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Tetrahedron
ELSEVIER
Tetrahedron 62 (2006) 9289–9293

4,4′-Dihydroxy-3,3′,5,5′-tetramethoxyazodioxybenzene: an unexpected dimer formed during hydroxylamine extractions of wheat flour

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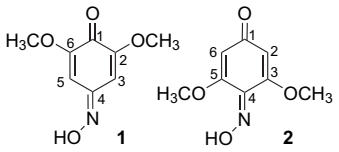
Received 31 January 2006; revised 15 May 2006; accepted 1 June 2006
Available online 4 August 2006

Abstract—Neutral hydroxylamine extracts of wheat contained a product that was colourless at pH<5 (λ_{max} 340 nm) and yellow at pH>9 (λ_{max} 400 nm). ESI-MS showed a major ion *m/z* 184.0 and a possible parent ion *m/z* 367.2 (MH^+) suggesting that the product resulted from the reaction of 2,6-dimethoxy-*p*-quinone with hydroxylamine. However, mass spectral and other spectroscopic data indicated that the compound was neither of the 2,6-dimethoxy-*p*-quinone oximes. A product with identical absorbance, mass spectrum, electrophoretic mobility and HPLC retention time as the pigment from hydroxylamine extracts of flour was observed amongst the reaction products of hydroxylamine and 1,4-dihydroxy-2,6-dimethoxybenzene. The structure of this product was identified by NMR, 2D NMR and IR as 4,4′-dihydroxy-3,3′,5,5′-tetramethoxyazodioxybenzene.

1. Introduction

Yellow alkaline noodles (YAN) made from wheat flour, alkaline salts such as sodium and potassium carbonate and water, are an important part of the diet in many countries of eastern and south-eastern Asia.[1] A preliminary study by Mares et al.[2] indicated that the colour of alkaline noodles was due partly to xanthophylls and partly to compounds that could be extracted with aqueous solvents. These latter compounds, in contrast to the xanthophylls, were essentially colourless at neutral or acid pH, but turned yellow at higher pH. An efficient method for the quantification of these water-soluble pigments using hydroxylamine extraction has been recently reported.[3] Together with flavone-*C*-glycosides, another unknown pigment was identified as a possible contributor to the colour of YAN.[3] This pigment was relatively unstable, colourless at pH<5 (λ_{max} 340 nm) and yellow at pH>9 (λ_{max} 400 nm). Electrospray mass spectrum yielded a major ion *m/z* 184.0 but with a possible parent ion *m/z* 367.2 (MH^+).

If the ion-mass of 184 was an MH^+ ion, it could arise from a low molecular weight oxime formed by condensation of hydroxylamine with either an aldehyde or ketone. One possible carbonyl candidate, which forms an oxime with a mass of 183, was 2,6-dimethoxy-*p*-quinone. 2,6-Dimethoxy-*p*-quinone can be isolated from wheat germ fermented with baker's yeast.[4,5] This compound forms two oxime isomers, 2,6-dimethoxy-1,4-benzoquinone-4-oxime (**1**) and 3,5-dimethoxy-1,4-benzoquinone-4-oxime (**2**). These isomers were synthesised and their properties compared with those of the flour product.



2. Results and discussion

The two oxime isomers of 2,6-dimethoxy-*p*-quinone (**1**, **2**) were synthesised and shown to have similar mass spectra with major ions (**1**) *m/z* (relative intensity) 367.0 ($2M+H^+$, 0.10), 184.0 ($M+H^+$, 0.25), 170.2 (0.10), 167.2 (0.11), 166.0 (0.68), 155.2 (0.19), 152.0 (base peak), 151.0 (0.81), 140.2 (0.25), 112.0 (0.67), 111.2 (0.26) and (**2**) *m/z* (relative intensity) 367.0 ($2M+H^+$, 0.07), 184.0 ($M+H^+$, 0.20), 170.0 (0.08), 167.2 (0.36), 166.2 (0.80), 152.0 (base peak), 151.0 (0.70), 140.0 (0.09), 112.0 (0.17), 111.0 (0.26). The mass spectra were more complex than expected and resulted from the formation of cluster ions during the ionisation process. In contrast, a relatively simple mass spectrum was obtained for the product obtained from flour, which showed major ions at

Keywords: Wheat flour; Hydroxylamine; Hydroquinone; Oxime dimer.
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doi:10.1016/j.tet.2006.06.117

m/z (relative intensity) 367.2 ($M+H^+$, 0.25), 184.0 (base peak), 156.1 (0.37), 154.0 (0.47), 139.1 (0.26), 124.1 (0.08). These differences in fragmentation patterns, as well as differences in absorbance spectra and HPLC retention times, indicated that the structure of the flour product was neither (**1**) nor (**2**). The considerably larger intensity of the mass at *m/z* 367 and simpler fragmentation pattern of the flour product compared with the oxime isomers suggested this product was a dimer of 2,6-dimethoxy-*p*-quinone mono-oxime.

1-Hydroxy-2,6-dimethoxy-nitrosobenzene is a tautomeric analogue of 2,6-dimethoxy-*p*-quinone oxime. Many nitrosobenzenes dimerise under increasing concentration,[6] low temperature[7] or in the presence of organic solvents[8] to give azodioxybenzenes. Nitrosobenzene trans-dimers have a diagnostic, very strong IR band at 1253–1299 cm^{-1} due to the aromatic $\nu N^+–O^-$ frequency,[6,9] which is sensitive to the molecular environment.[10,11] Aromatic cis-dimers give two active NO stretching bands at 1389–1397 cm^{-1} and 1409 cm^{-1}. The synthetic dimeric species had a strong band at 1316 cm^{-1}, which is consistent with the trans-form of a nitroso dimer (Table 1). Another major band associated with the dimer was at 952 cm^{-1}. This band[12] has been attributed to $\nu N^+–O^-$ in compounds with aliphatic $\nu N^+–O^-$. None of the dimers described by Luttke[9] contained this band and is quite specific for the compound under investigation.

The IR OH stretching frequency (3300 cm^{-1}) of the dimer is strong while the band for both oxime monomers is either weak or missing. A strong OH stretching band indicates that the nitroso tautomer predominates over the oxime tautomer. Both oxime monomers show a medium band at approximately 1345 cm^{-1} due to $\nu N{=}O$ stretching,[6] which is absent in the dimer.

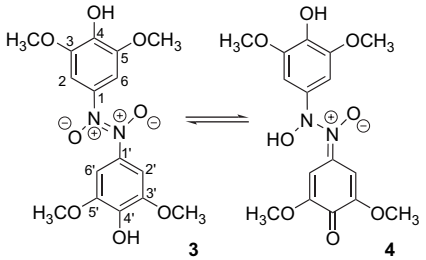
In organic solvents, such as chloroform and dichloromethane, *C*-nitrosobenzene compounds exist in monomer–dimer equilibria, with the cis-dimers being preferred over the trans-dimers, irrespective of the nature of the solid-state dimer structure.[8] However, the dimer was relatively unstable in chloroform and dichloromethane, but was stable in DMSO and water. No monomer–dimer equilibrium was observed in DMSO during the NMR experiments. The stability of dimer (**3**) and lack of monomer–dimer equilibrium are consistent with the hydroxyl groups acting as a strong electron withdrawing substituent.[6,19]

Table 1. Major peaks identified in the infrared spectra of 2,6-dimethoxy-1,4-benzoquinone-4-oxime (**1**), 3,5-dimethoxy-1,4-benzoquinone-4-oxime (**2**) and the dimer, 4,4′-dihydroxy-3,3′,5,5′-tetramethoxyazodioxybenzene (**3**)

1	2	3	ν
—	3300w	3268vs	OH
1626vs	1630vs	1644vs	C=O
1571vs	1575vs	1581vs	C=N
1452s	1454s	1455m	OH bending
1344m	1348m	—	N=O stretch
—	—	1316vs	Aryl $N^+–O^-$
1246s	1249s	1249s	=C-O-CH_3
1122vs	1125vs	1113vs	Aryl C–N stretch
1051vs	1052vs	1051s	=C-O-CH_3
—	—	952vs	$N^+–O^-$
860m	858m	852s	N–O bending
702s	704s	702m	

The aromatic protons of the dimer show a substantially higher δ (6.51 and 6.80 ppm) when compared with 2,6-dimethoxy-1,4-benzoquinone-4-oxime (**1**) (5.61 ppm) and 3,5-dimethoxy-1,4-benzoquinone-4-oxime (**2**) (doublet, 5.60 and 5.63 ppm) but lower δs than literature values for either unsubstituted or C-4 substituted cis-dimers (7.11–7.4 ppm) and trans-dimers (7.69–7.89 ppm) of nitrosobenzenes.[7] There is a significant difference ($\Delta\delta$ 0.29 ppm) between the aromatic protons of the dimer indicating the effect of shielding/deshielding. In contrast, no difference was recorded in the shifts for the 2 and 6 protons for the aromatic protons in dichloromethane and chloroform of either *cis*- or *trans*-nitroso dimers.[7]

It can be determined whether an isomer is either cis or trans in solution because the shielding/deshielding of aromatic protons in *cis*-$N_2O_2C_6H_{5-n}X_n$ is virtually negligible, whereas the shielding in the *trans*-$N_2O_2C_6H_{5-n}X_n$ is substantial.[7,13] Moreover, the aromatic proton signals for the cis-dimer should be shifted to the right compared to both the monomer and the trans-dimer. While shielding/deshielding was observed for the dimer, suggesting a trans-isomer, the aromatic proton signals were observed to be shifted to the left compared to the monomer, but shifted to the right compared to either *cis*- or *trans*-4-substituted nitrosobenzene dimers.[7] The higher δ values of the aromatic protons of our dimer were consistent with the formation of the azodioxybenzene compound (**3**). The hydroxyl group allows the contribution of the quinonoid canonical state and thus the aromatic protons were observed at lower δ values than other 4-substituted nitrosobenzenes. The double bond nature of the C–N bond and the possibility of formation of the tautomer (**4**) suggest that the energy barrier between cis and trans may not be great and the dimer may exist as both cis and trans in solution.



3 **4**

The ^{13}C NMR C1 shift of the dimer (δ 148.0) was in the range characterised by aromatic azodioxy dimers (δ 139–146) and is substantially less than the nitroso monomers (δ 162–176).[14] However, the C1 shifts of the two oximes (δ 137–138) are also substantially lower than the nitroso monomers and similar to the dimer. The exceptionally strong π-electron acceptor nature of the N=O substituent produces a strong deshielding effect causing C1 shifts to higher δ values, while the N_2O_2 and N–OH substituents have only a moderate effect.

The solvent used for NMR investigation is important. ^{13}C NMR data obtained in $CDCl_3$ or CD_2Cl_2 for nitrosobenzene monomers for the C3 and C5 and C2 and C6 carbons are

identical.[14–16] In DMSO, however, nitrosophenol monomers show differences between the C3 and C5, and the C2 and C6 carbons.[17] The position of the nitroso-oxime group in 3,5-dimethoxy-1,4-benzoquinone-4-oxime provides a larger difference between the ^{13}C shifts of quaternary carbons (C3 and C5) than the aromatic CH carbons (C2 and C6) suggesting the rotation around the C–N bond is restricted and *syn–anti* isomerism is slow.[18] However, 2,6-dimethoxy-1,4-benzoquinone-4-oxime has a broad peak at 102.4 ppm for the aromatic CH carbons (C3 and C5) suggesting the *syn–anti* isomerism is rapid and splitting is minimised.

Similar to the nitrosobenzene monomers, ^{13}C NMR studies of azodioxybenzenes[14–16] in $CDCl_3$ and CD_2Cl_2 also show no difference in the ^{13}C chemical shifts between either the C2 and C6 or the C3 and C5 carbons. However, in solid-state ^{13}C NMR, *trans*-4,4′-dichloro-azodioxybenzene $(4\text{-}ClC_6H_4NO)_2$ showed a distinction between the C2 and C6 signals ($\Delta\delta$=4.1).[8] This was thought to arise from the locked nature of the phenyl rings in the solid state and the chemical shift represents the shielding anisotropy of the azodioxy group. Similarly, the dimer (**3/4**) exhibited large differences in the ^{13}C shifts between the C3 and C5 carbons as well as the C2 and C6 carbons when measured in DMSO. The larger difference in shifts for the aromatic CH carbons (C2/C2′ and C6/C6′) compared with the quaternary carbons (C3/C3′ and C5/C5′) suggests that the azodioxy moiety is attached proximal to the aromatic CH carbons. gHMQC assignments together with differences in shifts due to shielding/deshielding magnetic anisotropy allowed the assignment of all carbons (Table 2; Fig. 1).

Table 2. Proton, carbon and gHMBC correlations of NMR of the dimer, 4,4′-dihydroxy-3,3′,5,5′-tetramethoxyazodioxybenzene (**3**)

Carbon number	^{13}C δ	^{1}H δ	gHMBC
1	148.0	—	H2[a] (2[b]), H6[a] (2)
2	94.5	6.5 (d)	H6 (3), methyl[a] (4)
3	151.9	—	H6 (4), methyl (3)
4	185.2	—	H2 (3), H6 (3)
5	153.6	—	H2 (4), methyl (3)
6	108.6	6.8 (d)	H2 (3), methyl[a] (4)
Methyl	55.5, 55.6	3.71, 3.73	—

[a] Weak association.
[b] Number in brackets refers to 2-, 3-, or 4-bond correlations.

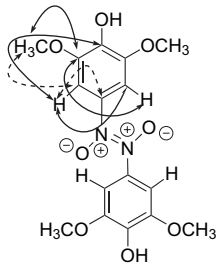
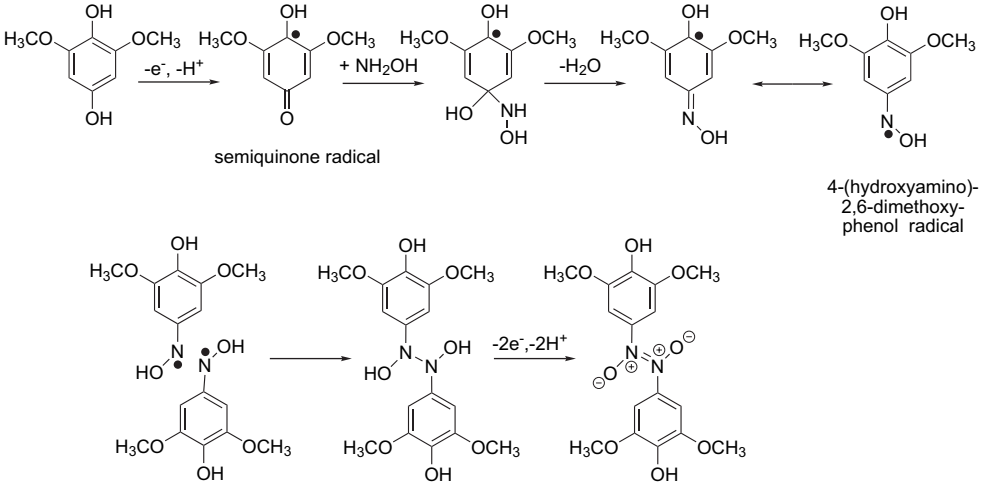


Figure 1. Correlations observed in the gHMBC spectrum of 4,4′-dihydroxy-3,3′,5,5′-tetramethoxyazodioxybenzene (**3**).

Additional evidence for the structure of the dimer arises from the absorbance spectral data. The molar extinction coefficients of the unionised oximes and the dimer are identical, while the π–π* UV band of the dimer shows a bathochromic shift of 40 nm compared with the oxime monomers due to a lengthening of the chromophore. In comparison, the π-levels of nitrosomesitylene (1,3,5-trimethyl-2-nitrosobenzene) are not changed by dimerisation[6] and there is no effect on either λ_{max} or extinction coefficient of the UV bands. The C–N bond of nitrosomesitylene has single bond character, and the nitroso group is not co-planar with the benzene moiety and is well insulated from the benzene ring in both monomer and dimer. Unlike the nitrosomesitylene dimer, the N^+–O^- group in the dimer is contiguous with the benzene moiety and the C–N bond shows some double bond character.

As most azodioxybenzenes are formed from their nitroso monomers and in the absence of strong intramolecular hydrogen bonding, 4-hydroxy species occur principally as oximes[20] and thus dimerisation is unlikely,[9] another mechanism is required for the formation of dimer (**3**). A related compound, 4,4′-dihydroxy-3,3′-dimethyldiphenyl-*N*,*N*′-dihydroxyhydrazine, detected by mass spectrometry in photographic effluent,[20] can be synthesised by reacting 2-methyl-*p*-benzoquinone with hydroxylamine in a reductive solution containing sulfite and carbonate. Therefore, a possible reaction mechanism for the synthesis of dimer (**3**) is suggested (Scheme 1). A partial oxidation of 1,4-dihydroxy-2,6-dimethoxybenzene to create 2,6-dimethoxysemiquinone is necessary prior to reaction with hydroxylamine.



Scheme 1. Suggested mechanism for the synthesis of 4,4′-dihydroxy-3,3′,5,5′-tetramethoxyazodioxybenzene (**3**).

In wheat, however, it is postulated that, 1,4-dihydroxy-2,6-dimethoxybenzene occurs as a glycoside even though this glycoside has never been isolated.[21,22] Is possible that during the deglycosylation process, 2,6-dimethoxysemiquinone radical is released, which then reacts with hydroxylamine.

3. Experimental methods

3.1. LC–mass spectrometry

The sample (5 μL) was loaded onto an HPLC column (Spherisorb S5 ODS2, 250×1 mm, Waters Corporation). The separation was performed with solvent A (5% formic acid) and solvent B (5% formic acid, 80% acetonitrile) by using a gradient system: 10–35% of solvent B in 35 min, kept constant at 35% for 5 min and then 35–95% solvent B in a further 20 min, at a flow rate of 25 μL/min. The HPLC column was connected to a UV–vis detector (HP1100, Hewlett–Packard) monitoring at 280 and 340 nm, followed by a mass spectrometer with an ion spray ion source (API-300, PE Sciex, Thornhill, Ontario, Canada). The mass spectrometer was operated in positive ion mode and was scanned from *m/z* 250 to 1000 in 1.88 s. Ion spray and orifice potentials were set at 5.5 kV and 30 V, respectively. Curtain and nebuliser gases were nitrogen and air, respectively. All mass spectral data were processed using Bio-Multiview software (version 1.2ß3, PE Sciex).

3.2. IR, NMR and melting points

Infrared spectra were collected using a Perkin–Elmer (Shelton, CT, USA) Spectrum 1 Fourier Transform Infrared (FTIR) instrument equipped with a diffuse reflectance sampling accessory. The data were exported to GRAMS/AI (Thermoelectron Corporation, Woburn, MA, USA) for processing. NMR spectra were acquired on a Varian Inova-600 NMR spectrometer, at an ^{1}H frequency of 600 MHz and ^{13}C frequency of 150 MHz. All NMR experiments were acquired at 25 °C. All spectra were processed on a Sun Microsystems Ultra Sparc 1/170 workstation using VNMR software (version 6.1A). Melting points were obtained on a hot stage microscope (C. Reichert Optische Werke A.G., Vienna, Austria).

3.3. HPLC

Separation of compounds was performed using a Hewlett–Packard HPLC 1100 instrument using a 250×4 mm analytical column (Merck, Darmstadt, Germany) packed with spherical LiChrospher 100 RP-18 (5 μm), fitted with a 4×4 mm guard column using the same packing material. Separation was carried out with solvent A (1% formic acid) and solvent B (1% formic acid, 4% acetonitrile, 95% methanol) by a gradient system elution program: 0–3 min, isocratic 10% B; 3–8 min, gradient 10–24% B; 8–11 min, isocratic 24% B; 11–18 min, gradient 24–34% B; 18–28 min, gradient 34–44% B; 28–35 min, gradient 44–65% B; 35–40 min, gradient 65–95% B; 40–55 min, isocratic 95% B; 55–60 min. A flow rate of 0.65 mL/min, detection at 340 and 280 nm and temperature set at 30 °C were used.

3.4. HVPE

The electrophoretogram, consisting of chromatography paper (Chr. 1; Whatman, England) soaked in the appropriate buffer was placed over a glass rod to minimise surface contact between two wells containing buffer of a gel electrophoresis unit (Model 715; Betheseda Research Laboratories, Gaithersburg, MD, USA). A voltage gradient of 7.5 V/cm was used. The buffers employed were borate (0.05 mol/L; pH 10.0) and citrate (0.05 mol/L; pH 7.0) and formic/acetic (0.75/1.04 mol/L; pH 1.76).

3.5. Extraction of the flour product

For direct comparison, flour (200 g) was extracted with 1 L 0.1 M hydroxylamine hydrochloride for 2 h. This was filtered and 100 mL of the filtrate was extracted with 3×100 mL dichloromethane. The dichloromethane was evaporated and the residue dissolved in DMSO for MS-analysis. Found: ES-MS, *m/z* (relative intensity) 367.2 ($M+H^+$, 0.21), 184.1 (base peak), 156.1 (0.42), 154.0 (0.26), 139.1 (0.41) and 124.0 (0.15); HPLC retention time was 21.4 min; absorbances (aq) λ_{max} 340 nm at pH 2.5 and λ_{max} 400 nm at pH 10.

3.5.1. Synthesis of 2,6-dimethoxy-1,4-benzoquinone-4-oxime (1). The *title compound* **1** (2,6-dimethoxy-4-oximino-2,5-cyclohexadienone-1) was synthesised from 2,6-dimethoxy-1,4-benzoquinone and hydroxylamine according to Bolker and Kung.[23] Found: pale yellow plates; mp 214–215 °C dec (lit[23] mp 218.8 °C dec); ES-MS, *m/z* (relative intensity) 367.0 ($2M+H^+$, 0.07), 184.0 ($M+H^+$, 0.20), 170.0 (0.08), 167.2 (0.36), 166.2 (0.80), 152.0 (base peak), 151.0 (0.70), 140.0 (0.09), 112.0 (0.17), 111.0 (0.26); HPLC retention time was 19.1 min; absorbances (aq) λ_{max} 300 nm (ε=16,000), 395 nm (ε=1200) at pH 2.5 and λ_{max} 353 nm (ε=25,300) at pH 10; δ_H (600 MHz DMSO-d_6) 3.71 (6H, s, OC*H*$_3$), 5.61 (2H, s, H2 and H6); δ_C (150.9 MHz DMSO-d_6) 56.1 (OCH$_3$), 102.4 br (C3 or C5), 137.7 (C4), 185.6 (*C*1), quaternary carbons (*C*2 and *C*6) were not observed; ν_{max} (KCl) 3233w, 3176w, 3064 (br), 2943w, 2750s (br), 2644w, 2366w, 2247w, 2174w, 2100w, 1844w, 1744w, 1626vs (C=O), 1571vs (C=N), 1452s (C–O stretch), 1430m, 1403m, 1344w, 1321w, 1246s (C–O stretch), 1228s, 1192m, 1122vs (aryl C–N stretch), 1051vs (N–OH), 1019w, 986w, 930m, 908m, 860s, 810m, 795m, 702s.

3.5.2. Synthesis of 3,5-dimethoxy-1,4-benzoquinone-4-oxime (2). The *title compound* **2** was prepared by nitrosodemethylation of 1,3,5-trimethoxybenzene (Sigma–Aldrich) according to Shpinel et al.[24] Found: pale yellow needles; mp 166–167 °C commenced sublimation, 216–217 °C dec (lit[17] mp 223–224 °C); ES-MS, *m/z* (relative intensity) 367.0 ($2M+H^+$, 0.10), 184.0 ($M+H^+$, 0.25), 170.2 (0.10), 167.2 (0.11), 166.0 (0.68), 155.2 (0.19), 152.0 (base peak), 151.0 (0.81), 140.2 (0.25), 112.0 (0.67), 111.2 (0.26); HPLC retention time was 25.4 min; λ_{max} (aq) 298 nm (ε=18,000), 395 nm (ε=1400) at pH 2.5, 353 nm (ε=29,500) at pH 10.0; δ_H (600 MHz DMSO-d_6) 3.72 (3H, s, OC*H*$_3$), 3.74 (3H, s, OC*H*$_3$), 5.60 (1H, s, *H*2), 5.63 (1H, s, *H*6); δ_C (150.9 MHz DMSO-d_6) 56.1 (O*C*H$_3$), 56.2 (O*C*H$_3$), 102.1 (*C*2 or *C*6), 103.3 (*C*2 or *C*6), 137.5 (*C*4), 157.6 (*C*3 or *C*5), 161.1 (*C*3 or *C*5), 185.6 (*C*1), in general agreement

with Maleski;[17] ν_{max} (KCl) 3236w, 3182w, 3062, 2951w, 2811w, 2800s (br), 2650w, 2249w, 2102w, 1851w, 1749w, 1630vs (C═O), 1575vs (C═N), 1465w, 1454vs (C–O stretch), 1442, 1431, 1409s, 1348w, 1249vs (C–O stretch), 1230s, 1194, 1125vs (aryl C–N stretch), 1066w, 1052vs (N–OH), 1019w, 988w, 934, 911, 858s, 809, 796, 704s.

3.5.3. Reaction of 1,4-dihydroxy-2,6-dimethoxybenzene with hydroxylamine (synthesis of 4,4′-dihydroxy-3,3′,5,5′-tetramethoxyazodioxybenzene 3). Approximately 10 mg of 1,4-dihydroxy-2,6-dimethoxybenzene and 20 mg hydroxylamine hydrochloride were added to 2 mL of water and adjusted to pH 7. This mixture was allowed to react for 16 h at 45 °C. The solution was extracted with dichloromethane. KCl was added and the dichloromethane was carefully evaporated under reduced pressure. Found: pale brown plates; mp 110–111 °C commenced sublimation (yellow needles), 183–184 °C dec; ES-MS, *m/z* (relative intensity): 367.2 ($M+H^+$, 0.25), 184.0 (base peak), 156.1 (0.37), 154.0 (0.47), 139.1 (0.26), 124.1 (0.08); λ_{max} (aq) 340 nm (ε=16,000) at pH 2.5, 400 nm (ε=17,000) at pH 10.0 (note this was estimated using HPLC and NMR data by comparing the concentration and absorbance of 2,6-dimethoxy-1,4-benzoquinone-4-oxime with the synthetic product); HPLC retention time was 21.4 min; δ_H (600 MHz DMSO-d_6) 3.71 (6H, s, OCH_3), 3.74 (6H, s, OCH_3), 6.51 (2H, d, *J* 2.1 Hz, *H*2 and *H*2′), 6.80 (2H, d, *J* 2.1 Hz, *H*6 and *H*6′); δ_C (150.9 MHz DMSO-d_6) 55.5 (OCH_3), 55.6 (OCH_3), 94.5 (*C*2, *C*2′), 108.6 (*C*6, *C*6′), 148.0 (*C*1, *C*1′), 151.9 (*C*3, *C*3′), 153.6 (*C*5, *C*5′), 175.0 (*C*4, *C*4′); ν_{max} (KCl) 3268vs (br, OH), 3092, 2965w, 2942, 2837, 2650w, 1644vs (C═O), 1581vs (C═N), 1455m (C–O stretch), 1417w, 1407, 1316vs (N^+–O^-), 1249vs (C–O stretch), 1219s, 1192w, 1181w, 1113vs (aryl C–N stretch), 1051, 1014, 952s (N^+–O^-), 907, 852s, 797, 733, 702.

Acknowledgements

Financial support from the Grains Research & Development Corporation and the Value Added Wheat CRC is gratefully acknowledged. We would also like to acknowledge Yoji Hayasaka, The Australian Wine Research Institute, for mass spectra and Philip Clements, The University of Adelaide, for NMR analyses, and Dr. Max Tate, the University of Adelaide, for helpful comments.

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