## Glucosides of Vanillic and Syringic Acids in Deciduous Woods

*Sir:*

During the course of our investigations on the extractives of representative deciduous woods it was found that the 75% n-propyl alcohol extractives of each of 46 different species tested yielded vanillin, syringaldehyde, vanillic acid, and syringic acid upon alkaline hydrolysis.[1] Because of the proven presence of coniferaldehyde and sinapaldehyde in the extractives of these woods and because of the known formation of vanillin and syringaldehyde from these two cinnamaldehydes in alkaline solution by a reverse "aldol" mechanism, it was suggested that such a mechanism was responsible for vanillin and syringaldehyde in these alkaline hydrolysates. Further, it was suggested that because oxygenated three-carbon side chains in guaiacyl and syringyl model compounds are known to rearrange to "acyloin" configurations during isolation procedures and because many acyloins hydrolyze to the corresponding benzoic acids by boiling with alkali, an alkaline hydrolysis of "acyloin" side chains might be responsible for the presence of vanillic and syringic acids in the alkaline hydrolysates of the extractives of these deciduous woods.

We have recently subjected these same 75% n-propyl alcohol extractives to hydrolysis with 0.5N sulfuric acid and have analyzed the hydrolysates for sugars and for phenolic materials. Again, vanillin, syringaldehyde, vanillic acid, and syringic acid were found in the hydrolysates of all 46 hardwood extractives. The vanillin and syringaldehyde yields were approximately of the same order of magnitude as those found in the alkaline hydrolysates of the same extractives. However, the yields of vanillic and syringic acids were substantially greater in the case of the acid hydrolyses. In some instances, the increase was manifold. In all instances, the increase in vanillic and syringic acids was accompanied by an increase in glucose yield, and in those experiments that produced manifold increases in vanillic and syringic acid yield, the yield of glucose produced by acid hydrolysis was correspondingly great.

Although these recent data do not prove, they certainly do suggest that all deciduous woods contain as extractives glucosides of vanillic and syringic acids. Such phenolic glucosides would yield the free phenolic acids to a limited degree upon alkaline hydrolysis[2] but would be hydrolyzed completely by boiling with dilute sulfuric acid.

Detailed analytical results on all of the sugars and phenolic compounds obtained in the acid hydrolyses of the 46 representative hardwoods and their significance to taxonomy and to biosynthesis will be reported at a later date. Experiments are now under way on the isolation and identification of the above noted glucosides of vanillic and syringic acids from those extractives which appear to have them in largest quantity.

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## Organic Sulfur Compounds. I. Hydroperoxide Intermediates in the Co-oxidation of Mercaptans and Olefins

*Sir:*

Substituted hydroxyethyl sulfoxides were obtained by Kharasch and co-workers[1] by a co-oxidation reaction of mercaptans and olefins. They proposed two tentative chain mechanisms for the co-oxidation which involved the formation of peroxide intermediates. Recently Ford and co-workers[2] obtained 2-phenylmercapto-1-indanyl hydroperoxide by the co-oxidation of indene and benzenethiol at room temperature in 70% yield, although they did not isolate the product.

It was found, in these laboratories, that on introducing air into hydrocarbon solutions of aromatic mercaptans (benzenethiol, p-toluenethiol, 4-chlorobenzenethiol, 2-naphthalenethiol) and reactive olefins (styrene, α-methylstyrene, indene) at 0° or at lower temperatures, the peroxide intermediates of such co-oxidation reactions can be obtained. Intermediates of high hydroperoxide content separate as viscous liquids in the bottom of such solutions.

The new hydroperoxides containing sulfur usually rearrange at room temperature to the corresponding hydroxyethyl sulfoxides.

$$RSCH(R')C(R'')_2OOH \longrightarrow RS(O)CH(R')C(R'')_2OH$$
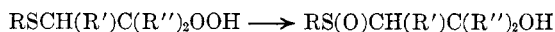
This rearrangement is accompanied by the loss of peroxide content, by a stronger absorption in the infrared at 3 microns (OH) and between 9–10 microns (SO), and by solidification where the hydroperoxides were liquid.

The co-oxidation product of 2-naphthalenethiol and indene, 2-(2-naphthylmercapto)-1-indanyl hydroperoxide, showed exceptional stability, m.p. 70° from benzene-n-heptane. (*Anal.* Calcd. for

(1) I. A. Pearl, D. L. Beyer, S. S. Lee, and D. Laskowski, *Tappi*, **42**, 61 (1959).

(2) C. E. Ballou, *Advances in Carbohydrate Chem.*, **9**, 59 (1954).

(1) M. S. Kharasch, W. Nudenberg, and G. H. Mantell, *J. Org. Chem.*, **16**, 524 (1951).

(2) J. F. Ford, R. C. Pitkethly, and V. O. Young, *Tetrahedron*, **4**, 325 (1958).

$C_{19}H_{15}O_2S \cdot$ C, 73.99; H, 5.23; S, 10.40. Found C, 74.12; H, 5.43; S, 10.3. Peroxide content by the iodide method 98%.) The pure compound was stable up to 70°. In benzene solution at 40° it was found to rearrange giving mainly 2-(2-naphthyl-sulfinyl)-1-indanol, mp. 138.5–139.5° with decomposition. (*Anal.* Calcd. for $C_{19}H_{15}O_2S$: C, 73.99; H, 5.23; S, 10.40. Found C, 74.26; H, 5.48; S, 10.3.) Other hydroxysulfoxide isomers now under investigation were also obtained on rearrangement.

A typical member of the new hydroperoxides is 2-hydroperoxy-2-phenylpropyl 2-naphthyl sulfide. This is obtained by co-oxidation of 2-naphtha-lenethiol and α-methylstyrene. (m.p., 10° by the freezing curve method, peroxide content 85% by the iodide method). A benzene solution containing 0.3 mole/l. of this compound deposits 2.3 g./100 ml. sediment on standing 16 hr. at 40°. After re-crystallization from benzene this sediment melts between 114 and 118°. (*Anal.* Calcd. for 2-hydroxy-2-phenylpropyl 2-naphthyl sulfoxide, $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84; S, 10.3. Found: C, 72.80; H, 5.85; S, 10.2.)

It is proposed that the co-oxidation of olefins and mercaptans which results in the formation of hydroperoxide intermediates is largely responsible for the peroxidation and subsequent color, gum, and sediment formation in untreated petroleum distillates.

Details of work on the co-oxidation of mercaptans and olefins will be reported later.

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