Guava aroma is highly desirable in processed products such as jellies and blended fruit drinks. Unlike our total guava extract the hydrocarbon fraction was devoid of fresh guava aroma. However, Shaw [6] has shown with certain essential oils that when a single hydrocarbon component is by far the major constituent, it can exert a profound influence on flavour in combination with minor oxygenated components. Therefore, caryophyllene might yet be shown to be important in guava aroma.

EXPERIMENTAL

Extraction methods. Wild Florida guavas (*Psidium guajava* L.) were used. *Ca* 100 kg of whole fruit was pureed in a Chisholm Ryder (Chisholm Ryder C., Inc., Niagra Falls, NY) finisher (5.1 mm screen) at 15 psi air pressure. The puree, about 75 kg, was placed in a cold walled stainless steel tank held at −1° and mixed with 19 l. CH_2Cl_2. The organic layer was allowed to settle to the bottom and removed through a valve; it was then concd in a rotary evporator at room temp. to afford 58 g dark brown residue (total extract) with a strong aroma characteristic of fresh guava.

TLC separation. The total extract, not readily separable by GLC because of its viscosity, was separated into 4 fractions by PLC on Si gel HF_{254} plates 1 mm thick, with hexane–Me_2CO (49:1). The least polar fraction, which contained the terpenes and sesquiterpenes, by far the largest of the 4 fractions, was removed, then eluted with developing solvent. The eluate was concd and then analysed by GC–MS and IR spectroscopy.

GC–MS analyses. The gas chromatograph used for GC–MS analyses was a Varian Model 1400 instrument equipped with a flame ionization detector and a 1:1 splitter. Injection port and detector temperature was 225°. A 0.76 mm × 305 m column coated with Carbowax 20 M was programmed from 70 to 200° at 1°/min with an He flow rate of 10 ml/min. GC–MS separations were obtained with a Bell & Howell Model 21-490 mass spectrometer at 70 eV coupled through a jet separator to GC

IR analyses. Separations for IR analyses were made by an F&M Model 700 gas chromatograph equipped with 5.1 mm × 6.1 m stainless steel columns packed with 40% Carbowax 20 M on 60–80 mesh Gas Chrom P. The thermal conductivity detector and injection port temps were 275 and 245°, respectively. Temp. was programmed from 100 to 220° at 1°/min at a He flow rate of 100 ml/min. IR spectra were determined as thin-liquid films.

REFERENCES

1. Bailey, L. H. and Bailey, E. Z. (1976) *Hortus Third* p. 527. Macmillan, New York.
2. Greany, P., private communication.
3. Misra, K. and Seshadri, T. R. (1965) *Phytochemistry* **7**, 641.
4. Smith, R. M. and Siwatibau, S. (1975) *Phytochemistry* **14**, 2013.
5. Stevens, K. L., Brekke, J. E. and Stern, D J. (1970) *J. Agric. Food Chem.* **18**, 598.
6. Shaw, P. E. (1977) in *Citrus Science and Technology* (Nagy, S., Shaw, P. E. and Veldhuis, M. K. eds) Vol. 1, p. 427. Avi, New York.
7. Wilson, C. W. (1969) *J. Food Sci.* **34**, 521.
8. Asakawa, Y., Komatsu, T., Hayashi, S. and Matsurra, T. (1971) *Flavour Ind.* **2**, 114.
9. Sutherland, O B. and Hutchins, R. F. N. (1972) *Nature* **23**, 1970.
10. Jacobson, M. (1972) *Insect Sex Pheromones* p. 251. Academic Press, New York.

Phytochemistry, 1978, Vol 17, pp 1436–1437 ©Pergamon Press Ltd Printed in England 0031-9422/78/0801-1436 $02 00/0

TWO MINOR DITERPENES FROM *EUPHORBIA* LATEX

RICHARD J. SCHMIDT and FRED J. EVANS
Department of Pharmacognosy, The School of Pharmacy (University of London), 29–39 Brunswick Square, London WC1N 1AX, U.K.

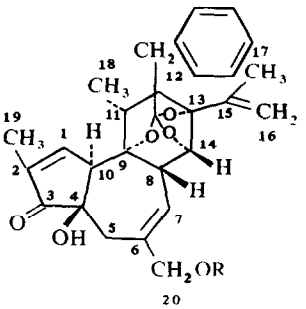
(*Received* 24 *January* 1978)

Key Word Index—*Euphorbia poisonii*; Euphorbiaceae; diterpenes; 20-*O*-acetyl-resiniferonol-9,13,14-*ortho*phenylacetate; 12-deoxyphorbol-13-O-[p-acetoxyphenylacetate]-20-acetate.

The section *Euphorbium* of the genus *Euphorbia* consists of succulent species indigenous to central and southern Africa. From the latex of several species of *Euphorbium* several novel ester diterpenes have been obtained [1–6]. *Euphorbia poisonii* is a member of the section *Euphorbium* from which esters of 12-deoxyphorbol, 12-deoxy-16-hydroxy-phorbol and resiniferonol have previously been isolated [7–9]. Further examination of the Et_2O fraction of the latex extract by means of both column chromatography and TLC yielded two new minor diterpene esters **1** and **3** in an impure form.

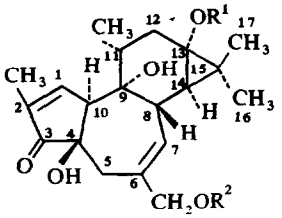
20-0-*Acetyl-resiniferonol*-9,13,14-ortho *phenylacetate* **1**

This ester was purified by partition TLC. Kieselguhr G plates (0.5 mm) were developed for 20 cm in 20% dipropylene glycol in Me_2CO and then air dried. The coated plates were developed twice in *n*-heptane–C_6H_6 9:1 (hR_f 32). After recovery of the ester [10], it was again purified by a second partition TLC step as before using *n*-heptane–benzene 17:3 (hR_f 51) as solvent and developing twice. The recovered resin produced a single black-orange spot on analytical TLC after spraying with 50% aq H_2SO_4 and heating. This compound was



1 R = CO.CH_3

2 R = H



3 R^1 = CO . CH_2—C$_6$H$_4$—O.CO.CH_3 R^2= CO.CH_3

4 R^1 = CO . CH_2—C$_6$H$_4$—OH R^2=H

5 R^1, R^2=H

6 R^1, R^2=CO . CH_3

obtained in 0.002% w/w yield from the latex. The MS of compound **1** (210°, 70 eV, measured values were within 10 ppm calculated values), exhibited significant ions at *m/e* 506 (6%, M^+·, $C_{30}H_{34}O_7$), 488 (2%), 446 (5%), 428 (2%), 370 (56%), 352 (4%), 341 (12%), 328 (21%), 310 (100%), 295 (10%), 292 (19%), 282 (20%). The IR spectrum exhibited V_{max} at 3450, 3040, 1740, 1715 and 1635 cm^{-1}. The PMR spectrum ($CDCl_3$, TMS, 60 MHz) exhibited signals at δ 7.49 (*bs*, 1H), 7.31 (*m*, 5H), 5.95 (*bs*, 1H), 4.76 (*s*, 2H), 4.57 (*s*, 2H), 4.28 (*d*, J = 2Hz, 1H), 3.23 (*s*, 2H), 3.14 (*m*, 2H), 2.42–2.06 (AB*q*, J = 7.3 Hz, 2H), 2.1 (*s*, 3H), 1.86 (*d*, *d*, 3H), 1.85 (*m*, 2H), 1.58 (*s*, 3H), 0.98 (*d*, J = 6.7 Hz, 3H), 2.25 (*s*, 1H, exchangeable with D_2O). Acid catalysed transesterification (1% $HClO_4$ in MeOH) produced resiniferonol-9,13,14-*ortho*phenylacetate **2** in 80% yield. This product was purified by partition TLC as before, using cyclohexane–EtOAc (7:3) (hR_f 36) as solvent. Compound **2** exhibited significant ions in the MS (200°, 70 eV) at *m/e* 464 (6%, M^+·, $C_{28}H_{32}O_6$), 446 (5%), 428 (1%), 328 (48%), 310 (100%), 295 (8%), 292 (13%), 282 (36%). In the IR spectrum V_{max} were evident at 3450, 3090, 1705, 1635 and 1610 cm^{-1}. The PMR spectrum ($CDCl_3$, TMS, 60 MHz) exhibited signals at δ 7.48 (*bs*, 1H), 7.32 (*m*, 5H), 5.89 (*bs*, 1H), 4.75 (*s*, 2H), 4.27 (*d*, J = 3Hz, 1H), 4.09 (*s*, 2H), 3.21 (*s*, 2H), 3.15 (*m*, 2H), 2.6–2.3 (AB*q*, J = 13.7 Hz, 2H), 1.84 (*m*, 2H), 1.82 (*d*,*d*, 3H), 1.54 (*s*, 3H), 0.99 (*d*, J = 6.7 Hz, 3H), 2.95 and 1.82 (*s*, 1H each, exchangeable with D_2O). Compound **2** was acetylated with AC_2O–Py for 2 hr at room temp and after removal of the reagents in a stream of N_2 the product was purified by partition TLC using *n*-heptane–C_6H_6 (17:3). The acetylated product was identical (TLC, MS, PMR) with 20-*O*-acetyl-resiniferonol-9,13,14-*ortho*phenylacetate **1**.

12-Deoxyphorbol-13-[p-acetoxyphenylacetate]-20-acetate **3**

This ester was obtained from the same column fraction of the Et_2O extract as **1**. Final purification of **3** was achieved by partition TLC using *n*-heptane–C_6H_6 (9:1) (hR_f 48) as solvent. The recovered resin produced a single orange–brown spot by analytical TLC after spraying with 50% H_2SO_4 and heating. Compound **3** was isolated in 0.0004% w/w yield from the latex. In the MS (180°, 70 eV) **3** exhibited significant ions at *m/e* 566 (0.6%, M^+·, $C_{32}H_{38}O_9$), 548 (0.4%), 506 (5%), 488 (1%), 417 (21%), 399 (27%), 372 (11%), 357 (16%), 354 (7%), 329 (15%), 312 (100%, $C_{20}H_{24}O_3$), 294 (73%), The CD spectrum (0.35 mg/ml MeOH), exhibited Cotton effects at 203 (ΔE = −17.2), 228 (ΔE = +12.7), 271 (ΔE = −0.74), 283 (ΔE = −0.44) and 335 nm (ΔE = −0.54). Acid catalysed transesterification of **3** as previously described produced the monoester **4**, which was identified as 12-deoxyphorbol-13-[*p*-hydroxy-phenylacetate] (MS, CD, PMR, TLC) [8]. Alkaline hydrolysis of **3** (satd $Ba(OH)_2$ in MeOH) produced the triol **5** which was acetylated as before and crystallised from MeOH (mp 138°). The diacetate **6** was identified as 12-deoxyphorbol diacetate (PMR, MS, TLC, GLC). Acetylation of **4** with AC_2O–Py at room temp followed by partition TLC purification as previously described afforded compound **3** (TLC, MS).

REFERENCES

1. Gschwendt, M. and Hecker, E. (1973) *Z. Krebsforsch.* **80**, 335.
2. Gschwendt, M. and Hecker, E. (1974) *Z. Krebsforsch.* **81**, 193.
3. Kinghorn, A. D. and Evans, F. J. (1975) *J. Pharm. Pharmacol.* **27**, 329.
4. Hergenhahn, M., Kusumoto, S. and Hecker, E. (1976) *Experientia* **30**, 1428.
5. Schmidt, R. J. and Evans, F. J. (1977) *Lloydia* **40**, 225.
6. Evans, F. J. (1978) *Toxicon* **16**, 51.
7. Evans, F. J. and Schmidt, R. J. (1976) *Phytochemistry* **15**, 333.
8. Schmidt, R. J. and Evans, F. J. (1976) *Phytochemistry* **15**, 1778.
9. Schmidt, R. J. and Evans, F. J. (1977) *Experientia* **33**, 1197.
10. Evans, F. J., Schmidt, R. J. and Kinghorn, A. D. (1975) *Biomed. Mass-spect.* **2**, 126.