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INTEGRIAMIDE[1]

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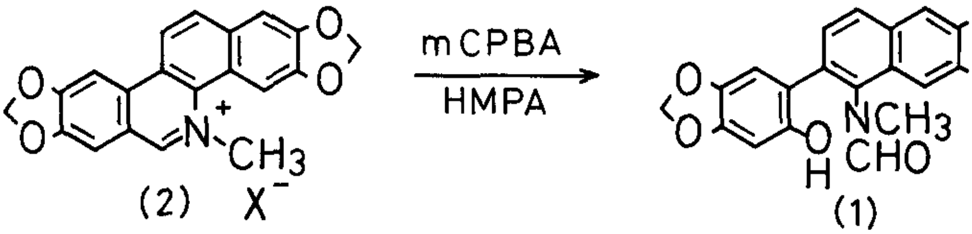
Abstract —— The structure of integriamide was established by preparing it due to the Baeyer-Villiger like oxidation of an immonium group of avicine.

In the course of studies on the chemical constituents of *Rutaceous* plants, we have isolated a new amide (1) from root-xylem of *Xanthoxylum integrifoliolum* (Merr.) Merr. (*Fagara integrifoliola* Merr.) [a Formosan *Rutaceous* plant, Japanese name; newata-no-ki][2] as a minor component together with other eighteen constituents and designated it as integriamide (1). In this report, we wish to report its structural establishment.

Integriamide (1) was obtained as colorless prisms, mp 302-304° ($CHCl_3$-MeOH), [IR ν (KBr): 1657 cm^{-1}] in 0.00021 % yield. In the nuclear magnetic resonance (NMR) spectrum [($CDCl_3 + CD_3OD$) δ] it shows a formyl proton [8.10(1H, s)] and two methylenedioxy groups [5.91 and 6.07(each 2H, s)] along with other signals [3.01(3H, s, NCH_3), 6.48, 6.53, 7.02, and 7.20(each 1H, s, arom. H), 7.28 and 7.74(each 1H, d, J=8.5 Hz, arom. H)]. In the previous papers,[3] we reported natural occurrence of new amide derivatives which were supposed to be formed by the Baeyer-Villiger like oxidation of an immonium group present in quaternary benzo[c]phenanthridine alkaloids. The fact that the signal pattern of the NMR spectrum of integriamide (1) is resemble to those of these new amides suggested that integriamide (1) is the oxidation product of avicine (2) which also occurred in a natural source.[4] This consideration led us to try the Baeyer-Villiger like oxidation of avicine (2).

Avicine (2) hydroxide which was obtained from avicine (2) sulfate[5] was dissolved in hexamethylphosphoric triamide (HMPA). After addition of a slight excess of trifluo-



roacetic acid, the solution was treated with m-chloroperbenzoic acid (mCPBA) at room temperature for 1 hr to give colorless prisms, mp 294-296° ($CHCl_3$-MeOH) in 79.0 % yield. The synthetic material was completely identical with the sample of naturally occurring integriamide (1) with respect to IR spectrum, TLC, and the mixed melting point. This result unambiguously shows that integriamide should be depicted by the formula (1).

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