With the exception of the dideuteriomalonic acid-d_2 (XII), all deuterium compounds were submitted to mass spectrometric analysis. Spectra of these products were compared with those of the light hydrogen analogues, which have been published by Ryhage and Stenhagen [8], and from that comparison the deuterium content of each product has been qualitatively determined. The high-mass end of the mass spectrum of the methyl deuterio-behenate reproduced in Fig. 1 shows a series of molecule-ion peaks from m/e 380 to m/e 397, corresponding to a series of esters of varying deuterium content from $C_{23}H_{20}D_{26}O_2$ to $C_{23}H_3D_{43}O_2$. The prominent peak at m/e 391 corresponds to the highest concentration of methyl heptatriadeuteriobehenate ($C_{23}H_9D_{37}O_2$) in the synthesized product. It is evident from Fig. 1 that molecules of mass 397, corresponding to the methyl perdeuterio-behenate (XVI), have been present, because the peak at m/e 397 is higher than that expected for the ^{13}C isotope peak of m/e 396.

Full details will be published later.

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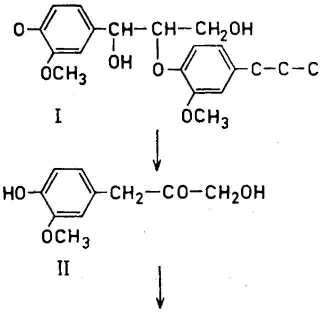
Isolation of 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone from Lignin

KNUT LUNDQUIST

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

According to the work of Hibbert [1], a series of guaiacylpropanones (III a—d) is formed from softwood lignin on heating with ethanolic hydrochloric acid for 48 h ("ethanolysis"). It was suggested [1] that these products originated from a structure of type II (3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone) or its enol form ("β-oxyconiferyl alcohol") assumed to be part of the lignin molecule. Later, it was proposed [2,3] that the ketones III originate from arylglycerol-β-aryl ether structures (I), the ketol II being an intermediate in the ethanolysis process rather than a genuine structural element of lignin. This view was supported by the finding that ethanolysis of model compounds of type I yielded "Hibbert ketones" (III a, c, d); similarly, ketones III c, d and e were obtained on "acidolysis" (heating with 0.2 N HCl in dioxane-water (9:1)) of lignin as well as of the model compounds of type I [3].

In order to obtain further evidence for the presence of structure I in lignin and of



$R{-}CO{-}CH(OC_2H_5){-}CH_3$ III a
$R{-}CH(OC_2H_5){-}CO{-}CH_3$ III b
$R{-}CH_3{-}CO{-}CH_3$ III c
$R{-}CO{-}CO{-}CH_3$ III d
$R{-}CO{-}CH(OH){-}CH_3$ III e
$R{-}CH(OH){-}CO{-}CH_3$ III f
(R=4-hydroxy-3-methoxyphenyl)

its role as a precursor of the Hibbert ketones, it was desirable to isolate the predicted intermediate II. Its formation as an intermediate in the acidolysis of model substances for structure I, *viz.*, guaiacyl glycerol and its β-guaiacyl ether, has recently been demonstrated in this laboratory [4].

It has now been possible to isolate II from the ether-soluble fraction (A) of the reaction products obtained on similar "acidolysis" (4 h) of spruce Björkman lignin. The presence of II in fraction A was demonstrated by paper chromatography (upper layer of a ligroin-water-chloroform-methanol 7:5:2:1 mixture [5], red-violet spot with diazotized sulfanilic acid, R_F 0.04) and by thin-layer chromatography on silica gel (benzene-acetone 4:1, spot with iodine vapour, R_F 0.16). The isolation of II was accomplished by chromatography on a silica gel column, benzene-acetone 9:1 being used as an eluent. The effluent fractions, which on examination by thin layer chromatography gave only one spot with R_F 0.16, were collected and yielded an oil (yield, 7 % of the lignin used). The infra-red spectrum of the oil was identical with that of synthetic II [6]. After distillation the product crystallized, m.p. 81—82°(lit.[6] 81—82°), no depression on admixture with authentic II.

Paper chromatography of the effluent fractions not containing II revealed the presence of vanillin, coniferyl aldehyde, α-hydroxypropioguaiacone (III e) and other unidentified constituents. In addition, small amounts of a phenolic ketone were isolated, which gave a blue colour reaction with 2,6-dibromo-N-chloroquinonimine (characteristic of *p*-hydroxybenzyl alcohols [7]), and an orange colour with diazotized sulfanilic acid. Its infra-red spectrum was very similar to that of guaiacylacetone (III c) between 1000—5000 cm^{-1} but showed an additional band at 1080 cm^{-1} (sec. alcohol). The substance was presumed to be 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (III f). While experiments regarding the structure of this acidolysis product were in progress, Gardner [8] published the synthesis of III f. The colour reactions and infra-red data reported for the synthetic sample are consistent with those of our product. Further work on the identification of the latter will be published later.

The results reported above constitute further experimental evidence for the presence of structural elements of type I in lignin [2,3,9,10] and for the mechanism of their acidolytic degradation proposed earlier [3,4a].

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