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DITERPENOID FURANS FROM *PTERODON* SPECIES

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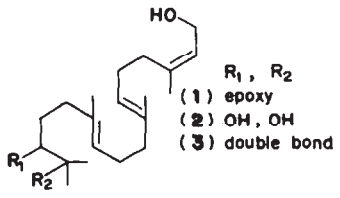
Key Word Index—*Pterodon pubescens*; *P. emarginatus*; *P. polygalaeflorus*; *P. apparicioi*, Leguminosae; diterpenes; geranylgeraniol derivatives; diterpenoid furans; vouacapanes; vinhaticanes.

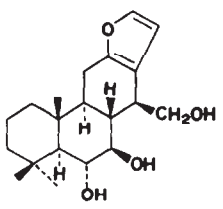
Abstract—Investigation of diterpenoids in four species of *Pterodon* show varying oxidation patterns on the vinhaticane or vouacapane skeletons.

The genus *Pterodon* (Leguminosae, Lotoideae) comprises 5 species native to Brazil, *P. pubescens* Benth. (Sucupira branca), *P. emarginatus* Vog., *P. polygalaeflorus* Benth., *P. apparicioi* Pedersoli [1], and *P. abruptus* Benth. Chemical investigation of these species was first promoted by the discovery [2] that the fruit oil of *P. pubescens* inhibited the penetration of the skin by schistosome cercariae, a property that was traced to 14,15-epoxygeranylgeraniol (**1**) [3] and later to the accompanying linear diterpenoid 14,15-dihydroxy-14,15-dihydrogeranylgeraniol (**2**) [3]. Geranylgeraniol (**3**) itself also occurs in *P. pubescens* [3], and as the characteristic floral odour of this diterpene and similar biological activity is observed in the fruit oils by *P. emarginatus*, *P. polygalaeflorus* and *P. apparicioi*, the presence of the same or related linear diterpenoids seems probable. Subsequently a number of diterpenoid furans were isolated [4–8] from the first three species mentioned and with further studies now reported on *P. apparicioi* and *P. polygalaeflorus*, the pattern of occurrence reported in Fig. 1 emerges.

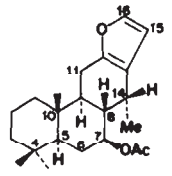
Chemical evidence for many of the structures presented has been reported earlier [4–8]. The new ester (**16**) was identical to the acetylation product of (**14**) [7] (*P. apparicioi*) and on $LiAlH_4$ reduction yielded the triol (**17**), previously obtained from the aldehyde (**10**) [4] and from other compounds of the series (**11**, **12**, **14**–**16**) [7,8]. Physical data which characterize the diterpenoids furans are tabulated in the Experimental.

Lactones of the type (**8**) are readily prepared from the corresponding furans (e.g. **7**) by peracid [6] or by Jones' chromic acid reagent [8]. (**8**) may therefore be an artefact of isolation. It is interesting that (**8**) shows high biological activity against *S. mansoni* cercariae and inhibits *Crithidia fasciculata* in culture at a concentration of 8 μg/ml. These activities are not shown by the corresponding furan (**7**).

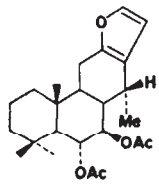




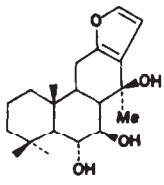
(**17**)



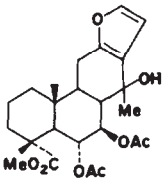
(**4**) *ap, em*



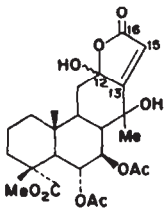
(**5**) *ap, em*



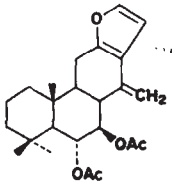
(**6**) *em, po*



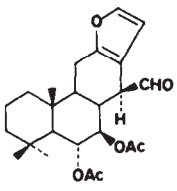
(**7**) *pu*



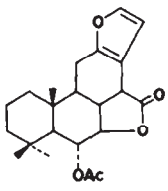
(**8**) *pu*



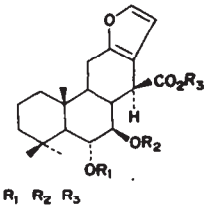
(**9**) *em*



(**10**) *pu*



(**11**) *em*



	R_1	R_2	R_3	
(**12**)	H	H	Me	*em, po*
(**13**)	H	H	H	*em, po*
(**14**)	Ac	H	Me	*ap, em, po*
(**15**)	H	Ac	Me	*em*
(**16**)	Ac	Ac	Me	*pu*

Table 1. NMR Data—Skeletal protons of the diterpenoid furans

Cpd.*	5α	$J_{5,6}$	6β	$J_{6,7}$	7α	$J_{7,8}$	8β	$J_{8,14}$	14	11 AB†
(4)				5·5; 10·5	4·75	10·5		6·5	2·79	2·45
(5)		11·5‡	4·85	9·0‡	5·24	10·0‡			2·64	2·45
(7)	1·42		5·29§		5·00§					2·52; 2·18
(8)			5·31		5·07					
(9)		10·0‡	5·50	9·0						2·5; 1·9
(10)	1·44	12·0	5·39	9·0	4·98	10·0	2·50	8·0	3·20	2·79; 2·30
(11)		10·5	5·52	9·5	4·13	10·5		11·0	3·20	
(12)			3·1–3·9		3·1–3·9				3·1–3·9	
(14)	1·39	11·5	5·23	9·0	3·91	10·5			3·50	2·56
(15)			3·7–4·1	9·0‡	4·84	10·5‡		8·5	3·37	
(16)	1·42	1·10	5·41	10·0	4·98	11·0			3·38	2·74

* **(6)** and **(13)** were too insoluble for NMR determinations.
† One datum only refers to one branch of the pattern the other being hidden in the envelope.
‡ Not firmly assigned.
§ NMDR did not permit elucidation of the proton coupling pattern. These assignments are made by analogy with other compounds of the series.

EXPERIMENTAL

The NMR spectra were determined at 60, 100 and 220 MHz (Varian instruments) and mass spectra on AEI, Atlas and Varian-Atlas low and high resolution mass spectrometers.

Isolation of diterpenoids from P. apparicioi. *P. apparicioi* fruits collected on the banks of the Rio Cipó, State of Minas Gerais, ground and percolated with hexane, to give after evaporation of the hexane a brown oil (300 g) from which 6α,7β-diacetoxyvouacapane **(5)** (4 g) crystallized directly. The oil (25 g) chromatographed over Si gel (380 g) in hexane–Me_2CO gave successively 7β-acetoxyvouacapane **(4)** (0·3 g), **(5)** (1·5 g) and methyl 6α-acetoxy-7β-hydroxyvouacapan-17β-oate **(14)** (0·1 g). All 3 compounds were recrystallized from Me_2CO by addition of hexane.

Isolation of diterpenoids from P. pubescens. A similar isolation procedure applied to *P. pubescens* fruits (collected near Brasília, DF) gave successively from 100 g oil, 6α,7β-diacetoxyvouacapan-14β-al **(10)** (5 g), 6α,7β-diacetoxyvouacapan-14β-oate **(16)** (2 g), methyl 6α,7β-diacetoxy-14-hydroxyvinhaticoate **(7)** (3 g) and methyl 6α,7β-diacetoxy-12,16-dihydro-12,14-dihydroxy-16-oxovinhaticoate **(8)** (0·3 g). Diterpenes **(10)** and **(15)** were recrystallized from Me_2CO by hexane addition; **(7)** from Me_2CO–MeOH by hexane addition; and **(8)** from *n*-PrOH [4,6].

Isolation of diterpenoids from P. polygalaeflorus. The crude oil was separated into acidic and neutral fractions by extraction with Claisen's alkali, followed by fractionation of the neutral fraction of Si gel, as described for *P. emarginatus* [8]. The following four compounds were obtained in the pure state and identified by direct comparison with authentic samples isolated earlier: [8] 6α,7β-dihydroxyvouacapan-17β-oic acid **(13)** (20% of the crude oil); methyl 6α,7β-dihydroxyvouacapan-17β-oate **(12)** (0·6%), methyl 6α-acetoxy-7β-hydroxyvouacapan-17β-oate **(14)** [7], and vouacapane-6α,7β,14β-triol **(6)** (2·5%).

Physical data of the diterpenoid furans. (a) *Melting points* (uncorr.) **(4)** 147–148°; **(5)** 167–168°; **(6)** 218–222°; **(7)** 100–105°; **(8)** 184–186°; **(9)** 157–158°; **(10)** 220–221°; **(11)** 279–280°; **(12)** 204–205°; **(13)** 273–274°; **(14)** 187–188°; **(15)** 210–212°; **(16)** 202–203°. (b) *Nuclear magnetic resonance data.* Chemical shifts (δ in $CDCl_3$, unless otherwise stated, TMSO) are given for skeletal protons in Table 1 and for functional groups in Table 2. (c) *Mass spectral data.* **(4)** 344(82), 284(28); 269(8); 160(31); 149(50); 147(100); 145(60); 133(13); 132(11); 131(12); 123(7); 119(9), 108(32). **(5)** 402(28); 283(30); 282(100); 267(13); 197(49); 158(21); 145(21); 133(54); 132(57); 109(16); 108(32); 105(13); 69(23); 55(16), 43(67). **(7)** 462(6); 447(7); 387(23); 341(17); 327(31); 267(40); 159(80); 124(48); 43(100). **(8)** 434(17); 416(7); 392(18); 391(18); 390(18); 374(33); 356(30); 331(38);

Table 2. NMR Data—Substituents in the diterpenoid furans

Cpd.*	Methyls 4α	Methyls 4β	Methyl 10	Methyl 14	CHO	CO_2Me	Furan† 15	Furan† 16
(4)	0·88;	0·96;	0·96	0·94 *d* J = 7 Hz			6·05	7·08
(5)	0·91;	1·00;	1·05	1·00 *d* J = 7 Hz			6·00	7·03
(7)	1·13;		1·22	1·44		3·67	6·32	7·20
(8)	1·01;		1·17	1·57		3·69	5·94	
(9)	0·95;	1·03;	1·12				6·42	7·25
(10)	0·96;	0·98;	1·12		9·14 *d* J = 5 Hz		6·10	7·24
(11)	1·00;	1·08;	1·08				6·60	7·30
(12)	1·00;	1·07;	1·16			3·73	6·15	7·22
(14)	1·03;	1·05;	1·16			3·71	6·09	7·20
(15)	1·03;	1·07;	1·17			3·73	6·12	7·23
(16)	0·96;	1·00;	1·11			3·68	6·07	7·20

* See note *, Table 1.
† $J_{15,16}$ = 2 Hz.

314(27); 296(51); 278(18); 173(62); 159(95); 109(69); 105(14); 91(9); 55(10); 43(100). **(10)** 416(7); 356(33); 314(19); 296(53); 285(17); 282(11); 268(16); 267(12); 183(22); 131(43); 43(100). **(11)** 372(66); 269(20); 268(56); 253(16); 197(12); 185(12); 184(15); 183(63); 167(33); 144(31); 132(10); 131(34); 119(32); 109(30); 43(100); 41(37). **(12)** 362(45); 327(13); 326(50); 303(17); 285(68); 284(42); 268(20); 267(98); 197(11); 191(18); 185(15); 161(25); 149(29); 147(33); 145(39); 137(53); 133(37); 131(85); 119(48); 109(34); 95(39); 91(46); 69(100); 55(49); 43(31); 41(65). **(14)** 404(13); 372(7); 344(57); 330(16); 326(20); 312(100); 285(15); 267(13); 178(81); 145(14); 137(16); 131(42); 123(24); 119(24); 109(23). **(15)** 404(14); 345(14); 344(56); 330(15); 312(100); 311(23); 285(16); 267(13); 179(10); 178(81); 177(16); 133(10); 131(42); 123(24); 119(24); 109(23); 69(48); 55(27); 43(71); 41(21). **(16)** 446(1); 386(19); 372(4); 354(6); 344(6); 326(100); 312(46); 267(12); 241(12); 229(21); 202(16); 178(25); 167(11); 137(18); 131(25); 123(18); 109(14).

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