the reported values [3]. (Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.60; H, 10.48%.)

Acknowledgements—We thank The Naito Foundation (1980, 1981) and the Toyota Foundation (1981) for financial aid, Dr. J. W. Rowe of the U.S. Department of Agriculture, Professor K. Takaki of Hiroshima University, and Professor K. Adachi of Osaka Institute of Technology, for kind discussions, and Eisai Co., Tokyo, for the bioassays.

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Phytochemistry, Vol. 22, No. 9, pp. 2085–2087, 1983.
Printed in Great Britain.
0031-9422/83 $3.00+0.00

6-HYDROXYTOXOL ESTERS AND A *SECO*-DAMMARANE DERIVATIVE FROM *ABROTANELLA FORSTERIOIDES**

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(*Received* 7 *February* 1983)

Key Word Index—*Abrotanella forsterioides*; Compositae; *p*-hydroxyacetophenone derivatives; toxol derivatives; triterpenes; *seco*-dammarane derivative.

Abstract—*Abrotanella forsterioides* afforded euparin, 6-hydroxytremetone and three 6-hydroxytoxol esters, one of them not being isolated previously. Furthermore a *seco*-triterpene was isolated. The tribal position of the genus *Abrotanella* in the Compositae is still an unsolved problem. Morphological investigations suggest that this genus should be transferred from the tribe Anthemideae to the Senecioneae [1, 2]. So far two species have been studied chemically; one afforded *ent*-kaurane derivatives, while both contained euparin and hydroxytremetone [3].

A reinvestigation of the roots of *Abrotanella forsterioides* Hook. fil. afforded, in addition to euparine (**1**) and 6-hydroxytremetone (**2**), the 6-hydroxy-3-epi-toxol esters **3**–**5** [4]. The senecioate **5** has not been isolated previously; its structure could be deduced from the ^{1}H NMR spectrum, which was close to that of **4** (see Experimental). Furthermore several triterpenes were present. In addition to stigmasterol, sitosterol and Δ^{12}-lupeol, a new *seco*-triterpene acetate was isolated. The molecular formula was $C_{32}H_{54}O_2$, while the ^{1}H NMR spectrum (Table 1) showed that four olefinic methyls were present, which required at least two double bonds. Thus, only three rings were present indicating a *seco*-triterpene. Accordingly, the signal of an acetoxymethylene group was apparent (4.03 *t*) and only one olefinic proton (5.09 *br t*). Three additional methyl singlets and one doublet indicated that a dammarane derivative may be present. Careful spin decoupling also, after addition of Eu(fod)$_3$, showed that a 4,5-double bond was very likely. Irradiation of the olefinic methyls caused a sharpening of one of the allylic threefold doublets (H-6), while both were coupled with a multiplet at δ 1.55 (H-7). After addition of Eu(fod)$_3$, the signals of the protons β to the acetoxy group could be assigned. Their multiplicity excluded any other position for the acetate group. The Eu(fod)$_3$-induced shifts further showed that the allylic proton were near the acetate group. Small differences in the shifts of the methyl singlets agreed with the assumption that a *seco*-dammarane was more likely than a euphane derivative. All data, therefore, agreed best with structure **6**. This proposal was further supported by the fragmentation pattern in the mass spectrum of **6**. A prominent peak m/z 287 could be explained as an elimination of both side chains ($-C_6H_{11}$ and $-C_5H_8O_2$, McLafferty). Probably **6** was formed via **7**. The aerial parts also afforded **1**–**5**.

The chemistry of *A. forsterioides* clearly showed that this genus cannot be placed in the tribe Anthemideae. Its position in the Senecioneae is supported by the occurrence of hydroxytoxol esters **3**–**5**. This type of *p*-hydroxyacetophenone derivative has been reported from nine *Senecio* species [4], though these compounds are also present in a few genera in other tribes.

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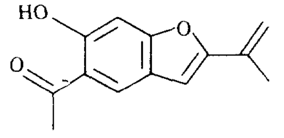
*Part 460 in the series "Naturally Occurring Terpene Derivatives". For Part 459 see Bohlmann, F., Zdero, C., Jakupovic, J., King, R. M. and Robinson, H. (1983) *Phytochemistry* (in press).



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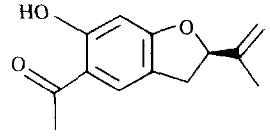

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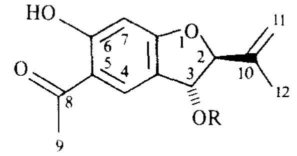

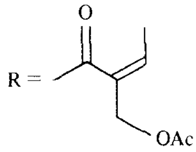

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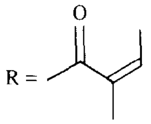

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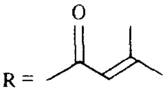

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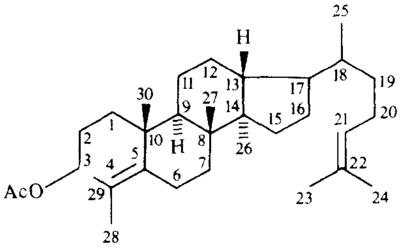

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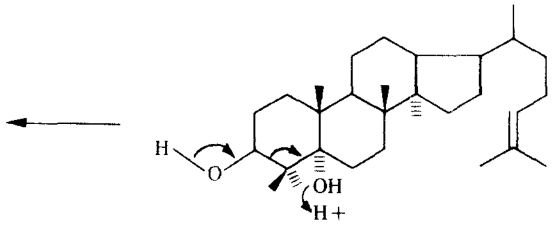

7

Table 1. ^{1}H NMR spectral data of **6** (400 MHz, $CDCl_3$, TMS and int. standard)

		+ Eu(fod)$_3$ at 40°
H-2	1.60 *m*	1.87 *m*
H-2′		1.79 *m*
H-3	4.03 *t*	4.56 *t*
H-6	2.25 *m*	2.29 *ddd*
H-6′	2.02 *m*	2.12 *br ddd*
H-7	1.50 *m*	1.55 *m*
H-7′		
H-20	2.02 *m*	2.02 *m*
H-20′	1.86 *m*	1.87 *m*
H-21	5.09 *br t*	5.09 *br t*
H-23	1.68 *br s*	1.68 *br s*
H-24	1.60 *br s*	1.60 *br s*
H-25	0.84 *d*	0.85 *d*
H-26	0.83 *s*	0.84 *s*
H-27	0.79 *s*	0.81 *s*
H-28	1.66 *s*	1.71 *s*
H-29	1.64 *br s*	1.67 *br s*
H-30	0.88 *s*	0.94 *s*
OAc	2.04 *s*	2.52 *s*

J (Hz): 2,3 = 6.5; 6, 6′ = 15; 6, 7 = 2.5; 6, 7′ = 8.5; 6′, 7 ~ 8; 6′, 7′ ~ 8; 6′, 29 ~ 1; 18, 25 = 6.5; 20, 21 = 6.7; 21, 23 = 21, 24 ~ 1.

EXPERIMENTAL

The air-dried plant material (collected in Tasmania, Mt. Field, with the voucher deposited at the Institute for Botany, University of Vienna) was extracted with Et_2O and the resulting extracts were separated by CC (Si gel) and repeated TLC (Si gel). Known compounds were identified by comparing their 400 MHz ^{1}H NMR spectra with those of authentic material. The roots (3.5 g) afforded 2 mg sitosterol, 1 mg stigmasterol, 15 mg Δ^{12}-lupeol, 20 mg **1**, 2 mg **2**, 10 mg **3**, 2 mg **4**, 2.5 mg **5** (Et_2O–petrol, 1:2) and 9.7 mg **6** (Et_2O–petrol, 1:10), while the aerial parts (140 g) gave 2 mg **1**, 8 mg **2**, 5 mg **3**, 2 mg **4**, 1 mg **5** and *ca* 10 mg unidentified triterpenes.

6-*Hydroxy*-3-*epi-toxol senecioate* (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700 (OH, hydrogen bonded), 1720, 1650 ($C=CCO_2R$), 1660 (PhCO); MS *m/z* (rel. int.): 316.131 $[M]^+$ (2) ($C_{18}H_{20}O_5$), 216 $[M-RCO_2H]^+$ (100), 201 $[216-Me]^+$ (85), 173 $[201-CO]^+$ (21); ^{1}H NMR ($CDCl_3$) 5.10 (*br d*, H-2), 6.03 (*d*, H-3), 7.84 (*s*, H-4), 6.45 (*s*, H-7), 2.55 (*s*, H-9), 5.05 and 4.95 (*br s*, H-11), 1.74 (*br s*, H-12), 5.64 (*qq*), 2.21 (*d*) and 1.91 *d* (*sen*) [*J* (Hz): 2, 3 = 2; 2′, 4′ = 2′, 5′ = 1.3].

3-*Acetoxy*-3,4-*seco-dammara*-4,21-*diene* (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1250 (OAc); MS *m/z* (rel. int.): 470.412 $[M]^+$ (12) ($C_{32}H_{54}O_2$), 455 $[M-Me]^+$ (8) 410 $[M-HOAc]^+$ (1), 369 $[M-CH_2CH_2CH_2OAc]^+$ (1), 287 $[M-C_6H_{11}, H_2C=CHCH_2OAc]^+$ (A) (27), 259 $[M-C_8H_{15}A]^+$ (10), 69 [Me_2C

$=CHCH_2]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589}{+45}\;\frac{578}{+48}\;\frac{546}{+55}\;\frac{436\,\text{nm}}{+95}\;(CHCl_3;\ c\ 0.97).$$

Acknowledgement—We wish to thank Professor F. Ehrendorfer, Institute for Botany, University of Vienna, for providing the plant material.

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Phytochemistry, Vol. 22, No. 9, pp. 2087–2088, 1983.
Printed in Great Britain.

0031-9422/83 $3.00+0.00
Pergamon Press Ltd.

CONSTITUENTS OF A HEXANE EXTRACT OF *PHOENIX DACTYLIFERA*

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(*Revised received* 18 *January* 1983)

Key Word Index—*Phoenix dactylifera*; Palmae; steroids; ketones; hydroxyketones; diketones.

Abstract—In addition to known compounds, two new steroid diones, 5α-stigmast-22-en-3,6-dione and 5α-campestan-3,6-dione, were isolated from stems of *Phoenix dactylifera.*

Phoenix dactylifera L. was collected at Parque Municipal of Elche (Alicante) and authenticated by Professor Mansanet, Department of Botany, University of Valencia. Previous work on this plant includes the chromatographic detection of flavonoids [1–3] and waxes [4] in a general taxonomic study of Palmae. The chemical constituents of the pollen [5] and palm-dates [6] have also been studied.

The neutral fraction from a dewaxed hexane extract of the stems of *P. dactylifera* was separated into six main fractions (I–VI) by CC. Fractions I, II and IV were mixtures of hydrocarbons (C_{26}–C_{31}), esters (alcohols: lupeol, β-sitosterol, stigmasterol and campesterol; fatty acids: 10, 12:1, 16, 18:1 and 18:2) and triglycerides (16, 18:2), respectively. Fractions III and V were lupyl acetate and lupeol. On analytical TLC, fraction VI was separated into a major component and four minor ones. The major component was separated by crystallization and was identified as a mixture of β-sitosterol, stigmasterol and campesterol.

Careful CC of the mother liquors of crystallization of fraction VI allowed the isolation of the four minor components (fractions VII–X) which were further purified by prep. TLC and recrystallization. The components of these preparations were identified by spectroscopy and by comparative GC, fraction VII: 3% SE-30, 300°, with natural authentic sample [7]; fraction VIII: 3% OV-17, 300° with natural [8] and synthetic [9] specimens; fractions IX and X: 3% OV-17, 300° (IX) and 3% OV-17, 310° (X) with synthetic specimens [10, 11]. Fraction VII was a mixture of stigmast-4-en-3-one [412 $[M]^+$ (86.2%)], stigmasta-4-22-dien-3-one [410 $[M]^+$ (7.9%)] and campest-4-en-3-one [398 $[M]^+$ (5.8)]; mp 86–87° (ether–methanol); $[\alpha]^{25}_D$ + 77.5°; IR ν_{max} cm^{-1}: 1670 (C=O), 1610 (C=C), 860 (C=C–H); ^{1}H NMR (CDCl$_3$): δ 5.75 (*br s*, –CO–CH=C), 2.2–2.4 (*m*, $-CH_2-CO-$); UV λ^{EtOH}_{max} 241 nm (log ε 4.15). Fraction VIII was a mixture of 5α-stigmastan-3,6-dione [428 $[M]^+$ (74.7%)], 5α-stigmast-22-en-3,6-dione [426 $[M]^+$ (12.9%)] and 5α-campestan-3,6-dione [414 $[M]^+$ (12.3%)]; mp 196–197° (chloroform–methanol); IR ν_{max} cm^{-1}: 1710 and 1720 (C=O); ^{1}H NMR (CDCl$_3$): δ2.1–2.6 (*m*, $3CH_2CO$ + $1CHCO$). 5α-Stigmastan-3,6 was known to occur naturally [8, 12–14]. However, this is the first report of the natural occurrence of the latter two diones. Fraction IX was a mixture of stigmast-4-en-3,6-dione [426 $[M]^+$ (92.6%)], stigmasta-4,22-dien-3,6-dione [424 $[M]^+$ (3.0%)] and compest-4-en-3,6-dione [412 $[M]^+$ (4.4%)]; mp 162–163° (methanol); IR ν_{max} cm^{-1}: 1680 (conjugated C=O), 1605 (C=C), 865 (=C–H); UV λ^{EtOH}_{max} 251 nm (log ε 4.01). Fraction X was a mixture of 6β-hydroxystigmast-4-en-3-one [428 $[M]^+$ (77.4%)], 6β-hydroxystigmasta-4,22-dien-3-one [426 $[M]^+$ (10.2%)], and 6β-hydroxycampest-4-en-3-one [414 $[M]^+$ (12.4%)]; mp 208–210° (ether); IR ν_{max} cm^{-1}: 3500 (O–H), 1695 (conjugated C=O), 1615 (C=C), 880 (=C–H); UV λ^{EtOH}_{max} 238 nm (log ε 4.12).

The isolation of steroid ketones, hydroxyketones and diketones from *P. dactylifera* is not unexpected [7, 8, 12, 13]; certainly they are not artifacts produced by air oxidation of sterols during the process of extraction,