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EUDESMANE TRIOLS FROM *VERBESINA VIRGATA**

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Key Word Index—*Verbesina virgata*; Compositae; structure elucidation; sesquiterpenes; eudesmanes; cinnamates.

Abstract—Chemical study of *Verbesina virgata* collected in several localities afforded two eudesmane triols as 4-cinnamates. Their structures were determined by chemical and spectroscopic means. The structure and stereochemistry of one of the triols was confirmed by X-ray crystallography.

INTRODUCTION

The large genus *Verbesina* (Heliantheae) is constituted of 150 species native to the New World [1]. The relatively few chemical studies of *Verbesina* species indicate that this genus elaborates sesquiterpenes with a great variety of hydrocarbon skeletons, such as elemane [2–4], cadinane [5] and eudesmane [6]. This paper reports the results of a chemical examination of *Verbesina virgata* Cav., collected in central Mexico.

RESULTS AND DISCUSSION

The aerial part of *Verbesina virgata* Cav., afforded the two triols **1a** and **2a** as 4-cinnamates.

The structure of the cinnamate **1a**, $C_{24}H_{32}O_4$, mp 170–171°, $[\alpha]_D^{20} - 21.1°$ ($CHCl_3$), is in complete agreement with its spectroscopic data: IR (1700, 1640 and 1580 cm^{-1}), ^1H NMR (Table 1), ^{13}C NMR (Table 2) and mass spectra. The presence of the cinnamoyl moiety indicated by the IR and ^1H NMR spectra is confirmed by the fragment at m/z 136 $[M - 148]^+$ and m/z 131 $[\phi - CH=CH-CO]^+$ in the mass spectrum. The presence of the two hydroxyl groups in the molecule (IR band at 3400 cm^{-1}), is confirmed by acetylation of **1a** to give the diacetate **1b**. The ^1H NMR spectrum shows the signals (Table 1) of the acetate methyl groups as two singlets. The signals attributed to the protons attached to hydroxyl substituted carbon atoms are shifted from δ 3.7 (1H, *ddd*, J = 10, 10, 4 Hz) and 3.15 (*d*, J = 10 Hz, 1H) to δ 5.15 and 4.05. The ^1H NMR spectrum also shows the signals for all methyl groups of the eudesmane skeleton, nevertheless the C-4 methyl is shown as a singlet at δ 1.6 indicating that the cinnamoyl ester is attached to this position.

Alkaline hydrolysis of **1a** yields the triol **1c** in whose ^1H NMR spectrum the signal of the C-4 methyl appears as a singlet at δ 1.2. The upfield shift ($\Delta\delta$ 0.4) is consistent with the C-4 position for the cinnamoyl moiety.

Compound **1a** contains a trisubstituted double bond as indicated by the ^1H NMR signal at δ 5.3 (1H) and formation of the epoxide **3**.

The hydroxyl groups are vicinal, since **1a** on treatment with H_5IO_6 affords the aldehyde **4**. The C-10 methyl group of **4** is moved downfield, indicating its vicinity to one of the newly formed aldehyde groups.

*Contribution No. 627.

Table 1. ^1H NMR chemical shifts of **1a**, **2a** and their derivatives ($CDCl_3$, TMS as int. standard)

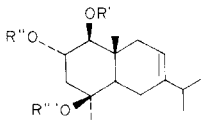
Compound	H-1	H-2	H-3ax.	H-3eq.	Me-4	H-8
1a	3.15 *d*(10)	3.75 *ddd*(10, 10, 4)	1.65 *dd*(14, 10)	3.27 *dd*(4, 14)	1.6 *s*	5.35 *m*
1b	3.78 *d*(10)	5.1 *dd*(10, 4)	1.6 *dd*(14, 10)	3.35 *dd*(4, 14)	1.6 *s*	5.3 *m*
1c	3.05 *d*(10)	3.9 *ddd*(10, 10, 4)	1.6 *dd*(14, 10)	2.2 *m*	1.2 *s*	5.37 *m*
3	2.95 *d*(10)	3.05 *ddd*(10, 10)	1.25 *dd*(14, 10)	3.2 *m*	1.6 *s*	2.95 *m*
4	9.45 *s*	9.55 *m*	—	3.5 *dd*(4, 14)	—	5.3 *m*
2a	3.85 *dd*(12, 8)	2.1 *m*	—	4.82 *br s*	1.65 *s*	5.35 *m*
2b	4.85 *t*(8)	1.8 *m*	—	5.9 *m*	1.45 *s*	5.2 *m*
5	—	3.3 *d*(12)*	—	—	1.65 *s*	5.35 *m*
		4.1 *d*(12)				

The coupling constants in Hz are in parentheses.
*AB system.

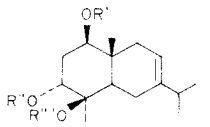
Table 2. ^{13}C NMR data of compounds **1a** and **2a** ($CDCl_3$, TMS as int. standard)*

C. No.	1a	2a
1	84.10 *d*	73.55 *d*
2	67.65 *d*	41.14 *t*
3	41.58 *t*	69.56 *d*
4	83.83 *s*	84.57 *s*
5	49.33 *d*	42.91 *d*
6	23.42 *t*	33.87 *t*
7	141.99 *s*	142.00 *s*
8	116.12 *d*	116.21 *d*
9	21.41 *t*	33.87 *t*
10	38.38 *s*	37.69 *s*
11	34.97 *d*	34.96 *d*
12	21.87 *q*	21.81 *q*
13	21.56 *q*	21.34 *q*
14	13.56 *q*	12.25 *q*
15	24.99 *q*	22.96 *q*
1′	166.10 *s*	166.07 *s*
2′	144.55 *d*	144.78 *d*
3′	130.31 *d*	130.31 *d*
4′	134.67 *s*	134.46 *s*
5′–9′	128.89 *d*	128.99 *d*
6′–8′	128.22 *d*	128.14 *d*
7′	119.90 *d*	119.57 *d*

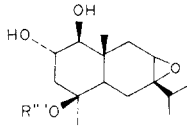
*Multiplicity estimated by off resonance.



1a R′ = R″ = H, R‴ = cinnamoyl
1b R′ = R″ = Ac, R‴ = cinnamoyl
1c R′ = R″ = R‴ = H



2a R′ = R″ = H, R‴ = cinnamoyl
2b R′ = R″ = Ac, R‴ = cinnamoyl



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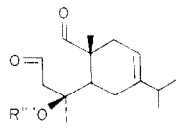

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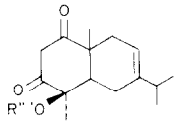

5

3–5 R‴ = cinnamoyl

The above discussion and the multiplicity of H-1 and H-2 signals (Table 1) lead us to select these positions for the free hydroxyl groups.

The C-1 hydroxyl group must be equatorially orientated according with the coupling constants of H-1 (*d*, $J_{1,2}$ = 10 Hz) and this is clearly observed after the addition of Eu(fod)$_3$ (7.8 mg). The doublet attributed to H-1 is moved downfield to δ 5.85 ($\Delta\delta$ 2.1). In this region there is no overlapping with other signals, thus permitting us to observe its coupling constant (J = 10 Hz) characteristic for an axial–axial interaction. H-2 is also shifted downfield, the same happened with H-3 eq. whose signal is located at δ 4.35 ($\Delta\delta$ 2.1) (1H, *dd*, J = 14, 4 Hz). When this signal is irradiated, that of H-2 collapses to a triplet (J = 10 Hz), thus indicating the axial orientation of H-1 and H-2 as shown in formula **1a**.

The stereochemistry of the C-1 hydroxyl group already established by ^1H NMR is congruent with the ^{13}C NMR data since the methyl group at C-10 resonates at δ 13.46 (Table 2), this high field chemical shift is explained by the shielding effect of the C-1 equatorial hydroxyl group, which has been reported for similar compounds [6].

The structure and stereochemistry of **1a** was unambiguously determined by X-ray diffraction analysis (Fig. 1). Two crystallographically independent molecules exist in the crystal, differing only in the conformations of the cinnamate and isopropyl side chains. One of the molecules, illustrated in Fig. 1 and designated by primes in Table 3, has the cinnamate group in the *s-trans* configuration and has a C-6′–C-7′–C-11′–C-13′ torsion angle of −62.7°. The other molecule designated without primes in Table 3, has its cinnamate group in the *s-cis* configuration and its isopropyl group rotated 136.7°.

The second eudesmane triol 4-cinnamate (**2a**), $C_{24}H_{32}O_4$, mp 137–138°, $[\alpha]_D^{20}$ −24.6° ($CHCl_3$), is an isomer of compound **1a**. The free hydroxyl groups of **2a** should be attached to positions C-1 and C-3. Chromic acid oxidation of **2a** yields the diketone **5** (IR 1710, 1635 cm^{-1}) which shows in its ^1H NMR spectrum the signals of the isolated methylene group (C-2) as an AB system. The C-1 hydroxyl group in compound **2a** must be equatorial as indicated by the H–H coupling constants and the shielding effect on the C-10 methyl group.

Both **2a** and **1a** contain α-methyl groups and β-cinnamates at C-4. The orientation of the C-4 methyl is

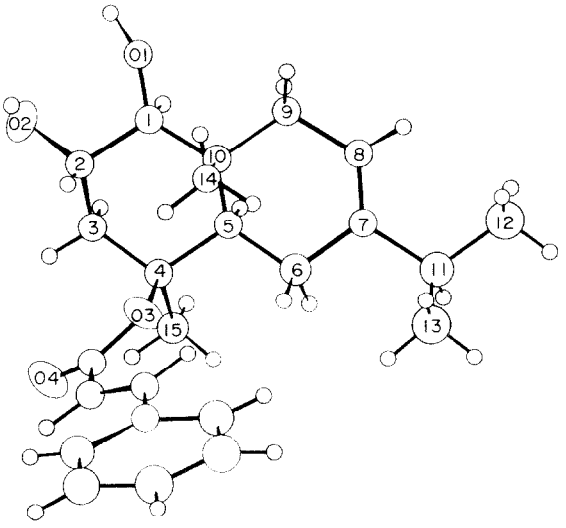

Fig. 1. Structure and stereochemistry of **1a** as determined by X-ray crystallography.

Table 3. Coordinates and thermal parameters for **1a**

Atom	x	y	z	B or Beq. Å^2	Atom	x	y	z	B. Å^2
O-1	1.2540(7)	0.4883(3)	0.8907(2)	5.0(3)	C-11	0.623(1)	0.6001(5)	1.0126(3)	5.2(2)
O-2	1.1436(8)	0.4895(3)	0.8062(2)	5.1(3)	C-12	0.457(2)	0.5575(7)	1.0079(4)	8.5(3)
O-3	0.8398(7)	0.6744(2)	0.8600(1)	3.4(2)	C-13	0.598(2)	0.6855(6)	1.0129(4)	8.3(3)
O-4	0.7753(8)	0.7118(3)	0.7940(1)	4.4(2)	C-14	1.095(1)	0.6235(5)	0.9220(2)	4.4(2)
C-1	1.081(1)	0.5014(4)	0.8799(2)	3.8(2)	C-15	0.587(1)	0.5939(5)	0.8449(3)	4.7(2)
C-2	1.068(1)	0.5392(4)	0.8367(2)	4.2(2)	C-16	0.833(1)	0.7247(4)	0.8281(2)	3.5(2)
C-3	0.883(1)	0.5505(4)	0.8247(2)	3.5(2)	C-17	0.916(1)	0.7975(4)	0.8413(2)	3.5(2)
C-4	0.776(1)	0.5948(4)	0.8569(2)	3.5(2)	C-18	0.953(1)	0.8525(4)	0.8148(2)	3.7(2)
C-5	0.806(1)	0.5617(4)	0.9007(2)	3.5(2)	C-19	1.034(1)	0.9262(4)	0.8249(2)	3.6(2)
C-6	0.708(1)	0.6064(4)	0.9347(2)	4.2(2)	C-20	1.062(1)	0.9492(5)	0.8657(3)	4.7(2)
C-7	0.744(1)	0.5755(4)	0.9776(2)	4.0(2)	C-21	1.134(1)	1.0204(5)	0.8749(3)	6.1(2)
C-8	0.869(1)	0.5284(4)	0.9850(2)	4.1(2)	C-22	1.175(1)	1.0695(6)	0.8402(3)	6.4(2)
C-9	0.995(1)	0.5004(4)	0.9528(2)	3.7(2)	C-23	1.155(1)	1.0465(5)	0.8003(3)	5.8(2)
C-10	0.996(1)	0.5494(4)	0.9133(2)	3.1(1)	C-24	1.081(1)	0.9752(5)	0.7921(3)	4.6(2)
O-1′	0.7014(7)	0.8514(3)	0.6586(2)	4.6(3)	C-11′	0.025(1)	0.7533(5)	0.5479(3)	5.5(2)
O-2′	0.6396(8)	0.8288(3)	0.7425(2)	4.9(3)	C-12′	0.040(2)	0.7934(6)	0.5064(3)	7.9(3)
O-3′	0.2976(7)	0.6581(3)	0.6881(1)	3.8(2)	C-13′	0.044(2)	0.6678(7)	0.5413(4)	8.6(3)
O-4′	0.2604(8)	0.6099(3)	0.7527(2)	5.6(3)	C-14′	0.522(1)	0.7237(4)	0.6224(2)	3.8(2)
C-1′	0.533(1)	0.8344(4)	0.6732(2)	3.5(2)	C-15′	0.062(1)	0.7376(5)	0.7145(3)	5.6(2)
C-2′	0.542(1)	0.7873(4)	0.7131(2)	3.8(2)	C-16′	0.300(1)	0.6021(4)	0.7165(2)	4.2(2)
C-3′	0.363(1)	0.7744(4)	0.7290(2)	4.0(2)	C-17′	0.357(1)	0.5278(4)	0.6991(2)	4.0(2)
C-4′	0.244(1)	0.7385(4)	0.6980(2)	3.9(2)	C-18′	0.377(1)	0.5134(5)	0.6589(2)	4.2(2)
C-5′	0.252(1)	0.7804(4)	0.6549(2)	3.6(2)	C-19′	0.435(1)	0.4414(4)	0.6399(2)	4.1(2)
C-6′	0.143(1)	0.7435(5)	0.6216(3)	4.7(2)	C-20′	0.510(1)	0.3831(5)	0.6636(3)	4.8(2)
C-7′	0.163(1)	0.7804(4)	0.5791(2)	4.0(2)	C-21′	0.563(1)	0.3144(5)	0.6434(3)	5.6(2)
C-8′	0.280(1)	0.8298(4)	0.5719(2)	4.0(2)	C-22′	0.540(1)	0.3056(5)	0.6013(3)	6.1(2)
C-9′	0.413(1)	0.8530(4)	0.6023(2)	3.9(2)	C-23′	0.467(1)	0.3611(5)	0.5787(3)	6.2(2)
C-10′	0.432(1)	0.7963(4)	0.6386(2)	3.2(1)	C-24′	0.414(1)	0.4308(5)	0.5975(3)	5.4(2)

Estimated s.d.s. in the least significant digits are shown in parentheses.

indicated by the low chemical shift (δ 22.9) in the ^{13}C NMR spectrum (Table 2) as observed in similar compounds [6].

Compound **2a** contains a trisubstituted double bond indicated by the signal at δ 5.3 (1H) in the ^1H NMR spectrum (Table 1) if the double bond is placed at the C-7–C-8 position as in compound **1a** the structure of the eudesmane triol is as depicted in **2a**.

EXPERIMENTAL

Mps are uncorr. Elemental analyses were determined by Dr. F. Pasher, Bonn, West Germany.

Isolation of 4*β-cinnamoloxy-*1*β*, 2*α-dihydroxyeudesm-*7*-ene* (**1a**) *and* 4*β-cinnamoyloxy-*1*β*, 3*α-dihydroxyeudesm-*7*-ene* (**2a**). *Verbesina virgata* Cav. was collected in May 1979 near Ixmiquilpan, Hgo. (voucher: MEXU-AOH15, No. Reg. 289952). Dried and ground leaves (2 kg) were extracted with $CHCl_3$ to give 180 g of an oily residue which was dissolved in $CHCl_3$ and chromatographed over Si gel (4 kg). The fractions eluted with $CHCl_3$–Me_2CO (4:1) were combined and crystallized from Me_2CO–hexane yielding **1a** (0.1%), mp 164–168°, $[\alpha]_D^{20}$ −21.1° ($CHCl_3$); UV $\lambda_{max}^{95\%\ EtOH}$ nm: 275 (ε 18 200); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1700, 1640, 1580. (Found: C, 74.99, H, 8.27; O, 16.70%. $C_{24}H_{32}O_4$ requires: C, 74.97; H, 8.27; O, 16.70%.) ^1H NMR (200 MHz, $CDCl_3$, TMS as int. standard): δ 7.62 (1H, *d*, *J* = 16 Hz, H-1′), 6.33 (1H, *d*, *J* = 16 Hz, H-2′), 7.33 (5H, *m*, Ar), 5.35 (1H, *m*, H-8), 3.77 (1H, *ddd*, *J* = 10, 10, 4 Hz, H-2), 3.3 (1H, *dd*, *J* = 14, 4 Hz, H-3eq.), 3.15 (1H, *d*, *J* = 10 Hz, H-1), 1.64 (3H, *s*, Me-4), 1.05 (6H, *d*, *J* = 6 Hz) 1.00 (3H, *s*, Me-10), MS *m/z*: 236 $[M-148]^+$ (41.6%), 131, 161 (100%).

The fractions eluted with $CHCl_3$–Me_2CO (7:3) yielded **2a** (0.15%), mp 133–135°, white crystals from Me_2CO–hexane, $[\alpha]_D^{20}$ −24.6°. UV $\lambda_{max}^{95\%\ EtOH}$ nm: 275 (ε 18 200); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1710 (carbonyl), 1640, 1580; ^1H NMR (Table 1) (80 MHz); MS *m/z* (rel. int.) $[M]^+$ 384, 236 $[M-148]^+$ (100), 174 (76.8) and 131 (68.5). (Found: C, 74.80; H, 8.39; O, 17.03%. $C_{24}H_{32}O_4$ requires: C, 74.97; H, 8.27; O, 16.70%.)

Saponification of **1a**. A soln of 4*β*-cinnamoyloxy-1*β*,2*α*-dihydroxyeudesm-7-ene (50 mg) in MeOH was treated with K_2CO_3 (500 mg) for 30 hr at room temp. Usual work-up gave 1*β*,2*α*,4*β*-trihydroxyeudesm-7-ene (**1c**) (16.5 mg), mp 120–121°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 2900; ^1H NMR (80 MHz): δ 5.35 (1H, *m*, H-8), 3.9 (1H, *ddd*, *J* = 10, 10, 4 Hz, H-2), 3.08 (1H, *d*, *J* = 10 Hz, H-1), 1.25 (3H, *s*, Me-4), 1.02 (6H, *d*, *J* = 6 Hz, Me-11), 1.00 (3H, *s*, Me-10); MS *m/z*: (rel. int.) 254 $[M]^+$, 236 $[2M-18]^+$ (14.6), 218 $[236-18]^+$ (5), 200 $[218-18]^+$ (2.4).

Acetylation of **1a**. Acetylation of 4*β*-cinnamoyloxy-1*β*, 2*α*-dihydroxyeudesm-7-ene (50mg) with Ac_2O–pyridine in the usual conditions yielded an oily product which after chromatography gave 4*β*-cinnamoyloxy-1*β*, 2*α*-acetoxyeudesm-7-ene (**1b**). **IR** $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1740, 1630 and 1580; ^1H NMR (80 MHz, $CDCl_3$, TMS as int. standard): δ 7.65 (1H, *d*, *J* = 16 Hz, H-1′), 6.33 (1H, *d*, *J* = 16 Hz, H-2′), 7.35 (5H, *m*, Ar), 5.35 (1H, *m*, H-8), 5.15 (1H, *ddd*, *J* = 10, 10, 4 Hz, H-2), 4.85 (1H, *d*, *J* = 10 Hz, H-1), 3.3 (1H, *dd*, *J* = 14, 4 Hz, H-3eq.), 2.15 (3H, *s*, AcO–), 2.00 (3H, *s*, AcO–), 1.64 (3H, *s*, Me-4), 1.05 (6H, *d*, *J* = 6 Hz, Me-11), 1.00 (3H, *s*, Me-10); MS (70 eV) *m/z* (rel. int.): 320 $[M-148]^+$ (1.2), 260 $[320-60]^+$ (6.5), 200 $[260-60]^+$ (1.4).

Epoxidation of **1a**. A soln of **1a** (50 mg) in CH_2Cl_2 (7 ml) was treated with *m*-chloroperbenzoic acid (50 mg). The mixture was stirred at room temp. for 20 min. Usual work-up gave **3** (20 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1720, 1640, 1580; MS (70 eV) *m/z* (rel int.): 252 $[M-148]^+$ (100), 234 $[252-18]^+$ (7.7), 212 (234 $-18]^+$ (2.5%).

Hydrogenation of **1a**. Compound **1a** (50 mg) in EtOAc was hydrogenated in the presence of Pd–C at room temp. The filtered soln was evaporated *in vacuo* and gave an oily gum (40 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1720, 1600; MS (70 eV) *m/z* (rel. int.): 386 $[M]^+$, 236 $[386-150]^+$ (40), 218 $[236-18]^+$, 200 $[218-18]^+$.

Dialdehyde **4**. 4β-Cinnamoyloxy-1β,2α-dihydroxyeudesm-7-ene (**1a**) (10 mg) was dissolved in dry Et_2O (5 ml) and treated with 10 mg HIO_4. The soln was stirred for 1 hr at room temp., washed with H_2O, 10% aq. $KHCO_3$ and satd aq. NaCl. The reaction mixture was dried (Na_2SO_4) and concd to give **4**. ^1H NMR (80 MHz, $CDCl_3$, TMS as int. standard): δ 9.55 (1H, *m*), 9.45 (1H, *s*), 7.6 (1H, *d*, *J* = 16 Hz, H-1'), 6.20 (1H, *d*, *J* = 16 Hz, H-2'), 7.35 (5H, *m*, Ar), 5.35 (1H, *m*, H-8), 1.6 (3H, *s*, Me-4), 1.25 (3H, *s*, Me-10), 1.1 (6H, *d*, *J* = 6 Hz, Me-11).

Diketone **5**. A soln of **2a** (300 mg) in cold Me_2CO (20 ml) was treated with Jones' reagent drop by drop until the soln was a persistent yellow colour. The reaction mixture was kept at room temp. for 30 min and then passed through a column packed with Tonsil. The solvent was eliminated and the substance was crystallized from Me_2CO–hexane affording 114 mg compound **5**, mp 118–120°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1715, 1665, 1180; MS *m/z*: 380 $[M]^+$, 232 $[M-148]^+$, 217 $[M-148-15]^+$, 214 $[M-148-18]^+$.

Crystal structure analyses for **1a**. X-ray data were collected using MoKα radiation in an Enraf–Nonius CAD4 automated diffractometer equipped with a graphite monochromater. Crystal data: $C_{24}H_{32}O_4$, MW 384.5, orthorhombic space group $P2_12_12_1$, $a = 7.897\,(3)$, $b = 17.336\,(4)$ $c = 32.192\,(4)$ Å, $Z = 8$, $d_c = 1.159$ g/cm, $\lambda = 0.71073$ Å, $\mu(MoK\alpha) = 0.835$ cm^{-1}. Intensity data were collected by $\omega - 2\theta$ scans of variable speed designed to yield $1 \simeq 50\sigma\,(I)$ for all observable reflections. All data in one octant having $1° < \theta < 25°$ were measured. Background, Lorentz and polarization corrections were applied to the data; no absorption corrections were necessary.

The structure was solved by direct methods (MULTAN) [7] and refined by full matrix least squares with unit weights. Oxygen atoms were refined anisotropically, while other heavy atoms were treated isotropically. Hydrogen atoms were located by difference maps and included in structure factor calculations, but were not refined. $R = 0.059$ for 2211 observed data. Co-ordinates of oxygen and hydrogen atoms are listed in Table 3.

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