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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8) R. Mechoulam, Z. Ben-Zvi, and Y. Gaoni, *Tetrahedron*, **24**, 5615 (1968).

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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

1) K.H. Lee, T. Ibuka, M. Kozuka, A.T. McPhail, and K.D. Onan, *Tetrahedron Letters*, **1974**, 2287, and references cited therein.

led to the isolation and characterization of an additional new sesquiterpene lactone, dihydroflorilenalin (II), which represents a structural variant in the lactone ring.

Dihydroflorilenalin (II), $C_{15}H_{22}O_4$, was isolated as a minor constituent in the form of colorless needles, mp 208° , from the mother liquor after the removal of florilenalin (I) by repeated silica gel column chromatography. The infrared (IR) spectrum (Nujol) of II showed, in addition to the presence of a γ -lactone ring (1740 cm^{-1}), two hydroxyl groups (3443 and 3343 cm^{-1}) which were confirmed by the presence of the prominent peaks at m/e 248 [$M-18$ (H_2O)] and 230 [$M-18$ (H_2O) -18 (H_2O)] in the mass spectrum. The nuclear magnetic resonance spectrum (NMR) (60 MHz) signal of these two hydroxyl protons appeared at *ca.* δ 3.47 as multiplets which disappeared upon addition of D_2O . Dihydroflorilenalin lacks the α -methylene group present in the lactone ring of florilenalin and proves to be the corresponding α -methyl- γ -lactone. Three-proton methyl group signals are found at δ 1.12 (C-11 methyl, d, $J=7\text{ Hz}$) and 1.13 (C-4 methyl, s). The lactonic proton at C-8 is seen as a multiplet at δ 4.58. The one-proton multiplet at δ 4.13 is assigned to the C-2 hydroxyl group proton since it is shifted down-field to δ 5.14 (overlapped m) upon acetylation with acetic anhydride in pyridine.²⁾ The remaining two low-field one-proton singlets which occur at δ 5.03 and 5.13 are comparable to those found in florilenalin (I) and consequently are assigned to the terminal methylene grouping at C-10.

I : florilenalin

II : R=H, dihydroflorilenalin
III : R=COCH₃

Considerations resulting from the biogenetic implications observed in the co-occurrence of florilenalin (I) and dihydroflorilenalin (II), coupled with the evidence presented above, suggested structure (II) for the latter, *i.e.* 11,13-dihydroflorilenalin. To further substantiate this, the identity of II was established by direct comparison (mixed melting point, thin-layer chromatography, and superimposable IR and mass spectra) with a synthetic sample of 11,13-dihydroflorilenalin prepared by the sodium borohydride reduction of florilenalin.

In order to establish the stereochemistry at C-11 and to obtain details of the molecular conformation, a single-crystal X-ray analysis of II was undertaken. Crystals are orthorhombic, space group $P2_12_12_1$, $a=12.89$ (1), $b=19.54$ (1), $c=5.47$ (1) Å, $z=4$. One octant of three-dimensional intensity data, recorded on an Enraf-Nonius CAD 3 diffractometer (Ni-filtered $Cu-K\alpha$ radiation, $\lambda=1.542$ Å) operating in the θ - 2θ scanning mode,³⁾ yielded 1118 reflections with $I>2.0\sigma(I)$. The structure was solved by direct phase-determining procedures using MULTAN⁴⁾ and 251 reflections for which $|E|>1.22$. Atomic parameters (anisotropic C, O; isotropic H) were refined by full-matrix least-squares calculations to R 0.0562. The absolute configuration was then established by including the anomalous scattering correction

2) This monoacetate, $C_{17}H_{24}O_5$, was obtained as an oil and had spectral properties all in accord with the assigned structure (III).

3) For further details see, D.L. McFadden, and A.T. McPhail, *J. Chem. Soc., Dalton*, **1974**, 363.

4) G. Germain, P. Main, and M.M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

Individual bond lengths and valency angles lie in the normal ranges. Endocyclic torsion angles⁶⁾ are shown in the Figure 1. The cyclopentane and γ -lactone rings adopt envelope conformations with C-5 and C-7 the out-of-plane atoms, respectively. Analysis of the cycloheptane ring torsion angles in terms of a chair conformation in which the C₂ axis bisects the C-7, C-8 bond and passes through C-1, and in terms of a twist-chair (C_s) form with C-7 as the axis carbon yields a $\sum_2/(\sum_2 + \sum_s)$ ratio⁷⁾ of 0.48. Thus the ring adopts a conformation intermediate between the more frequently encountered twist-chair and the less-favored chair forms.

Fig. 1. Endocyclic Torsion
Angles (deg.) in Di-
hydroflorilenalin (II)

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5) H. Hope and U. de la Camp, *Nature*, **221**, 54 (1969).

6) For a definition of the sign convention used see, W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).

7) A.T. McPhail and G.A. Sim, *Tetrahedron*, **29**, 1751 (1973).