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Light-induced Oxidation of Lignin. The Behaviour of Structural Units Containing a Ring-conjugated Double Bond*

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The methyl ethers of isoeugenol, coniferyl alcohol and coniferaldehyde, model compounds for end group units in spruce lignin, have been irradiated with near UV-light in the presence of oxygen. Veratric aldehyde and products arising from addition of solvent to intermediate peroxirane structures were isolated from the reaction mixtures indicating the participation of singlet oxygen.

This mechanism was verified (a) by retarding the reaction with specific singlet oxygen quenchers and (b) by reacting the same compounds with chemically generated singlet oxygen.

The results show that conjugated double bonds in lignin are susceptible to light-induced oxidation giving rise to carbonyl structures which are known to participate in the light-induced oxidation of phenolic units in lignin.

Due to a shortage in the supply of wood, the production of high yield pulps including mechanical pulp has become increasingly attractive. Recent technological improvements have made it possible to bleach mechanical pulp to a high brightness level and to maintain a high yield. Such pulps can substitute low yield, bleached chemical pulps in certain paper grades. One disadvantage of mechanical pulp, whether bleached or unbleached, is its rapid rate of yellowing on exposure to daylight. If a way could be found to improve the stability of such pulps towards the influence of light, the field of application of the pulps could probably be extended considerably. Great efforts have been made both technically and in the laboratory to find a solution to this problem, but these efforts have so far been unsuccessful.

In a recent series of papers much of our present understanding of the light-induced degradation of lignocellulosic materials was elucidated.[1–6] In that work it was shown that among the numerous structural elements present in lignin only a few were able to absorb ultraviolet light present in daylight, *viz.* arylpropane units containing α,β-double bonds, carbonyl groups in conjugation with aromatic rings and biphenyl structures. Furthermore, it was shown that conjugated carbonyl groups excited by light are capable of abstracting hydrogen from phenolic units thus generating phenoxy radicals. In subsequent reaction steps, these phenoxy radicals may react with oxygen to give coloured polymeric structures.

Double bonds in conjugation with aromatic rings are present in lignin end groups of the cinnamyl alcohol and cinnamaldehyde types.[7] In the present paper, studies are described which deal with the behaviour of non-phenolic model compounds of these types under the influence of UV-light with wavelengths between 300 – 400 nm, *i.e.* the UV-part of daylight radiation.

RESULTS

Coniferyl alcohol and coniferaldehyde structures are linked to the lignin polymer through their phenolic hydroxyl groups and/or the aromatic 5-positions.[7] The corresponding aryl methyl ethers (III, IV) were chosen as model compounds. These were irradiated in the presence of oxygen both in solution and absorbed on filter paper thus imitating the conditions

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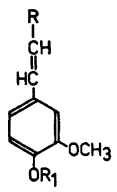
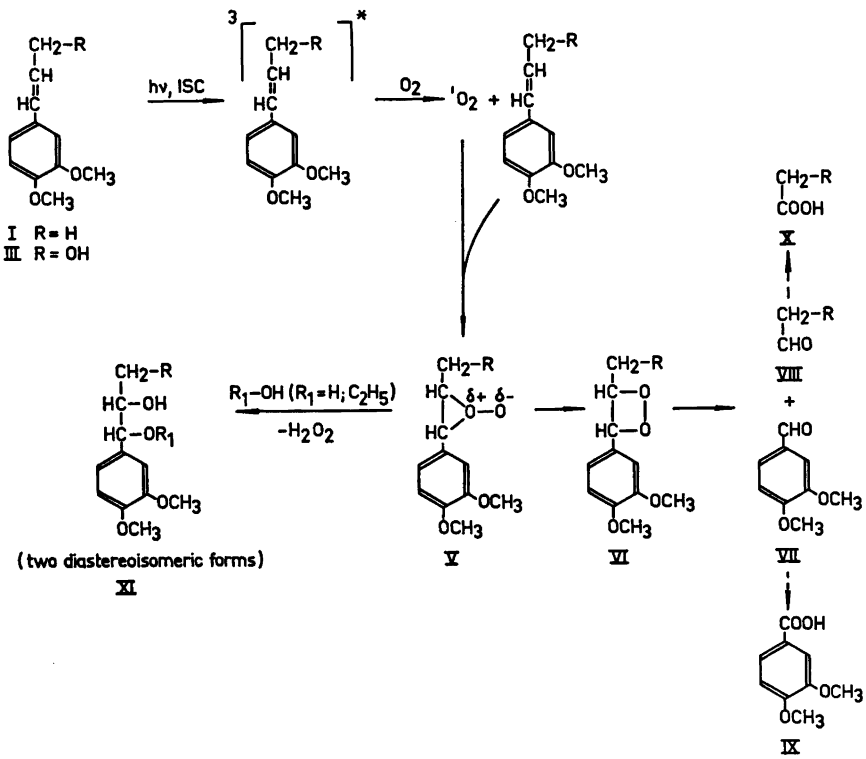


I R = R_1 = CH_3
II R = CH_3, R_1 = H
III R = CH_2OH, R_1 = CH_3
IV R = CHO, R_1 = CH_3

prevailing in a "mechanical pulp". Under these two sets of conditions, coniferyl alcohol methyl ether (III) and the simpler lignin model isoeugenol methyl ether (I) both afforded the same types of reaction products (see Scheme 1).

The reaction sequence may be rationalized in the following way. The model compound absorbs light and enters an excited singlet state. *Via* intersystem crossing (ISC), an excited triplet state is generated, oxygen quenching of which leads to the formation of singlet oxygen. (For comprehensive reviews of the physical and chemical properties of singlet oxygen see Refs. 8 and 9.) Singlet oxygen, which is known to react specifically with olefins, then adds to the double bond giving rise to a peroxirane intermediate (V) (*cf.* Ref. 10). This structure partly rearranges to a dioxetane (VI) which in turn cleaves to yield the two aldehydic fragments VII and VIII. A small amount of veratric acid (IX), formed by further oxidation of veratric aldehyde (VII), was also obtained. (The formation of VIII and its further oxidation to X have been described before [11,12]). At the same time, the peroxirane (V) is attacked directly by solvent with the formation of the glycol structures (XI). In addition, trace amounts of products arising by direct addition of solvent across the double bonds of III and I, respectively, were detected (see Experimental).

Comparative experiments carried out in the absence of oxygen also afforded products formed by addition of solvent across the double bond. In addition, various dimeric products were obtained (see Experimental).



Scheme 1.

In order to confirm the participation of singlet oxygen in the degradative reactions, quenching experiments were carried out. When solutions of isoeugenol methyl ether (I) were irradiated in the presence of β-carotene [13] or DABCO (1,4-diazabicyclo[2.2.2]octane) [14] strong retarding effects were observed, as shown by thin layer chromatography.

Singlet oxygen may also be generated chemically.[9] The simplest and most frequently used method is the oxidation of hydrogen peroxide with sodium hypochlorite. This method was used to oxidize isoeugenol methyl ether (I). As shown by thin layer chromatography, the reaction products were in all respects identical with those obtained from the photochemical oxidation.

In contrast to the methyl ethers of isoeugenol and coniferyl alcohol, coniferaldehyde methyl ether (IV) was remarkably stable when irradiated in solution or in the solid state. Thus, after several days of irradiation only a small amount of veratric aldehyde could be detected. The low degree of reactivity is obviously due to the presence of the aldehyde group which decreases the electron density at the double bond. This is in accordance with literature data. It has been repeatedly demonstrated that 1,2-cycloaddition between singlet oxygen and olefins requires the presence of an electron-rich double bond.[8,9]

In order to elucidate the reactions of phenolic units of the styrene type present in lignin, the light-induced oxidation of isoeugenol (II) was investigated. Contrary to the behaviour of the non-phenolic model compounds I and III, the sidechain double bond of II was attacked to only a minor extent. When the irradiation was carried out in solution only oligomeric coupling products were obtained. In the solid state, polymeric material was formed together with a small amount of vanillin (thin layer chromatography).

DISCUSSION

The results of these model studies indicate that daylight irradiation of lignin causes the degradation of non-phenolic end groups of the coniferyl alcohol type into an aromatic and aliphatic aldehyde fragment, as well as the conversion of such groups into arylglycerol structures. Previous investigations have shown that excited aromatic carbonyl structures exert a dominant influence upon the light-induced yellowing reaction of lignin.[2–6,15] The results here obtained show that arylpropane units containing α,β-double bonds may induce the same type of reaction after their partial conversion into aromatic aldehydes.

Most of the present knowledge about photooxidation of various model compounds for lignin is based upon results obtained in studies in which homogeneous solutions were irradiated. In a polymer matrix such as wood, functional groups, due to their restricted mobility may be widely separated in space. For this reason it is likely that, in addition to a direct hydrogen abstraction mechanism,[4] excited carbonyl structures may transfer energy to oxygen giving rise to the formation of singlet oxygen. Singlet oxygen is reasonably stable [9] and has the mobility required to transfer energy within a polymer matrix (*cf.* Ref. 16). Support for this view can be found in previous studies of dye-sensitised photochemical degradation of textile fibres [17] and in studies of the autoxidation of aromatics in polymer films [18,19] (*cf.* also Ref. 20). It is furthermore known that singlet oxygen may abstract hydrogen from phenolic hydroxyl groups and thus generate phenoxy radicals.[21,22] It thus seems justified to assume that singlet oxygen is an important participant in the lignin-yellowing reactions. As mentioned above, the major colour-forming reactions start with the addition of ground state oxygen to generated phenoxy radicals. The further reactions of the resulting hypothetical hydroperoxy intermediates and whether or not it is possible to generate radicals from structures in wood other than phenols under the influence of light are, however, still unknown and are important subjects for furture work in this field.

EXPERIMENTAL

Chromatography. TLC on silica gel HF_{254}. Preparative separations were carried out in a liquid chromatograph (Chromatronix Inc. Berkeley, Cal. USA) using silicic acid (Bio-Sil A 20–44 μm, Bio Rad Lab. Richmond, Cal. USA) as the stationary phase.

NMR. Perkin-Elmer R-12 (60 MHz, $CDCl_3$). Internal standard: Tetramethylsilane. Chemical shifts. δ-values.

MS. Perkin-Elmer 270. Electron energy: 20 eV. Temperature of probe heater: 50 °C. Relative intensities of the main peaks are given within parenthesis.

Model compounds: trans-Isoeugenol methyl ether (I) was prepared by methylation of *trans*-isoeugenol acetate (recrystallized twice from ethanol) with dimethyl sulfate in alkaline solution using water-dioxane (4:1) as solvent. Distillation under vacuum afforded the pure *trans* isomer.[23] $B.p._{0.05} = 79.5$ °C.

Coniferyl alcohol methyl ether (III). Reduction of 3,4-dimethoxycinnamic acid methyl ester[24] with $LiAlH_4$. M.p. 78–79 °C (benzene–hexane) (lit.[25] m.p. 78 °C) *trans*-3,4-dimethoxy-cinnamaldehyde (IV). Oxidation of eugenol methyl ether with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) for 3 days at room temperature in dioxane containing 0.5 % water;[26] (*cf.* also Ref. 27). M.p. 83–84 °C (benzene). (lit.[28] M.p. 83–84 °C.)

Irradiation. 1 g of the model compound concerned was dissolved in 100 ml ethanol-water (1:1) in a quartz flask. Air (nitrogen was used in some comparative experiments) was bubbled through the solution during irradiation in a photochemical reactor equipped with eight light tubes emitting light centered around 350 nm (Rayonet RPR-208, Southern New England Ultraviolet Co. Middletown, Conn. USA). After irradiation the solution was neutralized with aqueous sodium bicarbonate and evaporated to a small volume. Extraction with ethyl acetate afforded the neutral products. To the remaining aqueous solution, 2 ml 0.5 M tetrabutylammonium sulfate was added. Acidic reaction products were extracted as ion pairs with methylene chloride and reacted with methyl iodide yielding the corresponding methyl esters.[29]

Comparative experiments in the solid state were carried out by absorption of methylene chloride solutions of the model compounds on Whatman No. 1 filter paper sheets. After irradiation, the papers were extracted with acetone and the products investigated by TLC.

Products from isoeugenol methyl ether (I).

a) *Irradiation in O_2 for 48 h.* Neutral fraction: 920 mg. Acidic fraction: 60 mg of veratric acid methyl ester (identified by comparison with an authentic sample). The neutral fraction, after acetylation, was preparatively separated in light petroleum (60–70 °C)/ethyl acetate (gradient from 5:1 to 3:1).

Fraction 1 (fastest moving). Mixture of four components; 35 mg. Analysis by GLC-MS (10 % OV-1 on Chromosorb 100–200 mesh. 30 ml N_2/min): 1-(3,4-Dimethoxyphenyl)-1-ethoxypropane; MS, $m/e = 224(6)$, 195(55), 178(100), 167(24), 163(46), 139(36). 3,4-Dimethoxypropiophenone (comparison with an authentic sample); MS, $m/e = 194(8)$, 165(100), 137(12). 1-(3,4-Dimethoxyphenyl)-1,2-diethoxypropane (first form); MS, $m/e = 268(1)$, 222(20), 195(100), 167(34), 165(20), 151(16), 139(47). 1-(3,4-Dimethoxyphenyl)-1,2-diethoxypropane (second form); MS, see above.

Fraction 2. 1-(3,4-Dimethoxyphenyl)-1-ethoxy-2-acetoxypropane (first form); 70 mg. NMR, 1.17 (3 H, t), 1.21 (3 H, d), 1.91 (3 H, s), 3.41 (2 H, q), 3.84 (6 H, s), 4.21 (1 H, d), 5.0 (1 H, m), 6.81 (3 H, broad s); MS, $m/e = 282(3)$, 222(6), 195(100), 167(10), 165(5), 151(3), 139(5), 143(metastable). (Found: C 63.72; H 7.63; O 28.59. $C_{15}H_{22}O_5$ requires C 63.80; H 7.85; O 28.35).

Fraction 3. 1-(3,4-Dimethoxyphenyl)-1-ethoxy-2-acetoxypropane (second form); 170 mg. NMR, 1.06 (3 H, d), 1.14 (3 H, t), 2.00 (3 H, s), 3.38 (2 H, q), 3.84 (6 H, s), 4.14(1 H, d), 5.08 (1 H), 6.80 (3 H, broad s); MS, see fraction 2.

Fraction 4. Veratric aldehyde. 380 mg (comparison with an authentic sample).

Fraction 5. 1-(3,4-Dimethoxyphenyl)-1,2-diacetoxypropane (first form); 85 mg. NMR, 1.06 (3 H, d), 2.02 (3 H, s), 2.03 (3 H, s), 3.84 (3 H, s), 3.86 (3 H, s), 5.23 (1 H), 5.68 (1 H, d), 6.84 (3 H, broad s); MS, $m/e = 296(5)$, 236(11), 209(6), 195(10), 194(24), 178(11), 167(100), 151(19), 139(30). (Found: C 60.92; H 6.71; O 32.29. $C_{15}H_{20}O_6$ requires C 60.80; H 6.81; O 32.39).

Fraction 6. 1-(3,4-Dimethoxyphenyl)-1,2-diacetoxypropane (second form); 60 mg. NMR, 1.17 (3 H, d), 2.00 (3 H, s), 2.08 (3 H, s), 3.81 (3 H, s), 3.84 (3 H, s), 5.20 (1 H, m). 5.83 (1 H, d), 6.85 (3 H, broad s); MS, see fraction 5.

(b) Irradiation in N_2 for 72 h. Neutral fraction: 950 mg. No acids were found. Preparative separation (after acetylation) in light petroleum (60–70 °C)/ethyl acetate (gradient from 4:1 to 3:1).

Fraction 1 (fastest moving). Starting material. 580 mg.

Fraction 2. Dimer.C_2H_5OH; 15 mg. No detailed structure can be given. Mass peaks at $m/e = 402(1)$, 356(16), 178(100).

Fraction 3. Dimer.C_2H_5OH; 25 mg. No detailed structure can be given. Mass peaks at $m/e = 402(5)$, 356(35), 221(31), 195(22), 178(67), 149(100).

Fraction 4. Bis-(3,4-dimethoxyphenyl)-dimethylcyclobutane; 25 mg. NMR: 0.38 (3 H, d), 1.29 (3 H, d), 2.41 (2 H, m), 3.56 (3 H, s), 3.63 (3 H, s), 3.77 (6 H, s), 6.6(6 H) (signals of benzylic protons hidden by signals of OCH_3). MS: m/e = 356(1), 178(100).

Fraction 5. 1-*cis*-2-Bis(3,4-dimethoxyphenyl)-*trans*-3,*trans*-4-dimethylcyclobutane. 100 mg. M.p. 62.5–63.5 °C. NMR (*cf.* Ref. 30): 1.18 (6 H, d), 2.79 (2 H, m), 3.43 (2 H, d), 3.60 (6 H, s), 3.74 (6 H, s), 6.4 (6 H). MS: $m/e = 356(2)$, 178(100). (Found: C 74.88;

H 7.57; O 17.60. $C_{22}H_{28}O_4$ requires C 74.13; H 7.91; O 17.96).

Fraction 6. Dimer.C_2H_5OH; 30 mg. No detailed structure can be given. Mass peaks at $m/e = 402(2)$, 356(1), 196(42), 178(33), 168(100), 139(54), 115(metastable).

Fraction 7. 1-(3,4-Dimethoxyphenyl)-1-acetoxypropane 110 mg. NMR: 0.87 (3 H, t), 1.80 (2 H, m), 2.04 (3 H, s), 3.86 (3 H, s), 3.88 (3 H, s), 5.62 (1 H, t), 6.87 (3 H, s). MS: $m/e = 194(34)$, 178(23), 167(100), 139(71). 142, 116(metastable ions). (Found: C 65.64; H 7.72; O 26.65. $C_{13}H_{18}O_4$ requires C 65.53; H 7.61; O 26.86).

(c) Irradiation in O_2 for 48 h in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO). Irradiation was performed in the presence of 100 mg DABCO. Only small amounts of reaction products were formed (TLC).

(d) Reaction with chemically generated singlet oxygen ($^1O_2$). Isoeugenol methyl ether (I), dissolved in ethanol, was reacted with $^1O_2$ generated by oxidation of H_2O_2 with NaOCl following a procedure described by Foote *et al.*[31] The product mixture (TLC) consisted of starting material and the same reaction products as in experiment (a) (see above).

Irradiation of coniferyl alcohol methyl ether (III).

(a) In O_2 for 96 h. Neutral fraction: 1.36 g (after acetylation). Acidic fraction: 50 mg of veratric acid methyl ester. Preparative separation in light petroleum (60 – 70 °C)/ethyl acetate (gradient from 7:3 to 3:2).

Fraction 1 (fastest moving). 1-(3,4-Dimethoxypenyl)-1-ethoxy-3-acetoxypropane (impure material); 15 mg. Structure based on MS only. $m/e = 282(15)$, 195(100), 167(20), 139(30).

Fraction 2. Veratric aldehyde (comparison with an authentic sample); 210 mg.

Fraction 3. 1-(3,4-Dimethoxyphenyl)-1-acetoxy-2-propene. [Allylic rearrangement of the starting material (*cf.* Refs. 32, and 33)]; 85 mg. NMR, 2.03 (3 H, s), 3.82 (6 H, s), 4.81 (2 H, broad d), 5.7 (1 H, m), 6.57 (1 H, broad d), 6.78 (3 H, s); MS. $m/e = 236(100)$, 194(27), 193(43), 177(47), 176(33), 165(27), 151(18).

Fraction 4. 1-(3,4-Dimethoxyphenyl)-1-ethoxy-2,3-diacetoxypropane (first form); 185 mg. NMR, 1.14 (3 H, t), 1.89 (3 H, s), 2.01 (3 H, s), 3.39 (2 H, q), 3.85 (6 H, s), 4.3 (3 H), 5.2 (1 H), 6.81 (3 H, broad s); MS $m/e = 340(4)$, 280(1), 236(3), 221(3), 195(100), 167(29), 165(14), 151(5), 139(31). (Found: C 59.88; H 7.02; O 33.01. $C_{17}H_{24}O_7$ requires C 59.99; H 7.10; O 32.91).

Fraction 5. 1-(3,4-Dimethoxyphenyl)-1-ethoxy-2,3-diacetoxypropane (second form); 65 mg. NMR, 1.16 (3 H, t), 2.02 (6 H, s), 3.38 (2 H, q), 3.84 (6 H, s), 4.2(3 H), 5.2(1 H), 6.81 (broad s); MS, see fraction 4.

Fraction 6. 1-(3,4-Dimethoxyphenyl)-1,2,3-triacetoxy-propane (first form); 260 mg. NMR, 1.97 (3 H, s), 2.03 (3 H, s), 2.09 (3 H, s), 3.84 (3 H, s), 3.86 (3 H, s), 4.22 (2 H, d), 5.4 (1 H), 5.91 (1 H, d), 6.86 (3 H, broad s); MS, $m/e = 354(16)$, 294(20), 252(4), 234(4), 209(16), 192(46), 167(100), 165(12), 243(metastable). (Found: C 58.24; H 6.61; O 35.14. $C_{17}H_{22}O_8$ requires C 57.62; H 6.26; O 36.12).

Fraction 7. 1-(3,4-Dimethoxyphenyl)-1,2,3-triacetoxy-propane (second form); 370 mg. NMR, 2.02 (3 H, s), 2.04 (6 H, s), 3.83 (3 H, s), 3.86 (3 H, s), 4.14 (2 H, d), 5.4 (1 H), 5.89(1 H, d), 6.87 (3 H, broad s); MS, see fraction 6.

(b) In N_2 for 96 h. Neutral fraction 1.41 g (after acetylation). No acidic products. Preparative separation in light petroleum (60 – 70 °)/ethyl acetate (gradient from 7:3 to 3:2).

Fraction 1 (fastest moving). 1-(3,4-Dimethoxyphenyl)-3-ethoxy-1-propene (*cf.* Ref. 33); 40 mg. NMR, 1.24 (3 H, t), 3.52 (2 H, q), 3.84 (6 H, s), 4.09 (2 H, d), 5.88 – 6.31 (1 H, m), 6.53 (1 H, d, J 15.2 Hz), 6.9 (3 H, m); MS, $m/e = 222(100)$, 193(9), 177(15), 176(14), 165(16).

Fraction 2. 1-(3,4-Dimethoxyphenyl)-1-acetoxy-2-propene; 105 mg. NMR and MS data, see above. (Found: C 65.96; H 6.87; O 27.17. $C_{13}H_{16}O_4$ requires C 66.08; H 6.84; O 27.08).

Fraction 3. 1-(3,4-Dimethoxyphenyl)-1-ethoxy-3-acetoxypropane; 45 mg. NMR, 1.11 (3 H, t), 2.02 (3 H, s), 1.8 – 2.2 (2 H), 3.32 (2 H, q), 3.86 (6 H, s), 4.0 – 4.4 (3 H), 6.80 (3 H, broad s); MS, $m/e = 282(16)$, 236(1), 222(1), 195(100), 177(6), 176(9), 167(18), 139(17). Metastable ions at $m/e = 143$, 116. (Found: C 64.03; H 8.01; O 27.96. $C_{15}H_{22}O_5$ requires C 63.80; H 7.85; O 28.33).

Fraction 4. 1-(3,4-Dimethoxy-α-ethoxybenzyl)-2-(3,4-dimethoxyphenyl)-3-ethoxymethyl-cyclobutane; 30 mg. Tentative structure based mainly on MS. NMR, signals from two C_2H_5O-, four CH_3O-groups and six arom. H were clearly discernible; MS, $m/e = 444(9)$, 398(17), 386(11), 340(23), 339(33), 221(6), 195(100), 177(12), 167(16), 151(19), 139(14).

Fraction 5. 1,6-di-(3,4-Dimethoxyphenyl)-1,5-hexadiene; 45 mg. Tentative structure based mainly on NMR. NMR, 3.84 (12 H, s), 4.05 – 4.35 (4 H), 5.50 – 6.70 (4 H), 6.80 (6 H, broad s); MS $m/e = 354(1)$, 300(9), 178(100), 177(53). Six further fractions were obtained in a total amount of 800 mg. NMR and MS indicated dimers and possibly trimers.

Irradiation of coniferaldehyde methyl ether (IV) in O_2 for 150 h. Starting material and a small amount of veratric aldehyde (TLC).

Irradiation of isoeugenol (II) in O_2 for 48 h (*cf.* Refs. 34 and 35) Neutral fraction: 1000 mg. No acids were formed. Preparative separation (after acetylation) in light petroleum (60 – 70 °C)/ethyl acetate (gradient from 4:1 to 3:1).

Fraction 1 (fastest moving). Starting material. 560 mg.

Fraction 2. 4-(2,3-Dihydro-7-methoxy-3-methyl-5-propenyl-2-benzofuranyl)-2-methoxyphenyl acetate. (Dehydrodiisoeugenol acetate).

Identified by comparison with an authentic sample; 180 mg.

Fraction 3. 1-Ethoxy-1-(4-acetoxy-3-methoxyphenyl)-2-(4-propenyl-2-methoxyphenoxy)-propane; 110 mg (For NMR and MS data see Ref. 34). (Found: C 69.32; H 7.28; O 23.18. $C_{24}H_{30}O_6$ requires C 69.57; H 7.24; O 23.19.

Fraction 4. Trimer.C_3H_5OH (as diacetate); 60 mg. No detailed structure can be given. MS, $m/e = 618(1)$, 574(3), 532(5), 490(5), 414(3), 368(8), 326(5), 250(4), 223(54), 181(100), 164(24), 153(32), 152(84).

Irradiation of veratric aldehyde. When irradiated for 48 h in the presence of oxygen, veratric aldehyde was partially converted into veratric acid. From the aqueous solution, 160 mg of veratric acid methyl ester was obtained.

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