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Note

Synthesis and reactions of 2-methyl-5-(D-*arabino*-tetrahydroxybutyl)-3-furoylhydrazine

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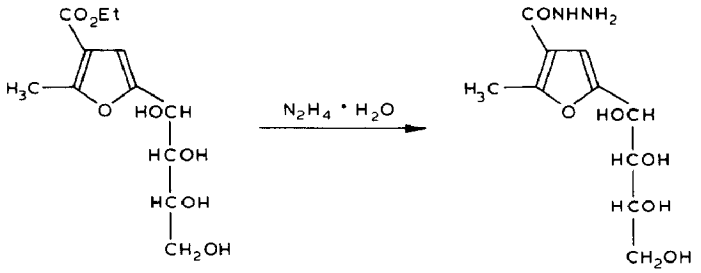
It has been shown that sugars or amino sugars react with β-dicarbonyl compounds in presence of dehydrating agents to give furan or pyrrole derivatives[1–8].

In the present work, 3-ethoxycarbonyl-5-(D-*arabino*-tetrahydroxybutyl)-2-methylfuran[1] (**1**) was boiled under reflux with hydrazine hydrate for one h to give 2-methyl-5-(D-*arabino*-tetrahydroxybutyl-3-furoylhydrazide (**2**) in 56% yield. The i.r. spectrum of this 3-furoylhydrazine derivative showed the disappearance of the ester band and the formation of an amide band at 1650 and 3200 cm^{-1}.



1 **2**

The newly prepared 2-methyl-5-(D-*arabino*-tetrahydroxybutyl)-3-furoylhydrazide (**2**) condensed with a series of aldehydes in acidic medium to give the corresponding *N*-2-methyl-(D-*arabino*-tetrahydroxybutyl)-3-furoyl)hydrazones (**3–9**), which were formed rapidly and in quantitative yields. Their i.r. spectra showed C=N bands at 1590–1605, amide bands at 1640–1650, NH bands at 3170–3220; and OH bands at 3300–3440 cm^{-1}.

Periodate oxidation of hydrazones (**3–9**) afforded the corresponding *N*-(5-formyl-2-methyl-3-furoyl)hydrazones (**10–14**). Their i.r. spectra revealed CHO bands at 1660–1685, C=N bands at 1580–1600, amide bands at 1640–1650, and NH bands at 3140–3180 cm^{-1}. ^{1}H-N.m.r. data (acetone-d_6) of the benzaldehyde derivative **10** and the *o*-hydroxybenzaldehyde hydrazone **13** are listed in Table I.

The aldehydes **10–14** reacted with benzoylhydrazine to give the corresponding hydrazones **15–19**. As expected, the i.r. spectra of these acylhydrazones showed the

disappearance of the aldehydic band, while the amide bands at 1640–1650, the C=N bands at 1590–1610, and the NH bands at 3160–3220 remained.

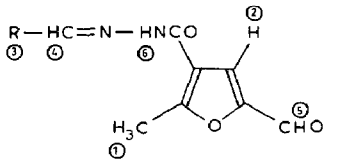
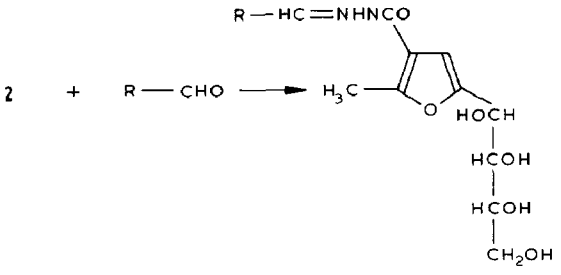


TABLE 1

^{1}H-n.m.r. spectra[a] of *N*-(5-formyl-2-methyl-3-furoyl)hydrazone

	δ p.p.m.					
R	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*
Ph	2.1	7.05	7.55–7.9	7.95	8.48	9.75
C_6H_4-*o*-OH[b]	2.15	7.05	7.35–7.58	7.63	8.00	9.80

[a] I_w acetone-d_6. [b] The OH proton resonated at δ 8.7 p.p.m.

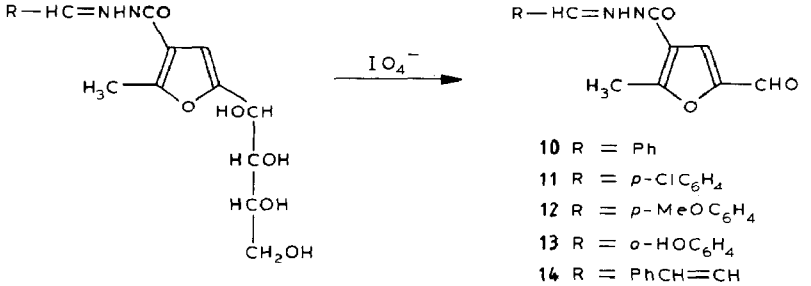


3 R = Ph
4 R = *p*-ClC$_6$H$_4$
5 R = *p*-MeOC$_6$H$_4$
6 R = *o*-HOC$_6$H$_4$

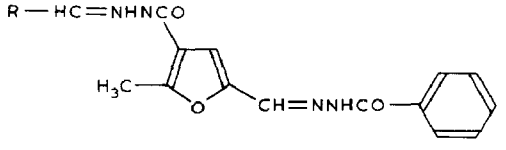
7 R = PhCH=CH

8 R = 

9 R = 



(3–7)



10 R = Ph
11 R = *p*-ClC$_6$H$_4$
12 R = *p*-MeOC$_6$H$_4$
13 R = *o*-HOC$_6$H$_4$
14 R = PhCH=CH
15 R = Ph
16 R = *p*-ClC$_6$H$_4$
17 R = *p*-MeOC$_6$H$_4$
18 R = *o*-HOC$_6$H$_4$
19 R = PhCH=CH

EXPERIMENTAL

General methods. — Melting points were determined on a Kofler block and are uncorrected. I.r. and u.v. spectra were recorded on Unicam SP 1025 and Unicam SP 2000 i.r. spectrophotometers, and a Unicam SP 1750 u.v. spectrophotometer, respectively. ^{1}H-n.m.r. spectra were recorded with a Varian EM-90 MHz n.m.r. spectrophotometer with Me_4Si as the internal standard.

Microanalyses were performed at the Faculty of Science, Cairo University, Cairo, Egypt. Solutions were evaporated under diminished pressure, unless otherwise stated.

*2-Methyl-5-(*D-arabino-*tetrahydroxybutyl)furoylhydrazine* (**2**). — 3-Ethoxycarbonyl-2-methyl-5-(D-*arabino*-tetrahydroxybutyl)furan (10 g) was boiled with hydrazine hydrate (20 mL) for one h. The mixture was then poured onto crushed ice, whereupon the hydrazine separated out, and was filtered off, washed with dilute EtOH and crystallised from EtOH as needles; yield 56%; m.p. 198°, υ_{KBr}, 1050 (CONH), 3200 (NH), and 3490 cm^{-1} (OH). Found C, 45.9, H, 6.1, N, 10.8%, $C_{10}H_{16}N_2O_2$ required C, 46.1; H, 6.2; N, 10.8%.

N′-*Arylidene*-N-[*2-methyl-5-(*D-arabino-*tetrahydroxybutyl)-3-furoyl]hydrazones* (**3–9**). — A solution of 2-methyl-5-(D-*arabino*-tetrahydroxybutyl)-3-furoylhydrazine (1.3 g, 5 mmol) in EtOH (10 mL) containing AcOH (0.1 mL) was treated with the required aldehyde (5 mmol). The mixture was refluxed for one h. After cooling, the required aldehyde hydrazone separated out and was crystallized from EtOH (Table II).

TABLE II

Analytical data for compounds **3–9**

Compound No.	*M.p.*	*Yield (%)*	*Mol. formula*	*Analysis C*	*(%) H*	*Calc/found N*
3	170	58	$C_{17}H_{20}N_2O_6$	58.6	5.7	8.0
				58.6	5.4	8.3
4	180	63	$C_{17}H_{19}ClN_2O_6 \cdot H_2O$	50.9	5.2	7.0
				51.1	5.4	7.0
5	187	53	$C_{18}H_{22}N_2O_7$	57.1	5.8	7.4
				56.8	5.6	7.1
6	185	66	$C_{17}H_{20}N_2O_7$	56.0	5.5	7.7
				55.7	5.2	7.4
7	204	75	$C_{19}H_{22}N_2O_6$	60.9	5.9	7.5
				60.6	6.0	7.8
8	160	65	$C_{15}H_{18}N_2O_7$	53.3	5.3	8.3
				53.2	5.5	8.6
9	190	51	$C_{15}H_{18}N_2O_6S$	50.8	5.1	7.9
				50.5	5.3	8.1

N′-*Arylidene*-N-[*5-formyl-2-methyl-3-furoyl]hydrazones* (**10–14**). — A solution of the *N*′-arylidene-2-methyl-5-[D-*arabino*-tetrahydroxybutyl)-3-furoyl]hydrazone (11 mmol) in distilled water (50 mL) was treated with a solution of $NaIO_4$ (3.4 mmol) in

distilled water (50 mL) dropwise with stirring for 3 h. The formyl derivative that separated out was filtered off, washed with water, dried, and crystallized from EtOH in needles. (Tables I and III).

N′-*Arylidene*-N-*(5-formyl)-2-methyl-3-furoyl)-hydrazines benzoylhydrazones* (**15–19**). — A solution of the *N*′-arylidene-*N*-(5-formyl-2-methyl-3-furoyl)hydrazine (1 mmol) in EtOH (10 mL) was treated with benzoylhydrazine (1 mmol) in EtOH (5 mL). The mixture was refluxed for one h on a water bath, whereby the benzoylhydrazine derivative separated out on cooling, filtered off washed with ethanol and crystallised from $CHCl_3$–EtOH mixture (Table IV).

TABLE III

Analytical data for compounds **10–14**

Compound No.	*M.p.*	*Yield (%)*	*Mol. formula*	*Analysis C*	*(%) H*	*Calc/found N*
10	105	69	$C_{14}H_{12}N_2O_3$	65.6	4.7	10.9
				65.2	4.6	11.2
11	225	63	$C_{14}H_{11}ClN_2O_3$	57.8	3.8	9.6
				57.6	3.5	9.9
12	100	74	$C_{15}H_{14}N_2O_4$	62.9	4.9	9.8
				62.6	4.7	9.6
13	200	67	$C_{14}H_{12}N_2O_4$	61.8	4.4	10.3
				61.7	4.6	10.5
14	115	77	$C_{16}H_{14}N_2O_3$	68.1	5.0	9.9
				68.0	4.8	10.1

TABLE IV

Analytical data for compounds **15–19**

Compound No.	*M.p.*	*Yield (%)*	*Mol. formula*	*Analysis C*	*(%) H*	*Calc/found N*
15	165	33	$C_{21}H_{18}N_4O_3$	67.4	4.8	14.97
				67.2	5.1	15.30
16	220	36	$C_{21}H_{17}N_4O_3Cl$	61.7	4.2	13.7
				61.2	4.5	14.0
17	230	19	$C_{22}H_{20}N_4O_4$	65.3	4.95	13.9
				65.5	5.20	14.2
18	175	42	$C_{21}H_{18}N_4O_4$	64.6	4.6	14.4
				64.3	4.3	14.3
19	200	26	$C_{23}H_{20}N_4O_3$	69.0	5.0	14.0
				69.3	4.9	13.8

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