Acid Reactions of Hydrobenzoins: Effects of Catalyst and Reaction Medium on Product Composition

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Acid treatment of hydroanisoin in dioxane–water mixtures results in the formation of 2,2-bis(4-methoxyphenyl)ethanal and 1,2-bis(4-methoxyphenyl)ethanone. The relative proportions of these products have been shown to be dependent on the nature of the catalyst and the composition of the reaction medium. The formation of the ketone was catalysed by HCl and by HBr; a variety of other catalysts (e.g. CF_3SO_3H, H_2SO_4, $HClO_4$ and HBF_4) gave only traces of this compound. Ketone formation is more effiently catalysed by HBr than HCl. The catalytic effect of HBr essentially disappeared when the solvent composition was changed from dioxane–water (9:1) to dioxane–water (7:3). Analogous results were obtained in studies of the acid degradation of hydroveratroin.

In addition to condensation reactions (see e.g. Refs. 1 and 2), the major initial irreversible reactions of various structural elements in lignins on acid treatment include abstraction of H_β (reaction route A) or elimination of the terminal CH_2OH group as formaldehyde (reaction route B); examples of these types of reaction appear in Figs. 1 and 2. Arylglycerol β-aryl ethers (1) constitute the most important type of structural element in lignins.[3] Fig. 1 shows alterna-

tive reaction routes for the acid-catalysed degradation of such lignin structures. The influence of reaction temperature and reaction medium on the relative rate of these reactions has been investigated by Sarkanen et al.[4] using veratrylglycerol β-guaiacyl ether (3) as a model compound and HCl as the catalyst. In previous work[5] we subjected the acid degradation of this model compound to further study and it was found that the rate of cleavage of the β-ether
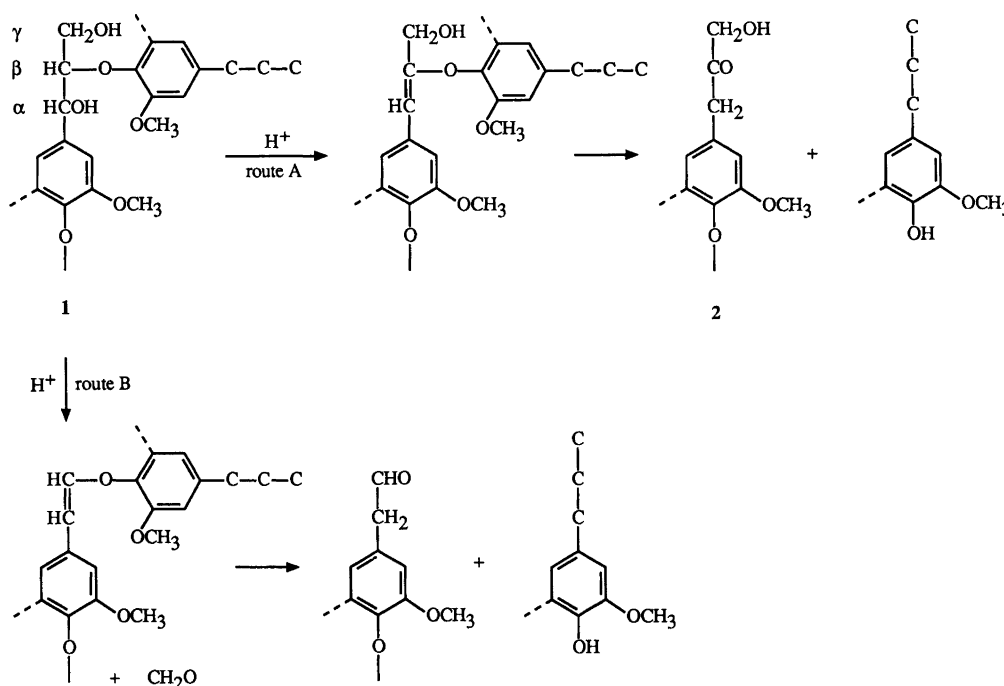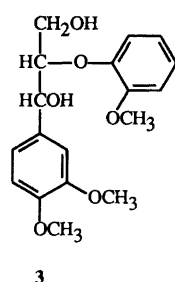

Fig. 1. Alternative reaction routes for the cleavage of arylglycerol β-aryl ethers (1) on acid treatment.

CH$_2$OH
HC—O
HCOH   OCH$_3$

OCH$_3$
OCH$_3$

3

bond was strongly dependent on the nature of the catalyst. HBr and HCl were shown to be comparatively efficient as catalysts. The experiments also indicated that the same catalysts favoured formation of the ketol **2** (reaction route A, Fig. 1) but clear-cut evidence for this was not obtained (Ref. 5 and unpublished data). The fact that liberated formaldehyde may take part in condensation reactions[6] complicates an evaluation of the relative importance of the two reaction routes (A and B, Fig. 1) on the basis of the product composition. Studies of model compounds for the β-1 type of structure, however, strongly suggest a catalytic effect of hydrochloric acid favouring elimination of H$_\beta$ (reaction route A, Fig. 2). Thus refluxing of **4** with 0.2 M hydrochloric acid in dioxane–water (9:1) gave a moderate yield of stilbene **5** and fairly large amounts of a series of aromatic carbonyl compounds (Fig. 2) formed via an elimination of H$_\beta$,[6] while refluxing with 0.1 M H$_2$SO$_4$ in the same medium gave the stilbene as the sole product.[7] Similar studies of model compounds representative of the β-5

type of lignin structure,[8,9] using HCl and H$_2$SO$_4$ as catalysts, suggest an analogous catalytic effect of HCl in the acid reactions of such compounds.

To obtain more information about the influence of catalysts as well as of reaction medium on lignin reactions in acid media, we used methoxy-substituted hydrobenzoins (**6, 7** and **12**) as model compounds. Such hydrobenzoins undergo two alternative reactions on acid treatment; both reactions include loss of the elements of water. A reaction involving an aryl group migration resulting in the formation of a diarylacetaldehyde competes with a reaction leading to a deoxybenzoin (Figs. 3 and 4); the latter reaction may proceed via reaction steps similar to those involved in reaction route A (Figs. 1 and 2). Methoxy-substituted hydrobenzoins have several advantages as model compounds in studies of acid-catalysed reactions of the above-mentioned types. The total yield of reaction products identified is high and the yield of each of them can be determined by ^{1}H NMR spectroscopic measurements since all of them exhibit ^{1}H NMR signals suitable for quantitative estimates. Furthermore, with hydrobenzoins as model compounds, the above-mentioned complications associated with the presence of formaldehyde among the reaction products is circumvented.

Results

Yields of products obtained on acid degradation of hydroanisoin by refluxing in 0.05 M solutions of a series of acids in dioxane–water (9:1) for 40 min are summarized in Table 1.
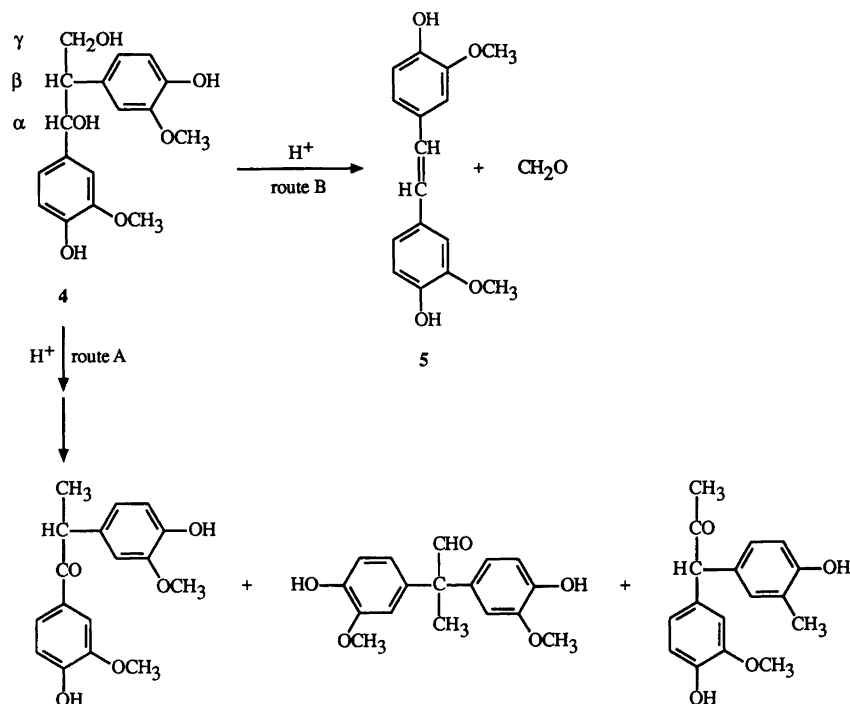
γ CH$_2$OH
β HC—⟨⟩—OH
α HCOH   OCH$_3$

OCH$_3$
OH

4

H$^+$
route B

OH
OCH$_3$

CH
HC   +   CH$_2$O

OCH$_3$
OH

5

H$^+$ | route A

CH$_3$
HC—⟨⟩—OH
CO   OCH$_3$

OCH$_3$
OH

+

CHO
HO—⟨⟩—C—⟨⟩—OH
        CH$_3$
OCH$_3$ OCH$_3$

+

CH$_3$
CO
HC—⟨⟩—OH
        CH$_3$

OCH$_3$
OH

Fig. 2. Reactions of a model compound (4) for lignin structures of the β-1 type on acid treatment.
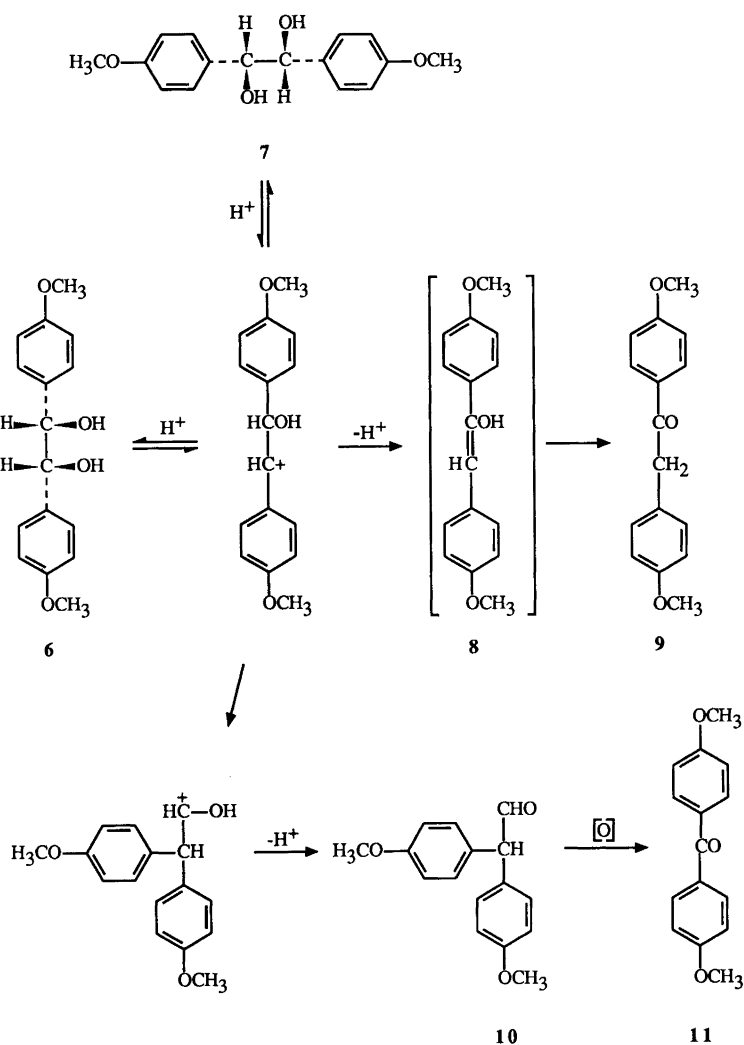
Fig. 3. Reactions of hydroanisoin on acid treatment.

The yields given in Table 1 were determined by ^{1}H NMR spectroscopy (see the Experimental). The aldehyde 10 is the predominant reaction product but substantial amounts of deoxybenzoin 9 are formed when HCl or HBr are used as catalysts. Small amounts of the benzophenone 11 are present in the reaction mixtures. This compound is formed, in the course of the acid treatment and/or handling of the sample, by oxidation of the initially formed 10; this compound is very prone to oxidation with formation of 11. As a rule, the *meso*-form of hydroanisoin (6) was used as starting material. Comparative experiments with methanesulfonic acid as a catalyst showed that the *meso*-form (6) and the (±)-form (7) of hydroanisoin gave reaction products of similar composition (Table 1). It is notable that a partial isomerization of the starting material occurred during the acid treatment. Experiments with aldehyde 10 and deoxybenzoin 9 showed that there was no interconversion of these two compounds under the reaction conditions prevailing during the acid degradation experiments with hydroanisoin (Table 1).

It is obvious from Table 1 that HCl and, to a greater extent, HBr catalyse the formation of deoxybenzoin 9. A few experiments with HI suggest that this acid is even more efficient in catalysing the formation of 9 but the aldehyde (10) was still the major product. Since solutions of HI are prone to oxidation with liberation of iodine, no further experiments with HI were performed. *meso*-Hydroanisoin (6) was essentially unchanged on refluxing with 0.05 M HF for 40 min. Heating (boiling-water bath) with 0.2 M HF for 6 h in a Teflon autoclave resulted in the partial degradation of 6 (71 % unchanged starting material) with formation of 15% 10, 2.6 % 9 and 3 % 11. The product composition may be interpreted as indicating a slight catalytic effect of HF, favouring deoxybenzoin formation. However, the low yields of 9, 10 and 11 and the low degree of conversion make this conclusion uncertain. Other acids examined as catalysts (HClO$_4$, *p*-toluenesulfonic acid, boron trifluoride–diethyl ether, HBF$_4$, HCOOH, CF$_3$COOH and H$_3$PO$_4$) either gave results similar to those given for CH$_3$SO$_3$H, CF$_3$SO$_3$H and H$_2$SO$_4$ in Table 1 (HClO$_4$, *p*-
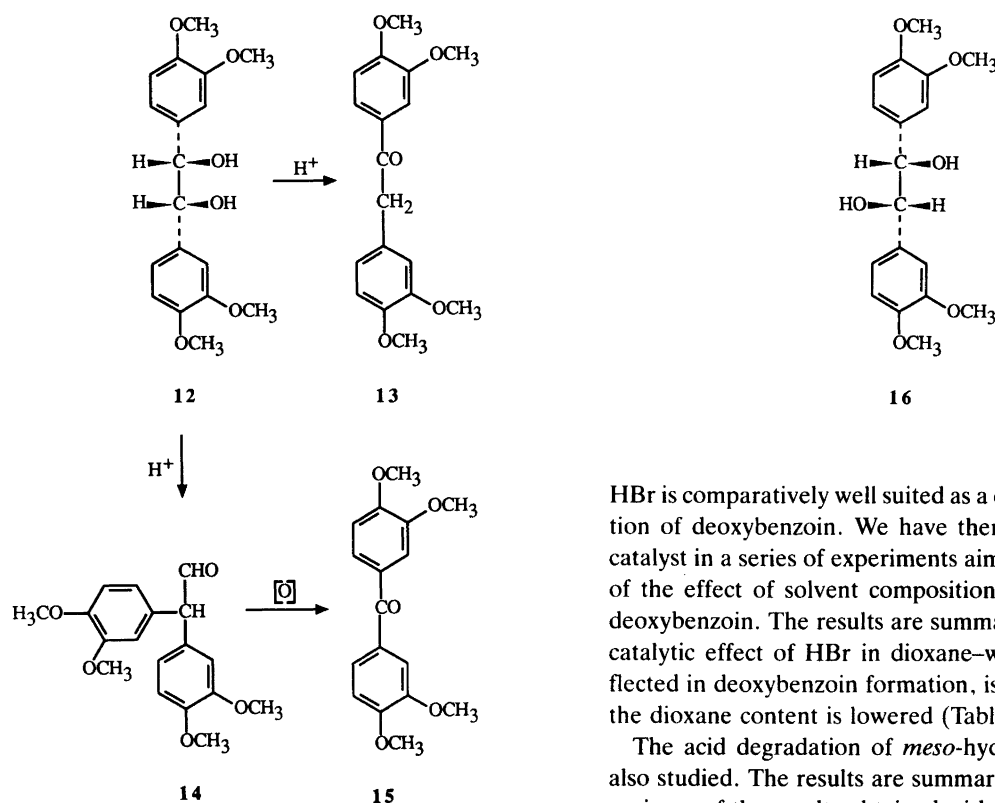
12 → **13**

H⁺ ↓

14 → [O] → **15**

Fig. 4. Reactions of hydroveratroin on acid treatment.

16

toluenesulfonic acid, boron trifluoride–diethyl ether and HBF$_4$) or left the starting material unchanged or essentially unchanged (HCOOH, CF$_3$COOH and H$_3$PO$_4$). None of them exhibited any significant catalytic effect with respect to deoxybenzoin formation. The experiments with boron trifluoride–diethyl ether and HBF$_4$ were performed with glass equipment (refluxing) as well as with a Teflon autoclave (heating at 100 °C); similar results were obtained in both series of experiments.

As is evident from the experiments described above,

HBr is comparatively well suited as a catalyst for the formation of deoxybenzoin. We have therefore used HBr as a catalyst in a series of experiments aiming at the elucidation of the effect of solvent composition on the formation of deoxybenzoin. The results are summarized in Table 2. The catalytic effect of HBr in dioxane–water mixtures, as reflected in deoxybenzoin formation, is essentially lost when the dioxane content is lowered (Table 2).

The acid degradation of meso-hydroveratroin (12) was also studied. The results are summarized in Table 3. Comparisons of the results obtained with hydroanisoin and hydroveratroin indicate that the catalytic effect leading to formation of deoxybenzoins is more pronounced in the case of hydroveratroin. Results from examinations of the phenolic model meso-hydrovanilloin [1,2-bis(4-hydroxy-3-methoxyphenyl)-1,2-ethanediol] were largely in accordance with those obtained with 6 and 12.

Discussion

Tadros et al.[10] have shown that deoxybenzoin 9 and aldehyde 10 are formed on acid treatment of hydroanisoin. In their work, however, the catalyst, as well as the reaction medium, was consistently varied in the experiments, i.e.

Table 1. Yields of aldehyde and ketones on refluxing hydroanisoin with 0.05 M solutions of various acids in dioxane–water (9:1) for 40 min. Results from such treatments of the aldehyde 10 and ketone 9 are also included in the table.

Compound	Acid	Product composition (%)		
		Ar$_2$CHCHO (10)	ArCH$_2$COAr (9)	ArCOAr (11)
6[a]	CH$_3$SO$_3$H	76	2	5
6	CF$_3$SO$_3$H	81	1	4
6	HBr	59	18	6
6	HCl	65	11	5
7[b]	CH$_3$SO$_3$H	76	1	5
9	CH$_3$SO$_3$H	0	96	0
10	HBr	78	0	6
6[a]	H$_2$SO$_4$	81	2	5

[a]About 5 % of the diastereomers of hydroanisoin was present in the reaction mixture (about equal amounts of 6 and 7).
[b]Hydroanisoin [mixture of starting material (7) and its diastereomer (6)] corresponding to 10 % of the original amount was present in the reaction mixture.

Table 2. Yields of aldehyde and ketones on refluxing *meso*-hydroanisoin (6) with HBr in dioxane–water mixtures with different compositions for 40 min. No starting material could be detected in the reaction mixtures.

Dioxane–water ratio	[HBr]/M	Product composition (%)		
		Ar$_2$CHCHO (10)	ArCH$_2$COAr (9)	ArCOAr (11)
9:1	0.05	59	18	6
8:2	0.1	85	7	7
7:3[a]	0.05	89	4	6
6:4	0.1	79	2	10

[a]Similar results were obtained with 0.1 M acid and refluxing for 60 min.

comparative experiments with different catalysts were not performed. It was experimentally supported in some cases and assumed in others that deoxybenzoin 9 found in the reaction mixtures is a conversion product of the initially formed aldehyde 10. Thus the formation of 9 as an initial product on acid treatment of hydroanisoin is demonstrated for the first time in the present study. Also it has not been recognized prior to our study that the reaction pattern is dependent on the particular acid used as a catalyst.

Yasuda *et al.*[7] discussed the differences in reaction patterns with respect to the formation of stilbene and aromatic carbonyl compounds, from lignin models of the β-1 type, on refluxing with 0.2 M HCl and 0.1 M H$_2$SO$_4$ in dioxane–water (9:1) and suggested that the size of the anion was of importance, a smaller anion being more efficient in H$_β$ elimination reactions (i.e. reactions leading to aromatic carbonyl compounds of the type shown in Fig. 2, see Ref. 6). This is not in accordance with our observations in the experiments with hydrobenzoins, since the bromide ion gives higher yields of deoxybenzoins than the smaller chloride ion (Tables 1 and 3). It is noteworthy that the efficiency of the halide ions as catalysts for deoxybenzoin formation parallels their nucleophilicity in aqueous solution. HBr is a stronger acid than HCl. However, the formation of deoxybenzoins can hardly be correlated with the acid strength of the catalyst, since the very strong trifluoromethanesulfonic acid gives a very low yield of 9 (Table 1). Thus the explanation of the observations made should be related to properties of the anions other than relative size. Since the catalytic effect of the bromide ion

resulting in the formation of 9 is diminished when the proportion of water in the reaction medium is increased, it would seem that the polarity of the reaction medium is of importance. We intend to carry out further studies in order to elucidate the reaction mechanism. One conceivable reaction route for the formation of deoxybenzoins comprises the formation of a benzylic cation and a subsequent release of a proton from the adjacent carbon atom, resulting in the formation of an enol intermediate of type 8 which tautomerizes to a deoxybenzoins (Fig. 3). In this context it is of interest to note that 'vinyl dehydration' of the type suggested in Fig. 3 is supposed not to occur in the semi-pinacolone rearrangement. As shown by isotopic labelling, this rearrangement involves migration of a hydrogen atom.[11] Assuming an analogous reaction route to be involved when hydrobenzoins are converted into deoxybenzoins, this reaction would be expected to proceed as shown in Fig. 5.

Experimental

Dioxane used was obtained by distilling reagent-grade dioxane over Na. Silica gel for flash chromatography was Merck Kieselgel 60 (230–400 mesh). The acid reagents used in the experiments were prepared by dilution of aqueous solutions of the acids with dioxane in volumetric flasks.

Thin layer chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60 F$_{254}$) with toluene–dioxane–acetic acid (90:25:4) as the eluent (R_f values: 16, 0.14; 12, 0.15; 7, 0.27; 6, 0.30; 15, 0.41; 14, 0.41; 13, 0.42; 11, 0.51; 9, 0.52; 10, 0.53). Spots were made visible with UV light and by spraying with formalin–H$_2$SO$_4$ (1:9) and subsequent heating.

Table 3. Yields of aldehyde and ketones on refluxing of *meso*-hydroveratroin (12) with 0.05 M solutions of HCl, HBr and CH$_3$SO$_3$H in dioxane–water (9:1) for 40 min.

Acid	Product composition (%)		
	Ar$_2$CHCHO (14)	ArCH$_2$COAr (13)	ArCOAr (15)
CH$_3$SO$_3$H[a]	75	3	5
HCl	62	16	8
HBr	48	24	8

[a]Hydroveratroin [mixture of starting material (12) and its diastereomer (16)] corresponding to 5 % of the original amount was present in the reaction mixture.
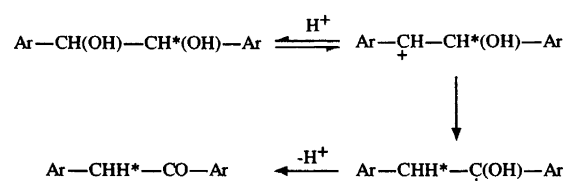

Fig. 5. Alternative reaction route for the formation of deoxybenzoins on acid treatment of hydrobenzoins (the migrating hydrogen atom is denoted H*).

Mass spectra (EI 70 eV). For GC–MS a Finnegan Mat 1020B instrument was used. GC column: 0.32 mm i.d., 30 m long, wide bore fused-silica capillary column [stationary phase: DB-1 (methylsilicone, bonded phase); JW-123103-20 (J&W Scientific)]. Column temperature: 60–250 °C (gradient, 10 °C min⁻¹). Carrier gas: He. Exact mass measurements were performed with a VG Analytical ZAB-HF instrument.

¹H NMR spectra were recorded at 270 MHz with a Bruker WH270 instrument or at 400 MHz with a Varian VXR-5000 instrument. ¹³C NMR spectra were recorded at 100.6 MHz with a Varian VXR-5000 instrument. Temperatures were ca. 300 K. Deuteriochloroform was used as the solvent (internal reference, TMS).

NMR spectral data for some compounds: ¹H NMR spectra.
meso-Hydroveratroin (12): δ 3.82 (6 H, s, OCH₃), 3.88 (6 H, s, OCH₃), 4.73 (2 H, s, CH–O), 6.80–6.85 (6 H, m; aromatic protons). (±)-Hydroveratroin (16): δ 3.76 (6 H, s, OCH₃), 3.83 (6 H, s, OCH₃), 4.62 (2 H, s, CH–O), 6.60–6.80 (6 H, m, aromatic protons). 1,2-Bis(3,4-dimethoxyphenyl)ethanone (13): δ 3.848 (3 H, s, OCH₃), 3.853 (3 H, s, OCH₃), 3.91 (3 H, s, OCH₃), 3.93 (3 H, s, OCH₃), 4.18 (2 H, s, CH₂), 6.75–7.75 (6 H, m, aromatic protons). meso-Hydroanisoin (6): δ 3.80 (6 H, s, OCH₃), 4.74 (2 H, s, CH–O), 6.80–7.25 (8 H, m, aromatic protons). (±)-Hydroanisoin (7): δ 3.76 (6 H, s, OCH₃), 4.64 (2 H, s, CH–O), 6.70–7.10 (8 H, m, aromatic protons). 1,2-Bis(4-methoxyphenyl)ethanone (9): δ 3.78 (3 H, s, OCH₃), 3.85 (3 H, s, OCH₃), 4.17 (2 H, s, CH₂), 6.85–8.05 (8 H, m, aromatic protons). 2,2-Bis(4-methoxyphenyl)-ethanal (10): δ 3.80 (6 H, s, OCH₃), 4.78 (1 H, d, J = 2.4 Hz; –CH<), 6.85–7.20 (8 H, m, aromatic protons), 9.88 (1 H, d, J = 2.4 Hz; CHO). Bis(4-methoxyphenyl)methanone (11): δ 3.89 (6 H, s, OCH₃), 6.90–7.85 (8 H, m, aromatic protons).

¹³C NMR spectra. 2,2-Bis(4-methoxyphenyl)ethanal (10): δ 55.3 (2 C, OCH₃), 62.5 (1 C, –CH<), 114.4 (4 C, aromatic carbon), 128.5 (2 C, aromatic carbon), 130.1 (4 C, aromatic carbon), 159.0 (2 C, aromatic carbon), 198.7 (1 C, CHO). 1,2-Bis(4-methoxyphenyl)ethanone (9): δ 44.4 (1 C, CH₂), 55.2 (1 C, OCH₃), 55.4 (1 C, OCH₃), 113.8 (2 C, aromatic carbon), 114.1 (2 C, aromatic carbon), 127.0 (1 C, aromatic carbon), 129.7 (1 C, aromatic carbon), 130.4 (2 C, aromatic carbon), 130.9 (2 C, aromatic carbon), 158.5 (1 C, aromatic carbon), 163.5 (1 C, aromatic carbon), 196.5 (1 C, CO).

Preparation of hydrobenzoins and their acidolysis products.
The preparation of the hydrobenzoins 6, 7, 12 and 16 has been described in a previous paper.[12] 1,2-Bis(4-methoxyphenyl)ethanone (9), 2,2-bis(4-methoxyphenyl)ethanal (10), 1,2-bis(3,4-dimethoxyphenyl)ethanone (13) and bis(4-oxyphenyl)methanone (11) were prepared following procedures described in the literature [9,[13] 10[10,14] (from hydroanisoin using acetic acid[10] as a dehydrating agent), 13,[15] 11[14]].

3,3',4,4'-Tetramethoxybenzophenone (15) was obtained as a by-product in acid degradation experiments with meso-hydroveratroin (12). M.p. 144–146 °C (from ethanol) (lit.[16] 146.0–147.2 °C). ¹H NMR: δ 3.94 (6 H, s, OCH₃), 3.97 (6 H, s, OCH₃), 6.85–7.50 (6 H, m, aromatic protons). ¹³C NMR: δ 56.07 (2 C, OCH₃), 56.08 (2 C, OCH₃), 109.8 (2 C, aromatic carbon), 112.4 (2 C, aromatic carbon), 124.7 (2 C, aromatic carbon), 130.8 (2 C, aromatic carbon), 148.9 (2 C, aromatic carbons), 152.6 (2 C, aromatic carbon), 194.4 (1 C, CO). The IR spectrum exhibited a band at 1632 cm⁻¹ (C=O) in agreement with a previous report.[17]

2,2-Bis(3,4-dimethoxyphenyl)ethanal (14) was prepared from meso-hydroveratroin analogously to the previously described[10] preparation of 2,2-bis(4-methoxyphenyl)ethanal from meso-hydroanisoin using phosphoric acid as the reagent. The product was obtained as an oil. 3,3',4,4'-Tetramethoxybenzophenone was present as a contaminant. Purification (column chromatography, separation via the sulfite complex) resulted in an essentially pure product but traces of 11 were still present in the product (¹H NMR; GC–MS, using the aldehyde as an internal standard the rel. retention time was 1.03 for the ketone). ¹H NMR: δ 3.84 (6 H, s, OCH₃), 3.88 (6 H, s, OCH₃), 4.78 (1 H, d, J = 2.7 Hz, CHAr₂), 6.65–6.95 (6 H, m, aromatic protons), 9.89 (1 H, d, J = 2.7 Hz, CHO). ¹³C NMR: δ 55.9 (2 C, OCH₃), 56.1 (2 C, OCH₃), 63.1 (1 C, CHAr₂), 111.5 (2 C, aromatic carbon), 112.3 (2 C, aromatic carbon), 121.3 (2 C, aromatic carbon), 128.7 (2 C, aromatic carbon) 148.6 (2 C, aromatic carbon), 149.4 (2 C, aromatic carbon), 198.4 (1 C, CHO). The IR spectrum exhibited peaks at 1722 (C=O) and 2721 cm⁻¹ (CH in the formyl group). The base peak in the mass spectrum (m/z 287) is attributed to the fragment ion (3,4-dimethoxyphenyl)₂CH⁺.

Exact mass measurements of the molecular ion (intensity, 7 % of the base peak) gave: m/z 316.128 (calc. for C₁₈H₂₀O₅: m/z 316.131).

Treatment of hydroanisoin and hydroveratroin with various acids and quantitative analysis of the reaction products by ¹H NMR spectrometry. Hydroanisoin or hydroveratroin (75 mg) was dissolved in 25 ml of the acid in dioxane–water [in most experiments 0.05 M acid in dioxane–water (9:1)] and the mixture was refluxed for 40 min (some experiments with HF, boron trifluoride–diethyl ether and HBF₄ involved heating the reaction mixture for the desired period of time in a Teflon autoclave at 100 °C). The reflux temperature was about 88 °C and the reflux temperature of other mixtures of dioxane–water used (Table 2) differed very little from this temperature. The reaction mixture was cooled in an ice-bath and the acidity reduced by addition of 10 ml 0.1 M NaHCO₃ solution. A solution (1.0 ml) of hexamethylbenzene in toluene (9.3 mg ml⁻¹) was injected into the reaction mixture. The reaction mixture was extracted with chloroform (25 + 2 × 10 ml) and the extract dried over Na₂SO₄.

A solution (1.0 ml) of docosane in toluene (8.0 mg ml⁻¹)

was added to the extract and solvents were removed by film evaporation. The residue was dissolved in 1 ml deuterio-chloroform and examined by ^{1}H NMR spectroscopy, and the amounts of the reaction products were determined by integration of suitable signals and comparison with the integrals of signals from the internal standards hexamethyl-benzene (signal at δ 2.23) and docosane [signals at δ 0.88 (CH$_3$) and 1.26 (CH$_2$); the latter signal was used in the estimates]. In addition to signals from formyl, methine and methylene groups, the following signals from aromatic protons were used in the quantitative estimates: 1,2-bis(4-methoxyphenyl)ethanone (**9**), δ 7.98 (2 H); 4,4′-di-methoxybenzophenone (**11**), δ 7.79 (4 H); 1,2-bis(3,4-di-methoxyphenyl)ethanone (**13**), δ 7.56 (1 H) and δ 7.66 (1 H); 3,3′,4,4′-tetramethoxybenzophenone (**15**), δ 7.43 (2 H) and δ 7.38 (2 H). The conditions for the recording (pulse width, pulse delay) were selected to ensure a quantitative result.

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