

silica-alumina 113 (in hexane and eluted with hexane 3% EtOAc). Crystallized from EtOAc; m.p. 253°; $[\alpha]_D^{20} +13$ (CHCl₃). The IR spectrum was identical to that of the sample obtained by HCl reaction on ursolic acid [3]. *Unsaturated ursolic acid lactone*. Separated from the same column and isolated as its acetate crystallized from EtOAc in microcrystals; m.p. 252°; $[\alpha]_D^{20} +46°$ (CHCl₃). IR and NMR spectra showed that the natural lactone was identical to the lactone obtained by LiAlH₄ reduction of 3-acetoxy-11-keto-ursolic acid [4]. It was thus proved to be 3 β -acetoxy-ursa-11,12-ene-oic-13,(28)-lactone. *Sitosterol*. Found only in the first residue from the branches; m.p. 137–138; $[\alpha]_D^{20} -36°$ (CHCl₃). Identified by co-TLC, IR and NMR spectra.

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ISOLATION OF PHORBOL FROM *EUPHORBIA FRANCKIANA*

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Key Word Index—*Euphorbia franckiana*; Euphorbiaceae; Diterpene; phorbol.

Plant material. *Euphorbia franckiana* is a succulent species indigenous to Southern Africa, which produces copious latex on incision of the leaves. During biological screening tests involving the mice ear irritant assay [1] we were able to show that the latex had a short term irritant effect reaching a maximum within four hours. This is in contrast to several other ingenol and phorbol ester containing *Euphorbia* and *Croton* species which have a maximum irritant activity only after 24 hr.

Present work. *E. franckiana* latex was collected from Kew Gardens into alcohol and immediately dried below 40°. The acetone extract of two samples of latex had ID₅₀'s on mice of 70 μ g/5 μ l and were non-irritant after 24 hr. Extraction of the polar extract with *n*-hexane removed the lipid and triterpenoid compounds and the irritants were extracted with CH₂Cl₂. The biologically active fraction was hydrolysed with KOH in MeOH to produce a resin a component of which (M⁺ C₂₀H₂₈O₆) was acetylated [2] and purified by TLC [3]. The recovered solid was recrystallized from MeOH m.p. 120–1° and was chromatogra-

phically pure by TLC [2] and GLC [4]. The high resolution MS gave parent ion *m/e* 490 (M⁺ C₂₆H₃₄O₉); fragment ions at *m/e* 430 (M-60); 388 (M-60 + 42); 387; 370 (M-120); 352 (M-120 + 18); 328; 310 (M-180); 292 (M-180 + 18); 282; 267; 227; 215; 199; 173; 159; 145; 133; 125; 121; 109; 95; 93; 91; 83 (base peak). The NMR spectrum (60 MHz), CDCl₃ (TMS $\delta = 0.00$) exhibited resonances at δ 0.93 (3Hd-18); 1.22 (2Me-16, 17); 1.76 (3Hd-19); 2.05 (3MeCO-12, 13, 20); 2.45 (2Hm-5); 2.72 (1 OH deuterium exchange); 3.22 (2H broad-8 and 10); 4.43 (2H-20); 5.27 (Hd-12); 5.45 (1OH deuterium exchange); 5.70 (Hd-7); 7.54 (Hm-1) ppm; C.D. (MeOH); 204 nm [ϵ] = -27291; 229 nm = +53295; 270 nm = -5181; 340 nm = -3984, confirming the presence of phorbol, isolated as its triacetate. This compound has been isolated from *Croton tiglium* seed oil [5], but from our own unpublished results of screening approximately 60 *Euphorbia* species the common diterpene of this genus is ingenol [3]. It occurs in the latex together with one or more of ingol [6], 16-hydroxyingenol [7] or 5-deoxyingenol [8]. Phorbol has

been reported from *E. tirucalli* [9] but a sample available to us was only found to contain 4-deoxy-4 α -phorbol [4]. The presence of phorbol in *E. franckiana* is therefore of chemotaxonomic interest. Phorbol was estimated to be 0.52% w/w of the acetone dried latex by means of GLC [4].

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C-GLYCOSYLFLAVONES IN THE BULBS OF SQUILL*

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Key Word Index—*Urginea maritima*; Liliaceae; squill; bulb; glycosylflavones.

Plant. *Urginea maritima* Baker (Liliaceae).
Source. Collected in Iberian Peninsula and Balearic Islands. Voucher specimen in Herb. of this University.

Previous work. Anthocyanins[1] and several flavonols and dihydro-flavonols-*O*-glucosides[2].

Present work. Six C-glycosylflavones were isolated from the EtOAc extract by PC; five of which were identified as vitexin, isovitexin, orientin, isoorientin, scoparin, by the usual degradative[3], chromatographic and spectrophotometric[4] methods, and further comparison with authentic samples (Fluka). A possible isovitexin-*O*-xyloside has also been isolated, but its structure is not yet definitive. Vicenin-2 was isolated from the ethanolic extract, after precipitating sinistrins with

MeOH-EtOAc (1:3), and separating cardiac glycosides on a celite column eluted with CHCl₃ and CHCl₃/MeOH. Further elution with aqueous MeOH afforded the flavonoid fraction; vicenin-2, was separated by PC and identified as above by comparison with an authentic sample.

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