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SYNTHESIS OF 3-SUBSTITUTED FURANS FROM 3-*C*-SUBSTITUTED HEXULOSES*

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ABSTRACT

Addition of Grignard reagents to the hexodiulose obtained from oxidation of 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose gave the corresponding 3-*C*-substituted hexuloses. A simple procedure for the direct conversion of these *C*-alkylated or -arylated hexuloses (heating with pyridinium chloride) to new 3-substituted 5-hydroxymethyl-2-furancarboxaldehydes is described.

INTRODUCTION

The 3-substituted furyl radical is the structural unit of various compounds that are of biological interest, for instance the natural defense substances of animals[1] and terpenes[2]. It is also a component of natural products and drug analogs[3]. The syntheses of 3-substituted furans[4] are generally multi-step procedures and often use substrates that are not readily available. Recently, new processes have been described starting from paraldehyde[5] or from heterocycles[6].

For a long time, it has been known that hexoses can be dehydrated to 5-hydroxymethyl-2-furancarboxaldehyde[7]. We previously demonstrated that treatment of hexoses (D-fructose for instance) with pyridinium salts, especially pyridinium chloride, is an easy and high-yielding procedure for preparing this furaldehyde[8]. We extended[9] this result to obtain a one-step access to a furan substituted by a chiral chain, namely, 5-(D-*glycero*-1,2-dihydroxyethyl)-2-furaldehyde prepared from sedoheptulosan, a natural heptulose. As the treatment of D-fructose with pyridinium chloride was shown to be a mild and high-yielding process giving a furan substituted at C-2 and -5, we made the assumption that the same reaction, applied to a *C*-3-branched-D-fructose, would provide a direct access to furans substituted at C-3 (see Scheme 1).

*Taken, in part, from the Docteur-Ingénieur Thesis of Catherine Fayet (Université de Clermont-Ferrand, June 26th, 1984).

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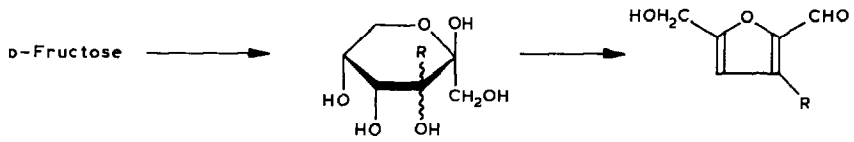
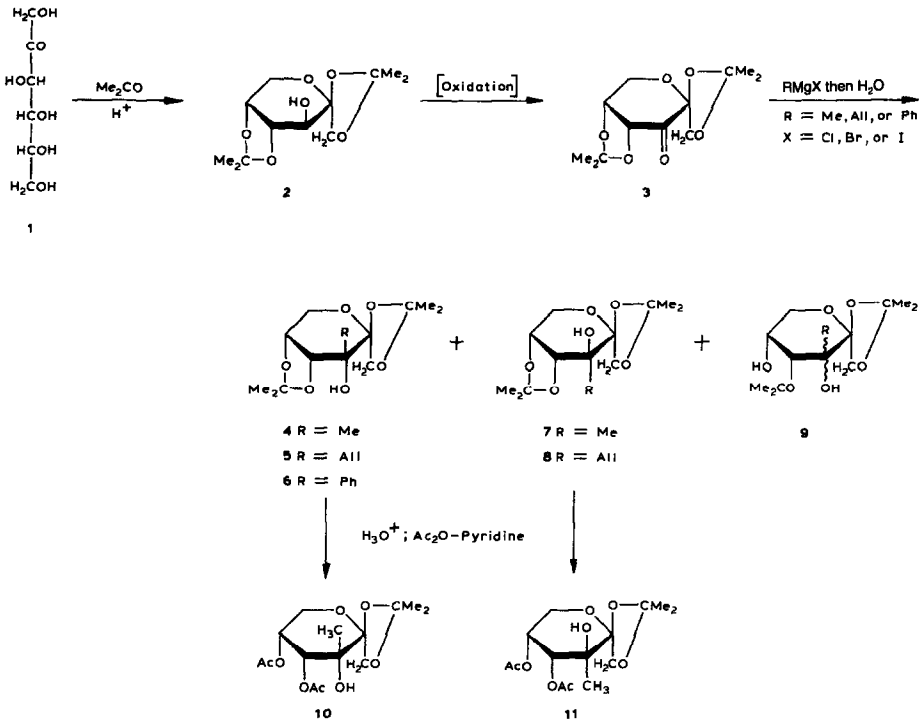


Scheme 1.

RESULTS AND DISCUSSION

The introduction of a substituent at C-3 of D-fructose (**1**) had been achieved by nucleophilic addition of Grignard reagents on the hexodiulose **3**, obtained in two steps from **1**. *O*-Isopropylidenation of **1** gave 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**2**) according to Brady[10]. This compound had been previously oxidized with dimethyl sulfoxide–acetic anhydride[11], but we found the procedure using pyridinium chlorochromate[12] quite convenient. In our hands, the latter reaction proceeded slower than that using pyridinium dichromate–acetic anhydride[13], but gave comparable yields.

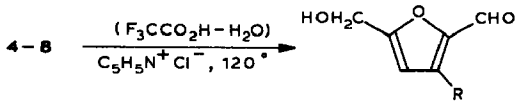


The addition of Grignard reagents to keto derivatives of monosaccharides is known (see, for instance, ref. 14 and references cited therein) to give addition, or reduction, or enolization depending on the experimental procedure. In the presence of a cyclic acetal, a ring opening of this protecting group can also be observed[15]. The action, at 0°, of methylmagnesium iodide in anhydrous ether on hexodiulose **3** gave a mixture of three compounds. One of them was very minor, but its proportion could be increased by repeating the reaction at higher temperature (reflux) in the presence of an excess of the Grignard reagent; it was isolated and its ^{1}H-n.m.r. spectrum showed [solvent ($^2H_6$)Me_2SO] a singlet and a doublet which were respectively due to a tertiary and a secondary hydroxyl group (which disappeared after addition of D_2O); a signal corresponding to a *tert*-butyl group was also observed. Thus, structure **9** was tentatively assigned and was confirmed by acetylation to give a compound, the ^{1}H-n.m.r. spectrum of which showed a multiplet at low field (δ 5.25) corresponding to H-5 (acetylation at O-4 would have given a completely different signal). The major derivatives were separated as pure crystalline compounds for which structures **4** (yield 30%) and **7** (yield 20%) are proposed. They correspond to both possible spatial orientations for the addition of the Grignard reagent. Structure **4** was initially assigned on the basis of its higher concentration due to the favored attack on the less-hindered side of the carbonyl group. This was confirmed by comparison (physical constants and ^{1}H- and ^{13}C-n.m.r. spectra) with the data published by Vass *et al.*[16] for the unique compound prepared by Raney nickel desulfuration of the corresponding dithiane, obtained from stereospecific addition of the dithianyl carbanion to hexodiulose **3**. The assignments are also in accordance (except for the melting points) with the data published[17] for the 3-*C*-methyl-β-D-fructopyranose (**7**) derivative. We can point out that the resonance of CH_3-3 occurred at a field higher for **4** than that of **7**. The molecular rotation was also found to be more negative ([M] −375) for **4** (D-*ribo* configuration) than ([M] −260) for **7** (D-*arabino* configuration)[16].

The general application of the method was tested by use of Grignard reagents for introducing an ethylenic double-bond and a phenyl group. In the case of the addition of allylmagnesium chloride, only the two expected stereoisomers were obtained, in a good yield, and separated as pure **5** (yield 40%) and **8** (yield 16%). The approximate proportion between them (~7:~3) showed that the reaction probably reflects a steric control approach and it does not sustain the assumption[17] that the poor stereoselectivity of the reaction with methylmagnesium iodide (~3:~2) could be due to an interaction of the magnesium atom of the complex with the glycosidic oxygen atom. This was confirmed by the addition of phenylmagnesium bromide to hexodiulose **3**, which gave a good yield of a unique derivative, isolated as a pure crystalline compound for which structure **6** was assigned. The presence of its stereoisomer could not be detected either by t.l.c. or by n.m.r. spectroscopy of the crude product.

In order to dehydrate the free sugars, compounds **4–8** were completely deprotected with 1:9 trifluoroacetic acid–water at room temperature. Regio-

selective cleavage of the 4,5-*O*-isopropylidene group was also possible with 1:3 acetic acid–water at room temperature. Starting respectively from compounds **4** or **7**, freeze-drying of the solution and acetylation (acetic anhydride–pyridine at 0°) gave **10** and **11**. The position of OAc-4 and OAc-5 was easily deduced from the ^{1}H-n.m.r. spectra.



12 R = Me
13 R = All
14 R = Ph

Heating of the totaly deprotected sugars obtained from **4–8** with anhydrous pyridinium chloride at 120° for 30 min afforded the furans **12–14** with fairly good yields (50–55%). The experimental conditions did not allow any distinction between the behavior of stereoisomers D-*psico* or D-*fructo* (or **10, 11**). Furthermore, the same furans were prepared directly by starting from the mixtures of **4,7** (or **10, 11**) **5,8**; or **6** still protected with acetal functions. In a first step, pyridinium chloride, like other pyridinium salts, is thus able to catalyze deacetalation as well as acetalation[15]; as soon as the free sugar is liberated, the high dehydrating power of the reagent[8] leads rapidly to furans, probably through the mechanism normally assumed for this type of reaction[7], which involves the enediol form of the sugar. It is interesting to note that the dehydration of D-fructose substituted at C-3 was as easy as that of D-fructose itself[8]. No formation of tar or by-products was detected in significant amounts. The furans **12–14** were identified by ^{1}H- and ^{13}C-n.m.r. spectroscopy. Comparison of their ^{1}H-n.m.r. spectra with that for 5-hydroxymethyl-2-furaldehyde[8] showed *inter alia* the disappearance of the doublet at δ 7.25 corresponding to H-3 and the persistance of a signal (doublet for 5-hydroxymethyl-2-furaldehyde, singlet for **12–14**), neat at δ 6.60, due to H-4. The ^{13}C-n.m.r. spectra also indicated that substitution at C-3 leads to a high-field shift of the C-6 signal.

In conclusion, this work demonstrates that readily available substituted derivatives of D-fructose are readily and rapidly dehydrated to furans with a mild and very simple procedure using anhydrous pyridinium chloride. The method can be directly applied to the crude mixture of stereoisomers (if any) of protected sugars obtained by the addition of Grignard reagents to an hexodiulose. As various substituents at C-3 are possible, this method opens a route to numerous furans, thus available as synthons, from D-fructose, with a few steps.

EXPERIMENTAL

General methods. — Optical rotations were measured with a Perkin–Elmer 141 polarimeter for solution in 1-dm tubes. ^{1}H-N.m.r. spectra were recorded with a Varian T 60 spectrometer and ^{13}C-n.m.r. spectra with a Jeol FX 60 spectrometer. Column chromatography was performed with Kieselgel 60 Merck and t.l.c. with precoated plates (Merck 5724), with detection by charring with H_2SO_4. Evaporations were performed under diminished pressure.

*1,2:4,5-Di-*O*-isopropylidene-*D*-fructopyranose* (**2**). — According to Brady[10], acetonation of D-fructose with 0.5% H_2SO_4 in acetone leads to 1,2:4,5-di-*O*-isopropylidene-D-fructopyranose; in contrast, with a higher concentration of H_2SO_4, 2,3:4,5-di-*O*-isopropylidene-D-fructose is obtained. D-Fructose (36 g, 0.2 mole) was suspended in acetone (700 mL) containing H_2SO_4 (3.5 mL). Vigorous stirring was continued for 2 or 3 h, until the starting material was dissolved. A solution of NaOH (11 g) in water (100 mL) was then added. After removal of acetone under diminished pressure, the aqueous layer was extracted with dichloromethane. The extracts were washed with water, dried, and evaporated to yield a white crystalline solid. One recrystallization from ether gave pure **2** as white needles (18 g, 35%), m.p. 117°, $[\alpha]_D^{20}$ +154.8° (*c* 0.1, acetone), +146.6° (chloroform); lit.[10] m.p. 119°, $[\alpha]_D$ +148.5° (acetone).

*1,2:4,5-Di-*O*-isopropylidene-β-*D*-erythro-2,3-hexodiulo-2,6-pyranose* (**3**). — *Method A.* A solution of **2** (5 g) in anhydrous benzene was stirred vigorously and refluxed. Pyridinium chlorochromate (15 g) was then added in small portions until monitoring by t.l.c. indicated disappearance of all starting material. The reaction mixture was filtered through Celite and the solvent removed. The crude solid product was crystallized from heptane to yield **3** as a pure, white crystalline powder (3 g, 60%), m.p. 102°, $[\alpha]_D^{20}$ −119.6° (*c* 0.1, chloroform); lit.[12] m.p. 102–103°, $[\alpha]_D$ −121° (chloroform).

Method B. Acetic anhydride (1.2 g) was added to a vigorously stirred solution of pyridinium dichromate (1 g) in dichloromethane. A solution of **2** (1 g) in dichloromethane was then added, and the mixture was refluxed for 2 h. T.l.c. indicated that the reaction was complete. The mixture was filtered through a Celite chromatography column to obtain the chromium salts, the product eluted with ethyl acetate, and the filtrate concentrated to dryness to give a syrup. Crystallization from heptane yielded the diulose **3** identified as described under Method A (0.6 g, 60%).

Addition of Grignard reagents. Synthesis of C-*3-branched* D-*hexulose derivatives.* — To a suspension of Mg turnings in anhydrous ether was added, at 0°, a solution of alkyl or aryl halide [iodomethane (8.5 g, 0.06 mol), 3-chloropropene (4.6 g, 0.06 mole), or bromobenzene (9.42 g, 0.06 mole)] in anhydrous ether. The mixture was stirred for 0.5 h, and then added dropwise to a solution of **3** (5.2 g, 0.02 mole) in ether until t.l.c. (1:1 ethyl acetate–hexane) indicated completion of the reaction. A saturated aqueous solution of $(NH_4)_2SO_4$ was added. The aqueous

layer was extracted with ether. The organic extracts were dried and evaporated. The syrupy residue was chromatographed on a silica gel column (1:4 ethyl acetate–hexane) to afford pure products.

When an excess of the Grignard reagent was added and the etherate solution boiled under reflux, traces of some minor compounds were detected by t.l.c. They derived from the ring-opening of the 4,5-*O*-isopropylidene group, and among them compound **9** was isolated by column chromatography.

*1,2:4,5-Di-*O*-isopropylidene-3-*C*-methyl-β-*D*-psicopyranose* (**4**). — Yield 30%, m.p. 80–81°, $[\alpha]_D^{20}$ −137° (*c* 0.1, chloroform); lit.[16] m.p. 91–92, $[\alpha]_D$ −129° (chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 4.32 and 3.95 (2 d, $J_{1,1'}$ 9.6 Hz, H-1,1'), 2.53 (s, OH-3), 1.60, 1.50, 1.45, and 1.40 [4 s, $C(CH_3)_2$] and 1.25 (s, CH_3); ^{13}C-n.m.r. ($CDCl_3$): δ 71.92 (C-1), 108.95 (C-2), 75.63 (C-3), 71.43 and 70.43 (C-4,5), 59.77 (C-6), 112.34 and 107.07 (CMe_2), 25.60–25.79, 25.92, and 26.31 [$C(CH_3)_2$], and 20.27 (CCH_3).

Anal. Calc. for $C_{13}H_{22}O_6$: C, 56.93; H, 8.03; O, 35.04. Found: C, 56.89; H, 8.02; O, 34.32.

*1,2:4,5-Di-*O*-isopropylidene-3-*C*-methyl-β-*D*-fructopyranose* (**7**). — Yield 20%, m.p. 76°, $[\alpha]_D^{20}$ −95° (*c* 0.1, chloroform); lit.[17] m.p. 84–86°, $[\alpha]_D$ −95° (chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 4.23 and 3.90 (2 d, $J_{1,1'}$ 9.6 Hz, H-1,1'), 2.63 [s, $C(CH_3)_2$]; ^{13}C-n.m.r. ($CDCl_3$): δ 71.27 (C-1), 108.90 (C-2), 77.90 (C-3), 73.03 and 72.21 (C-4,5), 62.63 (C-6), 110.45 and 105.97 (CMe_2), 24.82, 25.79, 25.99, and 26.44 [$C(CH_3)_2$], and 22.19 (CCH_3).

Anal. Calc. for $C_{13}H_{22}O_6$: C, 56.93; H, 8.03; O, 35.04. Found: C, 56.30; H, 8.05; O, 34.92.

*3-*C*-Allyl-1,2:4,5-di-*O*-isopropylidene-β-*D*-psicopyranose* (**5**). — Yield 40%, m.p. 65°, $[\alpha]_D^{20}$ −143° (*c* 0.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 4.40 and 3.96 (2 d, $J_{1,1'}$ 9.6 Hz, H-1,1'), 2.63 (s, OH-3), 6.05, 5.10, 4.96, and 1.32 [4 s, $C(CH_3)_2$]; ^{13}C-n.m.r. ($CDCl_3$): δ 71.08 (C-1), 108.83 (C-2), 72.32, 71.08, and 71.47 (C-3,4,5), 59.71 (C-6), 112.25 and 106.82 (CMe_2), 26.38, 26.05, 25.66, and 2540 [$C(CH_3)_2$], 40.67, 133.58, and 117.79 (CH_2–CH=CH_2).

Anal. Calc. for $C_{15}H_{24}O_6$: C, 60.00; H, 8.00; O, 32.00. Found: C, 59.43; H, 7.95; O, 32.65.

*3-*C*-Allyl-1,2:4,5-di-*O*-isopropylidene-β-*D*-fructopyranose* (**8**). — Yield 16%, syrup, $[\alpha]_D^{20}$ +149° (*c* 0.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 4.27 and 3.90 (2 d, $J_{1,1'}$ 9.6 Hz, H-1,1'), 2.77 (s, OH-3), 5.27, 5.08, 5.03, and 2.50 (3 m and d, CH_2–CH=CH_2), 1.50, 1.45, 1.32 [3 s, $C(CH_3)_2$]; ^{13}C-n.m.r. ($CDCl_3$): δ 72.38 (C-1), 109.15 (C-2), 74.07, 72.70, and 72.83 (C-3,4,5), 63.93 (C-6), 109.61 , and 105.39 (CMe_2), 26.57, 26.25, 25.34, and 24.62 [$C(CH_3)_2$], 38.79, 132.54, and 119.16 (CH_2–CH=CH_2).

Anal. Calc. for $C_{15}H_{24}O_6$: C, 60.00;, H, 8.00; O, 32.00. Found: C, 59.99; H, 7.98; O, 33.27.

*1,2:4,5-Di-*O*-isopropylidene-3-*C*-phenyl-β-*D*-fructopyranose* (**6**). — Yield 50%, m.p. 94–95°, $[\alpha]_D^{20}$ −171° (*c* 0.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 3.98 and

3.70 (2 d, H-1,1'), 3.13 (s, OH-3), 4.73 (d, H-5), 7.50 (m, C_6H_5), 1.62, 1.48, 1.35, and 1.16 [4 s, $C(CH_3)_2$]; ^{13}C-n.m.r. ($CDCl_3$): δ 71.80 (C-1); 109.15 (C-2), 76.43, 72.38, and 73.42 (C-3,4,5), 59.51 (C-6), 113.05 and 106.94 (CMe_2), 127.41, 127.61, and 139.04 (Ph), 23.54, 25.66, 26.35, and 26.57 [$C(CH_3)_2$].

Anal. Calc. for $C_{18}H_{24}O_6$: C, 64.29; H, 7.14; O, 28.57. Found: C, 64.44; H, 7.11; O, 28.96.

*4-*O*-tert-Butyl-1,2-*O*-isopropylidene-3-*C*-methyl-β-*D*-psicopyranose* (**9**). — Syrup, ^{1}H-n.m.r. ($CDCl_3$): δ 4.1 (dd, $J_{1,1'}$ 9.4 Hz, H-1,1'), 1.48 and 1.43 [2 s, $C(CH_3)_2$], 1.3 [s, $C(CH_3)_3$], and 1.18 (s, CH_3); [($^2H_6$)Me_2SO]: δ 5.46 (d, OH-5) and 5.06 (s, OH-3) (these latter two signals disappeared after addition of D_2O), 1.37 [2 s, $C(CH_3)_2$], 1.22 [s, $C(CH_3)_3$], and 1.06 (s, CH_3)

Selective deisopropylidenation of the diacetals **4** *and* **7**, *to monoacetals* **10** *and* **11**, *respectively.* — A suspension of the diacetal **4** or **7** in 1:3 acetic acid–water was stirred at room temperature until dissolution was complete (~1 h). T.l.c. (1:1 ethyl acetate–petroleum ether) indicated a slow migrating product. The solution was freeze-dried and acetylated conventionally to give **10** or **11** (yield 70%).

*4,5-Di-*O*-acetyl-1,2-O-isopropylidene-3-*C*-methyl-β-*D*-psicopyranose* (**10**). — Syrup, ^{1}H-n.m.r. ($CDCl_3$): δ 4.40 and 3.96 (2 d, H-1,1'), 3.20 (s, OH-3), 5.13 (d, H-4), 5.33 (m, H-5), 4.23 and 3.76 (2 d, H-6,6'), 1.20 (s, CH_3), 1.48 [2 s, $C(CH_3)_2$], 2.17 and 2.10 (2 s, $COCH_3$); ^{13}C-n.m.r. ($CDCl_3$): δ 69.26 (C-1), 108.25 (C-2), 73.62, 71.93, and 70.93 (C-3,4,5), 62.37 (C-6), 112.85 (CMe_2), 25.73 and 26.31 [$C(CH_3)_2$].

Anal. Calc. for $C_{14}H_{22}O_8$: C, 52.83; H, 6.92; O, 40.25. Found: C, 52.76; H, 6.88; O, 40.18.

*4,5-Di-*O*-acetyl-1,2-O-isopropylidene-3-*C*-methyl-β-*D*-fructopyranose* (**11**). — Syrup, ^{1}H-n.m.r. ($CDCl_3$): δ 3.10 (s, OH-3), 5.23 (m, H-4), 5.23 (m, H-5), 3.93 (dd, H-6,6'), 1.52 (s, CH_3), 1.37 and 1.43 [2 s, $C(CH_3)_2$], 2.13 and 2.06 (2 s, OAc); ^{13}C-n.m.r. ($CDCl_3$): δ 69.20 (C-1), 108.31 (C-2), 72.25, 70.24, 70.95 (C-3,4,5), 61.92 (C-6), 112.66 (CMe_2), 26.05 and 27.22 [$C(CH_3)_2$].

Anal. Calc. for $C_{14}H_{22}O_8$: C, 52.83; H, 6.92; O, 40.25. Found: C, 52.98; H, 7.01; O, 40.20.

Preparation of furans **12, 13**, *and* **14**. — Compound **4, 5, 6, 7**, or **8** (1–5 g) and crystalline anhydrous pyridinium chloride (1–5 g) were mixed and heated (oil bath at 120°) during 2 h. After being cooled at room temperature, the mixture was directly extracted with ethyl acetate. The organic layer was dried and evaporated to give the crude product which was further purified on a silica gel column (1:1 ethyl acetate–hexane) to yield the pure furan derivative.

5-Hydroxymethyl-3-methyl-2-furaldehyde (**12**). — Yield 50%, ^{1}H-n.m.r. ($CDCl_3$): δ 6.38 (s, H-4), 4.67 (s, CH_2-6), 4.08 (s, OH), 9.60 (s, CHO), and 2.37 (s, CH_3-3); ^{13}C-n.m.r. ($CDCl_3$): δ 177.4 (CHO), 160.4 (C-2), 136.2 (C-3), 112.8 (C-4), 148.1 (C-5), 57.4 (C-6), and 10.4 (CH_3-3).

Anal. Calc. for $C_7H_8O_3$: C, 60.00; H, 5.71; O, 34.29. Found: C, 59.05; H, 5.76; O, 34.42.

3-Allyl-5-hydroxymethyl-2-furaldehyde (**13**). — Yield 55%, ^{1}H-n.m.r.

($CDCl_3$); δ 6.60 (s, H-4), 4.63 (s, CH_2-6), 4.17 (s, OH), 9.70 (s, CHO), 1.92 (d, CH_2, allyl); ^{13}C-n.m.r. ($CDCl_3$): δ 177.4 (CHO), 160.7 (C-2), 136.9 (C-3), 107.2 (C-4), 146.2 (C-5), 57.3 (C-6), 18.8, 119.1, and 134.2 (CH_2–CH=CH_2).

Anal. Calc. for $C_9H_{10}O_3$: C, 65.06; H, 6.02; O, 28.92; Found: C, 65.20; H, 6.03; O, 29.10.

5-Hydroxymethyl-3-phenyl-2-furaldehyde (**14**). — Yield 45%, m.p. 46–48°; ^{1}H-n.m.r. ($CDCl_3$): δ 6.65 (s, H-4), 4.73 (s, H_2-6), 3.97 (s, OH), 9.50 (s, CHO), and 7.45 (m, C_6H_5); ^{13}C-n.m.r. ($CDCl_3$): δ 177.8 (CHO), 160.5 (C-2), 140.6 (C-3), 110.8 (C-4), 146.8 (C-5), 57.5 (C-6), 128.9, 129.3, and 130.4 (C_6H_5).

Anal. Calc. for $C_{12}H_{10}O_3$: C, 71.29; H, 4.95; O, 23.76. Found: C, 70.47; H, 5.05; O, 24.21.

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