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CABRALEA EICHLERIANA DC. (MELIACEAE)—I STRUCTURE AND STEREOCHEMISTRY OF WOOD EXTRACTIVES

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Abstract—From *Cabralea eichleriana* DC. (Meliaceae) nine compounds having a dammarane skeleton have been isolated and identified. They are cabraleone **2**, ocotillone **3**, cabraleadiol **4a**, cabralealactone **5**, cabralea-hydroxylactone **6a**, eichlerianic acid **7a**, shoreic acid **8a**, dammarenolic acid **9a** and eichlerialactone **10a**. The only limonoid present is *fissinolide* **1**. Compounds **7a** and **10a** are hereby reported for the first time as occurring in Nature. Configurations of ocotillone and cabraleone are revised and have been assigned 20*S*, 24*S* and 20*S*, 24*R* respectively.

Cabralea eichleriana DC. (Meliaceae) is a well known timber tree of Brasil. An examination of the petroleum ether extract of the wood for the presence of limonoids and their biogenetic congeners, led to the isolation of a series of triterpenoids with a dammarane skeleton. The only limonoid which could be isolated was fissinolide **1**, earlier reported[1] from the seeds of the same plant. In this paper, isolation, structure and stereochemistry of the triterpenoids are discussed.

The petroleum ether extract deposited fissinolide during concentration. The concentrate upon fractionation on silica gel followed by work-up as shown in Chart 2, led to the isolation of nine compounds characterised as cabraleone **2**, ocotillone **3**, cabraleadiol **4a**, cabralealactone **5**, cabralea-hydroxylactone **6a**, eichlerianic acid **7a**, shoreic acid **8a**, dammarenolic acid **9a** and eichlerialactone **10a**. Compounds **7** to **10** could be obtained crystalline only as their methyl esters, and **6** as its acetate.

Compounds **2**, **4**, **5** and **6** have been earlier isolated from *Cabralea polytricha*[2], **3** from the resin of *Dipterocarpus hispidus*[3] and the wood of *Dryobalanopus* sp[4], **8** and **9** from various species of *Shorea*.[5,6] This is the first report of the natural occurrence of eichlerianic acid **7a** and eichlerialactone **10a**.

Cabraleone **2**, $C_{30}H_{50}O_3$, which shows in the IR a strong carbonyl absorption (ν_{max} 1690 cm^{-1}), has an NMR spectrum indicating the presence of eight tertiary C-Me groups and one proton on a carbon carrying an oxygen function (δ 3·69 m) (Table 1). No signals in the downfield region are to be seen; however, the presence of a hydroxy-group was disclosed upon addition of trichloro-acetylisocyanate (TAI).[7] The nature of the side chain revealed by the fragmentation under electron impact: peaks at *m/e* 143 (100%, corresponding to $C_8H_{15}O_2$), 59 [for $(CH_3)_2\dot{C}{=}O$] and 399 (M^+-59), was confirmed by Jones oxidation of the compound to a trisnor-γ-lactone **5** (IR 1767 cm^{-1}, NMR six tertiary C-Me). The compound was finally identified by comparison with the reported physical and spectroscopic data of cabraleone earlier isolated from a related Brasilian species *C. polytricha*.[2]

Octillone **3**, analyses as in the previous compound for $C_{30}H_{50}O_3$, and the fragmentation pattern of the mass spectra of the two compounds are also identical. However, their IR and NMR spectra differ significantly. Instead of the eight distinct separate C-Me signals observed in the NMR spectrum of **2**, that of **3** showed only seven such signals, one of them corresponding to two methyls. Interestingly such a difference has been earlier reported for the two C-20*S*-ocotillol acetates epimeric at C-24. Compound **3** could then well be assumed to be an epimer of cabraleone **2**, and indeed, Jones oxidation of **3** afforded the same trisnor-lactone obtained from **2**. Since no epimerisation at C-20 was expected during the oxidation reaction, compound **3** can be formulated as the C-24 epimer of **2**, which corresponds to ocotillone.[4] This was confirmed by direct comparison with an authentic sample.

Cabraleadiol **4a**, is a hydroxy-compound having no carbonyl function (IR). It readily forms a monoacetate $C_{32}H_{54}O_4$ **4b**, the NMR spectrum of which shows eight C-Me signals, one acetate Me, one proton α- to the OAc group (δ 4·68, narrow triplet, $W_{1/2}$ 5·0 Hz, indicating a β-equatorial orientation), and one proton α-to an ether oxygen. The mass spectral fragments at *m/e* 443 (M^+-59) and 143 indicated the presence of a side chain similar to that of **2**, an observation confirmed by oxidation of **4b** to the trisnor-lactone **6b**. Sarett oxidation of **4a** gave a product identical in all respects with **2**, thereby establishing its structure.

Cabralealactone **5**, $C_{27}H_{42}O_3$, has a ketonic carbonyl and a γ-lactone (IR). Its NMR spectrum indicated the presence of six C-Me groups, five of which are placed in positions as in **2**. These facts indicated the loss of two Me groups from the side chain by oxidative degradation leading to the formation of the γ-lactone. This compound was found to be identical with the trisnor-γ-lactone obtained by the oxidation of **2** and **3**.

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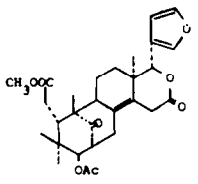
Table 1. NMR spectral data (δ values)

	Methyl groups at							24-H	Others
	4α	4β	10β	8β	14α	20	25		
Cabraleone **2**	0·96	1·05	1·10	1·03	0·90	1·12	1·17, 1·20	3·69(m)	
2 + TAI	0·96	1·03	1·07	1·03	0·89	1·17	1·54, 1·57	4·02(m)	NH 8·42 (s)
Ocotillone **3**	0·95	1·04	1·08	1·00	0·89	1·13	1·13, 1·21	3·78(q) J = 5·4, 7·6 Hz	
Cabralealactone **5**	0·95	1·04	1·08	1·01	0·91	1·37	—	—	
Cabraleadiol **4a**	0·83	0·85	0·93	0·96	0·88	1·10	1·13, 1·17	3·66(m)	3H 3·40 (t, $W_{1/2}$ 5·6 Hz)
Cabraleadiol-monoacetate **4b**	0·84	0·87	0·87	0·98	0·92	1·12	1·15, 1·19	3·67(m)	3H 4·68 (t, $W_{1/2}$ 5·0 Hz); OAc 2·08
Cabralea-hydroxy-lactone acetate **6b**	0·86	0·88	0·89	0·99	0·95	1·38	—	—	3H 4·63 (t, $W_{1/2}$ 5·0 Hz); OAc 2·09
Dihydromethyl-eichlerianate **7c**	0·82d, 0·92d (J = 6·5 Hz)		0·85	1·00	0·88	1·13	1·16, 1·20	3·67(m)	–COOCH$_3$, 3·67
Dihydromethyl-shoreate **8c**	0·80d, 0·91d (J = 7·0 Hz) =C–CH$_3$(29)		0·82	0·97	0·87	1·13	1·13, 1·21	3·74(m)	–COOCH$_3$, 3·66
Me eichlerianate **7b**	1·73		0·85	1·02	0·88	1·10	1·14, 1·18	3·66(m)	–COOCH$_3$, 3·67; =CH$_2$ 4·68(m), 4·87(m)
Eichlerianic acid **7a**	1·75		0·87	1·02	0·89	1·12	1·15, 1·20	3·70(m)	=CH$_2$ 4·70(m), 4·88(m)
7a + TAI	1·75		0·90	1·03	0·90	1·17	1·55, 1·57	4·14(m)	=CH$_2$ 4·70(m), 4·88(m); NH 8·45(s)
Me shoreate **8b**	1·72		0·83	1·00	0·88	1·11	1·11, 1·20	3·73(q) (J = 5·4, 7·6 Hz)	–COOCH$_3$, 3·73; =CH$_2$ 4·66(m), 4·83(m)
Shoreic acid **8a**	1·73		0·86	1·01	0·89	1·13	1·13, 1·21	3·57(m)	=CH$_2$ 4·69(m), 4·87(m)
Me eichleria lactone **10b**	1·73		0·85	1·00	0·90	1·35	—	—	–COOCH$_3$, 3·65; =CH$_2$ 4·67(m), 4·85(m)
Me dammarenolate **9b**	1·74		0·85	1·01	0·89	1·15	1·64, 1·71	=CH 5·16(m)	–COOCH$_3$, 3·66; =CH$_2$ 4·68(m), 4·87(m)
9b + TAI	1·73		0·84	0·99	0·90	1·51	1·61, 1·68	=CH 5·07(m)	–COOCH$_3$, 3·65; =CH$_2$ 4·64(m), 4·83(m) NH 8·18(s)



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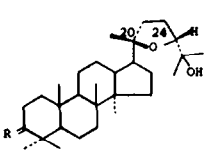
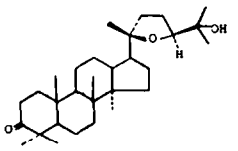


2 R=O
4a R=H, α-OH
4b R=H, α-OAc



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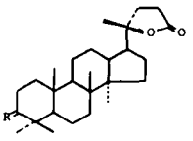
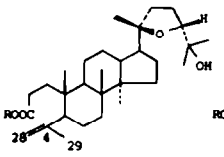


5 R=O
6a R=H, α-OH
6b R=H, α-OAc



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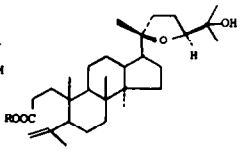

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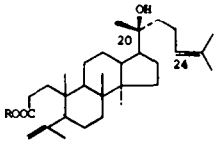
a, R = H; b, R = CH_3; c, R = CH_3, 4,28-dihydro



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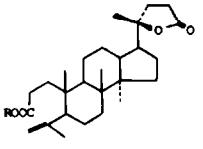

10

a, R = H; b, R = CH_3

Cabralea-hydroxylactone **6a**, could be purified only as its acetate **6b**. The IR spectrum of **6b** showed the presence of a γ-lactone, besides the ester carbonyl, and its NMR spectrum disclosed six C-Me groups, five of which were in similar positions as in cabraleadiol monoacetate **4b**. The identity of the compound was established by direct comparison with the oxidation product of **4b**.

Eichlerianic acid **7a**, though purified by repeated chromatography could, however, be crystallised only as its methyl ester **7b**. The NMR spectrum of the ester, showed the presence of six tertiary C-Me groups, one Me on a double bond (δ 1·73 broad singlet) one $-COOCH_3$, two vinylic protons, as well as one proton attached to a carbon bearing an oxygen function (multiplet partly hidden under the ester methyl signal).

Upon irradiation at δ1·73, the two vinylic proton signals collapsed into two doublets (J = 2·5 Hz), revealing thereby the presence of an isopropenyl group $(-C(CH_3)=CH_2)$.

The MS of **7b** showed peaks at *m/e* 59, 143 (100%) and 429 (M^+-59) revealing that the side chain is similar to that of **2** and **3**. This is further confirmed by oxidation of **7b** to the trisnor-γ-lactone **10b**. The isopropenyl group can, therefore, be accommodated only in a seco-ring A, an assumption supported by the co-occurrence of the 3-keto compounds **2** and **3**. Finally, the partial synthesis of the dihydro-methyl eichlerianate **7c** from cabraleone **2** confirmed the proposed structure. Irradiation of **2** in methanol with UV light gave a mixture which was fractionated on silica gel impregnated with silver nitrate. The major product (65% yield) was found identical with dihydro-methyl eichlerianate **7c**, obtained from **7b** by catalytic hydrogenation (Pd-C).

Methyl shoreate **8b**, has the same molecular formula as methyl eichlerianate **7b**, as well as an identical fragmentation pattern in the mass spectrum. That these two esters are epimeric at C-24 is shown by the difference in the C-Me region of their respective NMR spectra, which is of the same nature as encountered in the case of **2** and **3**. Furthermore, oxidation of both compounds gave the same trisnor-lactone **10b**. The identity of **8b** was unequivocally established by direct comparison with an authentic sample of methyl shoreate.[5]

Methyl dammarenolate **9b**, $C_{31}H_{52}O_3$, has four tertiary C-Me, three Me on double bonds, one ester Me and three olefinic protons (NMR). The presence of a hydroxyl group was revealed after addition of TAI,[7] and that of the isopropenyl group as in **7b** by double resonance, thereby suggesting an acyclic side chain with a terminal isopropylidene moiety. Its formulation as **9b** was supported by the physical constants and spectral properties which are in good agreement with the published data for methyl dammarenolate.[8]

Eichlerialactone methyl ester **10b**, $C_{28}H_{44}O_4$ (M^+ 444) is a γ-lactone (IR). Its NMR spectrum showed four tertiary C-Me, one Me on a double bond, one ester Me and two olefinic protons. Final identity of the compound was

established by direct comparison with the oxidation product of methyl eichlerinate **7b**, and of methyl shoreate **8b**.

Having established the identity of methyl shoreate among our compounds, an interesting stereochemical problem arose. Cabraleone **2** first isolated from *Cabralea polytricha* by Cascon and Brown, was assigned the 20*S*, 24*S* configuration.[2] Through its present degradation by photolysis to dihydro-methyl eichlerianate **7c**, cabraleone and eichlerianic acid **7a** have been interrelated, they both have, therefore, the same configuration in the side chain. Hence, it follows that ocotillone **3** and shoreic acid **8a**, which are the respective C-24 epimers, should have accordingly the 20*S*,24*R* configuration. This is, however, in conflict with the X-ray crystallographic analysis of methyl shoreate **8b** which was found to have the 20*S*,24*S* configuration.[6] A reexamination of the evidence leading to the configurational assignments at C-24 for cabraleone **2** and ocotillone **3** was therefore found necessary. It has been reported[9] that the treatment of betulafolienetriol **11** with NBS afforded a bromo-compound **12** whose structure has been rigorously established by X-ray analysis as being 20*S*,24*S*, whereas oxidation of **11** with perbenzoic acid gave two compounds epimeric at C-24 named oxides I and II (**13** and **14**).[10] The former has been related through a sequence of reactions shown in Chart 1 to ocotillone, whereas oxide II was obtained from the bromo-compound **12** by treatment with silver oxide. On these grounds, oxide II **14** was assigned the 20*S*,24*S* configuration as in **12**, and hence oxide I (and thereby ocotillone) were given the 20*S*, 24*R* configuration.

In another set of reactions oxidation of 3-acetyl dammarenediol **15** with p-nitroperbenzoic acid produced two compounds **16** and **17** epimeric at C-24.[11] Since **16** was related to ocotillone[3] and **17** to cabraleone[2] as shown in Chart 1, **17** and hence cabraleone were assigned the 20*S*, 24*S* configuration.

Since the configuration of the bromo compound **12** was established by X-ray crystallographic analysis,[9] it can be now assumed that the silver oxide treatment of **12** leading to the formation of oxide-II[10] involved an inversion of configuration at C-24 from $S \rightarrow R$, a possibility which was overlooked at the time, and led to the erroneous assignments in the whole series. Hence, the configuration of ocotillone need to be revised to 20*S*,24*S* **3** and that of cabraleone to 20*S*,24*R* **2** (for clarity and to avoid confusion, the revised stereochemistry is shown in Chart 1).

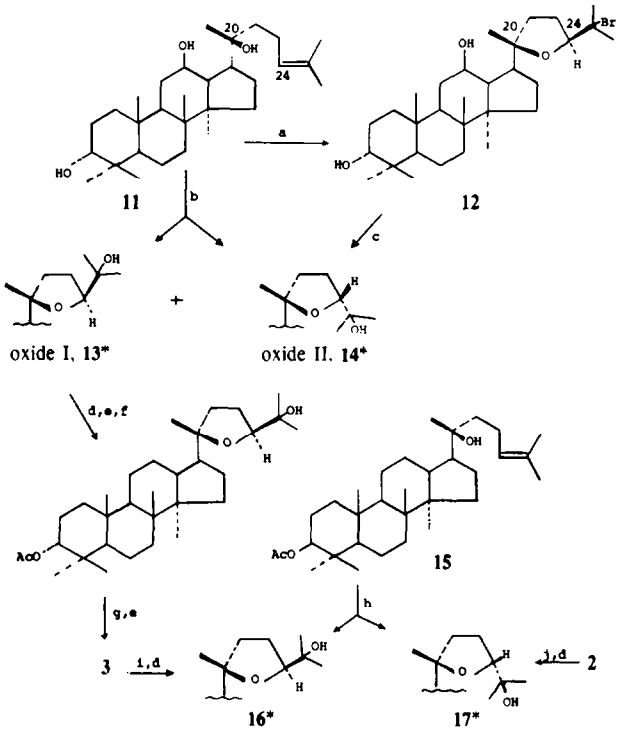

CHART 1. Relevant reaction sequences leading to the stereochemical assignments at C-24 of cabraleone **2** and ocotillone **3**.

*Revised structures.

Reagents: (a) NBS; (b) $C_6H_5CO_3H$; (c) Ag_2O/EtOH; (d) Ac_2O/Py; (e) CrO_3-Py; (f) Wolff-Kishner; (g) $\bar{O}H$; (h) p-NO_2-C_6H_4-CO_3H; (i) $NaBH_4$; (j) LAH.

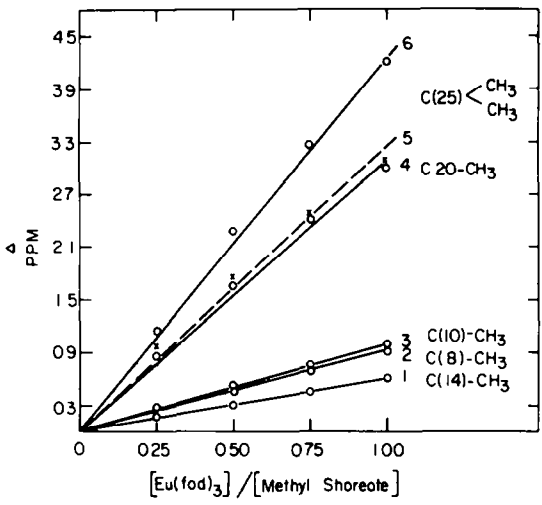

Fig 1. Eu(fod)$_3$ induced shifts of the six C-CH$_3$ groups in methyl shoreate **8b**.

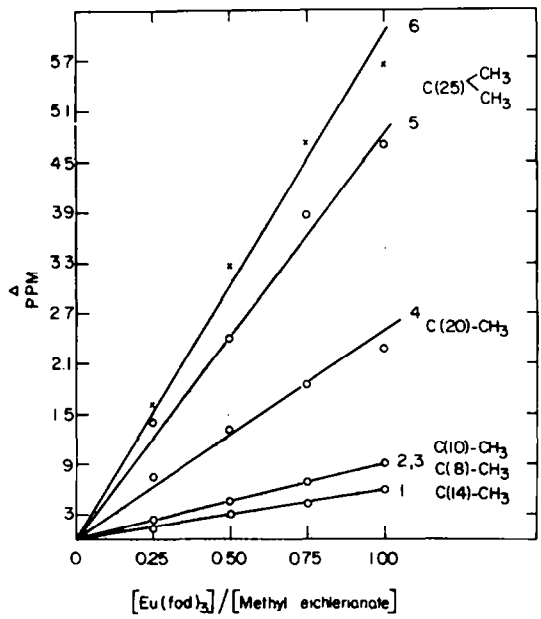

Fig 2. Eu(fod)$_3$ induced shifts of the six C-CH$_3$ groups in methyl eichlerianate **7b**.

In view of these changes direct and independent evidence for the stereochemistry at C-24 was sought. To this end, NMR studies using a lanthanide shift reagent were applied to methyl shoreate **8b** and methyl eichlerianate **7b**. In these compounds the C-25 hydroxyl group provides a convenient bonding site for Eu^{3+}. Since the isotropic shift decreases with increasing distance of the proton from the Eu^{3+}, in 20*S*,24*S* compounds, the C-20-Me, which is syn with the C-24-hydroxyisopropyl group, should be considerably more deshielded compared to the 20*S*,24*R* compounds, in which they are anti. The NMR spectra of methyl shoreate and methyl eichlerianate were measured with four different concentrations of Eu(fod)$_3$. The induced shifts fot the six C-CH$_3$ groups are plotted as a function of the Eu(fod)$_3$ concentration (Fig. 1 and 2). As it can be seen the C-20-Me in methyl shoreate is considerably more shifted as expected for a 20*S*,24*S* stereochemistry in accordance with the X-ray data,[6] whereas for methyl eichlerinate the corresponding shifts are much smaller, in accordance with the 20*S*,24*R* configuration, **7b**. Furthermore, the smaller values recorded for the C-25 methyls in methyl shoreate **8b** imply steric hindrance due to syn arrangement for the C-20 and C-24 substituents.

We thus conclude that cabraleone and eichlerianic acid should be assigned the 20*S*,24*R* configuration as shown in **2** and **7**, while ocotillone and shoreic acid are 20*S*,24*S* as in **3** and **8**.

Cabraleadiol **4a** has been converted to cabraleone **2** and therefore it also has the same 20*S*,24*R* configuration.

EXPERIMENTAL

Mps were taken on a Fisher-Johns apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer model 237B spectrophotometer and refer to KBr pellets. NMR spectra were recorded on a Varian A-60 spectrometer and refer to 5–10% solutions in $CDCl_3$, using TMS as internal standard. Decoupling experiments were carried out on a Brucker HFX-10 90 MHz spectrometer by Mr M. Greenberg, MS were recorded on an Atlas CH4 instrument under the direction of Dr Z. V. I. Zaretskii and the relative intensities of the peaks, given in parentheses, are reported with reference to the most intense peak taken as 100%. Optical rotations were recorded with an automatic Perkin-Elmer 141 polarimeter in $CHCl_3$ solution. Analyses were performed in the microanalytical laboratory of the Institute under the direction of Mr R. Heller. Silica gel 60 (Merck) 70–230 mesh was used for column chromatography. TLC were carried on chromatoplates of silica gel F. For preparative layer chromatography a thick layer (1·0 mm) of silica gel PF_{254} was used. Acetylations were carried out with Ac_2O/pyridine at room temp. for 20 h and worked up by removal of the reagents under reduced pressure on a hot water bath. Esterifications were performed using CH_2N_2 in ether solutions prepared from Diazald.

Extraction and isolation procedure. Finely chipped wood of *Cabralea eichleriana* (11 kg) was successively extracted with hot petroleum ether, C_6H_6 and MeOH. During concentration of the petroleum ether extract a crystalline material separated which was collected and crystallised from MeOH to give *fissinolide* **1** as colourless prisms, mp and mmp with an authentic sample 169–171°C.

Evaporation of the petroleum ether from the filtrate afforded an oily residue (140 g) from which a fraction (120 g) was dissolved for further purification in $CHCl_3$ (250 ml), intimately mixed with silica gel (200 g) and the mixture was evaporated to dryness. The residue

Eluent	Fractions		Product
n-Hexane to ether-hexane	2:3	1–110	"A" (oils, 80 g) (not investigated)
Ether-hexane	1:1	111–117	"B" cabraleone **2** (3·8 g)
Ether-hexane	1:1	118–121	"C" ocotillone **3** (0·65 g)
Ether-hexane	1:1	122–138	"D"
Ether-hexane	1:1	139–168	"E" see Chart 2
Ether		169–250	"F"

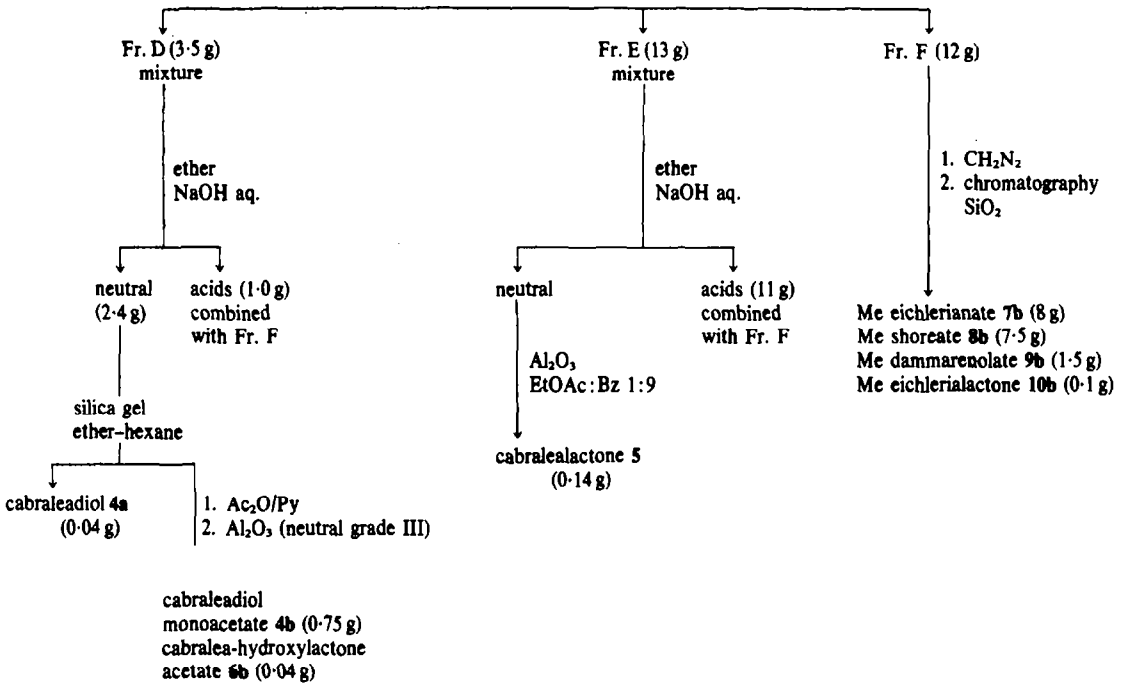

CHART 2. Isolation procedure for compounds 4 to 10

was placed on a dry column of silica gel (2·3 kg) and eluted with n-hexane with increasing quantities of ether. Fractions of about 250 ml each were collected and monitored by TLC and NMR. The fractions which appeared to be identical were combined as shown above and the procedure adopted for the isolation of the various components is outlined in Chart 2.

Carbraleone 2. Mp 163–166·5° (n-hexane), $[\alpha]_D$ + 60° (c, 1·2), ν_{max} 3520, 1690, 1085, 1064 cm^{-1}. MS *m/e* 459 (M^+ + 1) (0·5), 458 M^+ (0·4), 443 (6·7), 399 (41·4), 381 (8·8), 205 (17·2), 143 (100), 125 (31·3), 95 (21·2), 85 (32·3), 81 (21·2), 71 (23·2), 59 (34·3), 55 (24·2) and 43 (37·4). (Found: C, 78·38; H, 11·17; M^+ 458. $C_{30}H_{50}O_3$ requires C, 78·55; H, 10·99%; M.wt. 458·70).

Ocotillone 3. Mp 160–163° (MeOH), $[\alpha]_D$ + 63·7° (c, 0·7); ν_{max} 3483, 1694, 1463, 1381, 1370, 1356, 1147, 1089 and 1076 (all strong), 1033, 1022, 944, 896 and 885 cm^{-1} (all medium). MS *m/e* 459 (M^+ + 1) (0·2), 458 M^+ (0·1) 399 (22), 205 (6·9), 143 (100), 125 (10), 95 (8·6), 85 (11·5), 59 (10), 55 (8·9) and 43 (13·6). (Found: C, 78·52; H, 11·05; M^+ 458. $C_{30}H_{50}O_3$ requires C, 78·55; H, 10·99%; M.wt. 458·70).

Cabraleadiol 4a. The neutral component of fraction D (Chart 2) gave, on rechromatography, pure cabraleadiol (0·04 g), mp 176–178°, $[\alpha]_D$ + 13·6° (c, 1·0); [lit.[2] m.p. 175–176°, $[\alpha]_D$ + 18° (c, 1·0)]; ν_{max} 3432, 1065 and 1056 cm^{-1}. (Found: C, 78·12; H, 11·45. $C_{30}H_{52}O_3$ requires C, 78·20; H, 11·38%).

Cabraleadiol monoacetate 4b. Mp 149–151° (petroleum ether), $[\alpha]_D$ − 8·0° (c, 1·1); [lit.[2] m.p. 148–149°, $[\alpha]_D$ + 12° (c, 1·0)]; ν_{max} 3558, 3432, 1732 and 1246 cm^{-1}. MS. *m/e* 502 M^+ (very small), 487 (0·7), 443 (1·9), 383 (11), 284 (12), 264 (7), 256 (81), 213 (14), 185 (9), 143 (90), 129 (28), 73 (64), 69 (49), 60 (61), 57 (64), 55 (83) and 43 (100). (Found: C, 76·30; H, 10·85; M^+ 502. $C_{32}H_{54}O_4$ requires C, 76·44; H, 10·83%; M.wt. 502·8).

Hydrolysis of 4b. Cabraleadiol monoacetate 4b (150 mg) was refluxed with 6% methanolic KOH (20 ml, 5 h). After dilution with water (50 ml), the product was extracted with ether and the extract was washed with water and dried (Na_2SO_4). Removal of the solvent and crystallisation (CH_2Cl_2-hexane) gave 4a (120 mg), mp and mmp with the natural sample 176–178°.

Oxidation of 4a *to* 2. To a stirred solution of CrO_3 (125 mg) in pyridine (1·5 ml) a solution of cabraleadiol 4a (70 mg) in pyridine (1 ml) was added during 10 min. After 3 h of continued stirring water (50 ml) was added, and the product was extracted with ether, washed with water and dried (Na_2SO_4). The solvent was evaporated and the residue crystallized (hexane) to give colourless needles (55 mg), mp and mmp with cabraleone 2 163–165°, and also identical IR and NMR spectra.

Cabralealactone 5. Isolated from fraction E (see Chart 2); mp 182–184° (petroleum ether). $[\alpha]_D$ + 68·6° (lit[2] 181–183°, $[\alpha]_D$ + 70°); ν_{max} 1767 (γ-lactone), 1703 cm^{-1} (ketonic CO). MS *m/e* 414 M^+ (87·1), 399 (9·7), 396 (7·3), 329 (8·5), 328 (9·7), 316 (20·6), 315 (22·6), 205 (58), 195 (26), 135 (27), 121 (28), 109 (33·4), 107 (37·5), 99 (100), 95 (67), 81 (59), 69 (36), 67 (40), 55 (55) and 43 (67). This compound was found identical with the Jones oxidation product of cabraleone 2.

Cabralea-hydroxylactone acetate 6b. This compound isolated from fraction D was obtained pure after separation on a thick layer chromatoplate (Silica gel, C_6H_6-EtOAc 9:1) mp 185–186° (petroleum ether), $[\alpha]_D$ −2·6° (c, 0·4); ν_{max} 1772 (γ-lactone) 1745 (ester CO) and 1252 cm^{-1}. MS *m/e* 458 M^+, 443, 398, 383, 189, 135, 121, 107, 99, 81, 69, 55 and 43 (Cascon and Brown[2] reported a mp 125–127°, $[\alpha]_D$ + 17° (c 0·23); and ν_{max} 1760 and 1720 cm^{-1}. However, their NMR data are in agreement with ours).

Oxidation of 2 *to* 5. Jones reagent was added dropwise to a solution of cabraleone 2 (60 mg) in acetone (6 ml), while stirring, until the colour of the reagent persisted for 5 min. After addition of water, the acetone was removed under reduced pressure and the product was extracted with $CHCl_3$. The extract was washed with water, dried (Na_2SO_4) and evaporated to dryness to yield cabralealactone 5; mp 180–182° (petroleum ether).

Oxidation of **4b** *to* **6b**. A solution of cabraleadiol monoacetate **4b** (45 mg) in acetone (6 ml) was oxidized with Jones reagent as described above. The product crystallised from petroleum ether–CH_2Cl_2 as colourless prisms (26 mg), mp 185–187°, undepressed on mixing with cabralea-hydroxylactone acetate **6b** isolated from Fr. D (Chart 2).

Methyl eichlerianate **7b**. Isolated from Fr. F by methylation followed by chromatography (Chart 2), mp 109–110° (EtOH), $[\alpha]_D$ + 37·6° (c, 0·8); ν_{max} 3460, 3553 (w), 1743, 1635 and 896 cm^{-1}. MS *m/e* 488 M^+ (1·1), 473 (2·0), 455 (0·5), 429 (8·7), 411 (2·2), 263 (1·1), 249 (1·4), 237 (2·2), 175 (1·4), 161 (3·3), 143 (100), 125 (12·4), 59 (20·7), 55 (15·7) and 43 (23·3). (Found: C, 75·94; H, 10·65; M^+ 488. $C_{31}H_{52}O_4$ requires: C, 76·18; H, 10·72%; M.wt. 488·73).

Hydrogenation of **7b**. A solution of methyl eichlerianate **7b** (70 mg) in EtOH (10 ml) was stirred with H_2, in presence of 10% Pd–C (20 mg) until the rapid absorption ceased (30 min). After filtration, the solvent was removed to give a highly viscous semisolid which could not be induced to crystallise (the IR and NMR spectra indicated the absence of olefinic unsaturation). $\nu_{max}^{CHCl_3}$ 3542 (w), 1728 (s), 1158 (m) and 1051 (m) cm^{-1}. MS *m/e* 490 M^+ (very small), 475 (3·7), 472 (0·9), 457 (0·8), 441 (2·6), 431 (35·3), 413 (7·8), 389 (3·0), 143 (100), 125 (15·2), 109 (10·6), 95 (10·8), 81 (12·2), 71 (10), 69 (8·9), 59 (23·5), 55 (11·0) and 43 (14·8).

Jones oxidation of **7b**. Methyl eichlerianate **7b** (63 mg) was oxidised with Jones reagent and the product was purified using preparative chromatoplates (EtOAc-C_6H_6, 3:7) to give Me eichlerialactone **10b**, mp 126·5–127·5° (EtOH).

Methyl shoreate **8b**. Mp 82–83° or 94–94·5° (EtOH), $[\alpha]_D$ + 40·6° (c, 1·0); ν_{max} 3484 (m), 1739 (s), 1628 (w), 1280 (m), 1021 (s), 892 (m) and 883 (m) cm^{-1}. MS *m/e*, 488 M^+ (1·0), 473 (2·8), 470 (1·2), 429 (13·1), 411 (3·0), 389 (4·5), 161 (4·5), 143 (100), 125 (10·6), 85 (14·8), 59 (10·4), 55 (10·4) and 43 (13·7). (Found: C, 76·40; H, 10·71; M^+ 488. $C_{31}H_{52}O_4$ requires C, 76·18; H, 10·72%; M.wt. 488·73).

Jones oxidation of **8b** (90 mg) followed by chromatography of the product on a column of silica gel (n-hexane-ether 7:3) gave Me eichlerialactone **10b** (50 mg), mp 126–127°.

Methyl eichlerialactone **10b**. Isolated by methylation and chromatography of Fr. F (see Chart 2): mp 126–127° (EtOH); ν_{max} 1766 (γ-lactone) 1735 (ester CO) 1638, 1186, 1110 and 879 cm^{-1}. MS *m/e* 444 M^+ (12·9), 429 (6·5), 363 (92·3), 357 (49·1), 345 (8·8), 154 (23·5), 121 (32·6), 115 (20·0), 109 (32·6), 99 (100), 95 (57·6), 55 (78·8) and 43 (73·7).

Photolysis of Cabraleone **2**. A solution of cabraleone **2** (1·0 g) in MeOH (200 ml) was irradiated under N_2 atmosphere, with UV lamp (Hanovia 450 watt) with a pyrex filter until the reaction was complete (13 h). After removal of the solvent, the product was chromatographed on silica gel impregnated with $AgNO_3$. Elution with ether-hexane (1:4) gave a product (0·65 g) which would not crystallise. Its IR, NMR and MS spectra were identical with those of dihydro-methyl eichlerianate **7c**.

Methyl dammarenolate **9b**. This compound could not be obtained crystalline although homogeneous on chromatoplates, using different solvent systems (single spot). ν_{max} 3420, 1735, 1623, 1167 and 887 cm^{-1}. MS *m/e* 472 M^+ (0·1), 454 (64), 439 (2·8), 423 (4·1), 385 (38·5), 373 (20·5), 127 (31), 109 (100), 95 (56·4), 69 (89·7), 55 (43·6) and 43 (53·8).

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