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TERPENES AND SESQUITERPENES OF *CHAMAECYPARIS NOOTKATENSIS* LEAF OIL

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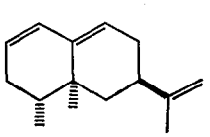
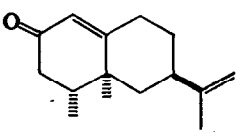
Abstract—The composition of the leaf oil of *Chamaecyparis nootkatensis* is reported. The terpene fraction consists of (−)-α-pinene, (+)-3-carene and (+)-limonene together with small amounts of (−)-β-pinene, myrcene and two unidentified hydrocarbons. The sesquiterpene fraction is largely a mixture of levoratatory α-, β-, and γ-curcumenes with lesser amounts of (−)-α-copaene, (+)-α-ylangene, (+)-longifolene, (+)-δ-cadinene, (+)-γ-cadinene, (+)-β-bisabolene, β-farnesene, (+)-*trans*-nerolidol and three substances which have not been fully characterized. One of these appears to be a mixture of diastereomeric "calamenenes"; the others are new sesquiterpenes which we designate as α- and β-alaskene. Valencene and nootkatene, previously reported from the heartwood oil of this species, were not detected in the leaf oil. The biogenetic and chemotaxonomic implications of these results are discussed.

INTRODUCTION

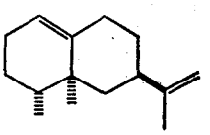
THE ALASKA yellow cedar (*Chamaecyparis nootkatensis*) is noted for the rot resistance and insect-repellant properties of its heartwood and the essential oil has been examined previously.[1-3] However, the insect resistance has not been completely explained in terms of the compounds isolated from the essential oil. *C. nootkatensis* seems to occupy a unique position in the genus and among the Cupressaceae in general, in containing nootkatane sesquiterpenes.[1] Recent studies suggest that nootkatene (I), nootkatone (II), and valencene (III) are the major sesquiterpenes of the heartwood oil.[1,4] Our general interest in the genesis and evolutionary importance of this class of sesquiterpenes (also elaborated by *Vetiveria* species[5]) led us to examine the essential oils derived from *C. nootkatensis*.



(I)



(II)



(III)

We chose to examine the leaf oil first due to the pleasant and enduring fragrance of fresh boughs, which contributes greatly to the forest aroma of stands of *C. nootkatensis*.

* National Science Foundation Predoctoral Fellow, 1968–69.

[1] An excellent review of the chemistry of the order Cupressales has appeared: H. ERDTMAN and T. NORIN, *Fortschr. Chem. organ. Naturstoffe* **24**, 206 (1966).

[2] B. CARLSSON, H. ERDTMAN, A. FRANK and W. E. HARVEY, *Acta Chem. Scand.* **6**, 690 (1952).

[3] R. H. CLARK and C. C. LUCAS, *Trans. R. Soc. Canada* **20**, 423 (1926).

[4] W. D. MACLEOD, JR., *Tetrahedron Letters* 4779 (1965).

[5] N. H. ANDERSEN, *Phytochem.* **9**, 145 (1970).

RESULTS

Steam distillation of fresh needles of *Chamaecyparis nootkatensis* produced a fragrant yellow essential oil in 2·5–3·4 per cent yield. The oil had the exact aroma of the fresh boughs but did not exhibit the highly "grapefruity" note associated with nootkatone.[4,6] Fractionation at reduced pressure (and GLC analysis of the fractions resulting) indicated that the oil consisted largely of terpene (~70 per cent) and sesquiterpene (~15 per cent) hydrocarbons with smaller amounts of oxygenated sesquiterpenes, and other high-boiling components together with traces of oxygenated terpenes. The characteristic aroma of the boughs was most distinct in the high boiling fraction containing the oxygenated sesquiterpenes.

An early study of the leaf oil identified α-pinene and limonene and suggested the presence of β-pinene, sabinene and *p*-cymene.[3] The present terpene hydrocarbon fraction was analyzed by GLC on four different columns (see Table 1)—five components (α-pinene, 35 per cent; β-pinene, 1 per cent; myrcene, 4 per cent; 3-carene, 43 per cent; and limonene, 12 per cent) were identified. Our analysis indicated the absence (<0·2 per cent) of *p*-cymene, tricyclene and camphene (see Table 2); however, one of three very minor components (unknown No. 1) might correspond to sabinene which was not available to us. Column chromatography on $AgNO_3/SiO_2$ followed by preparative GLC afforded pure samples of (−)-α-pinene, (+)-3-carene, (−)-β-pinene, (+)-limonene, and myrcene which displayed NMR spectra identical to those of authentic samples.

TABLE 1. GLC ANALYSIS OF *C. nootkatensis* TERPENE FRACTION

Component	Assignment§	Stationary phases* SF-96 (100°)	Apiezon-L (100°)	Carbowax 20M (75°)	DEGS† (100°)
1	α-Pinene	36·7% 938·0	34·1% 944·5	35% 1022·5	34·0% 1114
2	Unknown No. 1	1·2% 949·7	1·1% 960·1	1% ~1062	1·0% 1168
3	β-Pinene	2·1% 978·2	2·3% 993·0	2% 1103·4	2·2% 1227
4	Myrcene	4·0% 982·5	4·0% 975·8	47%‖	47·5%‖
5	3-Carene	42·5% 1009·1	44·4% 1020·9	~1141	~1264
6	Limonene	12·2% 1024·8	12·8% 1044·9	~12·5% 1187	12·7% 1323
7	Unknown No. 2	N.R.‡	N.R.‡	~0·5% ~1189·5	~0·5% 1324·5
8	Unknown No. 3	1·3% 1080·0	1·3% 1096·6	1% —	1·2% 1414·5

* The analysis of the terpene fraction on each phase is given together with the self-consistent Kovats' indices[7] for the peaks observed.
† Diethylene Glycol Succinate.
‡ Not resolved on the stationary phase.
§ Based on agreement (± 0·5) of self-consistent Kovats' indices with those obtained for authentic samples.
‖ Myrcene and 3-carene not resolved on this stationary phase.

[6] The characteristic "grapefruity" odor can usually be recognized in mixtures containing even small amounts of nootkatone, personal communication from H. U. DAENIKER (Givaudan Corp.).

TABLE 2. SELF-CONSISTENT KOVATS' INDICES FOR TERPENES

Standard	Stationary phases			
	SF-96 (100°)	Apiezon-L (100°)	Carbowax 20M (75°)	DEGS* (100°)
Tricyclene	928·5	936·6	1009·5	1111·5
α-Pinene	938·0	944·5	1022·5	1114
Camphene	952·4	965·9	1066·0	1185
β-Pinene	978·2	993·0	1103·4	1227
Myrcene	982·5	975·4	1148·9	1267
3-Carene	1009·1	1020·9	1140·8	1263·5
p-Cymene	1015·8	1034·2	1250·5	1427
Limonene	1024·8	1044·9	1187	1323

* Diethylene glycol succinate.

The GLC analysis of the terpene fraction deserves some further comment. Although we used the same stationary phases and temperatures as reported in a study of the essential oil of Douglas fir needles,[6] we were unable to reproduce the relative retentions, and even Kovats' indices, reported. We recently introduced a highly reproducible form of retention data for sequiterpene analysis which we termed "self-consistent Kovats' indices".[7] These indices are obtained using compounds of the same class as standards rather than *n*-alkanes[9] (see Ref. 7 for details) in order to offset differences in the temperature dependence of Kovats' indices between different classes of compounds. It also appears to eliminate the supposedly negligible effects of variable loading, column size, and column configuration on Kovats' indices.

Table 3 presents a comparison of our data on standard terpenes and that of W. G. Jennings *et al.*[8] The agreement is good only when our indices are compared to self-consistent indices calculated from the literature relative retention data. The literature data for the Carbowax 20-M column fit with the data presented in this paper only after a prior temperature coefficient correction. It appears that the retention data presented by Jennings *et al.*[8] was determined at 100° rather than 75° as stated.

TABLE 3. TERPENE RETENTION DATA ON SF-96 AT 100°, LITERATURE COMPARISON*

Compound	α-Pinene	Camphene	β-Pinene	3-Carene	Myrcene	Limonene	*p*-Cymene
RR†	0·572	0·628	0·741	0·904	0·762	1·000	0·944
Lit. RR	0·68	0·72	0·81	0·92	0·83	1·000	0·97
Lit. Kovats' index	942	956	983	1013	988	1028	1018
S.C. Kovats' index†	938·0	952·4	978·2	1009·1	982·5	1024·8	1015·8
S.C.K.I. lit.§	938‡	951	978	1006	983	1025‡	1017

* Lit. Ref. 8.
† Present work.
‡ Assigned as internal standards.
§ Self-consistent Kovats' indices calculated from the literature RR-value (see Ref. 7).

The sesquiterpene fractions [b.p. 84° (5 mm)—112° (1·5 mm)] proved to be complex mixtures which could not be resolved on any single stationary phase. Figure 1 shows traces of a representative sample on polar (DEGS) and non-polar (Apiezon-L) phases. In addition to the hydrocarbons indicated on these GLC traces, these fractions also contained a small amount of oxygenated sesquiterpenes from which *trans*-(+)-nerolidol could be isolated by preparative GLC.

[7] N. H. ANDERSEN and M. S. FALCONE, *J. Chromatog.* **44**, 52 (1969).
[8] T. SAKAI, H. MAARSE, R. E. KEPNER, W. G. JENNINGS and W. M. LONGHURST, *J. Agr. Food Chem.* **15**, 1070 (1967).
[9] E. KOVATS, *Helv. Chim. Acta* **41**, 1915 (1958).

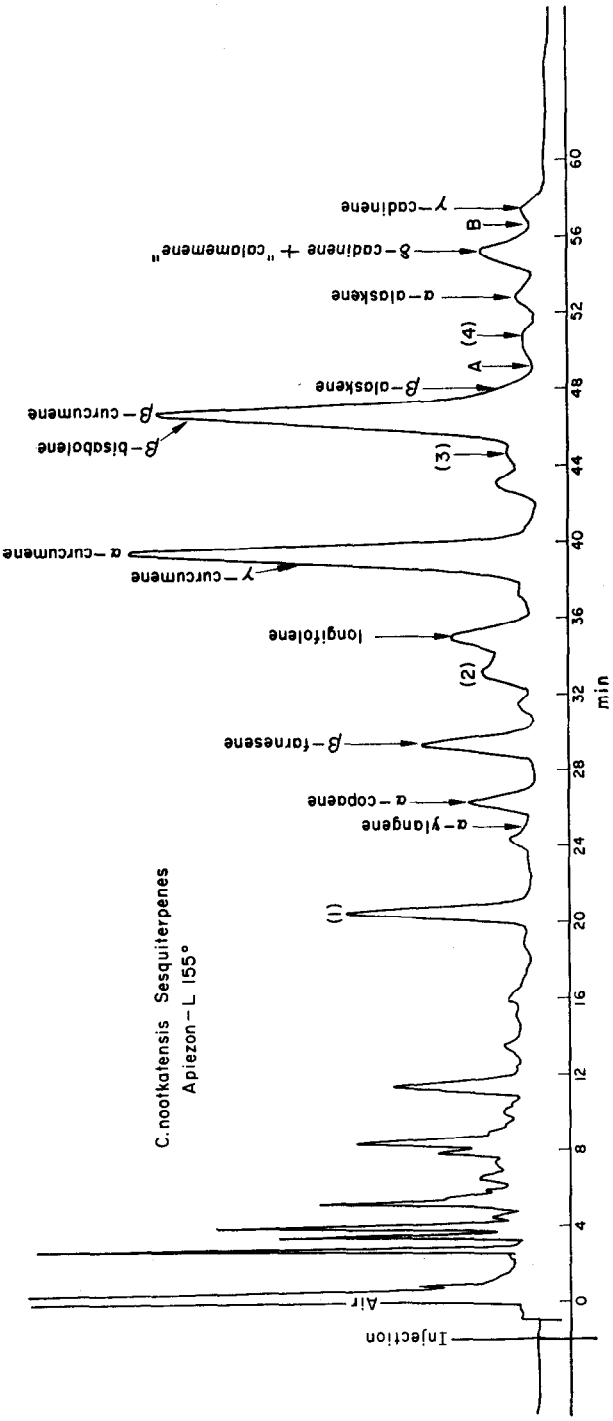

C. nootkatensis Sesquiterpenes
Apiezon – L 155°
Injection
Air
α – ylangene
α – copaene
β – farnesene
longifolene
γ – curcumene
α – curcumene
β – bisabolene
β – curcumene
β – elaskene
α – elaskene
β – cadinene + "calamemene"
γ – cadinene
(1)
(2)
(3)
(4)
A
B
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
min

FIG. 1a.

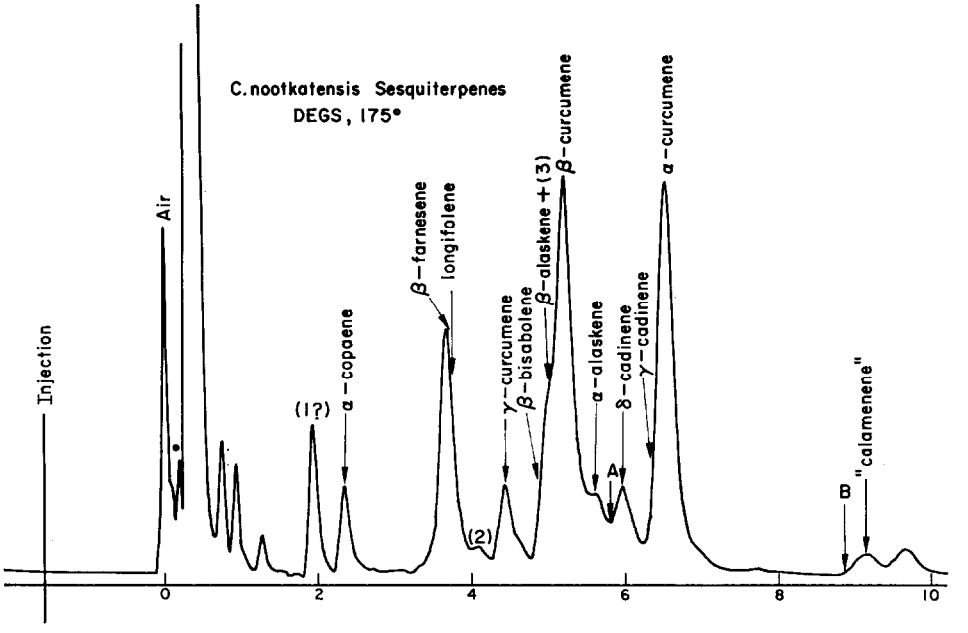


FIG. 1b.

FIG. 1. GLC TRACES OF A REPRESENTATIVE FRACTION OF SESQUITERPENES ON APIEZON-L (155°) AND DEGS (175°) COLUMNS.

Peaks corresponding to the isolated components are identified. The Kovats' indices of peaks 1–4 correspond to cubebene, caryophyllene, α-amorphene, and γ-bisabolene respectively, but these substances were not confirmed by isolation. Arrows marked A and B indicate the positions of authentic valencene and nootkatene respectively.

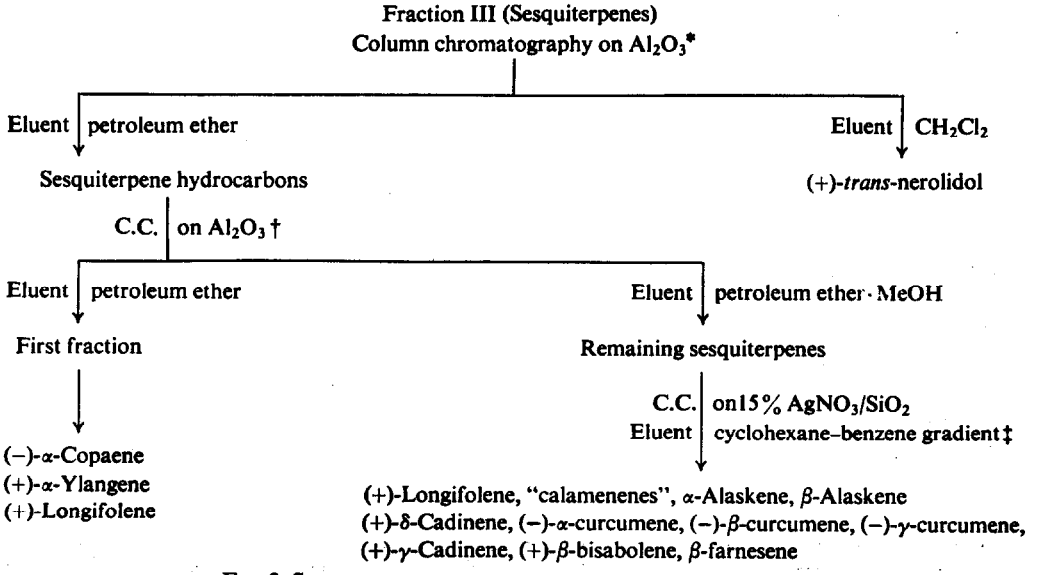
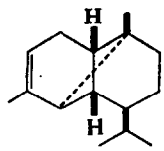


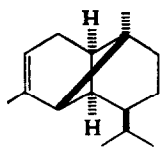
FIG. 2. SEPARATION SCHEME FOR THE SESQUITERPENE FRACTION.

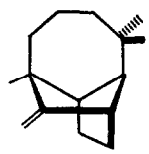
* Acid-washed, activity II–III.

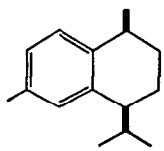
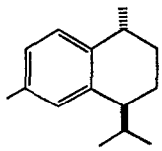
† Woelm basic alumina, activity I.

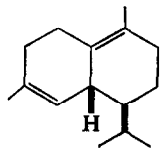
‡ Compounds listed in order of elution.

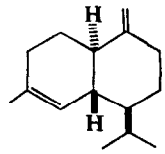

(−)-α-Copaene

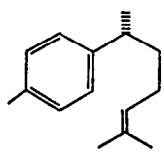

(+)-α-Ylangene

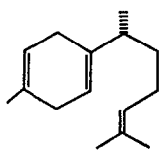

(+)-Longifolene

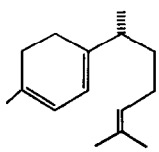


"Calamenenes"

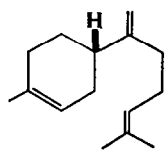

(+)-δ-Cadinene

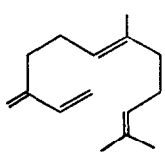

(+)-γ-Cadinene

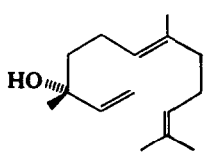

(−)-α-Curcumene


(−)-β-Curcumene


(−)-γ-Curcumene


(+)-β-Bisabolene


β-Farnesene


(+)-Nerlidol

The scheme employed for the separation of the sesquiterpene hydrocarbons (shown in Fig. 2) takes advantage of the high selectivity of chromatography on $AgNO_3/SiO_2$. Final purification of each substance was effected by chromatographic filtration (basic alumina, Woelm activity I) after preparative GLC.

The following substances were identified from "self-consistent Kovats' indices" on four or more GLC columns:[7] (−)-α-copaene, (+)-α-ylangene, (+)-longifolene, (+)-δ-cadinene, (−)-α-curcumene, (+)-β-bisabolene, and (+)-γ-cadinene; and showed i.r. and NMR spectra superimposable with those obtained from authentic samples[10] and in accord with the literature values where available.[11] β-Farnesene displayed i.r. and NMR spectra in accord with the literature values, and afforded farnesane (i.r. comparison) on hydrogenation.[12]

(−)-β-Curcumene and (−)-γ-curcumene have been only rarely encountered and have not been fully characterized (see Experimental). Our structural assignments rest largely on the NMR spectra of the isolated substances (see Experimental). Dehydrogenation (Se, 240°) of (−)-β-curcumene, $[\alpha]_D = -6{\cdot}6°$, afforded (−)-α-curcumene of 88 ± 8 per cent optical purity as judged by combined u.v., i.r. and ORD comparison with authentic (−)-α-curcumene isolated from *Curcuma aromatica*. Thus the elevated rotations reported[11] for levo- and dextrorotatory samples of supposed β-curcumene must be due to the impure states of

[10] The sources of authentic materials have been reported previously.[7]

[11] Physical constants and spectra of sesquiterpenes were obtained from G. OURISSON, S. MUNAVALLI and C. EHRET, *International Tables of Selected Constants, No. 15, Data Relative to Sesquiterpenoids*, Pergamon Press, Oxford (1966) and (b) R. BATES (University of Arizona) collection of NMR spectra. The work by OURISSON *et al.* was also used to check for sources of various sesquiterpenes.

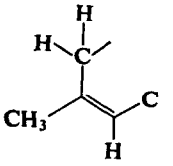
[12] Y. R. NAVES, *Helv. Chim. Acta* **49**, 1033 (1966).

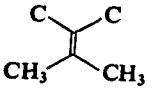
the samples isolated by the less-refined methods available at the time.[13] (−)-γ-Curcumene affords α-curcumene on standing. The rotation of the resulting α-curcumene was not determined, but the absolute configuration assigned to (−)-γ-curcumene seems secure in light of the fact that (+)-γ-curcumene co-occurs with (+)-α-curcumene in *Olearia paniculata*.[11,14]

The characteristic i.r. and NMR bands of the curcumenes and the other isolated sesquiterpenes are collected in Table 4.

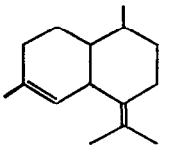
Three additional hydrocarbons were obtained in quantities too small for complete characterization. We designate two of these as α- and β-alaskene since they appear to be new substances. The third appears to be a mixture (~1:1) of two diastereomeric "calamenenes"; there are, however, certain inconsistencies between our data and the literature (see Experimental).

The alaskenes are isomeric sesquiterpenes of composition $C_{15}H_{24}$,[15] and both afford the same mixture of diastereomeric hydrocarbons ($C_{15}H_{28}$)[15] on hydrogenation, indicating a bicyclic skeleton with two double bonds. The i.r. and NMR spectra reveal only one vinyl hydrogen in each; thus one olefinic linkage is tetra-substituted. The NMR spectra of the two alaskenes are quite similar each showing a doublet methyl at δ ~0·87 and a composite signal at δ ~1·65 due to three vinyl methyl groups. Therefore the alaskenes must have an isopropylidene group and a trisubstituted double bond not at a ring fusion. The hydrogenation results and the differences in the vinyl hydrogen resonances (5·33 ppm, $W_{h/2} \sim 9$ Hz for α-alaskene, 5·42 ppm, $W_{h/2} \sim 11$ Hz for β-alaskene) argued that two differed in double bond position rather than in stereochemistry at the tertiary methyl. Our structures must incorporate the features shown below:

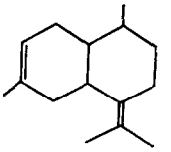




The cadalene skeleton readily incorporates these features generating possible structures for α- and β-alaskene as shown below:



α



β

The choice of the α and β structures being dictated by the peak widths for the vinyl hydrogen resonances.

We sought a verification of this tentative assignment by a careful GLC analysis of the hydrogenation product alaskane. Of the sixteen diastereomers (IV–VII, four each) that

[13] It would appear the best previous sample of β-curcumene isolated was the dextrorotatory sample of Y. R. NAVES, *Bull. Soc. chim. France* 990 (1951) with $[\alpha]_D = +27°$. However, 2–4% of oxygenated impurities were said to be present which could easily account for the large rotation.

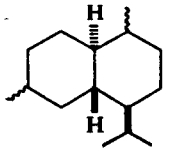
[14] R. E. CORBETT, G. A. JAMIESON and J. MURRAY, *J. Science Food Agr.* **14**, 349 (1963).

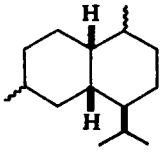
[15] Confirmed by exact mass of parent peak in the mass spectrum.

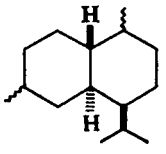
TABLE 4.

Compound	I.r. absorptions (cm^{-1})				NMR absorptions (δ)		
	C–H stretch	C=H stretch	C=C–H out-of-plane	Other	Vinyl H	Methyl res.	Other
(−)-α-Copaene	3030 (m)	1666 (w)	785 (s)		1H (5.23, bm)	$1CH_3$ (0·81, s) $2CH_3$ (~0·87, d) $1CH_3$ (1·68)	
(+)-Longifolene	3066 (mw)	1658 (ms)	874 (s)		1H (4·54, s) 1H (4·79, s)	$1CH_3$ (0·921, s) $1CH_3$ (0·972, s) $1CH_3$ (1·01, s)	1H (2·12, bm) 1H (2·65, bm)
"Calamenenes"	3040–3000 (w, sh)	1609 (mw)	812 (s)	1890 (w) 1493 (ms)		See Experimental	
α-Alaskene	3050–3020 (w, sh)		797 (m)	1372 (s) 757 (w)	1H (5·33, bs)	$1CH_3$ (0·879, d, 6·5) $3CH_3$ (1·73–1·6, n.r.)	
β-Alaskene	3035 (w)	1660–1675 (vw)	798 (m)	1368 (s) 757 (w)	1H (5·42, bs)	$1CH_3$ (0·854, d, 6·4) $3CH_3$ (1·75–1·63, n.r.)	
(+)-δ-Cadinene	3050 (sh)	1667 (w)	834 (m)		1H (5·45, m)	$1CH_3$ (0·77, d, 6·5) $1CH_3$ (0·95, d, 6·5) $2CH_3$ (1·67, bs)	
(−)-α-Curcumene	3100 (w) 3055 (w) 3025 (m)	1672 (w) 1650 (w)	818 (vs)	1893 (w) 1518 (vs)	1H (5·08, bt, 6)	$1CH_3$ (1·21, d, 7) $1CH_3$ (1·52, bs) $1CH_3$ (1·67, bs) $1CH_3$ (2·31, s)	4H (7·08, s)
(−)-β-Curcumene	3085 (w) 3020 (m)	1663 (w)	780 (s) 827 (m)	950 (s)	1H (5·10, t, 6) 2H (5·43, bs)	$1CH_3$ (0·992, d, 7) $1CH_3$ (1·58, bs) $2CH_3$ (1·67, bs)	4H (2·48, s)
(−)-γ-Curcumene	3073 (w) 3030 (m)	1653 (ms) 1604 (w)	822 (s)		1H (5·09, m) 2H (5·58, bs)	$1CH_3$ (0·984, d, 7) $1CH_3$ (1·58, bs) $1CH_3$ (1·67, bs) $1CH_3$ (1·77, s)	4H (2·05, s)
(+)-γ-Cadinene	3075 (m) 3047 (w) 3010 (m)	1663 (w) 1645 (ms)	885 (vs) 832 (m) 791 (m)		1H (4·58, bs) 1H (4·67, bs) 1H (5·48, bs)	$1CH_3$ (0·734, d, 7) $1CH_3$ (0·925, d, 7) $1CH_3$ (1·69, bs)	
(+)-β-Bisabolene	3085 (mw) 3050 (w) 3018 (m)	1675 (w) 1642 (ms)	889 (vs) 828 (m) 797 (ms)	915 (m)	2H (4·75, s) 1H (5·14, m) 1H (5·43, m)	$1CH_3$ (1·62, s) $2CH_3$ (1·67, bs)	
β-Farnesene	3090 (m) 3050 (w, sh) 3025 (m, sh)	1668 (w) 1643 (w) 1633 (ms) 1597 (ms)	892 (vs) 903 (sh) 990 (s)		2H (5·01, bs) 1H (~5·08, d, 11) 2H (~5·13, m) 1H (5·27, d, 17·5) 1H (6·50, dd, 11, 17·5)	$2CH_3$ (1·62, s) $1CH_3$ (1·68, s)	
(+)-*trans*-Nerolidol	3090 (w) 3055 (w, sh)	1647 (m)	998 (m) 920 (ms) 835–815 (m)	3460 (bs)	1H (5·06, dd, 1·8, 10·5) 2H (~5·17, m) 1H (5·20, dd, 1·8, 10·5) 1H (5·95, dd, 10·5, 17·5)	$1CH_3$ (1·275, s) $2CH_3$ (1·63, bs) $1CH_3$ (1·69, bs)	

could be expected from the tentative structures of the alaskenes, eight were available to us.[7] The hydrogenation of γ-cadinene produces three of the possible structures (IV), the hydrogenation of α-muurolene produces three of structure V, and the hydrogenation of α-amorphene produces two of structure VII. No bulgaranes (VI) were available.


(IV)


(V)


(VI)

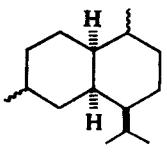

(VII)

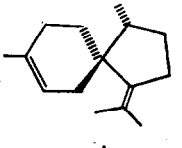
TABLE 5. GLC COMPARISON (S.C.K.I.)* OF ALASKANES, CADINANES, MUUROLANES, AND AMORPHANES

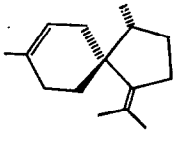
		Apiezon L (155°)	C-20M (165°)	DEGS (175°)
Alaskanes	I (60%)	1508·5	1620 ± 1	1765
	II (25%)	1516·2	1630 ± 1	~1780
	III (10%)	1484·8	1590 ± 3	1734
	IV (5%)	1499·5	1630 ± 5?	N.R.‖
Cadinanes†	I (64%)	1503·2	1618	1760
	II (29%)	1493·5	1597	1728
	III (7%)	1477·5	1567	1686
Muurolanes‡	I (45%)	1497·2	1582	1713
	II (32%)	1535·6	1659	1808
	III (16%)	1503·2	1610	1767?
Amorphanes§	I (44%)	1489·8	1593	1718
	II (41%)	1524·4	1648·5	1794

* Self-consistent Kovats' indices.[7]
† From authentic γ-cadinene.
‡ From authentic α-muurolene.
§ From authentic α-amorphene.
‖ Not resolved.

Alaskane appeared to contain all four possible diastereomers by GLC. However, none matched with those of the cadinanes, muurolanes, or amorphanes available on all three columns (see Table 5). Although these results do not eliminate the possibility that the alaskenes have a cadalene skeleton, they are clearly new sesquiterpenes and probably represent a new skeleton as well. Further structure elucidation will be pursued when larger samples are isolated.¶

¶ *Note added in proof*–The structures of α- and β- alaskene have now been shown to be i and ii respectively: N. H. ANDERSEN and D. D. SYRDAL, *Tetrahedron Letters*, in press.


i


ii

The fact that nootkatene (I) and valencene (III) were not present in the leaf oil, was confirmed by GLC peak enhancements (see Fig. 1) using authentic samples, which became available from other sources.[16]

DISCUSSION

This study of *Chamaecyparis nootkatensis* was initiated in hopes of gaining an understanding of the genesis of nootkatane sesquiterpenes such as those obtained from the heartwood oil of this species.[1,4] However, the leaf oil sample which we obtained contained no trace of either nootkatene or valencene. Furthermore, no selinenes or nootkatenes could be isolated. Although a number of minor sesquiterpenes from the leaf oil remain to be characterized, the results point to a striking differentiation in biogenetic development in the different parts of the plant—toward cyclodecadienyl cation VIII (proposed precursor of selinenes and nootkatenes[5,17]) in the wood and toward a precursor of cadelenes and curcumenes in the needles. (The question of a biogenetic link between the cadalene sesquiterpenes and the monocyclic bisabolenes and curcumenes is discussed below.)

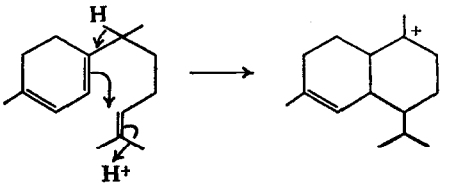
Superficially, *C. nootkatensis* no longer appears as chemotaxonomically unique—the predominance of nootkatane sesquiterpenes, which occur in no other Cupressaceae studied to date, has been cited as one of the indications that the systematic position of this species should be reconsidered.[1] As an example *C. obtusa* is known to produce (+)-longifolene, calamenene, (+)-δ-cadinene, and (+)-γ-cadinene, all present in *C. nootkatensis* leaf oil.[1,11] *C. lawsoniana* also contains cadinenes and β-bisabolene as do many junipers.[1,11] However, β-farnesene and (+)-nerolidol are known only in one other Cupressaceae (*Fokienia Hodginsii*) and the curcumenes are even less common—one example only, (+)-γ-curcumene, occurs in *Libocedrus Baldwilii*.[11]

However, the resemblance is only superficial. The β-bisabolene isolated from *C. lawsoniana* and junipers is the common levorotatory form, but *C. nootkatensis* elaborates (+)-β-bisabolene which has been previously encountered only once.[11] The curcumenes that occur in oils containing d-cadinenes have always been the dextrorotatory form—*C. nootkatensis* produces optically pure (−)-curcumenes as the major constituents of the leaf oil.* γ-Curcumene, although apparently rare in nature,† occupies a unique position as a possible biogenetic intermediate between the cadalene and monocyclic sesquiterpenes which is shown in Chart I.‡ Before discussing these hypotheses, some introduction to an admittedly "chemical" approach seems necessary.

* Those essential oils that produce curcumenes as major constituents generally produce (−)-curcumenes.[11]

† We found γ-curcumene to be unusually unstable. On standing at room temperature, one sample converted cleanly (GLC) to α-curcumene in 1 week. The apparent "rarity" of the γ-isomer and the "common" occurrence of the α-isomer may simply reflect this fact (see also experimental and Ref. 14).

‡ The reverse of this fragmentation has been suggested as one of three pathways leading to cadalenes.[18]



[16] Nootkatene and valencene were isolated from Reunion Oil of Vetiver, N. H. ANDERSEN, unpublished results.

[17] J. B. HENDRICKSON, *Tetrahedron* **7**, 82 (1959), and references therein.

[18] W. PARKER, J. S. ROBERTS and R. RAMAGE, *Quart. Rev.* **21**, 331 (1967).

To our knowledge, sesquiterpenes play no essential role in the "metabolic" pathways of plants and their frequently beneficial role in plants (insect control, as an example) can be considered as coincidence. The frequency of such coincidence in surviving species would, of course, increase due to the usual evolutionary forces. However, the amount of biochemical machinery mobilized in the synthesis of these substances should be minimal. For this reason we prefer biogenetic hypotheses employing the maximum amount of "chemical" reasoning rather than invoking enzymic control unnecessarily. The ideal (and almost certainly unrealistic) biogenesis would involve a single enzyme-controlled step generating a dissymmetric intermediate from which the wide variety of sesquiterpene types can be generated by chemical interconversions controlled by the usual steric and stereoelectronic effects associated with such rearrangements. We recently suggested a scheme by which a single cyclization of a *trans,trans*-farnesyl derivative (→ VIII) or a *cis,trans*-farnesyl derivative (→ IX)

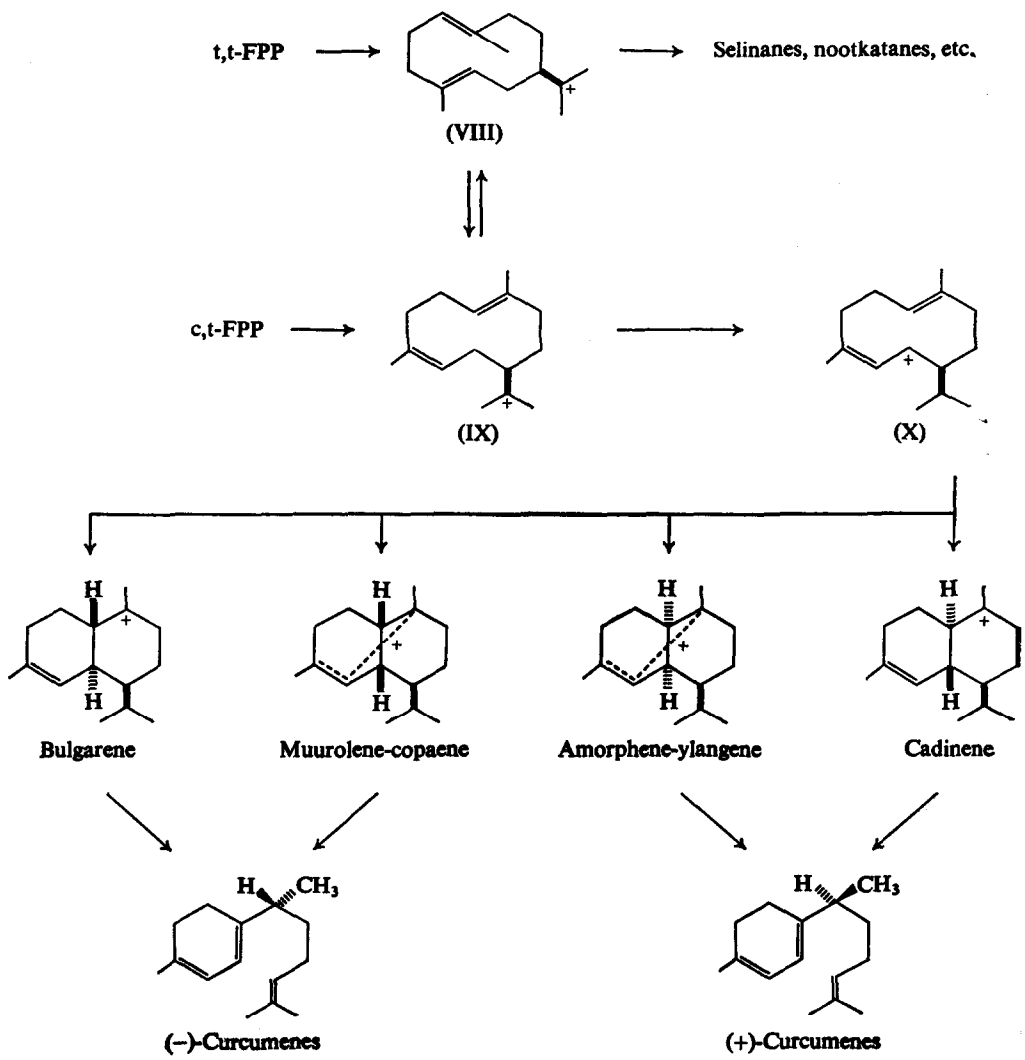
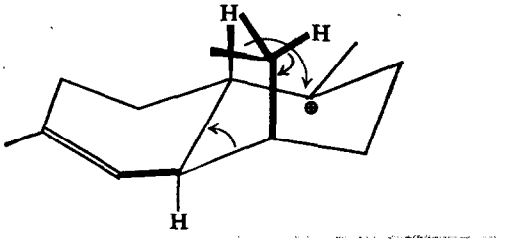


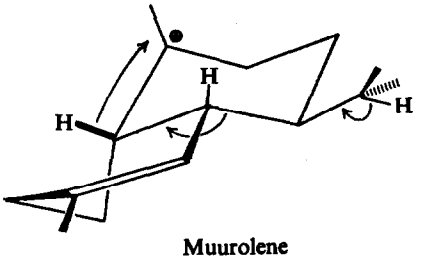
CHART I. CONDENSED BIOGENETIC SCHEME.

could lead to virtually all sesquiterpene types.[5] The essential feature of this scheme is the interconversion between a number of cyclodecadienyl cations including VIII, IX, and X in Chart I. Some of the further transformations of cation VIII (or the triene) have been discussed[5] and will not be considered here. Cation X could serve as the precursor of four stereochemical cadalene types[19] and of both the dextro- and levorotatory curcumene series as shown in Chart I. Bulgarenes and muurolenes should afford the (−)-curcumene series while cadinenes and amorphenes should yield the (+)-series by a concerted fragmentation.

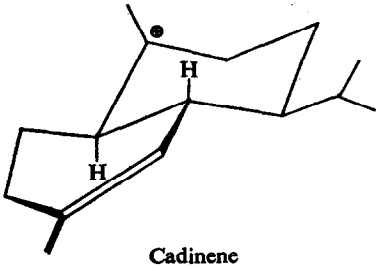
The observed levorotation of the curcumenes in curcumene-rich oils require that the fragmentation of bulgarenes and muurolenes should be facile relative to that of cadinenes or amorphenes. In the case of muurolene the stable conformation has the favorable antiparallel arrangement at the fusion. The *trans*-fused bulgarenes have an axial isopropyl group as shown—and the fragmentation to (−)-γ-curcumene should be favored (due to release of steric strain) even though the antiparallel relationship cannot be attained. Cadinene is, necessarily, in an unfavorable conformation and the favored, equatorial isopropyl, conformer of amorphene also lacks the antiparallel relationship leading to facile fragmentation. Thus the suggestion fits some available data. However, another implication, that curcumene-rich oils ought to contain minor amounts of bulgarenes, and perhaps also muurolenes and copaenes, has not been tested. Only one observation weighs against the proposal as stated above, i.e. the co-occurrence of substantial amounts of amorphenes and (−)-α-curcumene in the oil of *Amorpha fruticosa*.[20]



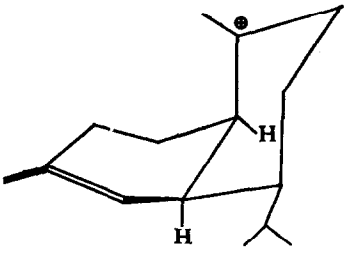
Bulgarene



Muurolene



Cadinene



Amorphene

Finally we must admit that any single species might well synthesize sesquiterpenes through a variety of unrelated or crossing routes, but only detailed examination of oil

[19] For similar discussion and a proof of stereochemistry for (+)-α-ylangene consistent with the proposal see Y. OHTA and Y. HIROSE, *Tetrahedron Letters* 1601 (1969).

[20] O. MOTL, M. ROMANUK and V. HEROUT, *Coll. Czech. Chem. Commun.* 31, 2025 (1966).

composition and experiments involving the incorporation of labeled materials will resolve this point. Until then chemical reasoning must stand as the guiding principle in the unravelling of sesquiterpene biogenesis.

EXPERIMENTAL

Isolation of the Essential Oil

Samples of the essential oil and of a turpentine-like oil were obtained in the following manner. 450 g of fresh frozen needles* was blended in batches with 1300 ml of water and the resulting slurries were added to a still pot containing 600 ml of ethylene glycol, 400 ml of water and 20 g of $CaCO_3$. Distillation over 3 hr removed virtually all of the water. The combined distillates were extracted with ether and CH_2CL_2 to yield a fragrant yellow essential oil (12–16 ml, 2·5–3·4%).† In another run, 330 g of needles afforded 8·5 ml of oil (2.4%) which separated spontaneously from the first 450 ml of distillate. This turpentine oil was colorless and lacked the characteristic odor.

Fractionation of the Whole Essential Oil

The whole essential oil (*ca.* 22 ml) was distilled at reduced pressure through a short Vigreaux column affording fractions as follows: I, b.p. 55–80° (25 mm), *ca.* 16 ml; II, b.p. 30–84° (5 mm), *ca.* 0·7 ml; III, b.p. 84–112° (5–1·5 mm), *ca.* 3 ml; IV, b.p. 50–160° (0·13 mm), *ca.* 2 ml.

Fraction I was further separated by means of column chromatography on $AgNO_3$ impregnated silica.‡ It (*ca.* 2 ml) was applied to a column (30 mm i.d., 30 cm high) and fractions were eluted with eluent composition ranging from 100% cyclohexane (H_2SO_4 and $KMnO_4$ washed) to 50% cyclohexane–50% benzene (distilled). The order of elution of the compounds was (−)-α-pinene, (+)-3-carene, (−)-β-pinene, unknown No. 1 and No. 2, (+)-limonene, and myrcene. (−)-α-Pinene and (+)-3-carene were eluted with 100% cyclohexane while (−)-β-pinene, (+)-limonene, and myrcene were eluted with increasing concentration of benzene.

GLC and TLC indicated fraction II was mainly terpene hydrocarbons contained in fraction I along with extremely small quantities of what appeared to be oxygenated monoterpenes. The further fractionation of fraction III is outlined in Fig. 2. Fraction IV is currently under investigation and would appear to consist mostly of oxygenated sesquiterpenes by VPC and TLC indications.

Purification and Identification of Fraction I Compounds

Each of the following compounds was isolated by preparative GLC of the appropriate chromatographic fractions on a ⅜ in × 16 ft, 6% FFAP-Chromosorb G (70–80 mesh) column at 120°. The collected compounds were all obtained in >98% purity according to analytical GLC analysis on several columns.

(−)-*α-Pinene.* $[\alpha]_D = -56 \pm 5°$ (lit. −50·0°[21]); NMR identical to that of R. Bates;[11] GLC indicated α-pinene (see Table 1).

(+)-3-*Carene.* $[\alpha]_D = +14 \pm 2°$ (lit. +17·1°[21]); NMR corresponds to authentic sample from commercial 3-carene; GLC indicated 3-carene (see Table 1).

(−)-*β-Pinene.* $[\alpha]_D$ is negative, ORD shows strong positive trend;§ NMR identical to that of R. Bates,[11] GLC indicated β-pinene (see Table 1).

(+)-*Limonene.* $[\alpha]_D = 103 \pm 3°$ (lit. +126·6[21]); NMR identical to that of sample isolated from celery-seed oil. GLC indicated limonene (see Table 1).

Myrcene. NMR corresponded to an authentic sample prepared from commercial myrcene; GLC indicated myrcene (see Table 1).

* The authors wish to thank Reynold Dickhaus (Georgia Pacific, Bellingham, Wash.) for supplying this collection (Nov., 1968). The needles were stripped from the fresh boughs within 24 hr and kept frozen until use (7–14 days).

† The extracts were dried ($NaSO_4$) and concentrated on a rotary evaporator (at 40°), with some loss of monoterpene hydrocarbons.

‡ Adsorbent was prepared by evaporation of a water slurry of 15% $AgNO_3$–85% Silicar CC-7 on a rotary evaporator at 70° for 12 hr. The adsorbent was further activated by heating at 80° (0·13 mm) for 6 hr and storage at 120° for 8 hr.

§ Solution concentration was unknown; however, the sample's ORD curve had the same shape as spectrum of a prepared commercial sample ($[\alpha]_D = -25°$, $[\alpha]_{300} = +144°$) (lit. $[\alpha]_D = -24°$[21]).

[21] J. Pliva, M. Horak, V. Herout and F. Sorm, *Die Terpene, Sammlung der Spektren und physikalischen Konstanten*, Teil II, *Monoterpene*, Akademie Verlag, Berlin (1960).

Purification and Identification of Fraction III Compounds

Each material was obtained by preparative GLC of the appropriate chromatographic fractions (⅜ in × 16 ft, 6% FFAP-Chromosorb G (70–80 mesh) column at 150–190°) in >95% purity according to subsequent GLC analysis on several columns. The self-consistent Kovats' indices[7] for these compounds are collected in Table 6.

TABLE 6. SELF-CONSISTENT KOVATS' INDICES OF *C. nootkatensis* SESQUITERPENES

Component	Apiezon-L (155°)	SF-96 (170°)	DC-710 (165°)	QF-1 (132°)	C-20M (165°)	DEGS (160°)	DEGS (175°)
α-Ylangene	1401·5	1396·1	1454·5		1538·5	1653	
α-Copaene	1410·2	1400·5	1459	1447	1551·3	1665	1692
β-Farnesene	1429·2			1509	1668	1818·5	1834
Longifolene	1464·0	1440·2	1517·5	1520	1643	1802·5	1840
γ-Curcumene	1481·9			1532·5			1895
α-Curcumene	1483	1480·4	1589	1557·5	1787·5	1992·5	2018·5
β-Bisabolene	1512·9	1510·3	1592·5	1548	1745·5	1909·5	1923
β-Curcumene	1513·6	1510·4		1547·5	1756	1922·5	1946·5
δ-Cadinene	1546·4	(1526·4)	1628·5		1784	1959	1990·5
γ-Cadinene	1554·9	1523·5	1623·5	1587	1792·3	1978·5	2015·0
β-Alaskene	1520·5				1738·3	1906·5	1938
α-Alaskene	1539·0				1763·0		1969
"Calamenenes"	1547–1548·5						2124–2130

(−)-α-*Copaene with* (+)-α-*ylangene*. $[\alpha]_D = +8 \pm 2°$ (lit. −6°[22], −19°[23]); ORD shows strong negative trend below 300 nm just as authentic (−)-α-copaene;[10] i.r. and NMR superimposable with spectra of authentic material.[10] GLC analysis on three columns[7] showed contamination with 15–20% α-ylangene. The positive rotation at the sodium D-line is due to (+)-α-ylangene (lit. $[\alpha]_D = +55·6$°[23]). See Ref. 22 for a similar discussion of a "dextrorotatory" α-copaene sample.

(+)-*Longifolene*. $[\alpha]_D = +27°$ (authentic sample[10] had +28·5°, lit. +45°[11]); $[\alpha]_{300} = +430°$ (authentic sample[10] had +570°); NMR and i.r. spectra superimposable with those of authentic material; MS, *m/e* 204 (parent), 187, 175, 161 (base), 147, 119 (base), 105, 79, 55, and 41.

"*Calamenene*", $C_{15}H_{22}$:[15] NMR ($CDCl_3$), δ 0·717 (½ CH_3, d, 6·5), 0·771 (½ CH_3, d, 6·5), 0·992 (½ CH_3, d, 7·5), 1·03 (½ CH_3 d, 6·5), 1·25 (1 CH_3, d, 6·7 Hz), 2·31 (1 CH_3, bs), 7·00 (3H, bm) ppm; i.r., ν 1890, 1642, 1609, 1510, *1494, 1453, 1380, 1370*, 1360, 1318, 1260, 1192, 1179, 1160, 1130, 1112, 1100, 1035, 1020, 980, 920, 900, 880, *812*, 730, 725 cm^{-1}; u.v. ($CHCl_3$), λ 278, 270, 264 nm. (ε 645, 672, 513 ± 10%); MS, *m/e* 202 (parent), 187, 159 (base), 145, 132, 105, 91, 41 with 159 five times as intense as 132, the second most intense peak.

The NMR spectrum can be well explained on the basis of a 50:50 mixture of the two possible diastereiomeric isomers of calamenene. The isopropyl group of each isomer could be expected to give two doublet methyl resonances integrating to six protons; whereas four doublet methyl resonances, integrating to six protons, are observed. The tertiary methyl of each isomer could be expected to produce a doublet integrating to three protons, and this is observed indicating this resonance happens to have the same chemical shift for each isomer. The aromatic methyl is at the expected δ value and integrates to three protons, indicating that the chemical shift is identical for this signal also.

The only NMR spectrum of calamenene reported in the literature[24] gives a pattern consistent with one diastereiomer of our mixture. However, the chemical shift values do not agree well: (δ, 0·71 (1 CH_3, d, 6·0), 0·98 (1 CH_3, d, 6·0), 1·23 (1 CH_3, d, 7·2), 2·24 (1 CH_3, s), 6·86 (3H, bm). The difference between the reported δ values and the δ values of one of our isomers is 0·007, 0·012, 0·02, 0·07, 0·14 δ, an error trend which is nearly linear with increasing δ value. Considering the rather low reported δ value for the aromatic protons, it is possible that a calibration error is the reason for the discrepancy in the literature values, which could then bring the spectrum of one of our isomers into good agreement with the previously reported spectrum.

The i.r. spectrum seems to correspond fairly well with other reported spectra for calamenene.[25,26] However,

[22] L. WESTFELT, *Acta Chem. Scand.* **20**, 2841 (1966).
[23] Y. OHTA, K. OHARA and Y. HIROSE, *Tetrahedron Letters* 4181 (1968).
[24] P. DE MAYO and R. E. WILLIAMS, *Tetrahedron* **21**, 619 (1965).
[25] F. SORM, K. VERES and V. HEROUT, *Coll. Czech. Chem. Commun.* **18**, 106 (1953).
[26] B. S. TYAGI, B. B. GHATGE and S. C. BHATTACHARYYA, *Tetrahedron* **19**, 1189 (1963).

because of minor discrepancies between the present spectrum and the literature values, which are also variable this cannot be used for positive identification.

The u.v. spectrum agrees quite well with those reported for calamenene. de Mayo and Williams[24] report λ_{max} 279, 270 nm (ϵ 765, 765) while Hayashi *et al.*[27] report λ_{max} 278, 269, 263 nm (ϵ 860, 940, 850).*

The mass spectrum of calamenene (occurring as an unspecified mixture with calacorene) has been determined under similar conditions to those employed in this investigation.[28] Fragments at *m/e* 187, 159, 145 were said to be due to the presence of calamenene. The mass spectrum of our mixture also contains these peaks with 159 being the base peak. However, the large majority of the reported spectrum would appear to be due to the calacorene presence, so comparison of the two spectra cannot be at all definitive.

α-Alaskene, $C_{15}H_{24}$.[15] NMR ($CDCl_3$), δ 0·879 (CH_3, d, 6·5 Hz), 1·6–1·73 (3-vinyl CH_3, n.r.), 5·33 (—CH=C<, $W_{h/2} \leq 9$ Hz) ppm; i.r. ν 3050–3020 (sh), 1430–1452, 1372, 1318, *1309*, 1273, *1189*, 1159, 1133, 1110, *1088*, *1069*, *1049*, *1011*, 1002 (sh), 996, 978, 962, *948*, 855, *826*, 808 (sh), *797*, *757*, 692 and 652 cm^{-1}; u.v. (CH_3OH) end absorption only, $\epsilon_{220} \simeq 1820$; MS, *m/e* 204 (parent), 189, 175, 161, 148, 136 (major), 121 (base), 105, 93, 79, 67, 55, 41, metastable at 107·7 confirms (136 → 121).

Hydrogenation afforded alaskane,† $C_{15}H_{28}$[15] (a mixture of stereoisomers, see Table 5): $[\alpha]_{300} = -44 \pm 25°$; i.r. ν 1456, *1386*, *1377*, *1368*, 1310–1320, 1236, 1160–1165, 1157, *1133*, 1105–1111, 1090, 1055, *1010*, *972*, 953, *931*, *914*, 896, and 836 cm^{-1}; MS 208 (parent), 165, 152, 124 (base), 109, 95, 81, 55, 44, 41.

The mass spectrum of α-alaskene is most interesting. Of thirty sesquiterpene hydrocarbons, representing nearly all skeletons known, whose mass spectra have been determined in this laboratory, none has had 121 as a base peak, nor has any had 136 as a major fragment. The fragmentation pattern as a whole is quite different from any of those taken.‡

β-Alaskene, $C_{15}H_{24}$.[15] NMR ($CDCl_3$), δ 0·854 (CH_3, d, 6·4 Hz), 1·63–1·75 (3-vinyl-CH_3, n.r.), 5·42 (—CH=C<, $W_{h/2} \leq 11$ Hz) ppm; i.r. ν 3035 (sh), 1660–1675 (vw), 1438, 1430, 1368, 1304, 1258, 1222, *1199*, *1170*, *1159*, 1140–1150, *1124*, *1076–1080*, 1040–1050, 1018, 1004, 963, *950*, *830*, *798*, *757*, and 688 (vw) cm^{-1}; u.v. (CH_3OH) end absorption only, $\epsilon_{220} \simeq 2040$. MS nearly identical to α-alaskene except that *m/e* = 136 is of somewhat greater relative intensity. Hydrogenation afforded the same mixture of diastereomers as obtained from α-alaskene.

(−)-*α-Curcumene* (+ ~ 25% (+)-*δ-cadinene*).§ NMR showed major constituent to be identical with α-curcumene from *Curcuma aromatica* (see Table 4); i.r. major peaks were identical to those of authentic sample (see Table 4); GLC five columns confirmed the presence of both α-curcumene and δ-cadinene; ORD, $[\alpha]_D$ was weakly dextrorotatory, difference between $[\alpha]_{300}$ and $[\alpha]_{230} = -1250°$ whereas that of authentic α-curcumene (from *C. aromatica*) = −2550°. Both of the ORD results strongly indicate that the δ-cadinene present in the mixture was dextrorotatory—both the positive $[\alpha]_D$ and the positive trend of the impurity; MS, see β-curcumene.

(−)-*β-Curcumene*, $C_{15}H_{24}$.[15] NMR ($CDCl_3$), δ 0·992 (CH_3, d, 7), 1·58 (vinyl-CH_3, bs), 1·67 (2 vinyl-CH_3, bs), 2·58 (2-CH_2 allylic, s), 5·09 (1H, *t*, 6 Hz), and 5·43 (2-vinyl-H, bs); i.r. ν 3080 (w, sh), 3055 (w, sh), 3020, 1662, 950 (s), 827 and 780 cm^{-1}; ORD $[\alpha]_D = -6·6 \pm 1°$, $[\alpha]_{300} = -52·5 \pm 3°$ (lit. $[\alpha]_D = +27°$ for dextrorotatory,[13] $[\alpha]_D = -48°$ for levorotatory[11]); MS, *m/e* 204 (parent), 189, 161, 119 (base), 105, 93, 69, 55, and 41.

The observed NMR spectrum contained the usual signals for the curcumene side-chain. In addition, two vinyl hydrogens give a broad singlet at δ 5·43 ppm and four doubly-allylic hydrogens produce a singlet at δ 2·58 ppm. These two facts suggest a 1,4 cyclohexadiene ring system with 1,4 substitution (to account for equivalence of chemical shifts for the allylic protons and the vinyl protons). R. Bates reports the NMR spectrum of γ-terpinene which contains the same ring system as β-curcumene.[11] This spectrum has a four-proton singlet at 2·61 δ and a two-proton, broad singlet at 5·47 δ, in very good agreement with our observed spectrum for β-curcumene.

Hydrogenation of (−)-β-curcumene (HOAc, H_2, PtO_2) produced the same two diastereomers obtained by hydrogenation of an authentic sample of β + γ-bisabolene[10] (confirmed by i.r. and GLC analysis on four columns). This is further support for the assigned structure.

* It is interesting to note that the ratio of extinction coefficients (which is quite precise regardless of the rather large amount of error in absolute value due to measurement errors) of the 278 nm and 270 nm absorptions is precisely intermediate to those same ratios in the reported values. This could be explained (as could the absence of a 263 absorption in de Mayo's sample) by postulating that Hayashi *et al.* had one diastereomer, de Mayo and Williams had the other, and the present mixture contains both.

† Hydrogenation performed by stirring acetic acid solution of the compound for 24 hr with Adams catalyst and in H_2.

‡ *Note added in proof*—The mass spectra are readily explained using the present spirane formulation.

§ These two compounds are separable by $AgNO_3$/silica chromatography; however, fractions containing each were inadvertently combined.

[27] S. Hayashi, K. Yano and T. Matsuura, *Bull. Chem. Soc. Japan* **37**, 474 (1964).
[28] N. Tsubaki, N. Nishimura and Y. Hirose, *Bull. Chem. Soc. Japan* **39**, 312 (1966).

Dehydrogenation of (−)-β-curcumene (~ 50 mg) with Se (~ 150 mg) at 240° resulted in a 3:1 mixture of α-curcumene and β-curcumene (GLC analysis). The α-curcumene produced was purified by preparative GLC (6% FFAP column), and had i.r. and NMR spectra superimposable with those of α-curcumene from *C. aromatica*. The u.v. spectra (MeOH) was identical to that of the authentic sample with λ_{max} 273, 267, 264·5, 259, 252 (sh) nm (ε 520, 433, 459, 342, 216). Optical purity of the α-curcumene produced was determined by a comparison of its ORD with that of the authentic α-curcumene. Authentic material had $[\alpha]_D = -46 \pm 10°$ (lit. +40 for dextrorotatory[29]) and $[\alpha]_{230} - [\alpha]_{300} = -2580°$. Our sample had $[\alpha]_{230} - [\alpha]_{300} = -2270 \pm 200°$ (optical purity 88 ± 8%). The original (−)-β-curcumene must be of this or greater optical purity.

(−)-γ-*Curcumene*, $C_{15}H_{24}$.[15] $[\alpha]_D = -11 \pm 30°$, $[\alpha]_{300} = -950 \pm 150°$ (lit. $[\alpha]_D = +32°$ for dextrorotatory isomer[30]); NMR ($CDCl_3$), δ 0·984 (1 CH_3, d, 7 Hz), 1·58 (1 CH_3, bs), 1·67 (1 CH_3, bs), 1·77 (1 CH_3, s), 2·05 (4 H, s), 5·09 (1 H, m), and 5·58 (2 H, bs) ppm; i.r. ν 3073, 3030, 1653, 1604, *1446*, 1430, 1370, 1335, *1230*, 1197, *1154*, 1105, 1080–1060, 1037, 1017, *980*, *880*, *822*, and 580 cm^{-1}; MS, *m/e* 204 (parent), 189, 159, 132, 121, 119 (base), 105, 93, 77, 69, 55, and 41; u.v. (MeOH), λ_{max} 276·5 (infl.), 266·5 (ε 3300), 258 (infl.) nm; u.v. ($CHCl_3$) λ_{max} 280 (infl.), 270 nm (ε ~ 4000); ORD shows Cotton effect centered about 271 nm (b = 30, a = −56).

The NMR of γ-curcumene was as expected. The usual signals for the curcumene side-chain were present. The four-ring CH_2 protons were a singlet (δ 2·05 ppm), as one would expect, due to their near equivalence. The chemical shift of the ring vinyl methyl (δ 1·77 ppm) was at a position very similar to that of the ring vinyl methyl of occidentalol (δ 1·81 ppm reported by R. Bates[11]), also at the terminus of a similar homoannular diene system.

The u.v. maxima agree well with literature values. Batt and Slater[30] report λ_{max} (cyclohexane) 267 nm (ε 3500). Birch[31] reports for synthetic γ-curcumene, λ_{max} (MeOH) 265 nm (ε 2900).

Air oxidation of the γ-curcumene afforded α-curcumene (identified by GLC analysis). This is further evidence for γ-curcumene and agrees with the findings of other investigators[32]

(+)-γ-*Cadinene*. $[\alpha]_D = +113 \pm 4°$, $[\alpha]_{300} = +855 \pm 20°$ (lit. $[\alpha]_D + 148°$[11]); NMR was superimposable on that of an authentic sample;[10] i.r. was identical to that of the authentic sample;[10] MS, *m/e*, 204 (parent), 189, 161 (base), 133, 119, 105, 41; GLC checked with authentic sample[10] using self-consistent Kovats' indices[7] (see Table 6).

(+)-β-*Bisabolene*. $[\alpha]_D = +52 \pm 20°$, $[\alpha]_{300} = +234 \pm 40°$ (lit. $[\alpha]_D = +75°$[11]); NMR identical to that of R. Bates;[11] i.r. corresponds to that of Die Terpene;[33] hydrogenation (H_2, HOAc, PtO_2) afforded the same compounds as hydrogenation of authentic β + γ-bisabolene[10] (GLC analysis on four columns); MS, *m/e*, 204 (parent), 189, 175, 161, 147, 119, 109, 93, 79, 69 (base), 55, and 41.

β-*Farnesene*. NMR agrees with that reported by Naves;[12] i.r. agrees with the reported spectrum;[12] u.v. (CH_3OH), λ_{max} 220 nm (lit. 223[11]); MS, *m/e*, 204 (parent), 189, 161, 133, 93, 69 (base), and 41; hydrogenation of β-farnesene (H_2, HOAc, PtO_2) afforded farnesane whose i.r. corresponds to that of Naves[12] (768, 730 cm^{-1} quite unusual).

(+)-trans-*Nerolidol*. $[\alpha]_D = +5·8°$ (lit. +14°[11]); NMR was identical with that reported by R. Bates[11] and with that of an authentic sample prepared from commercial *trans*-nerolidol (Aldrich); i.r. agreed with that reported in "Die Terpene"[33] and with that of the authentic sample; MS, *m/e*, 222 (parent), 161, 136, 107, 93, 69, 57, 44 (base), and 41. This mass spectrum was identical to that of the authentic sample.

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[32] The authors felt the α-curcumene present in *Olearia Paniculata* was an oxidation product of the major sesquiterpene, γ-curcumene, produced during isolation (see Ref. 14).
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