(H-5 at 6.01 ppm) and homoallylically coupled to a proton (H-6) at 5.26 ppm under the carbon carrying the methacrylic ester function. The sequence H-5 through H-9 was established by double resonance as in the case of goyazensolide and will not be discussed in detail. The presence of the dihydrofuran-3-one system C-10 through C-4 required by the formula was supported by the IR (bands at 1700 and 1590 $cm^{-1}$), UV ($\lambda_{max}$266 nm, $\epsilon$ 5600) and NMR spectrum (H-2 singlet at 5.70, methyl singlet at 1.51 ppm). Consequently, the new lactone is **1a** (15-deoxygoyazensolide). The stereochemistry shown in formula **1a** can be assigned on the basis of the same arguments used previously for goyazensolide [5].

## EXPERIMENTAL

*Extraction of* Vanillosmopsis erythropappa. Above-ground parts of the plant (except for the wood), wt 8 kg, collected by Dr. Hermogenes de Freitas Leitão Filho in Campos de Caraguatatuba, vicinity of Caraguatatuba, São Paulo State, Brazil, in May 1971, were extracted with hexane. The crude gum, wt 25 g, was chromatographed over Si gel–$AgNO_3$ (30%), wt 750 g, 200 ml fractions being eluted with hexane containing increasing amounts of EtOAc (hexane), EtOAc acetate and then with EtOAc–EtOH mixtures. The material from fractions 83–92 (hexane–EtOAc 5:1) was combined, wt. 1.29 g; a portion (0.5 g) was further purified by preparative TLC on silica gel (hexane–EtOAc, 2.5:1). The fraction which exhibited a violet fluorescence under UV light was eluted, to yield 45 mg of gum which was recrystallized from hexane to give an amorphous solid, mp 132–4°, $[\alpha]_{Hg}^{24}$ −38° ($CHCl_3$, 7.6 mg/ml), CD curve (MeOH) $[\theta]_{316}$ +13230, $[\theta]_{265}$ −7410, UV $\lambda_{max}$ 266 nm ($\epsilon$ 5600) and strong end absorption, IR bands at 1770, 1710, 1700, 1650, 1630, and 1590 $cm^{-1}$. The low resolution MS exhibited significant peaks at *m/e* 344 ($M^+$), 275 ($M^+ - C_4H_5O$), 260 ($M^+$–$C_4H_5O$–$CH_3$) and 232 ($M^+$–$C_4H_5O$–Me–CO) (Calc for $C_{19}H_{20}O_6$; C, 66.27; H, 5.85; 0, 27.88; MW, 344.1259. Found C, 65.99; H, 5.74; 0, 27.67; MW(MS), 344.1262).

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# A NEW DITERPENE GALACTOSIDE FROM *ACANTHOSPERMUM HISPIDUM**

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**Key Word Index**—*Acanthospermum hispidum*; Compositae; acanthospermol-β-galactosidopyranoside; structural determination.

*Plant and origin.* Aerial parts of *Acanthospermum hispidum* DC, Voucher specimen 9/73, JIPMER, collected in Pondicherry, India. The roots of this species contain the widespread tridecapentaynene [1]. The alcoholic extract of fresh aerial parts of *A. hispidum* DC yielded a crystalline compound which on acetylation gives a hexaacetate. The MS leads to the elementary formula $C_{38}H_{56}O_{14}$. The fragments *m/e* 389 and 331 correspond to the compositions $C_{24}H_{37}O_4$ and $C_{14}H_{19}O_9$ respectively and are in agreement with those of a glycoside of a diterpene triol. Acid hydrolysis gives galactose while the diterpene cannot be obtained in an unrearranged form. Also the PMR-spectrum of the hexaacetate is in agreement with an acetylated β-galactosidopyranoside (Table 1). Furthermore the spectrum shows three Me-singlets, a secondary OCOMe group [*dd* $\delta$ = 4.75($J$ = 2,2 Hz)], the group $CH_2C(Me)$=$CH\,CH_2OAc$, a methylene group (*s*(*br*) 4.91 and 5.10) as well as a further secondary ∩CHOR group [*dd* 4.43 ($J$ = 2,2)].These data correspond with a bicyclic diterpene with three O-functions. Manganese dioxide oxidation shows the presence of a primary allylic OH.

Further PMR studies lead to the structure **1**, its absolute configuration not being clear. Also the $^{13}C$ NMR-spectrum is in agreement with **1**. The correlation of the signals could be achieved by an "offresonance"-spectrum and by using $Yb(fod)_3$ as shift-reagent. The observed

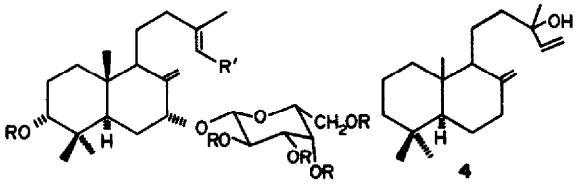
* Part 79. in the series "Naturally Occurring Terpene-Derivatives", Part 78. see Bohlmann, F., Zdero C. and Grent M. *Chem. Ber.* (in press).

Table 1. NMR data of compounds 1–3 ($\delta$-values, TMS as internal standard)

| | 1 ($CD_3OD$) | 2 ($C_6D_6$–$CDCl_3$ 2:1) | J(Hz) | 2 + Eu(fod)$_3$ Δ* | 3 ($CD_3OD$) | 2 $^{13}C(CDCl_3)$ + Yb(fod)$_3$ Δ* | | |
|---|---|---|---|---|---|---|---|---|
| 1–H | | | | | | C–1 | *t* 32.6 | 0.34 |
| 2–*H* | *m* 1.4–1.9 | *m* 1.5–1.8 | | | *m* 1.4–1.9 | C–2 | *t* 23.5 | 0.76 |
| 3–H | *m* 3.37 | *dd* 4.75 | $J_{2\alpha,3} = J_{2\beta,3}$ 2 | 4.92 | *m* 3.41 | C–3 | *d* 77.5 | 1.57 |
| 5–H | | *dd* 1.42 | $J_{5,6\alpha} = 3$ | | | C–4 | *s* 36.4 | 0.69 |
| 6–H | *m* 1.4–1.9 | *m* 1.31 | $J_{5,6\beta} = 12$ | | *m* 1.5–1.8 | C–5 | *d* 42.3 | 0.46 |
| 7–H | *dd* 4.51 | *dd* 4.43 | $J_{6\alpha,7} = J_{6\beta,7} = 2$ | 0.69 | *dd* 4.51 | C–6 | *t* 29.1 | 0.27 |
| 9–H | *m* 2.16 | *m* 2.25 | | | *m* 2.15 | C–7 | *d* 77.4 | 0.25 |
| 11–H | *m*1.4–1.9 | *m*1.5–1.8 | | | *m*1.5–1.8 | C–8 | *s* 144.9 | 0.22 |
| 12–H | *m* 2.16 | *m* 1.90 | | | *m* 2.15 | C–9 | *d* 51.1 | 0.26 |
| 14–H | *t*(*br*) 5.35 | *t*(*br*) 5.47 | $J_{14,15} = 7$ | 1.15 | *d*(*br*) 5.87 | C–10 | *s* 39.4 | 0.35 |
| 15–H | *d*(*br*) 4.07 | *d*(*br*) 4.63 | | 3.10 | *d* 9.95 ($J$ = 7.5) | C–11 | *t* 21.9 | 0.16 |
| 16–H | *s*(*br*) 1.66 | *s*(*br*) 1.68 | | 0.61 | *d* 2.21 ($J$ = 1) | C–12 | *t* 38.4 | 0.18 |
| 17–H | *s*(*br*) 5.13 | *s*(*br*) 5.04 | | 0.45 | *s*(*br*) 5.14 | C–13 | *s* 142.2 | 0.25 |
| 17–H | *s*(*br*) 4.87 | *s*(*br*) 4.82 | | 0.48 | *s*(*br*) 4.85 | C–14 | *d* 118.7 | 0.33 |
| 18–H | *s* 0.71 | *s* 0.57 | | 0.54 | 0.74 | C–15 | *t* 61.2 | 0.53 |
| 19–H | *s* 0.83 | *s* 0.68 | | 0.72 | 0.83 | C–16 | *q* 16.5 | 0.16 |
| 20–H | *s* 0.91 | *s* 0.82 | | 1.80 | 0.92 | C–17 | *t* 113.8 | 0.14 |
| 1'–H | *d* 4.14 | *d* 4.37 | $J_{1,2} = 8$ | 0.93 | *d* 4.14 | C–18 | *q* 13.5 | 0.20 |
| 2'–H | *dd* 3.57 | *dd* 5.47 | $J_{2,3} = 10$ | 1.46 | *dd* 3.57 | C–19 | *q* 27.8 | 0.65 |
| 3'–H | *dd* 3.43 | *dd* 5.02 | $J_{3,4} = 3$ | 1.79 | *m* 3.41 | C–20 | *q* 21.9 | 0.16 |
| 4'–H | *d* 3.81 | *dd* 5.39 | $J_{4,5} \approx 1$ | 1.43 | *d* 3.81 | C–1' | *d* 96.4 | 0.21 |
| 5'–H | *m* 3.37 | *dd*(*br*) 3.46 | $J_{5,6} = 6.5$ | 0.86 | *m* 3.41 | C–2' | *d* 71.1 | 0.21 |
| | | *dd* 4.10 | | | | C–3' | *d* 70.6 | 0.21 |
| 6'–H | *m* 3.73 | *dd* 4.12 | $J_{6,6} = 11$ | 1.11 | *m* 3.74 | C–4' | *d* 68.8 | 0.72 |
| OAc | — | *s* 1.73 | | 0.56 | — | C–5' | *d* 67.2 | 0.21 |
| | | *s* 1.77 | | 0.71 | | C–6' | *t* 61.4 | 0.46 |
| | | *s* 1.80 | | 1.37 | | | | |
| | | *s* 1.83 | | 2.79 | | | | |
| | | *s* 1.93 | | 1.07 | | | | |
| | | *s* 1.98 | | 4.13 | | | | |

* *ca* 0.4 mol Eu(fod)$_3$ in relation to **2**.

position of the signals are in good agreement with those expected from known substituent effects, the special steric effects from steroids [2] and comparison with the values of a similiar diterpene (**4**) [3]. The position of the sugar moiety is also clear as a free 7-OH should have been oxidized with $MnO_2$.




**1**: R = H, R' = $CH_2OH$ **2**: R = Ac, R' = $CH_2OAc$
**3**: R = H, R' = CHO

**4**

The new glycoside we have named acanthospermol-$\beta$-galactosidopyranoside.

## EXPERIMENTAL

NMR $\delta$-values, TMS as internal standard; MS were recorded at 70 eV. Fresh leaves of *A. hispidum* (3.5 kg) were extracted with hot 95% EtOH. The extract was concentrated to *ca* 1.5 l. (vacuum), extracted after filtration with petrol (60–80°, 6 l.), with $Et_2O$ (6 l.) and finally with EtOAc (8 l.). The last extract after concentration to *ca* 150 ml yielded 4 g of the crude glycoside which after 3 recrystallizations from MeOH–$Me_2CO$ had a mp 223–24° (**1**). It had no measurable optical rotation. The glycoside **1** (100 mg) $Ac_2O$ in 2 ml and 0.1 ml Py was heated with 30 mg 4-pyrrolidino-pyridine for 30 min at 70°. After evaporation (vacuum) residue was dissolved in $Et_2O$ and washed with dil $H_2SO_4$ and $NaHCO_3$. PLC ($Et_2O$–petrol 2:1) gave 120 mg **2**, colourless oil, *IR*. OAc 1750, 1250 $cm^{-1}$. *MS*. [*m/e*] 736.366 (0.05) (M) (calc. for $C_{38}H_{56}O_{14}$ 736.367); 389.269 (26) (calc. for $C_{24}H_{37}O_4$ 389.269); 331.102 (86) (calc. for $C_{14}H_{19}O_6$ 331.103). The glycoside **1** (50 mg) in 3 ml MeOH was stirred for 3 hr with 500 mg $MnO_2$. After filtration and evaporation under vacuum the residue gave colourless crystals from MeOH–$Et_2O$,

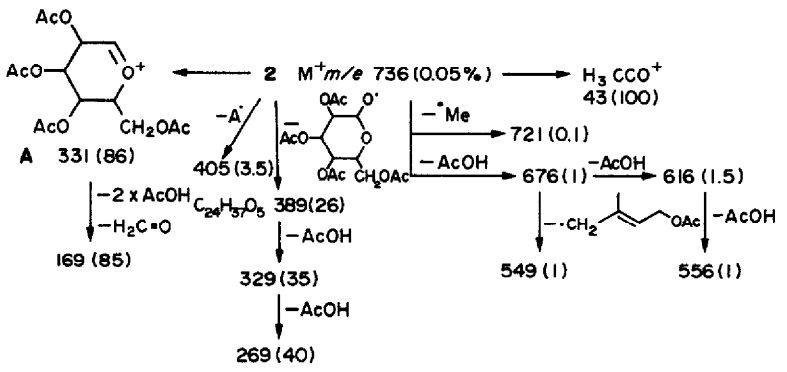



Fig. 1.

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).

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# A NEW AROMATIC ESTER DITERPENE FROM *EUPHORBIA POISONII*

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**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 $\nu_{max}$ at 3460, 1740 and 1715 $cm^{-1}$ and the UV spectrum exhibited $\lambda_{max}^{MeOH}$ 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 $M^+ - [acyl]$ 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-