As an analogous nitro-dealkylation, an anomalous nitration (nitro-dealkylation and nitro-deacylation) in polyalkylacyl-benzene series was reviewed,[8] and, recently, Cambie reported that nitration of 12-acetyl ester (V) yields methyl 12,14-dinitrodehydroabietate (nitro-deacylation) and methyl 12-acetyl-13-nitrodeisopropyldehydroabietate (nitro-dealkylation).[3b] However, there is a difference in the relative positions of isopropyl and carbonyl between X (*meta*) and Cambie's substrate (V) (*ortho*). Furthermore, it is interesting that nitro-deacylation type reaction did not occur at C-8 in X.

Application of this nitration reaction to other systems and under different conditions is being examined.

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[8] D.V. Nightingale, *Chem. Rev.*, **40**, 117 (1947).
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Synthesis of (±)-Fukugetin Heptamethyl Ether

In recent years, new biflavonoids having a carbon-carbon linkage between ring C and ring A′ have been found in the heartwood and bark of Guttiferae plants.[1]

Fukugetin is a flavonoid pigment occurring in the bark of *Garcinea spicata* HOOK. f. (Guttiferae). The structure, which has been under investigation for several decades, has recently been shown to be 3-luteolin-(8″)-yl-naringenin (I).[2] We now report the total synthesis of (±)-fukugetin heptamethyl ether (II) for the structure confirmation.

The first step of the synthesis was chloromethylation of 2-hydroxy-4,6-dimethoxyacetophenone (III) with chloromethyl methyl ether in acetic acid to prepare a chloromethylacetophenone derivative (IV), mp 133—135° (decomp.) (57%). The position of the chloromethyl group in IV was established by the fact that palladium charcoal-catalyzed hydrogenolysis of IV gave the known 2-hydroxy-4,6-dimethoxy-3-methylacetophenone (V).[3] IV was converted to a cyanomethyl compound (VI), mp 156—157° and then to a 3,4-dimethoxybenzoylester (VII), mp 202—203°. VII was rearranged with potassium hydroxide in pyridine (Baker–Venkataraman rearrangement) to produce a diketone (VIII), mp 180—182°. Treatment of VIII with sulfuric acid–acetic acid–water afforded 3′,4′,5,7-tetramethoxyflavon-(8)-yl-acetic acid (IX), mp 276—278° (84%).

Ketoflavone (X), a key intermediate for the synthesis of II, was shown to be obtained conveniently by the Fries rearrangement of a ester (XI), readily obtainable from the flavonylacetic acid (IX) and phloroglucinol dimethyl ether (XII) by means of triphenylphosphine-

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[1] *a*) C.G. Karanjgaokar, P.V. Radhakrishnan, and K. Venkataraman, *Tetrahedron Letters*, **1967**, 3195; *b*) B. Jackson, H.D. Locksley, F. Scheinman, and W.A. Wolstenholme, *J. Chem. Soc.* (*C*), **1971**, 3791.
[2] M. Konoshima, Y. Ikeshiro, A. Nishinaga, T. Matsuura, T. Kubota, and H. Sakamoto, *Tetrahedron Letters*, **1969**, 121.
[3] F.H. Curd and A. Robertson, *J. Chem. Soc.*, **1933**, 437.

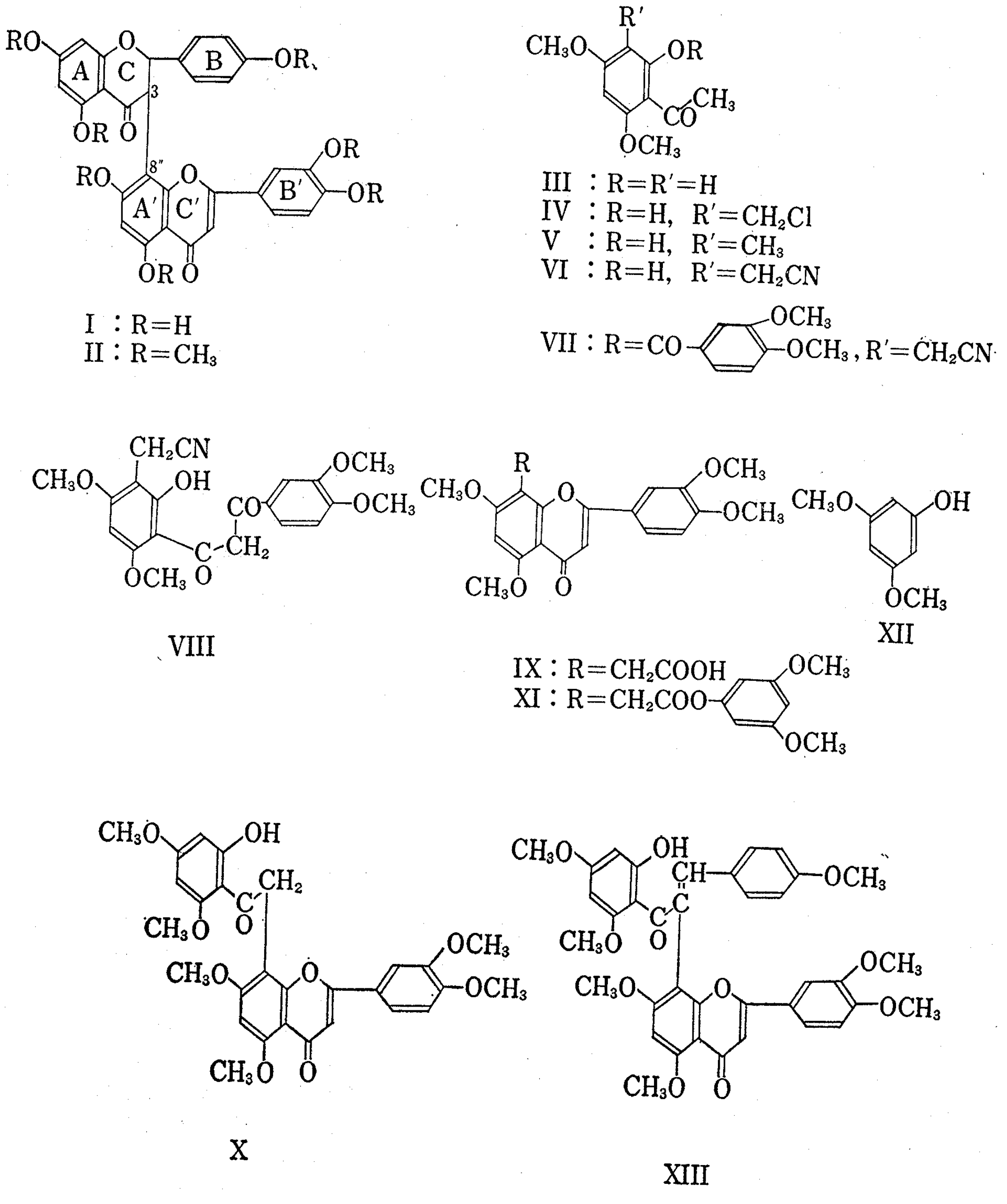

Chart 1

tetrachloromethane-*tert* organic base.[4] Thus, the acid (IX), the phenol (XII), triphenylphosphine, tetrachloromethane and triethylamine were refluxed together in chloroform for one hr to afford the ester (XI), mp 196—197° (42%), which was left standing with aluminum chloride in nitromethane at 0—5° for 48 hr (Fries rearrangement). After usual work-up the subsequent purification of the product was achieved through silica gel chromatography using chloroform as solvent to yield the ketoflavone (X) on concentration of the elute as colorless prisms, mp 233—234° (lit., mp 220—221° [2]) (41%). $FeCl_3$ test: violet brown and Mg+HCl test: red.

Condensation of the ketoflavone (X) with anisaldehyde in the presence of potassium hydroxide gave a chalcone (XIII), mp 135—137° (lit., 134—136°,[2] 130° [5]) in a low yield.

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[4] J.B. Lee, *J. Am. Chem. Soc.*, **88**, 3440 (1966); L.E. Barstow and V.J. Hruby, *J. Org. Chem.*, **36**, 1305 (1971), and related literatures.

[5] B.S. Joshi, V.N. Kamat, and N. Viswanathan, *Phytochemistry*, **9**, 881 (1970).

$FeCl_3$ test: dark brown, Mg+HCl test: red and $SbCl_5$ in CCl_4 test⁶⁾: intense red. The chalcone was finally cyclized by boiling with 2.5% sulfuric acid in acetic acid for 10 min to give the flavonylflavanone (II) as colorless needles from methanol, mp 212—213° (lit., 210°,⁵⁾ 212—213° ⁷⁾). $FeCl_3$ test: negative and Mg+HCl test: red. On the basis of melting points, mixed melting points and spectral data of infrared (IR) (Nujol) and nuclear magnetic resonance (NMR) ($CDCl_3$), the ketoflavone (X) and the flavonylflavanone (II) were shown to be identical, respectively, with the ketoflavone and (±)-fukugetin heptamethyl ether obtained from natural sources. All compounds gave satisfactory elemental analyses.

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6) G.B. Marini-Bettolo and A. Ballio, *Gazz. Chim. Ital.*, **76**, 410 (1946) [*C. A.*, **41**, 6565 (1947)].
7) A. Pelter, R. Warren, K.K. Chexal, B.K. Handa, and W. Rahman, *Tetrahedron*, **27**, 1625 (1971).