

sabinene and  $\Delta^4$ -carene, were found to be present as shown by GLC co-chromatography with reference compounds. The sesqui-terpene hydrocarbon fraction was divided into several smaller fractions on a  $\text{AgNO}_3$  column (Si gel containing 20%  $\text{AgNO}_3$ ). From these fractions the sesquiterpene hydrocarbons were isolated by preparative GLC. Their identity was established by comparing the IR and NMR spectra with those of pure reference substances. As far as known the presence of isocaryophyllene,  $\beta$ -selinene, selina-3,7(11)diene and of selina-4(14), 7(11)diene has not been reported previously. Further information on the identity of the 20 unknown sesqui-terpene hydrocarbons and the fraction containing the oxygen components in which pulegone and  $\alpha$ -bisabolol have been identified for the first time, will be given in a later communication.

From a chemotaxonomical point of view it is interesting to note that many of the components shown in Table 1 were present in the essential oil of *Humulus lupulus* L [6].

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## TRITERPENE ACETATES AND D-(+)-PINITOL FROM *DRYMARIA DRUMMONDII*

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**Key Word Index**—*Drymaria drummondii*; Caryophyllaceae; triterpenes; oleanolic acid acetate;  $\alpha$ -amyrin acetate; isoursenol acetate; pinitol.

*Drymaria drummondii* (alfombrilla), Voucher specimen. No. 7306 deposited in the Herbarium of Dept de Biología, ITESM Source: Chihuahua, Mex. Uses Unknown. Previous work—*Drymaria drummondii* and *D. arenarioides*, both known in northern Mexico as “alfombrilla”, and *D. pachyphylla* from Arizona are annually responsible for serious loss of cattle, particularly in drought years when other forage is not available [1]. Their toxicity has been well established [2], but no chemical studies have been reported.

Present work—The dried whole plant (5.0 kg) was Soxhlet extracted successively with light petrol

and  $\text{EtOH}$ . Each extract upon concentration yielded an oily residue on which preliminary tests for alkaloids, saponins and flavonoids were run [3]. Only saponins were detected in the  $\text{EtOH}$  extract.

The residue (62 g) obtained from the light petroleum extract, was chromatographed on Si gel. Elution with increasing gradients of  $\text{C}_6\text{H}_6$ — $\text{CHCl}_3$  gave first 0.6 g of oleanolic acid acetate, mp 266–268°,  $\text{C}_{32}\text{H}_{50}\text{O}_4$  ( $\text{M}^+$  at  $m/e$  498).  $[\alpha]$ , UV, IR, NMR, mmp co-TLC; on hydrolysis oleanolic acid was obtained, mp, mmp co-TLC  $[\alpha]$  IR. The second component proved to be  $\alpha$ -amyrin acetate

(15 mg). 224–226°,  $C_{32}H_{52}O_2$  ( $M^+$  at  $m/e$  468).  $[\alpha]_{D}^{25} + 34.8$ ;  $[\alpha]_{D}^{578} + 35.0$ ;  $[\alpha]_{D}^{546} + 40.1$   $[\alpha]_{D}^{436} + 68.8^\circ$ ,  $[\alpha]_{D}^{365} + 115.2^\circ$ ;  $[\alpha]_{D}^{316} + 187.2^\circ$ ; ( $CHCl_3$ ). UV, NMR, IR, ( $M \pm$  at  $m/e$  468, base peak at  $m/e$  203); hydrolysis gave isoursenol, mp  $[\alpha]_{D}$  IR, NMR.

The last crystalline compound was isoursenol acetate, (126 mg) mp 214–216°,  $C_{32}H_{52}O_2$ ;  $[\alpha]_{D}^{24} + 34.8$ ;  $[\alpha]_{D}^{578} + 35.0$ ;  $[\alpha]_{D}^{546} + 40.1$   $[\alpha]_{D}^{436} + 68.8^\circ$ ,  $[\alpha]_{D}^{365} + 115.2^\circ$ ;  $[\alpha]_{D}^{316} + 187.2^\circ$ ; ( $CHCl_3$ ). UV, NMR, IR, ( $M \pm$  at  $m/e$  468, base peak at  $m/e$  203); hydrolysis gave isoursenol, mp  $[\alpha]_{D}$  IR, NMR.

The ethanolic residue (80 g) was shaken with  $CHCl_3$  (600 ml) and filtered. A solid was obtained which on crystallization ( $H_2O$ –EtOH) afforded needles of (+)-pinitol (3.0 g) mp 187–189°  $[\alpha]_{D}^{24} + 51.1^\circ$  ( $CHCl_3$ ). IR, NMR, co-TLC mmp with an authentic specimen; pentacetate, mp, mmp and co-TLC. The  $CHCl_3$  soluble material was percolated on a Si gel column but no pure compounds were isolated.

This is only the second time that isoursenol (found earlier in *Olearia paniculata*, Compositae [4]) has been isolated from plant sources, and its presence in other members of the caryophyllaceae needs to be looked for.

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## TERPENOIDS AND STEROIDS FROM *MACARANGA TANARIUS*\*<sup>†</sup>

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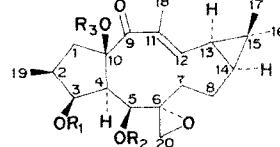
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**Key Word Index**—*Macaranga tanarius*: Euphorbiaceae; diterpenoids: 6:20-epoxylathyrol-5,10-diacetate-3-phenylacetate and macarangonol; triterpenoids:  $\beta$ -amyrenone,  $\beta$ -amyrin, friedel-3-ene, friedelin, friedelan-3 $\beta$ -ol; steroids: sitosterol, 5 $\alpha$ -stigmastan-3,6-dione, 6 $\beta$ -hydroxystigmast-4-en-3-one; ellagic acid.

**Plant.** *Macaranga tanarius* Muell.-Arg. (Hong Kong Herbarium voucher Specimen No. 23238). **Previous work.** Diterpene ketol, macarangonol from stems.\* Hardwoods for pulp and paper making [1]. On sister species: *M. triloba* (preliminary chemical and pharmacological screening) [2]. *M. denticulata* (taraxerone, 3-epitaraxerol and sitosterol [3]).

**Present work.** The light petrol extract of the stems of *M. tanarius* has been found to contain

diterpenoids: besides macarangonol\*, 6:20-epoxy-lathyrol-5,10-diacetate-3-phenylacetate (**1**) [4], which has previously been isolated only from *Euphorbia lathyris* (Euphorbiaceae), and triterpenoids: friedel-3-ene, friedelin, friedelan-3 $\beta$ -ol,  $\beta$ -amyrenone and  $\beta$ -amyrin. Friedel-3-ene was first prepared in the pure state by Brownlie *et al.* [5] by dehydration of friedelan-3 $\beta$ -ol, and its natural occurrence has been reported only from *Vaccinium*



(1)  $R_1 = PhAc$ ,  $R_2 = R_3 = Ac$

(2)  $R_1 = R_2 = R_3 = H$

\* Part X in the series "An Examination of the Euphorbiaceae of Hong Kong". For Part IX, see Hui W. H., Ng K. K., Fukamiya N., Koreeda M. and Nakanishi K. (1971) *Phytochemistry*, **10**, 1617.