purities, 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.

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RECEIVED JUNE 17, 1935

HINOKININ AS THE ENANTIOMORPH OF CUBEBINOLIDE

Sir:

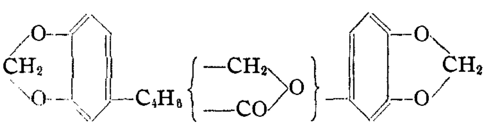
Erdtman [*Ann.*, **516**, 162 (1935)] has recently shown that eudesmin and the dimethyl ether of pinoresinol are enantiomorphs. From hinoki wood (*Chamecyparis obtusa*, Sieb. et Zucc.) Yoshiki and Ishiguro [*J. Pharm. Soc. Japan*, **53**, 73 (1933)] have isolated a crystalline compound, hinokinin, $C_{20}H_{18}O_6$, 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°

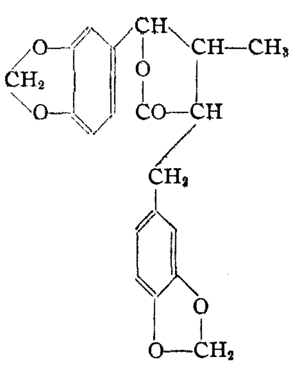
Both substances also yield piperonylic acid on oxidation. Based on the reactions of cubebinolide and the parent substance cubebin, Mameli has put forward the partial formula for cubebinolide (I). A substance of molecular formula $C_{20}H_{18}O_6$ containing two monosubstituted catechol methylene ether 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).

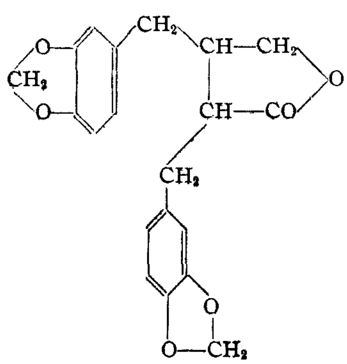
From the chemical reactions of matairesinol from the wood of *Podocarpus spicatus* [Easterfield and Bee, *J. Chem. Soc.*, **97**, 1028 (1910)], the constitution (IV) has been proposed for this resinol independently by Haworth (private communication) and the author [Briggs, Peak and Wooloxall, *Proc. Roy. Soc. N. S. Wales*, (in press)].



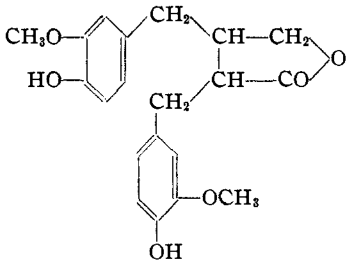
I



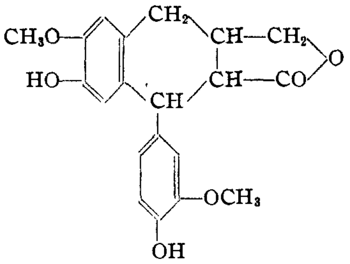
II



III



IV



V

Thus the structure suggested for cubebinolide (III) is very similar both to matairesinol and sulfite liquor lactone (tsugaresinol) (V) [Erdtman, *Ann.*, **513**, 229 (1934); Kawamura, *Bull. Imp. Forestry Expt. Sta. Tokyo*, No. 31, 73 (1932); Emde and Schartner, *Helv. Chim. Acta*, **18**, 344 (1935)].

The transformation of matairesinol into a substance of structure (III) is being attempted to prove this assumption.

DEPARTMENT OF CHEMISTRY
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L. H. BRIGGS

RECEIVED JUNE 19, 1935

THE SOLUTION OF TITANIC HYDROXIDE IN HYDROGEN PEROXIDE

Sir:

Several months ago, in the course of some attempts to crystallize a titanium per-salt, we observed an interesting phenomenon, to which there is apparently no reference in the literature. We found that freshly precipitated and well-washed titanic hydroxide dissolves in dilute hydrogen peroxide to give a clear yellow solution. Thus, 50 cc. of a suspension containing 0.0035 mole of $Ti(OH)_4$, treated with 0.4 cc. of 30% H_2O_2 (0.0035 mole), became clear after one hour at room temperature, or after a few minutes when warmed. Larger amounts of hydrogen peroxide hasten solution; much smaller amounts of hydrogen peroxide give solutions with pronounced opalescence.

The solution has colloidal properties. Diffusion through a collodion bag takes place to only a very slight extent. Nearly complete precipitation occurs on addition of small amounts of electrolytes, but high concentrations of hydrogen peroxide render the precipitation less complete. The precipitates in these cases are yellow and contain hydrogen peroxide.

Gels can be prepared by boiling down the solutions and then cooling. Some were obtained which could be remelted by warming. Some were also obtained which had the property, known for other gels, of temporarily liquefying on vigorous shaking.

The most nearly similar phenomenon of which we are aware is the solution of freshly precipitated and washed manganese dioxide in concentrated hydrogen peroxide (see *C. A.*, **5**, 2470 (1911)).

The solution not only is of some scientific interest, but also may find considerable application in the arts.

DEPARTMENT OF CHEMISTRY
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RECEIVED JUNE 21, 1935

THE POLYMERIZATION OF ETHYLENE INDUCED BY METHYL RADICALS

Sir:

In continuing our work on chain reactions induced by azomethane, we have found that ethylene is rapidly polymerized at temperatures near 300° by small quantities of azomethane. Over a ninety-fold range of azomethane pressure and a ten-fold range of ethylene pressure, and total pressures all below 60 mm., the initial rate depends