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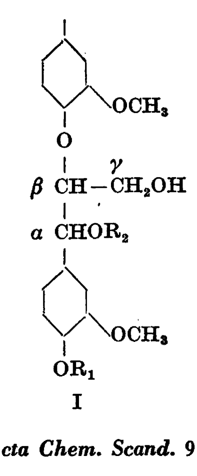
Note (added in proof): After this paper was submitted for publication the author's attention was drawn to a very recent paper by A. Hvidt, G. Johansen, K. Linderstrøm-Lang and F. Vaslow (*Compt. rend. trav. Lab. Carlsberg, Sér. chim.* **29** (1954) 129). The method used by these authors is essentially the same as that presented here, with the exception that it is used for larger volumes (~ 15 μl).

Guaiacylglycerol and its β-Guaiacyl Ether

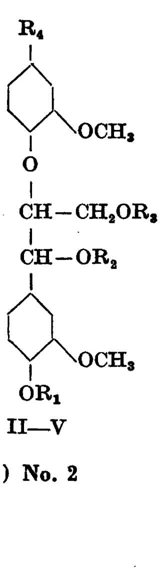
ERICH ADLER and EDGAR ERIKSOO

Institutionen för organisk kemi, Chalmers Tekniska Högskola, Göteborg, Sweden

According to the views expressed by Erdtman [1,2] regarding the course of the dehydrogenative dimerization and polymerization of *p*-propenylphenols, guaiacylglycerol-β-aryl ether structures (I), in addition to other structures, can be expected to arise when coniferyl alcohol is subjected to dehydrogenation. The same author discussed the occurrence of such structures in lignin. On the basis of experimental results concerning the behaviour of lignin in sulphonation with sulphite solutions, alkylation with alcoholic hydrochloric acid, and similar reactions, Adler and Lindgren [3,4] and Adler and Yllner [5] also suggested the presence of structure I in lignin.



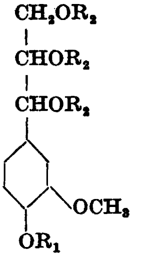
I



II—V

I. R_1 = H or the β-C-atom of a propane side-chain; R_2 = H or a C-atom of a propane side-chain
II. $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
III. $R_1 = R_2 = R_3 = R_4 = H$
IV. $R_1 = R_2 = R_3 = COCH_3$; $R_4 = H$
V. $R_1 = R_2 = R_3 = H$; $R_4 = CH{=}CH{-}CH_2OH$

The β-guaiacyl ether of α-(3,4-dimethoxyphenyl)-glycerol (II) was synthesized [3] and found to be a promising lignin model. It was sulphonated [3,4] and alkylated [3-6] in the expected manner, and also yielded formaldehyde on heating with strong sulphuric acid [3,4,7]. As in the case of α-(3,4-dimethoxyphenyl)-glycerol (VI) [8,7], the β-guaiacyl ether II yielded Hibbert's ”ethanolysis” products on prolonged heating with ethanolic hydrochloric acid. This reaction cannot be given by other dimeric systems like those present in dehydro-diconiferyl alcohol or in pinoresinol which also are assumed to occur in lignin (*cf.* Ref.[5]).



VI. $R_1 = CH_3$; $R_2 = H$
VII. $R_1 = R_2 = H$
VIII. $R_1 = R_2 = COCH_3$

Only one phenolic guaiacylglycerol compound, *viz.*, ”guaiacylglycerol” itself, *i. e.*, α - (3-methoxy-4-hydroxyphenyl) - glycerol (VII), has been available as yet. It had been obtained [8] as a syrupy mixture of the two possible pairs of optical antipodes, and yielded two crystalline tetraacetates (VIII), m.p. 84—85° and 113—114°, respectively. A sample of the syrupy product, which contained some water and had been kept in the refrigerator for several months, has now partly crystallized. Inoculation of other samples with the crystalline material induced rapid crystallization. Recrystallization from ethyl acetate, which was saturated with water, yielded needles, m. p. 82—84°. This compound contained one mole of water, which was removed at 60° (0.1 mm Hg). (Found: H_2O 7.71. Calc. for $C_{10}H_{14}O_5,H_2O$: H_2O 7.76.) The anhydrous product was a colourless glass. (Found: C 56.0; H 6.62; OCH_3 14.8. Calc.

for $C_{10}H_{14}O_5$: C 56.1; H 6.59; OCH_3 14.5.) Acetylation of the crystalline racemate or of the anhydrous product yielded a tetraacetate of m. p. 86—88°, identical with the previously [9] described acetate (VIII) of m. p. 84—85°, which obviously was not quite pure. Acetylation of the non-crystallizable residue obtained from the mother-liquors of the crystalline guaiacylglycerol furnished the second tetraacetate (VIII), m. p. 113—114°.

We further want to report the synthesis of the phenolic guaiacylglycerol-β-guaiacyl ether (III). It was carried out in a manner analogous to the preparation of the corresponding methyl ether (II). The reaction of ω-bromo-benzoyl-acetoguaiacone [1] with guaiacol in anhydrous methyl ethyl ketone in the presence of anhydrous potassium carbonate gave ω-(2-methoxy-phenoxy)-benzoyl-acetoguaiacone, which was treated in abs. ethanol with paraformaldehyde and potassium carbonate at room temperature. Reduction of the resulting α - (2-methoxy-phenoxy) - β - hydroxy-propioguaiacone with lithium aluminium hydride yielded the crude substance III as a syrup, from which a crystalline triacetate (IV), m. p. 106—108°, was obtained. (Found: C 62.0; H 6.08; OCH_3 14.06; CH_3CO 28.5. Calc. for $C_{23}H_{26}O_9$: C 61.8; H 5.86; OCH_3 13.90; CH_3CO 28.9.) The acetyl groups were removed from this triacetate by reduction with $LiAlH_4$. The guaiacylglycerol-β-guaiacyl ether (III) thus obtained was a practically colourless syrup. On re-acetylation the triacetate IV was again obtained.

Very recently, Freudenberg [10] has synthesized substance V by a similar procedure and has shown that one of the three dimeric products previously obtained on enzymatic dehydrogenation of coniferyl alcohol [11] is identical with this substance.

The view expressed by Adler and Lindgren [3-5] that guaiacylglycerol-β-aryl ether structures (I) may be essential elements in lignin has thus received further substantial support.

Details regarding the synthesis of III and of related compounds as well as their behaviour in typical lignin reactions, especially in ethanolysis, will be published later.

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Expansion of Condensed Monolayers of Normal Long Chain Fatty Acids on Admixture of *Iso*dextropimaric Acid

HENRIK H BRUUN

Institute of Physical Chemistry, Åbo Akademi, Åbo, Finland

Previous investigations [1,2] have shown that myristic and other long chain fatty acids, which give expanded monolayers in pure form, yield condensed monolayers when cholesterol and certain other bulky molecules are added to them. In the following an admixture-effect will be described which is the opposite of the above, *i. e.* an expansion of condensed fatty acid monolayers occurs on addition of a foreign substance, which alone forms a monolayer of the condensed type.

The study was conducted with a continuously recording surface balance of the Wilhelmy-Dervichian type [3]. The fatty acids investigated were palmitic, stearic, arachidic, behenic, lignoceric and myristic acids, of which the last-mentioned forms a monolayer of the expanded type. As the admixture-substance, *iso*dextropimaric acid *, a rosin acid, was employed.

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* For a detailed investigation of the monolayer properties of this and other rosin acids, see references 4 and 5.