handled in the same manner. The samples were also analyzed for the presence of trichlorodibenzo-p-dioxins and dichlorodibenzo-p-dioxins possibly formed as a consequence of the irradiation. Analyses were carried out by mass fragmentography using an LKB 2091-B gas chromatograph-mass spectromer operating in the EI mode, equipped with an LKB 2130 computer system for data aquisition and calculation.

The results summarized in the figure indicate that TCDD disappearance is directly related to the total dose of radiation absorbed. Although these data are merely preliminary, it is also clear that the type of solvent used is important for the efficiency of the degradation process.

Since it is known that substances chemically related to TCDD retain a high degree of toxicity, an analysis was carried out in order to identify compounds other than TCDD, present in irradiated solutions. In all these samples, it was possible to detect trichloro- and dichloro-dibenzo-p-dioxins, suggesting that the degradation process occurs, at least in part, with the loss of chlorine atoms from the TCDD molecule. Further studies are in progress to verify the possible application of this method to degradation of TCDD in contaminated soil samples.

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(±)9,10-dihydroxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol and (±)8,9-dihydroxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol: 2 new cannabinoids from *Cannabis sativa* L.[1]

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Summary. The structures of 2 new polyhydroxylated cannabinoids, (±)9,10-dihydroxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol and (±)8,9-dihydroxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol, obtained from a hexane extract of an Indian *Cannabis* variant were determined by spectral means and correlation with cannabinol.

To date more than 50 cannabinoids, among which the psychotomimetic Δ^9-tetrahydrocannabinol have been isolated and/or detected in *Cannabis*[3]. In a previous communication from our laboratory[4] we have reported the isolation and structure elucidation of 2 new cannabinoids, namely (+)-cannabitriol and (−)-10-ethoxy-9-hydroxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol from a *Cannabis* extract. The presence of these hydroxylated cannabinoids and reports on polyhydroxylated cannabinoids as minor constituents of *Cannabis*[5-8] have stimulated our interest in the isolation and characterization of minor components of *Cannabis.*

Material and methods. A polar fraction obtained by silica gel column chromatography of the hexane extract of an Indian variant of *Cannabis sativa* L. showed the presence of 2 phenols; **1a** and **2a**, with R_f 0.58 and 0.51 (EtOAc-$CHCl_3$; 1:1). These compounds were only observed in the GC as their TMS derivatives, **1b** and **2b** (RRT 0.28 and 0.35, respectively)[9]. Separation of the 2 compounds was achieved by repeated chromatography. For details on instrumentation as well as preparation of different derivatives see Elsohly et al.[4].

Results and discussion. Compound **1a**, R_f 0.58, $C_{21}H_{30}O_4$ (HRP-MS), was obtained as a yellow optically inactive oil. The IR-spectrum showed bands at ν_{max} ($CHCl_3$) 3500–3150 (br.) (OH) and 1620 cm^{-1} (C=C, Ar) and no carbonyl absorption. The UV-spectrum was characteristic for a styrene chromophore[10], λ_{max} MeOH 302 (sh, log ε 3.76) nm, 276 (3.88) and 228 (2.92).

The ^{1}H-NMR-spectrum was indicative for the olivetol moiety of a cannabinoid. The 2 aromatic protons were found at δ 6.40 (s, 1 H) and δ 6.44 (s, 1 H) and the terminal CH_3 group of the pentyl side chain at δ 0.97 (s, 3 H) and the benzylic protons at δ 2.28 (broad, m).

In addition resonances were found at δ 1.52 (s, 3 H), 1.47 (s, 3 H) and 1.28 (s, 3 H) assigned to methyl groups on oxygenated carbons and a singlet at δ 4.27 assigned to −CHOH−.

The mass spectrum of **1a** resembled that of cannabitriol reported by Elsohly et al.[4]. Peaks were observed at the same m/e-values but with different relative intensities.

These data were similar to but not identical with those of cannabitriol. The fact that no olefinic protons were observed in combination with the styrene type absorbance in the UV fixed the double bond between the 6a and 10a position. The carbon skeleton was thus established by refluxing **1a** with a trace amount of concentrated H_2SO_4 in MeOH for 1 h where cannabinol (**3**) was formed (TLC, GC, GC-MS). The formation of **3** also indicated that the nonphenolic hydroxyl groups were present in the terpene moiety of the molecule and not in the side chain.

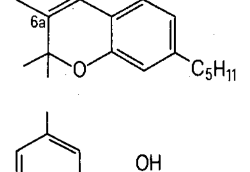
The TMS-derivative **1b** had MW 562 (GC-MS) which indicated the presence of 3 hydroxyl groups. Acetylation (acetic anhydride, pyridine) of **1a** yielded a diacetate, **1c**, the mass spectrum of which showed important ions at m/e 430 (20%) M^+; 415 (100) $(M\text{-}CH_3)^+$; 397 (49) $(M\text{-}CH_3{-}H_2O)^+$; 373 (31) $(M\text{-}CH_3{-}CH_2{=}C{=}O)^+$; 370 (18) $(M\text{-}CH_3COOH)^+$; 355 (62) $(M\text{-}CH_3{-}CH_3COOH)^+$; 337 (26) $(M\text{-}CH_3{-}H_2O{-}H_3CCOOH)^+$; 328 (88) $(M\text{-}CH_3COOH{-}H_2C{=}C{=}O)$; 313 (91) $(M\text{-}CH_3{-}H_2C{=}C{=}O{-}CH_3COOH)$ and 295 (44) $(M\text{-}CH_3{-}H_2O{-}H_2C{=}C{=}O{-}CH_3COOH)^+$. The formation of a diacetate instead of a triacetate suggested that the 3rd hydroxyl group must be a tertiary one and was therefore assigned to C_9. The mass spectrum points to the presence of a phenolic acetate and an aliphatic acetate. The presence of one phenolic OH group in **1a** was substantiated by the formation of the mono-methyl ether **1d** when **1a** was treated with diazomethane.

Periodate oxidation of **1a** gave a compound with MW 344, which excludes the possibility that the secondary OH is in position 7. Finally the secondary OH was assigned the C_{10} position, based on the ^{1}H-NMR-spectrum which showed a singlet for CHOH at δ 4.27. Thus **1a** was determined to be (±)9,10-dihydroxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol. The physical and spectroscopic data of **1a** were different from those reported for cannabitriol[4,8] which indicates that **1a** is a diastereomer of cannabitriol. Also, refluxing of **1a** with acetone/$HClO_4$ yielded a compound of which the mass spectrum was characteristic for an acetonide with important ions at m/e 386 (M^+); 371 $(M\text{-}CH_3)^+$; 328 $(M\text{-}CH_3COCH_3)^+$; 313 $(M\text{-}CH_3{-}CH_3COCH_3)^+$ and 311 $(M\text{-}CH_3{-}CH_3COOH)^+$ while cannabitriol isolated by Chan et al.[8] did not react with acetone.

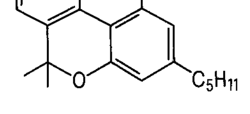
Compound **2a**, R_f 0.51, $C_{21}H_{30}O_4$ (HRP-MS), was also obtained as a yellow optically inactive oil. The physical data showed that this compound was closely related to **1a**. The IR-spectrum showed bands at ν_{max} ($CHCl_3$) 3500–3200 (br, OH) and 1620 cm^{-1} (C=C, Ar) and no carbonyl absorption. The UV-spectrum showed peaks at λ_{max}^{MeOH} 276 nm (log ε 3.76) and 228 (3.88) which indicate the presence of a styrene chromophore[10]. The ^{1}H-NMR-spectrum of **2a** was similar to that of **1a** except for a broad multiplet at δ 4.05 for −*C*HOH−. The carbon skeleton and the number and nature of the hydroxyl groups was determined in the same way as for the previous compound **1a**. Thus, refluxing **2a** with a trace of concentrated H_2SO_4 in MeOH yielded cannabinol **3** as shown by TLC, GC and GC-MS, excluding the possibility of having the hydroxyl groups in the side chain of the molecule. The absence of olefinic protons in the ^{1}H-NMR of **2a** indicated that the double bond should be in the 6a-10a position.

The TMS-derivative **2b** had mol. wt 562 which indicated the presence of 3 hydroxyl groups, while acetylation (acetic anhydride, pyridine) yielded a diacetate **2c** and methylation with diazomethane gave a monomethyl ether **2d**. These data supported by the mass spectrum of the acetate **2c**, indicated that **2a** had one tertiary, one secondary and one phenolic hydroxy group. The tertiary OH was assigned on carbon 9 as the only position in a cannabinol type structure. Potassium periodate oxidation of **2a** gave a compound with mol. wt 344 (MS) which can only be formed if the secondary OH is in position 8 or 10. Position 10 was ruled out because there are only 4 stereoisomers with 9 and 10 hydroxy substituents: 2 of these isomers were previously reported by Chan et al.[8] and Elsohly et al.[4] and the other 2 represent the racemic mixture **1a** previously described; **2a** was different from any of these (TLC, GC, IR). Thus, **2a** should be (±) 8, 9-dihydroxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol. The stereochemistry of all these poly-hydroxylated cannabinoids is yet to be determined.

The fact that compounds **1a** and **2a** are racemic mixtures indicates that these 2 compounds might be artifacts which could be derived from the intermediates 9,10-epoxy-$\Delta^{6a(10a)}$-tetra-hydrocannabinol and 8,9-epoxy-$\Delta^{6a(10a)}$-tetrahydrocannabinol respectively through the hydrolytic opening of the epoxide rings. Work is in progress to explore this possibility.



Cannabitriol and
1a $R^1{=}R^2{=}R^3{=}OH$; $R^4{=}H$
1b $R^1{=}R^2{=}R^3{=}OTMS$; $R^4{=}H$
1c $R^1{=}OH$; $R^2{=}R^3{=}OCOCH_3$; $R^4{=}H$
1d $R^1{=}R^2{=}OH$; $R^3{=}OCH_3$; $R^4{=}H$
2a $R^1{=}R^3{=}R^4{=}OH$; $R^2{=}H$
2b $R^1{=}R^3{=}R^4{=}OTMS$; $R^2{=}H$
2c $R^1{=}OH$; $R^2{=}H$; $R^3{=}R^4{=}OCOCH_3$
2d $R^1{=}R^4{=}OH$; $R^2{=}H$; $R^3{=}OCH_3$



3 Cannabinol

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