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Formation of Aromatic Compounds from Carbohydrates. VI.* Reaction of Dihydroxyacetone in Slightly Acidic, Aqueous Solution

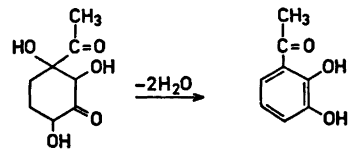
THOMAS POPOFF, OLOF THEANDER and ERIC WESTERLUND

Department of Chemistry, Agricultural College, Swedish University of Agricultural Sciences, S-750 07 Uppsala 7, Sweden

Treatment of dihydroxyacetone in aqueous solution of pH 4.5 at 96 °C yielded 2,5-hexanediones (*1*—*3*), 3-hydroxy-4*H*-pyran-4-ones (*4*—*7*), pyranopyrandiones (*8*—*9*), a *p*-benzoquinone (*10*), 1,2-benzenediols (*11*—*19*) and a benzo[*b*]furan (*20*). Only compound *4* has previously been obtained from dihydroxyacetone. The pyranopyrandiones (*8*, *9*), 3-hydroxy-5-methyl-4*H*-pyran-4-one (*6*), 3′,4′-dihydroxy-2′-methylacetophenone (*18*) and 2′,3′,4′,5′-tetrahydroxy-6′-methylacetophenone (*19*) appear to be new compounds.

The slow conversion of carbohydrates to brown polymers seems to be responsible, partly at any rate, for the yellowing of cellulosic products under both slightly acidic ageing conditions and alkaline pulping conditions. The process is accelerated by amino compounds (the Maillard reaction) [1] and may therefore give rise to colour, aroma and nutritional changes by thermal treatment of food. In order to trap low-molecular precursors, polymer formation in several simple model systems has been studied in aqueous solution at 96 °C. At high pH, D-glucose yielded 11 phenols and 2 enols, each product containing 6—9 carbon atoms.[2] Among the phenols, pyrocatechol (*11*) and its derivatives predominated. Similar yields (0.1 % or less) of the same low-molecular products were obtained from D-xylose. Although these products may well give rise to coloured polymers, their formation from the sugar must be complex, including fragmentation and recombination steps. The reaction at pH 4.5, which is more informative, has so far been investigated for hexoses,[3] pentoses and hexuronic acids.[4,5] Low-molecular compounds are now obtained in 0.5—3 % yields with no other cleavage of the carbon chain than decarboxylation of the uronic acids. These major products arise from the sugar by fairly obvious dehydration and cyclization reactions, sometimes accompanied by dimerization through aldol condensation. However, products, the formation of which must include fragmentation and recombination steps (from hexoses, C_7-C_9 and C_{11} compounds, and from pentoses and hexuronic acids, C_6-C_8 compounds), such as *11* and derivatives of *11* are still found in low yields, even in the presence of methylamine [6] or glycine.[7] Although the immediate precursor (*21*) of 2′,3′-dihydroxyacetophenone (*22*) was identified [4] (see Scheme 1), the fragmentation-recombination sequence leading to the phenolic products remains obscure. The investigation was therefore extended to simpler sugars. The present paper deals with the reaction of dihydroxyacetone in acetate buffer, pH 4.5. A paper on the reaction of D-erythrose under the same conditions is under preparation.

The mutual isomerization of trioses [8] and their dehydration to methylglyoxal [8,9] have



21 *22*

Scheme 1.

* Part V. See Ref. 6.

Table 1. Yields and chromatographic properties of compounds isolated after treatment of dihydroxyacetone at pH 4.5.

Compound	Yield (%)	R_c[b]	Colour	
			Spray a	Spray b
1	1.20	1.48	–	dark brown
2	1.10	0.87	–	pale brown
3	0.90	0.61	–	pale brown
4	0.30	1.96	brownish red	white
5	[a]	2.00	brick red	white
6	0.06	2.04	brownish red	white
7	0.10	1.96	bluish red	white
8	[a]	0.84	brownish red	dark yellow
9	[a]	1.08	brownish red	yellow
10	0.08	1.52	brownish	grey
11	[a]	1.00	bluish grey	red
12	0.03	0.36	bluish black	dark red
13	0.07	0.18	black	dark brown
14	[a]	1.41	black	red
15	[a]	1.17	greyish green	greyish red
16	0.03	0.52	bluish black	reddish brown
17	[a]	1.60	blue	reddish brown
18	0.05	0.88	bluish grey	pale brown
19	0.18	0.60	bluish black	brown
20	0.10	1.12	pale green	bluish black

[a] Trace amounts. [b] R_c, mobility relative to compound *11*.

been studied previously in acetate and other aqueous buffers. The base-catalyzed aldol and retroaldol condensations of trioses [10,11] and the reaction between dihydroxyacetone and glycine in water at 55 °C [12] have also been investigated. Under the conditions of technical sucrose production, dihydroxyacetone yields coloured products, believed to be of similar composition as those formed from a mixture of glucose and fructose.[13]

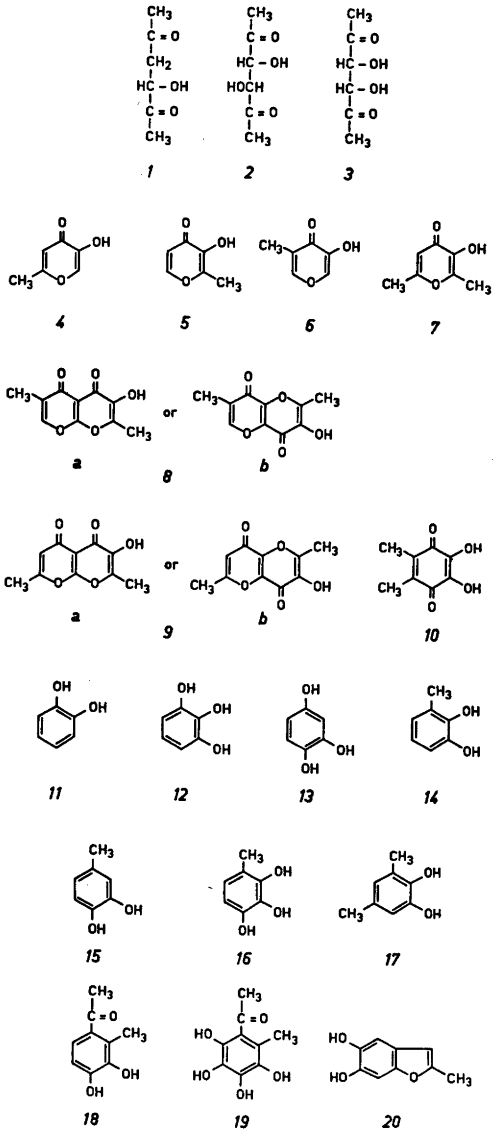
RESULTS

After chromatographic fractionation, the ethyl acetate-soluble part of the reaction mixture from the treatment of dihydroxyacetone in acetate buffer (pH 4.5, 96 °C, 24 h) yielded the compounds *1*–*20* given in Scheme 2 (where only one enantiomer of each of the racemic *1* and *2* is shown). The yields and chromatographic properties of the compounds are given in Table 1. It was proved that none of these compounds originated from solvents or chromatographic material or were present as impurities in the starting material. We have previously shown that acetate from the buffer does not react when pentoses or hexuronic acids are treated under the same conditions.[4]

Compounds *1*, *4*, *11*–*17* and *20* were identical (TLC, IR, MS, ^{1}H NMR) with authentic samples. Compounds *2* and *3* were identified by means of literature data (m.p., IR, MS, ^{1}H NMR)[14]. Each was converted to an equilibrium mixture of *2* and *3* under the reaction conditions. The bright red compound *10* and its dimethyl ether were identified by their melting points,[15] ^{1}H NMR and mass spectra. The structure of compound *18* was verified by synthesis.

Compounds *5* and *7* were only obtained as a 1:4 mixture, as shown by GLC analysis and by the ^{1}H NMR spectrum. The spectra of the components were consistent with those previously reported (for *5* and *7*),[16,17] see Table 2. The spectrum of the minor component was identical with that of authentic *5*.

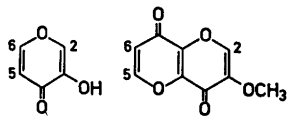
Structure *6* was fully established by comparing the ^{1}H NMR and MS spectra with those of the known pyrones *4*, *5* and *7*. As Table 2 shows, it is easy to decide from the shift of a methyl group or a single proton whether it is adjacent to the oxygen atom or the carbonyl group of a pyrone.[18,19] Moreover, a methyl



Scheme 2.

group adjacent to a free position is always revealed by allylic coupling ($|J|$*ca.* 1 Hz). Compound *6* was previously [20] reported to be a constituent of ginseng root but the ^{1}H NMR spectrum presented δ 2.36 (3 H, s), 6.38 (1 H, s), 7.66 (1 H, s) is in better support of structure *4*. Further, the melting point reported was 162–163 °C, whereas our product melted at 101–102 °C (*cf.* compound *4* at 153–154 °C).

Table 2. ^{1}H NMR spectral data for compounds *4*–*9* (in $CDCl_3$). Shifts for methyl groups are italicized.



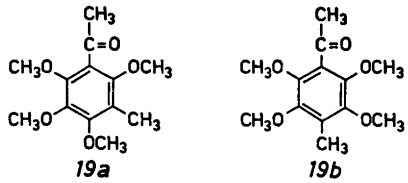
4–7 *8,9*

Compound	δ2	δ5	δ6	$\|J\|$ 5/6 (Hz)
4	7.76	6.26	*2.29*	0.7
5	*2.36*	6.42	7.70	6.0
6	7.85	*2.01*	7.70	1.1
7	*2.32*	6.20	*2.27*	0.7
8[a]	*2.51*	*2.05*	7.27	1.2
9[a]	*2.50*	6.36	*2.45*	0.7

[a] Numbered as above $\delta(OCH_3)$ 3.94.

The elemental composition (MS) of compounds *8* and *9* corresponded to $C_{10}H_8O_5$. The MS fragmentation pattern and colour with spray reagent *a* in TLC (Table 1) indicated pyranopyrandiones and the IR spectra excluded lactones. The ^{1}H NMR spectrum of each compound after methylation (CH_2N_2) showed the presence of two methyl groups, one methoxyl group and one single proton. The positions of the groups were established as described above for compound *6* (Table 2). The small amounts of compounds *8* and *9* available did not permit us to rule out the isomers *8a* and *9a*, but the fact that the 3-hydroxypyrones *6* and *4* were found in the reaction mixture in significant amounts makes the alternatives *8b* and *9b* more likely.

The elemental composition (MS) of compound *19* corresponded to $C_9H_{10}O_5$, and the reaction towards spray reagent *a* was similar to that of compound *12*. The ^{1}H NMR spectrum showed no aromatic protons, but two singlets at δ 2.28 and 2.55 indicated a benzene ring carrying one methyl, one acetyl and four hydroxyl groups. This was further verified by the ^{1}H NMR spectrum after methylation (CH_2N_2), which showed the occurrence of four different methoxyl groups. The methylated compound *19* was not identical with the synthesized isomer *19a* (see Scheme 3), and since the symmetrical iso-



Scheme 3.

mer *19b* was ruled out by the ^{1}H NMR spectra, compound *19* was assigned the proposed structure.

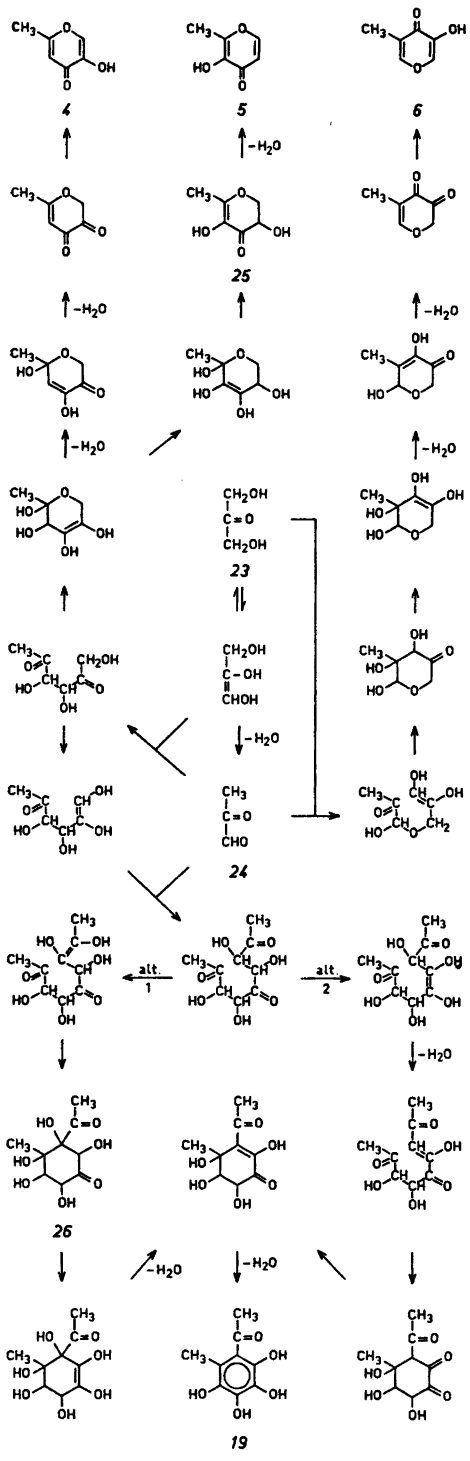
DISCUSSION

It was previously [8] reported from studies in acetate buffers (similar conditions as in the present investigation) of the mutual isomerization of dihydroxyacetone and glyceraldehyde and their dehydration to methylglyoxal (*24*), that a true equilibrium between trioses was not attained. After a certain reaction time, the concentration of dihydroxyacetone began to decrease more rapidly than that of glyceraldehyde, and unidentified compounds appeared. The pyrone *4* was previously isolated [12] from the treatment of dihydroxyacetone with glycine in water at 55 °C.

As discussed above, compound *4* (and probably not *6*) might also be a constituent of ginseng root.[20] Compound *5* was identified among the volatile compounds resulting from roasted starch [21] and from thermic degradation of D-glucose at pH 2.5 in the presence of proline,[22] and compound *7* has previously been prepared *via* oxidation of a dihydro-γ-pyrone.[17] Compounds *8* and *9* or any other pyranopyrandiones are to our knowledge not previously known as natural or carbohydrate degradation products, but the same skeleton is found in a series of compounds prepared by the reaction of γ-pyrones and lactones in the presence of trifluoroacetic acid.[23] The only report of the formation of quinones by degradation of carbohydrates in aqueous solution, besides the present compound *10*, seems to be on the formation of quinones by alkaline treatment of sucrose.[24]

As in the treatment of hexoses,[3] pentoses and hexuronic acids (after decarboxylation) [4,5] under similar weakly acidic conditions, the major products (yields >0.1 %) *1–4*, *7*, *19* and *20* from dihydroxyacetone seem to arise without carbon chain cleavage through dehydration and cyclization reactions (see Scheme 2). This general finding is probably not at variance with the fact that various components in the reaction mixtures may react further to other products by different rates and thus the total amount of a compound formed may much exceed that isolated. Of these compounds, the main products were *1–3*, previously only known as synthetic compounds, which apparently are reduction products. As we have previously [4] found by treatments under weakly acid conditions that exclusion of air seems to have little or no effect on the product pattern, these compounds are most likely formed *via* disproportionation reactions of, *e.g.*, the Cannizzaro type. We have, however, not looked for acids or other low-molecular oxidation products which may represent or arise from the corresponding higher stage of oxidation. It is also notable that so many phenolic compounds (*11*, *12*, *14–16* and *20*) were also found by treating hexoses [3] under the same conditions as in this experiment, but only compound *14* from pentoses.[4] Compound *19* does not appear to have been known hitherto.

Tentative mechanisms are given in Scheme 4 for the formation of compounds *4–6* and *19*, the structures of which indicate partial dehydration of the dihydroxyacetone (*23*) to methylglyoxal (*24*) before condensation to di- and trimers. By condensation of dihydroxyacetone (*23*) as its enol form with methylglyoxal (*24*), followed by cyclization and dehydration through β-eliminations, compounds *4*, *6* and *25* may thus be formed. The latter dihydro compound has previously been isolated as a reaction product of D-glucose, methylamine and acetic acid [25] and after treatment of D-fructose under slightly acidic conditions.[26] Compound *5* is formed in traces only, probably because the necessary α-elimination in *25* is a slower reaction than the β-eliminations. Compare also the strong conditions ($SOCl_2$) needed for its preparation.[26] Compound *19* may be formed *via* either of the two alternative routes given in the scheme. Alternative 1 seems most likely, since the proposed intermediate *26* is closely related to 3-acetyl-2,3,6-trihydroxycyclohexanone (*21*), an intermediate in the formation of



Scheme 4.

2′,3′-dihydroxyacetophenone (*22*), which we obtained by similar treatment of D-glucuronic acid.[4]

EXPERIMENTAL

General

Melting points are corrected. Concentrations were carried out at reduced pressure below 40 °C. TLC was performed on silica gel HF_{254} (Merck) with chloroform-acetic acid (9:1) as solvent. TLC plates were studied in UV light before treatment with (*a*) iron(III) chloride or (*b*) a solution (*v*/*v*) of *p*-anisaldehyde (5 %) and sulfuric acid (5 %) in ethanol, followed by heating (140 °C). Column chromatography was performed on Sephadex LH-20 with water-ethanol as solvent and on silicic acid (100 mesh Mallinckrodt) with (A) light petroleum-2-butanone (85:15), (B) dichloromethane-acetone (9:1), (C) light petroleum-2-butanone (2:1) and (D) dichloromethane-acetone (85:15) as solvent. The sublimations (or distillations) were performed at 0.5 mmHg in an electrically heated tube. ^1H NMR spectra were recorded at 100 MHz (Varian HA-100D) 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 MAT CH-7 instrument. The mass spectrometer was fitted with a Varian Aerograph 1740 equipped with a column containing 3 % STAP on Chromosorb W (100/120 mesh) and with a helium flow rate of 25 ml/min; GLC-MS of compounds *5* and *7* were obtained at 145 °C. High-resolution mass spectra were recorded on an AEI MS 902 instrument at the Institute of Medical Biochemistry, University of Gothenburg.

Title reaction procedure

Dihydroxyacetone (50 g) in 0.15 M acetate buffer of pH 4.5 (1.8 l) was kept at 96 °C for 24 h, with a stream of nitrogen bubbling through the solution. The cooled brown solution was extracted with ethyl acetate, first batchwise (3 × 0.7 l) and then in a percolator for 24 h. The combined ethyl acetate extracts were evaporated, and the residue (17.5 g) was fractionated on a Sephadex LH-20 column (4.7 × 100 cm). Six main fractions were collected by elution with water and a final one using ethanol as solvent. The fractions contained the following compounds: fraction I (6.75 g) compounds *1*–*3*, *8* and *9*; II (3.45 g) compounds *4*–*7* and *10*; III (2.45 g) compounds *10*–*12*; IV (0.71 g) compounds *13*–*16*; V (0.78 g) compounds *17* and *19*; VI (0.58 g) compound *18*; VII (1.38 g) compound *20*. The compounds were purified by repeated fractionation on silicic acid columns (compound *1*, solvent A; compounds *2*, *3*, *8*, *9* solvent B; compound *4*–*7* and *10* solvent C;

compounds *11–20*, solvent D) and further by crystallization (compounds *11*, *12*, *15*, *19* and *20*) and/or sublimation (compounds *2–4*, *6*, *7*, *11–15*, *17*, *18*, *20*).

Characterization and identification of compounds *1–10*, and *16–20*

The following products were identical (m.p. TLC, IR, ^{1}H NMR, MS) with samples, obtained commercially or synthesized according to the literature indicated: *11–15*, *16*,[2] *17*[27] and *20*.[3] The ^{1}H NMR spectral data for *4–9* are collected in Table 2.

Compound 1. Identical (NMR, MS, IR) with (±)-3-hydroxy-2,5-hexanedione synthesized[28] as previously described. Amorphous. MS [IP, 70 eV; *m/e* (% rel.int.)]: 112 (6, *M* − 18), 97 (6), 87 (70), 58 (8), 55 (18), 43 (*100*). ^{1}H NMR($CDCl_3$): δ 2.22 (3 H, s), 2.26 (3 H, s), 2.82 (1 H, dd, *J* 6.0 and 17.4 Hz), 3.00 (1 H, dd, *J* 4.3 and 17.4 Hz), 4.34 (1 H, dd, *J* 4.3 and 6.0 Hz). IR (film): 1705 (s), 1390 (m), 1355 (s), 1158 (m), 1093 (m) cm^{-1}.

Compound 2. Crystallization from ethyl acetate – light petroleum (b.p. 40–60 °C). M.p. 90–91 °C. The IR, MS and ^{1}H NMR spectral data and m.p. agreed with those reported.[14]

Compound 3. Crystals after sublimation. M.p. 60–61 °C. The IR, MS and ^{1}H NMR spectral data and m.p. agreed with those reported.[14]

Compound. 4. Identical (m.p., NMR, MS, IR) with an authentic sample of 3-hydroxy-6-methyl-4*H*-pyran-4-one. Crystallization from ethyl acetate. M.p. 153–154 °C. MS [IP, 70 eV; *m/e* (% rel. int.)]: 126 (*100*, *M*), 98 (12), 85 (9), 70 (10), 69 (31), 58 (25), 43 (44).

Compound 5 was only obtained in admixture with compound 7. The identity was confirmed by comparison of ^{1}H NMR and GLC-MS data with an authentic sample of 3-hydroxy-2-methyl-4*H*-pyran-4-one.

Compound 6. Crystals after sublimation. M.p. 101–102 °C. Anal. $C_6H_8O_3$; C, H. MS [IP, 70 eV; *m/e* (% rel. int.)]: 126 (*100*, *M*), 111 (7), 98 (12), 97 (11), 85 (10), 71 (11), 70 (11), 69 (32), 58 (10), 57 (16), 55 (25), 53 (13), 44 (18), 43 (50). IR (KBr): 1640 (m), 1600 (s), 1385 (m), 1325 (m), 1290 (m), 1180 (s), 1080 (s), 850 (m) cm^{-1}.

Compound 7. Obtained in admixture with compound 5. The identity was confirmed by comparison of ^{1}H NMR and GLC-MS data with those previously reported.[17] MS [IP, 70 eV; *m/e* (% rel. int.)]: 140 (57, *M*) 125 (10), 111 (15), 97 (12), 85 (32), 69 (27), 55 (11), 44 (15), 43 (*100*).

Compound 8. Crystallization from ethanol. M.p. above 250 °C. MS [IP, 70 eV; *m/e* (% rel. int.)]: 208 (*100*, *M*), 180 (6), 179 (6), 153 (5), 151 (10), 137 (11), 126 (8), 125 (12), 110 (6), 109 (7), 85 (14), 57 (10), 55 (22), 43 (46). IR (KBr): 1620 (s), 1590 (s, broad), 1420 (m), 1295 (m), 1240 (m, broad), 1165 (s), cm^{-1}. Mol. wt., obs. 208.036. Calc. for $C_{10}H_8O_5$: 208.037. Methylation (CH_2N_2) of compound *8* yielded the *methyl ether*. Crystals after sublimation. M.p. 202–204 °C. MS [IP, 70 eV; *m/e* (% rel.int.)]: 222 (*100*, *M*), 221 (20), 207 (14), 204 (27), 193 (8), 179 (17), 164 (27), 153 (9), 151 (6), 148 (23), 136 (15), 135 (10), 125 (16), 124 (32), 109 (15), 108 (21), 85 (44), 80 (13), 73 (10), 69 (12), 68 (20), 67 (39), 55 (13), 53 (16), 52 (11), 43 (87).

Compound 9. Crystallization from ethanol. M.p. above 250 °C. MS [IP, 70 eV; *m/e* (% rel. int.)]: 208 (*100*, *M*), 180 (6), 179 (9), 153 (5), 151 (12), 137 (10), 126 (9), 125 (19), 110 (7), 85 (33), 69 (14), 67 (12), 55 (18), 43 (74). IR (KBr): 1620 (s), 1585 (s), 1410 (m), 1320 (m), 1240 (s), 1215 (m), 1160 (m), 1110 (s) cm^{-1}. Mol. wt., obs. 208.037. Calc. for $C_{10}H_8O_5$: 208.037. Methylation (CH_2N_2) of compound *9* yielded the *methyl ether*. Crystals after sublimation. M.p. 224–226 °C (sealed capillary). MS [IP, 70 eV; *m/e* (% rel.int.)]: 222 (*100*, *M*), 221 (21), 207 (16), 204 (29), 193 (7), 179 (14), 164 (28), 153 (8), 151 (6), 148 (26), 136 (17), 135 (10), 125 (14), 124 (29), 109 (13), 108 (22), 85 (38), 80 (13), 69 (11), 68 (18), 67 (34), 55 (9), 53 (11), 43 (76).

Compound 10. Bright red crystals from ethanol. M.p. 177–183 °C. (dec.) MS [IP, 70 eV; *m/e* (% rel.int.)]: 168 (33, *M*), 141 (30), 140 (*100*), 139 (22), 123 (10), 122 (17), 111 (22), 97 (13), 94 (42), 83 (26), 67 (12), 66 (77), 65 (20), 58 (12), 55 (17), 53 (24), 51 (17), 43 (26). Mol. wt., obs. 168.042. Calc. for $C_8H_8O_4$: 168.042. ^{1}H NMR(CD_3OD): δ 1.97 (6 H, s). Methylation (CH_2N_2) of compound *10* yielded the *dimethyl ether*. Bright orange crystals from light petroleum (b.p. 60–80 °C). M.p. 60–62 °C. MS [IP, 70 eV; *m/e* (% rel.int.)]: 196 (*100*, *M*), 181 (40), 167 (12), 153 (29), 151 (82), 125 (29), 97 (44), 69 (14), 54 (32), 53 (23), 43 (13). ^{1}H NMR($CDCl_3$): δ 2.00 (6 H, s), 3.98 (6 H, s).

Compound 18. Identical (m.p., ^{1}H NMR, MS, IR) with 3′,4′-dihydroxy-2′-methylacetophenone obtained in poor yield along with the known 3′,4′-dihydroxy-5′-methyl- and 2′,3′-dihydroxy-4′-methylacetophenone by acylation of 3-methyl-1,2-benzenediol. This preparation was performed analogously to that of 2′,3′-dihydroxyacetophenone previously reported.[29] Compound *18* was separated on a silicic acid column (solvent B) from the two known products, which were identified by ^{1}H NMR and MS and by means of literature data (m.p., IR).[30] Crystals of *18* after sublimation. M.p. 149–152 °C. MS [IP, 70 eV; *m/e* (% rel.int.)]: 166 (44, *M*), 152 (40), 151 (*100*), 124 (14), 123 (21), 95 (12), 78 (12), 77 (18), 67 (10), 55 (13), 51 (13), 43 (19). ^{1}H NMR(CD_3OD): δ 2.36 (3 H, s), 2.50 (3 H, s), 6.68 (1 H, d, *J* 8.0 Hz), 7.28 (1 H, d, *J* 8.0 Hz). Mol. wt., obs. 166.062. Calc. for $C_9H_{10}O_3$: 166.063.

Compound 19. Light yellow crystals from methanol–water. M.p. 178–181 °C (dec.). MS [IP, 70 eV; *m/e* (% rel.int.)]: 198 (64, *M*), 184 (10), 183 (*100*), 180 (17), 155 (11), 43 (10). Mol. wt., obs. 198.053. Calc. for $C_9H_{10}O_5$: 198.053. ^{1}H NMR(CD_3OD): δ 2.28 (3 H, s), 2.55 (3 H,

s). Methylation (CH_2N_2) yielded the *tetramethyl ether* in about 20 % yield. Amorphous MS [IP, 70 eV; *m/e* (% rel.int.)]: 254 (70, *M*), 240 (15), 239 (*100*), 224 (16), 209 (20), 206 (12), 196 (10), 181 (11), 67 (12), 43 (19). ^{1}H NMR($CDCl_3$): δ 2.09 (3 H, s), 2.48 (3 H, s), 3.78 (3 H, s), 3.82 (3 H, s), 3.90 (3 H, s), 3.92 (3 H, s).

For comparison, 2′,3′,4′,6′-tetramethoxy-5′-methylacetophenone *19a* was synthesized as follows: methylation of 2′,4′,6′-trihydroxyacetophenone with iodomethane yielded 2′-hydroxy-4′,6′-dimethoxy-3′-methylacetophenone,[31] which was hydroxylated to 2′,5′-dihydroxy-4′,6′-dimethoxy-3′-methylacetophenone,[32] obtained in 10 % yield after silicic acid column separation with dichloromethane-ethanol (95:5) as solvent. Crystallization from methanol–water. M.p. 121–122 °C MS [IP, 70 eV; *m/e* (% rel.int.)]: 226 (*100*, *M*), 211 (81), 208 (13), 196 (15), 193 (17), 183 (20), 178 (11), 165 (30), 150 (11), 83 (12), 67 (16), 55 (12), 43 (49). ^{1}H NMR($CDCl_3$): δ 2.14 (3 H, s), 2.69 (3 H, s), 3.88 (3 H, s), 3.90 (3 H, s), 4.20 (1 H, broad s), 12.90 (1 H, broad s). Methylation of the compound with diazomethane was unsuccessful. The *tetramethyl ether* was hence prepared in 18 % yield as previously described[33] for 2′,3′,4′,5′,6′-pentamethoxyacetophenone. Amorphous. MS [IP, 70 eV; *m/e* (% rel.int.)]: 254 (43, *M*), 240 (14), 239 (*100*), 224 (15), 209 (16), 181 (25), 179 (18), 83 (10), 67 (11), 43 (40). ^{1}H NMR($CDCl_3$): δ 2.14 (3 H, s), 2.50 (3 H, s), 3.68 (3 H, s), 3.86 (9 H, s).

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