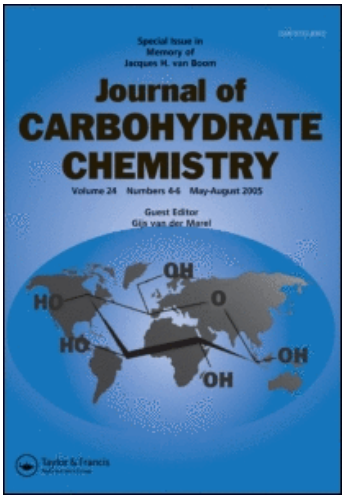


Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Synthesis and Rearrangement of Mono and Bis-(p-Fluorophenyl)Hydrazones of Dehydro-L-Ascorbic Acid

Yeldez El Kilany[a]; Nagwa Rashed[a]; Magda Mansour[a]; El Sayed H. El Ashry[ab]
[a] Chemistry Department Faculty of Science, Alexandria University, Alexandria, Egypt [b] Chemistry Department, Faculty of Applied Sciences and Engineering, Um Alquara University, Makkah, Saudi Arabia

To cite this Article Kilany, Yeldez El , Rashed, Nagwa , Mansour, Magda and Ashry, El Sayed H. El(1988) 'Synthesis and Rearrangement of Mono and Bis-(p-Fluorophenyl)Hydrazones of Dehydro-L-Ascorbic Acid', Journal of Carbohydrate Chemistry, 7: 1, 187 — 198
To link to this Article: DOI: 10.1080/07328308808058913
URL: http://dx.doi.org/10.1080/07328308808058913

J. CARBOHYDRATE CHEMISTRY, 7(1), 187-198 (1988)

SYNTHESIS AND REARRANGEMENT OF MONO AND BIS-(p-FLUOROPHENYL)HYDRAZONES OF DEHYDRO-L-ASCORBIC ACID[1]

Yeldez El Kilany,[+] Nagwa Rashed, Magda Mansour, and El Sayed H. El Ashry[*+]

Chemistry Department
Faculty of Science
Alexandria University
Alexandria, Egypt

Received September 11, 1986 - Final Form February 17, 1988

ABSTRACT

The mono- and bis-(p-fluorophenyl)hydrazones of dehydro-L-ascorbic acid were prepared. Oxidation of the bis(hydrazone) afforded 3,6-anhydro-3-C-(p-fluorophenylazo)-L-xylo-2-hexulosono-1,4-lactone-2-(p-fluorophenyl)hydrazone. Rearrangement of the bis(hydrazone) gave 1-(p-fluorophenyl)-3-(L-threo-glycerol-1-yl)-pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone, whose periodate oxidation gave 3-formyl-1-(p-fluorophenyl)pyrazolin-4,5-dione-3-4-(p-fluorophenyl)hydrazone that upon reduction gave 1-(p-fluorophenyl)-3-hydroxymethylpyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone. The compounds were characterized as their acetates and benzoates.

INTRODUCTION

One of the main objectives in this laboratory is the synthesis of heterocyclic compounds from carbohydrate precursors, whose heterocyclisation may be achieved via their corresponding hydrazones.[2]

The importance of organic fluorine compounds[3] in general has become gradually apparent in the second quarter of this century, as evidenced

---

*To whom enquiries should be addressed.

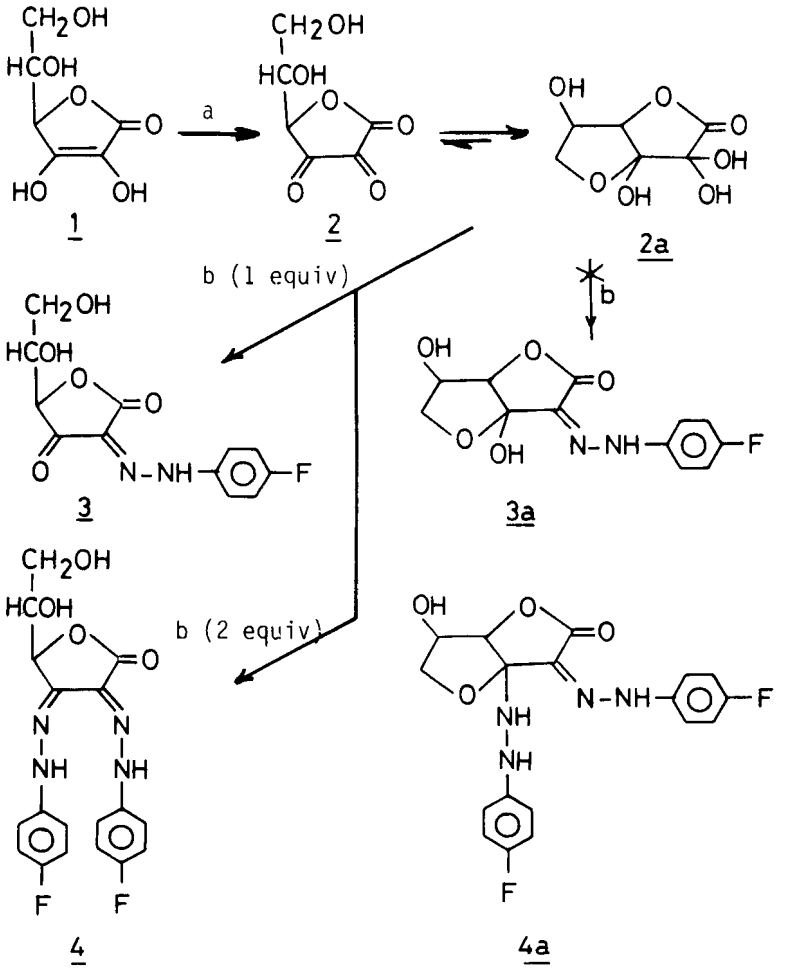
*+Present address: Chemistry Department, Faculty of Applied Sciences and Engineering, Um Alquara University, Makkah, P. O. Box 3711, Saudi Arabia.

for example, in their use as insecticides, and in a continuing interest in their preparation and manufacture. The replacement of hydrogen by fluorine in naturally occurring compounds has been shown to alter their biological properties dramatically. Such observations, combined with the main objectives of this laboratory, undoubtedly had a profound influence on our decision to research the synthesis of some fluorinated hydrazones from carbohydrate precursors and study their heterocyclisation reactions. The carbohydrate precursor used in this study was dehydro-L-ascorbic acid that has been characterized[4] in solution as 3,6-anhydro-L-xylo-hexulono-1,4-lactone-2-hydrate (**2a**, Scheme 1). However, the reaction of **2a** with p-fluorophenylhydrazine did not afford the corresponding derivatives **3a** and **4a**, but it gave **3** and **4**, respectively.

RESULTS AND DISCUSSION

In the present work, two types of hydrazones were prepared from dehydro-L-ascorbic acid as precursors for the synthesis of heterocyclic compounds. Oxidation of L-ascorbic acid (**1**) in aqueous solution gave dehydro-L-ascorbic acid, whose reaction under controlled conditions with a molar equivalent of p-fluorophenylhydrazine, as used by El Ashry et al.[2] for other arylhydrazines, afforded the yellow crystalline product, identified as L-threo-2,3-hexodiulosono-1,4 lactone 2-(p-fluorophenyl)-hydrazone (**3**), and not the hemiacetal **3a**. The structure of the monohydrazone **3** was deduced from its infrared (IR) spectrum which showed two bands in the carbonyl stretching region, one at 1760 cm^{-1} (due to the lactone carbonyl) and the other at 1675 cm^{-1} (due to the C-3 carbonyl). The structure of the p-bromophenyl analog was confirmed by X-ray crystallography.[5]

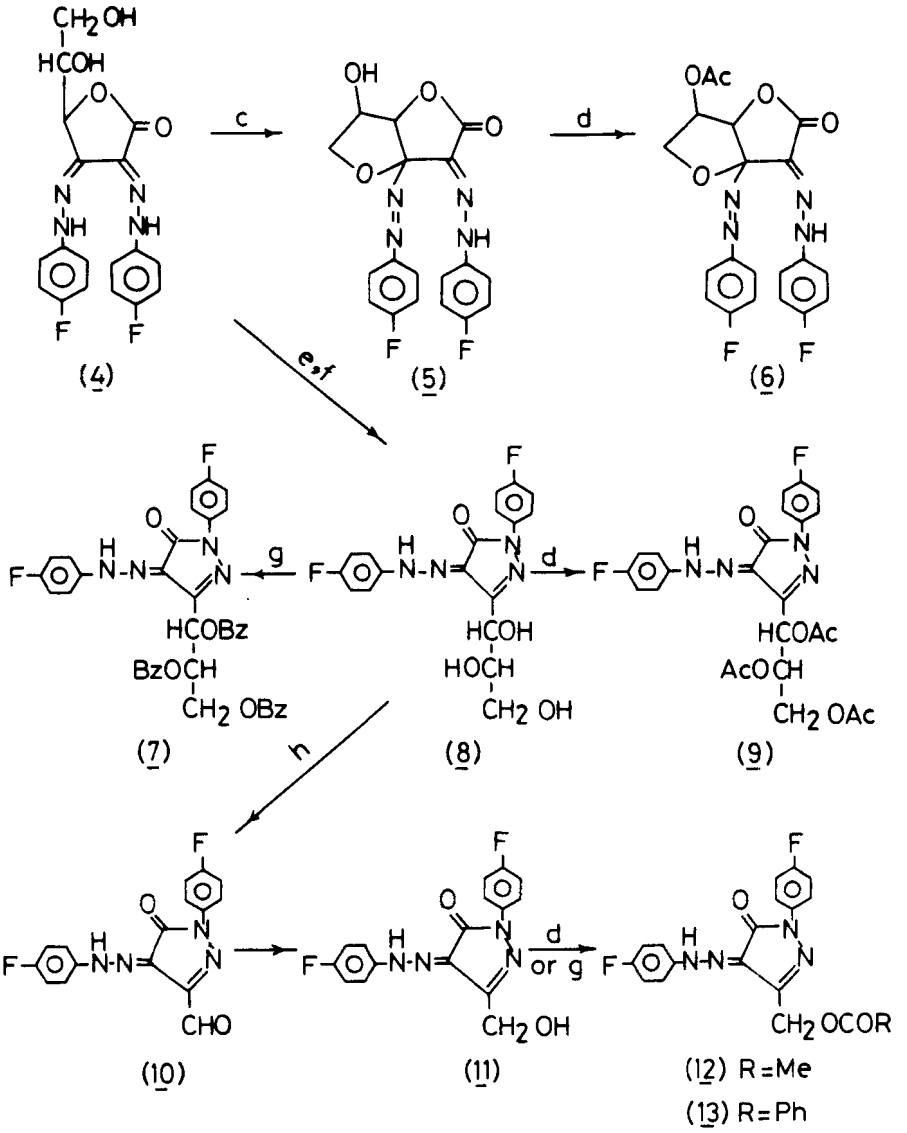
It has been shown that compounds possessing pyrazolinedione ring are of chemotherapeutic interest.[6] Consequently compounds with various substituents on that ring have been prepared.[2] Since the bis(hydrazones) of 1,4-butyrolactones are excellent precursors for their



a) O_2 ; b) p-F-C_6H_4-NH-NH_2

SCHEME 1

syntheses, L-threo-2,3-hexodiulosono-1,4-lactone 2,3-bis(p-fluorophenyl) hydrazone (**4**) was prepared by the reaction of **2** with two molar equivalents of p-fluorophenylhydrazine in the presence of acetic acid. The structure **4** was based on the accepted structure[7] for the phenyl analog. Heating a solution of **4** in sodium hydroxide, followed by acidification, caused its rearrangement to 1-(p-fluorophenyl)-3-(L-



(4) (5) (6) (7) (8) (9) (10) (11) (12) R=Me (13) R=Ph

c) $CuCl_2$; d) Ac_2O/C_5H_5N ; e) NaOH ; f) AcOH

g) $BzCl/C_5H_5N$; h) IO_4^- ; i) $NaBH_4$

SCHEME 2

threo-glycerol-1-yl)-pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone (**8**, Scheme 2). The IR spectrum of **8** showed a band at 1660 cm^{-1} (due to the OCN group), whereas the lactone carbonyl band at 1745 cm^{-1}, as found in precursor **4**, was absent, confirming that the rearrangement had taken place.[2] Acetylation of **8** with acetic anhydride in pyridine yielded 3-(1,2,3-tri-O-acetyl-L-threo-glycerol-1-yl)-1-(p-fluorophenyl)pyrazolin-4,5-dione-4-(p-fluorophenyl) hydrazone (**9**). The IR spectrum of this acetate showed the presence of a band at 1750 cm^{-1} (due to OAc), in addition to a band at 1660 cm^{-1} (due to OCN). Its ^1H NMR spectrum showed the presence of the three acetyl groups as two singlets of six and three-protons intensity at δ2.06 and 2.13, respectively. The H-3 and H-3' of the glycerolyl side chain appeared as two quartets at δ4.4 and 4.2, respectively. The smaller couplings ($J_{2,3}$ = 4.5 Hz and $J_{2,3'}$ = 6 Hz) in each quartet were due to the coupling with H-2, and the larger coupling ($J_{3,3'}$ = 12 Hz) was due to geminal coupling. The H-2 and H-1 appeared as a multiplet and a doublet at δ5.8 and 6.2, respectively. The aromatic protons appeared at δ 7.1-8.0, and the imino proton appeared at δ 13.7. The latter signal disappeared upon deuteration, which confirmed its assignment. Benzoylation of **8** with benzoyl chloride in pyridine yielded 1-(p-fluorophenyl)-3-(1,2,3-tri-O-benzoyl-L-threo-glycerol-1-yl)-pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone (**7**). Its IR spectrum showed bands at 1725 cm^{-1} (due to OBz) and 1660 cm^{-1} (due to OCN). Periodate oxidation of **8** gave 1-(p-fluorophenyl)-3-formyl pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone (**10**). Its IR spectrum showed two bands in the carbonyl frequency region, one at 1670 (due to OCN) and the other at 1700 cm^{-1} (due to the CHO group). The ^1H NMR spectrum of **10** showed the presence of one aldehydic proton as two separate signals at δ9.95 and 9.65 in a ratio of 4:3. The imino proton appeared also as two separate signals at δ13.9 and 13.3, indicating the presence of two species which may be attributed to the possible isomerism of the aldehydic group.

Reduction of the aldehyde **10** with sodium borohydride yielded 1-(p-fluorophenyl)-3-hydroxymethyl pyrazolin-4,5-dione-4-(p-fluorophenyl)-hydrazone (**11**), whose IR spectrum showed the disappearance of the band due to the aldehyde at 1700 cm^{-1} and appearance of a hydroxyl band at 3320 cm^{-1}. Acetylation of **11** with acetic anhydride in pyridine yielded 3-acetoxymethyl-1-(p-fluorophenyl)pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone (**12**), whose IR spectrum showed the presence of a band at 1745 cm^{-1} (due to OAc), in addition to a band at 1660 cm^{-1} (due to OCN). Its ^1H NMR spectrum showed the presence of one acetyl group as a singlet at δ 2.12. The singlet at δ 5.2 was assigned to the CH_2 group. The aromatic protons appeared at δ 7.1-8.0, and the imino proton appeared at δ 13.6. The presence of one acetyl group indicated that there was one hydroxyl group in **11** which resulted by reduction of the aldehydic group, thus confirming the structure of the aldehyde **10** and, consequently, the triol precursor **8**. Benzoylation of **11** with benzoyl chloride in pyridine yielded 3-benzoyloxymethyl-1-(p-fluorophenyl)pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone (**13**), showing in its IR spectrum bands at 1730 cm^{-} (due to OBz) and 1660 cm^{-1} (due to OCN).

It is known[8] that the bis(arylhydrazone) of 1,2-dicarbonyl compounds, as well as sugar bis(hydrazones), can be converted into triazoles by the action of oxidising salts. On the other hand, when 2,3-bis(phenylhyrazono)-butyro-1,4-lactone was boiled with an ethanolic solution of cupric chloride, partial hydrolysis occurred, and 2-phenylhydrazono-3-oxo-butyro-1,4-lactone[9] was obtained. Moreover, when bis(arylhydrazones) of **2** were subjected to similar reaction conditions, only a loss of two hydrogen atoms took place.[8] Thus when the reaction was extended to **4**, a yellow product could be separated and identified as 3,6-anhydro-3-C-(p-fluorophenylazo)-L-xylo-2-hexulosono-1,4-lactone-2-(p-fluorophenyl)hydrazone (**5**). The IR spectrum of **5** showed bands at 1725 and 1740 cm^{-1} (due to the carbonyl lactone), in addition to a band at 3440 cm^{-1} (due to the hydroxyl group). The ^1H NMR spectrum of **5** showed a singlet at δ 5.1 (due to H-4), a multiplet at δ 4.6 (due to H-

5), and multiplet at δ4.2 (due to H-6 and H-6'), in addition to a multiplet at δ7.1-8.0 (the aromatic protons) and a singlet at δ12.0 (NH). The hydroxyl proton appeared as a doublet at δ2.5. Acetylation of **5** with acetic anhydride in pyridine afforded 5-O-acetyl-3,6-anhydro-3-C-(p-fluorophenylazo)-L-xylo-2-hexulosono-1,4-lactone-2-(p-fluorophenyl)hydrazone (**6**) whose IR spectrum showed the presence of a band at 1745 cm^{-1} (due to the OAc) and a band at 1795 cm^{-1} (due to the carbonyl lactone). The ^1H NMR spectrum of the acetate **6** showed the presence of the acetyl group at δ2.0 and the H-4,5,6,6' at δ4.2, 5.3, and 4.2, respectively. The aromatic protons appeared as multiplets at δ7.1-7.9, and the NH appeared at δ12.0. These spectral data and the mode of the reaction confirmed the assigned structure. The formation of **5** from **4** may proceed through **4a**.

EXPERIMENTAL

General procedures. Melting points (uncorrected) were determined with a "Meltemp" apparatus equipped with a 76-mm immersion thermometer. Infrared (IR) spectra were recorded with a Unicam SP 1025 spectrometer. ^1H NMR specta were determined with a Varian EM-390 spectrometer for solutions in chloroform-d or dimethyl sulfoxide-d_6 with tetramethylsilane (Me_4Si) as internal or external reference, respectively. The spectra are reported with chemical shifts downfield from Me_4Si. Microanalyses were carried out in the unit of Microanalysis, Faculty of Science, Cairo University, Cairo, Egypt.

L-threo-2,3-Hexodiulosono-1,4-lactone-2-(p-fluorophenyl)hydrazone (3). A cold solution of **2**, obtained by the oxidation of **1** (1.76 g, 0.01 mol) in water (50 mL) with iodine, was treated with a solution of p-fluorophenylhydrazine hydrochloride (1.63 g, 0.01 mol) in ethanol (25 mL). Sodium acetate (0.8 g, 0.01 mol) and a few drops of glacial acetic acid were then added. The reaction mixture was cooled for 10 min and kept overnight at room temperature, whereby a yellow crystalline product separated out. The product was filtered, washed sequentially with

water, ethanol, and ether, and then dried. It was crystallized from ethanol as yellow crystals (1.7 g, 60% yield): mp 182 °C; ν_{max}^{KBr} 1675 (CO), 1760 (OCO), and 3430 (OH) cm^{-1}. Anal. Calcd for $C_{12}H_{11}FN_2O_5$: C, 51.1; H, 3.9; N, 9.9. Found: C, 51.4; H, 3.6; N, 9.8.

L-threo-2,3-Hexodiulosono-1,4-lactone-2,3-bis(p-fluorophenyl)-hydrazone (4). A solution of 2, obtained by the oxidation of 1 (1.76 g, 0.01 mol) in water (100 mL), was treated with a solution of p-fluorophenylhydrazine hydrochloride (3.26 g, 0.02 mol) in ethanol (50 mL) with sodium acetate (1.6 g, 0.02 mol) and glacial acetic acid (2 mL). The reaction mixture was heated on a boiling water bath for 30 min, whereby the bis(hydrazone) separated out. It was filtered after cooling, washed sequentially with water, ethanol, and ether, and then dried. It was recrystallized from ethanol to give red needles (2.2 g, 56% yield): mp 215 °C; ν_{max}^{KBr} 1745 (OCO), 3315 (NH), 3430 (OH) cm^{-1}. Anal. Calcd for $C_{18}H_{16}F_2N_4O_4$: C, 55.4; H, 4.1; N, 14.4. Found: C, 55.7; H, 4.0; N, 14.3.

1-(p-Fluorophenyl)-3-L-threo-glycerol-1-yl) pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone (8). A suspension of **4** (0.78 g, 2 mmol) in water (25 mL) was heated at 80 °C with 2 N sodium hydroxide (30 mL) for 30 min, whereby the bis(hydrazone) was completely dissolved. The resulting solution was acidified with glacial acetic acid, and the product that separated out was filtered, washed several times with water and ethanol, and dried. It was recrystallized from ethanol in orange crystals (0.55 g, 71% yield): mp 205 °C; ν_{max}^{KBr} 1660 (OCN), 3420 (OH) cm^{-1}. Anal. Calcd for $C_{18}H_{16}F_2N_4O_4$: C, 55.4; H. 4.1; N, 14.4. Found: C, 55.5; H, 4.0; N, 14.0.

1-(p-Fluorophenyl)-3-(1,2,3-tri-O-acetyl-L-threo-glycerol-1-yl)-pyrazolin-4,5-dione-4-(p-fluorophenyl) hydrazone (9). A cold solution of **8** (0.936 g, 2.4 mmol) in dry pyridine (5 mL) was treated with acetic anhydride (5 mL), and the mixture was kept overnight at room temperature. The reaction mixture was poured onto crushed ice, and the product that separated out was filtered, washed sequentially with a

dilute solution of sodium bicarbonate, water, and ethanol. It was recrystallized from ethanol in orange crystals (1.1 g, 89% yield): mp 138 °C; ν_{max}^{KBr} 1660 (OCN) and 1750 (OAc) cm^{-1}; ^1H NMR ($CDCl_3$): δ13.7 (bs, 1H, NH), 7.8, 7.4, and 7.1 (3 m, 8H, aromatic protons), 6.2 (d, 1H, $J_{1,2}$ = 6 Hz, H-1), 5.8 (m, 1H, H-2), 4.4 (q, 1H, $J_{2,3}$ = 4.5 Hz, $J_{3,3'}$ = 12 Hz, H-3), 4.2 (q, 1H, $J_{2,3'}$ = 6 Hz, H-3'), 2.13 (s, 3H, CH_3CO), and 2.06 (s, 6H, 2 CH_3CO). The singlet at δ13.7 disappeared upon addition of D_2O. Anal. Calcd for $C_{24}H_{22}F_2N_4O_7$: C, 55.8; H, 4.3; N, 10.8. Found: C, 55.7; H, 3.9; N, 10.4.

1-(p-Fluorophenyl)-3-(1,2,3-tri-O-benzoyl-L-threo-glycerol-1-yl)-pyrazolin-4,5-dione-4-(p-fluorophenyl) hydrazone (7). A cold solution of **8** (0.936 g, 2.4 mmol) in dry pyridine (5 mL) was treated with benzoyl chloride (0.2 mL), and the reaction mixture was kept for 24 h at room temperature. It was then poured onto crushed ice, and the solid that separated out was filtered and washed repeatedly with water. It was recrystallized from ethanol to give orange needles (1.3 g, 77% yield): mp 148 °C; ν_{max}^{KBr} 1660 (OCN) and 1725 (OBz) cm^{-1}. Anal. Calcd for $C_{39}H_{28}F_2N_4O_7$: C, 66.6; H, 4.0; N, 8.0. Found: C, 66.1; H, 4.0; N, 8.4.

1-(p-Fluorophenyl)-3-formyl-pyrazolin-4,5-dione-4-(p-fluorophenyl)-hydrazone (10). A suspension of **8** (3.9 g, 0.01 mol) in distilled water (50 mL) was treated with a solution of sodium metaperiodate (5.4 g, 0.025 mol) in water (20 mL), and the mixture was stirred at room temperature. The product was filtered off and recrystallized from ethanol to give orange needles (2.3 g, 70% yield): mp 225 °C; ν_{max}^{KBr} 1670 (OCN) and 1700 (CHO) cm^{-1}; ^1H NMR (DMSO-d_6): δ13.9, 13.3 (2 bs, 1 H, NH), 9.95, 9.65 [2 s, (4 : 3), 1H, HCO], 7.9, 7.5, and 7.1 (3 m, 8H, aromatic protons); the signal due to NH disappeared upon addition of D_2O. Anal. Calcd for $C_{16}H_{10}F_2N_4O_2$: C, 58.5; H, 3.1; N; 17.1. Found: C, 58.9; H, 3.2; N, 17.3.

1-(p-Fluorophenyl)-3-hydroxymethyl-pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone (11). A solution of **10** (0.56 g, 1.7 mmol) in a mixture

of N,N-dimethylformamide (15 mL) and methanol (10 mL) was treated with sodium borohydride (0.7 g), and the mixture was stirred at room temperature for 2 h, then left for an additional 4 h. The reaction mixture was diluted with water, and the precipitate was filtered, washed with water, and dried. The product was recrystallized from ethanol to give orange crystals (0.5 g, 84% yield): mp 219 °C; ν_{max}^{KBr} 1660 (OCN) cm^{-1}. Anal. Calcd for $C_{16}H_{12}F_2N_4O_2 \cdot H_2O$: C, 55.2; H, 4.1; N, 16.1. Found: C, 55.2; H, 3.7; N, 15.8.

3-Acetoxymethyl-1-(p-fluorophenyl)pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone (12). A cold solution of **11** (0.835 g, 2.4 mmol) in dry pyridine (5 mL) was treated with acetic anhydride (3 mL), and the mixture was kept overnight at room temperature. The reaction mixture was poured onto crushed ice, the product was filtered, washed repeatedly with water, and dried. It was recrystallized from ethanol to give orange crystals (0.8 g, 90% yield): mp 155 °C; ν_{max}^{KBr} 1660 (OCN) and 1745 (OAc) cm^{-1}; ^1H NMR ($CDCl_3$): δ13.6 (bs, 1H, NH), 7.8, 7.4, and 7.1 (3 m, 8H, aromatic protons), 5.2 (s, 2H, CH_2O), and 2.12 (s, 3H, CH_3CO). Anal. Calcd for $C_{18}H_{14}F_2N_4O_3$: C, 58.1; H. 3.8; N, 15.0. Found: C, 57.6; H, 3.9; N, 14.7.

3-Benzoyloxymethyl-1-(p-fluorophenyl)pyrazolin-4,5-dione-4-(p-fluorophenyl)hydrazone (13). A solution of **11** (0.1 g, 0.28 mmol) in dry pyridine (3 mL) was treated with benzoyl chloride (0.1 mL) and left overnight at room temperature. The reaction mixture was poured onto crushed ice, the product was filtered, washed repeatedly with water, and dried (0.1 g, 77% yield). It was recrystallizsed from ethanol to give orange needles: mp 205-206 °C; ν_{max}^{KBr} 1660 (OCN) and 1730 (OBz) cm^{-1}. Anal. Calcd for $C_{23}H_{16}F_2N_4O_3$: C, 63.6; H, 3.7; N, 12.9. Found: C, 63.2; H, 4.1; N, 12.5.

3,6-Anhydro-3-C-(p-fluorophenylazo)-L-xylo-2-hexulosono-1,4-lactone 2-(p-fluorophenyl)hydrazone (5). A suspension of **4** (1.0 g, 2.56 mmol) and cupric chloride (2.0 g, 14.8 mmol) in ethanol (20 mL) was heated on a boiling water bath for 30 min. The mixture was diluted with hot water

and then cooled. The precipitated product was filtered, washed with water, ethanol, and dried. It was then recrystallized from ethanol to give yellow crystals (0.8 g, 81% yield): mp 185 °C; ν_{max}^{KBr} 1725, 1740 (OCO), and 3440 (OH) cm^{-1}; ^1H NMR ($CDCl_3$): δ12.0 (s, 1H, NH), 7.9, 7.1 (2 m, 8H, aromatic protons), 5.1 (s, 1H, H-4), 4.6 (m, 1H, H-5), 4.2 (m, 2H, H-6, -6'), and 2.5 (d, 1H, OH); the singlet at δ12.0 and the doublet at δ2.5 disappeared upon addition of D_2O. Anal. Calcd for $C_{18}H_{14}F_2N_4O_4$: C, 55.7; H, 3.6; N, 14.4. Found: C, 55.4; H, 3.3; N, 14.8.

5-O-Acetyl-3,6-anhydro-3-C-(p-fluorophenylazo)-L-xylo-2-hexulosono-1,4-lactone 2-(p-fluorophenyl) hydrazone (6). A cold solution of **5** (0.2 g, 0.52 mmol) in dry pyridine (3 mL) was treated with acetic anhydride (3 mL). The mixture was kept overnight at room temperature, then poured onto crushed ice, and the product that separated out was filtered, washed sequentially with a dilute solution of sodium bicarbonate, water, and ethanol. It was recrystallized from ethanol to give yellow needles (0.16 g, 72% yield): mp 175 °C; ν_{max}^{KBr} 1745 (OAc) cm^{-1}; ^1H NMR ($CDCl_3$): δ 12.0 (s, 1H, NH), 7.8, 7.1 (2 m, 8H, aromatic protons), 5.3 (m, 1H, H-5), 5.2 (s, 1H, H-4), 4.2 (m, 2H, H-6,6'), and 2.0 (s, 3H, CH_3CO). Anal. Calcd for $C_{20}H_{16}F_2N_4O_5$: C, 55.8; H, 3.7; N, 13.0. Found: C, 56.2; H, 4.0; N, 12.9.

REFERENCES

1. Heterocycles from Carbohydrate precursors, Part 37. For Part 36, see E. S. H. El Ashry, Y. El Kilany and A. Mousaad, and M. El Habrouk, Ar. J. Sci. Eng., in press.

2. E. S. H. El Ashry in Ascorbic Acid: Chemistry, Metabolism and Uses, P. A. Seib and B. M. Tolbert, Eds, Advances in Chemistry Series, Vol. 200, American Chemical Society, Washington, DC, 1982; Y. El Kilany, H. Abdel Hamid, and E. S. H. El Ashry, Carbohydr. Res., **125**, 77 (1984); E. S. H. El Ashry, Y. El Kilany, and C. Schuerch, Abstr. Papers Am. Chem. Soc. 182nd National Meeting, New York, Carb-31 (1981); E. S. H. El Ashry, M. M. A. Abdel Rahman, Y. El Kilany, and A. Amer, Carbohydr. Res., **86**, C5 (1981); E. S. H. El Ashry, Y. El Kilany, and F. Singab, Carbohydr. Res., **56**, 93 (1977); **67**, 415 (1980); **79**, 151 (1980); **82**, 25 (1980).

3. A. A. E. Penglis, Adv. Carbohydr. Chem. Biochem., **38**, 195 (1981).

4. K. Pfeilsticker, F. Marx, and M. Bockisch, Carbohydr. Res., **45**, 269 (1975).

5. J. Hvoslef and S. Nordenson, Acta Crystallogr., Sect. B, **32**, 448 (1976).

6. F. S. G. Soliman and R. M. Shafik, Pharmazie, **30**, 436 (1975); H. G. Garg, J. Med. Chem., **15**, 446 (1972).

7. P. Pollet and S. Gelin, Tetrahedron, **36**, 2955 (1980).

8. H. S. El Khadem and E. S. H. El Ashry, J. Chem. Soc., 2251 (1968).

9. H. S. El Khadem, Z. M. El Shafei, E. S. H. El Ashry, and M. El-Sadek, Carbohydr. Res., **49**, 185 (1976).