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Cannabichromevarin and Cannabigerovar, Two New Propyl Homologues of Cannabichromene and Cannabigerol¹⁾

Two new neutral cannabinoids, cannabichromevarin and cannabigerovar, were isolated from the "Meao variant," Thailand Cannabis and their structures were determined to be the homologues of cannabichromene and cannabigerol which have a propyl side-chain, respectively, on the basis of spectral and chemical evidences.

In recent years much research has been directed towards the isolation and identification of propyl homologues of cannabinoids from local Cannabis,²⁻⁵⁾ such as cannabidivarin (CBDV),²⁾ tetrahydrocannabivarin (THCV)³⁾ and cannabivarin (CBV).⁴⁾

We now wish to describe the isolation and the structure elucidation of two new neutral cannabinoids, the homologues of cannabichromene (CBC) and cannabigerol (CBG) which have a propyl side-chain from the "Meao variant," Thailand Cannabis.

After the benzene percolate of the leaves harvested in the vegetative phase was decarboxylated by heating at 160° for 20 min, the neutral cannabinoids fraction was repeatedly column-chromatographed over silica gel with solvent benzene or benzene-hexane-diethyl amine (20:10:1) to give four propyl homologues besides the usual neutral cannabinoids. Two propyl homologues were identified with CBDV²⁾ and THCV.³⁾ The third new cannabinoid (I) gave a brownish red color with diazotized benzidine and the physical constants were as follows; I, C₁₉H₂₆O₂ (Calcd.: 286.193, Found: 286.191), colorless oil, $[\alpha]_D^{25} +58^\circ$ ($c=4.28$, CHCl₃), UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (ϵ): 281 (7577), 289 (7192, shoulder), IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3320 (OH), 1623, 1576 (C=C), 1430, 1090, 1040, NMR (in CDCl₃) δ : 0.92 (3H, triplet, ω -CH₃), 1.26 (3H, singlet, C₁₀-CH₃), 1.58, 1.67 (3H $\times$ 2, each singlet, C_{8,9}-CH₃), 2.45 (2H, triplet, α -CH₂), 5.10 (1H, triplet, C₆-H), 5.45 (1H, doublet, $J=10$ Hz, C₂-H), 6.12, 6.26 (1H $\times$ 2, each singlet, C_{3',5'}-H), 6.62 (1H, doublet, $J=10$ Hz, C₁-H), Mass Spectrum m/e : (M⁺) 286 (7.2%), 271 (3.8%), 204 (15.8%), 203 (100%), 187 (3.3%), 174 (12.8%).

The nuclear magnetic resonance (NMR) is similar to CBC^{6,7)} except for the methylene region and the mass spectrum (MS) has a characteristic fragmentation pattern of CBC,⁷⁾ with the differentiation that all masses are 28 unit (C₂H₄) smaller. All of the properties of I

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- 7) U. Claussen, F.V. Spulak, and F. Korte, *Tetrahedron*, 22, 1477 (1966).

mentioned above strongly confirm that I is cannabichromevarin (CBCV), the propyl homologue of CBC.

The last cannabinoid (II) gave an orange color with diazotized benzidine and a violet color with Beam's test.⁸⁾ The physical constants are as follows; II, $C_{19}H_{28}O_2$ (Calcd.: 288.213, Found: 288.209), mp 52–53°, colorless prisms, UV λ_{max}^{MeOH} nm (ϵ): 273 (923), 280 (878, shoulder), IR ν_{max}^{KBr} cm^{-1} : 3420 (OH), 1639, 1583 (C=C), 1520, 1448, 1150, 1040, 1017, NMR (in $CDCl_3$) δ : 0.92 (3H, triplet, ω - CH_3), 1.60, 1.68, 1.81 (3H $\times$ 3, each singlet, $C_{8,9}$ and 10 - CH_3), 2.47 (2H, triplet, α - CH_2), 3.42 (2H, doublet, $J=6$ Hz, C_1 -H), 4.90–5.40 (3H, multiplet, $C_{2,6}$ -H and OH), 6.27 (2H, singlet, $C_{3,5}$ -H), Mass Spectrum m/e : (M^+) 288 (23.8%), 273 (2.3%), 219 (32.3%), 203 (38.8%), 165 (100%).

Each aspect of II suggests that II must be cannabigerovarín (CBGV), the propyl homologue of CBG. II was identified with CBGV synthesized by the modified Mechoulam's method⁹⁾ (mixed mp: 53–54°, UV, IR, NMR and MS).

The neutral cannabinoids of the propyl homologues such as CBGV, CBDV, THCV and CBCV should exist as the cannabinoid acids in intact *Cannabis* and the studies on these cannabinoid acids are in progress.

cannabichromevarin (CBCV)

cannabigerovarín (CBGV)

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Structure and Absolute Stereochemistry of Dihydroflorilenalin, A New Sesquiterpene Lactone from Florida *Helenium autumnale* L.

The structure and absolute stereochemistry of dihydroflorilenalin, a new guaianolide isolated from *Helenium autumnale* L., have been determined on the basis of physicochemical data, chemical transformation, and X-ray crystallographic analysis.

The isolation and structure determination of a new guaianolide, florilenalin (I), from Florida *Helenium autumnale* L. were reported in a previous communication.¹⁾ Further investigation of the polar terpenoid fraction from the chloroform extract of this same plant has

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