Constituents of *Cannabis sativa* L. I: Propyl Homologs of Cannabinoids from an Indian Variant

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Abstract □ Cannabidivarin and tetrahydrocannabivarin are shown to be present in an Indian variant of *Cannabis sativa* L. (marijuana) in Mississippi. GC and mass spectrometry were used for identification. Indications are that these compounds are present as acids in fresh material.

Keyphrases □ *Cannabis sativa* L.—identification of cannabidivarin and tetrahydrocannabivarin, GLC, mass spectroscopy □ Marijuana—identification of cannabidivarin and tetrahydrocannabivarin, GLC, mass spectroscopy □ Cannabidivarin—GLC and mass spectroscopic identification as constituent of *Cannabis sativa* □ Tetrahydrocannabivarin—GLC and mass spectroscopic identification as constituent of *Cannabis sativa* □ Cannabinoids, propyl homologs—identified as constituents of *Cannabis sativa*, GLC, mass spectroscopy

Previous publications showed the presence of propyl homologs of cannabinoids in samples of *Cannabis sativa* L. (1–5). The samples used were either hashish or tinctures. In view of the instability of some of the cannabinoids, the age and preparation of these samples indicated a need to investigate the content of fresh plant material. In this report, evidence is presented for the presence of propyl homologs of cannabinoids in fresh plant material, specifically in an Indian variant of *C. sativa* L.

GC and GC–mass spectrometry were used as methods of analysis. TLC was used as an auxiliary tool.

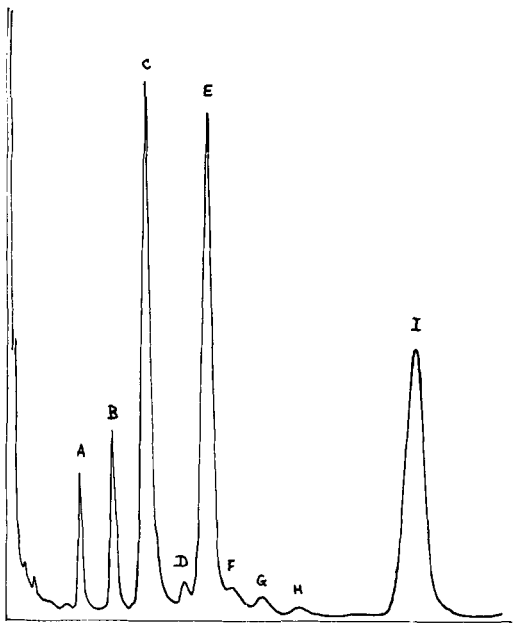

Figure 1—*Chromatogram of 1971 variant of Indian* C. sativa *L. (I-B). Key: A, cannabidivarin; B, (−)-Δ⁹-trans-tetrahydrocannabivarin; C, cannabidiol; D, (−)-Δ⁸-trans-tetrahydrocannabinol; E, (−)-Δ⁹-trans-tetrahydrocannabinol; F, cannabigerol; G, cannabinol; H, unknown peak; and I, 4-androstene-3,17-dione (internal standard used by NIMH).*

Variants of *C. sativa* L. from all over the world have been grown on the campus of the University of Mississippi, some dating back to the start of the marijuana project in 1968 (6). Each year the variants are analyzed both quantitatively and qualitatively for the presence of certain cannabinoids, using GC (7). In 1970, two Indian variants of *C. sativa* were obtained and grown on campus[1]. The chromatograms of all samples of one variant (I-B) showed the presence of two additional major peaks. Again in 1971 these peaks were present in the plant material grown from this same variant (I-B) (Fig. 1). These peaks were not found in significant quantities in any other variants of *C. sativa.*

Figure 2 shows the chromatograms of two variants of *C. sativa* commonly produced in the garden. The other Indian variant (I-A) looks similar to the Mexican (Fig. 2). The two additional peaks (A and B in Fig. 1) had relative retention times of 0.18 and 0.26, respectively, when analyzed by GC using 4-androstene-3,17-dione as the internal standard.

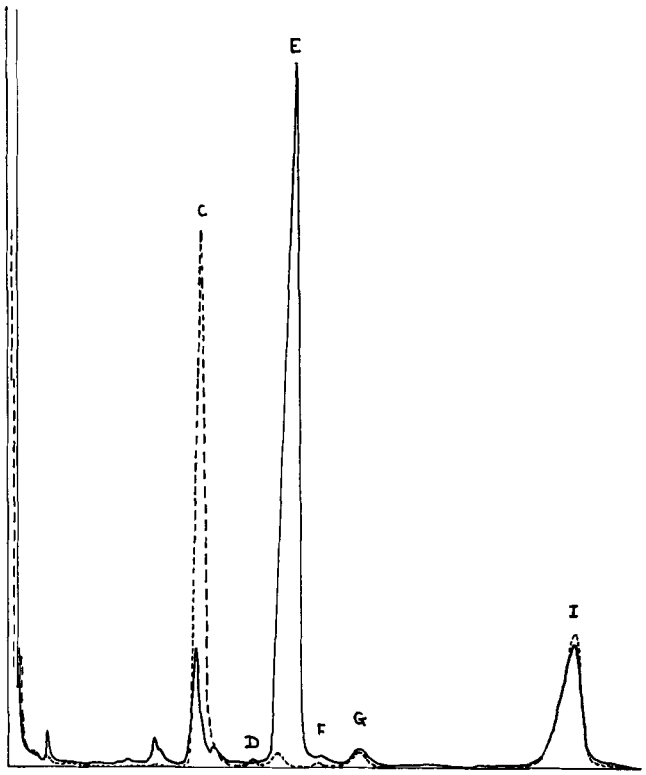

Figure 2—*Overlay of chromatograms of a Mexican and of a Turkish variant of* C. sativa *L. Key: ---, Turkish variant; and ——, Mexican variant. Peaks are lettered as in Fig. 1.*

[1] Seeds for the Indian variant (I-A) wre obtained through Dr. Milton Joffe of the National Institute of Mental Health. Seeds for the variant (I-B) were obtained by Professor Norman J. Doorenbos from Dr. C. K. Atal of the Regional Research Lab., Jammutawi, India.

Table I—Relative Retention Times of Cannabinoids

Cannabidivarin	0.18
(−)-Δ^9-*trans*-Tetrahydrocannabivarin	0.26
Cannabidiol	0.34
(−)-Δ^8-*trans*-Tetrahydrocannabinol	0.44
(−)-Δ^9-*trans*-Tetrahydrocannabinol	0.49
Cannabigerol	0.56
Cannabinol	0.63
Unknown	0.72
4-Androstene-3,17-dione	1.00

EXPERIMENTAL

Samples were prepared for chromatographic analysis by the method reported by Fetterman *et al.* (7). The GC separations were performed on 2-mm. i.d. × 1.8-m. (8-ft.) glass columns packed with 2% OV-17 (phenyl methyl silicone) on Chrom WHP[2]. Gas chromatographs[3] with flame-ionization detectors were used. The inlet temperature was 230°, the column was 210°, and the detector was 250°. Nitrogen was used as a carrier at 30 and 10 ml./min. for close calculation of relative retention times.

Hashish samples obtained from Europe[4] were used initially to identify the compounds by relative retention times (Table I). In addition, a synthetic sample[5] of (−)-Δ^9-*trans*-tetrahydrocannabivarin was used for further identification.

For further identification, GC–mass spectrometry was used[6]. A stainless steel, SE-30 column was used with helium as the carrier. The mass spectrometer was operated at 70 ev.

RESULTS AND DISCUSSION

The mass spectrum of the first major peak (A) showed a molecular ion at *m/e* 286 with major peaks at *m/e* 271, 218, 174, and 165. These data agree with the mass spectral data of cannabidivarin reported by Vollner *et al.* (3). The second major GC peak gave mass spectral peaks at *m/e* 286 (molecular ion), 271, 243, and 203. These data agree with the mass spectral data reported by Gill (2) for (−)-Δ^9-*trans*-tetrahydrocannabivarin.

The present work shows peaks A and B from fresh *C. sativa* of an Indian variant (I-B) to be cannabidivarin and (−)-Δ^9-*trans*-tetrahydrocannabivarin, respectively. Gill *et al.* (1) showed that tetrahydrocannabivarin or the propyl homolog of (−)-Δ^9-*trans*-tetrahydrocannabinol produces a cataleptic state in mice; however, they stated that it is more rapid in onset and decay in experiments on isolated organs than is (−)-Δ^9-*trans*-tetrahydrocannabinol, the compound often referred to as the main cause of psychotomimetic effects in *C. sativa* L. (2).

Further work on the GC–mass spectrometer indicated that the propyl homologs found in the fresh plant material were present as their acids, as in the case of (−)-Δ^9-*trans*-tetrahydrocannabinol and cannabidiol (8). These data will be reported later.

CONCLUSIONS

Propyl homologs are, indeed, naturally present in *C. sativa* L. but, as is the case with other cannabinoids, they may be present in significant or nonsignificant amounts, depending on the variant.

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[2] Beckman Instrument Co., Fullerton, Calif.

[3] Beckman GC 45 and GC 72-5.

[4] Supplied by Dr. F. W. H. M. Merkus and Dr. R. A. de Zeeuw.

[5] Supplied by Dr. L. Hollister.

[6] The gas chromatograph was a Varian series 1400 and was in combination with a DuPont 21-492 high resolution mass spectrometer.