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Formation of Aromatic Compounds from Carbohydrates. Part III.* Reaction of D-Glucose and D-Fructose in Slightly Acidic, Aqueous Solution

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The reaction of D-fructose in aqueous solutions of pH 4.5 at 96 or 160 C° yielded 5-(hydroxymethyl)-2-furaldehyde (*1*), 5,5′-oxy-dimethylene-bis(2-furaldehyde) (*2*), 5-(acetoxymethyl)-2-furaldehyde (*3*), 1-(2-furyl)-2-hydroxyethanone (*4*), 1,2-benzenediol (*5*), 1,2,3-benzenetriol (*6*), 6,7-dihydroxy-1(3*H*)-isobenzofuranone (*7*), 3-methyl-1,2,benzenediol (*8*), 4-methyl-1,2-benzenediol (*9*), 4-methyl-1,2,3-benzenetriol (*10*), 3-hydroxy-6-hydroxymethyl-2-methyl-4*H*-1-benzopyran-4-one (*11*), 1-(3,4-dihydroxy-6-methylphenyl)-2-hydroxyethanone (*12*), 3,4-dihydroxybenzaldehyde (*13*), and 2-methylbenzofuran-5,6-diol (*14*). The reaction of D-glucose at pH 4.5 and 96 °C gave the same compounds but in lower yields. Compounds *7*, *11*, *12*, and *14* as well as the synthesised 4,5-dihydroxy isomer of *7* seem to be new compounds. The ^{1}H NMR-spectra of *o*-dihydroxy- and *o*-dimethoxy-1(3*H*)-isobenzofuranones are discussed.

Acid-catalyzed dehydration reactions of D-fructose and D-glucose in aqueous solution have been extensively studied [1–4] (for a recent summary, see Ref. 1), primarily with respect to nonenzymatic browning and the formation of flavours in foods. 5-(Hydroxymethyl)-2-furaldehyde (*1*), 1-(2-furyl)-2-hydroxyethanone (*4*), levulinic acid and formic acid are long-known major products of these reactions. More recently Shaw *et al.*[3,4] also identified 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, 2-acetyl-3-hydroxyfuran (isomaltol), 5-methyl-2-furaldehyde, and 3,4,5-trihydroxy-3,5-hexadiene-2-one (acetylformoin) as minor products from acid treatment of D-fructose.

We recently isolated a series of cyclic degradation products, including many catechols and chromones, from the treatment of hexuronic acids and pentoses in slightly acidic, aqueous solution.[5,6] In the present investigation, we have studied the possible formation of phenolic compounds by the similar treatment of D-fructose and D-glucose.

RESULTS AND DISCUSSION

The ethyl acetate soluble part of the reaction mixture from treatment of D-glucose and D-fructose yielded the compounds given in Scheme 1 after chromatographic fractionation. These included the furan derivatives *1*, *2* and *4* previously obtained from hexoses [1,2] and the phenols *5*, *6* and *8* resulting from hexuronic acids under similar conditions.[5] The yields and chromatographic properties of the compounds are given in Table 1. It was shown that none of these compounds originated from solvents or chromatographic material or were present as impurities in the original carbohydrates.

Compounds *1*, *3*, *5*, *6*, *8*, *9*, *10*, and *13* were identical (IR, MS, NMR) with authentic samples and the identification of compounds *2* and *4* was based on NMR, MS and a comparison of their melting points with those previously reported.[2]

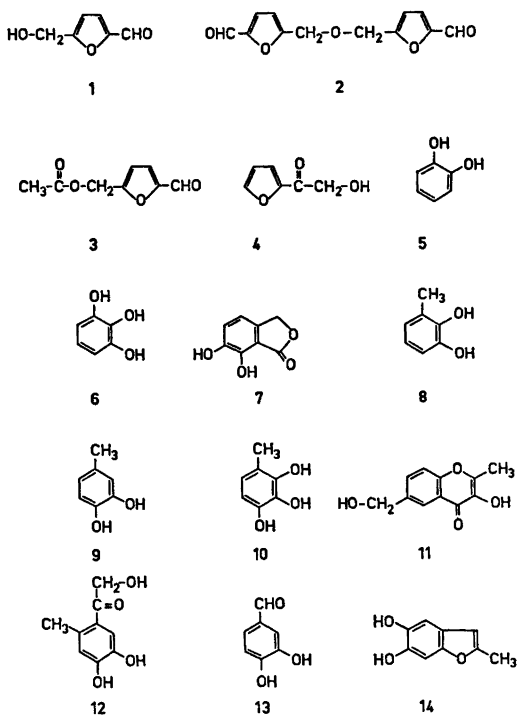
Elemental analysis of compound *7* corresponded to $C_8H_6O_4$. The NMR data of *7* and its dimethyl ether indicated an isobenzofuranone structure containing two hydroxyl groups and two adjacent aromatic protons but did

* Part II. See Ref. 15.

Table 1. Yields and chromatographic properties of compounds isolated after treatment of D-fructose and D-glucose at pH 4.5.

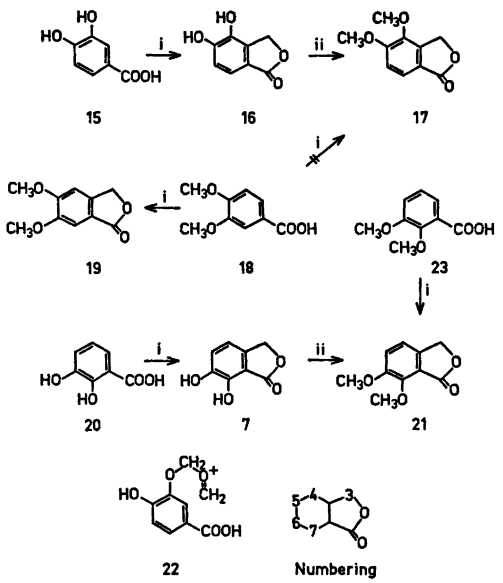
Compound	Yield %				Colour	
	Exp. A	Exp. B	Exp. C	R_C[c]	Spray A	Spray B
1	2.60	1.40	3.40	0.88	orange	–
2	0.01	0.02	0.09	1.88	orange	–
3	0.04	0.01	0.06	2.00	orange	–
4	0.04	0.01	0.07	1.58	brownish yellow	–
5	[a]	[a]	0.02	1.00	gray	bluish gray
6	[a]	[a]	0.03	0.40	grayish green	black
7	0.03	0.01	0.13	0.71	grayish yellow	blue
8	[a]	[a]	0.02	1.42	grayish red	black
9	[a]	[a]	0.01	1.04	grayish brown	grayish green
10	[a]	[a]	0.01	0.60	brown	bluish black
11	[a]	[a]	0.02	0.30[b]	–	violet
12	[a]	[a]	[a]	0.30	–	blue
13	[a]	[a]	[a]	0.52	orange	bluish green
14	[a]	[a]	0.02	0.98	greenish yellow	pale green

[a] Trace amounts. [b] Tailing. [c] Mobilities relative to compound *5*.



not distinguish between the 4,5-, 6,7- and 4,7-dihydroxy derivatives. The two former isomers (*16* and *7*, respectively) were synthesised from the 3,4- and 2,3-dihydroxybenzoic acids (*15* and *20*, respectively; see Scheme 2). The synthetic sample of *7* was identical in all respects (IR, NMR and MS) with that obtained in experiments A, B and C. The dimethyl ether of 7 was identical with the previously known compound meconin (*21*),[7] synthesised from 2,3-dimethoxybenzoic acid (*23*). In the syntheses of the isobenzofuranones (Scheme 2), we found it notable that reaction of 3,4-dihyhroxybenzoic acid (*15*) with formaldehyde in concentrated hydrochloric acid gave the 4,5-dihydroxy derivative (*16*), while 3,4-dimethoxybenzoic acid (*18*) gave the 5,6-dimethoxy derivative (*19*). The formation of *16* from *15* might be explained by primary attack on the *meta*-hydroxyl group by the protonated, dehydrated dimer of formaldehyde to give the intermediate *22*. Similar attack on the *para*-hydroxyl group is disfavoured by resonance involving the carboxyl group. Although the yield is modest, the synthesis of *17* from *15* via *16* is much simpler than the previously reported procedure.[8]

The NMR spectral data for the isobenzofuranones are collected in Table 2. All assignments of the protons were confirmed by appropriate spin decoupling experiments. The $|J|$ values (0.2 – 0.3 Hz) referring to a methoxyl group and its *ortho* proton are as expected.[9] As to the $|J|$ values involving an aromatic proton and those of the ring methylene group, the position in the benzene ring may be arranged in the order 4 > 6 > 7 > 5. This is con-



i: HCHO in conc. HCl ; ii: CH_2N_2 in CH_3-OH

sistent with the order $o > p > m$ for the corresponding toluene constants.[10] The order 7 > 5 may be explained by the more extended, zigzag-like path between a methylene proton and that in position 7.[10] Apparently, only the coupling to proton 4 has been observed previously.[11]

The mass spectrum of compound *11* was very similar to those of 3-hydroxy-2-methylchromones;[6] a molecular ion and losses of 28, 29, 55, and 71 mass units (m.u.). The elemental composition (MS) corresponded to $C_{11}H_{10}O_4$, indicating a hydroxymethyl or methoxy derivative of 3-hydroxy-2-methyl-chromone. The presence of a hydroxymethyl group was supported by the NMR spectra of the monomethyl ether and of the diacetate. The aromatic proton (H-5) in the latter spectrum showed up at δ 8.19. A comparison between this shift and that of H-5 in 2-methylchromone (δ 8.15) previously reported,[12] and our value [6] (δ 8.08) for the diacetate of 3,8-dihydroxy-2-methylchromone, indicated the structure 3-hydroxy-6-hydroxymethyl-2-methyl-4*H*-1-benzopyran-4-one, (3-hydroxy-6-hydroxymethyl-2-methylchromone) or its 7-hydroxymethyl-isomer. The former structure was assigned, however, based upon the small $|J|$-value (2.2 Hz) for H-5.

The elemental composition (MS) of compound *12* corresponded to $C_9H_{10}O_4$ and methylation gave a dimethyl ether. In the MS of compound *12*, the loss of 31 m.u. from the molecular ion (*m/e* 182) to give an intense peak at *m/e* 151 indicated the presence of a hydroxyacetyl group as in compound *4*. The NMR of compound *12* showed a broad three-proton singlet at δ 2.41, a two-proton singlet at δ 4,63 and two one-proton singlets at δ 6.67 (broad) and at δ 7.18. The high δ-values for the methyl group and one of the aromatic protons indicated

Table 2. ^{1}H NMR spectral data for 1(3*H*)-isobenzofuranones.[a]

Positions (s)	*16* in CD_3OD	*17* in $CDCl_3$	*19* in $CDCl_3$	*7* in CD_3OD	*21* in $CDCl_3$
δ values					
3	5.24	5.31	5.22	5.20	5.18
4		*3.95*	6.91	6.81	7.07
5		*3.96*	*3.98*	7.14	7.25
6	6.96	7.08	*3.94*		*3.91*
7	7.25	7.62	7.31		*4.09*
Coupling constants [J(Hz)]					
3,4			0.8	0.8	0.9
3,5				0.1	0.1
3,6	0.4	0.5			
3,7	0.1	0.3	0.3		
4,5			*0.2 – 0.3*	8.0	8.4
4,7			0.3		
5,6		*0.2 – 0.3*			*0.2 – 0.3*
6,7	8.2	8.2	*0.2 – 0.3*		

[a] Data for methoxyl groups are italicized; data for hydroxyl groups have been omitted.

ortho-position to the carbonyl group, and since no coupling between the aromatic protons was found, the structure 1-(3,4-dihydroxy-6-methylphenyl)-2-hydroxyethanone was assigned to compound *12*. For comparison, 1-(3,4-dihydroxy-6-methylphenyl)-ethanone was synthesised and found to have a very similar NMR spectrum as compound *12* (see EXPERIMENTAL). The elemental composition (MS) of compound *14* corresponded to $C_9H_8O_3$. The MS of compound *14* showed a very similar fragmentation pattern including a doubly charged ion (*m/e* 81.5 for *14*) to that of 2-methyl-benzofuran.[13] Methylation gave a dimethyl ether, established by NMR as 5,6-dimethoxy-2-methyl-benzofuran (see EXPERIMENTAL). The chemical shift and coupling constants of proton H-3 are in accordance with those reported for 2-methyl-benzofurans.[14]

To our knowledge compounds *7*, *11*, *12*, and *14*, isolated in the present investigation, as well as the synthesised compound *16*, are not previously reported.

The present results show that hexoses are degraded to various phenolic compounds, which might be active intermediates in the colour formation by heat treatment or storing of foods or solutions of fructose, glucose or sucrose under slightly acidic conditions. Naturally, the formation of these compounds, although formed to a much lower extent than the phenols from the corresponding treatment of pentoses and hexuronic acids,[5] might under more drastic treatments also introduce other non-wanted properties apart from discoloration to the products. The degradation products of hexoses described above differ markedly from those of pentoses and hexuronic acid,[5,6] and also from those of D-glucose produced in alkali.[15] Only compounds *5*, *9* and *13* were identified from both acid and alkaline treatments of this monosaccharide.

EXPERIMENTAL

Melting points are corrected. Concentrations were carried out at reduced pressure below 40 °C. TLC was performed on silica gel HF_{254} (Merck) with 9:1 chloroform/acetic acid as solvent. Silicic acid (100 mesh Mallinckrodt) and Sephadex LH-20 were used for column chromatography. TLC plates were studied in UV light before treatment with (A) *p*-anisidine hydrochloride (B) iron(III) chloride, (C) diazotised sulfanilic acid or (D) 25 % sulfuric acid (and heating) as spray reagents. The sublimations (or distillation) were done at 0.5 mmHg in an electrically heated tube. NMR spectra were recorded at 60 or 100 MHz (Perkin Elmer R 12 and Varian HA 100 D, respectively) and chemical shifts are given in δ units (d, dd, m, and s denote doublet, double doublet, multiplet, and singlet, respectively). Mass spectra were recorded on a Varian CH-7 and high resolution mass spectra on a Varian SM 1 instrument.

Experiment A. D-Fructose (400 g) in 0.3 M acetate buffer of pH 4.5 (2.0 l) was heated at 96 °C for 48 h with a stream of nitrogen bubbling through the solution. The cooled brown solution was continuously extracted for 2 days with ethyl acetate (2 × 1.3 l) The ethyl acetate extract (27.8 g) was fractionated on a Sephadex LH-20 column (4.7 × 110 cm). Six main fractions were collected by elution with water, and a final one using ethanol as solvent. In fraction I (3.36 g) no aromatic compounds detected; II (13.63 g) compound *1–4*; III (0.8 g) compounds *5–7* and *11*; IV (0.56 g) compounds *8–10*; V (0.78 g) compounds *12* and *13*; VI (0.57 g) compound *14*; and VII (1.91 g) unidentified strongly coloured products.

Repeated chromatography of fractions II–IV were made on silicic acid columns with 9:1 dichloromethane-acetone and of fractions V and VI with 8:2 dichloromethane-acetone. The individual compounds were sometimes further purified by sublimation (distillation). For yields and chromatographic properties of pure compounds see Table 1.

Experiment B. D-Glucose (400 g) was treated (as in Exp. A) and the ethyl acetate fraction (20.1 g) obtained was fractionated as in Exp. A (see Table 1).

Experiment C. D-Fructose (72 g) in acetate buffer of pH 4.5 (2.7 l) was treated in a stainless autoclave at 160 °C for 4 h and the ethyl acetate extract (10.2 g) obtained was fractionated as in Exp. A (see Table 1).

Characterization and identification of compounds *2–4*, *7*, *10–12* and *14*

Compound 2. Crystallization from light petroleum (b.p. 60–80 °C), m.p. 112–113 °C (lit. value[2] 112 °C) MS *m/e* (%): 234 (M^+, 3), 206(15), 125(9), 110(44), 109(100), 95(16), 82(36), 81(76), 53(56), 52(16), 51(13), 41(16). ^{1}H NMR, δ (100 MHz, $CDCl_3$): 4.63 (CH_2, s), 6.56 (H-4, d, $|J|$ 3.4 Hz), 7.20 (H-3, d, $|J|$ 3.4 Hz) and 9.63 (–CHO, s). Long range couplings (0.1–0.5 Hz) could also be detected between CHO and H-3, CHO and H_4, CH_2 and H-4 and between CH_2 and H-3.

Compound 3. Identical with acetylated (Ac_2O/Pyr) *1* (MS, NMR, IR). It could not be detected, however, from treatment of *1* in an acetate buffer as in Exp. A.

Compound 4. Crystals after sublimation m.p. 81.5–82.5 °C (lit. values 83–85 °C [2] and 79 °C [16]). MS *m/e* (%): 126 (M^+, 18), 96(9), 95(100), 67(7), 39(38), ^1H NMR, δ (100 MHz, $CDCl_3$): 4.74 (CH_2, s), 6.59 (H-4, dd, $|J|$ 1.8 and 3.5 Hz), 7.30 (H-3, dd, $|J|$ 0.8 and 3.5 Hz) and 7.63 (H-5, dd, $|J|$ 0.8 and 1.8 Hz).

Compound 7. Identical (m.p., mixed m.p., NMR, IR) with 6,7-dihydroxy-1(3*H*)-isobenzofuranone (yield 10 % after purification on a silicic acid column; eluant 4:1 dichloromethane-acetone) from 2,3-dihydroxybenzoic acid (*20*), in the same way as previously reported for the synthesis [7] of 6,7-dimethoxy-1(3*H*)-isobenzofuranone (*21*). Crystallization from ethanol, m.p. 221–222 °C (dec.). Found C 57.9; H 36. Calc. for $C_8H_6O_4$: C 57.8; H 3.6. MS, *m/e* (%. 166 (M^+, 90), 137(100), 120(46), 92(21), 81(28): 64(18), 63(19), 53(22), 52(18), 51(23). IR, ν max (KBr): 1720 (broad), 1615, 1520, 1450, 1405, 1310, (broad), 1280, 1220, 1095, 1000, 915.

Acetylation (Ac_2O/Pyr.) of compound *7* yielded the diacetate. Crystals after storage, m.p. 150.5–153.0 °C. MS, *m/e* (%): 250 (M^+, 1), 208(12), 166(55), 137(28), 97(16), 95(12), 85(13), 83(18), 81(15), 71(23), 69(25), 67(12), 57(43), 55(38), 43(100). ^1H NMR, δ (100 MHz, $CDCl_3$): 2.33 (3 H, s), 2.40 (3 H, s), 5.25 (2 H, broad s), 7.31 (1 H, d, $|J|$ 8.0 Hz) and 7.48 (1 H, d, $|J|$ 8.0 Hz).

Compound 10. Identical (m.p., mixed m.p., NMR, IR) with 4-methyl-1,2,3-benzenetriol, synthesised by reduction [17] of 2,3,4-trihydroxybenzaldehyde (prepared from 1,2,3-benzenetriol [18]). Recrystallization from ethanol, m.p. 142–143 °C (lit. value [17] 140–141 °C). ^1H NMR, δ (60 MHz, CD_3OD): 2.09 (3 H, broad s), 6.19 (1 H, d, $|J|$ 8.4 Hz) and 6.44 (1 H, d, $|J|$ 8.4 Hz).

Compound 11. Crystals after sublimation, m.p. 198–202.5 °C. MS, *m/e* (%): 206(M^+, 100), 205(31), 178(10), 177(53), 160(9), 151(16), 135(12), 105(14), 77(16), 44(17), 43(29). Found: *m/e* 206.0593. Calc for $C_{11}H_{10}O_4$: *m/e* 206.0579. Methylation (CH_2N_2) of compound *11* yielded the monomethyl ether (amorphous). MS, *m/e* (%): 220 (M^+, 27), 205(12), 151(11), 150(21), 149(24), 129(16), 111(19), 43(100). Peaks between *m/e* 43 and *m/e* 100 are omitted. ^1H NMR, δ (60 MHz, $CDCl_3$): 2.43 (3 H, s), 3.86 (3 H, s), 4.71 (2 H, s), 7.35 (1 H, d, $|J|$ 8 Hz), 7.67 (1 H, dd, $|J|$ 8 and 2 Hz) and 8.14 (1 H, d, $|J|$ 2 Hz).

Acetylation (Ac_2O/Pyr.) of compound *11* yielded the diacetate. Crystals after storage, m.p. 108–115 °C. MS, *m/e* (%): 290 (M^+, 2), 249(11), 248(70), 206(25), 205(20), 189(22), 188(24), 160(26), 133(11), 77(12), 43(100). ^1H NMR, δ (100 MHz, $CDCl_3$): 2.11 (3 H, s), 2.37 (6 H, s), 5.18 (2 H, s), 7.43 (1 H, d, $|J|$ 8.5 Hz), 7.65 (1 H, dd, $|J|$ 8.5 and 2.2 Hz) and 8.19 (1 H, d, $|J|$ 2.2 Hz).

Compound 12 (amorphous). MS, *m/e* (%): 182 (M^+, 10), 152(19), 151(100), 123(31), 77(17), 51(12), Found: *m/e* 182.0592. Calc. for $C_9H_{10}O_4$: *m/e* 182.0579 and found: *m/e* 151.0405. Calc. for $C_8H_7O_3$: *m/e* 151.0395. ^1H NMR δ (60 MHz, CD_3OD): 2.41 (3 H, broad s), 4.63 (2 H, s), 6.67 (1 H, broad s), and 7.18 (1 H, s).

Methylation (CH_2N_2) of compound *12* yielded the dimethyl ether (amorphous). MS, *m/e* (%): 210 (M^+, 21), 180(26), 179(100), 165(43), 151(50), 149(14), 138(17), 137(34), 122(10), 121(17), 108(10), 107(10), 93(14), 91(22), 78(10), 77(14), 65(20). ^1H NMR, δ (60 MHz, $CDCl_3$): 2.58 (3 H, broad s), 3.87 (3 H, s), 3.91 (3 H, s), 4.69 (2 H, s), 6.70 (1 H, broad s) and 7.11 (1 H, s). For comparison, 1-(3,4-dihydroxy-6-methylphenyl)-ethanone was synthesised by the same procedure as by the synthesis of 2,3-dihydroxy-acetophenone,[19] starting with 4-methyl-1,2-benzenediol. After purification on a silicic acid column using 9:1 dichloromethane-acetone as solvent, a yield of 10 % was obtained. Crystallization from aqueous ethanol, m.p. 170.5–171.0 °C (lit. value [20] 169 °C. MS, *m/e* (%): 167(10), 166(M^+, 50), 152(21), 151(100), 123(42), 87(21), 51(18), 43(16). ^1H NMR, δ (100 MHz, CD_3OD): 2.38 (3 H, broad s), 2.47 (3 H, s), 6.64 (1 H, broad s) and 7.32 (1 H, s).

Compound 14. Crystals after sublimation, m.p. 146–151 °C MS, *m/e* (%): 164 (M^+, 99), 163(100), 147(8), 136(6), 135(6), 118(6), 81.5(2), 77(10), 69(16), 65(10), 63(13), 43(16). Found: *m/e* 164.0470. Calc. for $C_9H_8O_3$: *m/e* 164.0473. ^1H NMR, δ (60 MHz CD_3OD): 2.30 (3 H, broad s), 6.15 (1 H, broad s) and 6.83 (2 H, broad s). IR, ν_{max} (KBr): 1610 (broad), 1490, 1475, 1350, 1320, 1265, 1200, 1165, 1145, 1095, 930, 880, 845, 810.

Methylation (CH_2N_2) of compound *14* yielded the dimethyl ether (amorphous). MS, *m/e* (%): 193(15), 192(M^+, 100), 191(14), 178(27), 177(63), 163(34), 149(23), 147(13), 135(13), 134(15), 131(14), 121(45), 106(23), 103(14), 91(14), 77(25), 69(25), 65(13), 63(15), 43(33). ^1H NMR, δ (100 MHz, $CDCl_3$): 2.42 (CH_3, d, $|J|$ 1.1 Hz), 3.91 (2 OCH_3, broad s), 6.26 (H-3, broad dd, $|J|$ 1.1 and 0.9 Hz), 6.94 (H-4, broad s), 7.0 (H-7, broad d, $|J|$ 0.9 Hz).

Synthesis of compounds *16*, *17*, *19* and *21*.

Compound 16. Synthesized from 3,4-dihydroxybenzoic acid (*15*) in the same way as *7* from 2,3-dihydroxybenzoic acid. Pure *16* was obtained in 17 % yield. Crystallization from water, m.p. 243.5–246 °C (dec.) Found: C 57.7; H 3.6. Calc. for $C_8H_6O_4$: C 57.8; H 3.6. MS, *m/e* (%): 166 (M^+, 64), 165(18), 137(100), 109(24), 108(11), 81(24), 63(17), 53(19), 52(16), 51(19). IR ν_{max} (KBr): 1720 (broad), 1625, 1610, 1530, 1410, 1300, 1240, 1090, 920.

Compound 17. Prepared by methylation (CH_2N_2) of *16*, m.p. 120–121.5 °C (lit. value[6] 122.5 °C).

Compound 19. Prepared in analogy with a previous procedure[21] from 3,4-dimethoxybenzoic acid (*18*), m.p. 154–156 °C (lit. value[21] 155 °C).

Compound 21. Prepared by a previous procedure[7] from 2,3-dimethoxybenzoic acid (*23*), as well as by methylation (CH_2N_2) of *7*, m.p. 99.5–100.5 °C (lit. value,[7,21] 101–103 °C). MS was in accordance with that previously reported.[22]

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