Lignin and related compounds. II. Studies using ruthenium and Raney nickel as catalysts for lignin hydrogenolysis

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Five cyclohexyl compounds, derived from lignin, have been isolated and identified from the products of the catalytic hydrogenolysis of spruce wood over ruthenium and Raney nickel catalysts. One of these, 3-(4-hydroxy-3-methoxycyclohexyl)-1-propanol, a previously unreported compound, has been synthesized and characterized.

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In a previous communication (1), the gas-liquid chromatograms of spruce lignin hydrogenolysis products obtained using excess Raney nickel, ruthenium on charcoal, and ruthenium on alumina as catalysts were illustrated. Of the 9 compounds represented as distinct peaks in these chromatograms, 4, labelled C, D, E, and F in Fig. 1, were identified as aromatic derivatives whereas the other 5 compounds, labelled 1 through 5, were reported as cyclohexyl derivatives but their structures had not been determined. This paper deals with the identification of these 5 compounds, the quantitative estimation of all 9 lignin derivatives, and suggestions as to their origin as a result of the hydrogenolysis process.

The chromatograms reproduced in the previous paper and that shown herein as Fig. 1, are of the ether-soluble fraction of the chloroformsoluble fraction obtained from the products of the catalytic hydrogenolysis of spruce lignin. Details of the hydrogenolysis, isolation, separation, and chromatography were given in the previous publication (1). Subsequent to the chromatographic work reported earlier, it was found that a better separation, for quantitative analytical purposes, could be obtained using a column packed with 10% SE-30 on Chromosorb W (80/100 mesh, DMCS treated, acid washed), operated under identical conditions. A pure sample of each compound was collected from the gas chromatograph and identified by comparison of its relative retention time and its mass, infrared (i.r.), and nuclear magnetic resonance (n.m.r.) spectra with similar spectra of an authentic sample.

Using dihydrosinapyl alcohol as the internal standard, the relative abundance of each of these 9 lignin degradation products was determined for each of the 3 catalyst systems under study and is given in Table 1 in terms of the percentage, by weight, of the total ether-soluble fraction; along with the total yield of all such products based on the original Klason lignin. Such values are recorded as obtained by the use of both a planimeter and the triangulation method; with the average of such values considered to be most suitable.

The results of the experiments reported in



FIG. 1. Gas-liquid chromatogram of spruce lignin hydrogenolysis products: 1, 4-ethylcyclohexanol; 2, 4-*n*-propylcyclohexanol; C, 4-methylguaiacol; 3, 3-cyclohexyl-1-propanol; D, 4-ethylguaiacol; E, 4-*n*-propylguaiacol; 4, 3-(4hydroxycyclohexyl)-1-propanol; 5, 3-(4-hydroxy-3-methoxycyclohexyl)-1-propanol; F, dihydroconiferyl alcohol.

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TABLE 1

Gas-liquid chromatographic analysis of ether-soluble spruce lignin hydrogenolysis products*

Catalyst	Abundance of chromatographable products [†] , [‡]											
	1	2	С	3	D	Е	4	5	F	Total	Yield of recovered lignin§	
Raney-Ni (10 g) Ru-C Ru-alumina	0.66 1.56 0.67	0.83 3.49 1.72	1.00 1.39 0.97	1.69 0.32 1.05	1.00 2.70 2.02	0.87 1.61 2.51	40.9 6.95 19.8	$12.6 \\ 4.52 \\ 12.2$	6.32 10.3 15.2	65.9 32.8 56.1	$16.5 \\ 11.8 \\ 14.6$	

*For details of isolation refer to reference 1.

*For details of isolation refer to reference 1. †Percent of total ether-soluble fraction as calculated subsequent to the measurement of average peak areas as obtained using the planimeter and the triangulation methods. ‡Product identity: C, 4-methylguaiacol; D, 4-ethylguaiacol; E, 4-*n*-propylguaiacol; F, dihydroconiferyl alcohol; 1, 4-ethylcyclohexanol; 2, 4-*n*-propylcyclohexanol; 3, 3-cyclohexyl-1-propanol; 4, 3-(4-hydroxycyclohexyl)-1-propanol; 5, 3-(4-hydroxy-3-methoxycyclohexyl)-1-propanol. §Percent of original Klason lignin.

Table 1 support the conclusion made in the previous publication (1), that the use of any of the catalyst systems (excess Raney nickel, ruthenium-on-charcoal, and ruthenium-on-alumina) results in a more extensive degradation of the lignin fraction along with a significant amount of ring reduction to the corresponding cyclohexyl derivatives. It may be of some significance that of the various compounds obtained, the major amount is represented by those of the 1-substituted-3-propanol structure. In this way, these 3 catalyst systems resemble more closely that of palladium-on-charcoal (1).

Authentic samples of each of the identified compounds were available or were synthesized as reported in the Experimental section. 1-(4-Hydroxycyclohexyl)-3-propanol and 1-(4hydroxy-3-methoxycyclohexyl)-3-propanol (peaks 4 and 5, Fig. 1) were prepared by the hydrogenation of dihydroconiferyl alcohol over ruthenium-on-alumina (5%) catalyst. As part of this synthetic study, it was of interest to note that a marked difference in the nature of the products was obtained depending on the conditions of the reaction. Under the conditions indicated in Table 2, negligible reaction occurred at a temperature below 120°. For hydrogenations carried out at 160, 175, and 195°, the nature of the products obtained is indicated in Table 2, with the approximate relative abundance as indicated by the relative ratio of peak areas, as observed by gas chromatography. The main reactions appear to be an initial ring saturation, followed by a reductive loss of methoxyl, followed by a reduction of the propyl alcoholic function and/or side chain cleavage of carbon-carbon bonds.

The suggestion that was made in the earlier

publication (1), that two types of ether linkage may exist in the lignin is supported by the observations recorded in this paper. All the compounds identified in Fig. 1 may be reasonably expected to be derived from either *n*-propylguaiacol (peak E) or dihydroconiferyl alcohol (peak F). That n-propylguaiacol should be considered as a primary lignin cleavage product along with dihydroconiferyl alcohol, and not a reduction product of the latter, is indicated in 2 ways. The production of the cyclohexyl derivatives is more readily explained as arising from the further reduction of each of these 2 compounds resulting in decreased yields of the 2 aromatic compounds relative to the total yield of recovered substances. In the second place, the Ru-alumina catalytic hydrogenolysis of pure dihydroconiferyl alcohol (Table 2) gave rise to no n-propylguaiacol suggesting that this secondary reaction is not the source of *n*-propylguaiacol found in the lignin products of a similar treatment of spruce wood.

This paper records the isolation, for the first time, of 3-(4-hydroxy-3-methoxycyclohexyl)-1propanol as a hydrogenolysis product of lignin; and also of its synthesis and characterization. The other cyclohexanols have been reported previously as lignin products (2).

Experimental

The ether-soluble spruce lignin hydrogenolysis products used in this study were those whose isolation and yields were recorded in the previous publication (1). They had been obtained by the hydrogenolysis of preextracted wood meal (10 g), in dioxane-water (1:1 v/v, 150 ml) at an initial hydrogen pressure of 500 p.s.i.g. at a temperature of 195° for 5 h over the appropriate catalyst (1 g for ruthenium-charcoal (5%) and ruthenium-alumina (5%)and 10 g for Raney nickel). For the study using Raney

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Dihydroconiferyl	Ru-alumina	Tomperature	Time	Ratio of peak areas of cyclohexyl derivatives and starting material [†] , [‡]					
(g)	(3 /o) (g)	(°C)	(h)	1	2	3	4	5	F
0.40 0.50 0.52	0.20 0.50 1.05	160 175 195	1 0.5 5	10 10	2.5 4	0.3 0.1	1 8	1 6	1.5

TABLE 2

Hydrogenolysis of dihydroconiferyl alcohol*

*Solvent: dioxane-water (1:1 v/v, 50 ml); hydrogen (initial pressure, 500 p.s.i.g.). †Product identity: 1, 4-ethylcyclohexanol; 2, 4-n-propylcyclohexanol; 3, 3-cyclohexyl-1-propanol; 4, 3-(4-hydroxycyclohexyl)-1-propanol; 3-(4-hydroxy-3-methoxycyclohexyl)-1-propanol; F, dihydrocomiferyl alcohol (starting material). ‡Other peaks appeared in the chromatogram but represented compounds that were not identified.

nickel (10 g), the ether-soluble fractions of the 2 runs recorded in Table 1 of the previous paper were combined, while for the study using Ru-alumina catalyst the run was used which had yielded 0.68 g of ether-soluble material. Chromatographic separation of the components of the ether-soluble fractions was made using an F & M Chromatograph, model 5750 with hydrogen flame detector and temperature programming. The column (1/8 in. \times 6 ft) was packed with 10% SE-30 on Chromosorb W (80-100 mesh, DMCS treated, acid washed). The chromatograms were obtained at a helium flow rate of 40 ml/min; temperature programmed from 100 to 250 °C at 4°/min; injection temperature 260°; detector temperature 270°; recorder chart speed 0.5 in./min.

The quantitative analytical data reported in Table 1 were obtained by a method similar to that reported earlier (1) but using 1-(4-hydroxy-3,5-dimethoxyphenyl)-3-propanol (dihydrosinapyl alcohol) as the internal standard. Each of the cyclohexyl derivatives obtained as lignin hydrogenolysis products was identified by comparison of its relative retention time with that of an authentic sample and by i.r., n.m.r., and mass spectra.

Source of Reference Compounds

Authentic samples of each of the cyclohexyl derivatives were obtained as indicated below. For analytical purposes, a fraction was obtained by gas-liquid chromatography (g.l.c.) using an Aerograph A90P machine, fitted with a column (1/4 in. \times 6 ft) packed with 15% SE-30 on Chromosorb W (80-100 mesh, DMCS treated, acid washed); column, detector, and injector temperatures of 190, 230, and 210° respectively; and a helium flow rate of 40 ml/min. In each case the identity of the compound was checked by means of its mass, i.r. and n.m.r. spectra. For 3-(4-hydroxy-3-methoxycyclohexyl)-1-propanol, details of its preparation and characterization are given because it is a previously unreported compound.

4-Ethylcyclohexanol

This alcohol was commercially available from Aldrich Chemical Company Inc.

4-n-Propylcyclohexanol

This hexanol was prepared by the catalytic hydrogenation (5% Rh-alumina, 175°) of eugenol or dihydroconiferyl alcohol; *a*-naphthylurethane derivative, m.p. 133-134°; reported (3) m.p. 134-135°.

3-Cyclohexyl-1-propanol

This propanol was prepared by the catalytic hydrogenation (5% Rh-charcoal, 100°) of 3-phenyl-1-propanol.

3-(4-Hydroxycyclohexyl)-1-propanol

This propanol was prepared by the catalytic hydrogenation (5% Rh-alumina, 160°) of dihydroconiferyl alcohol (see Table 2).

3-(4-Hydroxy-3-methoxycyclohexyl)-1-propanol

This propanol was prepared by the catalytic hydrogenation of dihydroconiferyl alcohol (0.5 g) in dioxane (50 ml) over 5% Ru-alumina (0.25 g) at an initial pressure of hydrogen of 500 p.s.i.g. for 1 h at 160°. By g.l.c. of the chloroform-soluble fraction a compound was obtained which had the same retention time (on two different columns) as compound 5 isolated from the products of lignin hydrogenolysis. This compound (as a mixture of its diastereoisomers) was shown to be 3-(4-hydroxy-3methoxycyclohexyl)-1-propanol as follows: m/e 188 (M⁺ 1.7), 170 (0.7, loss of water), 129 (100, characteristic loss of side chain (4)), 111 (27.2, loss of water from m/e 129 fragment), 98 (16.3), 97 (27.2, loss of methanol from m/e 129 fragment), 81 (27.2), 71 (22.2), 69 (27.2), 67 (28.4), 59 (7.2, side chain), 58 (22.2), 57 (20.8, characteristic of cyclohexanols (4)), 55 (27.2), 45 (53.1), 41 (50.7) and 31 (23.5); i.r. spectrum (KBr disc): 3380, 2910, 2840, 1440, 1180, 1075, 1050, 970 cm⁻¹; n.m.r. spectrum (CDCl₃): CH_2 OH, τ 6.4 (t, 2H); OCH_3 , τ 6.6 (s, 3H);

OH, 7.7 (s, 2H); C,
$$\tau$$
 5.9 (narrow m, 1/2H (equatorial)); τ 6.4 (broad m, 1/2H (axial)); C, τ 6.7

OH

(m, 1H); remaining protons as a broad m from ca. τ 7.9 to ca. τ 9. The n.m.r. spectrum of the diacetate of this compound confirmed the above assignments.

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