Photoreaction of Phenacyl Aryl Ether Type Lignols

Nobutaka Fukagawa[a]; Atsushi Ishizu[a]

[a] Department of Forest Products, Faculty of Agriculture, The University of Tokyo Bunkyo-ku, Tokyo, Japan

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Nobutaka Fukagawa and Atsushi Ishizu

Department of Forest Products, Faculty of
Agriculture, The University of Tokyo
Bunkyo-ku, Tokyo, Japan 113

ABSTRACT

Photoreactions of two dilignols, a trilignol and two tetralignols, all of which contain a phenacyl aryl ether type structure, were investigated. All lignols in ethanol yielded products showing the homolytic cleavage of a phenacyl aryl ether bond in this structure. As to tetralignols photodiscoloration was hardly observed in the absence of air, and the preexistence of a free phenolic hydroxyl groups showed no influence on discoloration even in the presence of air. Photoreaction on a filter paper revealed that main reactions are the recombination of radicals once formed by irradiation and the reaction of radicals with oxygen.

INTRODUCTION

Earlier studies have shown that yellowing of high yield pulps by light is partly due to aromatic carbonyl structures in lignin. Kringstad and Lin proposed a scheme that excited aromatic carbonyls abstract hydrogen radicals from phenolic hydroxyl groups and thereby generate phenoxy radicals which subsequently contribute to discoloration by oxidation[1]. Gellerstedt and Petterson proposed another scheme that singlet oxygen, which is produced by energy transfer from excited aromatic carbonyls to triplet oxygen in ground states, may abstract hydrogen radicals to yield phenoxy radicals[2]. Recently, Neumann and Machado reported that singlet oxygen was produced by excited quinonoid species

rather than by excited carbonyl species and participated in oxida-
tion of lignin[3].   However, Takagi and his coworkers reported
that singlet oxygen treatment had little or no effect on the
brightness of the bleached TMP[4].

In these schemes the presence of phenolic hydroxyl groups
is a prerequisite for the discoloration of high yield pulps.   In
accordance with this, Tschirner and Dence et. al. achieved nearly
complete photostabilization of TMP by alkylation with diazomethane
or propylene oxide following borohydride or dithionite reduction[5].
On the other hand, Gierer and Lin[6] found that phenoxy radicals
were produced together with phenacyl radicals by the cleavage of
phenacyl aryl ether bonds during photoreaction of phenacyl aryl
ether type compounds.   Recently, Castellan and his coworkers
studied the photodegradation of 3,4-dimethoxy-α-(2'-methoxy-
phenoxy)-acetophenone in detail and found the formation of α-
phenyl-acetophenone types of products which were produced by
the cleavage of the phenacyl aryl ether bonds followed by the
combination of phenacyl radicals with hexadieno-radicals which
resonate with the phenoxy radical[7].

In the present work, at first the relative reactivities of
acetoguaiacone (A), 4-hydroxy-3-methoxy-α-(2'-methoxyphenoxy)-β-
hydroxy-propiophenone (B) and 3,4-dimethoxy-α-(2'-methoxyphe-
noxy)-β-hydroxy-propiophenone (C) in Figure 1 to irradiation were
compared.   Then, the following three non-phenolic lignols were
irradiated in ethanol with light (>300nm), and their photoreactivi-
ties were discussed on the basis of discoloration measured by the
absorbance   at 450nm and of degradation products: dilignol C,
trilignol D, and tetralignol E (Figure 1).   Finally, each of lignols
B, E and F was irradiated in ethanol, in dimethoxyethane and in a
solid state on a filter paper, and their reactivities were investi-
gated.

RESULTS AND DISCUSSION
Irradiation to Phenacyl Aryl Ether Type Lignols in Ethanol

Figure 2 shows the absorption spectra of lignols A, B and C
after 3hr irradiation to their 0.02M ethanol solutions in the
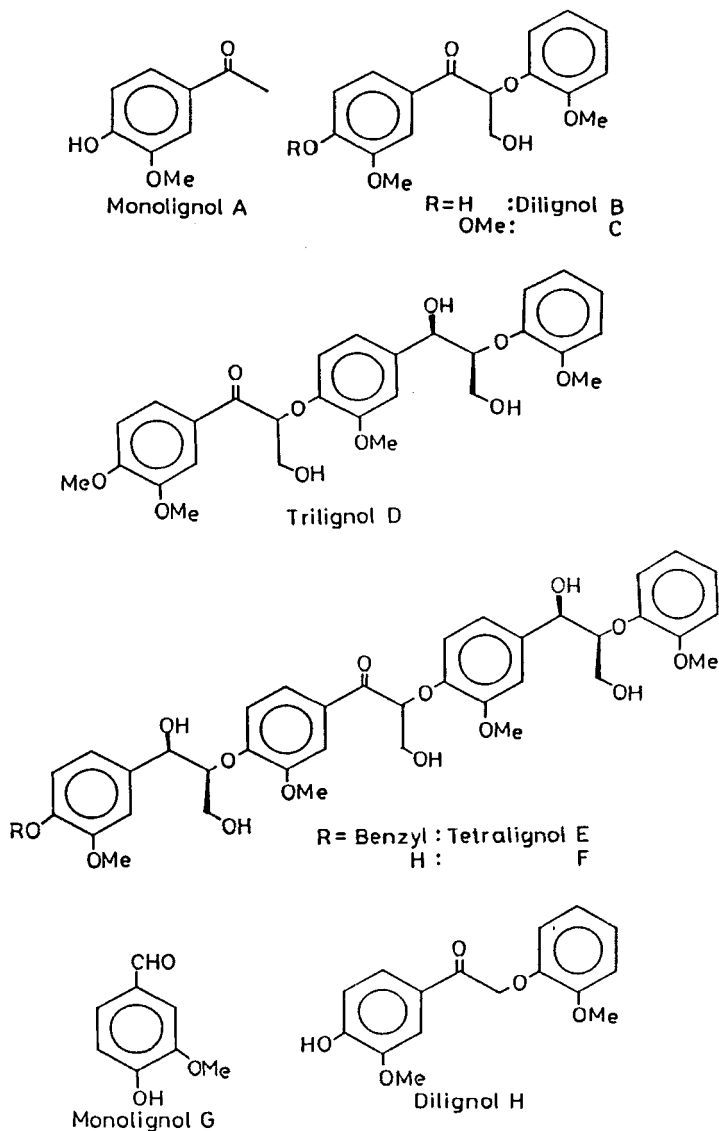
Figure 1. Aromatic carbonyl type lignols
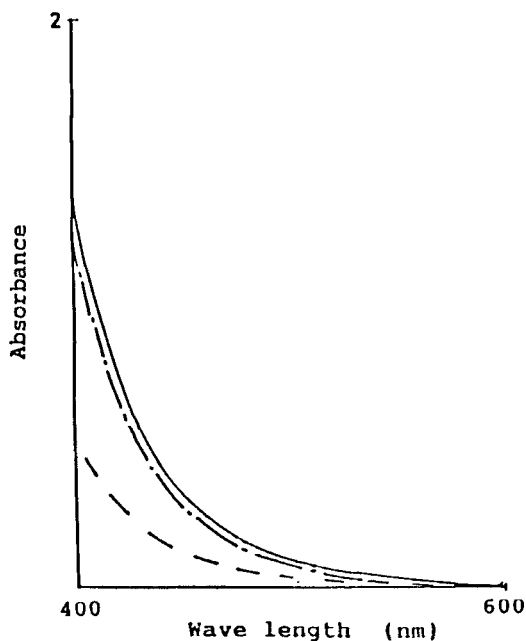
Figure 2.   Absorption spectra of 0.02 M ethanol solutions of
            aromatic carbonyl type lignols after 3 hr irradiation.

            – – – – – –   Acetoguaiacone
            —————————   Dilignol B
            —–·—–·——   Dilignol C

presence of air.   The   irradiated solutions of lignols B and C
showed almost equal   absorbance,   which are higher than that of
acetoguaiacone.   This result indicates that the preexistence of
phenolic hydroxyl groups is not always a dominant factor of the
photodiscoloration of phenacyl aryl ether type dilignols.   In our
another experiment the recoveries of acetoguaiacone (A), vanillin
(G), dilignol B and 4-hydroxy-3-methoxy-α-(2'-methoxyphenoxy)-
acetophenone (H) (Figure 1) after   1hr irradiation in the presence
of air   were found to be 97, 72, 45 and 42%,   respectively.   Das
and his coworkers suggested that aromatic carbonyl triplets

abstract hydrogen radicals from phenolic hydroxyl groups to be quenched.   At the same time, however, they implied that a nonnegligible fraction of the primary quenching events also regenerated the reagents.[8]   Although it is not clear whether this regeneration process occurred and contributed to high recoveries of monolignols A and G, phenoxy radicals formed by the homolytic cleavage of phenacyl aryl ether bonds must play a main part in photodiscoloration of lignols B, C and H rather than those formed by hydrogen abstraction from phenolic hydroxyl groups by aromatic carbonyl triplets.

Photoreaction of 4-hydroxy-3-methoxy-α-(2'-methoxyphenoxy)-β-hydroxypropiophenone

Photoreaction products of dilignol B were shown in Figure 3. The formation of guaiacol (B-VIII), compounds B-I and B-II supports the mechanism which was proposed for the photoreaction of 3,4-dimethoxy-α-(2'-methoxyphenoxy)-acetophenone   by   Castellan and his coworkers[7].   Namely,   the   phenacyl aryl ether bonds of dilignol B in excited states are cleaved to yield radicals R-I and R-II (Figure 4), which in turn recombine to yield B-I and B-II. Hydrogen abstraction from R-I by some active   species   may give compound B-V.   Radical R-I might yield compound B-III by losing a hydroxyl radical, although we haven't found out an example of such a type of reaction in literature.

Photoreaction of 3,4-dimethoxy-α-(2'-methoxyphenoxy)-β-hydroxy-propiophenone

Photoreaction products of dilignol C were shown in Figure 3. The compound corresponding to C-IV was not detected in B-series. On the other hand, the product corresponding to B-V was not detected in C series. These results suggest that the difference in the aromatic nuclei has some effect on the reactivity of R-I type of radicals in Figure 4.

Photoreaction of Non-phenolic Phenacyl Aryl Ether Type   Lignols

Tetralignol E and trilignol D disappeared much faster than dilignol C by irradiation (Figure 5). One reason for this result is the difference in absorption coefficients of these compound: dilig-

R = H   : B - I
·OMe : C - I

R = H   : B - II
  OMe : C - II

R = H   : B - III
  OMe : C - III

C - IV

B - V

R = H   : B - VI
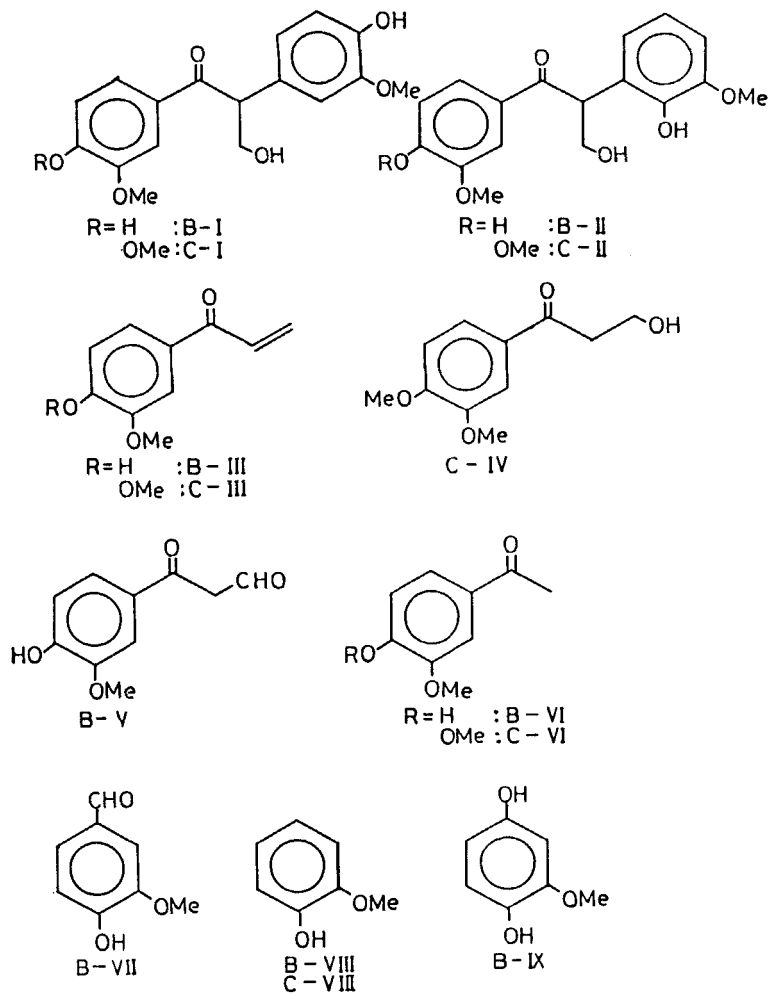 OMe : C - VI

B - VII

B - VIII
C - VIII

B - IX

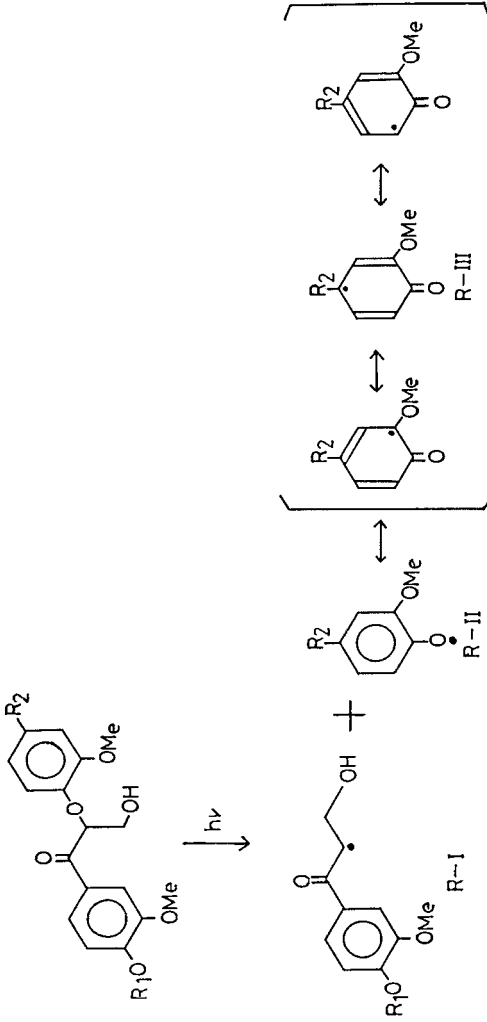Figure 3. Photoreaction products of dilignols B and C

Figure 4. Formation of radicals by irradiation to phenacyl aryl ether type structure.
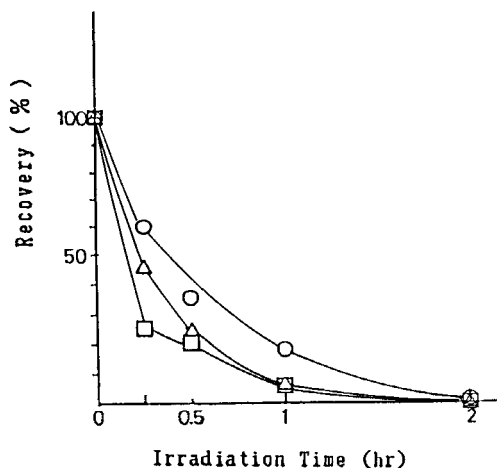
Figure 5.   Recoveries of lignols C, D, and E after
            irradiation in ethanol in the presence of air.

——— O ——— Dilignol C
——— △ ——— Trilignol D
——— □ ——— Tetralignol E

nol C; λ_{max}=308nm (ϵ 8700dm^{3}mol^{-1}cm^{-1}), trilignol D; λ_{max} =308nm (ϵ

9400dm^{3}mol^{-1}cm^{-1})   and   tetralignol E; λ_{max}=309nm (ϵ 9800dm^{3}mol^{-1}

cm^{-1}).   Another possible reason is the difference in physical

quenching rate of these compounds.   Scaiano and Netto-Ferreira

showed that intramolecular quenching process between a carbonyl

triplet and an aromatic ring of   excited α-phenoxyacetophenone

is   severely influenced by the conformational mobility between a

carbonyl carbon and a phenoxy-substituted carbon[9].   Having a

bulkier substituent, trilignol D and tetralignol E have lower con-

formational mobilities than   dilignol C.   As this result intramo-

lecular physical quenching from excited states of the former two

lignols is slower than that of dilignol C, and their quantum yields

of the cleavage of phenacyl aryl ether bonds become larger than

that for dilignol C.   Recently Palm and Dreeskamp showed that

significant homolytic cleavage of the phenacyl aryl ether bonds
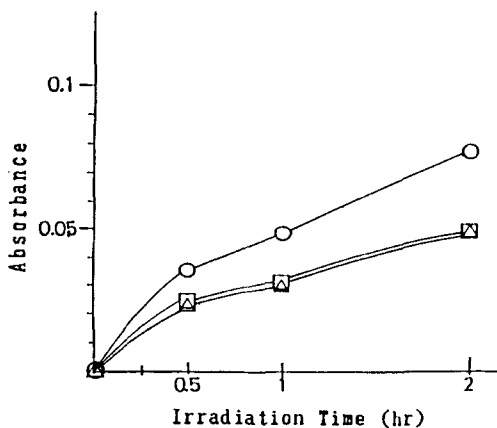
Figure 6.   Absorbance at 450 nm of 0.01 M ethanol solutions
             of lignols C, D and E after irradiation in the
             presence of air.

             ———O——— Dilignol C
             ———△——— Trilignol D
             ———□——— Tetralignol E

occurs from the excited singlet state of α-(2,6-dimethoxyphenoxy)-
acetophenone[10]. If this process also occurs for the singlet states
of lignols C, D and E, then factors other than intramolecular
quenching may affect the relative reactivities of these lignols.

On the other hand, the extent of photodiscoloration of
dilignol C was much higher than those of trilignol D and tetralig-
nol E (Figure 6).   Main photoreaction products of these lignols
(Figure 7)   indicate   that homolytic cleavage of   phenacyl aryl
ether bonds is a main process in photoreaction of these lignols.
As described above, however, trilignol D and tetralignol E disap-
peared faster than dilignol C.   Therefore, the order of discolora-
tion (C > D & E) seems to be due to the reactivities of phenoxy
radicals, which were produced by the homolytic cleavage, with
oxygen and/or other radicals.   Namely, the hexadieno-radicals
(R-III in Fig. 4) produced from dilignol C are thought to be more
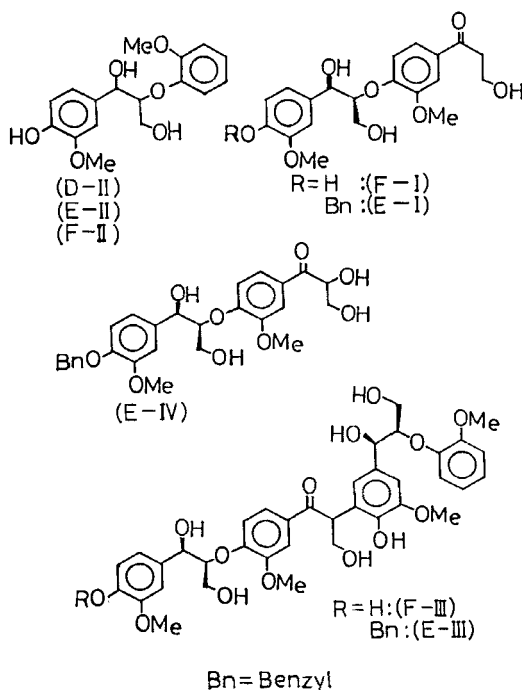
Figure 7.   Photoreaciton products of lignols D, E and F.

reactive than   those produced from trilignol   D and tetralignol E
to yield discolored products because   the bulkiness of a substitu-
ent of the former is much less than those of the latter two.
Photoreaction of Degassed and Aerated Ethanol Solutions
of   Tetralignols
        Absorption spectra of lignols B, E and F in ethanol and in
dimethoxyethane were shown   in Figures 8a and b, respectively.
Dilignol B was used as a reference.   Tetralignols E and F have
almost the same absorbance in the range of 300-400nm   both in
ethanol and in dimethoxyethane. Therefore, almost the same extent
of excitation may be caused by irradiation (>300nm) for these two
tetralignols.   Dilignol B in   ethanol has the same height of an
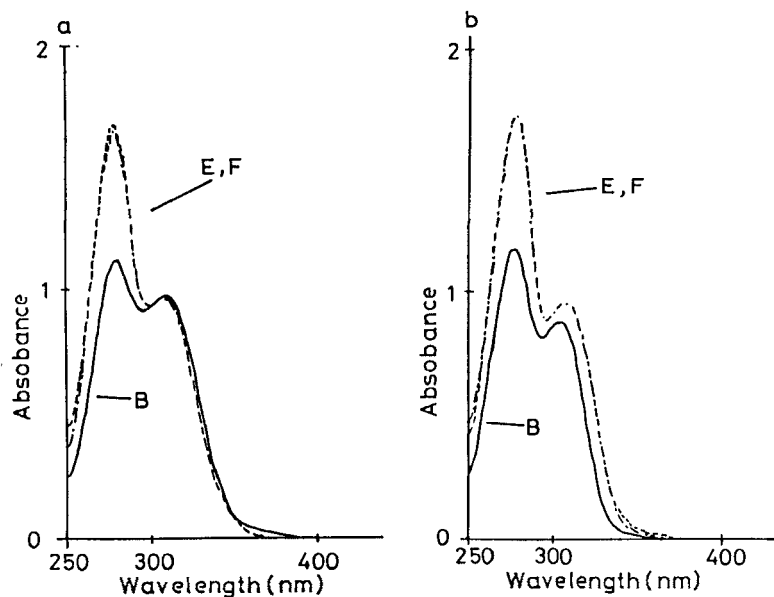
Figure 8. Absorption spectra of lignols B, E and F in ethanol
           (a) and in dimethoxyethane (b) in the range 250-400 nm.

——————————— Dilignol B
- - - - - - - - Tetralignol E
—— · —— · —— Tetralignol F

absorption maximum at about 310nm as tetralignols E and F and

a small absorption in the range of 350-400nm.   In dimethoxyeth-

ane, on the other hand, the maximum at 310nm shifted to a lower

wavelength and its height became a little lower.   And a small

absorption of 350-400nm was not observed.   These results indi-

cate that dilignol B in ground states and/or excited states are

solvated differently in ethanol and in dimethoxyethane.   All the

lignols showed no absorption in the range higher than 400nm.

        Recoveries of the starting materials and the absorbance at

450nm of degassed and aerated ethanol solutions of these lignols

after irradiation were shown in Figures 9 and 10, respectively.
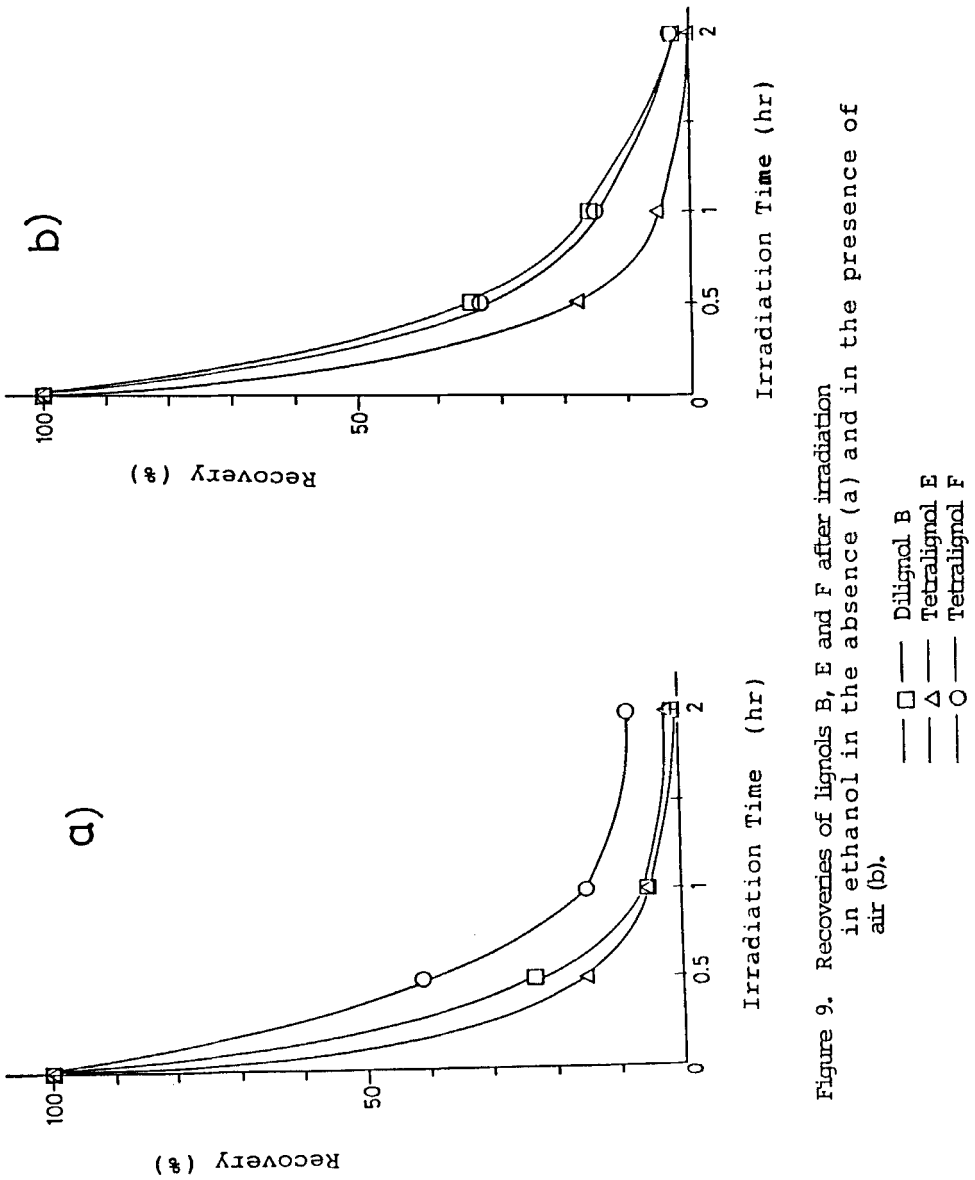
Figure 9. Recoveries of lignols B, E and F after irradiation in the absence (a) and in the presence of in ethanol in air (b).

Figure 10. Absorbance of 0.01 M ethanol solutions of lignols B, E and F at 450 nm after irradiation in the absence and in the presence of air.

———□——— Aerated solution of dilignol B
———△——— Aerated solution of tetralignol E
———○——— Aerated solution of tetralignol F
———■——— Degassed solution of dilignol B
———▲——— Degassed solution of tetralignol E
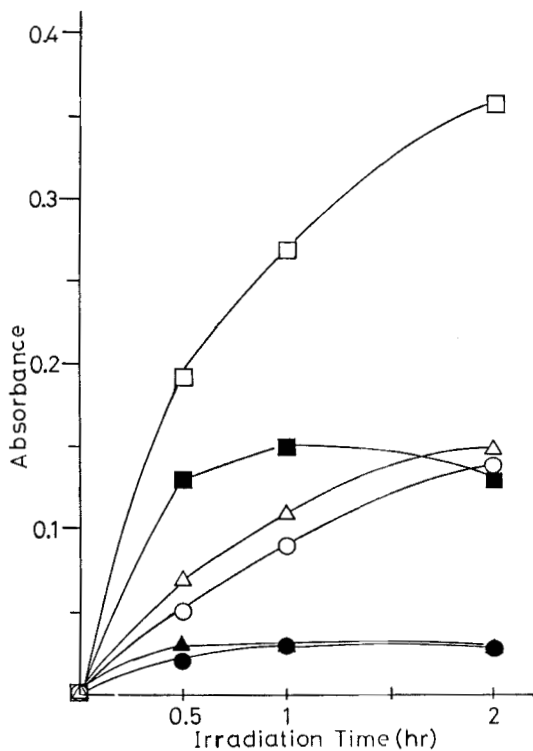———●——— Degassed solution of tetralignol F

Tetralignol E   disappeared faster than the other two lignols irrespective of the presence and the absence of oxygen. Tetralignol F disappeared most slowly.   The factors which influenced on this result have not been clear yet.

While the degassed ethanol solutions of tetralignols E and F showed only a small extent of photodiscoloration which was within the limit of experimental error, the degassed ethanol solution of dilignol   B discolored to   almost the same extent with aerated solutions of tetralignols E and F.   Photoreaction products (Figures 7) indicate that the homolytic cleavage of phenacyl aryl ether bonds is a main process in these photoreactions, too. The difference in the extent of discoloration may be ascribed to that in reactivities of hexadieno-radicals.

Photoreaction products F-I and F-II were formed not only in ethanol but also in dimethoxyethane.   Therefore, phenacyl and phenoxy type radicals (Figure 4) can abstract hydrogens not only from ethanol but also from other molecules.   Yields of compounds E-I, E-II or F-II and E-III under the degassed conditions are higher than those under the aerated conditions (Figures 11 and 12) This result shows that phenoxy and phenacyl radicals and/or photoreaction   products   were   further   oxidized   with   oxygen. As is evident from Figures 9 and 10, even after the greater part of tetralignol E disappeared, the extent of discoloration increased. Furthermore, although tetralignol F disappeared more slowly than tetralignol E, the discoloration of tetralignols E and F was almost equal.   Therefore, besides phenoxy radicals derived from the cleavage of phenacyl aryl ether bonds, those derived from hydrogen abstraction from phenolic hydroxyl groups preexisting and/or secondarily formed may contribute to the discoloration.

Photoreaction   of Tetralignol E Adsorbed on Filter Paper

Yields of compounds E-I and E-II, which were major photoreaction products in a solution (Figures 11 and 12), decreased for the photoreaction on a paper, but yield of E-IV which was thought to be produced by the addition of oxygen to a phenacyl type radical and the subsequent cleavage of a O-O bond increased.
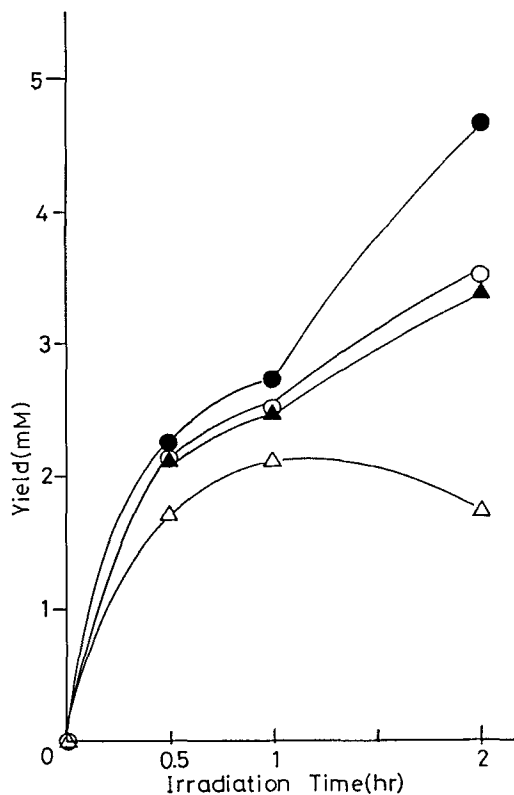
Figure 11.   Yields of compounds E-II and F-II after irradiation
              to 0.01 M ethanol solutions of tetralignols E and F.

——— ▲ ———   Degassed solution of tetralignol E
——— △ ———   Aerated solution of tetralignol E
——— ● ———   Degassed solution of tetralignol F
——— ○ ———   Aerated solution of tetralignol F

This result indicates that in a solid state, in which molecular
mobility is restricted, intermolecular radical abstraction between
substrates become more difficult than in a solution.   Thus, the
reaction of radicals with oxygen and recombination of radicals to
form a starting compound (although in this experiment occurrence
of this reaction was not clearly proved, slower disappearance of
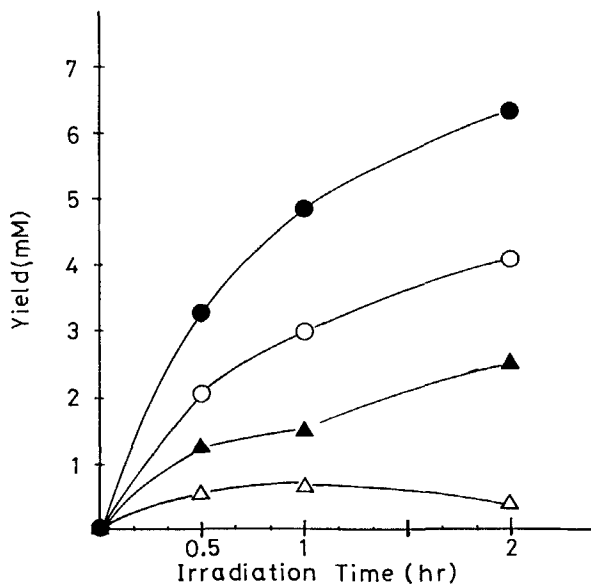
Figure 12.   Yields of compounds E-I and E-III after irradiation
             to 0.01M ethanol   solution of tetralignol E

——— ● ——— E-I in degassed solution of tetralignol E
——— ○ ——— E-I in aerated solution of tetralignol E
——— ▲ ——— E-III in degassed solution of tetralignol E
——— △ ——— E-III in aerated solution of tetralignol E

the starting lignols in a solid state than in a solution may partly
ascribed to this reaction) become   main reaction routes of R-I and
-II type of radicals.

EXPERIMENTAL

General Procedure

NMR spectra were recorded on a JEOL FX100, a Bruker AC300
and a Bruker AM600.   Tetramethylsilane was used as an internal
reference of chemical shift.   Phenylpropanes in dilignols, a
trilignol and tetralignols shown in Figure 1, 3 and 7 were num-
bered from the left to the right.

Mass spectra were recorded on a JEOL DX303. FAB-MS spectra were measured   with a glycerol matrix.

HPLC analyses were performed by the use of a Shimadzu LC4A. A Shimadzu shimpack-CLC-ODS reverse phased column (0.15m x 0.006m) and a Chemco reverse phased column (0.25m x 0.02m) were used for the separation of reaction products.

Irradiation was performed by the use of a RIKO-400MH, in which a 400W high pressure mercury lamp is equipped. Samples were irradiated in the 'merry-go-round' method.   Since a lamp was located in a pyrex glass tube, the light (>300nm) was irradiated to samples.

Syntheses of Lignols B and C

Acetoguaiacone (A) and vanillin (G) were commercially available.   4-Hydroxy-3-methoxy-α-(2'-methoxyphenoxy)-β-hydroxy-propiophenone (B) and 4-hydroxy-3-methoxy-α-(2'-methoxyphenoxy)-acetophenone (H) were synthesized according to the method of Hosoya and his coworkers[11]. 3,4-Dimethoxy-α-(2'-methoxyphenoxy)-β-hydroxy-propiophenone (C) was synthesized according to the method of Adler[12].

Synthesis of Trilignol D

Trilignol D (Figure 1) was synthesized by the method used for the preparation of tetralignol E and identified by NMR and FAB-MS.

FAB-MS: 551 (M+Na$^+$, Na$^+$ was included as a contaminant), 343 and 165.

^{1}H-NMR (in d$_6$-acetone): 3.6-3.8 (2-γ), 3.7-3.8 (OMe), 4.0 (1-γ), 4.1 (1-γ-OH), 4.2 (2-β), 4.5 (2-α-OH), 4.9 (2-α), 5.5 (1-β), 6.7-7.8 (aromatic).   These aliphatic connectivities were identified by a COSY experiment[13].

^{13}C-NMR (in d$_6$-acetone): 55.5-56.5 (OMe), 62.5 (2-γ), 65 (1-γ), 74.0 (2-α), 85.0 (1-β), 87.7 (2-β), 112.5, 113.5, 113.8, 114.5, 117.3, 119.0, 121.0, 122.4, 123.8 and 125.5 (tertiary aromatic carbons), 130.8, 137.5, 148.2, 149.5, 151.5, 151.8, 152.5 and 156.5 (quaternary aromatic carbons), 198.0 (1-α).
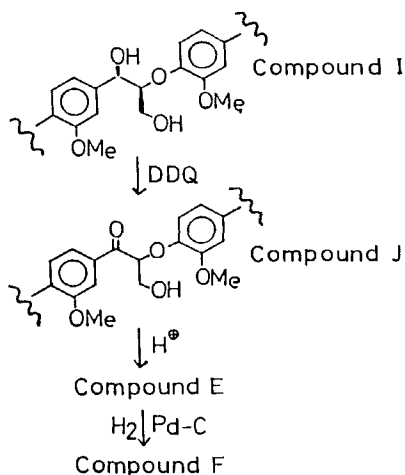
Figure 13.   The synthetic scheme of tetralignols E and F

Synthesis of Tetralignol E

The synthetic scheme is shown in Figure 13.   Intermediate I was synthesized according to the method of Hyatt[14].

a) Oxidation of a benzylic hydroxyl group

To a solution of 13g (15mmols) of compound I dissolved in 250mL of dioxane, 10.5g of 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) was added and the mixture was stirred for 24hr at room temperature.   Then, the precipitated 2,3-dichloro-5,6-dicyano-p-hydroquinone was filtered and washed with 50mL of dioxane. The filtrate combined with the washing was concentrated and partitioned between dichloromethane and 5% aqueous NaOH.   The dichloromethane layer was washed twice with 5% aqueous NaOH and once with brine, and then evaporated in vacuo after drying over Na_2SO_4.   The residue was fractionated on a silica gel column with ethyl acetate/n-hexane=2/1 giving 8g of a syrup.   On stand-ing overnight, this syrup (compound J) solidified.

b) Cleavage of isopropylidene

To a solution of 8g of compound J in 200mL of dioxane, 100mL of 5% aqueous HCl was added   and the mixture was   stirred   for 5hr at room temperature.   Then the reaction mixture was extract- ed with ethyl acetate.   The ethyl   acetate layer was washed with brine,   dried over Na_2SO_4, and then evaporated in vacuo.   The residue was purified on a silica gel column with acetone/n- hexane=2/1-3/1, giving 6g of a syrup.

HPLC analysis of this compound revealed the presence of two peaks in proximity.   The proportion in area of the peak with a short retention time to that with a long retention time was about 4/6.   The compounds corresponding to these two peaks were separated by HPLC with a reverse phased column and their ^{13}C- and ^{1}H-NMR spectra were measured.   These spectra of the two compounds were the same. Then ^{1}H-NMR spectra of these com- pounds were measured in 7% d_6-acetone solution containing 5% of Tris[3-(heptafluoropropyl-hydroxymethylene)-(+)-camphorato],euro- pium;Eu(hfc)$_3$. Two spectra were differed only in the range of 4.5- 5.5ppm.   Although their configuration could not be determined, these two compounds are thought to be optical isomers.

FAB-MS: 823 (M+Na$^+$), 505, 343 (320+Na$^+$), 175 (152+Na$^+$) and 137 in the case a trace amount of 1% aqueous NaCl was added; 839 (M+K$^+$), 271, 243, 179 and 151 in the case of a trace amount   of 1% aqueous KI was added.

^{1}H-NMR (in d_6-acetone): 3.7 (3-γ), 3.9 (1-γ), 3.7-3.8 (OMe), 4.0 (2-γ), 4.1 (2-γ-OH), 4.2 (3-β), 4.4 (3-α-OH), 4.6 (1-β), 4.9 (3-α), 4.9 (1-), 5.1 (Bn), 5.5 (2-β), 6.7-7.6 (aromatic).

Assignments of 1-β-^{1}H   and 3-β-^{1}H   were made by refer- ring   those of 2-β-^{1}H in lignol D   and β-^{1}H in *erythro*-form of compound E-II,   and aliphatic connectivities were identified by   a COSY experiment.

^{13}C-NMR (in d_6-acetone): 56.07-56.19 (OMe), 61.17 (3-γ), 61.96 (1- γ), 64.01 (2-γ), 71.35 (Bn), 73.51 (1-α),   73.55 (3-α), 83.78 (2-β), 84.69 (1-β), 86.18 (3-β), 112.29, 112.4, 112.84, 113.36, 114.40, 115.49, 115.93, 119.35, 120.01, 121.78, 123.25, 123.98, 128.32, 128.40 and

129.07 (tertiary aromatic carbons), 129.67, 135.75, 137.09, 137.18, 138.61, 147.71, 148.89, 148.99, 150.67, 151.08, 151.83 and 154.54 (quaternary aromatic carbons), 197 (2-α). These assignments were made by means of DEPT (Distortionless Enhancement by Polarization Transfer) and ^{13}C-^1H-heteronuclear shift correlation experiments[15].

Synthesis of Tetralignol F

To a solution of 2g of tetralignol E in 200mL of ethanol, 5g of 5% Pd-C was added and the suspension was stirred at room temperature being bubbled with hydrogen. After 4hr, the catalyst was filtered off and the filtrate was evaporated in vacuo. The residue was purified by the use of a silica gel column with acetone/hexane=4/1, yielding 1.5g of tetralignol F as a syrup. FAB-MS: 711 (M+H$^+$), 303 and 151; 733 (M+Na$^+$), 343 (320+Na$^+$), 265 and 207 in the case a trace amount of 1% aqueous NaCl was added; 749 (M+K$^+$), 359 (320+K$^+$), 303, and 150, in the case a trace amount of 1% aqueous KI was added.

^1H-NMR (in d$_6$-acetone): 3.7 (3-γ), 3.9 (1-γ), 3.7-3.8 (OMe), 4.0 (2-γ), 4.3 (3-β), 4.6 (1-β), 4.9 (3-α), 4.9 (1-α), 5.5 (2-β), 6.7-7.8 (aromatic).

^{13}C-NMR (in d$_6$-acetone): 56.18-56.26 (OMe), 61.72 (3-γ), 62.05 (1-γ), 64.0 (2-γ), 73.54 (1-α), 73.71 (3-α), 83.70 (2-β), 84.83 (1-β), 86.2 (3-β), 116.60, 112.45, 112.90, 113.43, 115.10, 115.53, 116.07, 119.43, 120.08, 120.64, 121.82, 123.31 and 124.04 (tertiary aromatic carbons), 129.59, 133.86, 136.92, 146.70, 147.34, 147.88, 148.81, 150.40, 150.76, 151.77 and 154.01 (quaternary aromatic carbons), and 197 (2-α). These assignments in aliphatic range are made by means of double quantum filtered COSY[16] and ^{13}C-^1H-heteronuclear shift correlation experiments.

Irradiation to Lignols A, B and C in Ethanol

a) Measurement of absorption spectra and recoveries of starting materials

Ethanol solutions (0.02M) of lignols A-C were irradiated for 3hr and their absorption spectra in the range of 400-600nm were

measured. Recoveries of starting materials were measured by HPLC under the following conditions.

    Column: Shimadzu CLC-ODS-C18 0.15m x 0.006m

    Eluate: $CH_3CN/H_2O=3/7$

    Flow rate: 1ml/min

    Detecting wavelength: 280nm

 b) Analysis of reaction products by GC-MS

    A part of reaction products was acetylated with 0.1ml each of pyridine and acetic anhydride at room temperature for 24hr and subjected to GC-MS analysis of which conditions were as follows:

    Column: Gasukurokogyo OV-1

Column temperature: kept for 1min at 100°C and raised at the rate of 4°C/min to 250°C and kept for 30min at 250°C.

    In this analysis, peaks corresponding to compounds (B', B-I', B-II', C', C-I' and C-II') produced by hydro-acyloxy-elimination from B, B-I, B-II, C, C-I and C-II were detected. These compounds were supposed to be artifacts in GC analysis, because they were not detected in HPLC analysis and because pure acetylated dilignol B showed predominantly the peak corresponding to B'.

 MS data of acetates are written in the order detected:

 B–series

    B-VIII and C-VIII: 166 (M^+), 124, 109 and 81

    B-IX: 224 (M^+), 182 and 140

    B-III: 220 (M^+), 178 and 151 (base ion)

    B': 342 (M^+), 300, 151 (base ion)

    B-I': 384 (M^+), 342, and 151 (base ion)

    B-II': 384 (M^+), 342 (base ion) and 151

 C–series

    C-VIII: 166 (M^+), 124, 109 and 81

    C-VI: 180 (M^+) and 165 (base ion)

    C-III: 192 (M^+) and 165 (base ion)

    C-IV: 252 (M^+), 192 and 165 (base ion)

    C': 314 (M^+), 283 and 165 (base ion)

    C-I' and C-II': 355 ($M-1^+$), 314, 283 and 165 (base ion)

C: 373 (M-1$^+$), 251, 165 (base ion) and 151

C-I and C-II: 356(M$^+$), 314, 283 and 165

c) Isolation and identification of reaction products

Photoreaction products were separated by HPLC under the following conditions.

Column: Chemco reverse phased column 0.25m x 0.02m

Eluate: $CH_3CN/H_2O=4/6-3/7$

Flow rate: 4ml/min

Each product was subjected to ^{13}C-NMR and MS analyses. β-C in compounds B-I, -II, C-I and -II were assigned on the basis of the results by Habu and his coworkers[17,18].

B-I: 3-hydroxy-1,2-bis(4'-hydroxy-3'-methoxyphenyl)-1-propanone

EI-MS (m/z): 318 (M$^+$), 300, 288 and 151 (base ion).

^{13}C-NMR (in CD$_3$OD): 55.87 (β-C), 56.26 and 56.28 (OMe), 65.60 (γ-C), 112.28, 112.74, 115.34, 116.03, 121.94 and 124.56 (tertiary aromatic carbons), 126, 127, 145, 146, 147 and 151 (quaternary aromatic carbons), 197(α-C).

B-II: 3-hydroxy-1-(4'-hydroxy-3'-methoxyphenyl)-2-
          (2"-hydroxy-3"-methoxyphenyl)-1-propanone

EI-MS (m/z): 318 (M$^+$), 300, 288 and 151 (base ion).

^{13}C-NMR (in CD$_3$OD): 48.63 (β-C), 56.23 and 56.31 (OMe), 64.20 (γ-C), 110.94, 112.31, 115.4, 120.19, 120.83 and 124.07 (tertiary aromatic carbons), 127, 129, 143, 147, 148 and 151 (quaternary aromatic carbons), and 197 (α-C).

B-III: 1-(4'-hydroxy-3'-methoxyphenyl)-2-propen-1-one

EI-MS (m/z): 178 (M$^+$) and 151 (base ion).

^{13}C-NMR (in CD$_3$OD): 56 (OMe), 110 (γ-C), 124 (β-C), 196 (α-C), 112.5, 128 and 132 (tertiary aromatic carbons), 129, 148 and 150 (quaternary aromatic carbons).

C-I: 3-hydroxy-2-(4"-hydroxy-3"-methoxyphenyl)-1-
          (3',4'-dimethoxy)-1-propanone

EI-MS (m/z): 331 (M-1$^+$), 313 and 165 (base ion).

FAB-MS (m/z): 334 (M+2H$^+$, base ion), 315, 287, 165 and 151.

^{13}C-NMR (in d$_6$-acetone): 55.97 (β-C), 56.04 and 56.14, 56.14 (OMe), 65.35 (γ-C), 111.24, 111.81, 112.53, 115.87, 121.76 and 123.97 (ter-

tiary aromatic carbons), 129.63, 130.86, 146.54, 148.37, 149.86 and 154.24 (quaternary aromatic carbons), 198.15 (α-C).

C-II: 3-hydroxy-2-(2"-hydroxy-3"-methoxyphenyl)-1-
(3',4'-dimethoxy)-1-propanone

EI-MS (m/z): 332 (M$^+$), 314, 165 (base ion) and 151.

FAB-MS (m/z): 334 (M+2H$^+$), 315, 287, 207, 165 and 150.

^{13}C-NMR (in d$_6$-acetone): 48.75 (β-C), 56.02 and 56.12, 56,30 (OMe), 64.16 (γ-C), 110.95, 111.51, 112.04, 123.62, 124.49 and 130.87 (tertiary aromatic carbons), 124.49, 130.87, 144.35, 148.45, 149.97 and 154.44 (quaternary aromatic carbons), 197.00 (α-C).

C-III: 1-(3',4'-dimethoxyphenyl)-2-propen-1-one

EI-MS (m/z): 192 (M$^+$), 165(base ion).

C-IV: 3-hydroxy-1-(3',4'-dimethoxyphenyl)-1-propanone.

EI-MS (m/z): 210 (M$^+$), 192, 180 and 165 (base ion).

^{13}C-NMR (in d$_6$-acetone): 41.41(β-C), 55.87 and 55.98(OMe), 58.45 (γ-C), 111.12, 111.27 and 123.13 (tertiary aromatic carbons), 131.12, 149.94 and 154.34 (quaternary aromatic carbons), 196 (α-C).

Irradiation to Non-phenolic Lignols

a) Measurement of absorption spectra and recoveries of starting materials

Ethanol solutions (0.01M) of lignols C, D and E were irradiated for 0.25, 0.5, 1, 2hr, respectively, and their absorbance at 450nm were measured.   Recoveries of starting materials were also measured by HPLC.

b) Separation and identification of photoreaction products

Photoreaction products of lignols D and E were separated by HPLC under the following conditions and identified by MS and NMR spectra.

Column: Chemco reverse phased column 0.25m x 0.02m

Eluate: CH$_3$CN/H$_2$O=4/6-3/7

Flow rate: 4ml/min

D-I: Retention time in HPLC and MS spectra were the same as those for C-IV.

D-II, E-II and F-II.   EI-MS: 320 (M$^+$), 272, 210, 196, 178, 165, 153 (base ion) and 124.

^{1}H-NMR (in d_6-acetone): 2.9, 4.3 (broad, aliphatic-OH), 7.4 (broad, Ph-OH), 3.7 (γ), 4.3 (β), 4.9 (α), 6.7-7.1 (aromatic). ^{13}C-NMR (in d_6-acetone): 55.80 and 55.87 (OMe), 61.38 (γ), 73.40 (α), 86.25 (β), 111.00, 113.11, 114.75, 119.21, 120.06, 121.46 and 111.91 (tertiary aromatic carbons), 146.23, 147.56, 148.63 and 151.53 (quaternary aromatic carbons).

E-I. FAB-MS: 483(M+H$^+$), 465, 437, 393, 242, 222, 197 and 153. ^{1}H-NMR (in d_6-acetone): 3.1 (2-γ), 3.8 and 3.85 (OMe), 3.9 (2-β), 4.6 (1-β), 4.9 (1-α), 5.1(Bn), 6.9-7.5 (aromatic). 1-γ was hidden by vast OMe peaks.

^{13}C-NMR (in d_6-acetone): 41.5 (2-β), 56.2 and 56.3 (OMe), 57.8 (2-γ), 59.6 (1-γ),   71.0 (Bn), 72.7 (1-α),   85.0 (1-β), 109.0, 109.5, 112.0, 114.0, 119.5, 123.5, 127.5 and 128.5 (tertiary aromatic carbons), 132.0, 136.5, 140.5, 148.5, 150.1, 150.5 and 153.0 (quaternary aromatic carbons), 197.5 (2-α).

E-III. FAB-MS: 823 (M+Na$^+$), 793, 549, 519, 175 and 151 in the case a trace amount of 1% aqueous NaCl was added; 839 (M+K$^+$), 320, 282 and 205, in the case a trace amount of 1% aqueous KI was added.

^{1}H-NMR (in d_6-acetone): 3.6 (3-γ), 3.7 (1-γ), 3.7-3.8 (OMe), 4.2 (3-β), 4.3 (2-γ), 4.5 (1-β), 4.7 (3-α), 4.9 (1-α), 5.0 (Bn), 5.3 (2-β), 6.7-7.7 (aromatic).

^{13}C-NMR (in d_6-acetone): 48.98 (2-β), 56.50-56.33 (OMe), 61.83 (3-γ), 61.96 (1-γ), 64.20 (2-γ), 71.48 (Bn), 73.68 (1-α), 73.90 (3-α), 85.07 (3-β), 86.63 (1-β), 109.99,   112.47, 112.90, 113.51, 114.59, 116.05, 119.38, 119.86, 120.16, 121.85, 123.38, 123.73, 128.44, 128.50 and 129.18 (tertiary aromatic carbons), 131.39, 134.20, 135.96, 138.75, 143.43, 148.03, 148.16, 148.65, 150.60, 150.84, 151.60 and 153.42 (quaternary aromatic carbons), 196 (2-α). These assignments in aliphatic region were made by DQF-COSY and HMQC[19] experiments.

E-IV.   FAB-MS: 521 (M+Na$^+$; Na$^+$ was included as a contaminant), 499 (M+H$^+$),   481, 243, 207, 151 and 137.

^{1}H-NMR (in d_6-acetone): 3.83 and 3.88 (OMe), 3.9 (1-γ), 4.7 (1-β), 5.0 (1-α), 5.0 (Bn), 5.1 (2-β), 7.0-7.6 (aromatic). 2-γ was hidden

by vast OMe peaks.   These aliphatic connectivities were identified by a DQF-COSY experiment.

^{13}C-NMR (in d$_6$-acetone): 56.1 and 56.3 (OMe), 62.0 (1-γ), 66.3 (2-γ), 71.5 (Bn), 73.8 (1-α), 75.3 (2-β), 85.1 (1-β), 112.5, 112.8, 114.6, 115.8, 119.9, 122.9, 128.4 and 129.1 (tertiary aromatic carbons), 133.0, 137.5, 148.5, 151.0, 151.5 and 154.0 (quaternary aromatic carbons), 197.5 (2-α).

Irradiation to Degassed and Aerated Ethanol Solutions of Tetralignols

a) Degassing operation and irradiation

Ethanol solutions (0.01M) of lignols B, E and F were frozen in ampules with liquid N$_2$ and degassed for 1min by means of vacuum lines and then allowed to melt at room temperature.   After this operation was repeated 5 times, ampules were closed.   Some ampules were closed after introduction of air (aerated samples). After 0.5, 1, 2hr irradiation, absorbance of solutions at 450nm and recoveries of starting materials were measured by HPLC.

b) Separation and identification of photoreaction products

Photoreaction products were analyzed by HPLC under the same conditions used in (b) of 'Irradiation to Non-phenolic Lignols'.

F-I.   FAB-MS: 393 (M+H$^+$), 345, 197 and 151.14

^{1}H-NMR (in d$_6$-acetone): 3.6 (2-γ), 3.8 (1-γ, hidden by vast OMe peaks), 3.8 and 3.9 (OMe), 3.9 (2-β), 4.6 (1-β), 4.9 (1-α), 6.8-7.6 (aromatic).

^{13}C-NMR (in d$_6$-acetone): 41.47 (2-β), 56.02 and 56.16 (OMe), 57.53 (2-γ), 61.90 (1-γ), 73.65 (1-α), 85.07 (1-β), 111.44, 111.99, 114.90, 115.81, 120.44 and 123.14 (tertiary aromatic carbons), 131.61, 133.89, 146.59, 147.76, 150.85 and 153.53 (quaternary aromatic carbons), 198.09 (2-α).

F-III. FAB-MS: 733(M+Na$^+$, Na$^+$ was included as a contaminant), 711 (M+H$^+$), 693, 615, 467, 347, 329, 207, 163 and 151; 733 (M+Na$^+$), 703, 545, 487, 429, 371, 313, 253 and 173, in the case a trace amount of 1% aqueous NaCl was added; 749 (M+K$^+$), 647, 554, 463, 389 and 297 in the case a trace amount of 1% aqueous KI was added.

^{13}C-NMR (d$_6$-acetone): 48.80 (2-β), 56.13-56.33 (OMe), 61.79 (3- γ), 61.83(1-γ), 64.97 (2-γ), 73.67 (1-α), 73.90 (3-α), 85.07 (3-β), 86.53 (1-β), 109.30, 111.01, 111.49, 112.75, 114.92, 115.94, 119.25, 119.42, 119.74, 121.70 and 123.16 (tertiary aromatic carbons), 129.09, 131.31, 133.90, 134.30, 137.39, 143.26, 146.60, 147.77, 148.17, 150.71, 153.25 and 156.65 (quaternary aromatic carbons), 196 (2-α).   These assignments of aliphatic carbons were made by reference to those in compound E-III.

ACKNOWLEDGMENT

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