized, their physicochemical properties determined, and their antitumor activity evaluated. During the past few years, a number of compounds synthesized in our laboratories have displaced carcinostatic activity. These compounds are dimethylarsino derivatives of thio and seleno sugars, thioamino acids and other biomolecules.[1–5] In the work herein reported, molecules of the type $GSAsR_2$ have been synthesized where G is 1- or 6-thioglucose tetraacetate. The primary goal has been to observe the effect, on carcinostatic activity, of varying the organic substituent, R.

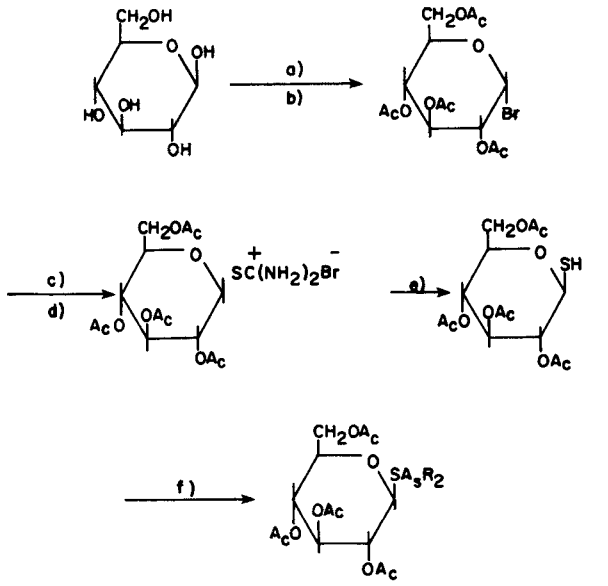
It is well known that thiols are intimately involved in various cytologic processes. Thiols in nucleoproteins have been observed to increase in concentration during normal growth processes, but even more so in neoplastic tissues.[6] It is logical to make these SH-containing nucleoproteins targets of chemotherapeuticals such as anti-memtabolites, and SH-inhibitors, such as arsenicals.

A biomolecule bonded to an organoarsenic group may function as a vehicle to transport the active arsenic moiety to a site of action. In this study, glucose has been chosen due to its ubiquity in biochemical systems. The 1-thio derivatives are of fundamental importance and the functionality of the glycosidic linkage in all living systems is well known.[7] The C-6 position is selected due to its reactivity and stereospecificity in crosslinking functions in polysaccharides.[8] The acetate groups are synthetically convenient and non-toxic. Also, they have been reported to increase the antitumor activity of some polysaccharides by raising the solubility and favoring changes of the polymeric structure.[9]

DISCUSSION

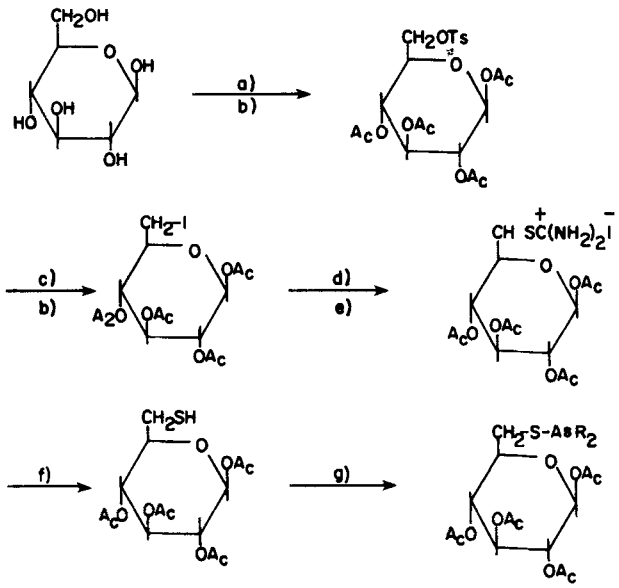
Schemes 1 and 2 depict the synthetic routes to the 1-thio and 6-thio diorganylarsino derivatives. As a general procedure, the thiol obtained from the thioureide was extracted into the organic phase which in the case of the 1-thio derivatives was chloroform or dichloromethane, while toluene was used for the 6-thio compounds. This solution was then treated with a stoichiometric amount of the diorganylhaloarsine followed by addition of an amine to remove the halo acid. Care was taken in this step to keep the pH of the reaction at values no higher than 8.0. The loss of the protective groups on the sugar ring may occur at higher pH values. After refluxing the reaction mixture for 1 hour, the product was isolated and purified as required. The course of the reaction was followed

† This work is partial fulfillment of graduate degree requirements for the Ph.D. degree from Texas A&M University.



SCHEME 1 Synthetic route to the 1-thioglucose series of compounds:

a) Bromine
b) Acetic anhydride
c) Thiourea
d) Acetone
e) Aqueous sodium bicarbonate
f) Diorganyliodoarsine



SCHEME 2 Synthetic route to the 6-thioglucose series of compounds:

a) Paratoluenesulfonyl chloride
b) Acetic anhydride
c) Sodium iodide
d) Thiourea
e) *n*-pentanol
f) Aqueous potassium bisulfite
g) Diorganyliodoarsine

by T.L.C. It was found that the size of the alkyl chain attached to the arsenic atom did not seem to affect the formation of the desired product which was in all cases obtained in quantitative yield. Also, the rate of the reaction did not appear to be much affected by the different alkyl groups used.

The proton NMR spectra of the compounds suggest that the configuration of the sugar diorganylarsino derivatives, is the same as that of the parent sugar thiol. On both materials, chemical shift values for the anomeric proton correspond to that of the β-anomer.[10] A qualitative estimation of the J (coupling constant) value for the anomeric proton gives a value of ≥ 6.5 Hz for the series of compounds, thus indicating that the conformation of the sugar ring is, in all cases, that corresponding to the $^4C_1$ chair.[11] The fact that the chemical shift values for the protons on the sugar ring remain virtually unchanged throughout the series, and when compared with those of the parent thiol, is also supportive of the observation that there is no change in configuration or conformation of the sugar ring, irrespective of the position and the size of the thiodiorganylarsino substituent. Chemical shift values for these protons have been assigned by comparison with literature values and the use of empirical rules[12] that state that equatorially oriented protons resonate at higher fields than those axially oriented. However, a definite assignment for each proton was not feasible in some instances due to the fact that the spectral signals are rather complex due to long-range coupling and substituent effects.

In the case of the 1-thio derivatives the most important variation detected is that of the upfield shift in chemical shift values of the protons *geminal* to the substituent at C-1 when sulfur replaces oxygen, as would be expected. The chemical shift values of the methylene protons at C-6 also are affected by the change in substituent, and they have been found at ca. 0.5 ppm downfield with respect to values observed for the acetoxy-substituted 1-thio compounds. This shift away from TMS suggests that the interactions of the resonating nuclei with the different substituents may arise not only from the differences in electronegativity of the atoms directly bound to the carbon, but from other effects caused by the chemical nature of

TABLE I

Significant ^1H NMR resonances for the 1- and 6-thioglucose esters of diorganyl-arsinous acids.[a,b]

Series	H-1	H-6	As—CH_2—
1-thio	5.3	2.6	1.7
6-thio	5.75	2.85	1.7

[a] Solvent, $CDCl_3$, References TMS.
[b] Chemical shifts in δ (ppm.)

TABLE II

Significant ^{13}C NMR resonances for the 1- and 6-thioglucose esters of diorganlyarsinous acids.[a,b]

Series	C-1	C-6	As-C
1-thio	83.4	61.5	22.5
6-thio	91.6	69.9	22.1

[a] Shift values in δ (ppm).
[b] Solvent $CDCl_3$, Reference TMS.

the substituent. This particular effect is also observed in the study of the ^{13}C NMR spectra.

The spectra of the diorganylarsino groups are more simple than those of the sugar moiety. The chemical shift values for the resonances of the methylene protons directly attached to the arsenic are found upfield from the typical values for —CH_2— resonances. In the case of the long chain derivatives, broad multiplets were obtained, and it was difficult to make assignments for each and all the methylene groups involved. It has been assumed that the value for the As—CH_2-methylene resonance would remain unchanged regardless of the chain as it is inferred from the integration of the areas below the various peaks of the multiplet. The terminal methyl group of the alkyl chain gives rise to a signal that has the following properties: it is well-separated from the methylene resonances; it is a recognizable triplet although somewhat distorted by long range coupling; it is the closest resonance to TMS in the spectra, and it has a consistent relative peak area.

Table I shows the assigned average chemical shift value of interest in these series of compounds. The complete assignments for each compound are presented in the experimental section.

^{13}C NMR spectra of the compounds were also obtained and assignments made by comparison with reported values for analogous compounds.[13] Basically, the trends observed in the ^1H NMR spectra, are also found in the ^{13}C spectra with respect to substituent effects on the sugar ring. For the 1-thio compounds, an upfield shift is observed on C–1 when sulfur replaces oxygen. In the case of 6-thio derivatives, such replacement results in a downfield shift of the resonance of the C–6. The resonance values for the ring carbons appear to be unaffected by the change in substituents and compare well with those values reported for the penta-acetylated glucopyranose.[14]

The ^{13}C chemical shift values for the diorganyl moiety are within agreement for those of an alkyl group. The characteristic feature is that of the As—CH_2-resonances which again are observed upfield with respect to the methylenes. This is more clearly observed in the spectra of the short chain derivatives where individual signals are readily resolved.

The more important ^{13}C average chemical shift values are listed in Table II.

Electron impact mass spectra of the compounds prepared, were obtained, from analytically pure samples. The data show that there exist a common fragmentation pattern for both series of derivatives. This involves the loss of the thiodiorganyl-arsino moiety as the first step. This behavior was observed in previous studies of similar compounds.[1,4] The remaining fragment, the sugar, follows a breakdown process which is typical of peracetylated pyranose.[1,4,15–20] The pyranosyl cation for the 1-thio series of compounds, m/e 331, undergoes the so-called *A* sequence on the breakdown process.[19] This is probably because the loss of the substituent at C–1 occurs so readily that the resulting glycosyl ion will undergo the direct loss of acetoxy substituents and any rearrangement process such as the one required for the *B* route[19] to take place, will be less favored.

For the 6-thio derivatives, it is found that their breakdown involves the loss of the thiodiorganyl-arsino fragment as the first step. In this case, the processes known as *A* and *C* series for the breakdown of the remaining sugar fraction are observed to take place. The occurrence of the *C* series differentiates the C–6 and C–1 fragmentation behavior. The loss of the thiodiorganylarsino group leaves the sugar ring virtually intact. The stability of the sugar fragment allows for a greater number of paths in its breakdown. For both types of compounds, the spectral data also show the presence of ions that are considered typical of acetoxy sugars,[17] e.g., triacetoxonium ion (m/e

145), diacetoxonium ion (m/e 103) acetic acid (m/e 60), acetate ion (m/e 59), acetoxyl (m/e 45) and ketene (m/e 42).

With respect to the arsine moiety, the data show that this fragment breaks down by the successive loss of two alkyl groups. In the case of the long chain derivatives this loss occurs in several steps with the probable generation of ethylene indicated by the presence of an m/e 28 fragment. In all cases it was possible to detect ions such as m/e 137 [$(CH_3)_2AsS$)], m/e 109 [H_2AsS] and m/e 107 [As—S] which are characteristic of the thioarsino compounds previously reported.[2,4]

Biochemical Testing

Compounds previously prepared in these laboratories have been evaluated[3,21,22] for carcinostatic activity. In all of these compounds a sulfur or selenium atom replaced one oxygen atom in the molecule. In general, sulfur containing compounds show higher degrees of activity. Also hydrophobic molecules, for example, peracetylated sugars are more active than their free (water soluble) hydroxy analogs. These results suggest that (a) the As—S bond is fairly stable under biochemical conditions, and (b) the solubility of the protected compound is such that it assists in the transport of the compound through the physiological environment to its site of action. All of the compounds which were the subject of this study were peracetylated (water insoluble) derivatives.

The compounds were tested against lymphocitic leukemia (P 388) in mice. By recording the survival time of groups of six mice treated with the drug, as well as a control group, the activity of the agents were evaluated. The NCI criterion for activity is the $\%\ T/C \geq 125$. This means that the group of animals receiving the drug survives at least 25 per cent longer than the control group. The results of preliminary screening tests are shown in Table III. From these preliminary results

TABLE III

Biochemical screening of compounds

Compounds[a]	N.C.I. Number	Host Sex	Tumor	Dose (mg/kg)[b]	Number of Injections	Vehicle[c]	% T/C
1	294973	F	PS	100	9	M	117
2	298838	F	PS	200	9	T	124
		F	PS	50	9	T	117
3	298840	F	PS	200	9	Z	181[d]
		F	PS	100	9	Z	180
		F	PS	50	9	Z	116
4	294971	M	PS	100	9	M	116
		M	PS	50	9	M	117
		M	PS	50	9	M	122
5	285224	M	PS	50	9	T	125
6	285227	F	PS	400	9	M	Toxic
7	288837	F	PS	200	9	T	118
8	285225	M	PS	100	9	T	125
		M	PS	200	9	T	119
		M	PS	50	9	T	119
9	285226	F	PS	25	9	M	120

[a] Key to compound numbers:
1—2,3,4,6-Tetra-O-acetyl-1-S-dibutylarsino-1-thio-β-D-glucopyranose
2—2,3,4,6-Tetra-O-acetyl-1-S-dipropylarsino-1-thio-β-D-glucopyranose
3—2,3,4,6-Tetra-O-acetyl-1-S-diethylarsino-1-thio-β-D-glucopyranose
4—2,3,4,6-Tetra-O-acetyl-1-S-2-hydroxyethylmethylarsino-1-thio-β-D-glucopyranose
5—2,3,4,6-Tetra-O-acetyl-1-S-dihexadecylarsino-1-thio-β-D-glucopyranose
6—2,3,4,6-Tetra-O-acetyl-1-S-dicyclohexylarsino-1-thio-β-D-glucopyranose
7—1,2,3,4-Tetra-O-acetyl-6-S-methyl-*n*-propylarsino-6-thio-β-D-glucopyranose
8—1,2,3,4-Tetra-O-acetyl-6-S-dihexadecylarsino-6-thio-β-D-glucopyranose
9—1,2,3,4-Tetra-O-acetyl-6-S-dicyclohexylarsino-6-thio-β-D-glucopyranose

[b] mg/kg body weight

[c] M-klucel (hydroxpropylcellulose), T-saline with tween-80, Z-saline + alcohol.

[d] Subsequent testing has failed to confirm these results. New tests are being conducted on a freshly synthesized sample of this compound.

it can be seen that the presence of organic substituents other than methyl attached to the arsenic atom can yield molecules which display carcinostatic activity.

EXPERIMENTAL

Chemicals

Arsenic trichloride was purchased from Alfa Products and from the Ventron Co. Diethylamine was dried over sodium hydroxide pellets, distilled over molecular sieve and used immediately. Hexadecyl bromide and dodecyl bromide were purchased from Eastman Kodak Products, Inc. and used without further purification. All other chemicals were purchased from Matheson, Coleman and Bell Chemicals. Anhydrous diethyl ether was obtained from Mallinckrodt and was dried over sodium wire and distilled prior to use. Methyl-*n*-propylarsinic acid, 2-hydroxyethylmethylarsinic acid and dimethylarsinic acid were obtained as gifts from Vineland Chemical Co. Di-*n*-octylarsinic acid was a gift from Dr. J. Flannery.

β-D-Glucose pentaacetate was purchased from Pfanstiehl Laboratories, Inc. β-D-Glucose (anhydrous analytical reagent) was purchased from Mallinckrodt Inc. and the American Drug and Chemical Co. Thiourea, reagent grade, was obtained from Matheson, Coleman and Bell Chemicals. All solvents used were reagent grade and were dried and distilled as required.

The materials used in thin layer chromatography were: flexible plastic-backed sheets (Baker–Flex) from J. T. Baker Chemical Co., silica gel IB-F and IB, and cellulose F. An iodine chamber was used to develop the chromatograms. The following materials were used in filtration: silicic acid from Baker's analyzed reagents, Celite 545 from Fisher Scientific Co., activated charcoal, Mallinckrodt Inc., silica gel and cellulose.

General Methods

Solvent evaporation was carried out with a Büchi Rotavapor-R at reduced pressure and varied bath temperatures. Melting points were determined with a Büchi–SMP–20 melting point apparatus and are not corrected.

^{1}H NMR spectra of crude and purified materials were recorded at 60 and 100 MHz. A Varian T-60 instrument was used for routine scanning and recording of spectra. A Varian A–60A was used for more detailed recordings.

A modified Varian Associates HA–100 spectrometer with a Hewlett–Packard Model 200 ABR radio oscillator and a frequency counter was used to measure the 100 MHz proton magnetic resonances. In all cases, spectra were recorded at ambient probe temperature (HA–100, 38°; A–60A, 32.5°, T–60, ~32°).

^{13}C Spectra were recorded by Steven N. Rosenthal, Chemistry Department, Texas A&M University. ^{13}C NMR measurements were made on a JEOL PS–100 PFT spectrometer equipped with a Nicolet 1080 computer and disc. The natural abundance ^{13}C NMR spectra were obtained at 25.03 MHz in the Fourier transform mode and a magnetic field strength of 23 KG. Samples were locked onto the internal deuterium of the solvent. All spectra were proton decoupled. The ambient probe temperature was 28 ± 1°C. The spectra were obtained with a spectral window of 5000 Hz, a pulse recycling time of 1 to 2 seconds, and a tip angle of 20°–30°. All ^{13}C NMR measurements were carried out on solutions in 10 mm O. D. Wilmad sample tubes. Individual ^{13}C chemical shift measurements were accurate to ±0.05 ppm.

The mass spectra of the products were recorded by Dr. R. Grigsby, Biochemistry Department, Texas A&M University. A DuPoint CEC 21–110 high resolution spectrometer operating at an ionized potential of 70 eV and ion current of 200 μA was used. The accelerating potential was 8 kV.

Carbon and hydrogen, and in some instances arsenic and sulfur microanalyses were performed by Galbraith Analytical Laboratories, Inc., Knoxville, Tennessee.

Preparation of Compounds

The haloarsines required for the synthesis of these products were prepared by the reduction of the corresponding arsinic acids which, in the case of the long chain arsines, were synthesized according to the method of Irgolic, *et al.*[23] Some of the short chain arsinic acids were obtained as gifts and were reduced to the arsines by treatment with hydriodic acid.[24] Still other arsines were prepared in these laboratories by conventional methods.[25]

The 1-thio derivative of β-D-glucose tetraacetate was prepared by well known procedures.[14] The method followed by Chen, Zingaro and Thompson,[4] was used to obtain the corresponding 6-thio derivative. The sugar in the form of the thiourеide was treated with potassium carbonate or sodium bisulfite in order to obtain the corresponding thiols. After treatment with the reducing agent, it was extracted with a suitable solvent and used directly in this solution. This was done with the purpose of minimizing the oxidation of the thiol to the disulfide by excessive exposure to air, and it was proven to be a satisfactory way to obtain quantitative amounts of the thio sugar with minimum contamination.

Minor changes in the techniques used to combine the reactants, were necessary in the preparation of several compounds and are described in the details of the preparations.

Preparation of 2,3,4,6 - Tetra - O - acetyl - 1 - thio - β - D - gluco - pyranose Derivatives

The general reaction scheme is shown in Figure 1.

2,3,4,6 - Tetra - O - acetyl - 1 - thio - β - D - glucopyranose was prepared following the method described by Wolfram and Whistler[9] as used by Zingaro and Thompson.[1]

2,3,4,6 - Tetra - O - acetyl - 1 - S - dihexadecylarsino - 1 - thio - β - D - glucopyranose 2,3,4,6-Tetra - O - acetyl - 1 - thio - 1 - S - β - D-glucopyranose, 1.5 g (4 mmoles) dissolved in 350 ml of methylene chloride was combined with 3.2 g (4 mmoles) of dihexadecyliodoarsine. Diethylamine was added until the pH reached 7. The mixture was then refluxed for one hour. Upon cooling a solid (diethylammonium iodide) formed and was removed by filtration. The methylene chloride was removed and a yellow waxy product remained. This product was further purified by recrystallization from hexane. However, all attempts to obtain a pure material were unsuccessful, and the final product, mp 43–45° was estimated to be ~95% pure, by integration of the proton NMR spectrum. ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ 5.30 (1 proton multiplet H-1), 4.35 (2 proton multiplet, H-3, 5), 4.1 (2 proton multiplet, H-2, 4), 2.9 (2 proton multiplet, H-6) 2.3, 2.1, 2.08, 2.0 (12 proton, singlets, $-CH_3$ acetate), 1.60 (8 proton multiplet, As$-CH_2-$), 1.85 (8 protons $-CH_2-$), 2.35 (10 proton multiplet, $-CH_2$), 1.1 (10 proton triplet, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.0, 168.5, 168.1, 167.9 (C=O), 96.0 (C–1), 72.0 (C–2), 73.7 (C–3), 67.9

(C-4), 76.0 (C-5), 61.5 (C-6), 20.1 (CH_3 acetate), 22.5 (C—As—), 32.4, 31.0, 29.5, 29.1, 28.0, 27.4, 25.9 (—CH_2—), 14.0 (—CH_3).

2,3,4,6 - Tetra - O - acetyl - 1 - S - Di - n - octylarsino - 1 - thio - β - D - glucopyranose 2,3,4,6-Tetra-O-acetyl-1-thiourea-1-S-β-D-glucopyranose pseudothiourea hydrobromide, 4.87 g (10 mmoles) was dissolved in 150 ml water and 7.5 g of K_2CO_3 (~50 mmoles) were added. The mixture was refluxed for ~15 min and after cooling, it was extracted with chloroform. Immediately, 2.8 ml (10 mmoles) of di-*n*-octyliodoarsine were added. Diethylamine was added until the pH remained constant at ~8. The solution was refluxed for one and a half hours. Upon cooling it was filtered, the solvent was removed and a yellowish powder was obtained. Thin layer chromatography revealed the presence of impurities after purification procedures (filtration, recrystallization) were carried out. The product melted at 122–125° and it was assumed to be ~95% pure, based upon the integration values from ^{1}H NMR. (60 MHz, $CDCl_3$, TMS): δ 5.25 (1 proton multiplet H-1), 4.35 (2 proton multiplet H-3, 5), 3.85–3.2 (2 proton multiplet, H-2, 4), 2.4 (2 proton multiplet H-6), 2.1, 2.09, 2.05, 2.02 (12 proton, singlets, CH_3 acetate), 1.85 (6 proton multiplet, As—CH_2—) 2.5–1.45 (18 proton multiplet, —CH_2—) 0.95 (8 proton triplet) —CH_3).

2,3,4,6 - Tetra - O - acetyl - 1 - S - dicyclohexylarsino - 1 - thio - β - D - glucopyranose A solution of 2,3,4,6 - tetra - O - acetyl - 1 - thio - 1 - S - β - D - glucopyranose (1.5 g, 4 mmoles) in methylene chloride was treated with dicyclohexyliodoarsine (1.7 ml, 4 mmoles). Diethylamine was added, until the pH remained at 7.5. The solution was refluxed for one hour. Upon cooling the solution was filtered and rinsed with H_2O to remove the ammonium salts. The solvent was removed under reduced pressure. The product was obtained in the form of light yellow crystals, melting at 53°, yield 65%. ^{1}H NMR, (60 MHz, $CDCl_3$ TMS): δ 5.7 (1 proton multiplet, H-1), 5.15 (2 proton multiplet, H-3, 5), 4.14–3.25 (2 proton multiplet, H-2, 4), 2.95 (2 proton multiplet H-6), 2.05, 2.03, 2.0, 1.98 (12H, singlets, CH_3 acetate), 1.5 (22 proton multiplet, —CH_2—). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.1, 169.3, 169.1, 168.8 (C=O), 91.6 (C-1), 72.6 (C-2), 74.0 (C-3), 70.2 (C-4), 75.8 (C-5), 62.3 (C-6), 20.6 (CH_3 acetate), 36.4 (—CH_2—As), 30.0, 29.6, 27.4 (—CH_2—). *Anal*: Calculated for $C_{26}H_{41}O_9SAs$ (found) %C 51.65 (51.8), %H 6.78 (6.82).

2,3,4,6 - Tetra - O - acetyl - 1 - S - diethylarsino - 1 - thio - β - D - glucopyranose Diethyliodoarsine (2.6 ml, 0.01 moles) was dissolved in 5 ml of anhydrous diethyl ether and diethylamine (~1 ml, 0.01 moles) was added. The reaction flask was kept under nitrogen. The diethylaminodiethylarsine formed was then treated *in situ* with 2,3,4,6-tetra-O-acetyl-1-thio-1-S-β-D-glucopyranose (3.63 g, 0.01 moles) dissolved in 300 ml of methylene chloride. The reaction mixture was refluxed for one hour. It was allowed to cool to room temperature, and then filtered to remove the ammonium salt. The solvent then was removed under reduced pressure, and a syrup remained. The product was recrystallized from carbon tetrachloride, and was very hygroscopic and sensitive to atmospheric moisture. ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ 5.1 (1 proton multiplet H-1), 4.1 (2 proton multiplet H-3, 5), 3.6–3.2 (2 proton multiplet H-2, 4) 2.6 (2 proton multiplet H-6), 2.03, 2.0, 1.98, 1.98 (12 proton multiplet, —CH_3 acetate), 1.7 (4 proton multiplet —As—CH_2—), 1.3 (6 proton triplet —CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.2, 169.8, 169.3, 169.1 (C=O), 83.1 (C—1), 72.6 (C—2), 74.0 (C—3), 68.8 (C—4), 76.0 (C—5), 62.5 (C—6), 20.5 (—CH_3 acetates), 21.1 (As—CH_2—), 10.3 (—CH_3). Yield 90%. *Anal*: Calculated for $C_8H_{29}O_9SAs$ (found) %C 43.51 (43.55); %H 5.80 (5.88).

2,3,4,6 - Tetra - O - acetyl - 1 - S - dipropylarsino - 1 - thio - β - D - glucopyranose 2,3,4,6 - Tetra - O - acetyl - 1 - thio - 1 - S - β - D - glucopyranose (1.3 g, 3.5 mmoles) was dissolved in 150 ml of chloroform and 1.5 ml, (3.5 mmoles) of dipropyliodoarsine were added. The pH was adjusted to 7–8 by the addition of triethylamine. The mixture was refluxed for one hour. After cooling it was filtered to remove insoluble impurities. After removal of the solvent and purification by filtering through Celite, the pure product was obtained in the form of yellow crystals which were very hygroscopic, melting point 47–48°, yield 90%. ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ 5.1 (1 proton multiplet, H-1), 4.1 (2 proton multiplet, H-3, 5), 3.5–3.1 (2 proton multiplet, H-2, 4), 2.7 (2 proton multiplet, H-6), 2.05, 2.03, 2.0, 1.98 (12 proton, singlets, —CH_3— acetate), 1.7 (4 proton multiplet, —As—CH_2—), 1.8 (8 proton multiplet —CH_2—), 1.0 (6 proton triplet, —CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.3, 169.9, 169.2, 169.0 (C=O), 83.3 (C-1), 72.2 (C-2), 73.9 (C-3), 68.1 (C-4), 75.8 (C-5), 62.0 (C-6), 20.6 (CH_3 acetates), 19.5 (As—CH_2—), 31.3 (—CH_2—), 16.1 (—CH_3). *Anal*: Calculated for $C_{20}H_{33}O_9SAs$ (found): %C 45.79 (54.70); %H 6.35 (6.39).

2,3,4,6 - Tetra - O - acetyl - 1 - S - dibutylarsino - 1 - thio - β - D - glucopyranose This compound was prepared by treating 3.7 g, (0.01 moles) of 2,3,4,6-tetra-O-1-thio-β-D-glucopyranose with 3.2 ml, (0.01 moles) of dibutyliodoarsine, using 150 ml of chloroform as the solvent. Triethylamine was added until the pH was 7–8. The reaction mixture was refluxed for one hour. Upon cooling, some white precipitate formed which was removed by filtration. The solvent was removed and the product was redissolved in warm methylene chloride, treated with activated charcoal and filtered through Celite. The product formed yellow hygroscopic crystals with a melting point of 51°, yield, 85%. ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ 5.3 (1 proton doublet, H-1), 4.3 (2 proton multiplet, H-3, 5), 3.8–3.2 (2 proton multiplet H-2, 4), 2.8 (2 proton multiplet, H-6), 2.08, 2.05, 2.02, 2.0 (12 proton, singlets, —CH_3 acetate), 1.7 (4 proton multiplet, As—CH_2—), 1.9 (12 proton multiplet, —CH_2—), 0.95 (6 proton triplet, —CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.5, 169.9, 169.3, 168.7 (C=O), 83.4 (C-1), 72.2 (C-2), 73.9 (C-3), 68.1 (C-4), 75.1 (C-5), 62.0 (C-6), 20.6 (CH_3 acetate), 24.5 (As—CH_2—), 29.6, 28.2 (CH_2), 13.6 (CH_3). *Anal*: Calculated for $C_{22}H_{37}O_9SAs$. (Found): %C 47.8 (47.79); %H 6.75 (6.81).

2,3,4,6 - Tetra - O - acetyl - 1 - S - methyl - n - propylarsino - 1 - thio - β - D - glucopyranose 2,3,4,6 - Tetra - O - acetyl - 1 - thio - β - D - glucopyranose (4 g, ~10 mmoles), was dissolved in 120 ml of chloroform and treated with 0.75 ml (10 mmoles) of methyl-*n*-propyliodoarsine. Triethylamine was added dropwise until the pH remained at 7–8, and the reaction mixture was refluxed for one hour. The solution was allowed to cool to room temperature. It was then filtered through Celite and the solvent was evaporated under reduced pressure. White crystals were obtained with a melting point of 51°, yield, 95%. ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ 5.3 (1 proton multiplet, H-1), 4.6–4.3 (2 proton multiplet H-3, 5), 4.0–3.4 (2 proton multiplet, H-2, 4), 2.8 (2 proton multiplet H-6), 2.2, 2.18, 2.03, 2.0 (12 proton, singlets, CH_3 acetate), 1.7 (2 proton triplet As—CH_2—), 1.9 (2 proton multiplet, —CH_2—), 1.1 (3 proton singlet, As—CH_3), 1.4 (3 proton triplet, —CH_3). ^{13}C NMR (100 MHz,

$CDCl_3$, TMS): δ 170.6, 170.0, 169.2, 169.1 (C=O), 87.1 (C-1), 69.7 (C-2), 75.4 (C-3), 67.9 (C-4), 75.8 (C-5), 61.5 (C-6), 20.6 (CH_3 acetate), 23.0 (As—CH_2—), 28.9 (—CH_2—) 14.0 (As—CH_3) 17.0 (—CH_3). *Anal:* Calculated for $C_{18}H_{29}O_9SAs$. (Found): %C 43.55 (43.54); %H 5.88 (5.92).

2,3,4,6 - Tetra - O - acetyl - 1 - S - 2 - hydroxyethylmethylarsino - 1 - thio - β - D - glucopyranose. A chloroform solution of 2,3,4,6 - tetra - O - acetyl - 1 - thio - β - D - glucopyranose (6.8 g, 20 mmoles) in 200 ml, was treated with 1.81 ml, (20 mmoles) of 2-hydroxyethylmethyliodoarsine. Triethylamine was added dropwise to the solution until the pH reached a value of 7 and the mixture was refluxed for one hour. It was allowed to cool and then it was filtered through Celite. The solvent was removed under reduced pressure and yellow crystals remained that melted at 46.5°. Purification on a silica gel column (eluent $CHCl_3$/EtOH 1:1) was necessary. This yielded light yellow crystals, with a melting point of 50°, yield 85%. ^1H NMR (60 MHz, $CDCl_3$, TMS): δ 5.2 (1 proton multiplet, H-1), 4.2 (2 proton multiplet, H-3, 5), 3.8–3.2 (2 proton multiplet, H-2, 4), 2.6 (2 proton multiplet, H-6), 2.1, 2.08, 2.05, 2.0 (12 proton, singlets, CH_3 acetate), 1.7 (2 proton triplet, —As—CH_2—), 3.1 (2 proton triplet, —CH_2—), 4.6 (1 proton singlet, —CH_2OH) 1.0 (3 proton singlet, —CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 170.6, 170.0, 169.6, 169.2, (C=O), 87.2 (C-1), 69.7 (C-2), 75.4 (C-3), 67.9 (C-4), 75.8 (C-5), 62.0 (C-6), 20.7 (—CH_3 acetate), 21.7 (As—CH_2—), 46.4 (—CH_2—), 14.9 (CH_3). *Anal:* Calculated for $C_{17}H_{27}O_{10}SAs$. (Found): %C 40.97 (41.09); %H 5.46 (5.48).

Preparation of 1,2,3,4 - Tetra - O - acetyl - 6 - thio - β - D - gluco - pyranose Derivatives 1,2,3,4-Tetra - O - acetyl - 6 - thio - β - D - gluco - pyranose was prepared as described by, Chen, Zingaro and Thompson[3] and references therein.

1,2,3,4 - Tetra - O - acetyl - 6 - S - dihexadecylarsino - 6 - thio - β - D - glucopyranose To 3.64 g (10 mmoles) of 1,2,3,4 - Tetra - O - acetyl - 6 - thio - β - D - glucopyranose dissolved in 100 ml of toluene, was added 7.5 g (10 mmoles) of dihexadecyliodoarsine. Triethylamine was added to pH 8, and the mixture was refluxed for two and a half hours. It was then filtered and the solvent was removed. A yellow powder was obtained that showed two spots on TLC, corresponding to the product and probably, the arsinic acid (the melting point of the fraction, corresponded to that of the acid, 122°). However, separation from the product was very difficult. A good degree of separation on TLC was achieved using the method outlined by Freeman and West for lipids and similar compounds. A TLC plate 15 × 8 cm (silica gel 1-B Baker flex) was spotted with a chloroform solution of the mixture. The plate was developed first in a chamber of: ethanol, hexane, diethyl ether 2:50:40 up to 11 cm. It was removed and allowed to dry in air and then put in a second chamber with diethyl ether-hexane 6:94 as eluent and developed up to 1 cm from the top. In this manner better, but still incomplete separation of the two compounds was achieved on a small scale, for purposes of characterization. It was found later that recrystallizations of the crude with mixtures of ether/hexane in which the amount of hexane is increased every time until only hexane is used, gave a good separation of the As(V) compound as a precipitate while the product remains in solution. After removal of the solvent, a white powder is obtained, that melts at 61°, yield 50–60%, impure material. ^1H NMR (100 MHz, $CDCl_3$, TMS): δ 5.75 (1 proton doublet, H-1), 5.15 (2 proton multiplet, H-3, 5), 4.35–3.75 (2 proton multiplet H-2, 4), 2.80 (2 proton multiplet H-6), 2.10, 2.08, 2.06, 2.02 (12 proton singlets, CH_3 acetate), 1.75 (6 proton multiplet, As—CH_2—), 2.30 (8 proton multiplet —CH_2—), 1.5, 1.35, 1.0 (64 proton multiplet, —CH_2), 0.90 (8 proton triplet, —CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 168.4, 166.5, 166.1 (C=O), 88.7 (C-1), 71.6 (C-2), 72.1 (C-3), 69.7 (C-4), 72.2 (C-5), 65.0 (C-6), 19.0 (—CH_3 acetate), 23.0 (—As—CH_2), 38.8, 29.2, 27.7 (—CH_2), 17.8 (CH_3).

1,2,3,4 - Tetra - O - acetyl - 6 - S - Didodecylarsino - 6 - thio - β - D - glucopyranose 1,2,3,4 - Tetra - O - acetyl - 6 - thio - β - D - glucopyranose 4 g, (0.01 moles) in toluene solution (150 ml) was treated with 5.5 g (0.01 moles) of didodecyliodoarsine. Diethylamine was added to pH 8. The mixture was refluxed for one hour. After cooling it was extracted once with water and then filtered through Celite. The solvent was removed and a white powder formed that melted at 55°. After purification by filtration through Celite of an hexane solution of the crude mixture, followed by removal of the solvent under reduced pressure, a white powder was recovered that melted at 62°, yield 60%. ^1H NMR (100 MHz, $CDCl_3$, TMS): δ 5.75 (1 proton doublet, H-1), 5.15 (2 proton multiplet, H-3, 5), 4.20–3.80 (2 proton doublet, H-2.4), 2.85 (2 proton multiplet, H-6), 2.15, 2.1, 2.08, 2.03 (12 proton, singlets, CH_3 acetate), 1.70 (4 proton multiplet, —As—CH_2—), 1.57 (25 proton multiplet, —CH_2—), 1.27 (42 proton multiplet, —CH_2—), 0.88 (10 proton triplet, —CH_3). *Anal:* Calculated for $C_{38}H_{69}O_9SAs$. (Found): %C 58.67 (59.43); %H 8.89 (9.72); %S 4.12 (4.33).

1,2,3,4 - Tetra - O - acetyl - 6 - S - di - n - octylarsino - 6 - thio - β - D - glucopyranose A toluene solution (170 ml) of 1,2,3,4-tetra - O - acetyl - 6 - thio - β - D - glucopyranose (7 g, ~20 mmoles) was treated with ~7 g, (20 mmoles) of di-*n*-octyliodoarsine. Diethylamine was added until the pH remained at ~8. The mixture was refluxed for one hour, and allowed to cool. It was then rinsed once with water. The solvent was removed and a brown syrup was recovered. After purification by treating with activated charcoal and filtering through Celite, a yellowish powder was obtained that melts at 75°, yield 65%. ^1H NMR (100 MHz, $CDCl_3$, TMS): δ 5.71 (1 proton multiplet, H-1), 5.10 (2 proton multiplet, H-3, 5), 4.35–3.86 (2 proton multiplet H-2, 4), 2.95 (2 proton multiplet H-6), 2.10, 2.05, 2.01, 2.00 (12 proton singlets, CH_3 acetate), 1.75 (4 proton multiplet, As—CH_2—), 1.63 (14 proton multiplet —CH_2—), 1.27 (10 proton multiplet —CH_2—), 0.88 (8 proton triplet —CH_3). *Anal:* Calculated for $C_{30}H_{53}O_9SAs$. (Found): %C 54.30 (55.14); %H 8.34 (8.89).

1,2,3,4 - Tetra - O - acetyl - 6 - S - dicyclohexylarsino - 6 - thio - β - D - glucopyranose. A toluene solution (350 ml) of 1,2,3,4-tetra - O - acetyl - 6 - thio - β - D - glucopyranose, 3.7 g (10 mmoles) was treated with 2 ml, (10 mmoles) of dicyclohexyliodoarsine. Diethylamine was added dropwise until the pH remained constant at 7-8. The reaction mixture was refluxed for 1 hour, and allowed to cool. Then, the mixture was filtered and the solvent was removed under diminished pressure. The resulting syrup was redissolved in warm chloroform, treated with activated charcoal and filtered through Celite. The solvent was again removed and the product, in the form of flaky pale yellow crystals, was recovered. The melting point was 51°. The yield was 87%. ^1H NMR (60 MHz, $CDCl_3$, TMS): 5.80 (1 proton doublet H-1), 5.25 (2 proton multiplet, H-3, 5), 4.30–3.80 (2 proton multiplet, H-2, 4), 3.0 (2 proton multiplet, H-6), 2.1, 2.09, 2.06, 2.0 (12 proton, singlets, —CH_3 acetate), 1.55 (22 proton

broad multiplet, —CH_2—). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 169.9, 169.4, 169.0, 168.7 (C=O), 91.4 (C-1), 72.8 (C-2), 75.0 (C-3), 70.6 (C-4), 75.7 (C-5), 69.7 (C-6), 20.5 (—CH_3 acetate), 36.9 (As—CH_2), 30.1, 27.5, 26.7 (—CH_2—). *Anal:* Calculated for $C_{26}H_{41}O_9SAs$. (Found): %C 51.65 (52.05); %H 6.78 (6.87).

1,2,3,4 - Tetra - O - acetyl - 6 - S - di - n - butylarsino - 6 - thio - β - D - glucopyranose 1,2,3,4 - Tetra - O - acetyl - 6 - thio - β - D - glucopyranose (~4 g, 0.01 moles) was dissolved in 300 ml of toluene. Dibutyliodoarsine (3.2 ml, ~0.1 moles) was added. Pyridine was added to maintain the pH of the solution at 7. The solution was refluxed for one hour, and then filtered. The solvent was removed under reduced pressure.

A yellow syrup was recovered, redissolved in chloroform and purified by chromatography on silica and Celite. Yellow, hygroscopic crystals were obtained that melted at 44.5°, yield 90%. ^1H NMR (60 MHz, $CDCl_3$, TMS): δ 5.7 (1 proton doublet, H-1), 5.1 (2 proton multiplet, H-3, 5), 4.4–3.7 (2 proton multiplet, H-2, 4), 2.7 (2 proton multiplet, H-6), 2.1, 2.09, 2.08, 2.05 (12 proton, singlets, —CH_3 acetate), 1.6 (4 proton multiplet, As—CH_2—), 1.9 (8 proton multiplet, —CH_2—), 0.90 (6 proton triplet, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 167.1, 166.3, 166.0, 165.7 (C=O), 94.0 (C-1), 71.3 (C-2), 73.3 (C-3), 70.4 (C-4), 73.2 (C-5), 68.3 (C-6), 18.4 (—CH_3 acetate), 22.1 (As—CH_2—), 27.6, 26.2, (CH_2), 11.7 (CH_3). *Anal*: Calculated for $C_{22}H_{37}SAs$. (Found): %C 47.81 (47.88); %H 6.75 (6.89).

1,2,3,4 - Tetra - O - acetyl - 6 - S - dipropylarsino - 6 - thio - β - D - glucopyranose Diethylaminodipropylarsine was prepared by addition of diethylamine (1 ml, 0.01 moles) to dipropyliodoarsine (3 ml, ~0.01 moles) dissolved in diethyl ether, (50 ml). The reaction flask was kept under nitrogen and the solution was immediately treated with 3.7 g (0.01 moles) of 1,2,3,4, - tetra - O - acetyl - 6 - thio - β - D - glucopyranose dissolved in 250 ml of diethyl ether. After refluxing for one and a half hours, the mixture was filtered through Celite and the solvent was subsequently removed. The product was obtained in the form of a syrup that crystallizes when subjected to reduced pressure, but reverted to a syrup upon exposure to the atmosphere. The yield was 70%. ^1H NMR (60 MHz, $CDCl_3$, TMS): δ 5.9 (1 proton doublet, H-1), 5.3 (2 proton multiplet, H-3, 5), 4.4–3.9 (2 proton multiplet, H-2, 4), 3.0 (2 proton multiplet, H-6), 2.1, 2.08, 2.06, 2.0 (12 proton singlets, —CH_3 acetates), 1.6 (4 proton multiplet, As—CH_2—), 1.8 (4 proton multiplet, —CH_2—), 1.2 (6 proton triplet, —CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.8, 169.1, 169.0, 168.5 (C=O), 91.6 (C-1), 72.8 (C-2), 75.5 (C-3), 72.4 (C-4), 75.5 (C-5), 70.5 (C-6), 20.7 (—CH_3 acetate), 23.6 (As—CH_2—), 32.5 (—CH_2—), 15.8 (CH_3). *Anal*: Calculated for $C_{20}H_{33}O_9SAs$. (Found): %C 54.79 (45.77); %H 6.35 (6.41).

1,2,3,4 - Tetra - O - acetyl - 6 - S - diethylarsino - 6 - thio - β - D - glucopyranose The diethylaminodiethylarsine was prepared by adding 1 ml (0.01 moles) of diethylamine to 2.8 ml (0.01 moles) of diethyliodoarsine dissolved in 50 ml of diethyl ether. The system was kept under nitrogen. A diethyl ether solution of 3.7 g, (0.01 moles) of 1,2,3,4 - tetra - O - acetyl - 6 - thio - β - D - glucopyranose was added. The mixture was refluxed for 1½ hr., filtered through Celite and the solvent was removed. Hygroscopic crystals were obtained that formed a syrup at room temperature. The yield was 85%. ^1H NMR (60 MHz, $CDCl_3$, TMS): δ 5.9 (1 proton doublet, H-1), 5.2 (2 proton multiplet, H-3, 5), 4.4–3.8 (2 proton multiplet, H-2, 4), 3.0 (2 proton multiplet H-6), 2.2, 2.18, 2.12, 2.0 (12 proton, singlets, CH_3—acetates), 1.7 (4 proton quartet, As—CH_2—), 1.3 (6 proton triplet, —CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.9, 169.5, 169.2, 168.9 (C=O), 91.8 (C-1), 72.9 (C-2), 74.9 (C-3), 70.5 (C-4), 74.9 (C-5), 70.3 (C-6), 20.7 (CH_3 acetate), 21.8 (As—CH_2—), 11.9 (—CH_3). *Anal:* Calculated for $C_{18}H_{29}O_9SAs$. (Found): %C 43.55 (43.62); %H 5.88 (5.94).

1,2,3,4 - Tetra - O - acetyl - 6 - S - methyl - n - propylarsino - 6 - thio - β - D - glucopyranose A solution made up of 3.8 g, (0.01 moles) of 1,2,3,4 - tetra - O - acetyl - 1 - thio - β - D - glucopyranose in 350 ml of toluene was treated with 2.8 ml (0.01 moles) of methyl-*n*-propyliodoarsine. Triethylamine was added until a constant pH of 7 was obtained. The mixture was refluxed for one hour and then filtered through Celite. The solvent was removed and light yellow hygroscopic crystals were deposited. They were dissolved in methylene chloride and filtered through Celite several times. After removal of the solvent, pale yellow crystals were obtained that melt at 50°. The yield was 95%. ^1H NMR (60 MHz, $CDCl_3$, TMS): δ 5.8 (1 proton doublet, H-1), 5.2 (2 proton multiplet, H-3, 5), 4.2–3.7 (2 proton multiplet, H-2, 4), 3.2 (2 proton multiplet, H-6), 2.1, 2.08, 2.04, 2.0 (12 proton, singlets, —CH_3 acetate), 2.4 (2 proton multiplet, As—CH_2—), 2.6 (2 proton multiplet, —CH_2—), 1.4 (3 proton triplet. CH_3), 0.90 (3 proton singlet, As—CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.0, 169.5, 169.1, 168.8 (C=O), 91.7 (C-1), 72.8 (C-2), 73.0 (C-3), 70.4 (C-4), 73.0 (C-5), 69.6 (C-6), 20.5 (—CH_3 acetate), 20.8 (As—CH_2—), 31.5 (—CH_2—), 15.3 (CH_3). *Anal:* Calculated for $C_{18}H_{29}O_9SAs$. (Found): %C 43.55 (43.64); %H 5.88 (5.95).

1,2,3,4 - Tetra - O - acetyl - 6 - S - 2 - hydroxyethylmethylarsino - 6 - thio - β - D - glucopyranose To a solution containing 5.5 g, (0.015 moles) of 1,2,3,4 - tetra - O - acetyl - 6 - thio - β - D - glucopyranose in 200 ml of toluene was added 4.5 ml, (0.015 moles) of 2 - hydroxymethylmethyliodoarsine. The arsine dissolved only upon heating. The pH was adjusted to 7 by the addition of triethylamine. The mixture was refluxed for one hour and the solution was filtered. When it was cooled, a yellow syrup formed which crystallized when subjected to reduced pressure. Purification of the product by treatment with activated charcoal, and column chromatography (silica, $CHCl_3$/EtOH 1 : 1) afforded a pure material in the form of yellow hygroscopic crystals that melted at 51°, with a yield of 87%. ^1H NMR (60 MHz, $CDCl_3$, TMS): δ 5.8 (1 proton doublet, H-1), 5.2 (2 proton multiplet, H-3, 5), 4.3–3.8 (2 proton multiplet, H-2, 4), 3.0 (2 proton multiplet, H-6), 2.1, 2.08, 2.04, 2.0 (12 proton, singlets, CH_3 acetate), 1.7 (2 proton triplet, As—CH_2—), 2.5 (2 proton multiplet, —CH_2—), 4.8 (2 proton singlet, CH_2—OH), 1.2 (3 proton singlet, —CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.0, 169.5, 169.1, 168.8 (C=O), 91.8 (C-1), 73.1 (C-2), 75.0 (C-3), 70.9 (C-4), 75.0 (C-5), 70.5 (C-6), 20.5 (—CH_3 acetate), 25.8 (As—CH_2—), 41.6 (—CH_2—OH), 14.3 (—CH_3). *Anal*: Calculated for $C_{17}H_{27}O_{10}SAs$. (Found); %C 40.97 (40.96); %H 5.46 (5.48).

ACKNOWLEDGEMENTS

We wish to acknowledge the financial support of the Robert A. Welch Foundation, Houston, Texas and the National Institutes of Health, Grant No. CA 16912. Also, Maria V. Rosenthal wishes to thank the CONACyT, (Mexico) for a scholarship.

REFERENCES

1. R. A. Zingaro and J. K. Thompson, *Carbohyd. Res.*, **24**, 147 (1973).
2. G. C. Chen, J. R. Daniel, and R. A. Zingaro, *Carbohyd. Res.*, **50**, 53 (1976).
3. J. R. Daniel and R. A. Zingaro, *Carbohyd. Res.*, **64**, 69 (1978).
4. G. C. Chen, R. A. Zingaro, and C. R. Thompson, *Carbohyd. Res.*, **39**, 61 (1975).
5. C. H. Banks, J. R. Daniel, and R. A. Zingaro, *J. Med. Chem.*, **22**, 572 (1979).
6. E. Schauenstein, *Phosphorus and Sulfur*, **2**, 198 (1976).
7. S. Hanessian and J. Banoub, *Synthetic Methods for Carbohydrates* (H. S. El Khadem, Ed., American Chemical Society, 1977) Chap. **6**, p. 36.
8. A. Mazur and B. Harrow, *Textbook of Biochemistry*, (W. B. Saunders Co., 1971) Chap. 7, 8, pp. 229, 263.
9. R. L. Whistler, A. A. Bushway, P. P. Singh, W. Nakahara, and R. Tokuzen, *Adv. Carbohyd. Chem. Biochem.*, **32**, 235 (1976).
10. D. Horton, *Methods in Carbohydrate Chemistry*, Vol. **2** (M. L. Wolfrom and R. L. Whistler, Eds., Academic Press, N.Y., 1963) p. 433.
11. G. Kotowycz and R. U. Lemieux, *Chem. Rev.*, **73**, 669 (1973).
12. S. J. Angyal, *Angew. Chem. Int. Ed.*, **8**, 157 (1969).
13. R. U. Lemieux, R. K. Kulling, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **79**, 1005 (1957).
14. S. N. Rosenthal and J. H. Fendler, *Adv, Phys. Org. Chem.*, 280 (1976).
15. J. Lonngreen and S. Svennson, *Adv. Carbohyd. Chem. Biochem*, **29**, 41 (1974).
16. G. R. Newcome, J. D. Sauer, V. K. Majestic, and N. S. Bhacca, *Carbohyd. Res.*, **48**, 1 (1976).
17. N. K. Kochetkov and O. T. Chizov, *Adv. Carbohyd. Chem.*, **21**, 39 (1966).
18. A. M. Hogg and T. L. Naggavitushan, *Tetrahedron Lett.*, **47**, 4827 (1972).
19. O. S. Chizov, V. A. Kadenstev, B. M. Zolotarev, A. B. Foster, M. Jarman, and J. H. Westwood, *Org. Mass Spectrom.*, **5**, 437 (1971).
20. O. S. Chizov, A. B. Foster, M. Jarman, and J. H. Westwood, *Carbohyd. Res.*, **22**, 37 (1972).
21. R. A. Zingaro, *Chem. Scripta*, **8A**, 51 (1975).
22. J. R. Daniel and R. A. Zingaro, *Phosphorus and Sulfur*, **4**, 179 (1978).
23. K. J. Irgolic, R. A. Zingaro, and M. R. Smith, *J. Organometall. Chem.*, **6**, 17 (1966).
24. K. J. Irgolic, R. A. Zingaro, and L. J. Edmonson, *Phosphorus*, **5**, 183 (1975).
25. Dimethyl, diethyl, dipropyl and dibutyliodoarsines were prepared by C. R. Mitchell. Dicyclohexyliodoarsine was supplied by K. C. Ehrhardt.
26. C. P. Freeman and D. West, *J. Lipid Research*, **7**, 324 (1966).