Synthesis and Characterization of Some New Glycosides Derived from The Sugar D-ribose of Expected Biological Activity

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ABSTRACT
This work describes the synthesis of new ribofuranosyl derivatives containing 1,2,3-triazoline or triazole rings derived from unsaturated D-ribose via 1,3 dipolar cycloaddition reactions. The strategy includes the conversion of D-ribose into allylic glycosides by treatment with unsaturated alcohol namely allyl alcohol. The conditions of the reaction are kinetically controlled to insure the formation of allylic furanosides and thermodynamically controlled to get pyranosides. Bothe type of glycosides were reacted with sodium azide in a 1,3 cycloaddition type of reactions to get the derivatives triazolinyl D-ribose. An attempt was carried out to oxidize the double bond of the glycosides with the objective of making both the dihydroxy and the carboxylic corresponding compounds. All products were identified by spectroscopic methods such as FT-IR and MNR spectroscopy. The purity of the products was examined by C.H.N analysis as well as t.l.c chromatography.

Keywords: D-ribose, Ribofuranosyl, triazoline, Derived, cycloaddition, allylic.
1. Introduction

D-Ribose plays an important role in metabolic processes. In addition, D-Ribose-5-phosphate is present in ribonucleotides and polyribonucleotides (RNA), whilst 2-deoxyribose is part of polydeoxyribonucleotides (DNA) H. P. Ramesh and N. Tanneerathan. (Wamhoff and Warnecke, 2001). D-Ribose is often marketed as a supplement for bodybuilders with a common recommended daily dose being 5 g. Some studies have found no evidence that there is a benefit, while others have found increased endurance, recovery and muscle output in healthy individuals. D-Ribose has also been used to reduce fatigue in fibromyalgia (FM) and chronic fatigue syndrome (CFS). D-Ribose has been found to be effective in the management of symptoms from myoadenylate deaminase deficiency, a metabolic disorder affecting the skeletal muscles. Ribose is used as a natural anti-anxiety and stress relief ingredient. It is also used to control stress-related eating and drinking that has the added value of being non-sedating with potential anti-depressant properties (Merck, 2010; Weast, 1981). Since the discovery of the Human Immunodeficiency Virus (HIV) as the etiologic agent of AIDS, intense efforts have been devoted to the synthesis and biological evaluation of compounds with potential anti-HIV activity (Hussain A et al, 2007). Most of the known triazole compounds possess low solubility in water, therefore the new researches include preparation of new glycosides derivatives containing 1,2,4-triazole and 1,2,3-triazole. (S.A. Nepogodiev, 2007; H. Wamhoff and H. Warnecke, 2001), these derivatives have high solubility in water and possessing possible biological activity. Triazoles have not been isolated in any naturally occurring compounds, however the triazol and triazolines moiety has been utilized in many applications ranging from industrial to pharmaceutical uses. The applications of triazol and triazolines are widespread, making -triazole derivatives a highly studied class of molecules. Triazo and triazolines belong to a class of compounds called azoles. (Nicotra F. et al, 2008). An azole contains a five-membered aromatic ring with at least one nitrogen atom and another heteroatom such as a nitrogen, sulfur, or oxygen. 1,2,3-Triazole links have emerged as a popular bridging units in carbohydrate chemistry because of the facile efficient method of their introduction, which referred to as "click chemistry" (Abu-Orabi S.T., 2002) "Review. The anomic atom of O-glycosides is susceptible to both acidic and enzymatic cleavage, whereas C-glycosides are resistant to hydrolysis, (Puol J. 2006). Synthesis of glycosides involving regio and stereo selectivity is an important and difficult area in synthetic organic chemistry, which is of prime concern to researchers working in this area. Glycosides are used as surfactants (Busch et al. 1994), colorants and flavoring agents (Sakata et al. 1998), sweeteners, antioxidants, anti-inflammatory (Wagner D, et al. 2002), antibiotics (Ishii H, 1980), antimicrobial and antifungal (Gupta R, et al. 1997). Alkyl and phenolic glycosides are even useful as detergents, cosmetics and food additives.

2. Experimental

2.1. Materials and methods

All solvents and chemicals were purified before used and were kept in special bottles containing, KOH, and CaCl2 for dryness. Evaporation was conducted under vacuum using Rotary Evaporator. FT-IR spectra were recorded in the (400 – 4000) cm⁻¹ frequency range by using FT-IR Spectrophotometer, Ministry of health, Sana’a, Yemen. NMR spectra (H1 were recorded on a Varian spectrometer at ambient temperature in an appropriate due treated solvent.
using trimethyl silane as the internal standard at ambient temperature located in King Abdul Aziz University, Jeddah, Saudi Arabia. The reactions were monitored by T.L.C made or aluminum plates covered with 0.2 mm of silica–gel F254 made by Mereck Company. Detection were achieved by iodine vapor and by spraying with conc. H2SO4 in EtOH followed by heating in an oven. C.H.N Elemental analysis was carried out sing an Elemental varrio EL analyzer. Column chromatography was performed with silica gel G60 using solvent system employed for TLC analyses which was ethyl acetate, ethyl methyl ketone, benzene and methanol.

2.2. Synthesis of Compounds

2.2.1. Synthesis of allyl – O – D – Ribofuranosides

D-Ribose (1.8g) was dissolved in a 0.5% hydrogen chloride in allyl alcohol which was prepared by adding acetyl chloride (0.25 ml) to allyl alcohol (26.5 ml) and leaving the mixture for about two hours. The reaction mixture was placed in 250 ml round bottomed flask and was stirred magnetically for three hours. The course of the reaction was monitored by T.L.C. using benzene – methanol (2:8 v/v). After all the sugar spot was disappeared, the reaction was stopped by neutralization with sodium hydroxide solution in allyl alcohol. The solvent was removed under reduced pressure and the syrupy product was purified on a silica -gel column chromatography using (ethyl methyl ketone: ethyl acetate) (1:1 v/v) as the solvent to give (1.3g, Browne color 83% Yield, R.F 0.7). FT-IR (KBr): cm-1 = 778, 657 (ring), 1085 (C – O – C), 1596 (C=C), 2930 (–CH2), 3400 (–OH). 1H. NMR data (D-DMSO) : δ (ppm) = 2.50 – 2.51 (3H,OH – sugar), 3.1 – 3.94 (4H, sugar), 3.95 – 4.0 (2H, O – CH2), 4.960 – 4.966 (2H, CH2=), 5.9 (1H, anomeric proton), 8.5 (H, – CH =). Carbon atoms. Anal. Calcd: C8H14O6, C 50.52,H 7.42%.; Found: C 50.12, H 7.12%.

2.2.2. Synthesis of Allyl – O – D – Ribopyranosides

These compounds were synthesized by adaptation of Abod method (Daiekh A,1983). D-Ribose (1.8 g) was dissolved in a 0.5% hydrogen chloride in allyl alcohol which prepared by adding acetyl chloride (0.5 ml) to allyl alcohol (26.5 ml) and leaving the mixture for about two hours. The reaction mixture was placed in 250 ml round bottomed flask and was stirred magnetically overnight. The course of the reaction was monitored by T.L.C. using benzene – methanol (2 : 8 v/v), to give (1.7g, Browne color 86% Yield, R.F 0.8). FT-IR (KBr): cm-1 = 1056 (C – O – C), 1607 (C=C), 2931 (–CH2), 3486 (–OH). 1H. NMR data (D – DMSO) : δ (ppm) = 2.50 – 2.51 (3H,OH – sugar), 3.1 – 3.94 (4H, sugar), 3.95 – 4.0 (2H, O – CH2), 4.960 – 4.966 (2H, CH2=), 5.9 (1H, anomeric proton), 8.5 (H, – CH =). Carbon atoms. Anal. Calcd: C8H14O6, C50.52, H 7.42%; Found: C 50.12, H 7.12%.

2.2.3. Synthesis of Allyl 2,3,4 – tri – O – acetyl – D – ribopyranosides

The product obtained from (2) was acetylated despite its impurity. The syrup (1g) was dissolved in pyridine (11 ml) and the solution was cooled in ice – water before acetic anhydride (8.5 ml) was added drop wise. The reaction solution was left for three days at room temperature after which the brown solution was powered into water (100 ml). Allyl – tri – O – acetyl – D – ribopyranosides was extracted with chloroform (10 x20ml) and the chloroform solution was dried over calcium chloride, filtered and evaporated under reduced pressure to a
thick syrup which was examined by T.L.C. using pet – ether/ethyl acetate (1 : 1 v/v). to give (2.5g, Brown colour 75% Yield, R.F 0.5). FT-IR (KBr): cm-1 = 1068 (C – O – C), 1595 (C=C), 1716 (OCOCH3 ), 2724(– CH2).1H. NMR data (D-Chloroform) : δ (ppm) = 1.63 – 2.5 (9H, COCH3)3.34 – 3.9 (4H, sugar), 3.9 (2H, OCH2), 4.6 – 5.2 (2H, CH2=), 6 (1H, anomic hydrogen), 8.4 (1H, =CH). Carbon atoms. Anal. Calcd. For: C14H19O8, C 53.33, H6.03%; Found: C 53.63, H6.53%.

2.2.4. Synthesis of triazolylmythyl 2,3,4 – tri – O – acetyl – D – ribopyranoside
The product obtained from (3) was acetylated despite its impurity. The syrup (1 g) was dissolved in pyridine (11 ml) and the solution was cooled in ice – water before acetic anhydride (8.5ml) was added drop wise. The reaction solution was left for three days at room temperature after which the brown solution was powered into water (100 ml).Triazolylmythyl Tri – O – acetyl–D– ribopyranosides was extracted with chloroform (10 x20 ml) and the chloroform solution was dried over calcium chloride, filtered and evaporated under reduced pressure to a thick syrup which was examined by T.L.C.to give (2.2g, 82% Yield, R.F 0.7). FT-IR (KBr): cm-1 = 1167 (C –O– C), 2344 (diazostrech), 1715 (COCH3), 2724 (– CH2).1H. NMR data (Chloroform): δ (ppm) = 2.9 – 3.41 (7H, sugar,NH, CH), 3.44 – 3.48 (2H – CH2), 7.94 (1H, anomic proton), 2.5 – 2.88(9H, COCH3). Anal. Calcd. For: C14H19N3O5, C 47.05, H 5.32, N 11.76%; Found: 47.45, H 5.82, N 12.32%.

2.2.5. Synthesis of triazolylmythyl – O – D – ribopyranoside
Ally – O – ribopyranoside (2g) was suspended in dimethyl form amide (DMF) (15 ml) with an excess of sodium azide (0.5g). the mixture was then heated under reflux conditions at 140 – 150 C for 72 hours. The reaction mixture was then cooled and was powered into iced water. The product was extracted with chloroform and dried with magnesium sulfate and chloroform was removed under vacuum to give (2.2g, 82% Yield, R.F 0.7) FT-IR (KBr): cm-1 = 1099 (C – O– C), 1610 (–N=N–), 2103 (diazostrech), 2928 (– CH2), 3388 (– OH).1H. NMR data (D – DMSO) : δ (ppm) = 2.500 – 2.504 (6H, OH – sugar, NH, – CH), 3.15 – 3.16 (2H – CH2), 3.934 – 3.937 (5H, sugar), 4.96 – 4.97 (2H – OCH2), 6. 1H, anomic proton). Analysis Calculated for: C8H15N3O5, C 41.20, H 6.48, N 18.02%; Found: C41.60, H 7.08, N 18.32%.

2.2.6. Synthesis of triazolylmythyl – O – D – ribofuranosides
Prepared by the seen procedure of compound (5) to give (2.5g, 81% Yield, R.F 0.9). FT-IR (KBr): cm-1 = 1084 (C –O– C), 1597 (–N=N–), 2042 (diazostrech), 2929 (– CH2), 3369 (– OH).1H. NMR data (D – DMSO) : δ (ppm) = 2.72 – 2.75 (4H, OH – sugar,NH), 1.7 (1H – CH), 2.76 – 2.88 (2H, O –CH2), 2.50 (2H – CH2),2.91 – 3.41 (5H, sugar), 7.94 (1H, anomic proton). Anal. Calcd. For: C8H15N3O5, C 41.20, C 6.03,H 6.48, N 18.02%; Found: C41.6, H 7.08,N 17.52%.

2.2.7. Synthesis by alkaline permanganate (conversion into hydroxyl groups)

2.2.7.1. 1,2 – di hydroxypropyl – O – D – Ribofuranoside
The compound (1) dissolved (1g) in pyridine (5 ml) and 10 ml of diluted alkaline solution of potassium permanganate. The mixture was stirred at room temperature for 30 minutes. It was then filter to remove precipitated MnO2. The solvent was then removed and a syrupy product was obtained (Deaik A,1983) .FT-IR (KBr): cm-1 = 1122 (C – O – C), 2959 (= CH2), 3401 (=
OH).1H NMR data (D – DMSO) : δ (ppm) = 1.2 – 2.5 (5H, OH – sugar), 2.6–3.7 (8H – sugar), 3.8 - 4 (2H, – OCH2), 8.5 (1H, anomeric proton). Anal. Calcd. For: C8H16O7, C 42.86, H 7.19%; Found: C43.36, H 7.80%.

2.2.7.2. 1,2-dihydroxypropyl - O – D – Ribopyranoside
The compound (2) was dissolved in pyridine (5 ml) and 10 ml of diluted alkaline solution of potassium permanganate. The mixture was stirred at room temperature for 30 minutes. It was then filter to remove precipitated MnO2. The solvent was then removed and a syrupy product was obtained. FT-IR (KBr): cm-1 = 1086 (C – O – C), 2943 (– CH2), 3368 (– OH).1H. NMR data (D – DMSO) : δ (ppm) = 2.73 (5H, OH – sugar), 2.9 – 3.35(8H – sugar), 3.36 (2H, –OCH2), 7.9 (1H, anomeric proton). Anal. Calcd. For: C8H16O7, C 42.86, H 7.19%; found: C 41.70, H 7.70%.

2.2.8. Synthesis by acidic permanganate (conversion into carboxylic acid)

2.2.8.1. Carboxymethyl – O – D – Ribofuranosides:
The compound (1) was dissolved in pyridine and 5 ml was added into 15 ml of permanganate potassium solution acidified with sulfuric acid. The mixture was heated for one hour. Filtered and solvent was evaporated under vacuum. The syrupy product was examined by FT-IR (KBr): cm-1 = 1040 (C – O– C), 1712 (OCOH), 2940 (– CH2), 3402 (– OH).1H. NMR data (D – DMSO): δ (ppm) = 8 (1H), 5.9 (1H, anomeric proton), 2.8 – 3 (2H, O– CH2), 2.71 (5H – sugar), 2.50 – 2.53 (3H, OH – sugar). Anal. Calcd. For: C8H16O7, C 42.86, H 7.16%; Found: C 43.22, H 8.10%.

2.2.8.2. Carboxymethyl – O – D – Ribopyranosides(10)
The compound (2) was dissolved in pyridine and 5 ml was added in to 15 ml of acidified with sulfuric acid solution of permanganate potassium. The mixture was heated and stirred magnetically for one hour. It was then filtered and solvent was evaporated under vacuum.(Daiekh A,1983 ). The syrupy product was examined by FT-IR (KBr): cm-1 = 1122 (C – O– C), 1715 (OCOH), 2957 (– CH2), 3415 (– OH). 1H. NMR data (D – DMSO): δ (ppm) = 10 (1H, OCOH), 7.9 (1H, anomeric proton), 3.4 – 3.6 (2H, OCH2), 2.7 – 2.8 (5H – sugar), 1.04 – 2.5 (3H, OH – sugar). Analysis Calculated For: C8H16O7, C 42.86, H 7.16%; Found: C 42.22, H 7.44%.

3. Results and Discussion

The objectives of this work are to synthesis new unsaturated glycosides of D-ribose as such compounds in general are expected to have biological activity as well as other important uses such as being used as enzyme substrates. The new glycosides, after being identified, are to be used as a key intermediate for new hetero nitrogen cyclic triazoline derivatives. This is a new approach to new triazolinyl derivatives of the sugars mentioned earlier. Identification using different possible instrumental analysis is a part of this work. The conversion of the unsaturated glycosides into the triazolinyl compound is accomplished via a 1,3-dipolar cycloaddition with sodium azide. Some of the glycosides and their corresponding triazolinyl derivatives were also converted to esters by treatment with acetic acid. The target compounds; The derivative allyl – O – D – ribofuranoside(1) as in schem (1), synthesized by reacting D–
ribose with allyl alcohol in hydrogen chloride solution prepared by adding acetyl chloride to allyl alcohol. The reaction mixture is stirred under kinetically controlled conditions for about 150 minutes at room temperature. The syrupy product obtained was identified by FT–IR spectrum. The C=C bond absorbed at 1596 cm\(^{-1}\) which could be considered as a characteristic peak for the new unsaturated glycosides as such a peak is absent in the spectrum of the free sugar, D-ribose. The peak at 1044 - 1085 cm\(^{-1}\) is due to C–O–C bonds of the etheric ring. The hydroxyl group appeared at 3369 - 3400 cm\(^{-1}\) and of the –CH2– group at 2930 cm\(^{-1}\). The 1H -NMR spectrum of compound (2) in the (scheme1) gives further evident for the structure of the compound. The signal at 8.5 ppm is due to hydrogen of the H-C=, which resonate at low field because of de shielding by the double bond and perhaps by the nearby glycosidic oxygen. The peaks at 2.50 – 2.51 ppm belong to three hydrogen of the hydroxyl groups. The peaks at 3.1 – 3.9 ppm are due to the sugar ring (H –2, H –3, H –4) and that of the anomeric hydrogen is at 5.9 ppm which is usually resonate down field due to the anomeric effect. The signals at 4.961 – 4.966 ppm is due to two hydrogen of =CH2, because of deshielding by the double bond. The signal at 3.9 – 4 ppm is may be of the two hydrogen the of ring methylene C.H.N analysis showed an acceptable agreement between calculated and the found values despite the fact that the product are examined without purification, which probably means that the produced mixture consist with only anomeric compounds.

Synthesized allyl – O – D –ribopyranoside (2) in the scheme(1) by reacting D-ribose with allyl alcohol in hydrogen chloride solution prepared by adding acetyl to allyl alcohol two hours prior to addition of D – ribose. The reaction mixture was then heated and stirred under reflux conditions at (90-110) °C for three hours. The syrupy product obtained was identified by FT – IR spectrum. The C=C bond absorbed at 1607 cm\(^{-1}\). The peak at 1056 cm\(^{-1}\) is due to C–O–C bonds of the etheric ring. The hydroxyl group appeared at 3486,3237 cm\(^{-1}\) and of the –CH2– group at 2931. The 1H -NMR spectrum of compound 2 gives further evident for the structure of the compound. The signal at 8.5 ppm is due to hydrogen of the H-C=, which resonate down field as a result of deshielding by the double bond and perhaps by the nearby glycosidic oxygen. Signal at 2.50 – 2.53 ppm belong to three hydrogen of the hydroxyl groups. The peaks at 3.1 – 3.9 ppm are due to five hydrogen of the sugars ring and that of the anomeric hydrogen is at 6.0 ppm which resonate down field due to the anomeric effect. The peaks at 4.9 – 5.4 ppm are due to two hydrogen of the =CH2. The signal at 3.9 ppm is due two hydrogen the of – O – CH2 group. C.H.N analysis showed an expectable agreement between calculated and the found values despite the fact that our product are examined without purification, which probably means that the produced mixture consist with only anomeric forms.
Scheme 1.

Synthesized allyl 2,3,4–tri – O – acetyl – D – ribopyranoside (3) as in schemes (2) by reaction of the product (2) was dissolved in pyridine and the solution was cooled in ice – water before acetic anhydride. It's left for three days at room temperature. Then tri acetyl was extracted with chloroform as showed in scheme 2. The syrupy product obtained was identified by its FT – IR Spectrum. The peak at 1068 cm\(^{-1}\) is due to C–O–C. The peak at 1595 cm\(^{-1}\) is due C = C. While carbonyl of ester groups appeared at 1716 cm\(^{-1}\) and of the –CH2 group at 2724 cm\(^{-1}\). The 1H - NMR spectrum of gives further evident for the structure of the compound. The signal at 8.47 ppm is due to hydrogen of theH–C=, Which came at are mark ably down field of de shielding by the double bond and perhaps by the nearby glycosidic oxygen. Signals at 1.63 – 2.50 ppm are due to 9H of the ester groups. The peaks at 3.34 – 3.39 ppm are due to five hydrogen of the sugar ring and that of the anomic hydrogen is at 6.1 ppm which is sometimes came at down field due to anomic effect. The peaks at 4.7 – 5.2 ppm are due to 2H of =CH2, The signal at 3.39 ppm is due to two hydrogen of the O – CH2 group. Triazolinylmethyl 2,3,4–tri – O – acetyl D–ribopyranoside (4) as in scheme (2) was synthesized by reacting the product (3) which was dissolved in pyridine and the solution was cooled in ice – water before acetic anhydride was added. Then it was left for three days at room temperature. Then the tri acetyl was extracted with chloroform. The syrupy product obtained was identified by it's FT– IR Spectrum. The peak at 1167 cm\(^{-1}\) is due to C–O–C. Peak at 2344 cm\(^{-1}\) is due to diazo groups stretch. The ester groups appeared at 1715 cm\(^{-1}\) and of the –CH2 group at 2724 cm\(^{-1}\).The spectrum is now free of any hydroxyl absorption. The 1H -NMR spectrum of the triazolinylmethyl 2,3,4–Tri acetyl– O–D–ribopyranoside (4) prove the structure of the compound. The signals at 2.5 – 2.88 ppm are due to 9H of the O – CH3 group. Signal at 2.9 – 3.4 ppm are due to 7H of the sugar hydrogen, CH, NH and CH2 of the hetrocyclic ring. Except for the anomic hydrogen at 7.94 ppm which showed at down filed because of the anomic effect. The peaks at 3.44 – 3.48 ppm are due to 2H the of the O – CH2. Triazolinylmethyl – O – D – ribopyranoside(5) as in schemes (2). Was the product of treatment of allyl – O – D – ribopyranoside with sodium azide.
in DMF at 170°C over a period of three days. The product triazolinylmethyl – O – D – ribopyranoside, which was obtained, was identified by it's FT – IR spectrum which showed clearly the appearance of the N3 absorption at 2103 cm$^{-1}$. The peak at 1099 cm$^{-1}$ is due C – O – C bond. The hydroxyl group absorbed at 3388 cm$^{-1}$ and – CH2 – group at 2928 cm$^{-1}$. The 1H - NMR of the triazolinylmethyl– O – D – Ribopyranoside(5) prove the structure of the compound. The signals at 4.96 –4.97 ppm may belong to 2H of the methyl group of the triazolyl ring. Signals at 3.15 - 3.16 ppm are due to six hydrogen of the hydroxyl groups, NH and – CH of the triazolinyl ring. The peaks at 3.934 – 3.937 ppm are belong to the five hydrogen of the sugar ring. The anomic hydrogen which showed at because of the anomic effect. Signal at 4.96 – 4.97 ppm are may belong to 2H of the ring methyl group. Triazolinyl methyl – O – D –Ribofuranoside(6) as in schemes( 3): was obtained by treatment of allyl – O – D – ribofuranodides with sodium azide in DMF at 140-150°C for a period of three days. The produced new triazolinyl methyl – O – D – Ribofuranodides(6), was identified by it's FT –IR spectrum which showed clearly the appearance of the N3 absorption at 2042 cm$^{-1}$. The peak at 1044 cm$^{-1}$ is due to C – O – C bond. The hydroxyl groups appeared at 3369 cm$^{-1}$ and that of – CH2- group at 2929 cm$^{-1}$. The 1H -NMR of the triazolinyl methyl– O–D – ribofuranoside(6) provide good evidence for the structure of the compound. The signal at 2.72 – 2.75 ppm is due to 4H of the hydroxyl groups and– NH of the triazolinyl ring. The peak at 1.7 ppm is due to – CH of the heterocyclic ring. The signals at 2.76 – 2.88 ppm may belong to 2H of the – OCH2 group. Signal at 2.91 - 341 ppm could be of the 5H of the sugars ring. The anomic proton at 5.9 ppm which showed at downfield because of the anomic effect. The peak at 2.50 ppm is due to 2Hof the – CH2 of the heterocyclic ring. C.H.N analysis showed good agreement between calculated and the found values, which probably means that the produced mixture consist with only anomic products. It is clear that the stereo chemistry of the triazolinyl derivatives produced in this work required further close consideration as diastereomers are expected due to generation of a new stereogenic center on the carbon atom of the nitrogen hetero ring.
1,2 - dihydroxypropyl – O – D – ribofuranoside(7) as in scheme (3) was synthesized by reaction of the glycoside (1) which was dissolved in pyridine and diluted alkaline solution of potassium permanganate. Then the mixture was stirred at room temperature for 30 min. The syrupy product obtained was identified by its FT–IR spectrum. The peak at 1122 cm\(^{-1}\) is due to C–O–C bonds of the etheric ring. The peak at 3401 cm\(^{-1}\) is due to hydroxyl groups and of the –CH\(_2\) group at 2959 cm\(^{-1}\). This approach provides a reasonable route to glyceryl glycosides which is very difficult to be synthesized by direct Fischer glycosylation as the problem of how to get rid of excess of glycerol associated with high boiling point of glycerol. This is the first report on this route as far as we know. The 1H-NMR spectrum of the 1,2 dihydroxypropyl – O – D –ribofuranoside gives further evidence for the structure of the compound. The signal at
1.2 – 2.5 ppm belong to five hydrogen of the hydroxyl group. Signals at 2.6 – 3.7 ppm are due to 8H of the sugars ring hydrogen. The signals at 3.8 – 4 ppm are due to 2H of the methyl group. The peak at 5.8 ppm is due to anomic hydrogen well known to be affected by the anomeri position. 1,2-dihydroxypropyl – O – D – ribopyranoside(8) as in scheme (2) was synthesized by reacting the glycoside (3) which was dissolved in pyridine with diluted alkaline solution of potassium permanganate. Then the mixture was stirred at room temperature for 30 min. The syrupy product obtained was identified by it’s FT – IR spectrum. The peak at 1086 cm\(^{-1}\) is due to C–O–C bond of the etheric ring. The hydroxyl groups appeared at 3368 cm\(^{-1}\) and of the –CH2 group at 2943 cm\(^{-1}\). The 1H-NMR spectrum of the 1,2 dihydroxypropyl – O – D – ribopyranoside gives further evident for the structure of the compound. The peak at 2.73 ppm belong to five hydrogen of the hydroxyl groups. Signals at 2.89 – 3.35 ppm are due to 8H of the sugars ring hydrogens. While the anomic hydrogen is resonated at 7.9 ppm. Which showed at lower filed as a result of shielding by anomic effect. The peak at 3.36 ppm is due to 2H of the O – CH2 group. The carboxymethyl – O – D – ribofuranoside as in schemes(3) was synthesized by reacting the glycoside (1) which was dissolved in pyridine and added to permanganate potassium solution acidified with sulfuric acid. Then the mixture heated for 1 hour the syrupy product obtained was identified by it’s FT – IR spectrum. The peak at 1040 cm\(^{-1}\) is due to C–O–C. The peak at 3402 cm\(^{-1}\) is due to hydroxyl groups. The peak at 2940 cm\(^{-1}\) is due to –CH2 group. The peak at 1712 cm\(^{-1}\) is of the –COOH. The 1H-NMR spectrum of the carboxymethyl–O–D–ribofuranoside gives further prove for the structure of the compound. The signal at 8 ppm is due to carboxylic hydrogen which excepted to be deshielded by the carboxylic oxygen. The signal at 5.9 ppm is due to anomic hydrogen deshielded by the anomic effect. The peaks at 2.8 – 3 ppm are due to two hydrogen of ring methyl group. The signals at 2.71 ppm for the rest of the sugar ring hydrogen. The signal at 2.50 – 2.53 ppm are of the three hydroxyl groups. The CHN analysis showed an acceptable agreement between calculated and the found values indicating agreement with the suggested compounds molecular weight and reasonable purity of the product. Hydroxymethyl – O – D – Ribopyranoside(10) as in schemes(2) was synthesized by reaction of the glycoside (2) which was dissolved in pyridine and added to it an acidified potassium permanganate solution. Then the mixture heated for 1 hours. The syrupy product obtained was identified by it’s FT – IR spectrum. The peak at 1040 cm\(^{-1}\) is due to C–O–C. The peak at 3415 cm\(^{-1}\) is due to –OH. The peak at 2957 cm\(^{-1}\) is due to –CH2 group. The peak at 1715 cm\(^{-1}\) is due to .The 1H-NMR spectrum of the carboxymethyl–O–D–ribopyranoside shows signal at 10 ppm due to carboxylic hydrogen which excepted to be deshielded by the carboxylic oxygen. The signal at 7.9 ppm is due to anomic hydrogen resonates downfield because of deshielding of the anomic effect. The peaks at 3.4 – 3.6 ppm are due to two hydrogen the of methyl group. The signals at 2.7 – 2.8 ppm for the rest of the sugar ring hydrogen. Signal at 1.04 – 2.5 ppm are of the three hydroxyl groups.

4. Conclusion

The results of the present investigation showed that some of new glycosides were synthesized. In addition, both these newly introduced and methods of glycosylation can be tried in large scale preparations. It is also expected that this work employing carbohydrate derivatives as test chemicals will help further the development of medicines for human disease control. So it is hoped that the glycosides triazolines and triazoles, D-ribopyranoside and furanoside (1-9)
compound might show potential antiviral, anti-tubercular and anti-inflammatory activities. Glycosides were successfully synthesized. However, purification of this compound did not turn out to be simple. Using both column chromatography and a reverse phase C18 column the crude mixture of products remained inseparable. After several attempts, it was determined that this method of simple purification of glycosides was unsuccessful.

Acknowledgements

The author thanks all his coworkers. Thanks also due to Dr. Shaker AL-Zorige for providing the facility for recording the 1H-NMR, and C.H.N Elemental analysis in Saudia Arabia.

References


