Cannabichromevarin and Cannabigerovarin, Two New Propyl Homologues of Cannabichromene and Cannabigerol

Two new neutral cannabinoids, cannabichromevarin and cannabigerovarin, 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, such as cannabidivarin (CBDV), tetrahydrocannabinovarin (THCV) and cannabivarin (CBV).

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°C 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 CBDV and THCV. The third new cannabinoid (I) gave a brownish red color with diazotized benzidine and the physical constants were as follows; I, C_{19}H_{22}O_2 (Calcd.: 286.193, Found: 286.191), colorless oil, [α]_D^20 +58° (c=4.28, CHCl_3), UV 𝜆_{max} (nm) (e): 281 (7577), 289 (7192, shoulder), IR 𝜈_{max} (cm⁻¹): 3320 (OH), 1628, 1576 (C=C), 1430, 1090, 1040, NMR (in CDCl_3) δ: 0.92 (3H, triplet, −CH_3), 1.26 (3H, singlet, C_9−CH_3), 1.58, 1.67 (3H×2, each singlet, C_9−CH_3), 2.45 (2H, triplet, −CH_2−), 5.10 (1H, triplet, −CH−), 5.45 (1H, doublet, J=10 Hz, C_9−H), 6.12, 6.26 (1H×2, each singlet, C_8,CH−), 6.62 (1H, doublet, J=10 Hz, C_1−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 except for the methylene region and the mass spectrum (MS) has a characteristic fragmentation pattern of CBC, with the differentiation that all masses are 28 unit (C_2H_4) smaller. All of the properties of I

mentioned above strongly confirm that I is cannabinoremarvarin (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\(_{16}\)H\(_{28}\)O\(_8\) (Calcd.: 288.213, Found: 288.209), mp 52—53\(^\circ\), colorless prisms, UV \(\lambda_{\text{max}}^{\text{nm}} (\varepsilon)\): 273 (923), 280 (878, shoulder), IR \(\nu_{\text{max}}^{\text{cm}^{-1}}\): 3420 (OH), 1639, 1563 (C=C), 1520, 1448, 1150, 1040, 1017, NMR (in CDCl\(_3\) \(\delta\): 0.92 (3H, triplet, \(\delta\)-CH\(_3\)), 1.60, 1.68, 1.81 (3H×3, each singlet, C\(_{9,9'}\)=C\(_{10}\)-CH\(_3\)), 2.47 (2H, triplet, \(\alpha\)-CH\(_2\)), 3.42 (2H, doublet, \(J=6\) Hz, C\(_4\)-H), 4.90—5.40 (3H, multiplet, C\(_2,6\)-H and OH), 6.27 (2H, singlet, C\(_3,6\'),\(\alpha\')-\)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 cannabinigerovarin (CBGV), the propyl homologue of CBG. II was identified with CGBV synthesized by the modified Mechoulam's method\(^9\) (mixed mp: 53—54\(^\circ\), UV, IR, NMR and MS).

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

\[\text{cannabinoremarvarin (CBCV)}\]

\[\text{cannabinigerovarin (CBGV)}\]

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Structure and Absolute Stereochemistry of Dihydroflorilalenin, A New Sesquiterpene Lactone from Florida \textit{Helennium autumnae L.}

The structure and absolute stereochemistry of dihydroflorilalenin, a new guaianolide isolated from \textit{Helennium autumnae 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, florilalenin (I), from Florida \textit{Helennium autumnae L.} were reported in a previous communication.\(^1\) Further investigation of the polar terpenoid fraction from the chloroform extract of this same plant has