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A NOVEL STUDIES OF SYNTHESIS OF NANOPARTICAL OF SOME LACTOSYLATED DITHIOBIURETS AND THEIR XRD STUDIES

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Abstract: A huge number of research papers have appeared over the last decades on the application of microwave technology in organic synthesis. The chemistry of thiourea of carbohydrate is extensively elaborated and well documented. The use of microwave irradiation in organic synthesis has become increasingly popular within the pharmaceutical and academic arenas, because it is a new enabling technology for drug discovery and development. By taking advantage of this efficient source of energy, These compounds arouse interest as potential biologically active substances and versatile intermediates for preparing various derivatives. They have been found useful in the treatment of hypertension, as appetite suppersant and as a potential anti-oxidant cardio protective agent. Chemistry of sugar isothiocyanate with special reference to their utility as intermediate in the synthesis of nitrogen and sulphur containing open chain and cyclic compound. Several lactosyl dithiobiurets deravaives has been prepare by condensation of hepta-O-acetyl-B-D-lactosyl isothiocyanate with various aryl thiocarbamides by microwave method. The identities of newly synthesis compounds have been established on the basis of usual chemical transformation and IR, NMR, Mass spectral studies.

Keywords: Hepta-O-acetyl-B-D-lactosyl is thiocyanate, Aryl thiocarbamides, lactosyl dithiobiurtes.

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INTRODUCTION

Microwave technology has been applied beneficially into a number of organic reactions. The microwave assisted hydrolysis of esters is well-known but the regioselective hydrolysis of esters at the anomeric position in sugars under this condition has not been described.

Microwave assisted organic synthesis has become an important tool to medicinal chemists for rapid organic synthesis. A huge number of research papers have appeared over the last decades on the application of microwave technology in organic synthesis.[1] Some of the major advantages include spectacular decrease in reaction time, improved conversions, clean product formation and wide scope for the development of new reaction conditions.

The use of polymer-supported reagents and scavengers is a powerful technique for expedited synthesis and purification.[2] Rapid transformations using microwave technology has shifted the bottleneck from synthesis to the work-up and purification step. Therefore, chemists are increasingly looking for an expedited synthesis and purification strategy that would combine the use of microwave heating with polymer-assisted solution-phase organic synthesis. This overview [3] covers the recent literature on the significant new applications of polymer-supported reagents and scavengers using microwave heating.

Carbohydrates derivatives have been extensively investigated including synthesis, characterization and biological activity. Partly due to the facts that many natural occurring saccharides and synthesized analogues exhibit various and potent biological activities and they have been widely employed as agrochemicals and pharmaceuticals[4-7].

Carbohydrates exist in a large elemental as well as stereochemical variety, as they are built up from monosaccharides of various kinds, forming diverse branched or linear oligomers as well as different class of poly-saccharides. Carbohydrates possess large numbers of functionalities, at least one carbonyl and several hydroxyl functions per monosaccharides and often carry further kinds of functional groups. They are compounds with several steriocenter and thus the carbohydrate group consists of a large numbers of sterioisomers. Synthetic carbohydrate chemistry, as a result of the structural complexity of carbohydrates is a challenging field for organic chemist. The initial carbohydrate chemistry deals with the structure of carbohydrate and solved basic question of the stereochemistry problem connected with it. This was mainly due to Emil Fischer, who solved all these basic questions, by the end of nineteenth century. Later in the 1960's all main aspects of the roles play by carbohydrates in the storage and supply of energy in biochemical system were understand and the mechanism of biosynthesis and biodegradation of carbohydrates were clarified. The art of chemical transformations of monosccharides synthesis was further developed, motivated by the isolation of biological active compounds from micro-organism, such as antibiotics.

Because of tremendous biological importance, carbohydrates have aroused much interest to synthetic and medicinal chemistry[8-9].

The N-lactosylated compounds have been known for their great biological importance. They have been found several applications in paper[10], textile[11,12] and food industries[13]. Besides these applications they have been found use as divertic agents, analgesics, antidiabetic compounds, bacteriosatic agents and in many other

ways[14]. Some of them have been found to be valuable oxidation dyes[15] for printing and padding the animals and vegetable fibers by standard oxidation dyeing methods. Quite few of them have antitumor and tuberculostatic activity[16].

RESULTS AND DISSCUSSION:

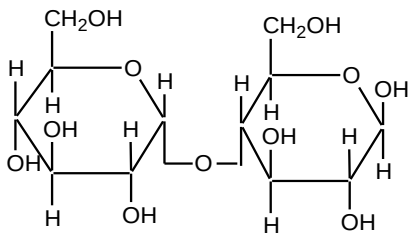
NANOPARTICLES:

A sub-classification of ultrafine particle with lengths in two or three dimensions greater than 0.001 micrometer (1 nanometer) and smaller than about 0.1 micrometer (100 nanometers) and which may or may not exhibit a size-related intensive property.

This term is a subject of controversy regarding the size range and the presence of a size-related property. Current usage emphasizes size and not properties in the definition. The length scale may be a hydrodynamic diameter or a geometric length appropriate to the intended use of the nanoparticle.

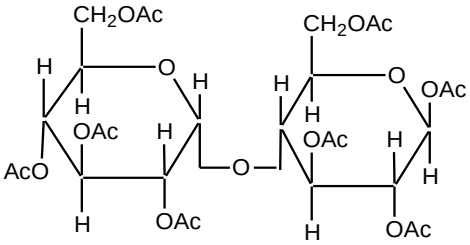
The chemistry of thiourea of carbohydrate is extensively elaborated and well documented. These compounds arouse interest as potential biologically active substances and versatile intermediates for preparing various derivatives

Reaction



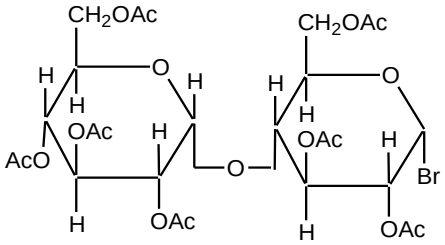
Lactose

Acetaylation



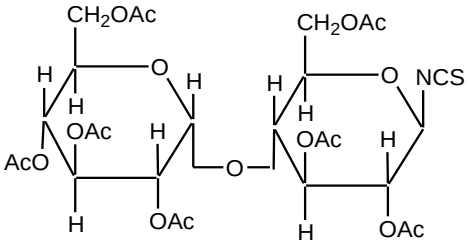
hepta-*O*-acetyl-β-d-lactosyl acetate

Bromination

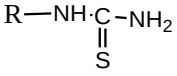


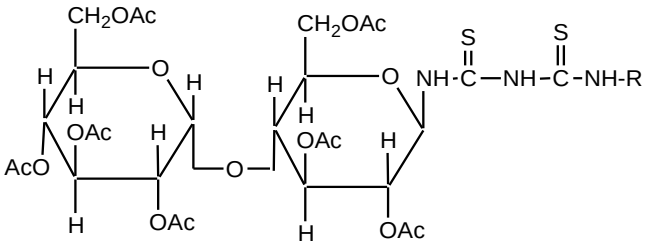
hepta-*O*-acetyl-β-d-lactosyl bromide

Pb-NCS



hepta-*O*-acetyl-β-d-lactosyl isothiocynate





hepta-*O*-acetyl-β-d-lactosyl-5-Aryl 2,4 dithiobiurets

R= a) *p*-toludine b) *p*-chloro-aniline c) *p*-amino benzoic acid

Several Lactosyl dithiobiurets deravaives has been prepare by condensation of Hepta-O-acetyl-B-D-lactosyl isothiocyanate with various aryl thiocarbamides by microwave method. Toluene solution of Hepta-O-

acetyl- β -D-lactosyl isothiocyanate (0.005 M, 1 g) was added to 4amino -1-phenyl thiocarbamide (0.21 gm in 20 ml) and the reaction mixture was under microwave irradiation It was then allowed to cool and pour it in petroleum ether with vigorous stirring; a white granular solid was separated out. The characterization of products was established by IR, ^{1}HNMR, MS XRD Spectral studies.

EXPERIMENTAL

Melting points were recorded on electro thermal melting point apparatus are uncorrected. Specificrotations were measured on Equip-Tronic digital polarimeter model no. EQ 800 at 30^{0}C in $CHCl_3$. IRspectra were recorded on a Perkin Elmer spectrometer. ^{1}H NMR were obtained on a Bruker DRX-300(300 MHz FT NMR) NMR spectrometer in $CDCl_3$ solution with TMS as an internal reference. The massspectra were recorded on a DART mass spectrometerwere recorded. Purity of the compounds was checkedby thin layer chromatography using Merck silica gel coated aluminum plates and petroleum ether: ethylacetate as eluent.

Synthesis of 1-hepta-O-acetyl-β-D-lactosyl-5-*p*-toludine-4-dithiobiuret

Benzene solution of Hepta-O-acetyl- β -D-lactosyl isothiocyanate (0.005 M, 1.9 g) was added to *p*-toludine (0.25g in 20 ml) and the reaction mixture was under microwave irradiation. It was then allowed to cool and pour it in water with vigorous stirring; a white granular solid was separated out, crystallized from aqueous ethnaol, m.p. 122°C. [Found C, 50.56; H, 5.54; N, 2.39; S, 6.80 $C_{21}H_{26}O_{10}N_3S_2$; requires; C, 50.30; H, 5.09; N, 2.80; S, 6.40%]

It was found soluble in alcohols acetone, chloroform and benzene while insoluble in water and petroleum ether. It charred when warmed with conc. sulphuric acid. The specific rotation was found to be $[\alpha]_D^{35}$ = -136° (c, 0.74 in chloroform). The purity was checked by TLC, and recorded Rf value 0.62 (CCl_4: EtOAc 3:2.1)

ANALYTICAL AND SPECTRAL DATA OF COMPOUNDS:

1) Synthesis of 1-hepta-O-acetyl-β-D-lactosyl-5-*p*-aminobenzoicacid-4-dithiobiuret

Yield 72 (%); Mp.122^{0}C;[□]$_D^{32}$242.42°(0.1, in $CHCl_3$);R*f* (Hexane:EtOAC)(1:1)0.59; **IR (KBr)cm- 1**:ν 3000-3292 (Ar-H)str ,1755 (C=O)str, 1543(C=N) str, , 1425 (C-N)str, 927(char. of glucopyranosyl ring), 758 (C=S) str.. **^{1}HNMR (CDCl3)ppm:** 7.46-6.32 (m,8H, Ar-H), 5.57-5.59 (m, 14H, lactosyl-H), 2.31-2.01 (m, 12H,OAc),. **MS**(m/z) : 535 (M+),511, 408, 331, 263, 261, 169, 108.(Anal.Calcd. For Found C, 50.56; H, 6.09; N, 2.39; S, 6.80 $C_{21}H_{24}O_{12}N_3S_2$; requires; C, 50.40; H, 5.20; N, 2.80; S, 6.40%]).

2) Synthesis of 1-hepta-O-acetyl-β-D-lactosyl-5-p-toludine -4-dithiobiuret

Yield72.8(%); Mp.95^{0}C;[□]$_D^{32}$+133 (0.1, in $CHCl_3$);R*f* (Hexane:EtOAC)(1:1)0.80;**IR**

(KBr)cm- 1:ν 3000-3292 (Ar-H)str ,1755 (C=O)str, 1543(C=N) str, , 1425 (C-N)str,

927(char. of glucopyranosyl ring), 758 (C=S) str. **^{1}HNMR (CDCl3)ppm:** 7.46-6.32

(m,8H, Ar-H), 5.57-3.87 (m, 7H, glucosyl-H), 2.31-2.01 (m, 12H,OAc),. **MS**(m/z) : 558

(M+),521, 408, 331, 263, 261, 169, 108.(Anal.Calcd. For Found C, 50.56; H, 5.54; N,

2.39; S, 6.80 $C_{21}H_{26}O_{10}N_3S_2$; requires; C, 50.30; H, 5.09; N, 2.80; S, 6.40%).

3) Synthesis of 1-hepta-O-acetyl-β-D-lactosyl-5-*p*-Cl-aniline-dithiobiurtes

Yield 80 (%); Mp.145-150^{0}C;[⍰]$_D^{32}$155.19(0.1, in $CHCl_3$);R*f* (Hexane:EtOAC)(1:1)0.87 **IR (KBr)cm- 1**:ν 3000-3292 (Ar-H)str ,1755 (C=O)str, 1543(C=N) str, , 1425 (C-N)str, 927(char. of glucopyranosyl ring), 758 (C=S) str.. **^{1}HNMR (CDCl3)ppm:** 7.46-6.32 (m,8H, Ar-H), 5.57-5.59 (m, 14H, lactosyl-H), 2.31-2.01 (m, 12H,OAc),.. **MS**(m/z) : 577 (M+),521, 408, 331, 263, 261, 169, 108.(Anal.Calcd. For Found C, 51.56; H, 5.89; N, 2.64; S; 6.78, $C_{20}H_{23}O_{10}N_3S_2Cl$; requires; C, 52.17; H, 5.17; N, 2.89'; S, 6.62%%).

Preparation of Nanoparticles of hepta-O-acetyl-β-D-lactosyl-4-amino benzoic acid-4-dithiobiurets:

Take about 1 gm of hepta-O-acetyl-β-D-lactosyl-4-amino benzoic acid-4-dithiobiurets and dissolve it completely in the 50ml of solvent in 250 ml beaker. Now put this beaker in sonicator. The highly penetrating acoustic waves are passed through mixture, which create high pressure bubbles in the beaker due to which breakdown of the bulk material is takes place and desired sized nanoparticles are formed. The size determination of nanoparticlesis done by the X-ray diffraction studies

Characterization of Nanoparticles:

1. Characterization using UV-Spectrophotometer: Single Beam UV-Spectrophotometer with software BI/CI/SP/SB-S-03 of Bio Era make. The UV-Visible Spectroscopy reveals the formation of Nanoparticles Characterization of Nanoparticles was done using visible Spectrophotometer by using model by showing different absorption those from bulk material.

2. Size determination of hepta-O-acetyl-β-D-lactosyl-4-amino benzoic acid-4-dithiobiurets. Nanoparticles by X-ray Diffraction studies: From the X-ray diffraction it comes to know that size of nano **hepta-O-acetyl-β-D-lactosyl-4-amino benzoic acid-4-dithiobiurets** is 42.29 nm.

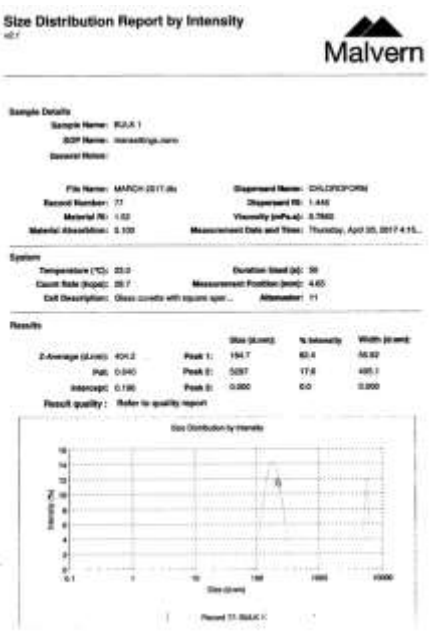


Table No.3:- Characterization data of synthesis of 1-hepta-O-acetyl-β-D-lactosyl-5-aryl-4-dithiobiurets

Sr. No.	Aryl dithiobiurets	1-hepta-O-acetyl-β-D-lactosyl-5-aryl-4-dithiobiurets	M.P. (^{0}C)	% yield	Optical Rotation $[\alpha]_D^{32}$	R_f value
1	4-toludine	1-hepta-O-acetyl-β-D-lactosyl-5-p-toludine-4-dithiobiurtes	95	72.80	$[\alpha]_D^{32}$ = +133.94° (c, 0.373 in chloroform).	0.80
2	4-Cl-aniline	1-hepta-O-acetyl-β-D-lactosyl-5-p-chloro-aniline-4-dithiobiuret	145 – 150	80.50	$[\alpha]_D^{32}$ = + 155.19° (c, 0.386 in chloroform).	0.87
3	4-amino benzoic acid	1-hepta-O-acetyl-β-D-lactosyl-5-p-amino benzoic acid-4-dithiobiuret	122	71.60	$[\alpha]_D^{32}$ = + 242.42° (c, 0.333 in chloroform).	0.59

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