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A MODEL STUDY OF THE MECHANISM OF THE BASE FRAGMENTATION OF LIGNOSULPHONATE

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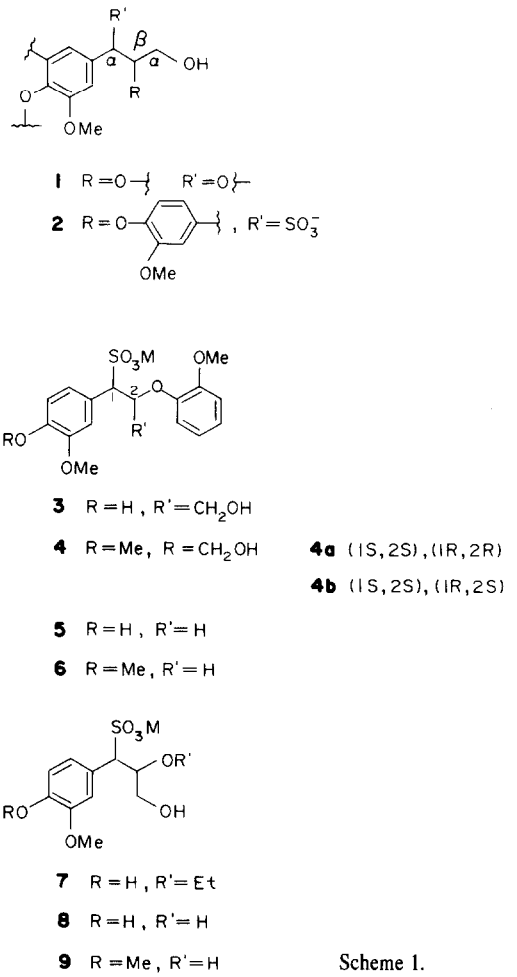
Abstract—The base fragmentation of the guaiacylglycerin-β-guaiacylether-α-sulphonate structural entity (**2**) of lignosulphonate,[1] was re-investigated by using the corresponding model compound (**4**). Isolation of the hitherto elusive[1] styrenic intermediate (**19**) resulted in a new mechanistic proposal.

Lignin, one of the two major components of wood, comprises a random polymer of highly oxygenated phenyl propane units (**1**).[2] During the bisulphite and acid sulphite pulping processes, lignin is converted (mainly by sulphonation of the benzylic or α-position of some of the phenyl propane units[3]) into water soluble lignosulphonate. Lignosulphonate constitutes a major part of spent sulphite pulping liquor (SSL) which generally poses a polution problem.[4] However, it also constitutes a potential source of chemical raw material.[5] The chemistry of this by-product has consequently been investigated since shortly after the invention of these pulping processes.[6,7] Initial research was concerned mainly with the sulphonation reaction itself. Later research involved structural studies, most of which consisted of degradation studies, model compound investigations, or a combination of these methods.[3] In this regard, the base fragmentation of lignosulphonate has been the subject of considerable attention.[3]

The base fragmentation of lignosulphonate was initially aimed at desulphonation,[8] but in 1904 Grafe[9] found that some vanillin (**15**) was produced by this treatment. Later, Kratzl *et al.*[10] found that both vanillin (**15**) and acetaldehyde (**17**) are produced under basic conditions. Their investigations showed that the sulphonic acid group is essential for aldehyde production, and labelling studies with ^{14}C showed that both aldehydes originate from the same phenyl-propane progenitor.[11] It was also shown that methylated lignosulphonate gave both vanillin (**15**) and its methyl ether veratric aldehyde (**16**), together with acetaldehyde (**17**).[12]

Model compound studies by the same authors[1,12] showed that these aldehydes originate from the guaiacylglycerin-β-guaiacylether-α-sulphonate structural entity (**2**) of lignosulphonate. Model compounds **3** (barium salt) and **4** (barium salt) afforded 71.3% vanillin (**15**), 58% acetaldehyde (**17**) and 73.9% guaiacol (**10**), and 53% veratric aldehyde (**14**), 60% acetaldehyde (**17**) and 73% guaiacol respectively, whilst models **5**, **7**, **8** and **9** (all Ba-salts) gave no aldehydes when treated with base.† From these results and from results obtained earlier on unsulphonated model compounds by Gierer,[13] it was concluded that the fragmentation of **3** and **4** proceeds *via* the initial elimination of guaiacol (**10**), rather than by direct substitution. Of the two possible elimination pathways (Scheme 1), pathway (a) was chosen. Strong



Scheme 1.

† It is not stated clearly whether **5** proposed any guaiacol.[1,12]

arguments were raised against the formation of the allyl alcohols (**18**) and **19**) by pathway (b) (*vide infra*), and furthermore no mechanism could be envisaged by which these intermediates would afford the observed aldehydes. The formation of intermediates **11** and **12** was favoured since they were expected to afford the observed products† *via* de-sulphonation followed by retro-aldol reaction.

Our recent isolation of one of the stereoisomers of **19** from the base treatment of the lignosulphonate model compound **4**[15] prompted a re-investigation of this mechanism.

In our initial study[15], reaction on **4** with 3,3N NaOH for 1 hr under reflux produced guaiacol **10** (65%) and one stereoisomer of **19** (38%). Since no provision had been made for the collection of the volatile aldehydes, we repeated the reaction under the conditions previously described by Kratzl *et al.*[1]

Model compound **4** (Na-salt) was treated with 2.5 M NaOH at b.p. for 1 hr. Oxygen free N_2 was bubbled continuously through the mixture and the volatile aldehydes were trapped as their 2,4-dinitrophenylhydrazones. The ether extract of the acidified mixture contained guaiacol **10** (72.4% yield) and veratric aldehyde **16** (1.7% yield) and veratric aldehyde **16** (traces). The aqueous phase contained starting material **4** (13.4% yield) and two other compounds. Separation of this mixture by semipreparative high pressure liquid chromatography (HPLC) gave the stereoisomers **19a**‡. (45.7% yield); $\delta(D_2O)$ 4.09 (d, 2H, J 6.6Hz, =CH–C$\underline{H}_2$–OH), 6.75 (t, 1H, J 6.6Hz, =C$\underline{H}$–), and **19b** (18.7% yield); $\delta(D_2O)$ 4.66 (d, 2H, J 5.5Hz, =CH–C$\underline{H}_2$–OH), 6.08 (t, 1H, J 5.5Hz, =C$\underline{H}$–).

The total yield of **19** (**a** + **b**, 64.6%) indicates that these compounds are intermediates in the conversion of model **4** to veratric aldehyde (**16**) and acetaldehyde (**17**). A reaction profile obtained by treating **4** with a 25 fold excess of NaOH over 24 hr (Fig. 1) shows that the initial rapid formation of **19a** and **19b** is followed by their slow conversion to the aldehydes **16** and **17**.

Kratzl *et al.*[1] originally argued that both the negative charge onthe sulphonate group, as well as the steric hindrance to anti-coplanarity which is required for the E_2 elimination of guaiacol (**10**) would hamper abstraction of the benzylic proton and formation of the allylic alcohol **19**. Our isolation of **19a** and **19b** refutes this argument. Furthermore, α-anion stabilization by sulphur through d-orbital participation could be expected to favour benzylic proton abstraction.

The possibility of neighbouring group participation[16] involving epoxide **20** formation and a corresponding reduction in the steric hindrance of the transition state complex required for eliminative epoxide ring opening, was shown to be unlikely. When model compound **6**, having a steric hindrance to anti-coplanarity comparable withthat of **4**, was subjected to base treatment, the elimination product **21**, $\delta(D_2O)$ 5.78 (s, 1H, =C$\underline{H}$H) and 6.12 (s 1H, =CH$\underline{H}$) was repidly formed (Fig. 2). Subsequent slow addition of hydroxide produced the alcohol **22**. This indicates: (a) that benzylic proton abstraction is a very facile process for this type of compound, and (b) that the steric hindrance to anti-coplanarity does not influence the reaction adversely. The formation of the allylic alcohols **19** from **4** therefore appears to proceed *via* the direct E_2 elimination of guaiacol **10**. The reaction conditions employed (strong base, high temperature) are also conductive to E_2 elimination reactions.

†The bis-demethoxy analogue of **12** has been shown to produce acetaldehyde (**17**) and benzaldehyde under similar conditions.[14]

‡Observed previously.[15]

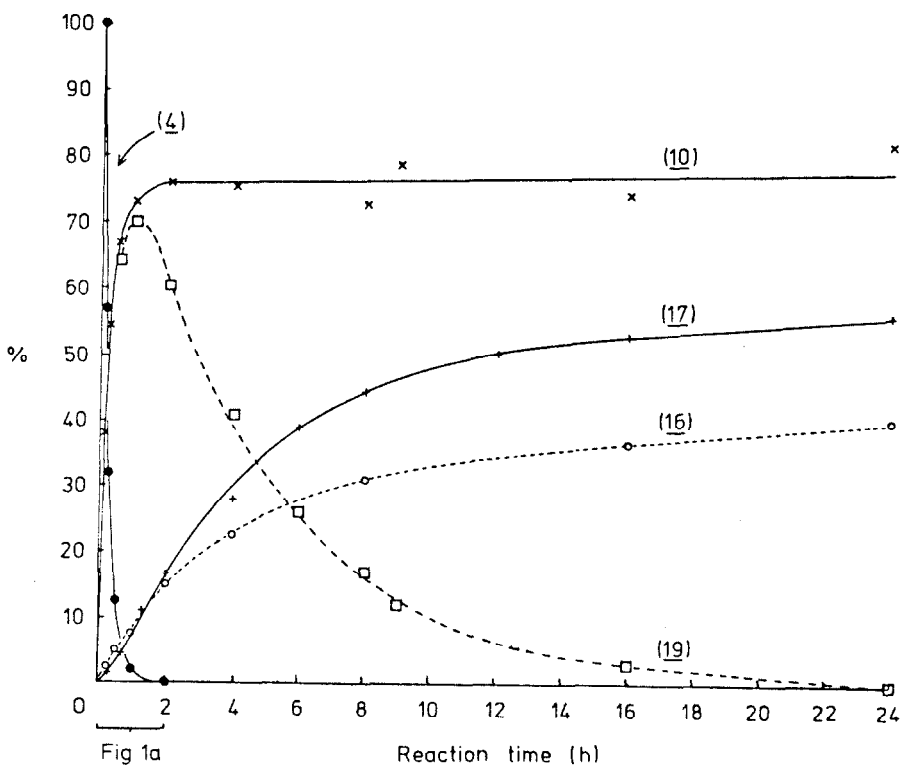


Fig. 1. Treatment of **4** with 2.5N NaOH at boiling point (Yields determined by HPLC).

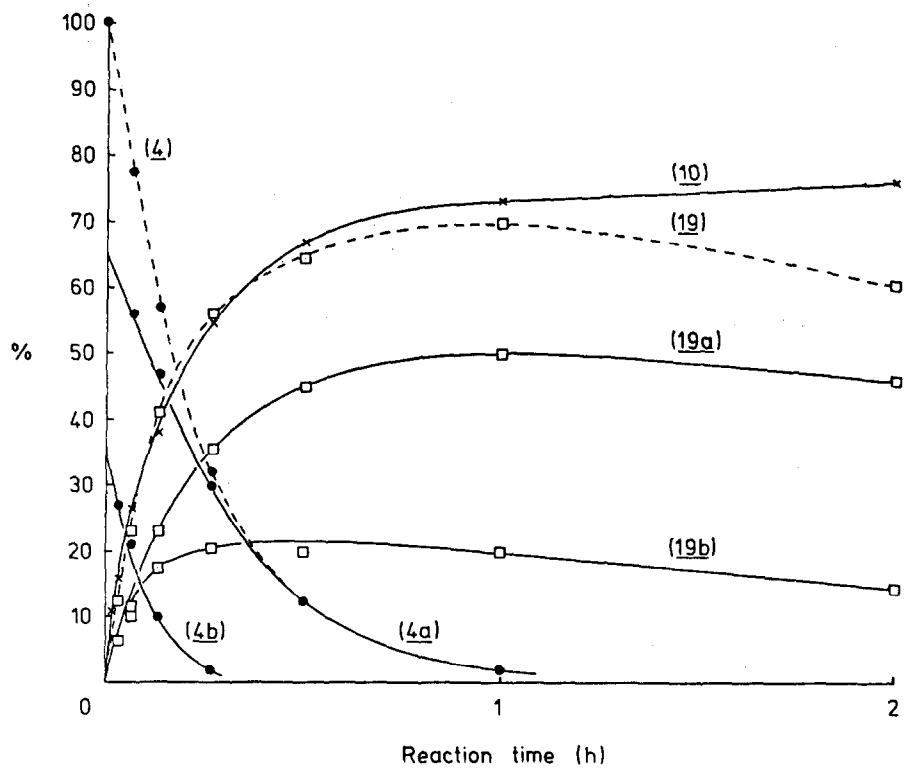


Fig. 1(a). Treatment of **4** with 2.5N NaOH at boiling point (Yields determined by GPLC).

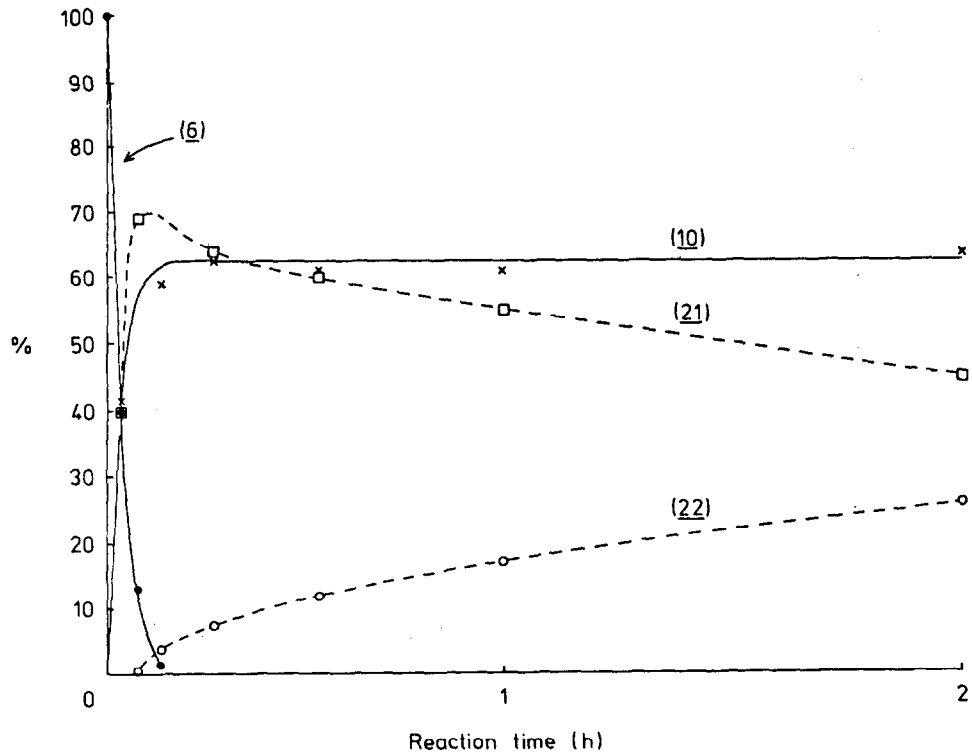
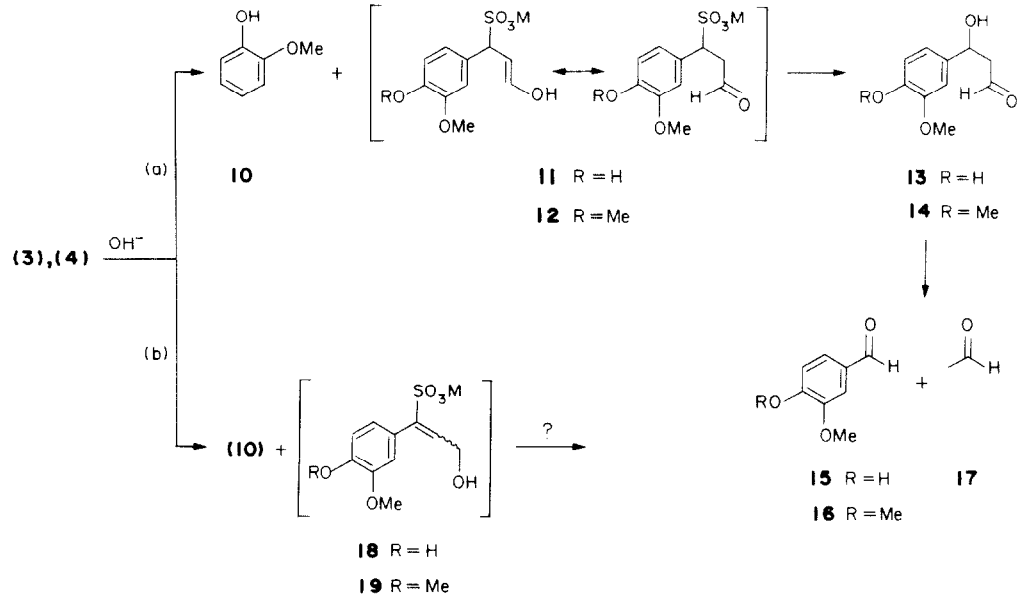
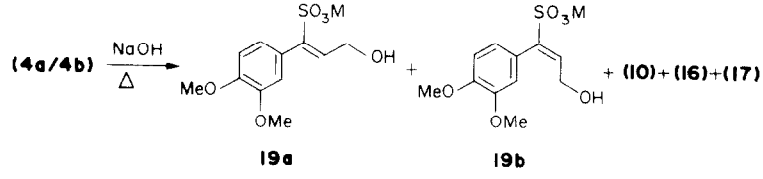


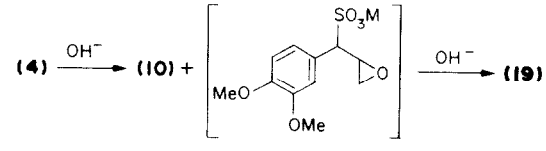
Fig. 2. Treatment of **6** with 1.6N NaOH at boiling point (Yields determined by HPLC).

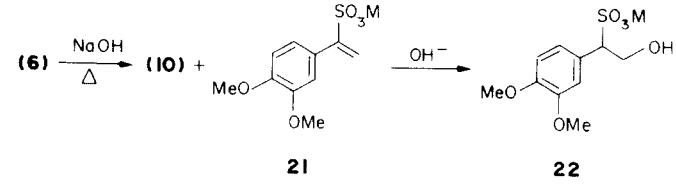


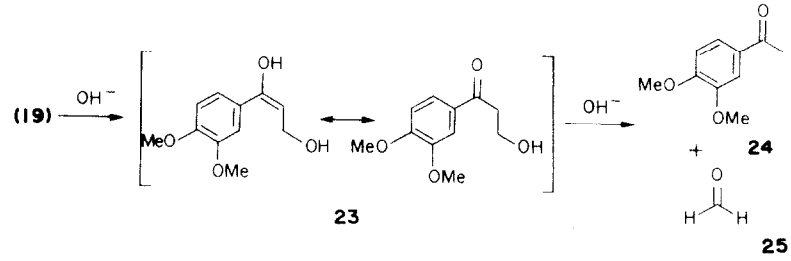
Two stereoisomers, **19a** (*Z*) and **19b** (*E*) are formed because compound **4** is a mixture of two diastereomeric racemates **4a** and **4b**. From Fig. 1a it is clear that **4a** produces the *Z*-isomer **19a** and **4b** the *E*-isomer **19b**. The anti-coplanarity required for guaiacol (**10**) elimination therefore indicates that diastereomeric racemate **4a** is a mixture of 1*R*; 2*R* and 1*S*; 2*S* enantiomers and diastereomeric racemate **4b** is a mixture **4b** is a mixture of 1*R*; 2*S* and 1*s*; 2*R* enantiomers.

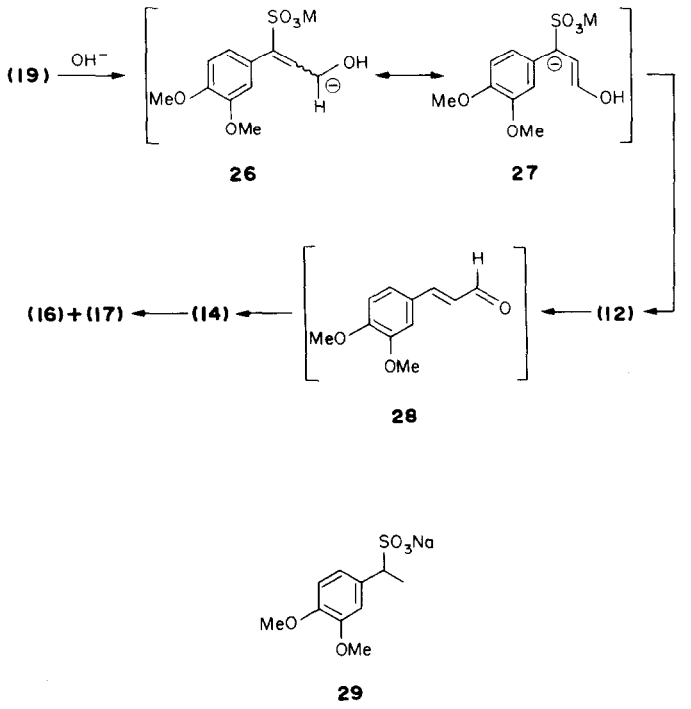
Several pathways exist for the further reaction of **19** with base. Addition of an OH group to the double bond of **19** as exemplified by the observed conversion of **21** to











22, Fig. 2, would lead to the formation of alcohol **9**. This compound has however previously been shown not o afford the observed aldehydes.[1] An alternative possiblity is the direct nucleophilic substitituion of the sulphonate group of **19** by an OH group. This process is unlikely in aqueous medium at 100°, and furthermore, would lead, *via* retro-aldol reaction of the intermediate **23**, to acetoveratrone (**24**) and formaldehyde (**25**), neigher of which could be detected in our study.† As a third alternative, the abstraction of aproton α to the OH group of **19** would result in the formation of the intermediate (**12**) proposed by Kratzl,[1] from which the formation of veratric aldehyde (**16**) and acetaldehyde (**17**) can be readily envisaged.

This abstraction is not a favoured process. However, once the intermediate anion (**26**) is formed, stabilization of its resonance form (**27**) by the benzylic sulphonate group (*vide supra*) will provide the driving force for its conversion to **12**.

The subsequent desulphonation of **12** to afford **14** has previously been suspected to proceed *via* a β-elimination yielding the corresponding cinnamyl aldehyde (**28**), rather than by direct substitution of the sulphonate group.[1] This presumption was confirmed b subjecting model compound **29** to the normal base treatment for 7 hr. Starting material was recovered quantiatively, showing that benzylic sulphonate groups are not substituted by OH ions under these conditions.‡ Thus, the sulphonate group of **12** appears to be lost by elimination *via* abstraction of the activated β-proton to afford 3.4-dimethoxy-cinnamaldehyde (**28**), which is subsequently hydrated to afford **14**.[14]

During the reaction, neither **12**, nor **28** nor **14** could be detected at any stage. This suggests that the proton abstraction from **19** represents the rate determining step of the reaction, which is followed by a faster conversion of **26** to the aldehydes **16** and **17**.

Thus it is clear that he base fragmentation of the lignosulphonate model compound **4** involves not only the intermediate **12** as proposed previously,[1] but also the intermediates (**19**) which we have isolated. The rapid E_2 elimination of guaiacol from model **4** *via* benzylic proton abstraction to give the allyl alcohol **19**, is followed by the slow base induced double bond migration to give the enol/aldehyde (**12**) which is readily converted to the observed aldehydes by desulphonation to hydroxy aldehyde (**14**) and subsequent collapse *via* retro aldol condensation.

While kinetic comparison of the model study results with those obtained on lignosulphonate itself[12] should be approached with caution,[1] it may be assumed that the guaiacylglycerin-β-guaiacylether-α-sulphonate structural entity (**2**) of lignosulphonate will fragment *via* the above mechanism to produce vanillin (**15**) and acetaldehyde (**17**).

EXPERIMENTAL

PMR and CMR spectra were determined on a Brucker WP-80 spectrometer (80 and 20 MHz respectively) in either D_2O [Ref. 3-(trimethylsilyl)propanesulphonic acid Na-salt] or $CDCl_3$ [ref. TMS]. Mass spectra were determined with a DuPont 21–492 B mass spectrometer with direct probe insertion operated with an ionizing potential of 70 eV. The probe inlet temp. and the percentage abundances of the base peak (100%) in each spectrum are given in parentheses.

Yields were determined by comparison with reference samples on a Knaur modular high pressure liquid chromagraph (HPLC). Water insoluble samples were analysed on a Knaur LiChrospher Si100 column with the eluant stated at a pump rate of 4 ml/min. Water soluble samples were analysed on a Knaur reverse phase

†Under certain conditions, Kratzl *et al.*[1,12] found trace amounts of **24** and **25**.

‡In aqueous base, benzyl sulphonic acid is converted to benzyl alcohol at temperatures above 345°.[17]

LiChrosorb RP-18 column withthe eluant stated at a pump rate of 4 ml/min. A valuable wavelength UV detector was employed at the wavelength stated, and hte chromatogram peaks were integrated for quantitative determinations by cutting out and weighing.

Sodium 1-(3',4'-dimethoxyphenyl)-2-(2''-methoxyphenoxy)-3-hydroxypropane-1-sulphonate (**4**, Na^+ salt)†

The model compound **4** was obtained (86% yield) as a 65:35 mixture of two diastereomers by sulphonation[18] of the corresponding benzylic alcohol diastereomeric mixture, which was available *via* the standard method of Adler *et al.*[19] Separation of the diastereomeric racemates by semi preparative HPLC (Knaur LiChrosorb RP-18 column with 16 mm internal diam, 25% MeOH eluant, 10 ml/min, 285 nm) afforded **4a**; δ (D_2O) 3.52, 3.60, 3.80 (3 × s, 3H each, 3x-OCH_3), 3.8–4.2 (m, 2H, -CH_2OH), 4.36 (d, 1H, J 8.3Hz, Ar-$CH(SO_3^-)$-), 5.0–5.2 (m, 1H, $W_{1/2}$ 13Hz, -$CH(SO_3^-)$-$CH(OAr')$-) and 6.7–7.2 (m, 7H, Ar-H); δ (D_2O) 58.04, 58.40 (-OCH_3), 65.49 (-CH_2-OH), 69.58 (Ar-$CH(SO_3^-)$-), 83.03 (-$CH(SO_3^-)$-$CH(OAr')$-), 113.95, 114.92, 115.56, 118.71 (Ar-C, o to oxygenated aromatic carbons), 123.77, 124.89, 126.55, 129.34 (Ar-C, m, p to oxygenated aromatic carbons), 149.94, 150.33, 150.51, 151.69 (oxygenated aromatic carbons) and **4b**; δ (D_2O) 3.82 (s, 6H, 2x-OCH_3), 3.86 (s, 3H, -OCH_3), 3.9–4.4 (m, 2H, -CH_2OH), 4.50 (d, 1H, J 5.9Hz, Ar-$CH(SO_3^-)$-), 5.0–5.3 (m, 1H, $W_{1/2}$ 14Hz, -$CH(SO_3^-)$-$CH(OAr')$-) and 6.8–7.4 (m, 7H, Ar-H); δ (D_2O) 58.49 (-OCH_3), 64.15(-CH_2OH), 68.36 (Ar-$O(SO_3^-)$-), 82.36 (-$CH(SO_3^-)$-$CH(OAr')$-), 114.35, 115.81, 116.21, 119.01 (Ar-C, o to oxygenated aromatic carbons), 124.29, 125.44, 125.60, 128.70 (Ar-C, m,p to oxygenated aromatic carbons), 148.79, 150.65, 150.95, 152.43 (oxygenated aromatic carbons).

Sodium 1-(3',4'-dimethoxyphenyl)-2-(2''-methoxyphenoxy)ethane-1-sulphonate (**6**, Na^+ salt)

Sulphonation of the corresponding benzylic alcohol[18] which was available *via* the standard method of Adler *et al.*,[19] afforded the model compound **6** (77%); δ (D_2O) 3.52, 3.77, 3.81 (3 × s, 3H each, 3x-OCH_3), 4.4–4.9 (m, 3H, Ar-$CH(SO_3^-)$- and -CH_2-) and 6.6–7.15 (m, 7H, Ar-H); δ (D_2O) 58.22, 58.34 (-OCH_3), 67.58 (benzylic C), 71.64 (-CH_2-), 114.35, 115.35, 115.59, 117.56 (Ar-C, o to oxygenated aromatic carbons), 123.95, 124.95, 125.10, 129.67 (Ar-C, m,p to oxygenate aromatic carbons), 149.76, 150.57, 150.85 and 151.57 (oxygenated aromatic carbons). The methyl ester of **6**[20] had M^+ 382.1092. $C_{18}H_{22}SO_7$ requires: M^+ 382.1086.

Base treatment of model compound **4**

(a) A soln of the mixture **4a/4b** (65:35) (2.00 g, 4.8 mmol) in water (20 ml) was heated with NaOH (2.0 g, 50 mmol) at b.p. (140° bath temp.) for 1 hr. Oxygen free N_2 was bubbled continuously through the mixture, whilst the water was replenished from time to time to keep the volume constant. The volatile aldehydes were trapped by passing the exiting N_2-vapour mixture through a soln of 2,4-dinitrophenylhydrazine (0.5 g 2,4-dinitrophenylhydrazine dissolved in 10 ml conc H_2SO_4 and then made up to 200 ml with H_2O). After 1 hr the mixture was cooled (ice bath), acidified (dil H_2SO_4, pH 2) and extracted with ether (4 × 50 ml). The combined extract was dried ($MgSO_4$) and analysed by HPLC (40% ether in hexane, 250 nm). Comparison with authentic samples showed **10** (72.4% yield) and **16** (1.7% yield). The precipitated 2,4-dinitrophenylhydrazones were extracted with CH_2Cl_2 (4 × 50 ml) and the combined extract dried ($MgSO_4$) and analysed by HPLC (15% ether in hexane, 250 nm). Comparison with 2,4-dinitrophenylhydrazones prepared by a standard procedure,[21] showed the hydrazones of **17** (4.3% yield) and **16** (traces). The extracted waterphase was neutralized (dil NaOHaq). HPLC analysis (2% and 15% MeOH, 217 nm) of an aliquot showed starting **4a** (13.4% recovered), and **19a** (45.7% yield) and **19b** (18.7% yield), reference samples of which were obtained as follows:

The waterphase was evaporated to dryness, and the resulting white solid was extracted with 92% n-BuOH (2 × 50 ml). Solvent evaporation afforded the crude product as a solid white foam. Semi-preparative HPLC (Knaur LiChrosorb RP-18 column with 16 mm internal dia., 4% MeOH eluant, 10 ml/min, 260 nm) afforded sodium (*Z*)- **19a**; δ (D_2O) 3.88, 3.89 (2 × s, 6H, 2x-OCH_3), 4.09 (d, 2H, J 6.5Hz, -CH_2OH), 6.75 (t, 1H, J 6.5Hz, =$CHCH_2OH$), 6.85–7.1 (m, 3H, Ar-H) and sodium (*E*)- **19b**; δ (D_2O) 3.87 (s, 6H, 2X-OCH_3), 4.66 (d, 2H, J 5.5Hz, -CH_2OH), 6.08 (t, 1H, J 5.5Hz, =$CHCH_2OH$), 7.0–7.2 (m, 3H, Ar-H). Methylation[18] of a portion of the crude product, followed by chromatography over SiO_2 (gradient from 20% EtOAc/hexane to 100% EtOAc) afforded methyl-(*Z*)-1-(3',4'-dimethoxyphenyl)-3-hydroxypropen-1-sulphonate; δ ($CDCl_3$) 1.92 (br.t, 1H, J = 5.9, -OH, D_2O exchangeable), 3.75 (s, 3H, -SO_3CH_3), 3.88, 3.90 (2 × s, 6H, 2x-OCH_3), 4.24 (app.t, 2H, J 5.9Hz, -CH_2-OH; D_2O: d, 2H, J 6.1Hz), 6.8–6.95 (m, 3H, Ar-H) and 7.09 (t, 1H, J 6.1Hz, =$CHCH_2OH$); *m/e* (100°) 288 (10%), 193 (24), 164 (55) and 55 (100); [Found M^+ 288.0660. $C_{12}H_{16}SO_6$ requires: M^+ 288.0667], and methyl-(*E*)-1-(3',4'-dimethoxyphenyl)-3-hydroxypropen-1-sulphonate; δ ($CDCl_3$) 2.38 (m, 1H, $W_{1/2}$ 11Hz, -OH, D_2O exchangeable), 3.72 (s, 3H, -SO_3CH_3), 3.89 (s, 6H, 2x-OCH_3), 4.74 (m, 2H, $W_{1/2}$ 11Hz, -CH_2-OH; D_2O: d, J 5.4Hz) 6.55 (t, 1H, J 5.4Hz, =$CHCH_2OH$), and 6.8–7.1 (m, 3H, Ar-H); *m/e* (110°) 288 (18%), 193 (40), 163 (78), 91 (32), 77 (38) and 55 (100): [Found M^+ 288.0663 $C_{12}H_{16}SO_6$ requires M^+ 288.0667].

(b) A soln of mixture **4a/4b** (65:35) (4.0 g, 9.52 mmol) in water (100 ml) was heated with NaOH (10.0 g, 250 mmol) as above. Aliquots (1 ml) were taken periodically from the mixture, worked up and analysed as before. The 2,4'-dinitrophenylhydrazone soln was replaced periodically, extracted and analysed as before. The analytical results, depicted in Fig. 1, were corrected for loss caused by aliquot removal.

Base treatment of model compound **6**. (Fig. 2)

A soln of **6** (806 mg, 2.06 mmol) in water (80 ml) was heated with NaOH (5.0 g, 125 mmol) at b.p. as before. Aliquots (2 ml) were removed periodically, acidified (0.3 M H_2SO_4, 20 ml) and extracted with CH_2Cl_2 (2 × 20 ml). The combined extract was dried and analysed by HPLC (40% ether/hexane, 250 nm) for **10**. No aldehydes could be detected. No 2,4-dinitrophenyhydrazones were formed. The aliquots were then neutralized (dil NaOHag), and analysed by HPLC (5% and 25% MeOH, 217 nm) for starting material (**6**), and **21** and **22**. Reference samples were obtained as follows:

After 2 hr the reaction was quenched by cooling (ice bath), acidified (dil H_2SO_4) and extracted with CH_2Cl_2 (2 × 50 ml). The waterphase was neutralized and evaporated to dryness. The solid residue was extracted with 92% n-BuOH (2 × 50 ml) to afford, after solvent evaporation, the crude product. A portion of the crude product was separated by semi-preparative HPLC (Knaur LiChrosorb RP-18 column with 16 mm internal dia. 24% MeOH eluant, 10 ml/min, 237 min) to afford **21**; δ (D_2O) 3.87 (s, 6H, 2X-OCH_3), 5.78 (s, 1H, =CHH *cis* to -SO_3Na), 6.12 (s, 1H, =CHH *trans* to -SO_3Na) and 6.95–7.3 (m, 3H, Ar-H), and **22**; δ (D_2O) 3.87, 3.88 (2xs, 6H, 2X-OCH_3)3.5–4.5 (m, 3H, -CH(SO_3Na)CH_2OH), and 7.0–7.5 (m, 3H, Ar-H). Methylation of the remainder of the crude product,[18] followed by chromatography over SiO_2 (gradient from 20% EtOAc/hexane to 100% EtOAc) afforded methyl 3',4'-dimethoxyphenylethene-1-sulphonate; δ ($CDCl_3$) 3.77 (s, 3H, -SO_3CH_3), 3.90 (s, 6H, 2x-OCH_3), 6.08 (s, 1H, =CHH *cis* to -SO_3CH_3), 6.42 (s, 1H, =CHH *trans* to -SO_3CH_3), and 6.8–7.25 (m, 3H, Ar-H); *m/e* (62°) 258 (48%), 163 (100), 148 (36), 119 (24), 89 (28), 77 (26) and 51 (32); [Found M^+ 258.0562, $C_{11}H_{14}SO_5$ requires: M^+ 258.0562], and methyl 1-(3',4'-dimethoxyphenyl)-2-hydroxyethane-1-sulphonate; δ ($CDCl_3$) 2.54 (br.m, 1H, $W_{1/2}$ 14Hz, -OH, D_2O exchangeable), 3.72 (s, 3H, -SO_3CH_3), 3.89 (s, 6H, 2X-OCH_3), 3.65–4.65 (m, 3H, -$CH(SO_3CH_3)CH_2OH$), and 6.7–7.1 (m, 3H, Ar-H); *m/e* (75°) 276 (11%), 181 (100), 151 (30), 149 (60), 138 (40), 121 (82), 91 (36), and 77 (42); [Found: M^+ 276.0658. $C_{11}H_{16}SO_6$ requires: M^+ 276.0667.].

Base treatment of model compound **29**

Compound **29** (prepared by sulphonation of the corresponding benzylic alcohol[18]) was treated with NaOH as before for 7 hr. No 2,4-dinitrophenylhydrazones were formed. Workup and analysis of the waterphase (HPLC; 10% MeOH, 217 nm) showed starting material (100%).

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