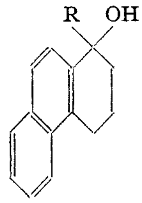
67 g. of the anilide. Reaction of the acid anilide with phosphorus pentachloride followed by reduction of the product by stannous chloride and hydrogen chloride in absolute ether yielded the new phenanthrene aldehyde 1-phenanthraldehyde (m. p. 110–111°; yield, 65%). These reactions now make it possible to prepare many 1-substituted phenanthrene derivatives hitherto difficult to obtain, and we are engaged in the preparation of such compounds. Reduction of the aldehyde to the carbinol (m. p. 165°), followed by a malonic ester condensation with the carbinol bromide (m. p. 97°) gave β-(1-phenanthryl)-propionic acid (m. p. 189–189.5°); experiments on the cyclization of this acid are not yet complete.

The excellent researches of Cook and coworkers [Cook, Dodds, Hewett and Lawson, *Proc. Roy. Soc.* (London), **114,** 278 (1934)] have shown that oestrogenic property is possessed by a variety of polycyclic compounds; and we are having the keto-cyclopentenophenanthrenes and derivatives tested for this property. We have also prepared three 1-hydroxy-1-alkyl-1,2,3,4-tetrahydrophenanthrenes (III) in crystalline state in which the alkyl group R is methyl (m. p. 86–86.5°), ethyl (m. p. 57–57.5°) and *n*-propyl (m. p. 86–87°); these compounds likewise are being tested for oestrogenic activity.



(III)

The physiological tests are being made by Dr. James Bradbury at the University of Michigan Hospital. The details of the experiments will be published later.

CHEMISTRY LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
W. E. BACHMANN

RECEIVED JUNE 13, 1935

THE PREPARATION OF MONOCHLOROACETOCATECHOL

Sir:

In the synthesis of adrenaline according to the method of Stolz [*Ber.*, **37,** 4149 (1904)] the preparation of monochloroacetocatechol is necessary. Chloroacetic acid, catechol and phosphorus oxychloride are mixed together and refluxed on the steam-bath. At the end of an hour the material in the flask is recrystallized from hot water. Using this method as it stands, repeated preparation shows large amounts of tars which obliterate much of the yield. Oxidation of the catechol must also be repressed for greater yields. To carry out this purpose the following method was used.

Fifty grams each of monochloroacetic acid, catechol, and *freshly distilled* phosphorus oxychloride were mixed together in a one-liter short-necked flask fitted with reflux condenser and a tube through which sulfur dioxide was passed. A tube was attached to the end of the reflux condenser to lead away hydrogen chloride gas evolved in the reaction, and the sulfur dioxide. After the flask was filled with the sulfur dioxide from a tank, heating was started, a steady stream of gas always flowing. At the end of an hour heating was stopped, the purple crystals of crude chloroacetocatechol crystallized from hot water, decolorized with acid, Norite and sodium sulfite, and again crystallized. The light violet tinged crystals were washed with absolute alcohol, and finally ether. The yield was 53.6 g., m. p. 173°. Without these modifications, namely, the sulfur dioxide atmosphere and freshly distilled phosphorus oxychloride, the yield was 8.3 g.

COLUMBIA UNIVERSITY
NEW YORK CITY
HENRY D. HOBERMAN

RECEIVED JUNE 15, 1935

THE RAMAN SPECTRUM OF RUBBER

Sir:

It has been previously reported that the Raman effect is exhibited by rubber as a continuous scattering together with the presence of broad bands [Franklin and Laird, *Phys. Rev.*, **36,** 147 (1930); Busse, *J. Phys. Chem.*, **36,** 2862 (1932)]. Busse attributed this result to the viscosity of the solutions or to the possibility that the rubber groups respond to a wide range of frequencies. However, viscous solutions of polysterol in carbon tetrachloride give a line spectrum [Signer and Weiler, *Helv. Chim. Acta*, **15,** 649 (1932)]. As to the second explanation, this does not seem to be the nature of the Raman effect [Bär, *Helv. Phys. Acta*, **4,** 369 (1931); Bär, *Z. Physik*, **79,** 455 (1932)]. The Raman effect has been investigated extensively for terpenes other than rubber.

The bands and continuous background for rubber appear to be due to fluorescence of impurities, oxidation products, or the rubber hydrocarbon. The acetone extract of rubber is fluorescent as observed in ultraviolet light. The intensity of the bands and background for rubber decreases as the rubber is purified. However, acetone extraction and two diffusions with ethyl ether did not remove the fluorescence entirely, as could be seen by examination between complementary light filters. Some of the background is undoubtedly unmodified radiation, that is, Tyndall scattering by the colloidal structure and by motes. This can be reduced by a monochromatic light filter.

In contrast to the previous results, a line spectrum has now been observed for rubber. Gels made with diffusion rubber [Memmler, "Science of Rubber," Am. Ed., Reinhold Publishing Corp., New York, 1934, p. 174)] give Raman lines of sufficient intensity to be seen against the background. A mixture of 43% carbon bisulfide and 57% carbon tetrachloride is suitable as a solvent since this mixture has about the same refractive index as rubber and has a simple Raman spectrum. Carbon tetrachloride has been used alone with petroleum ether diffusion rubber. Concentrations of rubber used were from 10 to 40% by volume. The preparations were clear, colorless gels, free from any gross optical imperfections. They were protected from ultraviolet light by being completely surrounded by a filter solution. They did not show any perceptible darkening due to the exposures. The Raman lines were excited by the 4358 Å. mercury line.

The three most intense Raman frequencies for rubber are 1672, 1460 and 1382 cm.$^{-1}$. Isoprene has frequencies of 1640, 1426 and 1388 cm.$^{-1}$ [Dadieu and Kohlrausch, *J. Opt. Soc. Am.*, **21**, 286 (1931); Bourguel and Piaux, *Bull. soc. chim.*, **51**, 1041 (1932)]. Thus the 1640 frequency for isoprene, ascribed to the double bond, is smaller than the corresponding frequency in rubber. However, trimethylethylene has three frequencies which agree closely with these most intense lines for rubber. Thus the Raman spectrum data appear to confirm the generally accepted views regarding the chain structure of rubber although a cyclic structure is not definitely excluded, since cyclic terpenes have a spectrum of this nature.

The group of lines at 2900 cm.$^{-1}$, characteristic of the aliphatic C–H linkage, can be observed readily for rubber. Measurements of the fainter lines for rubber will be possible with further reduction in the background intensity.

RESEARCH LABORATORIES
GOODYEAR TIRE & RUBBER CO.
AKRON, OHIO
S. D. GEHMAN

RECEIVED JUNE 17, 1935

HINOKININ AS THE ENANTIOMORPH OF CUBEBINOLIDE

Sir:

Erdtman [*Ann.*, **516**, 162 (1935)] has recently shown that eudesmin and the dimethyl ether of pinoresinol are enantiomorphs. From hinoki wood (*Chamecyparis obtusa*, Sieb. et Zucc.) Yoshiki and Ishiguro [*J. Pharm. Soc. Japan*, **53**, 73 (1933)] have isolated a crystalline compound, hinokinin, $C_{20}H_{18}O_6$, while Mameli [*Gazz. chim. ital.*, [ii] **42**, 551 (1912); [ii] **51**, 353 (1921)] has obtained a lactone, cubebinolide, $C_{20}H_{18}O_6$, from the oxidation of cubebin, $C_{20}H_{20}O_6$. That these substances are also enantiomorphs is apparent from the following comparison.

	Hinokinin	Cubebinolide
Molecular formula	$C_{20}H_{18}O_6$	$C_{20}H_{18}O_6$
M. p., °C.	64–65	63–64
Rotation	$[\alpha]^{32}_D$ −32.39° (2% alcohol)	$[\alpha]_D$ +33.69° (chloroform)
Dinitro derivative	M. p., °C. 183–184	183–184
	$[\alpha]^{22}_D$ −90.51° (acetone)	.....
Dibromo derivative	M. p., °C. 137–138	137
	$[\alpha]^{22}_D$ −26.94° (chloroform)	.....
Sodium salt of free acid	M. p., °C. 200–205	205–207
	$[\alpha]^{15}_D$ −7.61°	.....
Chloro methyl ester	M. p., °C. 92–93	95
	$[\alpha]^{15}_D$ (−?) 14.64° (chloroform)	$[\alpha]_D$ +13.89°

Both substances also yield piperonylic acid on oxidation. Based on the reactions of cubebinolide and the parent substance cubebin, Mameli has put forward the partial formula for cubebinolide (I). A substance of molecular formula $C_{20}H_{18}O_6$ containing two monosubstituted catechol methylene ether nuclei and a lactone group can only be tricyclic (including the lactone ring), so that the residue C_4H_6 must be saturated and acyclic.

On phytochemical grounds it is thus possible that cubebinolide has one of the alternative formulas (II) or (III). A substance of formula (II) should give the stable piperonoylformic acid as well as piperonylic acid on oxidation but the former acid has not yet been detected in the oxidation products. For this reason the author prefers formula (III).

From the chemical reactions of matairesinol from the wood of *Podocarpus spicatus* [Easterfield