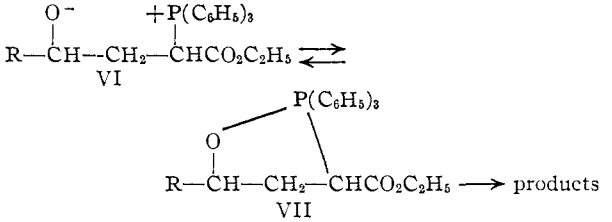
acid was converted to the amide, m.p. 190.5–192° (reported[4] 187–188°). I also reacted with III at 210–220° under nitrogen to give triphenylphosphine oxide (97% of crude material) and 26% of the ester (V), b.p. 70–75° at 0.4 mm. (reported[5] 75–80° at 0.5 mm). The ester was converted to the amide, m.p. 109–110°. (reported[5] 107–107.5°). Under similar conditions, 180° for five hours, cyclohexene oxide and I gave only recovered I and cyclohexene oxide. No cyclopropane ester could be detected.

Although no definite information is available on the mechanism of this reaction, it seems reasonable to suggest that the initial step involves nucleophilic displacement by the phosphorane on the epoxide to give an intermediate zwitterion (VI) which is in equilibrium with the pentacovalent phosphorus compound (VII).



Several paths can be envisioned for the decomposition of VII. If VI is an intermediate, then the possibility exists of preparing cyclopropanes from compounds similar to VI. These compounds could be prepared by a variety of methods. This approach is now being investigated, as are the reactions of other phosphoranes with a variety of epoxides.

(4) E. Buchner and J. Geronimus, *Ber.*, **36**, 3784 (1903).

(5) K. Hofmann, O. Jucker, W. R. Miller, A. C. Young, Jr., and F. Tausig, THIS JOURNAL, **76**, 1799 (1954).

SCHOOL OF CHEMISTRY DONALD B. DENNEY
RUTGERS THE STATE UNIVERSITY
NEW BRUNSWICK, NEW JERSEY MARVIN J. BOSKIN

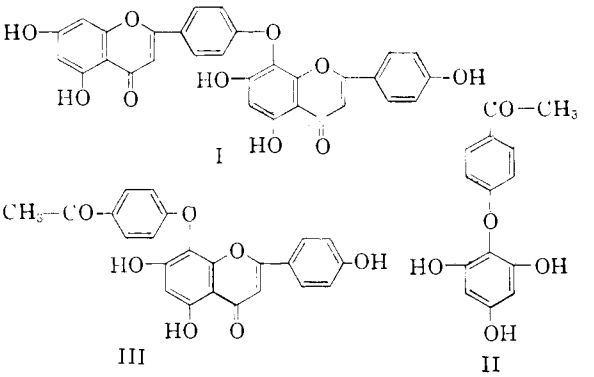
RECEIVED OCTOBER 26, 1959

THE STRUCTURE OF HINOKIFLAVONE, A NEW TYPE BISFLAVONOID

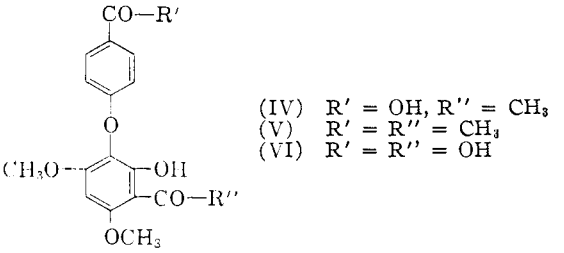
Sir:

Hinokiflavone, $C_{30}H_{18}O_{10}$, a bisflavonoid having a skeleton different from other bisflavonoids has been isolated.[1] The structures of ginkgetin and sciadopitysin recently were established as diflavonyls joined by a carbon–carbon linkage.[2,3] We now report that hinokiflavone is a diflavonyl ether represented by formula (I).

When treated with potassium hydroxide, hinokiflavone produces *p*-hydroxyacetophenone, a phenolic ketone (II), m.p. 201° (found: C, 64.83; H, 4.75. Calcd. for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65) and a ketoflavone $C_{23}H_{16}O_7$, m.p. 258° (III), which gave *p*-hydroxyacetophenone and II on further degradation. II has an acetyl and three hydroxyl groups. The trimethyl ether of II was oxidized to a carboxylic acid $C_{16}H_{16}O_6$, m.p. 192°, which was decarboxylated to 2,4,6-trimethoxydiphenyl ether m.p. 94.5°, which was newly synthesized from potassium phenoxide and bromophloroglucinol trimethyl ether. The infrared absorption spectra of II and its derivatives suggest *p*-substitution. This information, taken with that summarized below, allows the assignment of structures II and III.



Hinokiflavone has five hydroxyl groups. Its pentamethyl ether, treated with potassium hydroxide, gave anisic acid, *p*-methoxyacetophenone, 2,4-dimethoxy-6-hydroxyacetophenone, a phenolic acid (IV), m.p. 198° (found: C, 61.71; H, 4.75; OCH_3, 18.33. Calcd. for $C_{15}H_{10}O_5(OCH_3)_2$: C, 61.44; H, 4.85; OCH_3, 18.67) and a phenolic diketone (V), m.p. 147° (found: C, 65.28; H, 5.46; OCH_3, 18.30. Calcd. for $C_{16}H_{12}O_4(OCH_3)_2$: C, 65.44; H, 5.49; OCH_3, 18.77). The methyl ethers of IV and V were oxidized to the same



(IV) R′ = OH, R″ = CH_3
(V) R′ = R″ = CH_3
(VI) R′ = R″ = OH

dicarboxylic acid $C_{16}H_{14}O_8$ (VI methyl ether), m.p. *ca.* 110° (dec.), which was decarboxylated to 2,4,6-trimethoxydiphenyl ether. IV and V are positive to the Gibbs reagent and the infrared absorption spectra of IV and V also suggest *p*-substitution.

By boiling in methanolic barium hydroxide solution,[4] hinokiflavone pentamethyl ether produced 2,4-dimethoxy-6-hydroxyacetophenone (77% yield), IV (76% yield) and anisic acid (86% yield), and it can be deduced easily that hinokiflavone pentamethyl ether is constructed by condensation of these three fragments with loss of four molecules of water. Therefore, the structure of hinokiflavone must be represented by formula I. Now, it can be presumed that apigenin is a precursor in the biogenesis of hinokiflavone as well as in that of the other bisflavonoids such as ginkgetin and sciadopitysin.

Grateful acknowledgment is offered to Dr. T. Kariyone for his interest and encouragement.

PHARMACEUTICAL FACULTY
UNIVERSITY OF NAGASAKI YOSHIO FUKUI
NAGASAKI, JAPAN NOBUSUKE KAWANO

RECEIVED SEPTEMBER 11, 1959

(1) T. Kariyone and T. Sawada, *Yakugaku Zasshi*, **78**, 1020, 1023 (1958); *Chem. Abstr.*, **53**, 3203, 3204 (1959).

(2) N. Kawano, *Chemistry & Industry*, 368, 852 (1959).

(3) W. Baker, A. C. M. Finch, W. D. Ollis and K. W. Robinson, *Proc. Chem. Soc.*, 91 (1959).

(4) T. Kariyone, N. Kawano and H. Miura, *Yakugaku Zasshi*, **79**, 1182 (1959).