NOTES

Lignin and Related Compounds. III. An Improved Synthesis of 3-(4-Hydroxy-3-methoxyphenyl)-1-propanol and 3-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanol

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3-(4-Hydroxy-3-methoxyphenyl)-1-propanol (dihydroconiferyl alcohol) (**1**) and 3-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol (dihydrosinapyl alcohol) (**2**) have been synthesized in good yields from 4-allyl-2-methoxyphenol (eugenol) and 4-allyl-2,6-dimethoxyphenol by means of the hydroboration reaction.

L'(hydroxy-4 méthoxyphényl-3)-3 propanol-1 (alcool dihydroconiferyle) (**1**) et l'(hydroxy-4 diméthoxyphényl-3,5)-3 propanol-1 (alcool dihydrosinapyle) (**2**) ont été synthétisés avec un bon rendement à partir de l'allyl-4 méthoxy-2 phénol (eugénol) et l'allyl-4 diméthoxy-2,6 phénol au moyen d'une réaction d'hydroboration.

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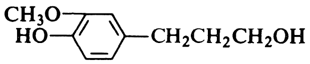
Introduction

Studies in these laboratories on the catalytic hydrogenolysis of spruce and aspen lignins (1, 2) have shown that significant quantities of 3-(4-hydroxy-3-methoxyphenyl)-1-propanol (dihydroconiferyl alcohol) (**1**) and 3-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol (dihydrosinapyl alcohol) (**2**) may be obtained. In order to study the properties and potential uses of these compounds it was necessary to synthesize them in adequate amounts. Previously reported syntheses involved the ultimate reduction of ethyl dihydroferulate or ethyl dihydrosinapate using either sodium in alcohol or lithium aluminum hydride (3–5). The preparation of these esters from the available starting materials, vanillin and syringaldehyde, involved several steps resulting in low overall yields.



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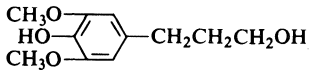

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This note reports the direct conversion by hydroboration and subsequent alkaline oxidation of the commercially available compounds, 4-allyl-2-methoxyphenol (eugenol) and 4-allyl-2,6-dimethoxyphenol, into **1** and **2** respectively. The required primary alcohol isomer is the major product representing ninety percent of the total. Separation of the two isomers may be achieved by repeated recrystallization from carbon tetrachloride – chloroform (5:1) mixture to give white crystals of the desired products **1** and **2** in approximately 80 and 75% yields, respectively. The success of the synthesis is dependent on the use of rigorously anhydrous conditions.

The characterization of the products was confirmed through their n.m.r. and mass spectra.

Experimental

Synthesis of 3-(4-Hydroxy-3-methoxyphenyl)-1-propanol (1)

Eugenol (9.7 g), obtained by fractional distillation (b.p. 78–80°/1 mm), was added to a 500 ml, three-necked flask which had been dried for 1 h at 110°. The flask was immediately fitted with a thoroughly dry pressure equating dropping funnel, a calcium chloride drying tube, and an inlet for dry nitrogen. Tetrahydrofuran (50 ml) previously dried over calcium hydride for 12 h and redistilled from $LiAlH_4$, was added to the flask which was then stoppered.

Borane (1 *M* in tetrahydrofuran) (60 ml) was added dropwise (30 drops per min) through the funnel to the stirred solution in the flask which was maintained at 0° by an ice bath. The solid, substituted borane separated near the end of the addition. Stirring was continued for an extra 30 min, at which time water (20 ml) was added to decompose the excess borane. This was followed by the addition of 3 *M* NaOH (24 ml), after which the mixture was allowed to warm to room temperature and 30% H_2O_2 (14 ml) added carefully and stirring continued for 1.5 h. The resulting pale yellow solution was extracted with diethyl ether (6 × 50 ml), saturated with NaCl, acidified with HCl (50 ml 2 *M*) and further extracted with ether (3 × 50 ml). The combined ether extracts were dried and concentrated to leave a yellow oil which slowly crystallized on standing at −15 °C. A gas chromatographic analysis (using a 6 ft, 1/8 in. stainless steel column packed with 10% SE30 on Chromosorb W, programmed from 100 °C at 4°/min) showed the two isomeric alcohols separated by 6.2 min.

Two crystallizations from carbon tetrachloride – chloroform (5:1) gave 3-(4-hydroxy-3-methoxyphenyl)-1-propanol (**1**), 8.7 g, (81%), m.p. 64–65° (reported m.p. 63–65° (4)).

Synthesis of 3-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanol (2)

Using the same procedure as described above, 4-allyl-2,6-dimethoxyphenol (10.7 g) was converted into 3-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol (**2**), 9.0 g (77%) m.p. 75–76° (reported m.p. 75–76.5° (4)).

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An Approach to Stereochemical Analysis by Ion Cyclotron Resonance. Distinguishing *exo*- and *endo*-Norborneol

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The ion cyclotron resonance spectra of mixtures of biacetyl and *exo*- or *endo*-norborneol show differences in the acetylation of the alcohol by the *m*/*e* 129 ion formed from biacetyl. The differences may be interpreted as a difference by a factor of four in rates of acetylation; a steric effect is proposed as the cause of the difference.

Les spectres de résonance cyclotron-ion de mélanges de biacétyle et d'*exo*- ou d'*endo*-norbornéol, montrent des différences dans l'acétylation de l'alcool, par l'ion *m*/*e* 129 qui se forme à partir du biacétyle. Les différences peuvent être interprétées comme une différence dans les vitesses d'acétylation par un facteur de quatre; il est suggéré qu'un effet stérique est la cause de cette différence.

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The reaction rates of *exo*- and *endo*-norborneol with acetylated biacetyl in the gaseous phase (eq. 1) differ by a factor of 4.

$$[1] \quad C_7H_{11}OH + C_6H_9O_3^+ \rightarrow C_7H_{11}O(H)OC_2H_3^+ + C_4H_6O_2$$

We have proposed that ion–molecule reactions studied by ion cyclotron resonance (i.c.r.) may be of use in the identification of organic functionality (1). Thus, 2,3-butanedione undergoes an ion–molecule reaction with itself (eq. 2) to give a species ("triacetyl", **1**) capable of transferring a specific (2) acetyl group to most oxygen- and nitrogen-containing functional groups (eq. 3). Our purpose in pursuing such studies is to explore the possibilities for reactions capable of distinguishing epimers, a problem which has been

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