m/e 363 ($C_{21}H_{31}O_5$) produced by this cleavage. In addition, we also find fragments at *m/e* 345 ($C_{21}H_{29}O_4$, 363-H_2O, m* 328.0), 327 ($C_{21}H_{27}O_3$, 345-H_2O, m* 310.2), 300 ($C_{19}H_{24}O_3$), all of which constitute characteristic fragments obtained with crustecdysone[5,11]. These and other significant peaks are reproduced in Table I.

On the basis of the spectroscopic data and melting points, commisterone (mp 146–151°) is not identical with any of the related compounds with molecular formula of $C_{27}H_{44}O_7$, with insect-moulting properties so far reported: crustecdysone (I), mp 235–236°[7], 22-isocrustecdysone, mp 259–260°[9], pterosterone, mp 229–230°[10], inokosterone, mp 255 (decomp.)[12], and ponasterone C, mp 270–272°[13]. Pterosterone[10] and ponasterone C[13] would be excluded since they give doublets at 9.00 (J = 6, pyridine), while commisterone as also crustecdysone[14] give singlets at 8.91[15] and 8.87[16] respectively.

Comparison of the IR-spectrum of commisterone with that of crustecdysone[5] in KBr shows essential identity in the region 400–1500 cm^{-1} but great dissimilarity in the fingerprint region. Similarly, comparison of the NMR-spectra of the 2 compounds shows close resemblance but not identity of the resonance signals of principal groups (Table II).

From the foregoing information, we infer that commisterone has the same skeletal and side chain structure as crustecdysone and must be stereoisomeric with it. Work is now in progress on the stereochemistry of commisterone[17].

Zusammenfassung. Aus den zerkleinerten Blättern von *Cyanotis vaga* (Commelinaceae) wurde durch Benzolextraktion und Chromatographie mit Silikagel eine neue Substanz isoliert: $C_{27}H_{44}O_7$ (Sp. 146–151°), die nach den spektrometrischen Daten (IR, NMR, UV, MS) mit dem Insektenhormon Ecdysteron stereoisomer ist.

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National Research Council of the Philippines Diliman, Q. C. (Philippines), 6 April 1970.

Table II. Proton chemical shifts of commisterone and crustecdysone in τ values, relative to TMS

Compound	C-18, C-19	O-H	H-7	C-26,
Crustecdysone[14,16]	9.18 (3 H) 9.10 (3 H)	5.43 (1 H) 5.66 (2 H) 5.79 (1 H) 5.91 (1 H) 6.50 (1 H)	4.35	8.87 (9 H)
Commisterone[15]	9.21 (3 H) 9.15 (3 H)	5.29 (1 H) 5.56 (1 H) 5.64 (2 H) 5.85 (1 H) 6.41 (1 H)	4.32	8.91 (9 H)

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[15] In dimethylsulfoxide.
[16] In hexadeuterodimethylsulfoxide containing deuterochloroform, using hexamethyldisiloxane (HMDS) as internal standard. Value given has been corrected to give chemical shift relative to tetramethylsilane.
[17] We wish to express our gratitude to the National Research Council of the Philippines for supporting this work.
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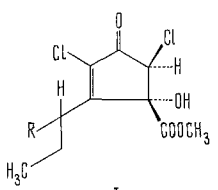
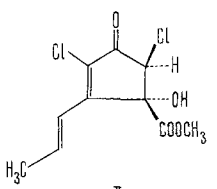
The Total Synthesis of Racemic Cryptosporiopsin, a Fungitoxic Antibiotic

Synthesis of a racemic dihydro derivative (I, R=H) of the fungitoxic metabolite cryptosporiopsin II[1,2], by a four-step sequence involving skeletal rearrangement of *meta-n*-propyl phenol through the agency of alkaline hypochlorite, has recently been reported[3]. Conversion of synthetic dihydrocryptosporiopsin to racemic cryptosporiopsin has now been realized, constituting a total synthesis of the antibiotic.



I



II

Synthetic dihydrocryptosporiopsin[3] was converted in 98% yield to the crude crystalline allylic bromide I (R=Br) by the WOHL-ZIEGLER reaction[4]. A sample, recrystallized from cyclohexane, had mp 116–121°; it displayed a molecular ion at *m/e* 344 (with appropriate isotope peaks[5]) in the mass spectrum, and UV λ_{max} (EtOH) at 252 nm (ε 7500).

Reaction with dimethylformamide[6] proved to be the most effective method for converting I (R=Br) to racemic cryptosporiopsin. Attempts to effect the required dehydrobromination under a variety of other conditions were attended by extensive decomposition. Thus, a solution of I (R=Br) (1.03 m*M*) in dry dimethylformamide (5 ml) was heated at 135–140 °C for 20 min in a nitrogen atmosphere. Preparative layer chromatography of the

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product on silica gel plates afforded a 17% yield of racemic cryptosporiopsin[7], whose identity was established by comparison of IR- (CCl_4), UV-, NMR- and mass-spectra, as well as TLC behavior, with those of natural cryptosporiopsin.

The synthetic racemic antibiotic was assayed for its activity against sporangial germination of *Phythophthora infestans*[8] in aqueous solution. Germination was almost completely prevented at a concentration of 12.5 µg/ml. Natural (dextrorotatory) cryptosporiopsin showed about the same degree of inhibition at 6.25 µg/ml. (Control; 70% germination.) These results suggest that the dextrorotatory enantiomer alone is responsible for the observed inhibition of sporangial germination.

Résumé. L'antibiotique cryptosporiopsine, produit métabolique de *Sporormia affinis* ainsi que d'une espèce de *Cryptosporiopsis* a été synthétisé à partir de la dihydrocryptosporiopsine synthétique.

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[7] The yield was 20% based on unrecovered starting material.

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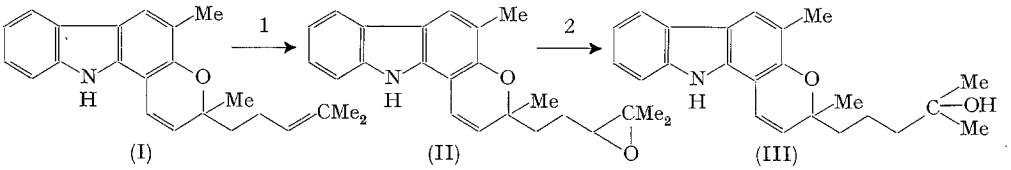
Terpenoid Alkaloids from *Murraya koenigii* Spreng. IV[1] Structure and Synthesis of Mahanimbinine[2]

Murraya koenigii Spreng. has proved to be a rich source of terpenoid carbazole alkaloids. Up to date 12 of these have already been reported[3–11]. The present communication describes the structure and synthesis of one more base – a congener of mahanimbine (I) from the leaves of this plant.



Reagents: 1, *m*-Chloroperbenzoic acid. 2, $LiAlH_4$

The alkaloid named mahanimbinine, $C_{23}H_{27}NO_2$ (M^+, 349), mp 179°; ν_{max} ($CHCl_3$) 3580 (OH), 3450 (NH), 1630 and 1600 cm^{-1} (unsaturation and aromatic system) had an UV-spectrum, λ_{max} (EtOH), 238, 288, 329, 344, and 359 nm (log ε 4.64, 4.61, 3.83, 3.87, and 3.82 respectively). The NMR-spectrum ($CDCl_3$) showed the following signals: τ 8.80, *s*, 6, $-O-C(CH_3)_2$; 8.59, *s*, 3, $-O-\underset{|}{C}-CH_3$; 7.67, *s*, 3, ar. CH_3; 8.14–8.65, *m*, 6, methylene protons; 4.42, *d* (J 10 Hz), 1, olefinic *H*; 3.40, *d* (J 10 Hz), 1, benzylic methine *H*; 2.35, *s*, 1, 4-*H*; 2.07, *m*, 1, 5-*H*. There were 3 more aromatic protons in the region 2.55–2.94 τ.

The mass spectrum of the base showed, apart from the molecular ion peak, M^+ 349, abundant ions at *m/e* 334, 331, 330, 316, 276, 275, 261, 260, 249, 248 (base peak), 247, 234, 218, 210, 204, and 180. The combined data and particularly the correspondence of the base peak with that obtained from mahanimbine[10] (I), the absence of olefinic protons in the side-chain, the presence of a –OH group in the IR-spectrum and the M^+ at *m/e* 349 (18 units higher than that of mahanimbine) led to constitution (III) for mahanimbinine.

This was confirmed by its synthesis as follows: (+)-mahanimbine (I) stirred 3 h at room-temperature with m-chloroperbenzoic acid in dry ether gave the epoxy compound (II) as the major product. Reduction of (II) with $LiAlH_4$ followed by purification of the product on silica-gel column gave a compound in 30% yield, mp 148° (benzene) which on the basis of elemental analysis, TLC, UV-, IR- and NMR-spectra, was identical, apart from its partial racemic nature, with the natural product. Since the synthesis of mahanimbine has already been reported[1], this constitutes the total synthesis of the new base. The partial racemization of this base as well as of some other members in this series will be discussed in a subsequent communication.

Zusammenfassung. Die Struktur (III) des Mahanimbinins, eines Verwandten des Mahanimbins aus den Blättern von *Murraya koenigii* Spreng., ist spektroskopisch und durch Synthese aufgeklärt worden.

S. P. Kureel, R. S. Kapil and S. P. Popli

Central Drug Research Institute, Lucknow (India), 20 April 1970.

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