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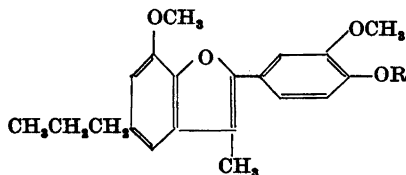
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Dehydrogenation of Dihydro-Dehydro-Di-Isoeugenol and its Methyl Ether

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For various purposes, especially in relation to work on the U.V.-absorption spectra of lignin and lignin derivatives compound I and its methyl ether II were required.



I R = H

II R = CH₃

These substances are easily obtained by sulphur dehydrogenation of the corresponding coumarane derivatives, dihydro-dehydro-di-isoeugenol and its methyl ether. For spectrochemical studies compare G. Aulin-Erdtman¹.

Experimental. 3-Methyl-5-propyl-7-methoxy-2-(4-hydroxy-5-methoxy-phenyl) coumarane (I): Dihydro-dehydro-di-isoeugenol (12.5 g) and sublimed sulphur (1.3 g) were mixed in a 25 ml Claisen distillation flask and heated in a salt bath. The temperature was slowly raised and at 215° evolution of hydrogen sulphide began. It ceased completely after 30 minutes, by which time the temperature had reached 250°. The reaction vessel was arranged for vacuum distillation and at 220–240° (1

mm) a yellow substance (9.0 g) was collected. The distillate was dissolved in benzene, filtered through aluminium oxide and evaporated to give an almost colourless substance (5.5 g) melting at 85–87°. Recrystallization from ligroin and from 50% acetic acid raised the m.p. to 86.5–87.5° (needles). The substance exhibits a blueish violet fluorescence in U.V. light. (Found: C 73.6; H 6.78. Calc. for C₂₀H₂₂O₄ (326.4): C 73.6; H 6.80.)

Acetate: The phenol (I) was acetylated with acetic anhydride in pyridine. The reaction mixture was poured into water and the product crystallized from ethanol in needles, m.p. 124–125°. (Found: OCH₃ 16.9. Calc. for C₂₀H₁₈O₅ (OCH₃)₂ (368.4): OCH₃ 16.9.)

3-Methyl-5-propyl-7-methoxy-2-(4,5-dimethoxyphenyl) coumarane (II):

A. The phenol (I) was methylated with dimethyl sulphate and alkali in the usual way giving the methyl ether which crystallized from methanol in cubes, m.p. 91.5–92.0°. The substance exhibits a violet fluorescence in U.V. light. (Found: OCH₃ 27.5; Calc. for C₁₈H₁₈O (OCH₃)₂ (340.4): OCH₃ 27.4.)

B. Dihydro-dehydro-di-isoeugenol methyl ether² was dehydrogenated as described for the phenol above. Evolution of hydro-

gen sulphide began at 200°. Distillation at 220–225°, 1 mm, gave about the same yield of crude product as above. Purification by filtration through aluminium oxide was in this case without success but repeated crystallization from methanol gave the pure compound m.p. 91–92°, undepressed on admixture with the substance obtained according to method A.

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