mp ~ 200° (decomp.) (3). IR(KBr): C=CHO 2750, 1700, 1620 cm^{-1}. Compound 1 (137 mg) was heated 2 hr with 12 ml 7% H_2SO_4 at 100°. After extraction with Et_2O the H_2O phase was neutralized with K_2CO_3, evaporated under vacuum and the residue dissolved in MeOH. The sugar obtained was identical in all properties with authentic galactose (PMR, PC and GLC of the TMSi ether).

Acknowledgement—A.G.R.N. thanks U.G.C., New Delhi for a research grant.

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A NEW AROMATIC ESTER DITERPENE FROM *EUPHORBIA POISONII*

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(*Received* 6 *April* 1976)

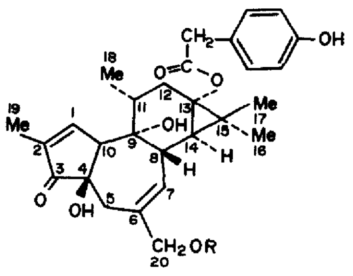
Key Word Index—*Euphorbia poisonii*; Euphorbiaceae; 12-deoxy-4β-hydroxyphorbol-13-*p*-hydroxyphenylacetate-20-acetate; proresiniferatoxin; diterpenes.

As a result of screening sixty species of the genus *Euphorbia* for diterpenes [1] it was found that 12-deoxyphorbol was one of the most common of this group of compounds to occur in the plant latices. This diterpene normally occurs as either mono- or diesters of aliphatic fatty acids varying from acetic to dodecenoic [2, 3]. Aromatic acids have only rarely been found as acyl moieties of 12-deoxyphorbol, the C-13 phenylacetate [4], and the corresponding C-20 acetyl diester [5, 6] being the only examples to date. We have isolated a series of esters from the latex of *E. poisonii* consisting of ortho-ester-tricyclic types [4] and *o*-acyl-esters of 12-deoxyphorbol. In this communication we describe the identification of two minor esters which were base line TLC products in the initial extraction. Both of these toxins demonstrate potent inflammatory effects on mammalian skin [7], and one of these is a new aromatic ester diterpene.

Plant material. E. poisonii latex, collected into ethanol in West Africa in 1974.

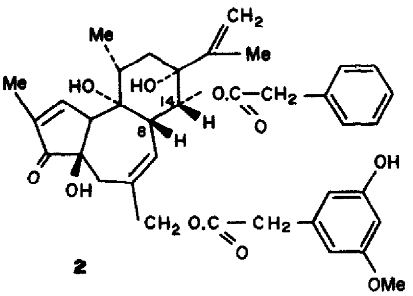
Present work. Dried latex was exhaustively extracted with acetone. After removal of solvent the cream white solid had an irritant dose 50% (I.D.$_{50}$) of 0.1 μg/5 μl/ear on mice. Residue was dissolved in 50% MeOH and extracted with hexane to remove lipids and triterpenoids, and the diterpenes were then extracted from the polar phase with ether. Removal of ether afforded a friable colourless resin, I.D.$_{50}$ = 0.06 μg/5 μl/ear, which was separated into several components by column chromatography followed by PLC. (30% butanone in cyclohexane, kieselguhr G 0.75 mm, 120° for 1 hr, impregnated by developing with 20% digol in acetone and air dried.)

12-deoxyphorbol-13-p-hydroxyphenylacetate-20-acetate (**1**). Yield 0.002% of latex, produced an orange spot by TLC in the system above ($R_f = 0.35$ after three developments) when sprayed with 60% aq. H_2SO_4 and heated. The IR spectrum (KBr discs) exhibited ν_{max} at 3460, 1740 and 1715 cm^{-1} and the UV spectrum exhibited λ_{max}^{MeOH} at 238 (log ε 3.8) and 290 (log ε 3.4) nm. (Bathochromic shift to 304 nm with addition of NaOH). The high resolution electron impact MS exhibited an M^+ ion at *m/e* 524.2411 (<5%, $C_{30}H_{36}O_8$) and significant fragmentation ions in the upper region of the spectrum at *m/e* 506 (<5%; $M^+ - 18$); 464 ($C_{28}H_{32}O_6$; 10%); 417 (40%, $M^+ - 107$); 399 (32%, $M^+ - [107 + 18]$); 339 (34%, $M^+ - [107 + 18 + 60]$); 372 (22%, $M^+ - 152$); 354 (11%, $M^+ - [152 + 18]$); 312 (100%, $M^+ - [152 + 60]$); 294 (70%, $M^+ - [152 + 60 + 18]$). The remainder of the spectrum was identical to 12-deoxyphorbol diacetate [8]. In the NMR spectrum (100 MHz, $CDCl_3$) signals were evident at δ 7.59 (1H, *bs*, C-1); 7.23–6.73 (4H, *q*, *J* 8 Hz, aromatics); 5.69 (1H, *d*, *J* 4 Hz, C-7); 4.46 (2H, *s*, C-20); 3.55 (2H, *s*, $-CH_2-\phi$); 3.28 (1H, *m*, C-8); 3.02 (1H, *m*, C-10); 2.44 (2H, *s*, C-5); 1.82 (3H, *m*, C-19); 1.075 (6H, *d*, *J* 3 Hz, C-16, C-17); 5.43, 5.05, 2.48 (3H, OH deuterium exchange); 0.89 (3H, *d*, *J* 6 Hz, C-18); 0.77 (1H, *d*, *J* 6.0 Hz, C-14). The CD spectrum (MeOH) exhibited a positive cotton effect at 228 nm and negative cotton effects at 205, 270 and 339 nm. Mild hydrolysis of (**1**) in 0.05 M KOH in MeOH for 30 min produced **1a** the desacetyl compound. The MS of **1a** was typical of a mono-ester of 12-deoxyphorbol [8], exhibiting an M^+ ion at *m/e* 482 and a typical $M^+ - [\text{acyl}]$ ion at *m/e* 330. The NMR spectrum was similar to (**1**) with the exception that the 3H signal at δ 2.06 due to the acetyl methyl group was absent and the 2H signal at δ 4.46 had moved upfield to δ 3.99, confirming the absence of a primary acetyl moiety at C-20 in **1a**. Complete hydrolysis of **1** in barium hydroxide–methanol under nitrogen produced two products. The first of these was the parent diterpene, 12-deoxy-4β-hydroxyphorbol identified as its diacetate (TLC, GLC, CD, MS, NMR) and the second was the aromatic acid *p*-hydroxyphenyl-



1 R = Ac

1a R = H



2

acetic acid, identified as its methyl ester (GLC, MS, NMR). Acetylation of **1a** produced **1** (TLC, MS) confirming the structure of **1** as the new natural product 12-deoxy-4β-hydroxyphorbol-13-*p*-hydroxyphenyl-acetate-20-acetate.

Pro-resiniferatoxin (**2**) [9], yield 0.02% of latex, produced an orange–black spot in the same system as before. (R_f 0.30 after four developments). The IR spectrum (KBr discs) exhibited ν_{max} at 3340, 2970, 1735, 1715 and 1630 cm^{-1}. In the MS, **2** produced an M^+ ion at *m/e* 646 (<2%, $C_{37}H_{42}O_{10}$) and a larger $M^+ - [18]$ ion (30%, $C_{37}H_{40}O_9$) at *m/e* 628. The rest of the spectrum was similar to resiniferatoxin [4]. The NMR (60 MHz, $CDCl_3$) exhibited signals at δ 7.54 (1H, *bs*, C-1); 7.34 (5H, *s*, aromatics); 6.80 (3H, *s*, aromatics); 5.55 (1H, *m*, C-7, superimposed on δ 5.49); 5.49 (1H, *s*, phenolic OH, superimposed on δ 5.55); δ 5.17 (2H, *bs*, C-17, superimposed on δ 5.05); δ 5.05 (1H, *d*, C-14, superimposed on δ 5.17); δ 4.48 (2H, *bs*, C-20); 3.89 (3H, *s*, φ–OMe); 3.60 (2H, *s*, φ–CH_2–); δ 3.54 (2H, *s*, φ–CH_2–, superimposed on δ 3.45); 3.45 (1H, *m*, C-8, superimposed on δ 3.54); 3.04 (1H, *m*, C-10); 2.65 (1H, *m*, C-11); 2.50–2.18 (4H, complex, C-5, C-12); 1.80 (3H, *m*, C-19); 1.71 (3H, *s*, C-16); 0.91 (3H, *d*, *J* 6.75 Hz, C-18); 3 OH between δ 2.2–δ 3.1 (deuterium exchange). (Double resonance demonstrated that the C-14 proton at δ 5.05 was coupled with the C-8 proton at δ 3.45). Pro-resiniferatoxin (**2**) when heated in organic solvent, using a trace of trifluoracetic acid produced the ortho-ester, resiniferatoxin [9] (TLC, MS, NMR). On mild hydrolysis in KOH–MeOH resiniferatoxin was converted to 20-hydroxytinyatoxin [4] (TLC, MS, NMR) which, upon acetylation, produced a mono-acetate [4] (MS, TLC). Resiniferatoxin exhibits cotton effects in its CD spectrum (MeOH) at 240 nm, $\Delta E = +8.35$; 225 nm, $\Delta E = +11.40$ and 200 nm, $\Delta E = -20.05$, whilst pro-resiniferatoxin produces cotton effects at 244 nm, $\Delta E = +6.80$; 230 nm, $\Delta E = +7.48$ and 195 nm, $\Delta E = -11.29$, suggesting that the *trans*-junction between rings A and B in resiniferatoxin is common to pro-resiniferatoxin (**2**).

Taxonomic significance. E. poisonii is a succulent species which is morphologically similar to *E. unispina*, and is indigenous to similar areas of North-west Africa. Neither of these species was classified in the major work on the genus [10], but *E. unispina* on the basis of spine characteristics was erected as a new sub-section monocanthium by Anton [11]. We have found that under certain conditions of habitat these species are difficult to distinguish, even if quantitative measurements are made as suggested by others [12]. Both species contain resiniferatoxin, tinyatoxin, pro-resiniferatoxin and 12-deoxyphorbol-13-phenylacetate-20-acetate; however 12-deoxy-4β-hydroxyphorbol-13-*p*-hydroxyphenylacetate-20-acetate (**1**) appears to be unique to *E. poisonii*, and may therefore be useful in the identification of the two species on chemical grounds.

Acknowledgements—We are grateful to Dr. L. Phillips and Mr. J. Bergess for the 100 MHz NMR spectrum, and to the Central Research Fund, University of London, for a travel grant.

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