A New Synthesis of Model Compounds for the $\beta$-5 Structural Unit in Lignins

GÖSTA BRUNOW * and KNUT LUNDQUIST

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

The $\beta$-5, or phenylcoumaran linkage is an abundant structural element in lignins. Until recently, the only practical synthetic route to this structure was the oxidative dimerization of p-propenylphenols such as isoeugenol and coniferyl alcohol. Apart from the fact that the desired dimers have to be separated from large amounts of other products formed in the reaction, this synthesis is unsuited for unsymmetrical phenylcoumarans and for oligomeric model compounds containing three or more phenylpropane units. A "rational" synthesis that avoids these problems has recently been reported. Here we describe an alternative and shorter synthetic route to the phenylcoumaran structure.

The synthesis is an extension of our recently published synthesis of $\beta$-1 model compounds (1,2-diarylp propane-1,3-diols). It starts with the formation of chalcone 1 which is formed in good yield from easily available starting materials. Epoxidation under phase transfer conditions afforded epoxide 2. Rearrangement of 2 with boron trifluoride diethyl etherate in refluxing diethyl ether and subsequent reduction of the product with sodium borohydride yielded a mixture which, after column chromatography, gave 38% of crystalline 1,2-diarylp propane-1,3-diol 3. This is probably the erythro isomer in analogy with other 1,2-diarylp propane-1,3-diols prepared in a similar manner.

Debenzylation with hydrogen over a palladium catalyst in dry dioxane gave a quantitative yield of 4. This compound is to our knowledge the first synthetic "open" structure corresponding to a phenylcoumaran. No spontaneous ring closure was observed with 4 either in dioxane solution or on evaporation of the solvent. Only after addition of a catalytic amount of hydrochloric acid to the dioxane solution did a cyclization to the phenylcoumaran 5 take place. When debenzylation of 3 was done using methanol as solvent, normal work-up (filtration of the catalyst and evaporation of the solvent) gave 5 directly.

The $^1$H NMR spectrum of the diacetate of 5 was similar to that of dihydrodihydrodiconiferyl alcohol and dehydrodiosoneugenol indicating that the substituents at the coumaran ring are trans as shown in the Formula.

The unexpected stability of 4 supports the assumption that such units can exist as such in lignins. They have in fact been found in certain naturally occurring lignans.

Experimental. $^1$H NMR spectra were recorded on a Bruker WH 270 instrument with chloroform-$d$ as solvent. The high resolution mass spectrum was obtained with a VG Analytical ZAB instrument. Melting points were determined using a Mettler hot stage on a polarizing microscope.

1-(4-Benzylxylo-3-methoxyphenyl)-3-(2-benzylxylo-3-methoxyphenyl)-2-propen-1-one (1). The compound was prepared from the benzyl ethers of 1-(4-hydroxy-3-methoxyphenyl)ethanone and 2-hydroxy-3-methoxybenzaldehyde using the procedure described in Ref. 5. The product was a yellow oil which crystallized slowly on standing. Recrystallized from ethanol, m.p. 91°C, yield 83%. $^1$H NMR spectrum: δ 3.89 (3 H, s; OCH$_3$), 3.92 (3 H, s; OCH$_3$), 5.04 (2 H, s; CH$_2$), 7.53 (1 H, d, $J$=15.9 Hz; vinyl proton), 6.8–7.6 (16 H,
m; aromatic protons), 7.99 (1 H, d, J=15.9 Hz; vinyl proton).

1-(4-Benzoyl-3-methoxyphenyl)-3-(2-benzyl-
3-methoxy-3-methoxyphenyl)-2,3-epoxy-1-propa
one (2). Chalcone 1 (9.6 g, 20 mmol) was dissolved in
50 ml dichloromethane. A mixture of 10 ml 35 %
hydrogen peroxide and 30 ml 3 M aqueous
NaOH was added with cooling (ice bath) to
below 4 °C. With vigorous stirring, 1.4 g of solid
tetraethylammonium hydrogen sulfate were
added in small portions during 10 min. The
mixture was stirred for 1 h at 4 °C and for 2 h at
room temperature. The organic layer was sep-
arated and washed twice with 1 % aqueous ammo-
nium sulfate, dried (Na2SO4) and the solvent
evaporated. Yellow oil 8.8 g (89 %). 1H NMR
spectrum: δ 3.90 (3 H, s; OCH3), 3.92 (3 H, s;
OCH3), 4.10 (1 H, d, J=1.9 Hz; -CH<), 4.22 (1
H, d, J=1.9 Hz; -CH<), 5.00 (2 H, AB
spectrum, J=11.0 Hz; CH2), 5.20 (2 H, s;
CH2)=7 (16 H, m; aromatic protons).

1-(4-Benzoyl-3-methoxyphenyl)-2-(2-benzyl-
3-methoxyphenyl)-1,3-propanediol (3). To 2
(4.7 g, 9.5 mmol), dissolved in 300 ml dry diethyl
ether was added 13.4 g freshly distilled BF3-
diethyl etherate (95 mmol). The mixture was
refluxed for 30 min and the reaction was then
stopped by the careful addition of water (200 ml).
Dried (Na2SO4) and evaporated to a small
volume. The syrupy residue was dissolved in
dioxane (75 ml) and a solution of 1 g sodium
borohydride in 25 ml 0.1 M sodium hydroxide
was added dropwise (vigorous reaction). After 48
h at room temperature the mixture was acidicified
(0.1 M HCl) and extracted with ether (200 ml in
three portions). The ether layer was washed with
saturated sodium hydrogen carbonate solution
and with water. After drying (Na2SO4), evapora-
tion of the solvent left an oil (5 g) which was
crystallographed on a silica gel column (120 g,
CH2Cl2:EtOAc 4:1, 10 ml fractions). Fractions
19–31 yielded a colourless oil (1.8 g, 38 %)
which crystallized slowly on standing. Recrystal-
lization from diethyl ether gave small white
needles m.p. 97–100 °C. 1H NMR spectrum of
the acetate derivative: δ 1.88 (3 H, s; CH3CO),
1.89 (3 H, s; CH3CO), 3.70 (3 H, s; OCH3), 3.86
(3 H, s; OCH3), 3.91 (1 H, dd, J=6.3 and 10.7
Hz; CH3), 4.05 (1 H, m; Hβ), 4.20 (1 H, dd, J=6.0
and 10.7 Hz; Hβ), 4.62 (1 H, d, J=11.0 Hz;
methylene proton), 4.94 (1 H, d, J=11.0 Hz;
methylene proton), 5.09 (2 H, s; CH2), 6.05 (1 H, d,
J=8.1 Hz; Hα), 6.6–7.5 (16 H, m; aromatic
protons).

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-hydroxy-
3-methoxyphenyl)-1,3-propanediol (4). The
dibenzyl ether 3 (0.31 g) was subjected to
catalytic hydrogenation in dioxane (15 ml) with
0.1 g 10 % Pd/C as catalyst. After 1 h the