equation. Under these circumstances, any extrapolation to zero distance is arbitrary. The concentration profiles shown in Fig. 7 of *Reference 1* are speculative since the actual interfacial concentration and the initial concentration gradient cannot be assessed from the experimental data with sufficient accuracy. In addition, the assumption of a constant nonsaturated interfacial concentration independent of the initial concentration gradient (as shown in Fig. 7) is not consistent with a transport model involving two consecutive rate processes.

Since the telegraph equation is not applicable, it is meaningless to ask whether the random-walk model with autocorrelation is appropriate to the descending column. However, even if perfect agreement had been obtained with the equation, this would not be more than a formal quantitative description. The authors' attempt to establish a mechanistic analogy between their descending dissolution and the mutual displacement of two miscible phases in a porous medium would still be questionable.

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Total Rate Equation for Decomposition of Prostaglandin E₂

Sir:

Monkhouse *et al.* (1) recently presented the 60° log rate–pH profile for the dehydration of prostaglandin E₂ (PGE₂)[1] from pH 1 to 10. Between pH 4 and 10, the log of the rate data was correlated by a straight line with a slope of about 0.3. Our 60° rate data substantially agree

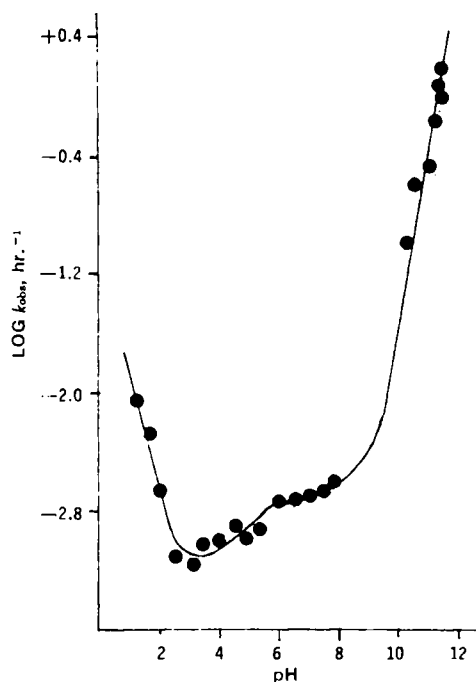[1] PGE₂ is 11α,15(S)-dihydroxy-9-oxo-5-cis,13-trans-prostadienoic acid.

Figure 1 —*Log rate–pH profile for decomposition of PGE₂ at 25.0°.*

with the reported (1) 60° profile. However, we recently completed a 25° log rate-pH profile from pH 1 to 12 which appears to shed more light on the nature of the decomposition reaction between pH 4 and 10.

Figure 1 shows the log rate–pH profile for the decomposition of PGE₂ in water–methanol (95:5 v/v) at 25.00 ± 0.05°. The apparent first-order rates were determined in hydrochloric acid and formate, acetate, phosphate, carbonate, and sodium hydroxide buffers at a constant ionic strength of 0.10. The apparent first-order rate constants were determined by following the disappearance of the substrate by a TLC procedure specific for PGE₂.

Although it may initially appear that the region between pH 4 and 9 is linear, the observed 25° rate constants (k_{obs} values) were best correlated by a rate equation depending upon the pKa of the prostaglandin[2]:

$$k_{obs} = k_H \cdot a_H \cdot (1 - \alpha) + k_{H_2O}(1 - \alpha) + k_{OH} \cdot a_{OH} \cdot (\alpha) + k'_{H_2O}(\alpha) + k^{11}(\alpha) \quad (\text{Eq. 1})$$

where k_H is the specific hydrogen-ion catalytic constant, k_{H_2O} is the catalytic constant for the water reaction of PGE₂, k_{OH} is the specific hydroxide-ion catalytic constant, k'_{H_2O} is the catalytic constant for the water reaction of ionized PGE₂, and k^{11} represents a catalytic constant for a reaction of PGE₂ in the ionized form. The hydrogen- and hydroxide-ion activities are represented by a_H and a_{OH}, respectively, and $(1 - \alpha)$ and (α) represent the fractions of PGE₂ in the unionized and ionized form, respectively.

The line in Fig. 1 was calculated from Eq. 1, and the points correspond to the experimentally observed apparent first-order rate constants. Buffer catalysis and isomerization at C₈ and C₁₅ (2) did not appear to contribute significantly to the overall rate expression.

[2] The pKa of PGE₂ under the conditions of the kinetic experiments was determined to be 5.00.

A more detailed account of this work will be published.

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Constituents of *Cannabis sativa* L. VI: Propyl Homologs in Samples of Known Geographical Origin

Sir:

Recent developments in identifying propyl homologs of cannabinoids prompted this communication. We wish to report the presence of cannabidivarin[1] and (−)-Δ⁹-*trans*-tetrahydrocannabivarin in freshly grown cannabis from known geographical locations. We routinely employed GLC and TLC[2] to identify the C_3-homologs. Some samples were identified by combined GLC–mass spectrometry[3].

Vollner *et al.* (1) identified cannabidivarin (I) from a sample of hashish in 1969. Gill *et al.* (2) later identified (−)-Δ⁹-*trans*-tetrahydrocannabivarin (II) from a sample of tincture of cannabis. Merkus (3) reported the presence of cannabivarin (III) in samples of Nepal hashish. This research group reported the presence of I and II in a sample of freshly grown *Cannabis sativa* L. from Indian seed stock (IN-B) grown in Mississippi (4).

De Zeeuw *et al.* (5) reported that propyl cannabinoids seem to depend on sample origin: samples from countries like India, Nepal, and Pakistan contained significant amounts of propyl cannabinoids, whereas samples from

[1] Since Vollner *et al.* (1) used cannabidivarin (divarinyl group) for the C_3H_7 side chain of cannabidiol (olivetyl group C_5H_{11}), and Merkus (3) used cannabivarin for the C_3H_7 side chain of cannabinol, we shall use the following trivial names: cannabidivarin, (−)-Δ⁹-*trans*-tetrahydrocannabivarin, and cannabivarin. Gill *et al.* (2) used "divarol" for the C_3H_7 side chain: (−)-Δ⁹-*trans*-tetrahydrocannabidivarol.
[2] Beckman GC-45, GC-72-5, and GC-5. Procedures described by Turner and Hadley (7) were used. Silica gel G precoated plates from Brinkmann were used for TLC analysis; petroleum ether–ether (4:1) was the solvent.
[3] Varian Series 1400 gas chromatograph interfaced with Dupont 21-492.
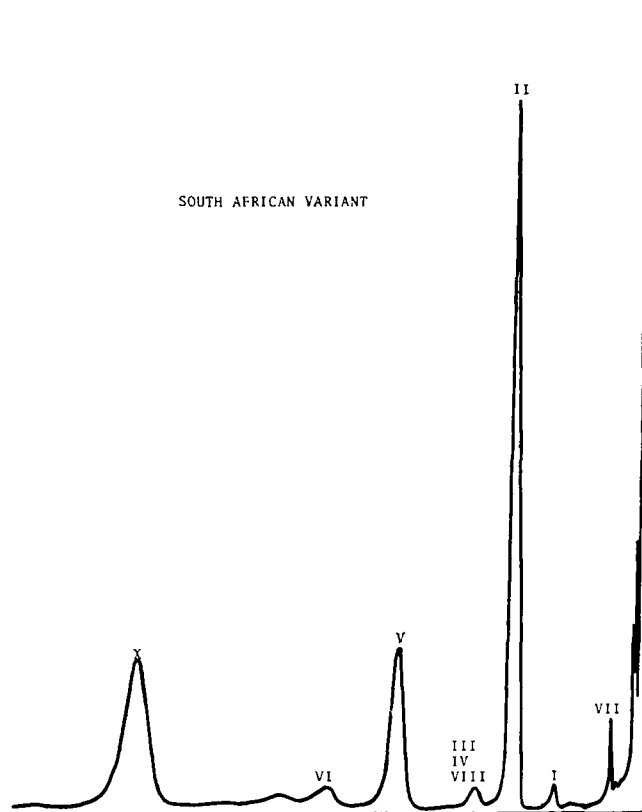
Figure 1—*Chromatogram of South African C. sativa L. (coded SA-E). Key: I, cannabidivarin; II, (−)-Δ⁹-trans-tetrahydrocannabivarin; III, cannabivarin; IV, cannabichromene; V, (−)-Δ⁹-trans-tetrahydrocannabinol; VI, cannabinol; VII, (−)-Δ⁹-trans-tetrahydrocannabiorcol; VIII, cannabidiol; and X, 4-androstene-3,17-dione (internal standard).*

Middle Eastern and Mediterranean countries contained much lower amounts. Our own findings using only those variants from exact geographical locations confirm and extend the previously thought abundance of propyl cannabinoids in freshly grown *C. sativa* L. (Table I).

The percentages of I and II given in Table I are normalized reports. Each cannabinoid is reported as its percentage in regard to total cannabinoid content. These data were obtained by a GLC–computer[4] analysis based on relative retention times of routine cannabis analysis[5].

Figure 1 of an African variant (seed code SA-E) contained 1.70% of I; 53.69% of II; 2.75% of III, cannabichromene (IV), and cannabidiol (VIII); 23.41% of (−)-Δ⁹-*trans*-tetrahydrocannabinol (V); and 4.38% of cannabinol (VI). Peak number VII was tentatively identified as (−)-Δ⁹-*trans*-tetrahydrocannabiorcol[6], first reported by Vree *et al.* (6).

Figure 2 of an Afghanistan variant (seed code AF-A) contained 8.35% of I; 5.34% of II; 12.48% of III, IV, and VIII; 1.94% of cannabigerol monomethyl ether (IX); 58.93% of V; and 2.03% of VI. The age of the material analyzed in Figs. 1 and 2 was 20 weeks. A previous literature report (7) showed that cannabinoid contents vary within each variant according to age.

[4] Digital PDP-8 computer.
[5] A comprehensive listing of the relative retention times can be found in *Reference 7*.
[6] The methyl side chain of (−)-Δ⁹-*trans*-tetrahydrocannabinol as named by Vree *et al.* (6).