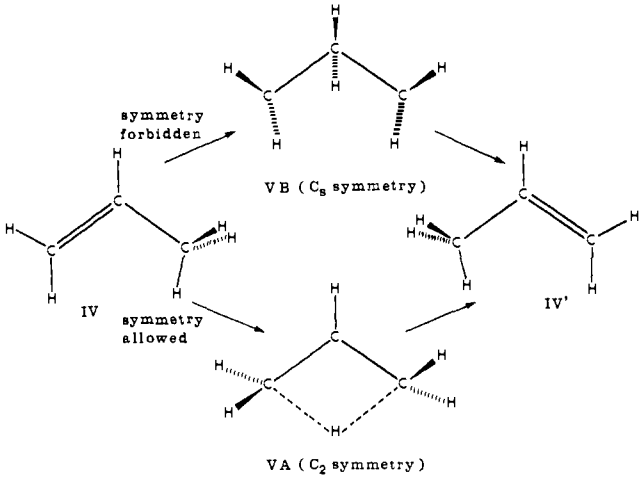

Figure 2. 1,3-Sigmatropic shift in propene.

Table II. Calculated Total Energies (E, Hartrees) and Relative Energies (ΔE, kcal mol^{-1})

Species	STO-3G		4-31G	
	E	ΔE	E	ΔE
I	−150.91668	18.4	−152.66632	11.7
IIIA	−150.77020	110.3	−152.53144	96.4
IIIB	−150.68740	162.3	−152.49927	116.5
II	−150.94599	0	−152.68499	0

version of the Gaussian 70 series of programs[10] and the STO-3G[11] and 4-31G[12] basis sets. Optimized STO-3G geometries for vinyl alcohol (I)[13] and acetaldehyde (II) and for the transition states (IIIA, IIIB, Figure 1), separating them, were obtained using direct search procedures described elsewhere[15,16] and are summarized in Table I. Calculated energies are shown in Table II.

We begin by noting that, for the isoelectronic hydrocarbon propene, the analogous, and in this case degenerate, 1,3-sigmatropic shift IV → IV′ is symmetry allowed if antarafacial (VA) and symmetry forbidden if suprafacial (VB, Figure 2).[17] Although it is somewhat less satisfactory to apply the orbital symmetry considerations to our less symmetrical vinyl alcohol → acetaldehyde rearrangement, we note that our transition-state structures IIIA and IIIB resemble the symmetry-allowed (VA) and symmetry-forbidden (VB) structures, respectively. An important structural feature in IIIA is the manner in which the bridging hydrogen causes a narrowing of the CCO angle to 102.6° compared with values of 126.9° in I, 124.3° in II, and 124.6° in IIIB. We may think of IIIA as the transition state on a pathway involving a direct 1,3-hydrogen shift. In the transition state IIIB, the short distance (1.164 Å) between the migrating hydrogen and the central carbon is worth noting. The reaction path in this case may be considered to proceed via successive 1,2 shifts.

Both basis sets predict (Table II) that the "symmetry-allowed" structure IIIA is the favored transition state. Our better (4-31G) calculations predict an activation energy for the vinyl alcohol → acetaldehyde transformation of 85 kcal mol^{-1} and an energy difference between vinyl alcohol and acetaldehyde of 11.7 kcal mol^{-1}. The latter result is in reasonable agreement with an indirect experimental estimate[18] of 13.2 kcal mol^{-1}. Although our results, particularly for the "symmetry-forbidden" transition state IIIB may be modified in a more sophisticated treatment, i.e., one which uses a larger basis set and which incorporates electron correlation, our calculated activation energies are sufficiently large that we predict with some confidence that vinyl alcohol is stable with respect to intramolecular rearrangement. The apparent ease with which vinyl alcohol is converted to acetaldehyde in the laboratory must be due to complicating *inter*molecular or ionic reactions.

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Synthesis and Enzymatic Formation of a *C*-Glucuronide of Δ^6-Tetrahydrocannabinol

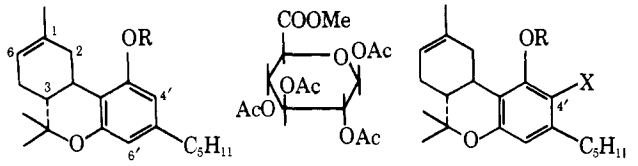
Sir:

The primary metabolic pathways of Δ^1- and Δ^6-tetrahydrocannabinol (Δ^1-THC and Δ^6-THC (**1a**)) have been thoroughly investigated.[1] However, little is known about the nature of the water-soluble conjugates, which are frequently the predominant components of the THC excretion products.[2] Indirect evidence has suggested the presence of glucuronides.[3,4] Indeed, recently Harvey et al. reported the formation of *O*-glucuronides of cannabidiol (a cannabinoid related to THC) and some of its metabolites in mouse liver after administration of cannabidiol.[5]

We considered the possibility that, if THC conjugates were indeed glucuronides, they could be (in part at least) of the very rare *C*-glucuronide type.[6] This conjecture was based on published observations that in several chemical reactions,[7] including glucosidation,[8] the C-4′ aromatic position in some cannabinoids was substituted preferentially to the free phenolic group. In order to facilitate the identification of possible *C*-glucuronides produced in metabolic processes, we initially synthesized the appropriate *O*- and *C*-glucuronides. We chose to work in the Δ^6-THC series, rather than in the pharmacologically more important Δ^1-THC series, in order that the attempted syntheses of glucuronides (which involve acidic

conditions) would not be complicated by the presence of the acid labile double bond in Δ^1-THC. In any case, most metabolic pathways of Δ^1-THC parallel those of Δ^6-THC.

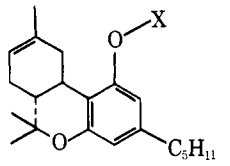
Condensation of Δ^6-THC (**1a**) in dry benzene with an equimolar amount of methyl (tetra-*O*-acetyl)-β-D-glucopyranuronate (**2**) at room temperature for 4 h in the presence of



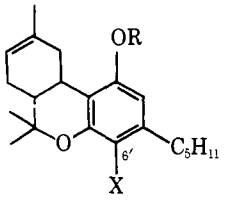
1a, R = H
b, R = Ac

2

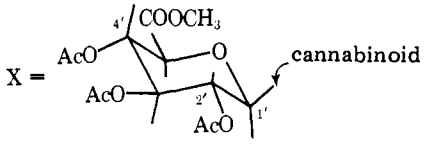
3a, R = H
b, R = Ac



4



5a, R = H
b, R = Ac



boron trifluoride etherate gave, on purification on preparative layer chromatography (PLC), Δ^6-THC-*C*-4′-glucuronide methyl ester triacetate (**3a**): 20% yield; $[\alpha]_D^{EtOH}$ −160°; λ_{max}^{EtOH} 288 nm (bathochromic shift to 304 nm on addition of base); δ ($CDCl_3$) 0.90, 1.05, 1.35 (pyran ring and side-chain CH_3s), 1.69 (2 CH_3, olefinic and C-2′ sugar $OCOCH_3$),[8,9] 2.02, 2.06 (2 sugar $OCOCH_3$), 3.80 ($COOCH_3$), 4.02–4.37 (C-5′ sugar H), 4.80 (br d, J = 10 Hz, C-1′ sugar H), 5.14–5.64 (4 H, olefinic and C-2′, C-3′, C-4′ sugar H), 6.18 (s, arom H), 7.45 (OH); *m/e* (rel intensity) 630 (20), 570 (4.5), 511 (17), 450 (38), 391 (53), 367 (100), 351 (59), 349 (48), 327 (41), 283 (41), 271 (57).

On acetylation the tetraacetate (**3b**) was obtained: $[\alpha]_D^{EtOH}$ −141°; λ_{max}^{EtOH} 276, 286 nm; δ ($CDCl_3$) 0.95, 1.05, 1.36 (pyran ring and side-chain CH_3s), 1.66 (olefinic CH_3) 1.83 (C-2′ sugar $OCOCH_3$), 2.03 (2, $OCOCH_3$), 2.33 (phenolic $OCOCH_3$), 3.72 ($COOCH_3$), 3.83–4.28 (C-5′ sugar H), 4.60 (br d, J = 10 Hz, C-1′ sugar H), 5.0–5.67 (4 H, olefinic and C-2′, C-3′, C-4′ sugar H), 6.68 (s, arom H); *m/e* (rel intensity) 672 (23), 630 (100), 612 (9), 547 (11), 511 (53), 493 (15), 451 (41), 450 (35), 449 (15), 409 (18), 366 (59), 349 (53).

The presence of a *single* aromatic proton in **3a,b,** the bathochromic shift caused by base in **3a,** and the formation of the *tetra*acetate **3b** (mol wt 672) indicate the formation of a *C*-glucuronide rather than an *O*-glucuronide.

Condensation of Δ^6-THC (**1a**) with **2** (molar ratio 3:1) in dry benzene in the presence of *p*-toluenesulfonic acid (reflux, 12 h) gave a mixture which on separation on PLC gave three compounds. The least polar compound (10% yield) was identified as the Δ^6-THC-*O*-glucuronide methyl ester triacetate (**4**): mp 149 °C; $[\alpha]_D^{EtOH}$ −166°; λ_{max}^{EtOH} 276, 281 nm (no bathochromic shift on addition of base); δ ($CDCl_3$) 0.90, 1.06, 1.35 (pyran ring and side-chain CH_3s), 1.56 (olefinic CH_3), 1.70 (C-2′ sugar $OCOCH_3$), 2.05 (2, $OCOCH_3$), 3.80 ($COOCH_3$), 4.07–4.37 (C-5′ sugar H), 4.90 (br d, J = 8 Hz, C-1′ sugar H), 5.2–5.55 (4 H, vinylic and C-2′, C-3′, C-4′ sugar H), 6.45, 6.52 (2 arom H); *m/e* (rel intensity) 630 (8), 570 (8), 317 (48), 314 (71), 257 (94), 231 (100). Compound **4** did not undergo acetylation. These data, in particular the presence of *two* aromatic protons, the lack of bathochromic shift in the UV spectrum on addition of base, the absence of a hydroxyl band in the IR spectrum, and the molecular ion indicate that **4** has an *O*-glucuronide structure.

The above-described Δ^6-THC-*C*-4′-glucuronide derivative (**3a**) was obtained in ~10% yield. In addition the Δ^6-THC-C-6′ isomer (**5a,** 1% yield) was also isolated. The IR and NMR spectra[10] of **5a** and of the tetracetate **5b,** are similar to, but not identical with, those of **3a** and **3b,** respectively.

We assume that **3, 4,** and **5** are β-glucuronides on the basis of the large coupling constant observed (J = 10 Hz) for the C-1′ H in the sugar moiety.[9] The α anomer has a much smaller constant owing to the axial–equatorial relationship of the C-1′, C-2′ protons. Also, the condensation of **2** with phenols in the presence of *p*-toluenesulfonic acid has been shown to lead mostly to β anomers.[11] We also assume that the sugar in **3a** is attached to the C-4′ aromatic position and in **5a** it is attached to the C-6′ position. We deduce this from several observations: (a) the free phenol **3a** is *less* polar than its acetate **3b,** suggesting the existence of an internal hydrogen-bonded phenolic group in **3a** (as expected the free phenol **5a** is *more* polar than its acetate **5b**); (b) in the IR spectrum of **3a** the band due to the hydrogen-bonded phenolic group (at 3440 cm^{-1}) was unchanged on dilution in the concentration range of 5–0.005% in CCl_4, indicating an internal hydrogen bond; (c) in the NMR the aromatic protons in **3a** and **3b** are at a lower field than the corresponding ones in **5a** and **5b,** which follows precedence.[7c]

The enzymatic conjugation of Δ^6-THC (**1a**) with glucuronic acid was done as follows. A solution of uridine-5′-diphosphoglucuronic acid sodium salt (UDPGA Na^+) (2 mg), UDPglucuronyltransferase prepared from lyophilized crude microsomal preparation from rabbit liver (Sigma Co) (10 mg), and $MgCl_2$ (0.47 mg) in Tris buffer (100 mM), ph 7.4, in isotonic KCl solution (up to 1 mL) was equilibrated for 5 min at 37 °C. [C-3-^{3}H]-Δ^6-THC (2.7 mg, 2 × 10^6 dpm) in dimethyl sulfoxide (0.01 mL) was then added, and the mixture was incubated in a shaker for another 30 min under nitrogen. After lyophilization the total mixture (of 20 identical runs) was esterified with diazomethane and then acetylated with acetic anhydride in pyridine. The crude product obtained was chromatographed on Sephadex LH-20 using chloroform as eluent. Two main radioactive fractions were isolated, Δ^6-THC acetate (**1b**) and Δ^6-THC-*C*-4′-glucuronide methyl ester tetraacetate (**3b**). Unchanged Δ^6-THC acetate was by far the major recovered material. The crude glucuronide was further purified thrice on silica gel TLC (elution, 1:1 ether–petroleum ether).

On TLC, **3b** originating from the enzymatic reaction showed a single spot with a R_f value equivalent to that of the synthetic sample. It differed from those of **4** and **5b.** The mass spectrum of the enzymatically produced **3b** had a mass peak at *m/e* 672 and contained all the major peaks (with approximately equivalent relative intensities) observed in the spectrum of synthetic **3b** taken under identical conditions.

The enzymatic production of the *C*-glucuronide of Δ^6-THC represents a very unusual pathway of conjugation and is the first recorded case of such an in vitro reaction. This conjugation is unusual also because it takes place on a molecule which contains a free phenolic group. Whether parallel in vivo metabolism takes place is yet to be determined. We expect this to be the case (possibly only to a minor extent) as the enzymatic production was achieved with an enzyme which is widely distributed and is nonspecific with respect to the chemical structure of the substrate. From an organic-chemical point of view the C-glucuronidation of Δ^6-THC is also unusual, though, as mentioned above, not unexpected.[7,8,12,13]

Acknowledgment. This work was generously supported by the National Institute on Drug Abuse under Grant DA 00021. We thank Mr. David Linder for his dedicated help in the mass spectral work.

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(4) The water-soluble metabolites of cannabinoids apparently are not all of the same chemical type. β-Glucuronidase type L-1 has been reported to release only ~30% of "conjugated" cannabinoids present in rat bile.[2a]

(5) D. J. Harvey, B. R. Martin, and W. D. M. Paton, *Biochem. Pharmacol.*, **25**, 2217 (1976). After this communication was submitted for publication, we were informed by Dr. D. J. Harvey that *O*-glucuronides of seven cannabinoids and some of their hydroxy and acid metabolites were identified by the Oxford group, as in vivo liver metabolites (D. J. Harvey, B. R. Martin, and W. D. M. Paton, *Res. Commun. Chem. Pathol. Pharmacol.*, **16**, 265 (1977)). It was pointed out, however, that these conjugates are not the only type of water-soluble metabolites present.

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(10) Δ^6-THC-*C*-6′-glucuronide methyl ester triacetate (**5a**): NMR ($CDCl_3$) δ 0.85, 1.00, 1.32 (pyran ring and side-chain CH_3s), 1.61 (olefinic CH_3), 1.69 (C-2′ sugar $OCOCH_3$), 1.98, 2.00 (2 sugar $OCOCH_3$), 3.63 ($COOCH_3$), 3.83–4.30 (C-5′ sugar H), 4.50 (br d, J = 10 Hz, C-1′ sugar H), 5.00–5.60 (4 H, olefinic and C-2′, C-3′, C-4′ sugar H), 6.0 (arom H); mass spectrum (rel intensity) *m/e* 630 (46), 611 (5), 571 (7), 570 (7), 547 (19), 511 (10), 510 (8), 467 (8), 451 (100), 421 (13), 409 (66), 343 (27), 299 (15), 231 (20), 221 (27). Δ^6-THC-*C*-6′-glucuronide methyl ester tetraacetate (**5b**): nmr ($CDCl_3$) δ 0.9, 1.10, 1.35 (pyran ring and side-chain CH_3s), 1.68 (olefinic CH_3), 1.75 (C-2′ sugar $OCOCH_3$), 2.01, 2.03 (2, $OCOCH_3$), 2.25 (phenolic $OCOCH_3$), 3.70 ($COOCH_3$), 3.90–4.35 (C-5′ sugar H), 4.62 (br d, J = 10 Hz, C-1′ sugar H), 4.98–5.75 (4 H olefinic and C-2′, C-3′, C-4′ sugar H), 6.38 (arom H); mass spectrum (rel intensity) *m/e* 672 (50), 630 (27), 613 (13), 612 (9), 589 (16), 547 (11), 511 (14), 510 (11), 493 (68), 451 (100), 409 (27), 391 (25), 349 (43), 343 (18), 299 (17), 231 (14), 221 (25).

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(12) The formation of a *C*-glucuronyl derivative obtained as a by-product in the synthesis of the *O*-glucuronyl derivative of equilenin has been described: R. B. Conrow and S. Bernstein, *J. Org. Chem.*, **36**, 863 (1971).

(13) After this communication was submitted for publication we were informed by Professor C. Fenselau that in her laboratory *O*-glucuronides of cannabinol, cannabidiol, Δ^1- and Δ^6-THC (characterized by GLC–mass spectrometry) were obtained by an enzymatic synthesis closely related to the one used by us. However the partially purified UDPglucuronyltransferase used by the Baltimore group was immobilized on cyanogen bromide activated sepharose, while ours was a commercially available enzyme. This difference may perhaps explain the divergency of results (M. A. Lyle, S. Pallante, K. Head, and C. Fenselau, *Biomed. Mass Spectrom.*, **4**, 190 (1977)).

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Unusual Reactions of a Bridged Hydride Ligand in Aqueous Solution

Sir:

Bennett, Brencic, and Cotton[1,2] synthesised the salt $Cs_3Mo_2Cl_8H$ (compound I) and analogous salts $M^I_3Mo_2X_8H$ (M^I = Cs, Rb; X = Cl, Br). The complex ion $Mo_2Cl_8H^{3-}$ was shown to have two bridging chlorides and one bridging hydride between the two molybdenum(III) atoms.[2] The band at 1245 cm^{-1} in the IR spectrum of I was assigned to the anti-symmetric Mo-H-Mo stretching by Cotton and Kalbacher[2] and was shifted to 904 cm^{-1} in the deuterium-substituted salt[2] $Cs_3Mo_2Cl_8D$. These authors also observed that the decomposition of the ion $Mo_2X_8H^{3-}$ by water was accompanied by evolution of H_2 gas. Using the deuterium-substituted salt in H_2O they discovered that the main product of the reaction was HD, thereby proving that the bridging D^- was oxidized by an aqueous proton, $D^- + H^+ \rightarrow HD$.

The Mo species produced in the decomposition of I in water was examined in this laboratory. When the reaction is carried out in dilute aqueous acids (e.g., HCl 1 M or *p*-toluenesulfonic acid 1 M) the yellow solution of $Mo_2Cl_8H^{3-}$ quickly turns red, and then is slowly converted to a green end product. The second stage is accompanied by H_2 evolution. The green species was identified by ion-exchange chromatography and UV-vis spectrum, as the dichloromolybdenum(III) dimer[3] $Mo_2(OH)_2Cl_2^{2+}$. The net apparent oxidation number per molybdenum atom in compound I was $2\frac{1}{2}$ as determined by permanganate titration in which molybdenum(III) is oxidized to 6+ and H^- to H^0 (H_2 is evolved during the titration). The same result is obtained with the intermediate red species which is probably a partially aquated product of I. During the conversion of the red species to the green molybdenum(III) dimer, the oxidation number increases until it reaches 3+ at the end of the reaction, as expected.

When fresh yellow solution of I reacts with acetic acid, a deep violet solution is formed. The oxidation number at this stage remains $2\frac{1}{2}$+. The violet solution decomposes slowly, *without* any formation of gaseous H_2, to a yellow solution. The oxidation number *drops* during this stage from $2\frac{1}{2}$+ to 2.0+. The spectrum of the yellow end product is identical with that of $Mo_2(OAc)_4$ and crystals of this compound are slowly precipitated from the solution. The reduction of the molybdenum atoms from 3+ to 2+ can only be explained by an accompanying oxidation of the H^- ligand to H^+.

$$2Mo^{III} + H^- \rightarrow 2Mo^{II} + H^+$$

This reaction is, in fact, the reversal of the reaction in which I is obtained from $Mo_2(OAc)_4$ by hot concentrated HCl.[1] Similar violet species are obtained from I with other carboxylic acids, amino acids, and other ligands containing a carboxylate group. All these violet species are slowly converted to the respective molybdenum(II) compounds. The violet species, obtained from I with glycine was absorbed on an ice-cooled cation-exchange column (Dowex 50X2) and eluted as a distinct band by 3 M acid (HCl or H_2SO_4). The eluted violet species did not contain any chloride. The visible absorption spectrum had maxima at 660 nm (ϵ 45), 538 (75), and 410 (sh) (58). The oxidation number was $2\frac{1}{2}$+. H_2 was produced during the titration by permanganate as with I. The structural relation of the violet species to I was demonstrated by reversing the substitution reaction of Cl^- by glycine: addition of concentrated HCl to the violet species followed by CsCl precipitates the salt I. The retention of the μ-hydrido bridge in the violet species was further supported by the use of $Cs_3Mo_2Cl_8D$. This salt was prepared following the procedure of Cotton and Kalbacher.[2] It was reacted with glycine in H_2O and the violet species was separated chromatographically. Finally I was precipitated by