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SYNTHESIS OF 3-DEOXY-4-*O*-β-D-GALACTOPYRANOSYL-D-*erythro*-HEXOS-2-ULOSE AND OF SOME OF ITS DERIVATIVES FROM LACTOSE*

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ABSTRACT

3-Deoxy-4-*O*-β-D-galactopyranosyl-D-*erythro*-hexos-2-ulose (**1**) was obtained from lactose by reaction with benzoylhydrazine in the presence of a slightly acidic solution of *p*-toluidine, followed by hydrazinolysis of the product, 3-deoxy-4-*O*-β-D-galactopyranosyl-D-*erythro*-hexos-2-ulose bis(benzoylhydrazone) (**3**), with benzaldehyde. A variety of derivatives of **1** and **3** was prepared. Lactose aroylhydrazones were also prepared. Quantitative determination of the oxidant during the periodate oxidation of **3** was studied. Periodate oxidation of monosaccharide arylhydrazones gave glyoxal mono(arylhydrazones) which afforded the corresponding, mixed bis(hydrazones).

INTRODUCTION

The non-enzymic browning (Maillard) reaction[1-3] is a complex set of reactions known to occur, during storage or processing of many foodstuffs, between reducing sugars and amino acids (free, or combined as proteins or peptides), leading to the formation of dark-colored and insoluble products, as well as to flavor deterioration. 3-Deoxyhexosuloses have been postulated[2-4] as intermediates in such reactions through a process of β-elimination. Moreover, it has been suggested that such compounds are responsible for the antitumor activity of several antibiotics[5,6].

In addition to these biological aspects of the 3-deoxyhexosuloses, they are also of considerable importance from the chemical[2] point of view, such as in study of the Lobry de Bruyn–Alberda van Ekenstein transformation. They occur as intermediates in the conversion of sugars by acids into furfurals, and by alkalis into metasaccharinic acids.

As lactose (4-*O*-β-D-galactopyranosyl-D-glucopyranose) is one of the constituents of milk, it might be supposed that, owing to the foregoing aspects, its 3-deoxyosulose derivative, 3-deoxy-4-*O*-β-D-galactopyranosyl-D-*erythro*-hexos-2-ulose (**1**) is of particular importance. Its synthesis has now been achieved by the hydrazinolysis of (new) bis(aroylhydrazones).

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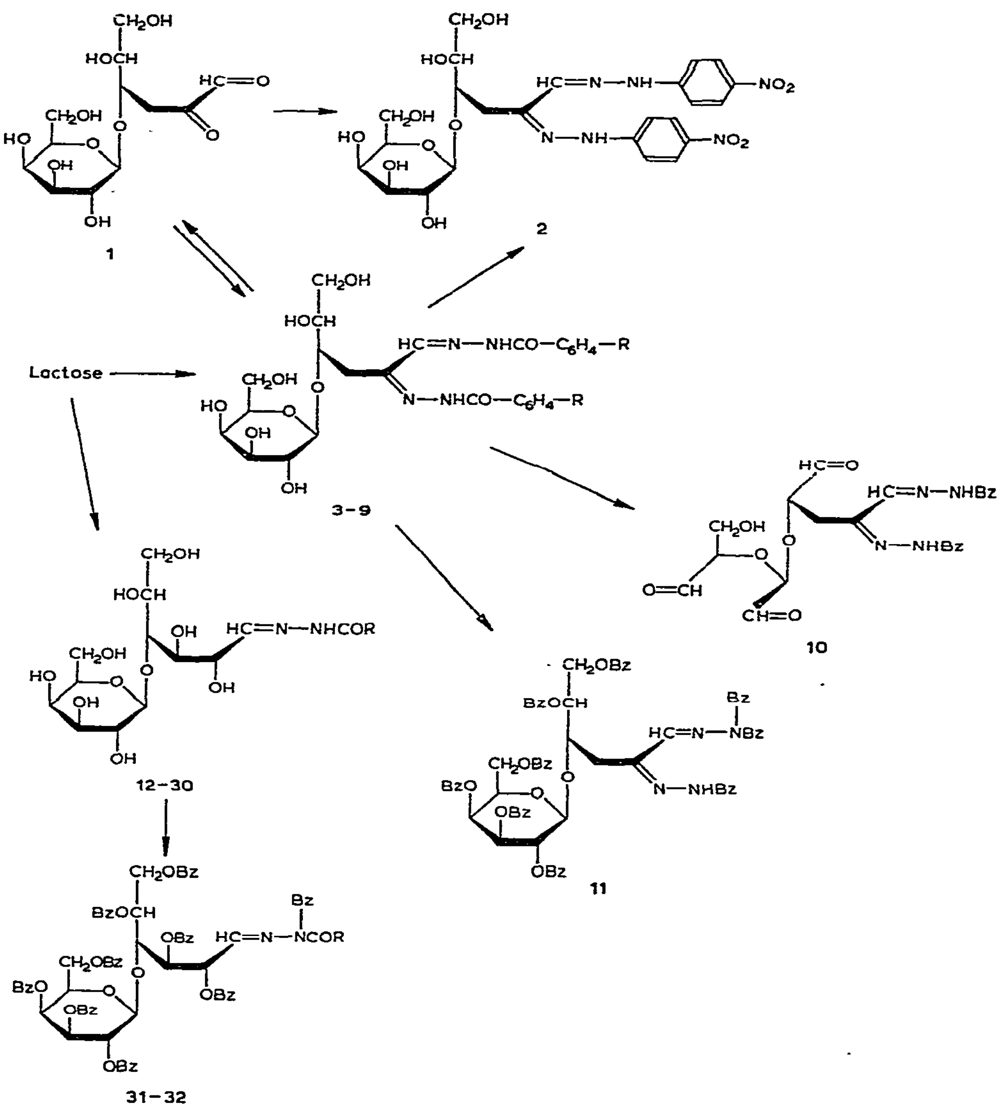
*The Scope of the Reactions of Hydrazines and Hydrazones, Part VI.

Aroylhydrazones of monosaccharides are excellent precursors for the synthesis of their heterocyclic derivatives[7-9], such as 1,3,4-oxadiazoles, which are of biological interest[10-13]. It seemed likely that such derivatives having oligosaccharide side-chains might possess greater solubility and, consequently, better chemotherapeutic values than those from monosaccharides. The first step in this work was the preparation of a number of lactose aroylhydrazones (and their structures are discussed).

RESULTS AND DISCUSSION

On reviewing the literature on the methods available for synthesizing 3-deoxyaldos-2-uloses, it was found that a number of methods have been suggested for their preparation: (*1*) conversion of 3-deoxyaldoses into 3-deoxyaldosuloses *via* their reaction with arylhydrazine, and hydrazinolysis[14,15], (*2*) action of alkali on 3-*O*-benzylated aldoses[16-18], (*3*) decomposition of *N*-butyl-aldosylamines by acetic acid[15], (*4*) decomposition of di-D-fructoseglycine[19,20], (*5*) the action of acids on D-fructose[21], (*6*) a sequence of reactions[22] (starting with a 2-deoxyaldonic acid chloride), $\text{-CH}_2\text{COCl} \rightarrow \text{-CH}_2\text{COCHN}_2 \rightarrow \text{-CH}_2\text{COCH=N-N=PPh}_3 \rightarrow \text{-CH}_2\text{COCHO}$, and, recently, (*7*) a simpler route[23-25], including the hydrazinolysis of 3-deoxyaldosulose bis(aroylhydrazones) obtained by the reaction of the appropriate aldoses with aroylhydrazines in the presence of *p*-toluidine. It seemed that the last is the route of choice for preparing this class of compound, as the others either give a low yield of the aldosulose, or the isolation thereof is a tedious process. Thus, the reaction of lactose with *p*-toluidine in acidified ethanol, followed by treatment with benzoylhydrazine, gave a colorless product identified as 3-deoxy-4-*O*-β-D-galactopyranosyl-D-*erythro*-hexos-2-ulose bis(benzoylhydrazone) (**3**, R = H). Similarly, variants (**4**–**9**) of **3** were prepared having different aroyl substituents (such as *o*-hydroxybenzoyl, *m*-toluoyl, *p*-toluoyl, *p*-methoxybenzoyl, *p*-chlorobenzoyl, and *p*-nitrobenzoyl). As, with the arylamines, lactose is known to give the *N*-aryllactosylamines, which are capable of undergoing the Amadori rearrangement, it seems possible that the rearranged product gives the corresponding 3-deoxyaldos-2-ulose, which reacts, *in situ*, with the aroylhydrazine to afford the bis(aroylhydrazone) (**3**–**9**). The n.m.r. spectra of **3** and **6** (**3**, R = C_6H_4-Me-*p*) showed the sugar protons as a multiplet at δ 3.9–5.2, and the aromatic protons as multiplets in the regions δ 7.0–8.0 and δ 8.2–9.1 for both compounds. In addition, compound **6** showed two singlets, at δ 2.1 and 2.2, due to the two methyl groups of the *p*-toluoyl rings.

Hydrazinolysis of the bis(aroylhydrazone) residues with benzaldehyde in ethanolic solution, in a manner similar to that used in the preparation of 3-deoxy-D-aldos-2-uloses[23] and D-*arabino*-hexosulose[26], gave benzaldehyde benzoylhydrazone and 3-deoxy-4-*O*-β-D-galactopyranosyl-D-*erythro*-hexos-2-ulose (**1**) in 20% yield; this could be transformed into a crystalline bis(*p*-nitrophenylhydrazone) (**2**), whereas its bis(phenylhydrazone) could not be isolated in crystalline form. The osulose **1** reacted with benzoylhydrazine to afford the original 3-deoxy-4-*O*-β-D-galactopyranosyl-D-*erythro*-hexos-2-ulose bis(benzoylhydrazone) (**3**, R = H), indicating that the hydra-



zinolysis does not affect the rest of the molecule (particularly, the glycosidic linkage).

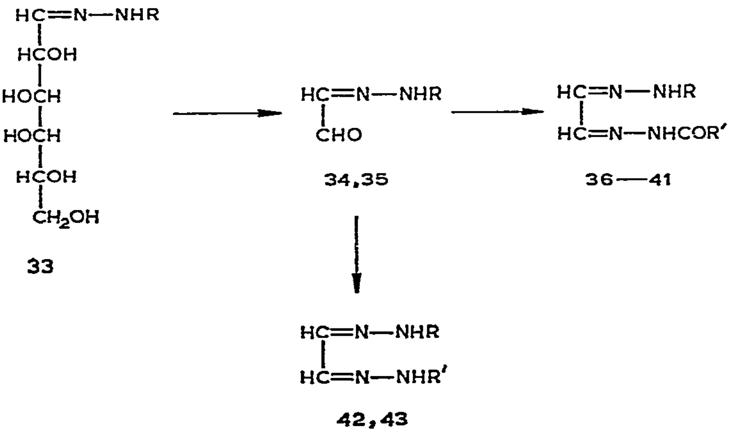
On periodate oxidation, 3-deoxy-4-*O*-β-D-galactopyranosyl-D-*erythro*-hexos-2-ulose bis(benzoylhydrazone) consumed the calculated amount of the oxidant within five hours, followed by the consumption of 2–3 moles per mole during the next 3 days, with the isolation of a colorless compound tentatively assigned the structure 2,4,6-triformyl-1-hydroxy-3,5-dioxanonane-8,9-dione 8,9-bis(benzoylhydrazone) (**10**).

Acetylation of **3** gave an amorphous product, whereas benzoylation with benzoyl chloride in pyridine gave hexa-*O*-benzoyl-3-deoxy-4-*O*-β-D-galactopyranosyl-D-*erythro*-hexos-2-ulose 2-(2-benzoylhydrazone) 1-(2,2-dibenzoylhydrazone) (**11**).

Direct treatment of lactose with aroylhydrazines afforded the corresponding aroylhydrazones (**12**–**30**) having a variety of aroyl substituents, such as benzoyl, *o*-hydroxybenzoyl, *m*-hydroxybenzoyl, *p*-hydroxbenzoyl, *m*-toluoyl, *p*-toluoyl, *p*-methoxybenzoyl, *o*-chlorobenzoyl, *p*-chlorobenzoyl, *p*-bromobenzoyl, *o*-iodobenzoyl, *p*-iodobenzoyl, and *p*-nitrobenzoyl, in addition to nicotinoyl, isonicotinoyl, veratroyl, piperonoyl, *p*-tolylsulfonyl, and phenylacetyl.

Benzoylation of lactose aroylhydrazones [**12**, R = Ph, and **20** (**12**, R = C_6H_4Cl-*p*)] with benzoyl chloride in pyridine gave octa-*O*-benzoyl derivatives (**31** and **32**, respectively) which showed, in their i.r. spectra, bands at 1720 cm^{-1} due to the OBz groups, in addition to a band at 1640 cm^{-1} due to the OCN group (which also appeared in the spectra of their precursors).

Periodate oxidation of lactose benzoylhydrazone gave a product identical with that isolated from monosaccharide benzoylhydrazones[27], which may be taken as evidence for the presence of the former in the (partially) open-chain structure. O'Donnell and E. Percival[28] studied the periodate oxidation of D-galactose phenylhydrazone, and the product was formulated as glyoxal mono(phenylhydrazone). We extended this periodate oxidation to D-galactose *p*-bromo- and *p*-iodo-phenylhydrazones (**33**) and the products were formulated as glyoxal mono-(*p*-bromo- and *p*-iodo-phenyl)hydrazones (**34** and **35**, respectively), which showed, in their i.r. spectra, the aldehydic groups at 1660 cm^{-1}. These monohydrazones reacted with a number of aryl- and aroyl-hydrazines, affording the corresponding, mixed bis(hydrazones) (**36**–**43**).



EXPERIMENTAL

General methods. — Melting points were determined with a Kofler-block apparatus and are uncorrected. I.r. spectra were recorded with a Unicam SP-200 spectrometer. U.v. spectra were recorded with a Unicam SP-800 spectrophotometer. Microanalyses were performed in the Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt.

TABLE I

MICROANALYTICAL AND INFRARED ABSORPTION DATA FOR 3-DEOXY-4-*O*-β-D-GALACTOPYRANOSYL-D-*eyrthro*-HEXOS-2-ULOSE BIS(AROYLHYDRAZONES) (3–9)

Compound No.	*R*	*Yield (%)*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol} *(cm⁻¹)*		
					C	*H*	*N*	*C*	*H*	*N*			
3	Ph	38	235	$C_{26}H_{32}N_4O_{10} \cdot H_2O$	54.0	5.9	9.7	53.7	6.2	9.5	1655	1685	3400
4	C_6H_4OH-*o*	28	238–240	$C_{26}H_{32}N_4O_{12}$	52.7	5.4	9.5	52.7	5.5	9.7	1640	1660	3400
5	C_6H_4Me-*m*	37	185	$C_{28}H_{36}N_4O_{10}$	57.1	6.2	9.5	56.7	6.4	9.5	1635	1660	3340
6	C_6H_4Me-*p*	42	253–255	$C_{28}H_{36}N_4O_{10}$	57.1	6.2	9.5	56.7	6.1	9.2	1630	1675	3390
7	C_6H_4OMe-*p*	40	232–234	$C_{28}H_{36}N_4O_{12}$	54.2	5.9	9.0	54.1	5.7	8.9	1645	1660	3445
8	C_6H_4Cl-*p*	55	271–273	$C_{26}H_{30}Cl_2N_4O_{10}$	49.6	4.8	8.8	49.2	5.2	8.5	1640	1680	3400
9	$C_6H_4NO_2$-*p*	32	216–218	$C_{26}H_{30}N_6O_{14}$	48.0	4.6	12.9	47.8	5.2	12.6	1640	1680	3390

*3-Deoxy-4-O-β-*D*-galactopyranosyl-*D-erythro*-hexos-2-ulose bis(aroylhydrazones)* (**3–9**). — A solution of lactose (0.01 mol) and *p*-toluidine (0.01 mol) in a mixture of ethanol (50–100 mL), water (5–10 mL), and acetic acid (2 mL) was boiled under reflux for 30 min. The aroylhydrazine (0.03 mol) was then added, and the mixture was further refluxed for 15–25 h. The resultant solution was kept for 2 days, during which, the product separated out; it was filtered off, washed successively with alcohol and ether, and dried. Recrystallization was effected from ethanol, to give colorless needles (see Table I).

*3-Deoxy-4-O-β-*D*-galactopyranosyl-*D-erythro*-hexos-2-ulose* (**1**). — A solution of compound **3** (2.0 g) in ethanol (60 mL), water (100 mL), acetic acid (2.5 mL), and freshly distilled benzaldehyde (3.5 mL) was boiled under reflux for 6 h on a water bath; after 3 h, benzaldehyde benzoylhydrazone started to separate out. Ethanol was removed by evaporating off 60 mL of the solution, with simultaneous dropwise addition of water (100 mL). After 18 h, the precipitated benzaldehyde benzoylhydrazone was filtered off, and the filtrate was concentrated to 40 mL, washed with ether, and evaporated to a thick syrup (yield 20%). Reaction of the syrup with benzoylhydrazine afforded the bis(benzoylhydrazone) **3**.

*3-Deoxy-4-O-β-*D*-galactopyranosyl-*D-erythro*-hexos-2-ulose bis(*p*-nitrophenylhydrazone)* (**2**). — A solution of syrupy **2** (0.56 g), (*p*-nitrophenyl)hydrazine (0.5 g), and 1 drop of acetic acid in water (10 mL) was heated for 1 h at 40°. The bis-hydrazone that separated out was filtered off, and successively washed with ethanol and ether (yield 93%). The product was recrystallized from ethanol–water, to give red needles, m.p. 195°; ν_{max}^{Nujol} 3330 cm^{-1} (OH).

Anal. Calc. for $C_{24}H_{30}N_6O_{11} \cdot H_2O$: C, 47.1; H, 5.3; N, 13.7. Found: C, 47.1; H, 4.9; N, 13.9.

2,4,6-Triformyl-1-hydroxy-3,5-dioxanonane-8,9-dione 8,9-bis(benzoylhydrazone) (**10**). — To a stirred solution of sodium metaperiodate (2.4 g) in distilled water (25 mL) was added compound **3** (2.0 g). The mixture was kept in the dark overnight at room temperature, and the product that separated out was filtered off, washed successively with water and aqueous sodium thiosulfate solution, and dried (yield 64%). It was recrystallized from ethanol, to give colorless needles, m.p. 205°; ν_{max}^{Nujol} 1690 (C=O), and 1655, 1640 cm^{-1} (OCN); λ_{max}^{EtOH} 240, 265, and 340 nm (log ε 3.81, 3.83, and 3.33); λ_{min}^{EtOH} 248 and 318 nm (log ε 3.80 and 3.26).

Anal. Calc. for $C_{24}H_{24}N_4O_8$: C, 58.1; H, 4.9; N, 11.3. Found: C, 58.3; H, 4.6; N, 10.9.

*Hexa-O-benzoyl-3-deoxy-4-O-β-*D*-galactopyranosyl-*D-erythro*-hexos-2-ulose 2-(2-benzoylhydrazone) 1-(2,2-dibenzoylhydrazone)* (**11**). — A solution of compound **3** (0.1 g) in dry pyridine (10 mL) was treated dropwise with benzoyl chloride (1 mL), and the mixture was kept overnight at room temperature. It was then poured onto crushed ice, and the precipitate was filtered off, washed successively with water and aqueous sodium hydrogencarbonate, and dried (yield 86%). The product was recrystallized from ethanol, to give colorless needles; m.p. 140°; ν_{max}^{Nujol} 1720 (OBz), 1710 and 1690 cm^{-1} (OCN).

TABLE II

MICROANALYTICAL AND INFRARED ABSORPTION DATA FOR LACTOSE AROYLHYDRAZONES (12–30)

Compound No.	*R*	*Yield (%)*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*				*Found (%)*				ν_{max}^{Nujol} *(cm^{-1})*	
					C	*H*	*N*	*X*	*C*	*H*	*N*	*X*		
12	Ph	89	198–199	$C_{19}H_{28}N_2O_{11} \cdot 2H_2O$	46.0	6.5	5.6		46.2	6.6	5.6		1640	3400
13	C_6H_4OH-*o*	60	200	$C_{19}H_{28}N_2O_{12} \cdot 2H_2O$	44.5	6.3	5.4		44.7	6.7	5.6		1640	3300
14	C_6H_4OH-*m*	65	208–210	$C_{19}H_{28}N_2O_{12}$	47.9	5.9	5.8		47.9	6.2	5.4		1640	3290
15	C_6H_4OH-*p*	53	182	$C_{19}H_{28}N_2O_{12}$	47.9	5.9	5.8		48.1	6.0	5.4		1660	3340
16	C_6H_4Me-*m*	51	169	$C_{20}H_{30}N_2O_{11} \cdot 2H_2O$	47.1	6.7	5.5		46.9	6.9	5.3		1635	3390
17	C_6H_4Me-*p*	53	165	$C_{20}H_{30}N_2O_{11} \cdot H_2O$	48.7	6.5	5.7		48.6	6.1	6.0		1640	3440
18	C_6H_4OMe-*p*	60	172	$C_{20}H_{30}N_2O_{12} \cdot 2H_2O$	45.6	6.5	5.3		45.4	6.8	5.3		1645	3385
19	C_6H_4Cl-*o*	52	190	$C_{19}H_{27}ClN_2O_{11}$	46.1	5.5	5.6	7.2	45.9	5.7	5.4	7.1	1640	3340
20	C_6H_4Cl-*p*	53	199	$C_{19}H_{27}ClN_2O_{11}$	46.1	5.5	5.6	7.2	45.8	5.5	5.2	7.3	1645	3345
21	C_6H_4Br-*p*	73	207	$C_{19}H_{27}BrN_2O_{11}$	42.3	5.0	5.2	14.8	42.4	5.4	5.0	14.6	1640	3340
22	C_6H_4I-*o*	67	175	$C_{19}H_{27}IN_2O_{11} \cdot H_2O$	37.8	4.5	4.6	20.9	37.8	4.8	4.8	20.7	1660	3390
23	C_6H_4I-*p*	57	179	$C_{19}H_{27}IN_2O_{11}$	38.9	4.6	4.8	21.6	38.4	4.8	5.0	21.5	1650	3300
24	$C_6H_4NO_2$-*p*	74	224	$C_{19}H_{27}N_3O_{13}$	45.1	5.4	8.3		44.9	5.6	8.3		1650	3340
25	C_5H_4N	56	175	$C_{18}H_{27}N_3O_{11} \cdot 2H_2O$	43.5	6.3	8.4		43.5	6.2	8.8		1660	3300
26	C_5H_4N-*iso*	54	219	$C_{18}H_{27}N_3O_{11}$	46.9	5.9	9.1		47.0	6.2	8.8		1660	3390
27	$C_6H_3(OMe)_2$-*m,p*	40	213	$C_{21}H_{32}N_2O_{11}$	48.5	6.1	5.4		48.0	6.5	5.4		1650	3400
28	$C_6H_3(CH_2O_2)$-*m,p*	40	173	$C_{20}H_{28}N_2O_{13}$	47.6	5.6	5.6		47.6	5.9	5.5		1655	3400
29	$C_6H_5CH_2$	79	238	$C_{20}H_{30}N_2O_{11}$	50.6	6.4	5.9		50.3	6.1	6.0		1660	3400
30	$(SO_2)^aC_6H_4$-Me-*p*	90	159	$C_{19}H_{30}N_2O_{12}S$	44.7	5.9	5.5	6.3	44.5	5.6	5.0	6.5		3330

$^a SO_2$ instead of CO.

TABLE III

MICROANALYTICAL AND INFRARED ABSORPTION DATA FOR OCTA-*O*-BENZOYLLACTOSE 2-AROYL-2-BENZOYL HYDRAZONES (**31, 32**)

Compound No.	*R*	*Yield (%)*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)* C	H	N	Cl	*Found (%)* C	H	N	Cl	ν_{max}^{Nujol} *(cm^{-1})*	
31	Ph	54	153	$C_{82}H_{64}N_2O_{20}$	70.5	4.5	2.0		70.2	4.5	2.3		1640	1745
32	C_6H_4Cl-*p*	49	140	$C_{82}H_{63}ClN_2O_{20}$	68.8	4.4	1.9	2.5	68.8	4.1	1.6	2.3	1640	1720

TABLE IV

MICROANALYTICAL AND INFRARED ABSORPTION DATA FOR GLYOXAL MONO(ARYLHYDRAZONES) AND THEIR DERIVATIVES[a] (**34–43**)

Compound No.	*R*	*R'*	*Yield (%)*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)* C	H	N	*Found (%)* C	H	N	ν_{max}^{KBr} *(cm^{-1})*	
34	C_6H_4Br-*p*	—	70	142–146	$C_8H_7BrN_2O$	42.3	3.1	12.3	42.3	3.2	12.4	1660	3260
35	C_6H_4I-*p*	—	60	150–152	$C_8H_7IN_2O$	35.1	2.6	10.2	35.1	2.5	9.9	1660	3290
36	Ph	C_5H_4N	62	235–238	$C_{14}H_{13}N_5O$	62.9	4.9	26.2	63.1	5.2	26.1	1640	3300
37	C_6H_4Br-*p*	Ph	72	259–262	$C_{15}H_{13}BrN_4O$	52.2	3.8	16.2	52.5	4.1	16.3	1640	3300
38	C_6H_4Br-*p*	C_6H_4Me-*p*	70	279–281	$C_{16}H_{15}BrN_4O$	53.5	4.2	15.6	53.2	4.4	15.4	1635	3290
39	C_6H_4Br-*p*	C_6H_4OMe-*p*	65	250–253	$C_{16}H_{15}BrN_4O_2$	51.2	4.0	14.9	51.6	4.3	14.9	1635	3290
40	C_6H_4I-*p*	Ph	63	239–241	$C_{15}H_{13}IN_4O$	45.9	3.3	14.3	46.0	3.4	14.3	1640	3300
41	C_6H_4I-*p*	C_6H_4OMe-*p*	65	234–236	$C_{16}H_{15}IN_4O_2$	45.5	3.6	13.3	45.7	3.3	13.2	1630	3250
42	C_6H_4Br-*p*	Ph	72	177–179	$C_{14}H_{13}BrN_4$	53.0	4.1	17.7	53.3	4.1	17.5		3300
43	C_6H_4I-*p*	Ph	70	285–288	$C_{14}H_{13}IN_4$	46.2	3.6	15.4	46.0	3.4	15.6		3300

[a] Some of these compounds were prepared by S. Mancy.

TABLE V

ULTRAVIOLET ABSORPTION DATE FOR SOME OF THE COMPOUNDS DESCRIBED

Compound No.	$\lambda_{\max}^{\mathrm{EtOH}}$ *(nm)*	*log* ε	$\lambda_{\min}^{\mathrm{EtOH}}$ *(nm)*	*log* ε
12	208(sh), 225	3.94, 3.76		
13	220(sh), 235, 300	3.83, 3.94, 3.71	277	3.52
15	215, 255	3.62, 4.07	224	3.50
16	210, 230	3.73, 3.83	220	3.60
18	215, 253	3.53, 4.00	220	3.50
25	223, 263	3.80, 3.67	245	3.62
36	204, 245, 273, 385	4.08, 3.94, 3.91, 4.43	231, 263, 314	3.89, 3.89, 3.49
37	205, 238, 268(sh), 317(sh), 372	4.26, 4.12, 4.06, 3.96, 4.63	217, 295	4.02, 3.81
38	204, 249, 274, 316(sh), 370	4.3, 4.15, 4.07, 3.95, 4.63	233, 296	4.03, 4.84
39	204, 217(sh), 271, 316(sh), 360	4.29, 3.98, 4.18, 4.01, 4.67	239, 304	4.03, 3.98
41	204, 216(sh), 270, 319(sh), 371	4.33, 4.19, 3.98, 4.67	238, 308	4.01, 3.91
42	205, 225(sh), 256, 309, 373	4.1, 3.89, 3.84, 3.79, 4.41	242, 276, 320	3.79, 3.44, 3.79

Anal. Calc. for $C_{75}H_{60}N_4O_{17}$: C, 69.9; H, 4.7; N, 4.2. Found: C, 70.0; H, 4.7; N, 3.9.

Lactose aroylhydrazones (**12–30**). — A solution of lactose (2 mmol) in water (2 mL) was treated with an aroylhydrazine (2 mmol) in ethanol (4 mL), and the mixture was boiled under reflux for 1 h. The resulting solution was concentrated, and then cooled, whereupon the product separated out. It was filtered off, washed with ethanol, dried, and recrystallized from ethanol, to give colorless needles (see Table II).

Octa-O-benzoyllactose (2-aroyl-2-benzoyl)hydrazone (**31**, **32**). — A solution of lactose aroylhydrazone (**12**, or **20**) (0.1 g) in dry pyridine (5 mL) was treated with benzoyl chloride (1 mL), and the mixture was kept overnight at room temperature. The mixture was poured onto crushed ice, and the product that separated out was filtered off, successively washed with water and sodium hydrogencarbonate solution, and dried. It was recrystallized from ethanol, to give colorless needles (see Table III).

Glyoxal mono(arylhydrazones) (**34**, **35**). — To a stirred solution of sodium metaperiodate (0.04 mol) in distilled water (25 mL) was added the D-galactose arylhydrazone (0.01 mol) in portions. The mixture was kept overnight in the dark at room temperature, and the product was filtered off, washed successively with water and aqueous sodium thiosulfate solution, and dried. It was recrystallized from ethanol, to give red needles (see Table IV).

Glyoxal 2-(aroylhydrazone) 1-(arylhydrazone) (**36–41**). — A hot solution of glyoxal mono(arylhydrazone) (0.2 mol) in ethanol (20 mL) was treated with the calculated amount of the aroylhydrazine, and the mixture was heated for 2 min on a steam bath. On cooling, the mixed hydrazone separated out; it was recrystallized from ethanol, to give yellow needles (see Table IV).

Glyoxal 1-(arylhydrazone) 2-(arylhydrazone) (**42**, **43**). — A hot solution of the glyoxal mono(arylhydrazone) (0.2 mol) in ethanol (20 mL) was treated with the calculated amount of the arylhydrazine, and the mixture was treated as in the preceding experiment (see Table IV).

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