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SESQUITERPENES OF *BARBILOPHOZIA* SPECIES*

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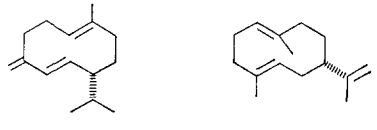
Abstract—Two isomeric olefins, α- and β-barbatene, apparently of a new tricyclic sesquiterpene skeleton (that of gymnomitrol), have been found in the liverworts *Barbilophozia barbata*, *B. floerkei*, *B. lycopodioides*, and *B. attenuata*. Additional components identified are alkanes, calamenene and α-alaskene. GLC suggests the presence of caryophyllene, longifolene, bazzanene and α-cedrene in minor amounts.

INTRODUCTION

THE LAST few years have seen a major development in the study of the essential oils of lower plants. The liverworts are remarkable in producing oils[1] which have yielded a number of novel sesquiterpenes: bazzanene[2] and related compounds,[3] myliol,[4] an enantiomeric santonin relative,[5] chiloscyphone,[6] (−)-longifolene,[7] and *ent*-α-selinine.[8] These results suggest the operation of biogenetic pathways in liverworts that follow the general outlines of those found in conifers. However, the elaboration of enantiomeric sesquiterpenes[5,7,8] places the liverworts in a unique position in the plant kingdom,[9] and raises the question of

* Part XIII in the series "Constituents of Mosses and Liverworts". For Part XII see Ref. 13.

[1] HUNECK, S. and KLEIN, E. (1970) *J. Hattori Bot. Lab.* **33**, 1.
[2] HAYASHI, S. and MATSUO, A. (1969) *Experentia* **25**, 1139; MATSUO, A. (1971) *Tetrahedron* **27**, 2757
[3] HAYASHI, S. and MATSUO, A. (1970) *Experentia* **26**, 347.
[4] BENESOVA, V., SEDMERA, P., HEROUT, V. and SORM, F. (1971) *Tetrahedron Letters* 2679.
[5] KNOCHE, H., OURISSON, G., PEROLD, G. W., FOUSSERAEU, J. and MALEVILLE, J. (1969) *Science* **166**, 239.
[6] MATSUO, A. (1972) *Tetrahedron* **28**, 1203; and ref. therein.
[7] HUNECK, S. and KLEIN, E. (1967) *Phytochemistry* **6**, 383.
[8] ANDERSEN, H. N., SHUNK, B. and COSTIN, C. R. (1973) *Experentia* in press.
[9] Enantiomeric sesquiterpenes of some classes have been encountered in plants previously, but these can be explained in a number of ways without requiring the cyclization producing enantiomeric germacrenes



i ii

(i or ii). See, for example, ANDERSEN, N. H. and FALCONE, M. S. (1971) *Chem. Ind.* (*London*) 62. The only confirmed occurrence of enantiomeric germacrenes (or related products) is the report of (−)-germacrene-*A* (ii) in a marine invertebrate.[10]
[10] WEINHEIMER, A. J., YOUNGBLOOD, W. W., WASHECHECK, P. H., KARNS, T. K. B. and CIERESZKO, L. S. (1970) *Tetrahedron Letters* 497.

the stage in the phylogeny of higher plants at which the exclusive formation of 7β-isopropyl compounds evolved.[11]

These considerations have led us to a systematic examination of the sesquiterpenes of the essential oils of lower plants, in particular of the Hepaticae and Musci.

TABLE 1. GLC ANALYSIS OF *Barbilophozia* SPECIES

Component	R_f	% of oil	Self-consistent Kovats' indices[12,*] $I_A^{190°}$	$I_A^{155°}$	$I_B^{170°}$	$I_C^{150°}$	$I_C^{165°}$	$I_D^{160°}$	Assignment
B. barbata	No. 2	2	1433	(1420?)			1552	1670	
	7	2	~1475·5	1448			1660		(Caryophyllene)
	10	16	1500	1470	(1440·5)	1626	1647	1812	α-Barbatene
	11	1	(1502)	1474·2			1640	1786·5	(α-Cedrene)
	12	5	1519				(~1712?)		
	13	7	1534·5	1502·5	(1472·5)	1689	1712	1902·5	β-Barbatene
	15	30	1555	~1539		1748	1764·5	1938·5	(−)-α-Alaskene
	16	4	1567·8	1551	(1524)		1791	~1978·5	Calamenene
	18	3	1586·8	~1574			1816		
B. floerkei	No. 3	10	1403·5		1391	1564·5			Alkane
	6a	2	1498		1439 5	1632			α-Barbatene
	6b	4	1493		1458·5	1632			Alkane?
	9	20	(1539)		1473	1692 0			β-Barbatene
	10	18	(1530 or 1539)		(~1498)	1735			
	11	18	(1530 or 1539)		(~1498)	1741·5			
	14	2	1583 5		1530·5	1786 5			(Bazzanene?)[13]
	15	5			1634 5				
B. lycopodioides	No. 1	50	1270				1496·5		
	2	12	1404				~1496·5		
	3	9					1582		
	4	3	1499				1656		
	5	3	1523				1749?		
	6	10	1539				1716		(β-Barbatene)
B. attenuata	No. 1	18	1268				1493		
	2	12	1403				~1493		
	3	12	?				1581		
	4	8	1421				1617		
	5	4	1483				1698		
	6	12	1537·5				1715·5		(β-Barbatene)
	7	4	~1536 or 1560				1771·5		
	8	9	1568				1812		

* The subscripts indicate the stationary phases, A—apiezon-L; B—SF-96; C—carbowax 20-M; and D—diethylene glycol succinate.

RESULTS AND DISCUSSION

The steam volatile ether extracts of dried plant material of four *Barbilophozia* species have been examined by GLC on four stationary phases. The GLC traces revealed mixtures of sesquiterpenes in each case. The composition of the oils, as revealed by these analyses, is

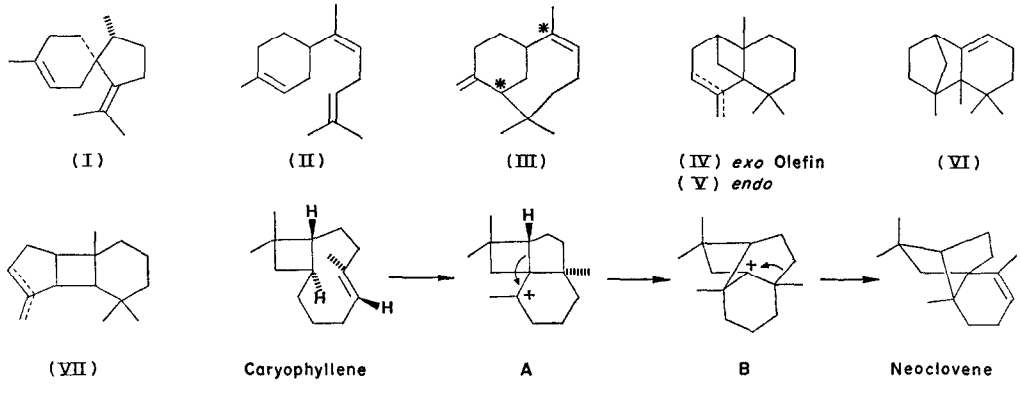
[11] ANDERSEN, N. H. (1970) *Phytochemistry* **9**, 145.
[12] ANDERSEN, N. H. and FALCONE, M. S. (1969) *J. Chromatog.* **44**, 52.
[13] ANDERSEN, N. H. and HUNECK, S. (1973) *Phytochemistry* **12**, 1818.

shown in Table 1. A number of components were tentatively identified from the correspondence of Kovats' indices on the wide variety of stationary phases employed.[12] These assignments are placed in parentheses. The major hydrocarbons which were stable to Al_2O_3 chromatography were isolated by subsequent preparative GLC for further study.

The peak identified as (−)-α-alaskene, (I)[14] from *B. barbata* was isolated by direct preparative GLC.[15] The assignment was fully confirmed by spectral and chiroptical measurements as well as chemical reactions (see Experimental). Component 16 was identified as calamenene from its IR spectrum.[15]

Components 10 and 13 of *B. barbata*, designated α- and β-barbatene, were isolated by direct preparative GLC and by $AgNO_3$–Al_2O_3 chromatography of *Barbilophozia floerkei*. Initial GLC analyses of *B. lycopodioides* and *attenuata* also showed peaks assignable to the barbatenes (see Table 1). In fact every liverwort oil examined thus far at U.W. (12 species) has displayed a peak for at least one of the barbatenes: β-barbatene is by far the more prevalent. We present here our initial studies on the constitution of the barbatenes.

The barbatenes are isomeric $C_{15}H_{24}$ olefins of a tricyclic skeleton. The NMR spectrum revealed, in the case of β-barbatene, 3 singlet methyls and an exomethylene grouping accounting for 4 termini of farnesane suggesting one of the normal modes of cyclization. The α-barbatene spectrum indicated 3 singlet methyls, a vinyl hydrogen, and a vinyl methyl, suggesting its assignment as the *endo*-olefin isomer of β-barbatene. This relationship was confirmed by hydrogenation which afforded the same saturated hydrocarbon ($C_{15}H_{26}$) from either barbatene. The relationship was later shown more directly: β-barbatene affords α-barbatene in essentially quantitative yield on treatment with formic acid at ambient temperature. The IR spectra suggested a $-CMe_2$ unit. We therefore considered structures in the humulene–caryophyllene → longifolene sequence. The NMR spectra did not correspond to the known compounds: longifolene, longipinenes,* neoclovene,[16] and several other caryophyllene rearrangement products.[17]



* Both longipinenes have been isolated from *Scapania undulata* (unpublished work).

[14] ANDERSEN, N. H. and SYRDAL, D. D. (1972) *Tetrahedron Letters* 899. See Ref. 15 and also ANDERSEN, N. H. and SYRDAL, D. D. (1970) *Tetrahedron Letters* 2277.

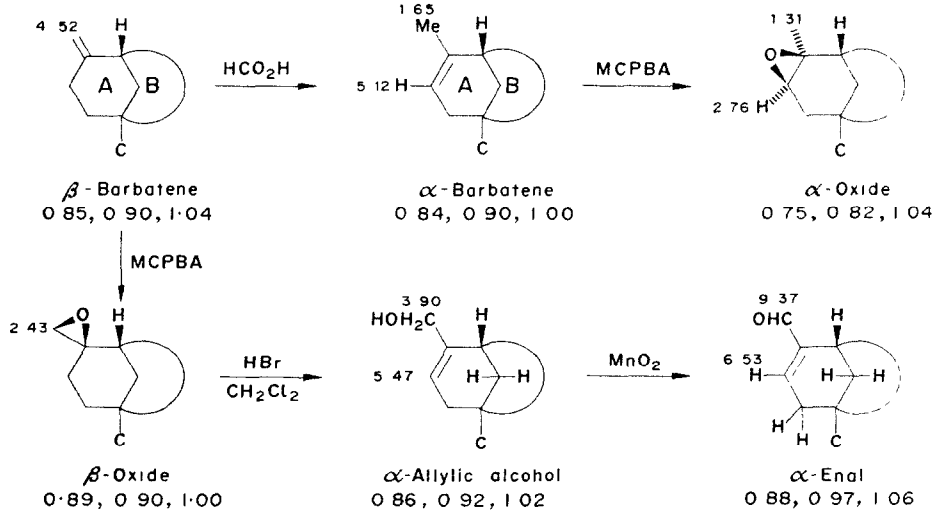
[15] The methods employed for chromatography on $AgNO_3$–Al_2O_3 and preparative gas chromatography appear in: ANDERSEN, N. H. and SYRDAL, D. D. (1970) *Phytochemistry* **9**, 1325; and SYRDAL, D. D., Ph.D. Thesis, University of Washington. (1971).

[16] MCKILLOP, T. F. W., MARTIN, J., PARKER, W. and ROBERTS, J. S. (1967) *Chem. Commun.* 162.

[17] GOLLNICK, K., SCHADE, G., CAMERON, A. F., HANNAWAY, C., ROBERTS, J. S. and ROBERTSON, J. M, (1970) *Chem. Commun.* 248; GOLLNICK, K., SCHADE, G., CAMERON, A. F., HANNAWAY, C., ROBERTSON. J. M. (1971) *Chem. Commun.* 46.

In this category the unknown isomeric olefins based on the hirsutane and protoilludane skeleton as well as the 2 + 2 cyclization products (VII) of γ-humulene should be considered. Ion A from the established mechanism[16] for the rearrangement of caryophyllene producing, in part, neoclovene, offers another possibility. An additional possibility can be envisioned based on bazzanene (III),[2] a minor constituent of *B. floerkei*. Isomeric olefins (IV, V) would result from cyclobutane formation by linking the asterisked positions of bazzanene.

All of these possibilities except IV, V and the olefins related to ion A were rapidly eliminated by degradative studies detailed below. The stability of α-barbatene to formic acid seemed to argue against the olefins from ion A. The barbatenes undergo a further rearrangement in high yield on exposure to HCO_2H–CF_3CO_2H (1 : 1) at 50°. The crystalline product, an isomeric olefin displaying four singlets due to tertiary methyl groups, was not neoclovene. On this basis we tentatively favored structures IV and V, for β- and α-barbatene respectively, and viewed the rearrangement product as VI. Recently careful $Eu(FOD)_3$ shifted NMR studies of the degradation products led to a revision of this structure. The degradative studies are summarized in the scheme below (NMR chemical shifts are in ppm downfield from TMS in CCl_4—for each substance the shifts of the three singlet methyls are given):



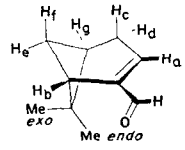
The allylic substitution pattern was established by the presence of 3 proton signals (2·2–2·65 ppm) and a triplet vinyl hydrogen at 6·53 ppm (J 4 Hz) in the spectrum of the enal. The ring size and its rigid *meta*-fused nature were assigned by comparison of the α-oxide with α-cedrene oxide—δ 1·36 (Me, *s*) and 2·85 ppm (oxirane-H, *d*, 4·4 Hz). The sharp doublet (J 3·8 Hz) oxirane proton resonance (even though there are two vicinal hydrogens) implies that ring B is 4- or 5-membered. The epoxide of β-barbatene gave an allylic alcohol rather than the bromohydrin on exposure to aqueous HBr, again reminiscent of the established chemistry of pinenes and cedrenes.[18] On this basis, we compared the spectra

[18] The same rearrangement has been observed with strong bases, alumina, and with Lewis acids: ESCHINASI, E. E. (1968) *Israel J. Chem.* **6**, 713; CHRETIEN-BESSIERE, Y. and MEKLATI, B. (1971) *Tetrahedron Letters* 621; KERGOMARD, A. and PHILIBERT-BIGOU, J. (1959) *Bull. Soc. Chim. Fr.* 1381.

TABLE 2. $Eu(FOD)_3$ INDUCED SHIFTS IN THE NMR OF MYRTENAL.

0·6 M Myrtenal/$CDCl_3$ + 0·5 M $Eu(FOD)_3/CCl_4$ (0·0–0·3 molar equiv.)

H	δ (ppm)	LIS (ppm)
CHO	9·52	N.D.
H_a	6·71	4·52
H_b	2·87	12·5
H_c, H_d	2·58	4·11
H_e	2·50	3·61
H_f	1·06	4·63
H_g	2·21	2·39
exo Me	1·36[5]	2·42
endo Me	0·76	3·47



$J_{e,f} = 10·4$ Hz
$J_{b,e}$ $J_{b,g}$ $J_{c,g}$ * 5·6 Hz
ave $J_{a,c}$, $J_{a,d}$, $J_{c,g}$, $J_{d,g} \approx 3$ Hz
$J_{a,b} \sim 1·3$ Hz
$J_{b,f}$ $J_{f,g} < 1·0$ Hz

of the allylic alcohol and enal in the presence of the shift reagent, $Eu(FOD)_3$,[19] with those of myrtenol and myrtenal. The use of the shift reagent allowed complete assignment of all resonances of both terpenes, and demonstrated the substitution pattern of ring A and ring B for the barbatene derivatives. The argument, in the case of the aldehydes, follows. The

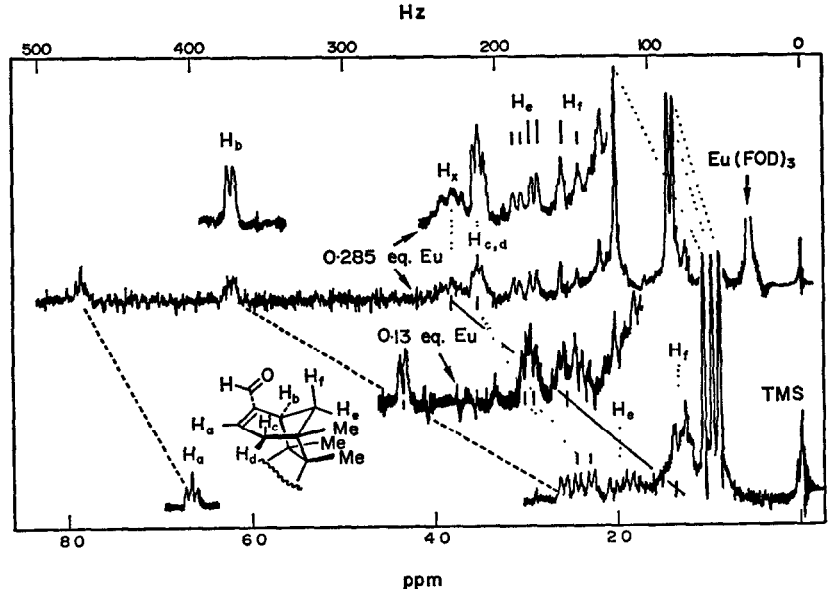
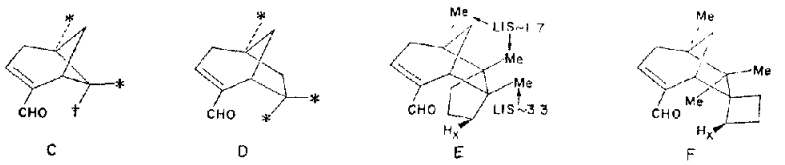


FIG. 1. NMR SPECTRA OF THE BARBATENE ENAL (0·08 M $CDCl_3$) WITH INCREMENTAL ADDITION OF $Eu(FOD)_3$, δ (LIS): CHO, 9·52 (N.D.); H_a, 6·67 (4·15); H_b, 2·60 (10·36); H_c, 2·47 (3·75); H_d, 2·30 (4·21); H_e, 2·00 (3·5); H_f, 1·33 (4·15); H_x, 1·43 (8·4); Me groups 1·09 (3·3), 0·99 (1·65), and 0·91 ppm (1·86 ppm); $J_{ef} = 11·2$, $J_{eb} = 4·3$, $J_{c,a} = 3·6$, $J_{da} = 4·0$, $J_{ab} \sim J_{bf} < 1·4$.

myrtenal values (see Table 2) were used as the model for ring A and for expectation LIS-values for methyl groups at various distances for the carbonyl oxygen.[19] The initial and representative shifted spectra for the enal derivative of barbatene are shown in Fig. 1.

[19] For a discussion of the basis for the use of this reagent and the method of structure analysis, see: ANDERSEN, H. N., BOTTINO, B. J. and SMITH, S. E. (1972) *Chem. Commun.* 1193.

The assignment of proton resonances *a* through *f* was obvious from the combination of chemical shift and LIS* comparison with the model. Assuming either a bicyclo-[3.1.1]- or bicyclo-[3.2.1]-part skeleton; the simple doublet H_b resonance and the absence of additional coupling with H_c and H_d implies methyls or ring residues at the asterisked positions. The sharp doublet displayed for H_f implies a group at the endo position of the pinane like skeleton, almost certainly the fast shifting methyl (LIS = 3·3). However, the *endo*-Me would have been upfield in the initial spectrum based on analogy to myrtenal and other pinene derivatives. Thus the cedrene like skeleton appeared more likely. The appearance of an additional proton (H_x) which shifts rapidly proved key to further structure refinement. The observation implied an endo ring residue. Structures E and F show the only possibilities which would display 3 singlet Me resonances. No firm decision between these was possible.



C D E F

At this point, the communication of the structure elucidation of gymnomitrol (IX) appeared.[20] An impure hydrocarbon isolated from *Gymnomitrion obtusum* in connection with the gymnomitrol work appears (from NMR comparison[21]) to be identical to β-barbatene. The data of Connolly *et al.* do allow a decision between skeletons E and F and the barbatenes must be VIII and X. The CD comparison of the barbatenes and cedrenes confirms the absolute stereochemistry assigned to gymnomitrol. In addition the distinctly different olefin CD[22] data for pinenes and longipinenes indicates that such comparison distinguishes between bicyclo[3.1.1]heptene and bicyclo[3.2.1]octene.

β-Cedrene $\Delta\varepsilon_{200} = -4\ 7$[22]
α-Cedrene $\Delta\varepsilon_{198} = -5\ 2$[14]

(−)-β-Pinene $\Delta\varepsilon_{198} = +15\ 2$[22]
(−)-α-Pinene $\Delta\varepsilon_{186} = +3\ 8$
(+)-β-Longipinene $\Delta\varepsilon_{201} = +9\ 8$[22]
( )-α-Longipinene $\Delta\varepsilon_{187} = -4\ 8$

(VIII) R = H β-Barbatene $\Delta\varepsilon_{195} = 1\ 7$
(IX) R = OH Gymnomitrol

(X) α-Barbatene $\Delta\varepsilon_{201} = +5\ 0$

This assignment leaves only one question: what is the structure of the ultimate olefinic product of the acid-catalyzed rearrangement of the barbatenes?* This point is under investigation.

EXPERIMENTAL

NMR spectra were determined in CCl_4 at 60 MHz using TMS as an internal standard ($\delta = 0{\cdot}0$). The NMR samples were obtained directly from column fractions or by preparative gas chromatography. Rotation and CD data were obtained on a Cary 60. Further purification for determination of rotation (*c* 0·01, pentane), CD (1–5 mM, pentane), and UV spectra was effected by filtration through Al_2O_3

* The slightly lower LIS-values for the barbatene enal reflect the increased dissociation of the 2:1 complex at 0·08 M vs 0·6 M.

[20] CONNOLLY, J. D., HARDING, A. E. and THORNTON, I. M. S. (1972) *Chem Commun.* 1320.
[21] The spectrum was kindly supplied by Professor Connolly.
[22] ANDERSEN, N. H., COSTIN, C. R., SYRDAL, D. D. and SVEDBERG, D. P. (1973) *J. Am. Chem. Soc.* **95**, 2049.

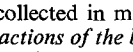
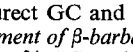
(Woelm, Act. I, basic) with pentane just prior to use. GLC analyses were performed and data reduced according to Ref. 12. The general procedures for $AgNO_3$–Al_2O_3 and related column chromatography and preparative GLC have been outlined.[15] The pinene and cedrene compounds were available from natural sources or were prepared from the natural products by known procedures.

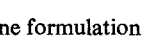
Liverwort oil samples. Barbilophozia barbata (Schreb.) Loeske. Dried plant material (120 g) was extracted with Et_2O. Dissolution in 5 ml of hexane and cooling to 0° afforded a crop of crystals, barbilophozin.[23] The mother liquor afforded a 0·3% yield of hydrocarbon fraction on hexane elution through a column of Al_2O_3 (act. II, neutral). *Barbilophozia floerkei* (Web. and Mohr) Loeske. 408 g of dried plant material[23] was extracted with Et_2O. Steam distillation of the extract afforded 3·17 g (0·77%) of essential oil. *Barbilophozia attenuata* (Mart.) Loeske (= *B. gracilis* (Schleich) K. Mull). 69 g of dried plant material (9–67) afforded a 0·28% yield of oil by the procedure above. *Barbilophozia lycopodioides* (Wallr.) Loeske. Afforded an essential oil in 0·5% yield.[23]

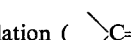
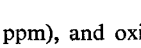
Isolated sesquiterpene hydrocarbons. α-Barbatene (ex. *B. barbata*). MS (*m/e*): 204 ($C_{15}H_{24}$), 136, 121, 119, 108, 95, 93 (base); ORD: $[\alpha]_D$ +96 ± 20°, $[\alpha]_{300}$ +510 ± 30°; CD: $\Delta\epsilon_{201}$ +5·0 ± 0·5; ν_{film} 1630, 882 and 795 cm^{-1}; NMR (δ): 0·84, 0·90, 1·00 (Me *s*), 1·65 (=C–Me, *bs*), ~2·0 (2 allyl - H), and 5·12 ppm (=CH–, $w_{1/2}$ ~ 7 Hz). Hydrogenation (PtO_2, HOAc) afforded essentially a single diastereomer. MS (*m/e*): 206 ($C_{15}H_{26}$); $I_A^{190°}$ = 1560. *β-Barbatene* (ex *B. barbata*). MS (*m/e*): 204 ($C_{15}H_{24}$), 136, 121, 108, 96 (base), 93, 81; ORD: $[\alpha]_D$ +12 ± 10°, $[\alpha]_{300}$ −50 ± 15°; CD: $\Delta\epsilon_{195}$ +7 ± 1; NMR (δ): 0·85, 0·90, 1·04 (Me singlets), 1·80, 2·11 (sharp lines), and 4·52 ppm (C=CH_2) see Fig. 1. From *B. floerkei* this material displayed $\Delta\epsilon_{196}$ +9 ± 2. β-Barbatene from *Chiloscyphus polyanthus* ($\Delta\epsilon_{195}$ = +ve), *Bazzania trilobata* ($[\alpha]_D$ −21°, $[\alpha]_{300}$ −42°, $\Delta\epsilon_{196}$ +7·2 ± 1·0),[13] and *Scapania undulata* ($\Delta\epsilon_{196}$ = +8·2 ± 1·0) also appear to be the same enantiomer. Hydrogenation of β-barbatene afforded the same saturated hydrocarbon as obtained from α-barbatene. (−)-*α-Alaskene* (ex *B. barbata*). MS (*m/e*): 204 ($C_{15}H_{24}$), 136, 121 (characteristic of α-alaskene); ORD: $[\alpha]_{300}$ −230° (lit. −500°); CD: $\Delta\epsilon_{213}$ −2·7, $\Delta\epsilon_{202}$ 0, $\Delta\epsilon_{192}$ +7·8 (reported $\Delta\epsilon_{213}$ = −3·2)[14,15]; NMR (δ) identical to reference spectrum: 5·24 (vinyl-H) 1·67, 1·64,[5] 1·58 (3 vinyl-Me), and 0·86 ppm (CH_3, *d*, 6·7 Hz). Hydrogenation (Adams catalyst, HOAc) afforded a mixture of four alaskanes in identical ratio to that observed previously for α-alaskene (ex. Alaska cedar).[15] Treatment with formic acid afforded a single rearrangement product identified as α-cedrene by GLC.[24] *Calamenene* (ex *B. barbata*) was collected in minute quantities by direct GC and identified from its film IR spectrum.[15]

Reactions of the barbatenes. Acid treatment of β-barbatene. HCO_2H (50 μl) was added to a stirred solution of 5 μl of β-barbatene in 50 μl of *n*-decane.[24] GC analysis of the decane layer revealed complete conversion to α-barbatene in 1 hr at room temp. The reaction was repeated on a 30 mg scale using heptane in place of decane. Quenching with water followed by filtration of the heptane layer through alumina afforded, on concentration *in vacuo*, material judged to be pure α-barbatene by NMR, GC and CD.

Ozonolysis of β-barbatene. On treatment with O_3–O_2 at −78° an ethyl acetate solution of 30 mg of β-barbatene afforded after workup five products (TLC on silica). None of these were simple cyclic ketones. The only isolable product displayed a 2 proton doublet (6·5 Hz) at 4·98 ppm for which no structure assignment can be suggested.

Epoxidation of α-barbatene. α-Barbatene (30 mg) in 1·5 ml of CH_2Cl_2 was treated with 40 mg *m*-chloroperbenzoic acid (MCPBA) in 1·5 ml of CH_2Cl_2 at 0°. After 2 hr, 10% aq. Na_2SO_3 was added. The resulting organic layer was washed with aq. $NaHCO_3$, brine, and then dried (Na_2SO_4). Preparative layer chromatography (SiO_2, 20:1, hexane–EtOAc) afforded 20 mg of the pure epoxide as an oil: $C_{15}H_{24}O$ by MS; NMR: 2·76 ( –*H*, *d*, 3·8 Hz), 1·31 (*CH*$_3$– ), 1·04 (me *s*), 0·82 and 0·75 ppm (2—me, 2 *s*). On reaction in the two phase system (CH_2Cl_2, 48% HBr) the epoxide failed to yield a bromohydrin.

Epoxidation of β-barbatene. β-Barbatene (290 mg) was epoxidized as above. GC analysis indicated a single product (Apiezon-L 190°, RR_{A-cad} = 2·17). The NMR spectrum of the oily product was consistent with the oxirane formulation: δ 2·43 ( , *s*), 1·00 (Me, *s*), 0·90 and 0·89 ppm (2–Me, 2 *s*).

Rearrangement of β-barbatene oxide. The oxide from above (200 mg) in 15 ml CH_2Cl_2 was treated with 5 ml 48% aq. HBr at 0°. After 10 min, the reaction was quenched with excess water. Evaporation of the base washed, dried, organic layer afforded 203 mg of crude product. Preparative layer chromatography afforded the major product, an allylic alcohol: $C_{15}H_{24}O$ by MS; NMR: 5·47 (1 vinyl-H), 3·90 (=C–CH_2OH, *bs*), 2·07 (2 allylic-H), 1·0, 0·92 and 0·86 ppm (Me, *s*). Its nature, an allylic primary alcohol, was established by acetylation ( : 5·51, 4·36, 1·98 ppm), and oxidation MnO_2/CH_2Cl_2 ( :

[23] The detailed description of the isolation of some of the essential oils examined here has been reported in connection with another study: HUNECK, S. and OVERTON, K. H. (1971) *Phytochemistry* **10**, 3279.

[24] Essentially the procedures used in the conversions nerolidol → bisabolene → cedrene: ANDERSEN, N. H. and SYRDAL, D. D. (1972) *Tetrahedron Letters* 2455.

2·2–2·65; 6·53, 4 Hz *t*; 9·37 ppm). The NMR spectra of the oxidation product in $CDCl_3$ with and without added shift reagent appear in Fig. 2.

Acid treatment of α-barbatene. A 10% solution of α-barbatene in *n*-decane was stirred with various acids with the following results:[24] HCO_2H at room temp gave only unchanged α-barbatene ($I_C^{165} = 1650{\cdot}5$); at 80°C, HCO_2H gives 30% conversion to a new compound, $I_C^{165} = 1664\ 5$, in 19 hr; a 1:1 mixture of HCO_2H and CF_3CO_2H at 65° leads to the $I_C^{165} = 1664{\cdot}5$ component ($t_{1/2} \sim 1$ hr). The new compound was prepared in greater than 85% yield from β-barbatene. A solution of 45 mg β-barbatene in 1·6 ml heptane was treated with 0·6 ml HCO_2H with stirring for 12 hr at room temp (GC analysis at this point shows only α-barbatene in the hydrocarbon layer.) After addition of 0 8 ml CF_3CO_2H and 5 hr of stirring at 55°, the reaction mixture was diluted with 60 ml of pentane and washed with H_2O Evaporation afforded 40 mg of crystalline residue which displayed a single peak on GC: $I_A^{190°} = 1501$, $I_A^{155} = 1482{\cdot}5$, and $I_C^{165°} = 1664{\cdot}5$ Preparative GC afforded the novel hydrocarbon (original assignment, structure VI, now considered to be of undefined structure) in pure state: m.p. 56°; ORD: $[\alpha]_D$ +20°, $[\alpha]_{300}$ +197°; CD: $\Delta\epsilon_{209}$ −1·44, $\Delta\epsilon_{193}$ +10·1; and NMR (δ): 5·26 (–CH=C$\diagdown\!\!\diagup$ *bs*,); 1·17 1·10, 1·03, and 0·96 ppm (Me *s*).

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