trated to dryness. The residual oil solidified on standing. This material had no well defined melting point and left an ash on combustion. It weighed 10.7 g. (74% yield, calculated as the sodium salt of *o*-hydroxybenzylamine) and its infrared spectrum was devoid of any carbonyl absorption. It was taken up in a minimum quantity of water and treated carefully with dilute hydrochloric acid until no more precipitate formed. Filtration and drying gave 6.71 g. of *o*-hydroxybenzylamine (V), m.p. 121–123°. This material could be recrystallized from water, but the melting point varied greatly (114 to 120°) with the apparent degree of hydration of the resulting crystals. Completely anhydrous material was not obtained.

A mixture of 2.8 g. (*ca.*, 0.02 mole) of *o*-hydroxybenzylamine (V), m.p. 118–119°, and 2.96 g. (0.02 mole) of phthalic anhydride was heated in an oil bath at 170–180° for 0.5 hr. After cooling, the resulting solid was taken up in boiling methanol, filtered, and cooled. Crystalline product thus obtained was added to several further crops obtained by concentration of successive filtrates to give 3.3 g. (65%) of crude N-(2-hydroxybenzyl)-phthalimide (III), m.p. 171–173°. Several recrystallizations from ethanol gave pure III, m.p. 177°; λ_{max}^{Nujol} 2.98, 5.67, 5.90 μ; $\lambda_{max}^{CHCl_3}$ 275 (3200), 280 (3250), 297 mμ (ϵ 2150).

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38. Found: C, 71.09; H, 4.59.

N-Phenoxymethylphthalimide (VI).—To a stirred suspension of 2 g. (0.084 mole) of sodium hydride in 50 ml. of 1,2-dimethoxyethane was added dropwise a solution of 7.9 g. (0.08 mole) of phenol in 50 ml. of 1,2-dimethoxyethane. After stirring 1 hr. at room temperature, a solution of 19.2 g. (0.08 mole) of N-bromomethylphthalimide in 1,2-dimethoxyethane was added dropwise, and stirring was continued overnight at room temperature. The reaction mixture was filtered from sodium bromide and concentrated to dryness under reduced pressure. The solid residue was triturated with acetone, filtered, and dried to give 8.17 g. (42%) of crude VI, m.p. 133–135°. Recrystallization from acetone (charcoal) gave pure N-phenoxymethylphthalimide (VI), m.p. 140–141°; $\lambda_{max}^{CHCl_3}$ 5.60, 5.80 μ, no OH absorption.

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38. Found: C, 71.19; H, 4.33.

Attempted Rearrangement of the Ether VI to II or III.—When a benzene solution of the ether VI was refluxed for 5 hr. in the presence of a continuous stream of either dry hydrogen chloride or hydrogen bromide, it was recoverable quantitatively. When phenol was used as a solvent and hydrogen bromide was continuously bubbled through the mixture for 5 hr. at steam-bath temperature, no starting ether VI could be recovered. A 9% yield of N-(4-hydroxybenzyl)phthalimide (II), m.p. 205–206°, was isolated, but the bulk of the product consisted of a refractory polymeric mixture.

Phenolysis of N-Bromomethylphthalimide. A. In Benzene.—A solution of 3 g. (0.0125 mole) of N-bromomethylphthalimide and 2 g. (0.021 mole) of phenol in 10 ml. of dry benzene was refluxed for 3 hr. The solvent was then removed by distillation under reduced pressure and the residue was suspended in hot (60–80°) water, collected at the filter, and washed thoroughly with more hot water. Drying gave 1.60 g. (51%) of product which, after thorough grinding to ensure homogeneity was found, by thin-layer silica gel chromatography, to consist of a mixture of *o*- and *p*-substituted phenols II and III. Neither the disubstituted phenol VIII nor the phenyl ether VI was present. Quantitative column chromatography (described later) showed that this mixture consisted of 54% *para* isomer II and 49% *ortho* isomer III. Thus, within the limits of experimental error of detection, II and III are the only products identifiable in this reaction mixture.

When the foregoing procedure was repeated in the presence of 4.1 ml. (*ca.* 0.021 mole) of β-pinene, as expected, no hydrogen bromide evolution was detectable. Working up the reaction in the usual way gave a semisolid mixture which contained (thin-layer chromatography) a large amount of the bromide I together with smaller amounts of II, III, the phenyl ethyl VI, and a fourth unknown substance (possibly bornyl bromide). Trituration of the product with ether followed by filtration gave a crude solid whose infrared spectrum was qualitatively identical to that of the starting bromide I.

B. In Phenol.—A mixture of 3 g. of N-bromomethylphthalimide and 2 g. of phenol was heated on the steam bath for 3 hr. and worked up as in the foregoing procedure. There was obtained 2.68 g. (85%) of a mixture which thin-layer chromatography showed to be mainly II and III, together with a small amount of an unknown substance which remained at the origin. Again, neither the phenyl ether VI nor the disubstituted phenol VIII was detectable. Quantitative column chromatography showed the presence in the mixture of 53% *para* isomer II and 40% of *ortho* isomer III.

A sample of the mixture was fractionally crystallized from a benzene–pentane mixture to give pure N-(*p*-hydroxybenzyl)-phthalimide (II), m.p. 205–206°, identical (infrared spectrum and mixture melting point) with an authentic sample.

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38. Found: C, 71.35; H, 4.11.

Several fractions of the chromatographic eluate, which, judging from the plotted chromatogram ($E_{1\,cm}^{1\%}$ *vs.* fraction number), contained the *ortho* isomer III, were combined and distilled to dryness under reduced pressure. The residue proved to be identical (infrared spectrum and qualitative thin-layer chromatography) with an authentic sample of N-(2-hydroxybenzyl)phthalimide (III).

Thin-Layer Silica Gel Chromatography.—Solutions of the compounds or their mixtures were prepared in a 1:1 methanol–chloroform mixture, and 5-λ volumes were spotted at the origins of the plates. After drying the spots, a solvent mixture, composed of 9 volumes of benzene to 1 of ethyl acetate was employed to develop the chromatograms. After drying once more, the resolved spots were visualized by means of iodine vapor. Under these conditions, the following R_f values were observed: N-(4-hydroxybenzyl)phthalimide (II), 0.2; N-(2-hydroxybenzyl)-phthalimide (III), 0.5; and N-phenoxymethylphthalimide (VI), 0.65. The disubstituted phenol could be identified by the observation that, unlike the other three substances, it could not be cleanly resolved under these conditions. It usually smeared out over a considerable portion of the chromatogram or, at best, gave spots much too elongated for the determination of any meaningful R_f value.

Column Chromatography.—A solution of the mixture of isomers (0.10 g.) in a minimum amount of a methanol–chloroform or ethyl acetate–chloroform mixture was placed on a column (2 × 28 cm.) of silica gel (100–200 mesh) previously packed in chloroform. Development was effected with pure chloroform (150–200 ml.) and elution was accomplished with chloroform containing gradually increasing amounts (2.5 → 10%) of ethyl acetate. Eluate was collected in 20-ml. fractions and the quantity of phenolic material in each fraction was determined spectrophotometrically using the optical density at 280 mμ. The $E_{1\,cm}^{1\%}$ values employed in the calculations were 127 for the *ortho* isomer III and 86.5 for the *para* isomer II. A plot of absorbance *vs.* volume of eluate in a successful chromatogram gave two peaks separated by a trough extending very nearly to the base line. The first peak represented the quantity of *ortho* isomer III and the second that of the less mobile *para* isomer II. A complete chromatogram usually required less than 400 ml. of eluate. Some chromatographic experiments failed to give appreciable separation. This was usually ascribable to the difficulty of applying the mixture to the top of the column in a sufficiently small volume of solvent.

On the Occurrence of Hydronootkatinol in the Heartwood of *Cupressus Lindleyi* Klotsch

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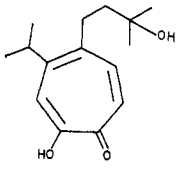
Continuing our investigations[1] of the tropolones present in heartwood of *Cupressus* species, we examined *Cupressus lindleyi* Klotsch, a species native to Mexico.

(1) E. Zavarin, *J. Org. Chem.*, **27**, 3368 (1962).

On cooling the *n*-hexane solution of the total tropolonic fraction, a crystalline solid deposited. Purification yielded pale yellow needles, m.p. 107–108°.

The material obtained had correct analysis for $C_{15}H_{22}O_3$ with two active hydrogens and gave ferric chloride and copper acetate reactions for tropolones. The electronic and infrared absorption spectra agreed with the tropolonic structure. In infrared, in addition to a tropolonic hydroxyl at 3230 cm.$^{-1}$, the compound showed two peaks at 3620 and 3430 cm.$^{-1}$, which did not disappear upon chelation with copper acetate and were derived from an alcoholic hydroxyl. N.m.r. spectrum of the isolated material was in complete agreement with structure I, which relates to nootkatin (II)[2] by double bond hydration according to the Markownikoff rule.

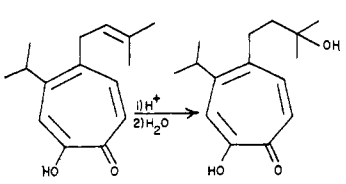


I

The final proof for structure I was obtained by adding elements of water to the double bond of nootkatin using 85% phosphoric or concentrated sulfuric acids. The resulting tropolone was found to be identical with the isolated material, termed hydronootkatinol (I).

As the isolation of I involved dissolution of the tropolonic fraction in 85% phosphoric acid, it was repeated avoiding low pH conditions. Paper chromatography indicated that hydronootkatinol, in addition to nootkatin, was still present in the extract, although in a somewhat decreased amount. Thus hydronootkatinol should be regarded as a true heartwood constituent and not as an artifact.

A survey of literature indicates that this is the first instance of identification of a tropolonic sesquiterpene alcohol in wood of *Cupressaceae*. The formation of hydronootkatinol from nootkatin with mineral acids should be kept in mind whenever the phosphoric acid procedure of Lin, Lo, and Wang[3] is used for the separation of tropolones from other constituents. This also explains the tailing of nootkatin on paper chromatograms impregnated with phosphoric acid,[4] as hydronootkatinol has a much smaller R_f value than nootkatin.



II I

Experimental

Isolation of Hydronootkatinol.—A 559-g. portion (14% moisture content) of heartwood sawdust of *Cupressus lindleyi* Klotsch, collected at La Venta near Mexico City, was extracted with acetone in a Soxhlet extractor for 16 hr. The material obtained was evaporated to dryness and the residue extracted with isooctane on a steam bath. The resulting solution was extracted with 5% sodium hydroxide, the aqueous phase acidified with acetic acid, neutralized with an excess of ammonia, and treated with an excess of 5% ammoniacal copper acetate solution. This material was extracted with chloroform, the extract evaporated to dryness, the residue dissolved in acetone, and the bound chelated copper precipitated with hydrogen sulfide. The precipitate was filtered, the filtrate evaporated to dryness, the residue taken up in chloroform, and the resulting solution extracted with four 25-ml. portions of 85% phosphoric acid. The acidic extracts were combined, diluted to 500 ml. with water, neutralized with ammonia, and extracted with chloroform. The extract was evaporated to dryness, and the residue dissolved in 200 ml. of boiling *n*-hexane. On cooling and stepwise evaporation of the solvent, a white crystalline solid precipitated. The crude material collected was purified by treatment with active carbon in boiling carbon tetrachloride–chloroform solution, filtration through Celite, cooling, and recrystallization of the resulting solid from the same solvent to give 1.0 g. of pale yellow needles, m.p. 107–108° (0.2% yield dry wood weight).

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86; active H, 0.81; CH_3–C, 12.01; mol. wt., 250.3. Found: C, 71.77; H, 8.65; active H, 0.79; CH_3–C, 7.33; mol. wt., 258 (camphor).

To determine the presence of hydronootkatinol *in situ* the same isolation procedure was followed except that the phosphoric acid extraction step was omitted. For determination of hydronootkatinol, paper chromatography on dimethyl sulfoxide impregnated paper[5] was employed using the total mixture of phenols and tropolones. Visual comparison of the intensity of the spots on chromatograms sprayed with 5% ferric chloride indicated a decrease in intensity of the hydronootkatinol spot. The hydronootkatinol spot was present at a R_β[6] of 0.09 and at 0.05 using, respectively, the dimethyl sulfoxide and 17% phosphoric acid (toluene as developer)[7] chromatographic procedures.

Spectroscopy of Hydronootkatinol.—Electronic absorption: λ_{max} 322 mμ (log ε 3.87), 240 (4.47); λ_{min} 268 mμ (log ε 2.92), acetonitrile as solvent. The spectrum was very similar to that of nootkatin.

Infrared absorption (cm.$^{-1}$): 3620 w, 3430 m, 3230 w, 2975 s, 2460 w, 1620 s, 1605 s, 1555 s, 1490 s, 1473 s, 1455 s, 1390 m, 1373 m, 1343 m, 1270 s, 1242 s, 1175 m, 1155 m, 1122 m, 1025 m, 995 w, 974 w, 924 m, 908 m, 857 m, 828 w, 681 w, 657 w (chloroform as solvent).

Nuclear Magnetic Resonance.—Shifts are in p.p.m. relative to tetramethysilane as 0.0; deuteriochloroform as solvent; run at 100 and 60 m.c.: 1.27 relative intensity (RI), 3.0 (first peak of the isopropyl doublet); 1.34, RI, 9.0 (second peak of the isopropyl doublet superimposed on the other two methyl peaks); 1.72 (sextuplet) RI, 2.0 (methylene, β to the nucleus); 2.78 (sextuplet) RI, 2.0 (methylene, α to the nucleus); 3.28 (heptuplet)RI, 1.0 (tertiary isopropyl hydrogen); 5.27 RI, 2.0 (aromatic and aliphatic hydroxyls); 7.18, 7.32, 7.39 RI, 3.0 (aromatic hydrogens).

For comparison the spectrum of nootkatin was run under the same conditions; 1.32, 1.20 (isopropyl methyl doublet); 1.73, 1.76 (peak due to double bond methyls); 3.28 (heptuplet), (tertiary isopropyl hydrogen); 3.39 (methylene doublet); 5.13 (double bond hydrogen triplet); about 7.33 (aromatic hydroxyl); 7.47 (weak), 7.40, 7.27, 7.22, 7.02 (weak) (aromatic multiplet).

The **copper chelate** was prepared by the usual procedure and recrystallized from carbon tetrachloride–chloroform mixture; m.p. 237.5–241.0° dec.

Anal. Calcd. for $C_{30}H_{42}O_6Cu$: C, 64.09; H, 7.53. Found: C, 63.79; H, 7.40.

In infrared (potassium bromide pellet), the material exhibited a hydroxyl band at 3435 cm.$^{-1}$; the tropolonic hydroxyl band at 3230 cm.$^{-1}$ disappeared; and the carbonyl band shifted to 1593 cm.$^{-1}$

Synthesis of Hydronootkatinol.—A 10.8-mg. portion of nootkatin (m.p. 94.6–95.8°) was dissolved in 10 ml. of 85% phos-

(2) (a) For isolation and characterization see G. Aulin-Erdtman, *Acta Chem. Scand.*, **4**, 1031 (1950); G. Aulin-Erdtman and H. Theorell, *ibid.*, **4**, 1490 (1950); R. B. Campbell and J. M. Robertson, *Chem. Ind.* (London), 1266 (1952); B. Carlsson, H. Erdtman, A. Frank, and W. E. Harvey, *Acta Chem. Scand.*, **6**, 690 (1952); H. Erdtman, and W. E. Harvey, *Chem. Ind.* (London), 1267 (1952); (b) for structure determination, see S. R. Duff and H. Erdtman, *ibid.*, 432 (1954).

(3) Y. T. Lin, T. B. Lo, and K. T. Wang, *J. Chinese Chem. Soc.* (Taiwan), **5**, 54 (1958).

(4) E. Zavarin, R. M. Smith, and A. B. Anderson, *J. Org. Chem.*, **24**, 1318 (1959).

(5) C. A. Wachtmeister and B. Wickberg, *Acta Chem. Scand.*, **12**, 1335 (1958).

(6) R_β is defined as the ratio of the distance migrated by a certain tropolone to the distance migrated by β-thujaplicin.

(7) E. Zavarin and A. B. Anderson, *J. Org. Chem.*, **21**, 332 (1956).

phoric acid and allowed to stand overnight at room temperature. The resulting solution was diluted with 100 ml. of water, neutralized with ammonia, and extracted with chloroform. The chloroform extract was dried with sodium sulfate, filtered, and evaporated to dryness. The residue was extracted with boiling *n*-hexane and allowed to cool. The deposited crystals were collected to give 6.9 mg. of material, m.p. 106.5–107.5° (59.1% yield). The melting point of the isolated material was undepressed on admixture with the natural hydronootkatinol; their infrared spectra were identical.

Paper chromatography of the crude reaction product revealed an intense spot for hydronootkatinol and the absence of nootkatin. Similar results were obtained with concentrated sulfuric acid.

Acknowledgment.—An acknowledgment is made to Mr. Richard Scheible for his help in collecting the necessary wood samples.

The Structure of the Solid State Photodimer of 3-Benzylidenephthalide

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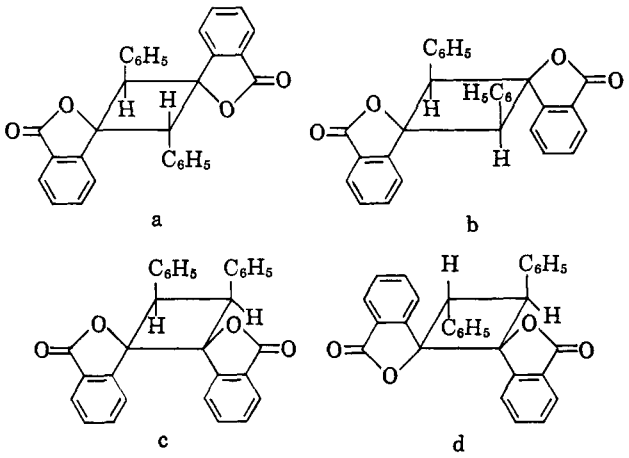
Of the wealth of photodimers which have been reported[1] the number of those whose structure has been fully elucidated remains small. With growing interest in the mechanism of the photodimerization reaction, structural delineation of photochemical dimerization products has acquired renewed importance. While the mechanism of solution photodimerization is still being debated,[2] the structural consequences of solid state dimerization are thought to be dictated by the alignment of the monomers in the crystal lattice.[3] This generalization is based only on few examples,[4-6] an extensive correlation being impossible because of the lack of photodimers whose structure can be considered as firmly established. It was deemed desirable for this reason to investigate additional photodimeric compounds, of which the photodimer of 3-benzylidenephthalide was a particularly convenient example.

3-Benzylidenephthalide was found to dimerize readily in the solid state in yields of 30% by irradiation with a 275-watt sunlamp.[7] The photodimer, m.p. 294–296°, infrared absorption at 5.64 μ, lacks vinyl proton absorption in the n.m.r. spectrum,[8] the latter exhibiting outside the aromatic region only one sharp signal at τ 4.82 (p.p.m.).

Formation of a cyclobutane ring structure is corroborated by the n.m.r. spectrum as well as by the observation that the dimer reversed to the monomer upon irradiation in solution with a Hanovia mercury arc lamp. The presence of a single aliphatic proton absorption in the n.m.r. spectrum is in accord with the expected formation of a symmetrical dimer. Rejecting from consideration the possibility of *cis–trans* isomerization,[9] the number of photodimeric structures among which the choice has to be made is reduced to a total of four, the *cis–trans* isomeric pairs of either the head–tail structure (Ia, b) or of the head–head structure (Ic, d). the following evidence establishes the structure of the photodimer as being Ia, the head–tail formulation.

Upon mild alkaline hydrolysis the photodimer was found to yield a carboxylic acid II, which readily eliminated water reverting to starting material.[10] The corresponding methyl ester, found to be somewhat more stable, was assigned the mono ester–lactone structure III on the strength of its infrared spectrum (bands at 2.90, 5.65, and 5.92 μ) and its n.m.r. spectrum, the latter providing conclusive evidence for the streochemistry of III and, hence, for that of the photodimer from which it is derived. With the loss of symmetry in the molecule, the two hydrogens become dissimilar in the ester–lactone derived from three of the four possible dimeric structures. A photodimer of structure Ib would give rise to an ester–lactone which retains a plane of symmetry and the two ring hydrogens remain in an identical environment. Of the remaining three structures, the head–head structures Ic and Id, when transformed into an ester–lactone, will have their ring hydrogens on adjacent carbons and since they are now nonequivalent, they should give rise to a doublet.[11] In fact, the ester obtained showed, in addition to the



I

(1) See, for example, A. Mustafa, *Chem. Rev.*, **51**, 1 (1952); A. Schönberg, "Präparative Organische Photochemie," Springer Verlag, Berlin, 1958, pp. 22–35.

(2) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344, 2454 (1962).

(3) T. Sadeh and G. M. J. Schmidt, *ibid.*, **84**, 3970 (1962); D. Cohen and G. M. J. Schmidt, in "Reactivity of Solids," J. H. de Boer, Ed., Elsevier Publishing Co., Amsterdam, 1961, p. 556.

(4) P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.*, **80**, 6150 (1958) and forthcoming publication.

(5) G. W. Griffin, J. E. Bassinski, and L. I. Peterson, *ibid.*, **84**, 1012 (1962).

(6) G. M. J. Schmidt, *Acta Cryst.*, **10**, 793 (1957); H. J. Bernstein and W. C. Quimby, *J. Am. Chem. Soc.*, **65**, 1845 (1943).

(7) The dimerization of 3-benzylidenephthalide in solution has been reported to give one photoproduct of unknown structure [A. Schönberg, N. Latif, R. Moubasher, and W. I. Awad, *J. Chem. Soc.*, 374 (1950)]. In the present study it was found that three dimers resulted from solution dimerization, one in predominant amounts and none identical to Ia. The n.m.r. spectra exhibited only singlet proton signals in the 5-τ region.

(8) The vinylhydrogen in the monomer gives rise to a signal at τ 3.62 (p.p.m.).

(9) *cis–trans* isomerization in the solid state is unlikely in this case. The cross-over mechanism *via* a cyclobutane dimeric structure advanced for the solid state isomerization of cinnamic acid (G. M. J. Schmidt, Photochemistry Symposium, Rochester, N. Y., March, 1963) cannot hold in our example, as the photodimer remains unchanged upon further irradiation. We are indebted to a referee for bringing to our attention the above unpublished results.

(10) The facile formation of photodimer precludes cyclobutane ring opening or other skeletal changes under these conditions. More vigorous base treatment caused cyclobutane ring cleavage.

(11) Coupling of vicinal nonequivalent *cis* or *trans* cyclobutane protons is expected; *cf.* ref. 2 and spectra of distilbenes in J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McHraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 290–291.