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## COMMUNICATIONS TO THE EDITOR

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### THE TOXIC PRINCIPLES OF POISON IVY

Sir:

We have investigated the active principles of poison ivy and find that the toxic oil is a complex of at least three active components and several innocuous concomitants.

Hill and his co-workers<sup>1</sup> isolated a toxic yellow oil from poison ivy with the stated boiling point of 210° (0.5 mm.), and presented evidence to prove that it was identical with urushiol, the boiling point of which was quoted as 210° (0.4–0.6 mm.). From this toxic oil they prepared a series of derivatives, identical when crystallizable with those prepared from urushiol, but no yields were reported.

"Urushiol" is a name first applied by Majima<sup>2</sup> to an extract of Japan lac which boiled over a range of 210–222° ((0.4–0.6 mm.), and, upon redistillation, from 195° to "above 210°." It was shown to consist of four components<sup>3</sup> the structures of which were partially elucidated.

Since it is known that plants of the *Anacardiaceae* family, to which both poison ivy and Japan lac belong, elaborate a number of vesicant mono- and dihydric alkyl phenols with fifteen and seventeen carbon side chains, the derivatives prepared by Hill only prove the presence of a compound or compounds with a 3-pentadecacatechol skeleton in the distillate. This is a property it possesses in common with urushiol.

Essentially we followed Hill's method of isolation; our concentrate boiled over a range, the major portion distilling at 185–250° (2 microns) with considerable resinification. Redistillation in a Hickman molecular still yielded three fractions at bath temperatures up to 125°, 165° and 170°, the principal superficial difference being one of color. The products, although containing innocuous concomitants, were all toxic, 0.5 gamma of oil per sq. cm. of hypersensitive skin being sufficient to elicit a strong characteristic poison ivy reaction.

Chromatographed under nitrogen on barium carbonate-Hyflo Super Cel (Johns Mansville Sales Corporation), fraction 1 was separated into

an unsaturated acid (or acids, hydrogenation yielding a solid, m. p. 66–67°, depressed by palmitic but not stearic acid; C, 75.4; H, 12.5; amide m. p. 105–106°, depressed by palmitamide but not stearamide; therefore stearic acid<sup>4</sup>) and a phenolic oil,  $\log \epsilon$  265  $m\mu$  = 3.02,  $\log \epsilon$  273  $m\mu$  = 3.09 in absolute ethanol. In twenty-four hours absorption decreased to  $\log \epsilon$  265  $m\mu$  = 2.72 and the ferric chloride test became negative in the original concentration, 6 mgm./100 cc. This suggests that the presence of drying oils in the vesicant-bearing sap accounts at least in part for the extraordinary stability of the toxic principles in their natural environment.

Chromatographed on alumina (Alorco) deactivated with 90% ethanol, fraction 1 yielded six bands, from the top: orange, four colorless with bright blue-white fluorescence under ultraviolet light, and yellow. One fluorescent band, eluted with 90% ethanol, was phenolic and auto-oxidized with extreme rapidity. The other fluorescent bands could not be removed without major destruction, but were shown to be highly toxic, while the remaining fractions were not. We conclude that at least three toxic components are present, and are engaged in improving this technique and elucidating the structures of the toxic compounds. The exigencies of the day have required this short report at this time.

(4) We are indebted to Dr. Arthur T. Ness for the microchemical analyses.

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### THE MECHANISM OF THE DIELS-ALDER REACTION

Sir:

It is noteworthy that in the usual case the Diels-Alder reaction involves, on the one hand, a substance, *e. g.*, a diene, of relatively low ionization potential and, on the other, a molecule of high electron affinity, *e. g.*, an  $\alpha,\beta$ -unsaturated carbonyl compound. We may therefore expect an electron-transfer from the diene to the dienophile with the formation of an ion-pair intermediate of the type recently postulated in general for molecu-

(1) Hill, Mattacotti and Graham, *THIS JOURNAL*, **56**, 2736 (1934).

(2) Majima, *Ber.*, **42**, 1418 (1909).

(3) Majima, *et al.*, *ibid.*, **55B**, 172 (1922).