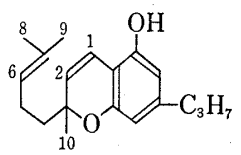
mentioned above strongly confirm that I is cannabichromevarin (CBCV), the propyl homologue of CBC.

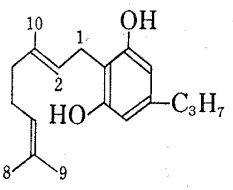
The last cannabinoid (II) gave an orange color with diazotized benzidine and a violet color with Beam's test.[8] The physical constants are as follows; II, $C_{19}H_{28}O_2$ (Calcd.: 288.213, Found: 288.209), mp 52—53°, colorless prisms, UV λ_{max}^{MeOH} nm (ε): 273 (923), 280 (878, shoulder), IR ν_{max}^{KBr} 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×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 cannabigerovarin (CBGV), the propyl homologue of CBG. II was identified with CBGV synthesized by the modified Mechoulam's method[9] (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)



cannabigerovarin(CBGV)

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8) R. Mechoulam, Z. Ben-Zvi, and Y. Gaoni, *Tetrahedron*, **24**, 5615 (1968).
9) R. Mechoulam and Y. Yagen, *Tetrahedron Letters*, **1969**, 5349.

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

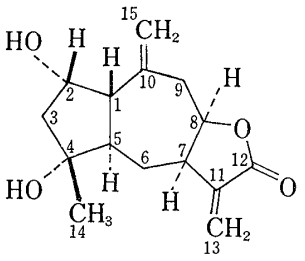
The structure and absolute stereochemistry of dihydroflorilenalin, a new guaianolide isolated from *Helenium autumnale* L., have been determined on the basis of physicochemical data, chemical transformation, and X-ray crystallographic analysis.

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

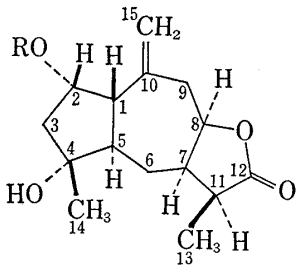
1) K.H. Lee, T. Ibuka, M. Kozuka, A.T. McPhail, and K.D. Onan, *Tetrahedron Letters*, **1974**, 2287, and references cited therein.

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 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=$COCH_3$

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) A, z=4. One octant of three-dimensional intensity data, recorded on an Enraf-Nonius CAD 3 diffractometer (Ni-filtered Cu-K_α radiation, λ=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 MULTAN[4] 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).

for oxygen[5] into the structure-factor calculations. R was 0.0560 for the enantiomer represented by (II) whereas for the mirror image it was 0.0565, thereby confirming that (II) correctly represents the absolute stereochemistry. This conclusion is entirely consistent with the absolute configuration derived earlier for florilenalin (I) using the anomalous scattering of iodine.[1] Further least-squares refinement of the atomic parameters reduced R to its present value of 0.0504.

Individual bond lengths and valency angles lie in the normal ranges. Endocyclic torsion angles[6] 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 C_2 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 $\sum_2/(\sum_2+\sum_s)$ ratio[7] of 0.48. Thus the ring adopts a conformation intermediate between the more frequently encountered twist-chair and the less-favored chair forms.

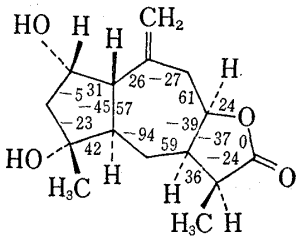


Fig. 1. Endocyclic Torsion Angles (deg.) in Dihydroflorilenalin (II)

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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).