Assuming the activity coefficients $\gamma_{\pm}$ at 25° C to be the average of results at 20° C and 30° C, changes in partial molal entropy were calculated from the expression

$$[3] \qquad \bar{S}_2 - \bar{S}_2^* = (\bar{H}_2 - \bar{H}_2^*)/T - 3.972 \ln (\gamma_{\pm} m / \gamma_{\pm}^* m^*).$$

The calorimetric results (1) were used for the enthalpy difference rather than the estimates of this quantity from osmotic data. The resulting curve is plotted in Fig. 3. The increase in entropy on micellization is about 5.5 cal mole^{-1} deg^{-1} and is of course equal to $\Delta H_M/T$. Goddard, Hoeve, and Benson (1) have drawn attention to the importance of changes in solvent structure in the process of micelle formation. The observed increase in entropy is explicable on this basis.

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THE SYNTHESIS OF A LIGNIN MODEL SUBSTANCE: 3-HYDROXY-1-(4-HYDROXY-3,5-DIMETHOXYPHENYL)-2-PROPANONE

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A study of the ethanolysis (1) of 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (I (R)) (β-oxyconiferyl alcohol) has provided considerable evidence for the presence in the lignin complex of the side chain —CH_2—CO—CH_2OH or its enolic form. Gardner has shown (1) that the four Hibbert monomers (II–V) are produced by the ethanolysis of I.

(R = 4-hydroxy-3-methoxyphenyl, R′ = 4-hydroxy-3,5-dimethoxyphenyl)

They have been shown previously to be released by the ethanolysis of spruce wood and various isolated lignins (2). Hibbert has proposed a series of interconversions (3) relating the production of II–V from I. Such a scheme would account for the proved absence of primary alcoholic groups in these isolated propylphenyl lignin monomers as contrasted with the presence of such groups in lignin derivatives obtained by other degradation procedures such as hydrogenation (2) and as evidenced from general analytical data. It

also explains the fact that carbon–methyl groups are present in these ethanolysis products and in other isolated lignins (4, 5) but not in protolignin itself (4).

From maple wood, by ethanolysis, the corresponding syringyl (R′ = 4-hydroxy-3,5-dimethoxyphenyl) analogues were isolated in addition to, and in greater yield than, the guaiacyl members, II–V (2). Although it is logical to assume that these monomers would be produced by the ethanolysis of the previously unreported 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone (VI), this assumption has yet to be proved. Of greater interest would be the comparison in yield of the rearrangement products obtained through ethanolysis of the two analogues. In the degradation of hardwood lignins, syringyl derivatives are obtained in greater abundance than are the corresponding guaiacyl members. A comparative study of the yield of the products obtained by the various established techniques of ethanolysis, oxidation, and hydrogenation as applied to I (R and R′) would assist in estimating the ratio of guaiacyl to syringyl nuclei in angiosperm protolignin.

This note records the synthesis of 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone. The method is similar to that used to prepare the analogous β-oxyconiferyl alcohol (6). Homosyringic acid, prepared by three different routes, was acetylated, then converted via the acid chloride, through the diazomethyl ketone, to the O-acetyl derivative of I (R′) which on hydrolysis gave I (R′). Several of the intermediate compounds are reported here for the first time. The yields of the syringyl derivatives are consistently lower than those of the corresponding guaiacyl compounds.

EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were measured with a Perkin–Elmer Model 21 spectrophotometer using sodium chloride optics.

Syntheses of Homosyringic Acid

Via Willgerodt Reaction (Kindler Modification)

Homosyringic acid was obtained starting from acetosyringone (7) by the adoption of the method used by Schwenk and Papa (8) to synthesize *p*-hydroxyphenylacetic. The product, obtained in only 6.7% yield, was recrystallized from water (Norite) to give fluffy white crystals, m.p. 130–131°; reported m.p. 132.5–134.5° (9). Previously a similar synthesis in these laboratories of homovanillic acid from acetovanillone had been achieved in a 43% yield. Arlt *et al.* (9) also reported the synthesis of homovanillic acid by this method.

Via Syringal Rhodanine

Syringal rhodanine.—To a mixture of syringaldehyde (41.0 g), rhodanine (29.9 g), and freshly fused sodium acetate (51.3 g) was added glacial acetic acid (365 ml) and the mixture refluxed for 40 minutes. The hot reaction mixture was decanted into vigorously stirred water (1030 ml), and after the mixture had been stirred for 3 hours, the product was collected, washed well with water, and dried under vacuum. The yield of crude syringal rhodanine was 59.4 g (89%), m.p. 242–246° (decomp.). Three recrystallizations from *n*-butanol (Norite) gave orange microcrystals, m.p. 258–258.5° (decomp.). Calc. for $C_{12}H_{11}NO_4S_2$: C, 48.5; H, 3.72; OCH_3, 20.9%. Found: C, 48.5; H, 3.74; OCH_3, 21.0%.

α-Thioketo-β-(4-hydroxy-3,5-dimethoxyphenyl)-pyruvic acid.—To syringal rhodanine (3.0 g) was added 15% sodium hydroxide (19 ml) and the mixture refluxed for 45 minutes. The red solution was cooled to 0° and acidified rapidly using 10% hydrochloric acid. The yield of the crude precipitated thioketo acid was 2.4 g (92.7%), m.p. 123–125°.

Several reprecipitations of the product from saturated sodium bicarbonate solution yielded dense, orange-yellow crystals, m.p. 130–131°. Calc. for $C_{11}H_{12}O_5S$: C, 51.5; OCH_3, 24.2%. Found: C, 51.1; OCH_3, 24.1%.

α-Oximo-β-(4-hydroxy-3,5-dimethoxyphenyl)-pyruvic acid.—Hydroxylamine hydrochloride (4.1 g) was dissolved in water (4.3 ml) and neutralized with a solution of sodium (1.75 g) in ethanol (45 ml). After filtration, the base was added to α-thioketo-β-(4-hydroxy-3,5-dimethoxyphenyl)-pyruvic acid (5.67 g) and the mixture refluxed on a steam bath for 60 minutes. Cooling to 0° gave fluffy white crystals, which were filtered, washed with ethanol, and dried. From the mother liquor was obtained a further 0.6 g, the combined yield being 4.2 g (75%), m.p. 219–220° (decomp.). Calc. for $C_{11}H_{13}NO_6$: OCH_3, 24.3%. Found: OCH_3, 24.2%.

Acetylhomosyringonitrile.—α-Oximino-β-(4-hydroxy-3,5-dimethoxyphenyl)-pyruvic acid (8.7 g) was treated with acetic anhydride (32.8 ml), the mixture warmed gently until solution of the oximino acid and the evolution of carbon dioxide were complete and then refluxed for 2 hours. Removal of the excess acetic anhydride yielded the crude nitrile, m.p. 84–89°. Several recrystallizations from petroleum ether (80–100°) (Norite) gave white crystals, m.p. 96–96.5°. Calc. for $C_{12}H_{13}NO_4$: OCH_3, 26.4%. Found: OCH_3, 25.8%.

Homosyringic acid.—Potassium hydroxide (7.84 g) was dissolved in a mixture of water (46.8 ml) and ethanol (52.1 ml) and this solution added to acetylhomosyringonitrile (6.0 g). After it was refluxed for 13 hours the solution was concentrated, under reduced pressure, to remove the ethanol. After it had cooled, the reaction mixture was acidified with dilute hydrochloric acid (40 ml) and the precipitated acid collected at 0° and dried. The yield of crude acid was 4.4 g (81.5%), m.p. 100–104°. Four recrystallizations from water (Norite) gave white needles, m.p. 126–128°.

Via Azlactone Synthesis

Homosyringic acid was also prepared from syringaldehyde by means of the intermediate azlactone (9). Recrystallizations of this product from water (Norite) gave white crystals, m.p. 130.5–132°.

Syntheses of 3-Hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone

Acetylhomosyringic Acid

Homosyringic acid (1.17 g) was dissolved in 37% sodium hydroxide (2 ml) containing crushed ice (ca. 3 g). After the addition of acetic anhydride (0.75 ml) the cooled solution was shaken for 2–3 minutes. Acidification with 6 *N* hydrochloric acid (5.3 ml) produced an oil which crystallized slowly. The yield of crude acetylhomosyringic acid was 0.92 g (65.6%), m.p. 117–119.5°. Recrystallization from water (Norite) gave white flakes, m.p. 120–121°. Calc. for $C_{12}H_{14}O_6$: C, 56.7; H, 5.55; OCH_3, 24.4%. Found: C, 55.9; H, 5.68; OCH_3, 24.3%.

Acetylhomosyringoyl Chloride

To a solution of acetylhomosyringic acid (1.5 g) in dry benzene (3.0 ml) was added freshly purified thionyl chloride (1.35 ml). The resulting solution was refluxed, under nitrogen, for 1.5 hours. The excess thionyl chloride was removed by the successive addition and distillation of 5×2.0 ml of benzene. Removal of the excess benzene left the crude acyl chloride as a red, viscous oil weighing 1.63 g.

Acetylhomosyringoyl Diazomethane

The above acetylhomosyringoyl chloride (1.63 g) was dissolved in dry benzene (4.3 ml) and the solution added dropwise to a vigorously stirred solution of diazomethane, at 0°, prepared by dissolving the diazomethane from 5.1 g of N-nitrosomethylurea in 60 ml of

diethyl ether. The solution was allowed to warm slowly to room temperature and react overnight. Removal of the solvents under reduced pressure (nitrogen) left a viscous, red oil weighing 1.7 g.

3-Hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone

Acetylhomosyringoyl diazomethane (1.7 g) was dissolved in chloroform (2.15 ml) and this solution added dropwise, with vigorous mechanical stirring, to water (45 ml) in a three-necked flask fitted with a stirrer and a condenser. The mixture was heated on a steam bath at 93° for 4 hours. Dilute hydrochloric acid (0.76 ml) was added to bring the solution to pH 1 and the heating and stirring continued for 1 hour. Decolorizing carbon (0.75 g) was added and the heating continued for a further 1 hour. The hot solution was filtered, the yellow filtrate cooled to 5°, and exhaustively extracted with 6×25-ml portions of ethyl acetate. These combined extracts were dried over anhydrous magnesium sulphate and the solvent removed under reduced pressure at room temperature to leave a viscous, pale red oil. Considerable difficulty was experienced in effecting crystallization, but after thorough drying by the addition and evaporation of three successive portions of dry benzene followed by cooling in a dry ice – acetone bath, with scratching, the oil crystallized (0.46 g). Five recrystallizations from dry benzene gave cream-colored crystals, m.p. 106.5–107.5°. Calc. for $C_{11}H_{14}O_5$: C, 58.4; H, 6.23%. Found: C, 58.8; H, 6.46%. Infrared spectrum: 3455 cm^{-1} (broad) and 3295 cm^{-1} (broad) (hydroxyls); 1700 cm^{-1} (carbonyl); 1611 cm^{-1} and 1515 cm^{-1} (aromatic ring).

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THE PREPARATION OF $\Delta^{\alpha\beta}$-BUTENOLIDE[1]

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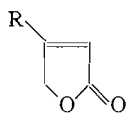
The syntheses of β-substituted derivatives of $\Delta^{\alpha\beta}$-butenolide (I) have been described by Rubin, Paist, and Elderfield (1). These investigators prepared the β-*n*-butyl,



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