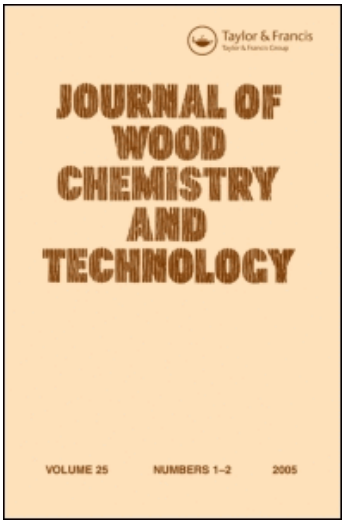

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Lignin and Related Compounds X. The Synthesis of Dimeric-Type Compounds Derived from Lignin

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LIGNIN AND RELATED COMPOUNDS X. THE SYNTHESIS OF DIMERIC-TYPE COMPOUNDS DERIVED FROM LIGNIN

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ABSTRACT

Four dimeric-type compounds (14, 15, 16, and 17) that had been isolated earlier from the catalytic hydrogenolysis products of aspen poplar lignin have been synthesized for structural verification.

INTRODUCTION

In a previous communication[1] evidence was presented in the form of NMR and MS data for the characterization of the dimeric-type compounds, 14, 15, 16, and 17, as products of the catalytic (Rh-C) hydrogenolysis of aspen poplar lignin. This paper reports the syntheses and characterization of these compounds as a final verification of their structure. The synthesis involves the base-catalyzed condensation of two appropriately substituted monomers, one a phenylmethyl chloride and the other an ethyl or methyl phenylethanoate. The appropriate starting materials, 1, 2, 3, 4, and 5 were prepared as follows and identified by comparison with reported analytical data. Conversion of vanillin (4-hydroxy-3-methoxybenzaldehyde) or syringaldehyde (4-hydroxy-3, 5-dimethoxybenzaldehyde) into the corresponding benzyl ethers[2,3]

and reduction with sodium borohydride gave the substituted benzyl alcohols[4,5]. Subsequent treatments of these alcohols with thionyl chloride in chloroform gave the required substituted benzyl chlorides, 1[6] and 2[5,6]. Further treatment of the chlorides with sodium cyanide gave the nitriles[5,6] which on hydrolysis yielded the ethanoic acids[5,7,8]. Esterification of the acids gave the required but previously unreported ethyl esters 3 and 4 and the reported methyl ester 5[9]. Overall yields starting from vanillin and syringaldehyde were 59 and 58 percent for 1 and 2, respectively, 26 percent for 3/5 and 25 percent for 4.

An alternative method for the preparation of the homoacids from acetoguaiacone (1-(4-hydroxy-3-methoxyphenyl)ethanone) and acetosyringone(1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone) using the Willgerodt-Kindler reaction[10] was less satisfactory.

The dimerization reaction, catalyzed by lithium N-isopropyl-cyclohexylamide[11], and the subsequent conversion to the required hydrogenolysis products was effected as shown in Scheme 1.

EXPERIMENTAL

A. Apparatus

^{1}H nmr spectra were recorded on either a Varian T-60 and/or EM-90 instrument with TMS as internal standard.

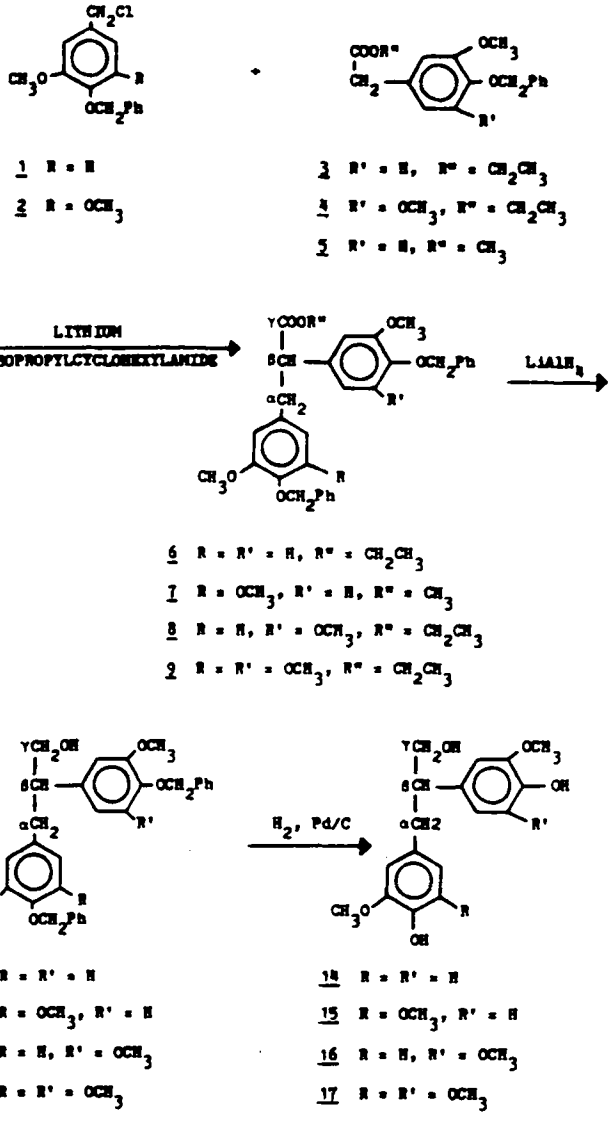
Mass spectra were obtained using an MS-12 mass spectrometer.

Column chromatographic separations were made using a column (60 cm x 2.8 cm) packed with Bio-Sil A (silica gel, 200 - 400 mesh). Thin layer chromatographic separations were made using Merck TLC aluminum sheets (20 x 20 cm) precoated with silica gel $60F_{254}$.

B. Synthesis of Monomeric Starting Materials

Ethyl 4-benzyloxy-3-methoxyphenylethanoate, 3, was prepared as a yellow oil by the esterification of the appropriately substituted ethanoic acid according to the method of Kametani et al[5]. Yield, 84%. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

SCHEME 1



1 R = H
2 R = OCH_3

3 R' = H, R'' = CH_2CH_3
4 R' = OCH_3, R'' = CH_2CH_3
5 R' = H, R'' = CH_3

6 R = R' = H, R'' = CH_2CH_3
7 R = OCH_3, R' = H, R'' = CH_3
8 R = H, R' = OCH_3, R'' = CH_2CH_3
9 R = R' = OCH_3, R'' = CH_2CH_3

10 R = R' = H
11 R = OCH_3, R' = H
12 R = H, R' = OCH_3
13 R = R' = OCH_3

14 R = R' = H
15 R = OCH_3, R' = H
16 R = H, R' = OCH_3
17 R = R' = OCH_3

Found: C, 71.75, H, 6.86%. ^{1}H nmr ($CDCl_3$) δ ppm 1.15 (t, 3H, CH_3, J = 6.5 Hz), 3.6 (s, 2H, CH_2), 3.9 (s, 3H, OCH_3), 4.3 (q, 2H, OCH_2CH_3, J = 6.5 Hz), 5.2 (s, 2H, $PhCH_2O$), 6.8-6.9 (m, 3H, Ph), 7.2 - 7.6 (m, 5H, $ArCH_2$). Mass spec. (70 ev) m/z 300 ($M^{+\cdot}$, 15%), 272 (31%), 227 (40%), 181 (10%) and 91 (100%).

Ethyl 4-benzyloxy-3,5-dimethoxyphenylethanoate, 4, was prepared from the appropriate starting materials as above. Yield, 82%. Calcd. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71%. Found: C, 69.18; H, 6.60%. ^{1}H nmr (acetone-d_6) δ ppm 1.2 (t, 3H, CH_3, J = 6.5 Hz), 3.5 (s, 2H, CH_2), 3.9 (s, 6H, OCH_3), 4.1 (q, 2H, OCH_2CH_3, J = 6.5 Hz), 4.7 (s, 2H, $PhCH_2O$), 6.6 (s, 2H, Ar-CH_2), 7.1 - 7.5 (m, 5H, Ph). Mass spec. (70 ev) m/z 330 ($M^{+\cdot}$16%), 302 (30%), 257 (45%), 211 (12%) and 91 (100%).

C. Synthesis of Dimeric Hydrogenolysis Products

The typical procedure used to effect the synthesis of the dimeric products is illustrated below by the condensation of 1 and 3 to produce 6 and its subsequent conversion through 10 to the required 14. The other dimers were prepared by similar procedures.

Ethyl 2,3-di(4-benzyloxy-3-methoxyphenyl) propanoate, 6.

To a magnetically stirred solution of N-isopropylcyclohexylamide (0.75g ~ 5.5 mmol) in dry THF (7.5 mL) contained in a 50 mL pear-shaped flask and cooled in a dry ice-acetone bath, was added, by syringe, 3.5 mL of 1.65M n-butyllithium (5.5 mmol) in hexane. To the stirred cold solution was added, by syringe, ethyl 4-benzyloxy-3-methoxyphenyl ethanoate (1.5g ~ 5 mmol) in dry THF (10 mL) and stirring continued for 15 minutes. After warming to room temperature this solution was added, by syringe, over a period of several minutes, to a stirred solution of 4-benzyloxy-3-methoxyphenylmethyl chloride (1.6g ~ 6.1 mmol) in dry DMSO (5 mL) in a round-bottomed flask (100 mL). After stirring at room temperature under nitrogen overnight, the resulting light brown solution which contained a small amount of solid was diluted with water (50 mL) and extracted with ether

(4 x 25 mL). The combined ether extract was washed with water (4 x 25 mL), hydrochloric acid (10%, 3 x 25 mL), saturated sodium bicarbonate solution (2 x 25 mL), saturated sodium chloride (2 x 25 mL), water (2 x 25 mL) and finally dried over anhydrous sodium sulfate. After filtration the solvent was evaporated to leave a viscous yellow-brown oil (2.8g). Purification by column chromatography using as eluant increasingly polar mixtures of ethyl ethanoate-Skelly B of v/v 1/9, 2/8, 3/7 gave several fractions from which those were combined that contained 15 as monitored by thin-layer chromatography. Evaporation of the solvents gave a crude crystalline compound which was recrystallized from cyclohexane. Yield 1.34g, 51%, m.p. 105-106°C. Calcd. for $C_{33}H_{34}O_6$: C, 75.26; H, 6.51%. Found: C, 75.16; H, 6.44%. ^1H nmr ($CDCl_3$), δ ppm 1.12(t, 3H, CH_3, J = 7.0 Hz), 2.90(q, 1H, α Ha, J = 6.8 Hz, J = 13.6 Hz), 3.33(q, 1H, α Hb, J = 8.6 Hz, J = 13.6 Hz), 3.68(q, 1H, β H, J = 6.8 Hz, J = 8.6 Hz), 3.76 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.06 (q, 2H, OCH_2CH_3, J = 7.0 Hz), 5.09 (s, 2H, OCH_2Ph), 5.11 (s, 2H, OCH_2Ph), 6.56 - 6.84 (m, 6H, Ar), 7.24 - 7.42 (m, 10H, $PhCH_2$). Mass Spec. (70ev), m/z 526 ($M^{+\cdot}$,5%), m/z = 453 (1.1%), 452 (0.55%), 299 (5%), 227 (62%), 91 (100%), 65 (16%), 107 (8%).

2,3-Di(4-benzyloxy-3-methoxyphenyl)-1-propanol, 10

To a magnetically-stirred solution of lithium aluminum hydride (0.13g ~ 3.43 mmol) in diethyl ether (10 mL) was added, by syringe, a solution of 6 (0.40g ~ 0.73 mmol in 25 mL dry ether). The resulting mixture was heated under reflux with stirring for 3 hours. After cooling, ether (10 mL) was added followed by water (50 mL) and hydrochloric acid (10%, 50 mL) and finally extracted with ether (4 x 25 mL). The combined ether extract was washed with water (2 x 25 mL), saturated sodium bicarbonate solution (2 x 25 mL), saturated sodium chloride solution (2 x 25 mL) , water (2 x 25 mL) and dried over anhydrous magnesium sulfate. After filtration the solvent was evaporated to give a sticky white solid 10 (0.3g, yield 81%), m.p. 90 - 92°C

(from benzene-cyclohexane). Calcd. for $C_{31}H_{32}O_5$: C, 76.84; H, 6.66%. Found: C, 76.62; H, 6.83%. ^{1}H nmr, ($CDCl_3$), δ ppm, 1.48(s, broad, 1H, OH), 2.67 - 2.89 (m, 3H, α H and β H), 3.58 - 3.68 (2H, γ H overlapped with OCH_3), 3.65 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 4.99 (s, 2H, OCH_2Ph), 5.02 (s, 2H, OCH_2Ph), 6.48 - 6.70 (m, 6H, Ar), 7.18 - 7.35 (m, 10H, $PhCH_2$). Mass spec. (70 ev), m/z 484 ($M^{+\cdot}$, 9%), 257 (32%), 227 (35%), 240 (6%), 107 (10%), 91 (100%), 65 (25%).

2,3-Di(4-hydroxy-3-methoxyphexyl)-1-propanol, 14

2,3-Di(4-benzyloxy-3-methoxyphenyl)-1-propanol 10 (0.12g) was dissolved in dioxane:acetic acid:water (2:2:1 v/v, 15 mL), Pd-black (0.02g) was added and the mixture stirred in the presence of hydrogen gas for 3 hours. After filtration the filtrate was extracted with chloroform (3 x 15 mL), the extract was washed with water (2 x 10 mL), dried over anhydrous sodium sulphate and evaporated to leave an oily residue. The oily mass was purified by micro pipette column packed with Bio-Sil silica gel. Calcd. for $C_{17}H_{20}O_5$: C, 67.10; H, 6.57%. Found: C, 67.29; H, 6.42%. ^{1}H nmr($CDCl_3$, D_2O) δ ppm 2.70 - 2.90 (m, 3H, α H and β H), 3.60 - 3.69 (m, 2H, γ H overlapped with OCH_3), 3.70 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 6.50 - 7.40 (m, 6H, Ar). Mass spec. (70 ev), m/z 304 ($M^{+\cdot}$, 16%), 150 (41%), 167 (100%), 137 (88%).

Methyl 2-(4-benzyloxy-3-methoxyphenyl)-3-(4-benzyloxy-3,5-dimethyoxyphenyl) propanoate, 7

It was prepared as described for compound 6, using methyl 4-benzyloxy-3-methoxyphenyl ethanoate (1.43g ~ 5 mmol) and 4-benzyloxy-3,5-dimethoxyphenyl chloride (1.46g ~ 5 mmol). Yield 1.27g ~ 47%, m.p. 106 - 108°C (Skelly B:ethyl ethanoate). Calcd. for $C_{33}H_{34}O_7$: C, 73.04; H, 6.32%. Found: C, 72.85; H, 6.08. ^{1}H nmr ($CDCl_3$), δ ppm 2.85 (q, 1H, α Ha, J = 7.0 Hz, J ~ 13.6 Hz), 3.25 (q, 1H, α Hb, J = 8.4 Hz), 3.52 - 3.63 (m, 1H, β H, overlapped with OCH_3). 3.52 (s, 3H, $COOCH_3$), 3.62 (s, 6H, OCH_3), 3.77 (s, 3H, OCH_3), 4.87 (s, 2H, OCH_2Ph), 5.03 (s, 2H, OCH_2Ph), 6.18 - 6.90 (m, 5H, Ar), 7.24 - 7.32 (m, 10H, OCH_2Ph). Mass

spec. (70 ev), m/z 542 ($M^{+\bullet}$, 5%), 483 (0.65%), 482 (0.4%), 285 (62%), 257 (23%), 107 (8%), 91 (100%), 65 (16%).

Ethyl 2-(4-benzyloxy-3,5-dimethoxyphenyl)-3-(4-benzyloxy-3-methoxyphenyl) propanoate, 8

It was prepared as described for compound 6, using ethyl 4-benzyloxy-3,5-dimethoxyphenyl ethanoate (1.65g ~ 5 mmol) and 4-benzyloxy-3-methoxybenzylchloride (1.57g ~ 5 mmol). Yield 1.32g ~ 48%, m.p. 110 - 112°C (Skelly B:ethyl ethanoate). Calcd. for $C_{34}H_{36}O_7$: C, 73.36; H, 6.52%. Found: C, 73.59; H, 6.18%. ^1H nmr, ($CDCl_3$), δ ppm 1.10 (t, 3H, CH_3, J = 7.2 Hz), 2.91 (q, 1H, αHa, J = 6.8 Hz, J = 13.7 Hz), 3.32 (q, 1H, α Hb, J = 8.6 Hz, J = 13.7 Hz, 3.66 (q, 1H, β H, J = 6.8 Hz, J = 8.6 Hz), 3.65 (s, 3H, OCH_3), 3.75 (s, 6H, OCH_3), 3.98 (q, 2H, J = 7.2 Hz), 4.97 (s, 2H, OCH_2Ph), 5.00 (s, 2H, OCH_2Ph), 6.48 - 6.90 (m, 5H, Ar), 7.22 - 7.48 (m, 10H, $PhCH_2$). Mass spec. (70 ev), m/z 556 ($M^{+\bullet}$,4%), 483 (0.7%), 482 (0.4%), 329 (5%), 227 (35%), 257 (18%), 107 (8%), 91 (100%), 65 (16%).

Ethyl 2,3-di(4-benzyloxy-3,5-dimethoxyphenyl) propanoate, 9

It was prepared as described for compound 6, using ethyl 4-benzyloxy-3,5-dimethoxyphenylethanoate (1.65g ~ 5 mmol) and 4-benzyloxy-3,5-dimethoxyphenyl chloride (1.46g ~ 5 mmol). Yield 0.88g ~ 30%, m.p. 96 - 98°C (cyclohexane:ethyl ethanoate). Calcd. for $C_{35}H_{38}O_8$: C, 71.65; H, 6.53%. Found: C, 71.73; H, 6.23%. ^1H nmr, ($CDCl_3$), δ ppm 1.11 (t, 3H, CH_3, J = 7.0 Hz), 3.32 (q, 1H, α Ha, J = 6.8 Hz, J = 13.7 Hz), 3.34 (q, 1H, α Hb, J = 8.6 Hz, J = 13.7 Hz), 3.67 (q, 1H, β H, J = 6.8, J = 8.6), 3.73 (s, 6H, OCH_3), 3.77 (s, 6H, OCH_3), 4.10 (q, 2H, OCH_2CH_3, J = 7.0 Hz), 5.00 (s, 2H, OCH_2-Ph), 5.09 (s, 2H, OCH_2Ph), 6.57 - 6.82 (m, 4H, Ar), 7.15 - 7.41 (m, 10H, $PhCH_2$). Mass spec. (70 ev), m/z 586 ($M^{+\bullet}$, 3.5%), 513 (0.8%), 329 (4%), 257 (61%), 107 (8%), 91 (100%), 65 (16%).

2-(4-Benzyloxy-3-methoxyphenyl)-3-(4-benzyloxy-3,5-dimethoxyphenyl)-1-propanol, 11

It was prepared as described for compound 14. Yield 0.37g ~ 79%, m.p. 94 - 96°C (Skelly B:ethyl ethanoate). Calcd. for

$C_{32}H_{34}O_6$: C, 74.69; H, 6.66%. Found: C, 74.58; H, 6.79%. ^1H nmr, ($CDCl_3$), δ ppm 1.45 (s, broad, 1H, OH), 2.68 - 2.90 (m, 3H, αH and βH), 3.57 - 3.70 (m, 2H, γH, overlapped with OCH_3), 3.67 (s, 6H, OCH_3), 3.80 (s, 3H, OCH_3), 4.98 (s, 2H, OCH_2Ph), 5.11 (s, 2H, OCH_2Ph), 6.47 - 6.80 (m, 5H, Ar), 7.16 - 7.41 (m, 10H, Ph proton). Mass spec. (70 ev), m/z 514 ($M^{+\cdot}$, 14%), 483 (0.6%), 257 (56%), 240 (6%), 149 (7%), 107 (10%), 91 (100%), 65 (25%).

3-(4-benzyloxy-3-methoxyphenyl-1-propanol, 12

It was prepared according to the method as described for compound 14. Yield ~ 78%, m.p. 98 - 100°C (Skelly B:ethyl ethanoate). Calcd. for $C_{32}H_{34}O_6$: C, 74.69; H, 6.66%. Found: C, 74.78; H, 6.50%. ^1H nmr, ($CDCl_3$), δ ppm 1.50 (s, broad, 1H, OH), 2.69 - 2.91 (m, 3H, αH and βH), 3.57 - 3.70 (m, 2H, γH overlapped with OCH_3), 3.66 (s, 3H, OCH_3), 3.76 (s, 6H, OCH_3), 5.00 (s, 2H, OCH_2Ph), 5.03 (s, 2H, OCH_2Ph), 6.50 - 6.80 (m, 5H, Ar), 7.20 - 7.50 (m, 10H, $PhCH_2$). Mass spec. (70 ev), m/z 514 ($M^{+\cdot}$, 13%), 287 (32%), 227 (33%), 270 (7%), 179 (5%), 107 (10%), 91 (100%), 65 (25%).

2,3-Di(4-benzyloxy-3,5-dimethoxyphenyl)-1-propanol, 13

It was prepared as described for the compound 14. Yield ~ 78%. Calcd. for $C_{33}H_{36}O_7$: C, 72.77; H, 6.66%. Found: C, 72.50; H, 6.27%. ^1H nmr, ($CDCl_3$), δ ppm 1.49 (s, broad, 1H, OH), 2.68 - 2.78 (m, 3H, αH and βH), 3.59 - 3.68 (m, 2H, γH, overlapped with OCH_3), 3.65 (s, 6H, OCH_3), 3.71 (s, 6H, OCH_3), 4.98 (s, 2H, OCH_2Ph), 5.00 (s, 2H, OCH_2Ph), 6.46 - 6.69 (m, 4H, Ar), 7.15 - 7.34 (m, 10H, $PhCH_2$). Mass spec. (70 ev), m/z 544 ($M^{+\cdot}$, 11%), 287 (33%), 257 (34%), 270 (5%), 179 (6%), 107 (10%), 91 (100%), 65 (25%).

2-(4-Hydroxy-3-methoxyphenyl)-3-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol, 15

It was prepared according to the method described for compound 14. Calcd. for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63%. Found: C, 64.86; H, 6.49%. ^1H nmr ($CDCl_3$, D_2O), δ ppm 2.69 - 2.89 (m, 3H, αH and βH), 3.60 - 3.69 (m, 2H, γH, overlapped with OCH_3),

3.68 (s, 6H, OCH_3), 3.75 (s, 3H, OCH_3), 6.49 - 7.50 (m, 5H, Ar). Mass spec. (70 ev), m/z 334 ($M^{+\cdot}$, 11%), 150 (37%), 167 (100%).

2-(4-Hydroxy-3,5-dimethoxy)-3-(4-hydroxy-3-methoxyphenyl)-1-propanol, 16

It was prepared according to the method described for compound 14. Calcd. for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63%. Found: C, 64.91; H 6.62%. ^1H nmr ($CDCl_3$, D_2O), δ ppm 2.67 - 2.88 (m, 3H, αH and βH), 3.59 - 3.68 (m, 2H, γH overlapped with OCH_3), 3.70 (s, 3H, OCH_3), 3.75 (s, 6H, OCH_3), 6.50 - 7.46 (m, 5H, Ar). Mass spec. (70 ev), m/z 334 ($M^{+\cdot}$, 13%), 180 (38%), 197 (100%), 137 (85%).

2,3-Di-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol, 17

It was prepared according to the method described for compound 14. Calcd. for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64%. Found: C, 62.92; H, 6.29%. ^1H nmr ($CDCl_3$, D_2O), δ ppm 2.68 - 2.77 (m, 3H, αH and βH), 3.58 - 3.69 (m, 2H, γH overlapped with OCH_3), 3.66 (s, 6H, OCH_3), 3.74 (s, 6H, OCH_3), 6.50 - 6.88 (d, 4H, Ar). Mass spec. (70 ev), m/z 364 ($M^{+\cdot}$, 10%), 180 (39%), 197 (100%), 167 (67%).

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