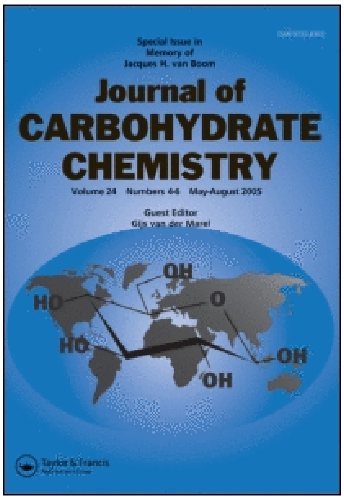

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REACTION OF 3-HYDRAZINO-5,6-DIPHENYL-1,2,4-TRIAZINE WITH SOME HEXOSES AND PENTOSES

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ABSTRACT

3-Hydrazino-5,6-diphenyl-1,2,4-triazine (1) reacts with D(-)fructose, D(+)glucose, D(-)ribose and D(-)arabinose to give the corresponding bis triazinyl hydrazones 4a and 7a. Reactions of these hydrazones with acetic anhydride and with phenyldiazonium chloride are described.

INTRODUCTION

Hydrazine derivatives react with aldoses and ketoses to give either the corresponding hydrazones or osazones. This prompted us to investigate the behaviour of 3-hydrazino-1,2,4-triazine derivatives towards aldoses and ketoses. Also the obtained products are potential biological agents as many 1,2,4-triazines exhibit pronounced biological activities.

RESULTS AND DISCUSSION

The synthesis of 3-hydrazino-5,6-diphenyl-1,2,4-triazine (1) has been described by different authors.[1-5] This hydrazine has now been prepared in a better yield and shorter time than that reported before.[3] This was achieved by heating together 3-methylthio-5,6-diphenyl-1,2,4-triazine (2) and hydrazine hydrate for one hour.

The present investigation deals with the study of the reaction of the triazine 1 with some monosaccharides, namely, D(-)fructose (3), D(+)glucose

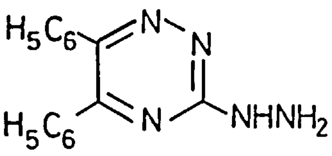
(5), D(-)ribose (6) and D(-)arabinose (8). Thus, when the sugars 3, 5, 6 and 8 were treated with compound 1 in dilute acetic acid, they gave the corresponding bis triazinyl hydrazones 4a and 7a. This is similar to the reaction of these sugars with phenylhydrazine to give the corresponding osazones. However 3-amino-5,6-diphenyl-1,2,4-triazine (11), which is expected as a by-product, could not be isolated.

On the other hand, treatment of each compounds 4a and 7a with hydrochloric acid followed by p-methoxybenzaldehyde gave the triazinyl hydrazone 9.[2] The formation of compound 9 may be attributed to the ready hydrolysis of the bis triazinyl hydrazones 4a and 7a to give compound 1, which is not isolated but reacts readily with the aldehyde in the reaction medium.

The structures of compounds 4a and 7a are inferred from the following facts: (1) The compounds give the corresponding correct analytical values. (2) Compound 4a is obtained from either D(-)fructose or D(+)glucose and compound 7a is obtained from either D(-)ribose or D(-)arabinose. (3) Compound 4a gives a postive test with Molisch's reagent (violet color). (4) The infrared absorption spectra of compounds 4a and 7a show OH and NH groups as broad bands in the 3100-3500 cm^{-1} region.

Compounds 4a and 7a were readily acetylated on treatment with acetic anhydride in pyridine to give the tetraacetate and triacetate derivatives 4b and 7b respectively. The infrared spectra of compounds 4b and 7b show bands at 1750 cm^{-1} ($O-COCH_3$), and no bands could be detected in the 1600-1700 cm^{-1} region (absence of $N-COCH_3$) confirming that acetylation has taken place on the hydroxyl groups only. Compound 4b has ^1H NMR ($DMSO-d_6$) δ 2-2.2 (4 singlets, 12H, 4 CH_3CO). 4.25 (d, 2H, H_a), 5.2 (m, 1H, H_b), 5.55 (dd, 1H, H_c), 5.8 (d, 1H, H_d), 7.1-7.7 (m, 10H, arom), and 8.1 (s, 1H, H_e) ppm.

The synthesis of the formazan derivative 10a has now been achieved by coupling compound 4a in pyridine with phenyldiazonium chloride. The infrared spectrum of compound 10a shows a broad band at 3150-3500 cm^{-1} (OH and NH). Compound 10a undergoes acetylation when treated with acetic anhydride in pyridine to give the tetraacetate derivative 10b. Compound 10b has also been obtained by coupling the tetraacetate derivative 4b in pyridine, with phenyldiazonium chloride. The infrared spectrum of compound 4b shows a band at 1745 cm^{-1} ($OCOCH_3$) and disappearance of the broad band in the 3100-3500 cm^{-1} region (OH) present in the parent compound 4a. Compound



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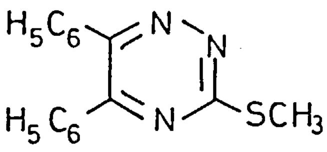

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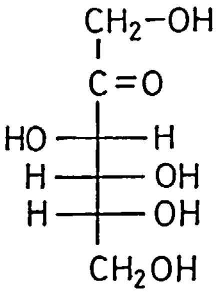

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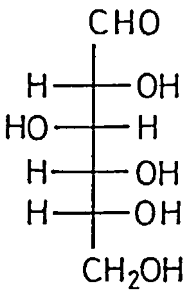

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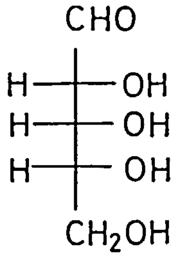

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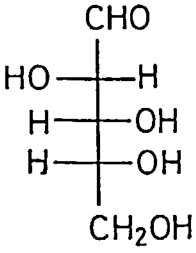

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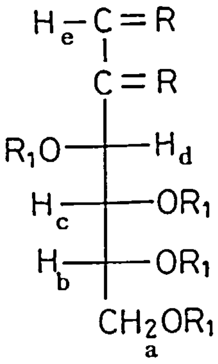

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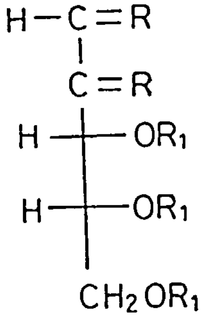

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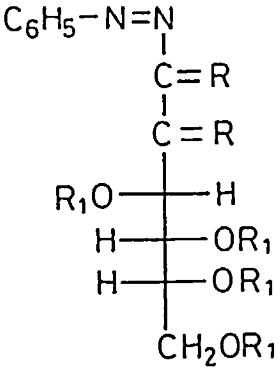
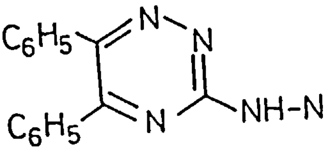
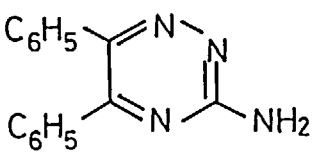


10

	R_1	R
4a ,7a,10a	H	
4b , 7b , 10b	$COCH_3$	





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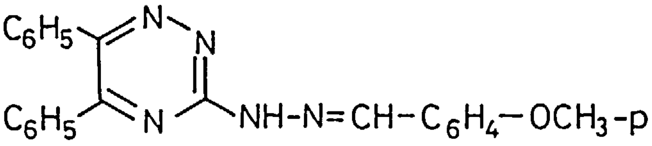

9

10b has ^1H NMR (DMSO-d_6) δ 1.95-2.1 (4 singlets, 12H, 4 CH_3CO), 4.2 (d, 2H), 5.25 (m, 1H), 5.5 (t, 1H), 5.7 (d, 1H), 7.2-8.0 (m, 25H, arom), 12.5 (s, 1H, NH), 13.45 (s, 1H, NH). ppm.

EXPERIMENTAL

All melting points are reported uncorrected. The IR spectra (potassim bromide) were recorded with a Unicam SP 1200 infrared spectrophotometer. The ^1H NMR spectra were recorded with a Varian EM 390 90 MHz spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane.

3-Hydrazino-5,6-diphenyl-1,2,4-triazine (1). A mixture of 3-methylmercapto-5,6-diphenyl-1,2,4-triazine (2) (0.03 mol) and hydrazine hydrate (80 mL, 85 %) was heated under reflux for 1 h. The reaction mixture was allowed to cool , then poured into cold water and allowed to stand overnight. The precipitate obtained was collected and recrystallized from methanol to give yellow crystals of compound 1, mp 172-173 °C (mixed mp with an authentic sample[5] showed no depression), yield ca. 97 %.

D-Arabino-hexos-2-ulose Bis-3-(5,6-diphenyl-1,2,4-triazinyl)hyrazone (4a). To a solution of D(-)fructose (0.6 g) in water (25 mL), was added compound 1 (1.2 g) followed by glacial acetic acid (10 mL). The flask containing the reaction mixture was immersed in a boiling water bath for 2 min. An additional amount of glacial acetic acid (5 mL) was then added portionwise till clear solution was obtained. After 5 min heating, a yellow product started to separate. Heating was continued for a further 10 min. The reaction mixture was allowed to cool. The precipitate obtained was collected and recrystallized from DMF as orange yellow crystals of compound 4a mp 214-215 °C (charring and decomposition), yield ca. 40 %.

Anal. Calcd for $C_{36}H_{32}N_{10}O_4$: C, 64.66; H, 4.82; N, 20.94. Found: C, 64.40; H, 5.10; N, 20.55.

The above procedure was repeated using D(+)glucose (5) instead of D(-)fructose and the same product 4a was obtained, mp 214 °C (charring and decomposition), yield ca. 30 %. Mixed mp of samples of compound 4a obtained from both sugars showed no depression; moreover, both samples have identical IR spectra, and they give a violet color with Molisch's reagent.

D-Erythro-pentos-2-ulose Bis-3-(5,6-diphenyl -1,2,4-triazinyl)hydrazone (7a) To a solution of D(-)ribose (0.5 g) in water (30 mL) was added compound 1 (1.0 g) followed by glacial acetic acid (9.0 mL). The flask containing the reaction mixture was immersed in a boiling water bath. After 10 min heating a precipitate started to separate. Heating was continued for a further 10 min and the reaction was allowed to cool. The precipitate obtained was collected and recrystallized from DMF as orange-yellow crystals of compound 7a, mp 243-245 °C (charring and decomposition), yield ca. 30 %.

Anal. Calcd for $C_{35}H_{30}N_{10}O_3$: C, 65.82; H, 4.73; N, 21.93. Found: C, 65.44; H, 5.10; N, 21.82.

The above procedure was repeated using D(-)arabinose (8) instead of D(-)ribose, and heating was continued for 45 min to give product 7a, mp 243-245 °C (charring and decomposition), yield ca. 25 %. Mixed mp with compound 7a obtained previously showed no depression and the IR spectra were identical.

Reaction of compounds 4a and 7a with hydrochloric acid and p-methoxybenzaldehyde. A suspension of compound 4a (0.1 g) in hydrochloric acid (10 mL, 5 M) was boiled, then ethanol (3 mL) was added to the hot solution, portionwise till a clear solution was obtained. The reaction mixture was then treated with p-methoxybenzaldehyde (0.1 mL) and boiled for 2 min. After cooling, the orange precipitate formed was filtered, washed with water and cold alcohol, respectively. Recrystallization from DMF gave the 3-(5,6-diphenyl-1,2,4-triazinyl)hydrazone (9), mp 268 °C, yield ca. 65 %. Mixed mp with an authentic sample[2] gave no depression.

The same procedure was repeated using compound 7a instead of compound 4a, and compound 9 was separated and identified as before, yield ca. 66 %.

D-Arabino-hexos-2-ulose Bis-3-(5,6-diphenyl-1,2,4-triazinyl)hydrazone-3,4,5,6-tetra-O-acetate 4b. To compound 4a (0.3 g) was added a mixture of pyridine (2 mL) and acetic anhydride (2 mL). The reaction mixture was left overnight at room temperature. It was then poured into water (25 mL) and the precipitate obtained was filtered, washed with water and recrystallized from butanol as orange crystals of compound 4b, mp 153 °C, yield ca. 60 %.

Anal. Calcd for $C_{44}H_{40}N_{10}O_8$: C, 63.15; H, 4.82; N, 16.73. Found: C, 62.80; H, 5.0; N, 16.41.

D-Erythro-pentos-2-ulose Bis-3-(5,6-diphenyl-1,2,4-triazinyl)hydrazone-3,4,5-tri-O-acetate (7b). The preceding procedure was applied to 7a (0.28 g). The product was recrystallized from ethanol to give yellow crystals of compound 7b, mp 168 °C, yield ca. 54 %.

Anal. Calcd for $C_{41}H_{36}N_{10}O_4$: C, 64.39; H, 4.74; N, 18.31.Found: C, 64.00 H, 5.10; N, 17.96.

Phenyldiazonium chloride reagent. Aniline (1 mL) was dissolved in hydrochloric acid (5 mL, 5 M), cooled to 5 °C and treated with an aqueous solution of sodium nitrite (0.8 g in 2 mL water), keeping the temperature below 5 °C.

1-Phenylazo-D-arabino-hexos-2-ulose Bis-3-(5',6-dipnenyl-1,2,4-triazinyl)-hydrazone (10a). Compound 4a (0.3 g) was dissolved in pyridine (10 mL), cooled to 0 °C and treated by dropwise addition of phenyldiazonium chloride reagent (3 mL). The reaction mixture acquired a red color. After 5 min ice-water (5 mL) was added, whereby a red residue was formed. The reaction mixture was allowed to stand for 15 min at room temperature. It was then diluted with five times its volume with water and left overnight. The reddish brown precipitate formed was collected and recrystallized from ethanol to give compound 10a mp 175-178 °C (charring and decomposition), yield ca. 28 %.

Anal. Calcd for $C_{42}H_{36}N_{12}O_4$: C, 65.27; H, 4.69; N, 21.74. Found: C, 64.90; H, 5.00; N, 21.40.

1-Phenylazo-D-arabino-hexos-2-ulose Bis-3-(5',6-diphenyl-1,2,4-triazinyl)-hydrazone-3,4,5,6-tetra-O-acetate (10b); Method (i). To compound 4b (0.15 g) was added a mixture of pyridine (2 mL) and acetic anhydride (2 mL). The reaction mixture was allowed to stand overnight at room temperature. It was then diluted with ice-cold water (25 mL). The precipitate formed was collected and recrystallized from ethanol as brown crystals of compound 10b, mp 128 °C, yield ca. 25 %.

Anal. Calcd for $C_{50}H_{44}N_{12}O_8$: C, 63.83; H, 4.67; N, 17.86. Found: C, 63.50; H, 5.00; N, 17.50.

Method (ii). To a solution of compound 4b (0.2 g) in pyridine (10 mL) cooled to 0 °C was added dropwise phenyldiazonium chloride reagent (3 mL). After standing for 15 min at room temperature, water (25 mL) was added, and the reaction mixture was allowed to stand overnight at room temperature. The residue obtained was collected and recrystallized from ethanol giving brown crystals of compound 10b, mp 128 °C, yield ca. 22 %. Compound 10b obtained by method (ii) was identical to that obtained by method (i) (mp and mmp showed no depression; both samples have identical IR spectra).

REFERENCES AND FOOTNOTES

1. R. Fusco and R. Trave, Rend. Ist Lombardo Sci Pt. I, 91, 202 (1957); Chem. Abstr., 52 11865h (1958).
2. A. Dornow, W. Abele and H. Menzel, Chem. Ber., 97, 2179 (1964).

3. W. W. Paudler and Teh-Kuei Chen, J. Heterocyclic Chem., 7, 767 (1970).

4. P. V. Laakso, R. Robinson and H. P. Vanderwala, Tetrahedron 1, 103, (1957).

5. M. F. G. Stevens, J. Chem. Soc. Perkin Trans. 1, 1221 (1972).