volume, and additional hydrogen sulfide and hydrogen chloride passed through the filtrate to precipitate a second crop. After filtration, air was drawn through the solid for a period, and the sintered glass funnel of dried solid stored in an evacuated desicator to remove excess hydrogen chloride and hydrogen sulfide. In this way, 5.5 g. (98%) of crude tri(*p*-fluorothiobenzaldehyde) was obtained. Similar treatment of 5.0 g. of *m*-fluorobenzaldehyde (Pierce) gave 4.7 g. (84%) of crude product. Starting with 6 g. of *o*-fluorobenzaldehyde (Pierce), in 50 ml. of absolute ethanol, the yield was 6.05 g. (96%).

Thin Layer Chromatography.—A Desaga apparatus and silicic acid according to Stahl (Merk silica gel G) were used for the thin layer chromatography. A non-adjustable t.l.c. applicator was used for applying standard layers of 250 μ. As solvents for the separation of the trimers of *m*- and *p*-fluorothiobenzaldehydes 5–8% diethyl ether in cyclohexane were used and the R_f values are listed in Table III. Freshly made solvent mixtures were allowed to travel the premarked distance of 10 cm. on the plates. The spots were developed by spraying the chromatograms with a mixture of 0.1 *M* copper acetate and 0.1 *M* silver nitrate in 3 *M* alcoholic ammonia. Brown spots appeared after heating at 100–120° for 20 min. to half an hour. The spray was prepared as follows: 1.7 g. of silver nitrate and 1.8 g. of copper acetate were dissolved in 20 ml. of concentrated ammonia, then absolute ethanol was added and the volume made up to 100 ml. The solution was filtered and kept in a brown bottle. Copies of the chromatograms can be taken by tracing as well as by photography or Xerography.

Separation of α- and β-Isomers by Column Chromatography.—One hundred grams of silicic acid (160 mesh) was dried and activated by heating overnight, then, after cooling, put in a beaker and mixed with 6% diethyl ether in cyclohexane. The resulting slurry was transferred to the column and excess solvent allowed to drain. One gram of crude trithiofluorobenzaldehyde was dissolved in ether and then mixed with a very small amount of silicic acid. This mixture was stirred well, left to dry at room temperature, and transferred as a dry powder to the top of the column. The material was covered with a thin band of silicic acid and sand at the very top. The column was developed with 6–7% diethyl ether in cyclohexane as solvent under pressure. The 10-ml. fractions which were collected by an automatic fraction collector were subjected to thin layer chromatography. In this way, the progress of the separation was traced. Fractions containing only α- or only β-isomer were combined and crystallized from a benzene–cyclohexane mixture. Analytical samples were crystallized from absolute ethanol. Fractions containing both α- and β-isomers were combined and rechromatographed. The results obtained from column chromatography are shown in Table IV. Other physical properties and analyses are listed in Table II.

Preparation of Isomeric Tri(*o*-fluorothiobenzaldehydes) by Unidimentional Multipass Chromatography on Thick Plates. (Preparative T.l.c.).—Since the R_f values of the isomeric α- and β tri(*o*-fluorothiobenzaldehydes) were very close, preparative t.l.c. was applied instead of column chromatography. The regular applicator was modified to produce thick plates by placing ten narrow strips of plastic adhesive tape on each end of the applicator. In this way, silicic acid plates were produced to a thickness of from 1–2 mm. The crude material was dissolved in acetone and spotted in a linear narrow strip of 10 cm. at the origin. The technique of unidimentional multipass chromatography was applied. The progress of separation of the isomeric products can be followed by developing a portion of the plate with saturated solution of iodine in chloroform as brown strips or, by distilled water as distinct white strips, or the chromatograms can be read as strips of different transparency by placing an electric lamp behind the plate.

When the separation of the isomeric products was satisfactory, the strips of silicic acid containing the separate isomers were scraped off and collected in separate beakers. Each isomeric product was extracted by ether and hot benzene or acetone and transferred to centrifuge tube. After centrifugation, the clear solution was transferred to a clean centrifuge tube and evaporated under a stream of nitrogen. Each isomeric product was washed with a small amount of cyclohexane and recrystallized several times from ethanol. Evaporation, washing, recrystallization, and subsequent drying of the sample were done in the same centrifuge tube. During the recrystallization procedure, the purity of the isomers were checked by unidimentional multipass chromatograms which were developed by the described copper–silver sulfur-sensitive spray. Six to eight plates are sufficient to give enough material (about 60–80 mg.) of each isomer for n.m.r., molecular weight determination, and analysis. The material used for n.m.r. and molecular weight determination can be recovered. The physical properties of the tri(*o*-fluorothiobenzaldehydes) are listed in Table II.

TABLE IV

YIELDS OF THE PRODUCTS FROM THE COLUMN

Tri(*m*-fluorothiobenzaldehyde)		
Alpha (α)	47% (crude)	0.47 g.
Beta (β)	25% (crude)	.25 g.
Red oil + impurities	6%	.06 g.
Yellow oil	6%	.06 g.
Tri(*p*-fluorothiobenzaldehyde)		
Alpha (α)	64% (crude)	.64 g.
Beta (β)	30% (crude)	.30 g.
$\alpha + \beta$ + impurities	6%	.06 g.

Acknowledgment.—The authors wish to thank Professor Walter Meyer, of this department, for assistance in interpreting the n.m.r. spectra.

Evidence of a Biphenyl Group in Lignin[1]

JOHN C. PEW

Forest Products Laboratory,[2] Forest Service, U. S. Department of Agriculture, Madison 5, Wisconsin

Received May 4, 1962

Studies of the ultraviolet spectra of lignin model compounds and enzymatic dehydrogenation of these substances indicate that biphenyl groups occupy an important rather than a minor role in coniferous lignin.

That coniferous lignin is a polymer of coniferyl alcohol and that the linkages occurring in dehydrodiconiferyl alcohol, in guaiacylglycerol-β-coniferyl ether, and in pinoresinol[3] are important contributors is now a widely accepted theory of lignin structure. Biphenyl groups, on the other hand, though they have been detected,[4] are generally assumed to occupy a minor role. Observations made during the past two years indicate a substantial number of such groups may be present.

Like coniferous lignin, I (Fig. 1), the simple model substance 4-propylguaiacol (II) has an ultraviolet absorption maximum at 280 mμ, but unlike that for lignin the curve falls abruptly to 0 at 300 mμ and nearly to 0 at 250 mμ before rising again, forming a deep

(1) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(2) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

(3) K. Freudenberg, *Nature*, **183**, 1152 (1959).

(4) G. Aulin-Erdtman, *Svensk Papperstid.*, **55**, 745 (1952).

TABLE I

ULTRAVIOLET SPECTRA OF LIGNIN MODEL COMPOUNDS[a]

No.	Compound	λ_{max}	$\epsilon \times 10^{-1}$[b]	λ_{min}	$\epsilon \times 10^{-1}$[b]	λ_{max}	$\epsilon \times 10^{-1}$	λ_{min}	$\epsilon \times 10^{-1}$
II	4-Propylguaiacol	280	296	250	24				
III	Eugenol	281	312	252	40				
IV	Dihydroconiferyl alcohol	281	304	250	20				
V	Guaiacylglycerol	279	272	250	24				
VI	Apocynol	279	284	250	24				
VII	Vanillyl alcohol	280	284	251	28				
VIII	Vanillyl ethyl ether	280	292	252	28				
IX	Creosol	281	284	250	28				
X	4-Propylveratrole	279	288	251	28				
XI	Veratrylglycerol	277	276	250	32				
XII	Veratryl alcohol	279	272	251	40				
XIII	4-Isopropylpyrocatechol	282	296	249	24				
XIV	Isocreosol	281	292	249	20				
XV	Hydrovanilloin	279	296	252	36				
XVI	Pinoresinol	280	332	252	36				
XVII	Isoeugenol dibromide	280	320	258	88				
XVIII	3,5-Dimethoxy-4-hydroxyphenylpropane	273	128	265	56				
XIX	4-Methyl-6-propylguaiacol	280	228	252	32				
XX	6-Propylvanillyl alcohol	281	228	253	40				
XXI	Dihydrodehydrodiisoeugenol	281	300	256	56				
XXII	5-Ethylcreosol	284	332	253	24				
XXIII	α-Conidendrin	283	352	255	40				
XXIV	4-Ethylphenol	278	192	245	8				
XXV	4-Methylanisole	278	196	245	8	285	160	283	148
XXVI	4,4′-Dipropyl-6,6′-biguaiacol	290	300	271	148				
XXVII	Coniferyl alcohol	265	1540	240	580				
XXVIII	4,4′-Dihydroxy-3,3′-dimethoxystilbene	333	2360	261	400				
XXIX	Coniferylaldehyde	341	2360	270	240	240	1040		
XXX	2-Ethoxy-1-(4-hydroxy-3 methoxyphenyl)-1-propanone	280	860	250	180	305	760	296	720
XXXIV	Dihydrodehydroiisoeugenol crystalline dehydrogenation product	288	284	270	188				
XXXV	Dehydrodipinoresinol	283	280	268	176				
XXXVI	Dehydrodivanillyl alcohol	288	276	271	146				
XXXVII	Dehydrodiapocynol	288	276	271	146				
XXXVIII	Dehydrodihydroconiferyl alcohol	290	268	271	136				

[a] Solvent—95% ethanol. [b] Per aromatic nucleus.

trough as shown in Fig. 1 (the spectra of the model compounds are on the basis of absorbance per unit containing one aromatic nucleus). A study of numerous other C-4 substituted guaiacyl and related compounds showed they invariably give similar and often almost identical curves, provided they do not have a C=C or C=O group conjugated with the aromatic ring. Thus the shaded area in Fig. 1 encloses the curves for the guaiacyl compounds III–IX, the veratryl compounds X–XII, the pyrocatechol compound XIII, and isocreosol, XIV, a compound in which the position of the hydroxyl and methoxyl groups is interchanged as compared to the above guaiacyl structures. Curves of dimers, not involving ring substitution (XV, XVI), also fall within this boundary. Even isoeugenol dibromide XVII, Table 1, though not wholly contained within the shaded area, is quite similar except for a somewhat narrowed trough.

The substitution of the aromatic ring in the 6-position with oxygen suppresses the absorption maximum decidedly, shifts the maximum to a lower wave length, and decreases the trough. This is illustrated in Fig. 2 with 3,5-dimethoxy-4-hydroxyphenylpropane (XVIII). Such structures are not commonly believed to occur in coniferous lignin, however. Substitution with C in this position (compounds XIX, XX) has much less effect, principally that of blunting the maximum somewhat as illustrated by XIX, Fig. 2. In the model dihydrodehydrodiisoeugenol (XXI), with one of the two rings so substituted, this effect is scarcely noticeable, but the trough is narrowed. C substitution in the 5-position also causes only small alteration, but the maximum is raised and shifted to a slightly higher wave length (XXII, XXIII, Table I, XXII, Fig. 2).

Since coniferous lignin contains some *p*-hydroxyphenylpropane-type groups, the spectra of these groups are of interest. As shown in Fig. 2, XXIV, and Table I, XXIV, XXV, they are roughly similar to the guaiacyl compounds, but the maximum absorption is considerably lower and the trough much wider. The coupling of two guaiacylpropane units in positions *ortho* to the phenolic hydroxyl groups (XXVI, Fig. 2) has a profound effect, the significance of which will be discussed later.

As for the conjugated compounds, Fig. 3, coniferyl alcohol (XXVII) with its maximum at about 265 mμ and about five times the absorption of the nonconjugated structures could, in admixture with these, tend to "fill in" the trough that they show. Coniferyl alcohol groups containing free phenolic hydroxyls are not believed to be present in isolated lignins to any considerable extent,[5] though etherified units could be a

(5) B. O. Lindgren and H. Mikawa, *Acta Chem. Scand.*, **11**, 826 (1957).

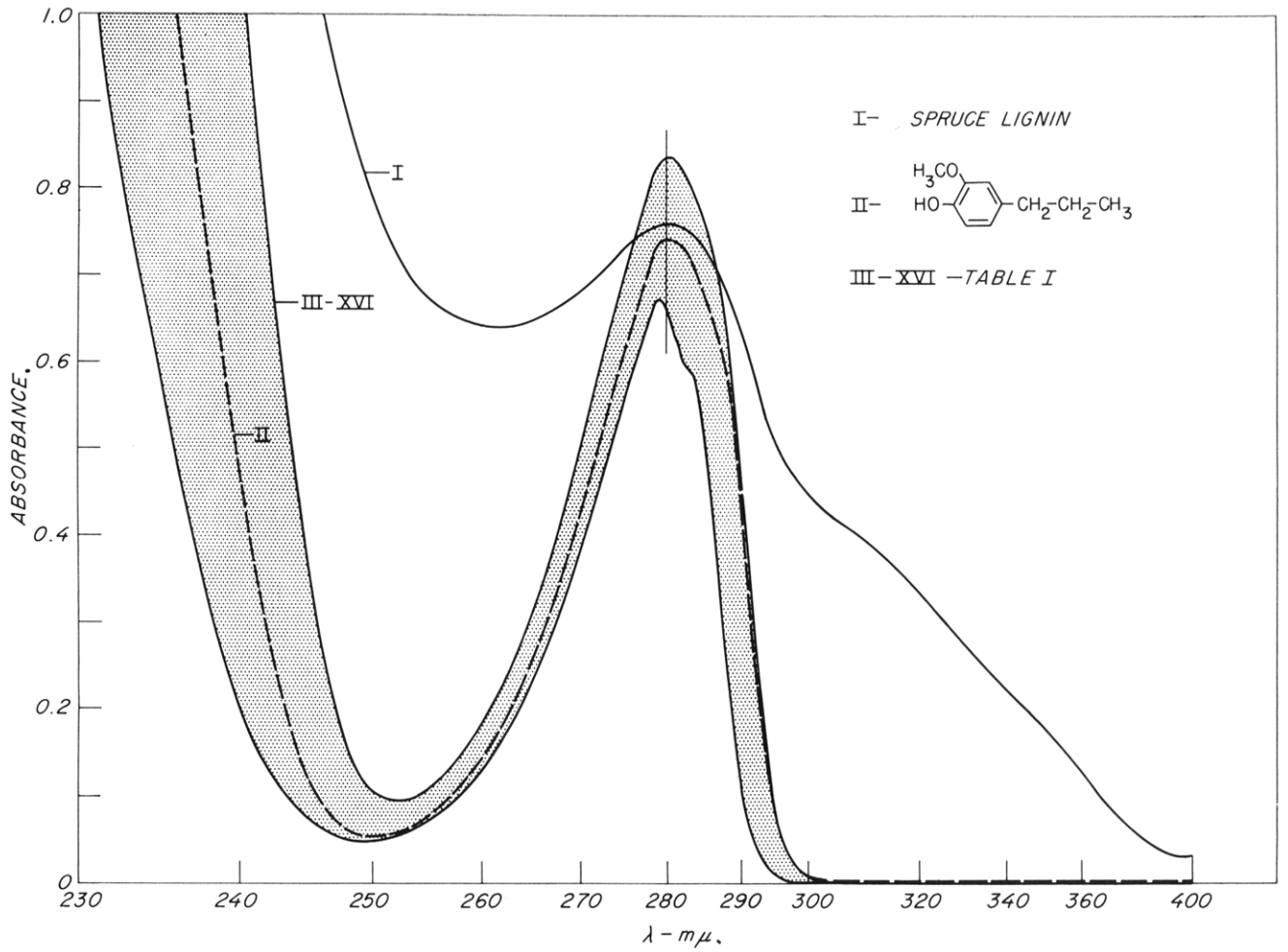

Fig. 1.—Ultraviolet spectra of spruce cellulytic enzyme lignin compared to that of C-4 substituted unconjugated guaiacyl compounds and related structures. Lignin—36 mg./l. of 95% aqueous Methyl Cellosolve; monomeric models—0.00025 *M* in 95% ethanol; dimers—half this concentration.

factor. Coniferylaldehyde, XXIX, has a maximum about eight times that of 4-propylguaiacol but the absorption occurs mostly in the 300–400-mμ range. 2-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone, XXX, with about three times the maximum absorption of the simple models, exhibits maxima at 305 mμ as well as at 280 mμ. The latter two types of structure are known to be present in coniferous lignin and, while they no doubt contribute to the well known shoulder occurring in the 300–400-mμ range, they cannot explain the filling in of the trough. Moreover, the effect of C=O systems in lignin can be eliminated by hydrogenation or reduction with sodium borohydride and is discernible by decreasing the shoulder in the ultraviolet curve. This is shown by XXXII in Fig. 4, a borohydride-reduced spruce cellulytic enzyme lignin (chosen because it is a mildly prepared soluble lignin and represents practically all the lignin in the wood).

A search was made for relevant structures that would decrease the trough shown by the simple models, since lignin is widely regarded as the result of enzymatic dehydrogenation of coniferyl alcohol, models which could be produced by analogous means were studied. When dilute hydrogen peroxide was gradually added to a solution of 4-propylguaiacol in 50% aqueous alcohol containing a little peroxidase, clouding began almost at once and soon crystals formed. The known 4,4′-dipropyl-6,6′-biguaiacol, XXVI, Fig. 2, was isolated in high yield. Although the maximum of this compound is at 290 mμ rather than 280 mμ, the curve has a more lignin-like appearance than the guaiacylpropane models; but, more important, absorption starts at 320 rather than 300 mμ and the absorption at 250 mμ is extremely high. Such structures could well contribute to "filling in" the trough shown by the simple models.

When dihydrodehydrodiisoeugenol was treated in a similar manner, an amorphous product was formed. Molecular weight and analytical values (C, H, OCH_3 and C, H, OCH_3, $CH_3C{=}O$ on the amorphous diacetate derivative) agree with the loss of 1 H per molecule of starting material and suggest an analogous coupling. The ultraviolet spectrum (XXXI, Fig. 4) has a maximum at 283 mμ, a relatively shallow trough, and appreciable absorption in the 300–320-mμ region. A material with the same spectra as well as physical and analytical properties was obtained by starting with dehydrodiisoeugenol (model for the corresponding coniferyl compound) and hydrogenating the product. The spectrum of these substances shows considerable resemblance to that of the reduced spruce lignin (XXXII). True, the absorption maximum is at slightly higher wave lengths than that of lignin, but with simple models the introduction of oxygen in the alpha C atom of the side chain and the conversion of the free phenol group to an ether tends to shift the

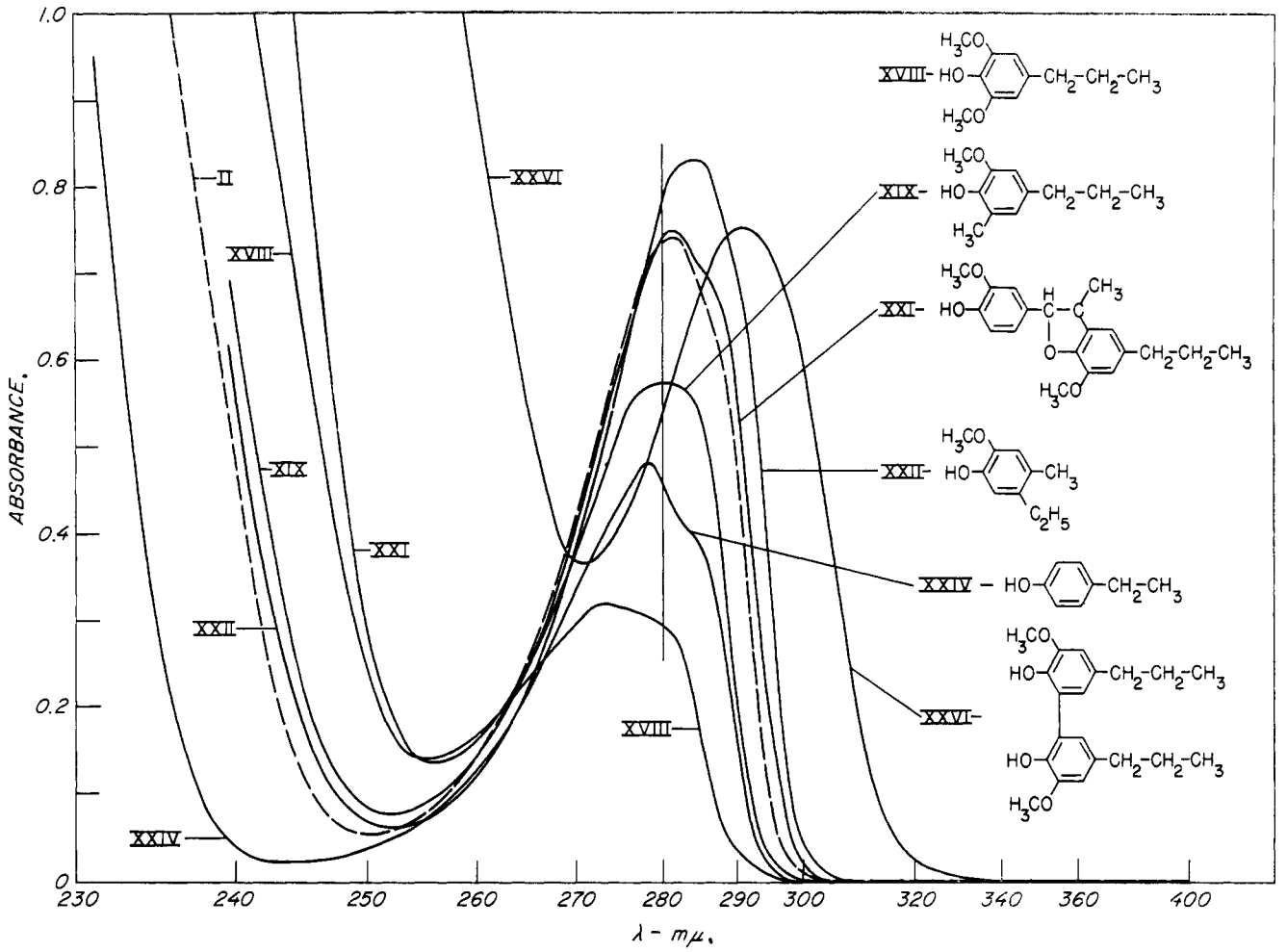

Fig. 2.—Effect of alteration in ring substitution of lignin models on ultraviolet spectra—0.00025 *M* in 95% ethanol.

maximum to slightly lower wave lengths. The admixture with uncondensed units (to explain vanillin formation) or with other nonbiphenyl-linked units could cause still further shifts. The spectrum of a mixture of the dehydrogenated dihydrodehydrodiisoeugenol with veratrylglycerol in such proportion as to give a ratio of one biphenyl-linked unit to two not so linked has a maximum at 280 mμ (XXXIII, Fig. 4).

Attempts to crystallize the above dehydrogenation product were at first unsuccessful, but finally crystals were obtained in 27% yield. This material gave a crystalline diacetate and, as with the amorphous product, analytical values were closely in accord with the loss of one hydrogen per molecule of starting material. The ultraviolet spectra of the compound (XXXIV, Fig. 4) is, however, different from the amorphous substance. The structure of the crystalline compound is presumably that indicated in the figure. When blended with veratrylglycerol to give a mixture with 33% biphenyl-linked units, a shallow trough and a maximum at 282 mμ is obtained. The material not isolated in crystalline form has an average molecular weight about one-fifth greater than the crystalline biphenyl and therefore contains some higher polymer along with other unknown products. It is being investigated further. A crystalline dehydrogenation product has also been obtained from dehydrodiisoeugenol with an analysis that agrees with the loss of one hydrogen per molecule.

The dehydrodipinoresinol of Freudenberg and Sakakibara[6] was prepared by means of hydrogen peroxide and peroxidase in the manner described above. Since it consists of an equal number of units with and without biphenyl links, it too has an absorption in the 300–320-mμ region and reduced trough height (XXXV, Fig. 4) somewhat like that of lignin.

Experiments with other lignin models containing a free phenolic hydroxyl and an unsubstituted *ortho* position indicate that biphenyl coupling is quite general. Vanillin gave 88% dehydrodivanillin and acetovanillone 66% of the analogous product. Eugenol gave dehydrodieugenol in moderate yield. With a restricted amount of peroxide, vanillyl alcohol (a simple model for the guaiacylglycerol-type dimer) gave 19% dehydrodivanillyl alcohol and no dehydrodivanillin. Thus it appears that all three of the major dimeric products of Freudenberg may undergo biphenyl condensation.

As with the monomeric C-4 substituted guaiacyl models, the spectra of the biphenyl compounds is nearly independent of the side chain provided there is no conjugation with the ring. Thus the spectra of dehydrodivanillyl alcohol and of dehydrodiapocynol (XXXVI, XXXVII, Table I) are identical and very similar to that of dehydrodihydroconiferyl alcohol XXXVIII and the 4,4′-dipropyl-6,6′-biguaiacol XXVI.

(6) K. Freudenberg and A. Sakakibara, *Ann.*, **623**, 129 (1959).

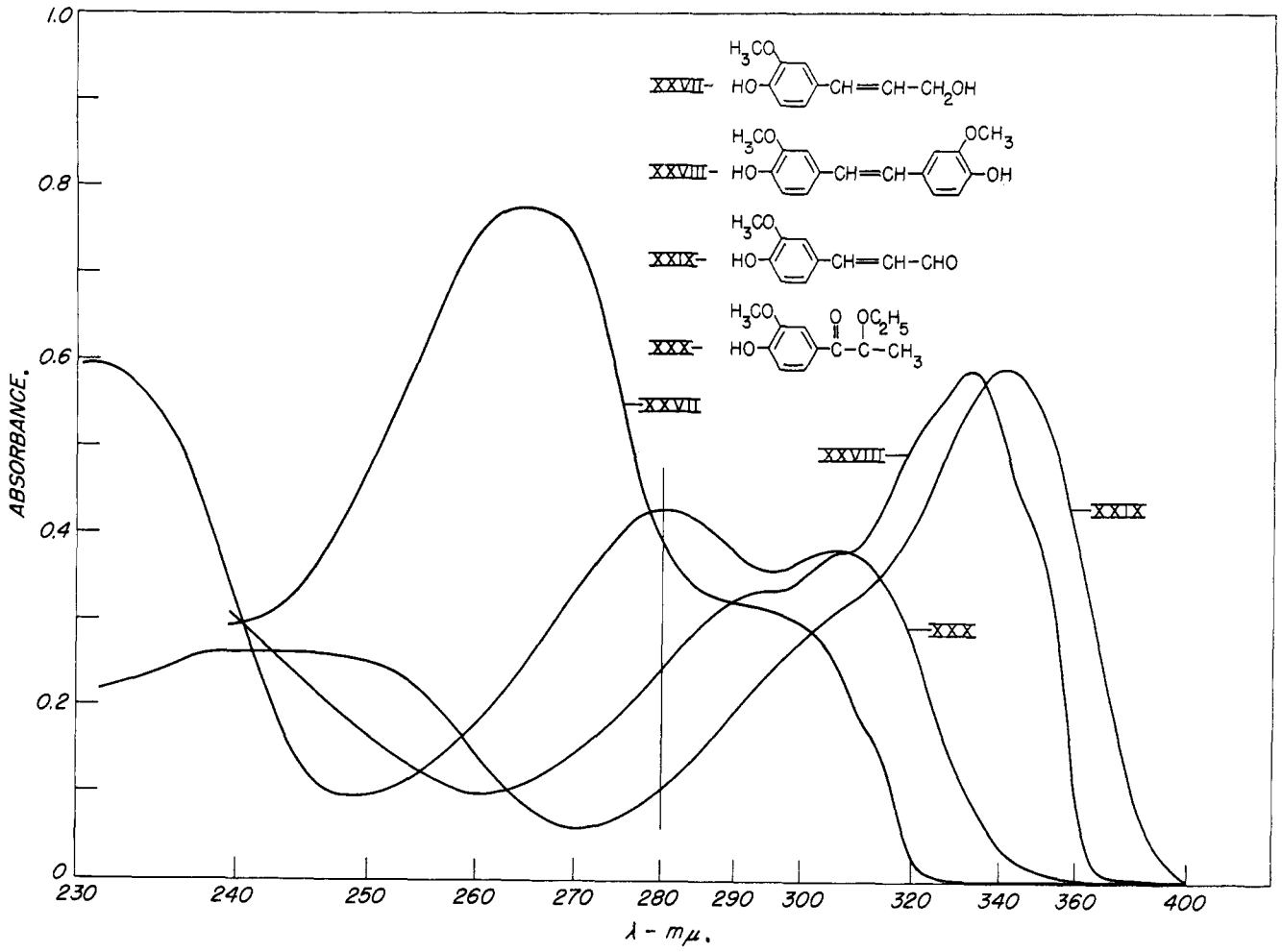

Fig. 3.—Effect of conjugation in the side chain on the ultraviolet spectra of lignin models. Coniferylaldehyde and stilbene compound—0.000025 *M*; others—0.000050 *M*.

On the other hand, methylation has considerably more influence in the case of the biguaiacol compound, and ring substitutions which affect the interplanar relationship of the two rings may have profound effect. An investigation of some of these factors as well as biphenyl linkage in positions other than *ortho* to the free phenolic hydroxyl group is in progress.

It is possible that in lignin formation the primary dehydrogenation by molecular oxygen produces hydrogen peroxide which, in turn, causes further dehydrogenation largely by ring coupling. Coniferous lignin may well contain 25% or more of biphenyl-linked units. While it is true that only small yields of dehydrodivanillin have been isolated by nitrobenzene oxidation of lignin,[7] some confirming evidence is to be found in the literature. Freudenberg, Lautsch, and Piazolo[8] solubilized spruce cuoxam lignin by treatment with metallic potassium in ammonia solution, methylated the product, and oxidized it with potassium permanganate. Though yields were small, as is usual with such experiments, almost equal amounts of veratric, isohemipinic, and dehydrodiveratric acid resulted. Since biphenyl-linked structures might conceivably produce isohemipinic acid as well as dehydrodiveratric acid, substantial quantities of biphenyl structures are indicated.

(7) J. C. Pew, *J. Am. Chem. Soc.*, **77**, 2831 (1955).

(8) K. Freudenberg, W. Lautsch, and G. Piazolo, *Chem. Ber.*, **74**, 1879 (1941).

Experimental[9]

Cellulytic Enzyme Lignin.—Extracted spruce wood meal was ground 8 hr. on a vibratory mill and 96% of the carbohydrate removed from the product by digestion with cellulytic enzyme.[10] For the spectra a quantity of this product containing the equivalent of 36 mg. of dry carbohydrate-free lignin was dissolved in 100 ml. of 90% aqueous Methyl Cellosolve. In the case of reduced lignin an amount equivalent to 40 mg. of lignin was dissolved in 5 ml. of 90% aqueous Methyl Cellosolve, 10 mg. of sodium borohydride added, and the mixture allowed to stand for 24 hr. The mixture was then made slightly acid with hydrochloric acid and diluted to 100 ml. with aqueous Methyl Cellosolve. Reduction with borohydride in dilute alkaline solution and by hydrogenation with palladium–carbon catalyst gave similar results.

Dehydrogenation of 4-Propylguaiacol.—To a solution of 1.00 g. of 4-propylguaiacol in 20 ml. of ethanol, 20 ml. of water containing 5 mg. of peroxidase (59 purpurogallin units per mg.) was added, and with vigorous stirring 3.5 ml. of 3% hydrogen peroxide (102% of theoretical) added dropwise over a period of 30 min. Stirring was continued 5 min.; the crystals which separated were collected and washed with 50% aqueous ethanol to yield 0.64 g., m.p. 145–150°. Recrystallization from ethanol gave 4,4'-dipropyl-6,6'-biguaiacol, m.p. 150–152° (lit.,[11] m.p. 152°).

Anal. Calcd. for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.60; H, 8.09.

Dehydrogenation of Dihydrodehydrodiisoeugenol.—A 1.00-g. sample of the material was dissolved in 50 ml. of warm ethanol in a centrifuge bottle. With vigorous stirring, 50 ml. of water containing 5 mg. of peroxidase was added and then, starting immediately, 6.0 ml. of 1% aqueous hydrogen peroxide (115%

(9) Melting points made on the Fisher–Johns apparatus in comparison with U.S.P. reference standards and are corrected.

(10) J. C. Pew, *TAPPI*, **40**, 553 (1957).

(11) H. Erdtman, *Biochem. Z.*, **258**, 177 (1933).

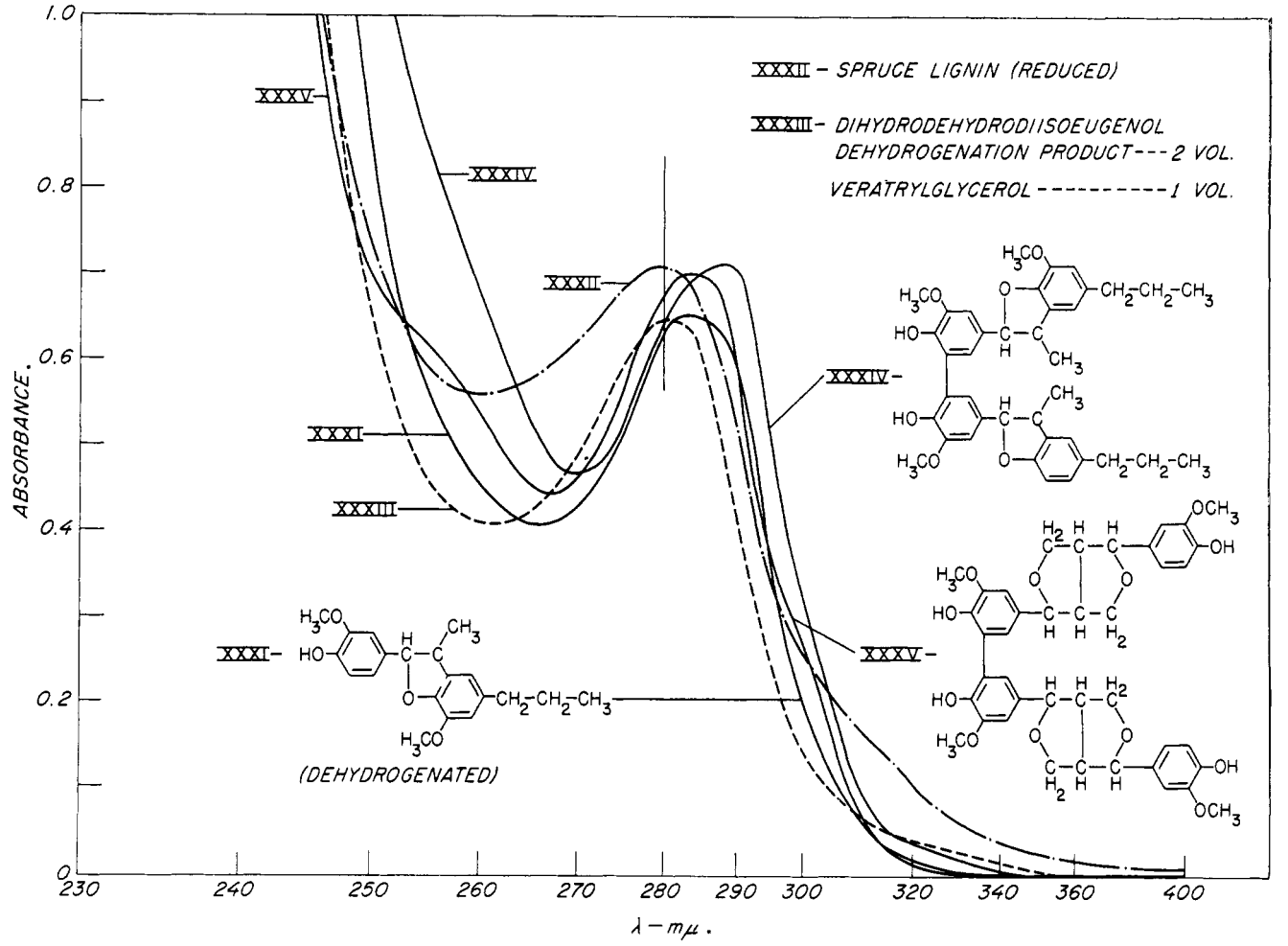

Fig. 4.—Ultraviolet spectra of spruce cellulytic enzyme lignin reduced with sodium borohydride, of the dehydrogenation product of dehydrodehydrodiisoeugenol, of a mixture of this product with veratrylglycerol, and of the dehydrogenation product of pinoresinol. Lignin—40 mg./l. of 90% aqueous Methyl Cellosolve; dehydrogenation products—0.00025 $M/4$; veratrylglycerol—0.00025 M in 95% ethanol.

of theoretical) was added dropwise over a period of 30 min. The mixture was allowed to stand 2 hr., was centrifuged, the liquid decanted, and the resinous residue redissolved in 50 ml. of ethanol. The bottle was cooled to −20° and 50 ml. of cold water (+2°) added causing the product to separate as a powder. The mixture was allowed to warm up and remain at room temperature for 2 hr. The reprecipitation process was repeated a second time but without warming and the precipitate centrifuged, washed, and dried. The yield was 80% of a nearly colorless powder.

Anal. Calcd. for $C_{20}H_{23}O_4$ (loss of 1 H atom): C, 73.36; H, 7.08; OCH_3, 18.98. Found: C, 73.25; H, 7.01; OCH_3, 19.01.

The material was acetylated with acetic anhydride and pyridine and recovered as a powder.

Anal. Calcd. for $C_{22}H_{25}O_5$ (loss of 1 H atom and no blocking of OH function): C, 71.52; H, 6.82; OCH_3, 16.80; $COOH_3$, 11.65. Found: C, 71.41; H, 6.84; OCH_3, 16.83; $COCH_3$, 11.57.

In another experiment the dehydrogenation was carried out as above but only 5.2 ml. of the peroxide (100% of theoretical) added. The crude resin, without reprecipitation, was dissolved in hot cyclohexane and the solution allowed to stand overnight. The crystals, after centrifuging and washing, amounted to 0.27 g., m.p. 122–125°. They were difficult to purify and obtain free of solvent. After several recrystallizations from cyclohexane, then ethanol, followed by drying in vacuum at 110° for several hours, the m.p. was 142–144°.

Anal. Calcd. for $C_{44}H_{50}O_9$: C, 73.36; H, 7.08; OCH_3, 18.98. Found: C, 73.21; H, 7.15; OCH_3, 18.89.

The crystals were acetylated with acetic anhydride and pyridine to give an acetate with m.p. 154–155° from ethanol.

Anal. Calcd. for $C_{44}H_{50}O_{80}$: C, 71.52; H, 6.82; OCH_3, 16.83; $COCH_3$, 11.57; mol. wt., 738. Found: C, 71.51; H, 6.86; OCH_3, 16.74. $COCH_3$, 11.65; mol. wt. (isothermal distillation), 744.

The noncrystalline fraction from the dehydrogenation was reprecipitated twice from 50% aqueous ethanol and then acetylated with acetic anhydride and pyridine. The molecular weight of the product determined by isothermal distillation was 885.

Anal. Calcd. for $C_{44}H_{50}O_{10}$: C, 71.52; H, 6.82; OCH_3, 16.74; $COCH_3$, 11.57. Found: C, 71.31; H, 6.92; OCH_3, 16.92; $COCH_3$, 11.73.

Dehydrogenation of Dehydrodiisoeugenol.—With vigorous stirring, 100 ml. of water containing 5 mg. of peroxidase was added to a solution of 1.00 g. of dehydrodiisoeugenol in warm ethanol. Over a period of 1 hr., 5.2 ml. of 1% hydrogen peroxide (100% of theoretical) was added dropwise, the stirring continued 15 min., and the white powdery precipitate filtered and washed with 50% aqueous ethanol. The yield was nearly quantitative.

Anal. Calcd. for $C_{20}H_{21}O_4$ (loss of 1 H atom): C, 73.82; H, 6.51; OCH_3, 19.08. Found: C, 73.70; H, 6.76; OCH_3, 19.03.

The crude product was dissolved in a small amount of boiling ethyl acetate. After standing overnight 0.20 g. of colorless microscopic needles separated, m.p. 172–174°. Recrystallization gave a product melting at 174–176°.

Anal. Calcd. for $C_{40}H_{42}O_8$: C, 73.82; H, 6.51; OCH_3, 19.08. Found: C, 73.66; H, 6.65; OCH_3, 19.14.

On acetylation of the crystals with pyridine and acetic anhydride two acetates, one melting at 140° and one melting at 184°, were formed. They had identical infrared spectra and are

probably dimorphic, the low melting variety tending to change into the higher melting form.

Anal. Calcd. for $C_{44}H_{46}O_{19}$: C, 71.90; H, 6.31; $COCH_3$, 11.72. Found: C, 72.00; H, 6.54; $COCH_3$, 11.60.

The crude dehydrogenation product of dehydrodiisoeugenol was hydrogenated at room temperature in ethanol over palladium-carbon. The product was practically identical to that formed by the dehydrogenation of dihydrodehydrodiisoeugenol in respect to analytical values and ultraviolet spectra and it gave an identical crystalline fraction.

Dehydrogenation of Pinoresinol.—To a solution of 1.00 g. of pinoresinol diacetate in 10 ml. of ethanol, 10 ml. of 1 *N* sodium hydroxide was added and the mixture refluxed 1 hr. The cooled solution was diluted with 6.5 ml. of 1 *N* hydrochloric acid and 3.5 ml. of water and then, with vigorous stirring, 2.0 ml. of 1% hydrogen peroxide (50% of theoretical) added dropwise over a 30-min. period. The resin which separated was dried, triturated with absolute ether, the ether decanted, and the residue extracted with boiling benzene. The benzene solution was allowed to stand at room temperature for several hours, the benzene decanted, and the residue recrystallized several times from benzene. The crystals after drying 3 days at 80° under vacuum (yield 6.8% based on pinoresinol) melted at 120–122° (lit.,[6] m.p. 119–121°). The acetylated material had m.p. 193–195° (lit.,[6] m.p. 195.5–197°).

Dehydrogenation of Dihydroconiferyl Alcohol.—To the compound (0.25 g.) in 5 ml. of ethanol was added 5 ml. of water containing 2.5 mg. of peroxidase and dropwise over a 30-min. period 20 drops of 3% hydrogen peroxide. A precipitate formed on keeping the solution at +2° for several hours. Recrystallization twice from ethanol gave a small yield of colorless crystals, m.p. 148–150°. The ultraviolet spectra closely agreed with that of the 4,4′-dipropyl-6,6′-biguaiacol.

Anal. Calcd. for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 65.98; H, 7.29.

Dehydrogenation of Eugenol.—Using the general methods described above, 1.00 g. of eugenol produced a resin which gave 0.42 g. of crystals from hexane, m.p. 96–100°. Recrystallization from ethanol gave pure dehydrodieugenol, m.p. and m.m.p. 104–105° (lit.,[11] m.p. 106°).

Isoeugenol, using 67% of the theoretical amount of hydrogen peroxide, gave 26% of the expected dehydrodiisoeugenol.

Dehydrogenation of Vanillin.—To a solution of 1.00 g. of vanillin in 100 ml. of ethanol and 10 ml. of water containing 5 mg. of peroxidase, 5 ml. of 3% hydrogen peroxide was added dropwise over a period of 1 hr. The mixture was allowed to stand overnight, the precipitate filtered, washed with water, then washed with acetone which removed an orange-colored resin. The product, 0.88 g. melting at 306–312°, was recrystallized from acetic acid giving pure dehydrodivanillin, m.p. and m.m.p. 315–316° (lit.,[12] m.p. 315–316°).

(12) J. G. Pew, *J. Am. Chem. Soc.*, **77**, 2833 (1955).

Dehydrogenation of Acetovanillone.—This was carried out as with the vanillin to give 0.66 g. of crude product, m.p. 306–312°, and pure crystals, m.p. 310–312° (lit.,[13] m.p. above 300°). The ultraviolet spectra was quite similar to that of dehydrodivanillin.

One gram of the material as prepared above was dissolved in 10 ml. of *N* sodium hydroxide and 0.2 g. of sodium borohydride added. The solution was allowed to stand overnight, acidified with acetic acid, extracted with ethyl acetate, and the solution was dried, concentrated, and cooled to −20°. The crystals (0.42 g.) had m.p. of 133–136°, or 138–140° on repeated recrystallization. The ultraviolet spectra was identical with that of dehydrodivanillyl alcohol.

Anal. Calcd. for $C_{20}H_{21}O_4$: C, 73.82; H, 6.51; OCH_3, 19.08. Found: C, 73.70; H, 6.76; OCH_3, 19.03.

Dehydrogenation of Vanillyl Alcohol.—To a solution of 1.00 g. of vanillyl alcohol in 10 ml. of hot water was added 10 ml. of water containing 5 mg. of peroxidase. With vigorous stirring 7.4 ml. of 1% hydrogen peroxide was added dropwise over a period of 1 hr. The solution was extracted with ether and the ether evaporated to give 0.28 g. of vanillyl alcohol containing a little vanillin. The solution was next extracted with ethyl acetate, the ethyl acetate evaporated, and the residue rubbed with a mixture of alcohol and acetone. Crystals, 0.153 g., m.p. 188–190°, separated. Reworking the mother liquor gave an additional 0.019 g. and the evaporated extracted solution 0.013 mg. or a total of 0.185 g. Recrystallization gave a product melting at 192–194° (lit.,[14] m.p. 187–190°). None of the highly insoluble dehydrodivanillin was detected.

The dehydrogenation of apocynol was attempted as described for vanillyl alcohol. Only starting material, resin, and a considerable amount of acetovanillone was recovered. The difficultly crystallizable biphenyl compound may have been produced but not successfully isolated. No dehydrodiacetovanillone was detected.

5-Propylvanillyl Alcohol.—A solution of 0.50 g. of 4-propylvanillin and 0.05 g. of sodium borohydride in 10 ml. of methanol was allowed to stand several hours and the methanol removed at room temperature. The residue was taken up in water, the mixture extracted with ether, the ether evaporated, and the residue recrystallized twice from hexane at −20°. The yield was 0.41 g., m.p. 45–50°. Repeated recrystallization from hexane gave crystals melting at 70–72°.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.33; H, 8.22; OCH_3, 15.82. Found: C, 67.23; H, 8.30; OCH_3, 15.71.

Acknowledgment.—The author is indebted to Professor E. Adler, Dr. J. A. F. Gardner, and Dr. I. A. Pearl for furnishing some of the model compounds investigated.

(13) F. Tiemann, *Ber.*, **18**, 3493 (1885).

(14) E. Adler, *Acta Chem. Scand.*, **9**, 332 (1955).

The Structure and Some Reactions of Isopropylidenemalononitrile Dimer

J. K. WILLIAMS

Contribution No. 788 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

Received August 30, 1962

Isopropylidenemalononitrile dimer is shown to exist predominantly as the aminocyclohexadiene IVa, which is in equilibrium with the tautomer IVb. It undergoes addition of nucleophiles, such as methoxide, to give cyclohexenes such as IXb. These undergo a reverse Diels–Alder reaction on heating near 150° to form isobutylene and dienes such as Xb. Gentle acid hydrolysis of the cyclohexenes (IX) leads to 1,4-transannular transfer of alkoxide to a cyano group to form imino ethers that subsequently undergo hydrolysis to the esters XX.

Isopropylidenemalononitrile dimer has been obtained by the base-catalyzed reaction of acetone with malononitrile[1,2] and by the piperidine-catalyzed dimerization of isopropylidenemalononitrile (I).[3] It has been suggested that the dimer is the cyclobutane II,[2] the imino diene IIIa,[2] and the tautomeric amino triene IIIb.[4] We have studied the dimer and conclude

(1) G. J. Ostling, *Oevers. Finska Vetenskaps-Soc. Forh.*, **57A**, No. 11, 1 (1915).

(2) R. Schenk and H. Finken, *Ann.*, **462**, 267 (1928).

(3) A. C. Cope and K. E. Hoyle, *J. Am. Chem. Soc.*, **63**, 733 (1941).

(4) D. M. W. Anderson, F. Bell, and J. L. Duncan, *J. Chem. Soc.*, 4705 (1961). Professors Anderson and Bell have examined the manuscript of this publication and have graciously suggested that we include a note stating that they agree with our structures and conclusions.