configuration for **1**. In fact the spectra were differentiated only by the expected[3] changes in the shifts of the carbons influenced by the different orientation of the acetoxy group in 12.

The structure of 12, 18-diepi-scalaradial (**3**) is based on the following evidence: $C_{27}H_{40}O_4$; UV (MeOH) 228 nm (ε 10,700), IR ($CHCl_3$) 2840, 1735, 1715, 1680 and 1640 cm^{-1}; PMR (C_6D_6) 9.96 (H-19, 1 H, d, J = 2.5 Hz), 9.22 (H-20, 1 H, s), 6.34 (H-16, 1 H, m), 5.02 (H-12, 1 H, dd, J = 4, 10 Hz), 3.66 (H-18, 1 H, d, J = 2.5 Hz), 1.76 (CH_3–CO, 3 H, s) δ; MS 428 (M^+, 2%), 368 (40%), 340 (92%), 258 (32%), 205 (67%), 191 (100%), 137 (50%), 123 (58%). The above spectral data are quite similar to those of **2**, with the exception that, in the PMR of **3**, the signals assigned to H-18 and H-19 are located downfield and, also, they show a smaller coupling constant. On the basis of this evidence, we conclude that in **3** the simple aldehyde group in 18 is axially oriented as in structurally related compounds[7]. CMR spectra of **3** (table) confirmed the suggested structure (**3**) and allowed the determination of its stereochemistry.

The biological activities of those substances have not been investigated. However, it has been reported[8] that natural polycyclic dialdehydes are often substances showing strong antifeedant, antifungal, antiyeast and plant-growth regulatory activities.

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Cannabiripsol: A novel *Cannabis* constituent[1]

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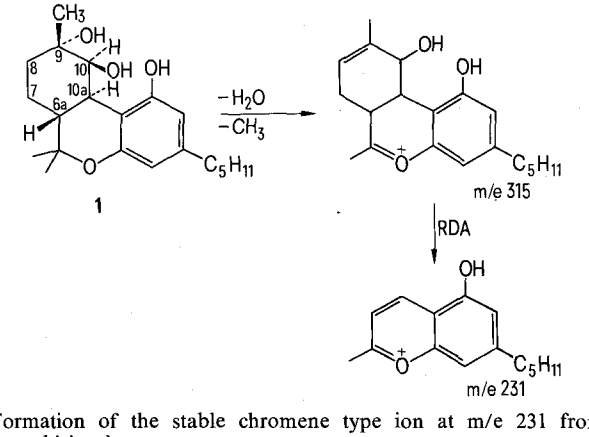
Summary. Cannabiripsol [(–)(6aR, 9S, 10S, 10aR)9, 10-dihydroxy-hexahydrocannabinol] (**1**), a new cannabinoid was isolated from a South African Cannabis variant. The structure was determined by spectral means and by synthesis.

In previous communications[3,4] we have reported the isolation and structure determination of (+)-Cannabitriol[3] and other polyhydroxylated cannabinoids[4] from *Cannabis*. In this communication we wish to report the isolation and characterization of a new polyhydroxylated cannabinoid.

Combined GC-MS analysis of the trimethyl silyl derivatives of a polar fraction obtained from the hexane extract of a South African *Cannabis* variant revealed the presence of a new phenolic constituent with relative retention time 0.24[5]. This compound (**1**) was isolated by repeated chromatography on silica gel and polyamide and was obtained as a light yellow oil, with R_f 0.38 [silica gel G, ethylacetate-chloroform (1:1)], $[\alpha]_D^{25}$ –122° and molecular formula $C_{21}H_{32}O_4$ (HRP-MS). IR ν_{max}^{KBr} 3350-3200 (br. OH), 2920 (CH), 1630 and 1585 (C=C_{Ar}) cm^{-1} and no carbonyl absorbance was observed; UV λ_{max}^{MeOH} 227 (log ε 3.39) and 286 (log ε 2.90) nm.

The ^{1}HNMR (60 MHz, $CDCl_3$) showed peaks characteristic for the olivetol moiety of a cannabinoid: the aromatic protons were observed at δ 6.26 (br. s, 1 H) and δ 6.09 (br s, 1 H), and the terminal methyl group of the pentyl side chain at δ 0.89. In addition, peaks were found at δ 1.09 (s, 3 H), δ 1.34 (s, 3 H), and δ 1.39 (s, 3 H) for methyls on oxygenated carbon atoms. A peak at δ 4.83 (br s, 1 H) was assigned to a proton under a hydroxy group. The TMS derivative of **1** had mol.wt 564 indicating 3 hydroxy groups, while acetylation (acetic anhydride/pyridine) gave a diacetate indicating that 1 of the hydroxy groups is tertiary. The tertiary hydroxy was assigned to C_9 because there are 3 methyls on oxygen carrying carbons. The broad singlet at δ 4.83 indicates the secondary hydroxy is at C_{10}. However, **1** could not be oxidized with KIO_4 suggesting that if **1** is indeed a glycol, then the hydroxyl groups must be trans-diaxial.

The mass spectrum of **1** was in agreement with these findings since a peak was observed at m/e 231 ($C_{15}H_{19}O_2$). This peak is very characteristic for certain cannabinoids and the formation and structure of this ion has been studied extensively[6–8]. Loss of a methyl radical and a molecule of H_2O will result in an ion which easily can undergo a retro-Diels-Alder reaction resulting in a stable chromene type ion (figure).



Formation of the stable chromene type ion at m/e 231 from cannabiripsol.

These data suggested that the compound might be the dihydro-derivative of 9,10-dihydroxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol. Assuming that the stereochemistry at C 6a and C 10a is the same as in the naturally occurring Δ^9-THC, four stereoisomers should be considered.

Synthesis of these isomers showed that (−) (6aR, 9S, 10S, 10aR)-9,10-dihydroxy-hexahydrocannabinol was identical (^{1}HNMR, IR, MS, UV, R_f [α]) with the isolated compound. The synthesis of **1** was accomplished by epoxidation of (−) (6aR, 10aR)-Δ^9-THC-acetate followed by alkaline hydrolysis and isolation by repeated chromatography of the reaction mixture. This is the first report of the isolation of (−) (6aR, 9S, 10S, 10aR)-9,10-dihydroxy-hexahydrocannabinol from *Cannabis* which we named cannabiripsol.

Due to the stereochemistry of cannabiripsol and other cannabinoids such as Δ^9-THC the 'activity' of cannabiripsol should more nearly mimic that of Δ^9-THC type cannabinoids than that of other dihydroxylated cannabinoids. The pharmacological profile of cannabiripsol is currently being investigated.

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9 The synthesis and spectral characteristics of all isomers as well as full details on the isolation of (−) (6aR,9S,10S,10aR)-9,10-dihydroxyhexahydrocannabinol will be described elsewhere.

(−)-Maalian-5-ol, a new enantiomeric sesquiterpenoid from the liverwort *Plagiochila ovalifolia*

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Summary. A new enantiomeric sesquiterpene alcohol named (−)-maalian-5-ol was isolated from the liverwort, and the structure and absolute configuration was determined to be the stereostructure **I** by chemical and spectral evidence.

In the course of our investigation on terpenoids from the liverworts (Hepaticae), which form a unique group in the plant kingdom, several enantiomeric sesquiterpenoids[2] being antipodes to the normal ones from vascular plants were isolated along with several novel carbon skeletal sesquiterpenoids[3]. The present communication deals with the isolation and the structure determination of an additional new enantiomeric sesquiterpene alcohol, named (−)-maalian-5-ol, from the leafy liverwort, *Plagiochila ovalifolia* Mitt. belonging to the Plagiochilaceae in the Jungermannineae.

The liverwort (860 g), collected at Kuju in Kyushu and dried in the shade for a few days, was digested with methanol. The methanol solution, after being concentrated in vacuo, was then extracted with ether and the solvent was distilled out at reduced pressure to afford a viscous matter (10.2 g). Part of the extract (6.8 g) was chromatographed over silica gel with a mixed solvent of chloroform and ether (v/v, 5:1) to isolate the new sesquiterpene alcohol (150 mg) as a major constituent. Spectroscopic evidence showed that the compound, $C_{15}H_{24}O$ (M^+ 222.1990), $[\alpha]_D$ +106° (c 2.5, $CHCl_3$), was a saturated tricyclic sesquiterpene alcohol containing a cyclopropane ring [δ_{CDCl_3} 0.4-0.8 (2H, complex)] together with a tertiary hydroxyl group [ν_{CCl_4} 3625 and 3500 cm^{-1}; no signal between δ 3.0 and 4.5], a secondary methyl [δ 0.93 (3H, d, J=7.5)] and 3 tertiary methyls [δ 1.00, 1.05 and 1.10 (each 3H, s)]. This structure was supported by the off-resonance ^{13}C-NMR spectrum which showed 3 singlets (δ 17.6, 36.4 and 75.0), 3 doublets (δ 20.4, 32.9 and 34.1), 5 triplets (δ 16.9, 21.6, 30.0, 31.0 and 37.0) and 4 quartets (δ 16.5, 16.5, 23.4 and 31.0). The alcohol (120 mg) was dehydrated with $SOCl_2$ in pyridine to yield 2 kinds of hydrocarbons, which were, respectively, isolated as a less polar (40 mg) and a more polar (40 mg) product by means of preparative TLC over silica gel using hexane as a solvent. The spectral properties of the former (**II**), $C_{15}H_{24}$ (M^+ 204); ν_{CCl_4} 1230, 1140, 1070, 973 and 953 cm^{-1}; δ_{CDCl_3} 0.83, 0.99 and 1.09 (each 3H, s), 1.57 (3H, br.s), coincided with those of (−)-β-maaliene reported by Büchi et al.[4], and the latter (**III**), $C_{15}H_{24}$ (M^+ 204); ν_{CCl_4} 3060, 1650, 1210, 985, 955, 900 and 885 cm^{-1}; δ_{CDCl_3} 1.15 (3H, d, J=8.0), 1.14 (3H, s), 4.65 and 4.78 (each 1H, br.s), 5.20 (1H, d, J=4.0), did with those of (+)-selina-5,11-diene[4]. However, the optical rotations of both the sesquiterpene hydrocarbons (**II**, $[\alpha]_D$ +129° and **III**, $[\alpha]_D$ −145°) derived from