Phytochemistry, 1977, Vol. 16. pp. 1731–1751. Pergamon Press. Printed in England

SESQUITERPENES OF NINE EUROPEAN LIVERWORTS FROM THE GENERA, *ANASTREPTA*, *BAZZANIA*, *JUNGERMANNIA*, *LEPIDOZIA* AND *SCAPANIA*

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(*Revised received* 23 *March* 1977)

Key Word Index—*Scapania*; Jungermanniales; Hepaticae; cadinene; *ent*-sesquiterpenes; gymnomitrol; bazzanene; myliol; sibirene; chamigrenes; ylangene; himachalene–longifolene-type sesquiterpenes; *cis*-fused selinenes.

Abstract—The essential oils of fourteen liverwort specimens from nine species of the Jungermanniales have been examined as to their sesquiterpenes. The barbatenes prove to be present in detectable amounts in all but one species. Bazzanene is frequently found with the barbatenes and new chemical evidence does not support the previously assigned structure but is consistent with a structure diastereomeric to trichodiene. This is consistent with a biogenetic rationale for the barbatene skeleton. Anasterptene, a novel crystalline tetracyclic hydrocarbon, has been found in numerous oils, and chemical degradation established a common skeleton with myliol. The samples of genus *Scapania* elaborate sesquiterpenes of the enantiomeric humulene–longifolene sequence. New members of this group found are (−)-β-longipinene, (−)-longipipanol, and (+)-γ-himachalene. The related germacrene series is represented by a cadinene, (−)-α-ylangene, and (−)-sativene. A series of *cis*-fused selinenes have also been found, which are more closely allied to the germacrene–sativene group than to typical *trans*-fused selinenes. One of these selinenes is shown to be the same as the material previously designated as sibirene. *Scapania undulata* also elaborates (+)-α- and β-chamigrene, and a number of novel hydrocarbons of still unknown structure.

INTRODUCTION

That the liverworts (Hepaticae) are an unusually rich source of sesquiterpenes has been convincingly demonstrated [1–5]. A number of unique sesquiterpene skeletons have been found such as those of myliol (**1**‖), [3b] β-barbatene (**2**) [4a, b, 2c] and gymnomitrol (**3**) [6], and bazzanene (**11**) [2a]. A number of these compounds are biogenetically related to the (−)-bisabolenes (**8**–**10**): the barbatenes distantly so; bazzanene (**11**) [2a, 4a]¶, (−)-cuparenes (**5**, **6**) [2b, f], α-alaskene (**12**) [4b], and calamenene (**7**) [4a] more directly. Another series including *ent*-selinenes [4c], (−)-δ-cadinene [3c, 4e], and *ent*-eudesmanolides [3d, 4d, 7] are related to *ent*-germacrenes. The production of sesquiterpene enantiomeric to vascular plant products extends to other skeletons as well [2d].

The first well-documented study on sesquiterpenes from liverworts indicated the presence of (−)-longiborneol (**13**) and (−)-longifolene (**14**) in *Scapania undulata* [1a]. Since then other representatives of the himachalene → longifolene family (**15**, **18** [2e], and **20** [8]) have been found in *Scapania* species or suggested as constituents from GLC surveys. In contrast, *Scapania parvitexta* is reported [2b] to elaborate β-cubebene, calamene (**7**), β-chamigrene, β-selinene, bazzanene (**11**), and cuparene (**5**); but no longifolene-related compounds.

During the past six years we have been re-examining liverwort essential oils previously isolated by one of us (S.H.) using high resolution GLC with authenticated sesquiterpene standards [9], and spectroscopic studies on components isolated by preparative GLC. In this article we report the results for nine European species of the Jungermanniales which indicate that β-barbatene is indeed a common marker for this order. In addition the study includes four *Scapania* species and has uncovered a number of the missing links in the biogenetic schemes illustrated above.

RESULTS

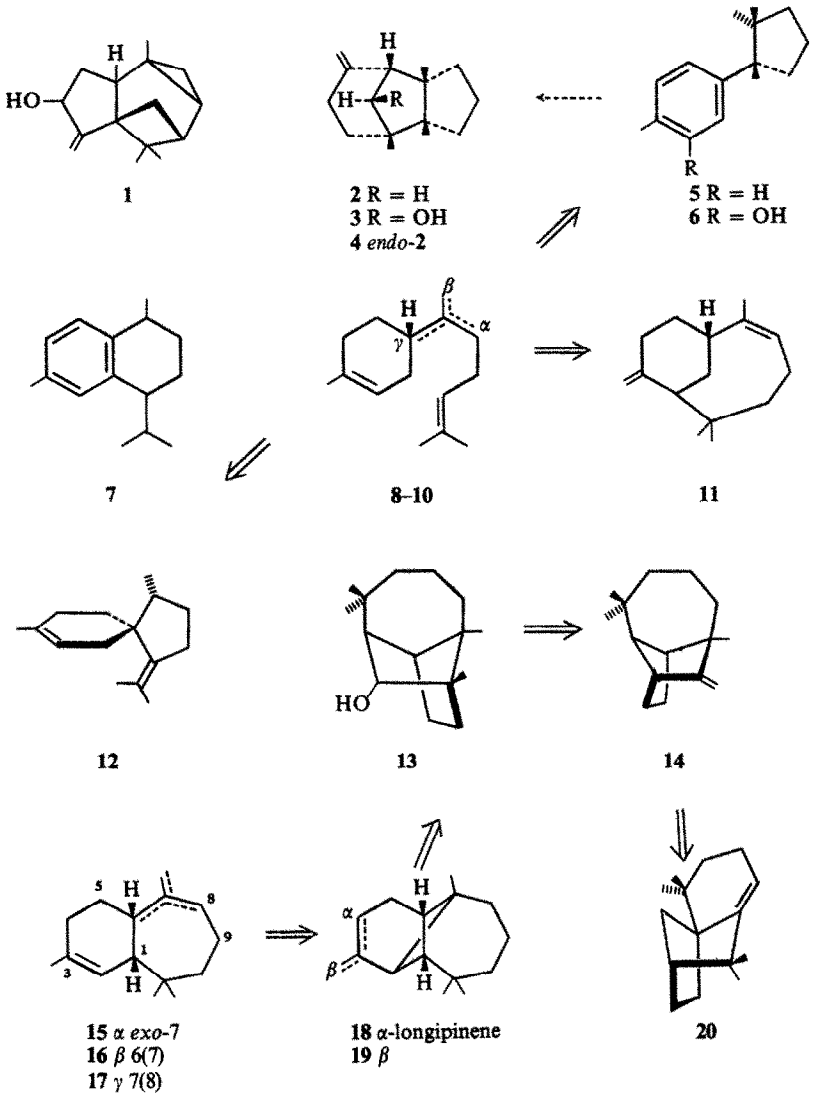
Each essential oil was examined directly by GLC on at least two stationary phases with the results shown in Table 1 (for the typical sesquiterpene hydrocarbon region of the GLC trace). A number of the oils were available in

* Alfred P. Sloan Research Fellow, 1972–1974; Dreyfus Teacher–Scholar, 1974–1979; NHA acknowledges support via an NIH Career Development Award (GM-00134).

‡ Senior post-doctoral associate, 1972–1974, supported by NIH grant GM-18143.

‖ Evidence presented for a related compound, anastreptene, described in this work were inconsistent with the myliol assignment in the literature (**1**). While this paper was being revised after reviewing, the structure of myliol was revised to **1b** based on an X-ray crystallographic study of the *p*-bromobenzoate [10].

¶ Bazzanene was found in a number of the species covered by this report and the evidence for structure **11** has been reconsidered in light of new evidence. Our structure proposal is given in the Results.



only minute quantities (*J. cordifolia*, *Scapania aequiloba* and *S. aspera*) and thus none of the components could be isolated for spectral comparison.

Identification based only on GLC data are considered tentative and are given in parentheses in Table 1. In most cases the GLC analyses of the oils available in only small quantity closely resemble those of more thoroughly studied oils of a related species, lending additional weight to the tentative assignments. As indicated in earlier work [4a–c], β-barbatene (**2**) was encountered in all species except *Scapania aequiloba*. In *S. aequiloba* as much as 10% of β-barbatene could have been present without being evident by GLC due to the masking effect of a novel sesquiterpene hydrocarbon designated aequilobene (see the discussion under *S. undulata*) showing very similar GLC retention data. Bazzanene was found in both *Bazzania* species. In the case of *B. trilobata*, NMR comparisons for the aromatic component clearly indicated calamenene (**7**), not (—)-cuparene (**5**)*. The major hydrocarbon from *Jungermannia cordifolia* appears to be new to Hepaticae and higher plants.

The hydrocarbon fraction of *Anastrepta orcadensis* is largely a novel $C_{15}H_{22}$ hydrocarbon designated as anastreptene, particularly when the oil sample is fresh or has been in storage with rigorous exclusion of atmos-

* *B. pompeana* is reported to contain bazzanene, both barbatenes, and cuparene as the major components [2f].

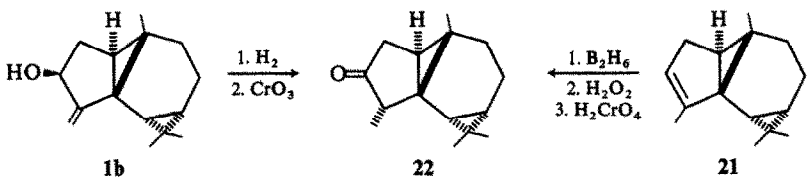


Table 1. GLC data for liverwort essential oils (sesquiterpene hydrocarbon region)

Liverwort	peak #	%	I_A^{190}	I_C^{150}	I_C^{165}	I_D^{160}	Assignment
*Anastrepta orcadensis**							
	1	tr–8	1068			1559	oxygenated terpene
	2	30–80	1405	1570	1582	1728	anastreptene
	3	~2	1491				
	4	~3	1520	1641?	1762?		
	5	10–50	1533	1689	1718	1901	β-barbatene
	6	~2	1556				
	7	1–9	1590	1754?		1843.5	
Bazzania trilobata†							
	1	3	1501	1628			α-barbatene
	2	2	(1523)	1644.5			
	3	26	1538	1693			β-barbatene
	6	2	—	1736			
	8	9	1568	1838.5			calamenene
	9	42	1590.5	1789.5			bazzanene
	10	3	1621	1834			
Bazzania tricrenata¶							
	1	6	(1497)	1540		1743	
	5	23	1532	1689		1893	β-barbatene
	11	15	1595	1790		2050	bazzanene
	12	8	1617	1790?		2074	
	13	34	1567	1841		2087	calamenene‡
Jungermannia cordifolia							
	2	49	1455	1577		1712	novel hydrocarbon?
	3	10	(1455?)			1745	
	5	5	1527	1687		1898	(β-barbatene)
	9	18	1562	1833		2087	§
Lepidozia reptans							
	3	3	1423.5	1524		1665	(α-longipinene)
	6b	3	1500	1628		1816	(α-barbatene)‖
	7	30–50	1533	1693		1897	β-barbatene
	10	20	1553?	1760		1897?	
	12	6	1568	1837		2086	§
Scapania aspera							
	2	30	1400	1569		1725	(anastreptene)
	6	10	1494	1643		1807	
	8	10	1523	1702.5		1889	(aequilobene?)
	8b	~3	1534	(1687)		1889?	(β-barbatene)
	9	9	(1587)	1743.5		1914	
	11	12	1596	1784.5		1992	(asperene)
	7	3	~1520	1687		1889	(α-himachalene)
Scapania aequiloba							
	2	7	1404	1564		1731	(anastreptene)
	4	2	1490	?		1798	(longifolene?)
	6	44	1522	1699		1895	(aequilobene)
	9	11	1554	1738		1932	(β-himachalene)
	11b	5	1594	~1780		1995	(asperene?)
Scapania ornithopodioides							
	1	5		1642			
	2	8		1668			
	3	10–20	1522	~1695			(aequilobene?)
	4	30–60	1531	1693			β-barbatene
	5	~8		1739			
	6	~4		1837			§
Scapania undulata							
	1	tr–0.5	1404	1564	1575		(anastreptene)
	2b	10–22	1423	1524.5	1541	—	α-longipinene
	2c	tr–2.8	1424	1523	—	—	α-ylangene
	3	~0.5	1433	1669.5			β-farnesene
	4a	1–3	1458	1558.5	1580	—	longicyclene
	4c	tr	1462.5	1576	1595		sativene
	4d	tr–0.8	1458	1594			sibirene
	5c	2–22	1475	1614	1626		β-longipinene
	5d	tr–0.5	1479	1638	—	—	caryophyllene
	6b	15–36	1494	1622	1640	1802.5	longifolene
	7a	~0.1	1500	1623			(α-barbatene)
	7c	1–2	1502	1683			α-helmiscapene
	7d	1–2	1506	1686			β-helmiscapene
	8a	1–4	1510	1736			α_2-bisabolene

Table 1—*Continued.*

9a	2.5–14	1519	1684	1698	1889	α-himachalene
9c	~0.5	1518	1708			aequilobene**
10a	5–9	1522.5	1665	1685	1841	scapanene
11a	2–7	1537	1693		1902	β-barbatene
12c	~1–2	1547	1777			α_1-bisabolene
12d	5–10	1546.5	1725	1737		γ-himachalene
13c	tr	1556	1736			(β-himachalene)
14	0.3–1.4	1560				β-chamigrene
15b	~0.7	1574	1778		1978	γ_1-cadinene?
16 (=15a)	0.7–1.6	1578	1765			α-chamigrene
17	tr	1594	1805			asperene**
18	0.4	1617	1812			undulatene

* The hexane extract contains substantial quantities of non-volatiles. † Analysis refers to hydrocarbon peaks only for a sample that was *ca* 40% oxygenated materials (see Experimental). ‡ Confirmed by NMR, less than 5% cuparene. § Without NMR spectra on separated components, cuparene and calamenene cannot be distinguished. || The preparative GLC fraction indicates that α-barbatene is only a component of a more complicated mixture. ¶ Analysis refers to hydrocarbon peaks only. The sample was 72% oxygenated materials based on GLC analysis on phase A (which does not retain alcohols as dramatically). **Obtained pure enough for NMR characterization, but identity with materials in *S. aequiloba* and *S. aspera* is based on GLC data only.

pheric oxygen. Anastreptene, mp 91–93°, is an extremely air sensitive substance.

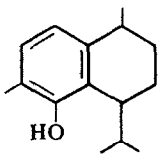
Degradative studies have correlated it with myliol (**1b**) via ketone **22** as shown, indicating structure **21** for anastreptene*. The stereochemical features follow from lanthanide-induced-shift studies on various degradation products and fit with the recent data for myliol [10] An unidentified compound throught to be an oxygenated terpene has also been isolated.

The remaining portions of this report will detail, in the order stated, our studies of the oxygenated components of the two *Bazzania* species, the structure of bazzanene, and a detailed examination of the components of *Scapania* oils. The latter comes largely from the exhaustive investigation of several oil specimens from *S. undulata*. Only the minimum data required for identification of these constituents will be presented here. The details of structure proofs and biomimetic interconversions will be the subject of other articles [11].

The GLC analyses of *B. trilobata* and *B. tricrenata*, and *Scapania undulata* on Apiezon-L (a non-polar phase) indicated sesquiterpene alcohols were present. These results are not reflected in Table 1.

A sample of the more polar fractions of the steam distilled ether extract (eluted from silica with benzene) was examined in order to isolate the oxygenated compounds. GLC analysis indicated three major sesquiterpene alcohols; unknowns ($RR_C^{200} = 0.876$, $RR_A^{190} = 0.823$; $RR_C^{200} = 2.39$, $RR_A^{190} = 1.31$) and drimenol ($RR_C^{200} = 2.87$, $RR_A^{200} = 2.05$). One unknown might be bazzanenol which was not available to us. The identity of drimenol was established by GLC coinjection with authentic material [1b].

The major portion (72%) of the oil from *Bazzania tricrenata* was a mixture of sesquiterpene alcohols none of which corresponded to those of *B. trilobata*. The two major alcohols were isolated in pure form by preparative GLC. The first (14%: $RR_A^{190} = 1.19$) corresponded to gymnomitrol (**3**) by NMR: δ_{CDCl_3} 4.63 (2H, C=CH_2), 3.69 (1H, *s*), 2.31 (*s*), 1.85 (*s*), and 1.25, 1.10 and 0.96 ppm (3 Me *s*)†. The second (32%: $RR_A^{190} = 1.37$, $RR_D^{200} = 2.49$) proved to be a phenol. The NMR—δ_{CDCl_3} 6.72 (2H, aryl-AB, $J_{AB} = 8$), 4.38 (1H, OH, *s*), 2.6–3.0 (2H, benzyllic-H, *m*), 2.17 (3, aryl-Me, *s*), 1.28 (Me, *d*, 7), 0.93 (Me, *d*, 7), and 0.89 ppm (Me, *d*, 7 Hz)—indicated the absence of δ-cuparenol (**6**) and was consustent with a structure such as **23**, our tentative assignment. This oxygenation pattern has been observed previously in liverwort products, as in chiloscyphone (**24**)



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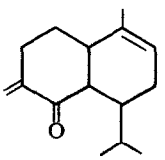

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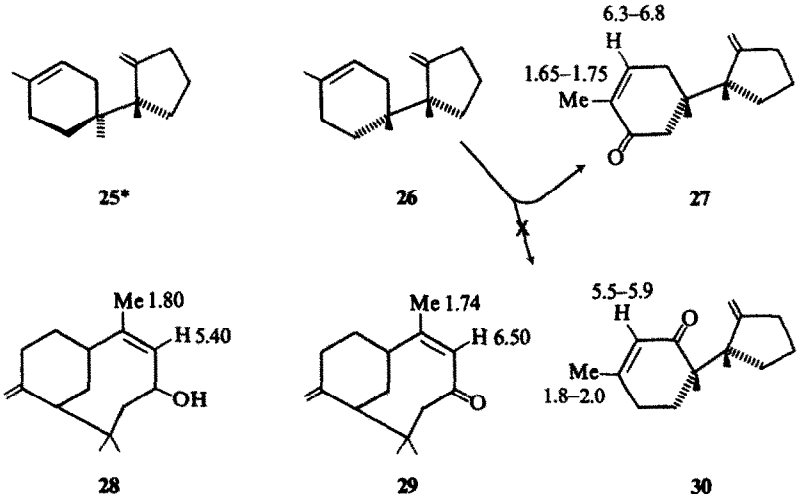
[2g]. Phenol **23** was not isolated in sufficient quantity for chemical degradation studies.

The sample of bazzanene isolated from both *Bazzania* species were identical by NMR and high resolution GLC. The NMR spectrum recorded in $CDCl_3$ was superimposable with one provided by Dr. Matsuo [2a] and but little changed in CCl_4: 5.305, 4.97, 4.83 (3 vinyl-H); ~2.25 (2 allyl-H), ~2.07 (1 allyl-H), 1.63 (vinyl-Me); and 1.025 and 0.84 ppm (2 singlet Me). Structure **11**, independent of the relative stereochemistry at the *meta*-fusion predicts a highly disymmetric environment for one or both olefinic bonds suggesting that large olefin CD bands should be observed [12]. Instead we find a very weak CD for bazzanene—$\Delta\varepsilon_{214} = +0.54 \pm 0.10$, $\Delta\varepsilon_{200} \simeq -0.7 \pm 0.3$, $\Delta\varepsilon_{194} \simeq +1.0 \pm 0.5$: barely above the detection limits due to the noise associated with the UV absorption of two olefinic bonds. The reported mass spectra of bazzanene and trichodiene (**25**) [13] are essentially identical and only minor differences appear in the NMR spectrum (reported δ_{CCl_4} for trichodiene:

* The stereochemical assignment and full details of the degradative studies on anastreptene will be presented in due course.

† The NMR spectrum of gymnomitrol was kindly supplied by Dr. Connolly [6].

5.23, 4.92, 4.71, 1.63, 1.04, and 0.85 ppm); these considerations led us to reexamine the structural evidence for bazzanene [14]. The key observations were the spectral data for bazzanenol [15] and ketone related to it and also obtained from allylic oxidation of bazzanene [2a]. The structures assigned (**28** and **29**) and pertinent NMR data are given below.



We have also included the two enones (**27**, **30**) which might result from structure **26**, the epimer of trichodiene, on oxidation. The chemical shift values indicated on structures **27** and **30** are expected values based on cyclohexenone data obtained in these laboratories and reported in the literature. Nakanishi reports similar values for the α (δ 5.9) and β protons (δ 6.8) of α,β-unsaturated ketones [17]. The vinyl hydrogen shift, δ 6.5, reported for bazzanenone is inconsistent with the structure assigned (**29**). Additional evidence supporting structure **26** for bazzanene is its facile dehydrogenation to cuparene (**5**) [2a]†. Further evidence for structure **26** comes from the acid catalyzed rearrangement studies conducted on β-bazzanene,‡ α-barbatene, and (+)-α-chamigrene (**35**, isolated from *Scapania undulata, vide infra*)§.

On stirring with HCO_2H–*n*-heptane, β-bazzanene affords primarily the endocyclic isomer (62%) and a tricyclic product (18%). The tricyclic material, although very similar to α-barbatene by GLC and NMR was clearly distinguishable as a new substance and displayed the opposite CD sense of the olefin transition [12] suggesting structure **36**. The major product from β-bazzanene displays an NMR consistent with a diastereomeric mixture (**31** + **32**) in which the cyclohexene olefinic linkage has equilibrated (the new diastereomer, **32**, = α-trichodiene, is the intermediate leading to structure **36**). This diastereomeric mixture was shown to have the same skeleton as β-bazzanene by hydrogenation, which gave the same tetrahydro products (identical retention indices on all 15 m GLC columns) obtained from β-bazzanene.

Because our efforts to confirm the β-bazzanene structure (**26**) by demonstrating the conversion to α-barbatene (**26** → **33** → **4**) failed in HCO_2H, apparently due to the isomerization (**31** ⇌ **32**), we turned to more ionizing media which might favor a longer life for ion **33**, and thus cyclization in the proper sense. It is known [4b] that the barbatenes afford a rearranged tricyclic compound designated isobarbatene [18b] in nearly quantitative on treatment with CF_3CO_2H–*n*-decane. When β-bazzanene and α-chamigrene (**35**) are treated under these isomerization conditions complex mixtures result (see Table 5, Experimental). GLC comparison of the two product mixtures shows that 85% of each are made up of ten common constituents indicating that each compound reaches the stage indicated by an equilibration of ion **33** and **34**. Moreover 29% of the β-bazzanene derived material is shown to be isobarbatene. The major process is dehydrogenation [18] in the case of α-chamigrene, affording ar-himachalene (35%).

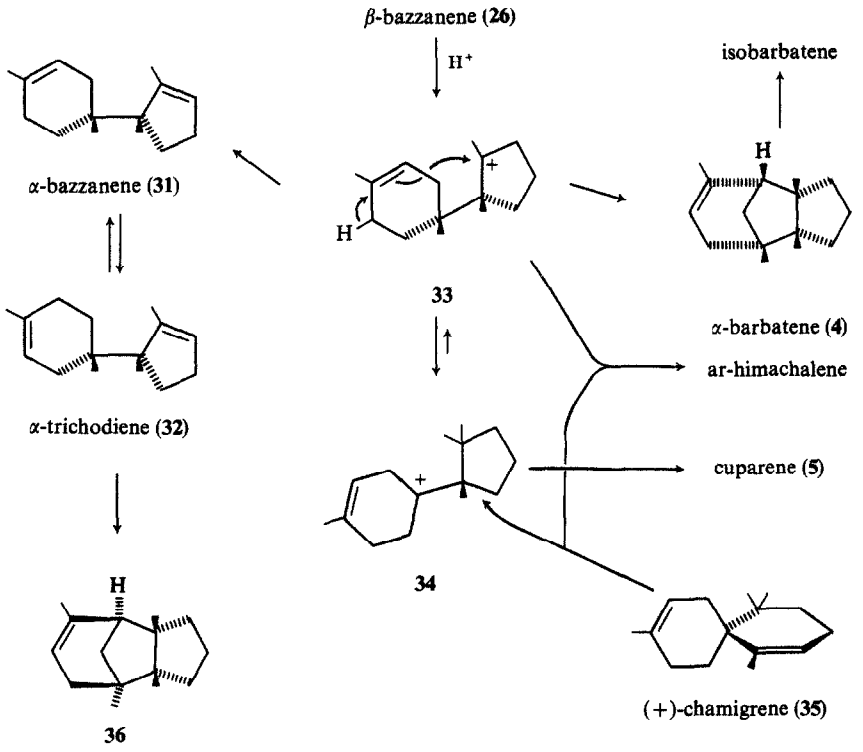
Turning to the *Scapania* species, only in the case of *Scapania undulata* has extensive separation and isolation work been completed. The assignments for the other oils follow from the GLC data and comparison with known values and those observed in *S. undulata*. Three samples of *S. undulata* were examined, in each case the entire oil obtained by steam distillation of ether extracts was examined by GLC directly with the results summarized in Table 1. The hydrocarbon analyses obtained in this way are deceptive for two reasons: (1) the oils typically contain 15–40% of oxygenated compounds largely a mixture of longiborneol (**13**) and longipinanol (**37**), a novel sesquiterpene; and (2) longipinanol

* The diastereomeric nature of trichodiene was not established in the structure elucidation [13], but can be correlated with that of the trichothecanes based on the high yield incorporation of trichodiene into trichothecanes by the synthesizing enzyme system [16].

† This dehydrogenation is also observed under milder conditions, CF_3CO_2H at 25° [18] (*vide infra*).

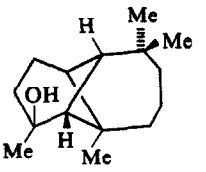
‡ In light of the production of the endocyclic isomer (**31**) we now designate natural bazzanene as the β-isomer.

§ This component was originally thought to have structure **31** based on a hydrogenation comparison with β-bazzanene and its GLC retention data which are indistinguishable from those of the HCO_2H rearrangement product of β-bazzanene on columns of moderate resolution. GLC (15 m packed columns, and 15 m capillary columns) established nonidentity with the endocyclic isomer mixture (**31** + **32**) and of the hydrogenation products.



is not stable to GLC analysis affording, in a ratio of 3:1, α- and β-longipinene (**18**, **19**). Further the ratio of these two alcohols varies greatly with the origin of the plant specimen. Samples from the Ore Mountains (Erzgebirge, Sachsen) which elaborate scapanin [19] contain little or no longipinanol (**37**) and in the separated hydrocarbon fraction constituents **18**, **19**, and **14** are present in the ratio 5–7:1–4:10. Specimens from the Thuringian Forest contain varying ratios of **13** and **37**, from 1:1 to 1:3, and separated hydrocarbons contain **18**, **19**, and **14** in the ratio 2.5:0.4–1:10. The Thuringian samples are depleted in longipinenes but show increased content of all three himachalenes. The extracts of Thuringian samples do not yield scapanin [20].

The present study of *Scapania undulata* confirms the presence of optically pure (−)-longiborneol and (−)-longifolene [1a]. In the case of longiborneol this was established from the CD data for derived longicamphor. In accord with biogenetic pathway we find (−)-α-longipinene (**18**) and (+)-α-himachalene (**15**) as other major hydrocarbons; these substances have also been obtained from Japanese specimens [2e]. The Erzgebirge samples contained, in moderate amounts (4–17% of the hydrocarbon portion), the previously unknown exocyclic isomer (**19**), (−)-β-longipinene. The relationship to β-pinene was evident in the NMR and IR spectra. Ozonolysis afforded a cyclohexanone ($\nu_{C=O}$ 1715 cm^{-1}) whose NMR spectrum corresponded to that of the racemic ketone used in the synthesis of the longipinenes [21]. Hydrogenation of α- and/or β-longipinene afforded, according to GLC analyses, the same saturated hydrocarbon. The structure assignment was confirmed by the observation that the major alcohol from the Thuringian sample afforded both longipinenes. This alcohol, designated longipinanol, has been assigned structure **37** based on the experiments detailed below.



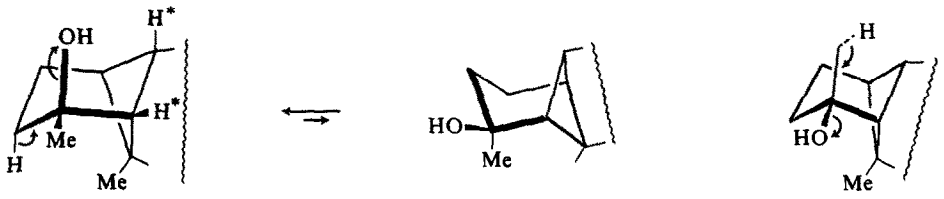
GLC 260° → 75% **18** + 25% **19**
$SOCl_2$, Py → 70% + 14%

37 mpl 82.5–83°
$[\alpha]_D = -50°$ (n-C_5H_{12})

The Thuringian Forest samples of *Scapania undulata* yield a crystalline (mp 63–65°, from pentane) mixture of **13** and **37**, which is extremely difficult to separate by adsorption chromatography. The simplest procedure for isolating pure longipinanol consists of oxidation (H_2CrO_4) of this mixture: longipinanol is readily separated from longicamphor. Dehydration ($SOCl_2$, pyridine) of longipinanol afforded α- and β-longipinene identical in all respects (IR, NMR, CD) to the compounds isolated from the hydrocarbon fraction of the same oil.

In contrast, the epimeric alcohol (**38**) prepared in a total synthesis of the longipinenes on comparable dehydration affords 48% α and 36% β-longipinene [21]. The relative stereochemistry of longipinanol [**37a**] follows from NMR shift experiments using Eu(FOD)$_3$ (see Experimental): in particular from the large and nearly identical shifts observed for the two asterisked bridgehead hydrogens. Both the coupling constants in the cyclohexane portion of longipinanol and a detailed analysis [22] of the lanthanide incuded shifted indicated a preference for a conformation intermediate between the half chair and **37a**. This conformational preference also reationalizes the dehydration results.

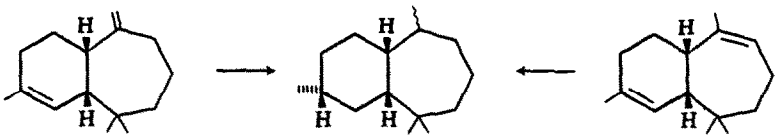
The GLC analysis of the hydrocarbon fractions of *Scapania undulata* oils indicated 18 components (on



37a 37b 38

Apiezon-L, which gives the best resolution in this case), but on chromatography on $AgNO_3$–Al_2O_3 or $AgNO_3$–SiO_2 (using a cyclohexane–benzene gradient) it was clear that most GLC peaks were due to two or more constituents of differing affinity for $AgNO_3$. The components are numbered in order of elution from the Apiezon-L GLC column with the letter designations (a, b, or c) indicating the order of elution from the Ag-adsorption column for substances with similar GLC retention data on Apiezon-L. Only the major and identified hydrocarbons are listed in Table 1.

Further member of humulene–longifolene series were identified from NMR spectra and GLC data: longicyclene, β-himachalene, and γ-himachalene (**17**),



15 39 γ-himachalene (**17**)

Upon hydrogenation of α- and γ-himachalene each afforded a mixture of the same tetrahydro compounds confirming the *cis*-fusion in the new γ-isomer. We first isolated γ-himachalene, $[\alpha]_D = +14°$, in 1971 and were unaware of the isolation of the enantiomeric substance ($[\alpha]_D = -29°$) first communicated in Sao Paulo in 1971 [23]. With a full report on this work now available [24], a NMR comparison confirms the isometric identity beyond doubt. Concerning the report of another γ-himachalene ($[\alpha]_D = -7°$, from Anise oil([25]: as reported, the ^{1}H-NMR is not *identical*, $\Delta\delta = 0.08$ for the Me singlets compared to $\Delta\delta = 0.05$ for our substance, but the reported ^{13}C-NMR corresponds (± 0.08 ppm, largest error 0.21 ppm) for all fifteen carbons to the values observed for our sample. All γ-himachalenes reported are thus *cis*-fused and bear identically arrayed olefinic linkages.

We could not find isolongifolene (**20**) in our samples of *Scapania undulata*. In one case our studies were so detailed that we can exclude the presence of trace amounts as small as 0.03 %. On this basis the gas chromatographic identification is *iso*-longifolene in a number of *Scapania* [8], including *S. undulata*, is suspect. Based on our GLC data, β-longipinene is virtually indistinguishable from isolongifolene on non-polar phases. The nature of the co-eluting substance on a polar phase such as Carbowax-20 M is not clear. Isolongifolene may then be the most thoroughly studied unnatural sesquiterpene, for we know of no confirmed occurrence in a natural oil.

The barbatenes, β-farnesene, and the α-bisabolenes were recognized by the full complement of spectral comparisons. The retention data for these compounds and other liverwort hydrocarbons together with updated rotatory data are collected in Table 3. In the case of α-bisabolene both isomers (*cis/trans*) were obtained. The earlier eluted isomer corresponded to the α-bisabolene from *Opoponax* oil [26, 27a], which has been assigned the *trans* stereochemistry. The *cis,trans* assignment of α-bisabolene appears to be based on unpublished NMR spectral analyses by A. F. Regan [27, 29, 30]. The NMR spectra of our samples are very similar and we are chary of making an assignment. What is clear is that the natural product, tentative assignment *trans*, occurs widely and has been synthesized [29]. The later eluting material found in *Scapania undulata* corresponds to the major α-isomer from nerolidol [28, 30] and also is produced on dehydrochlorination of bisabolene trihydrochloride [27b]. The later eluted material corresponds to the major α-isomer obtained on acid-catalyzed cyclization of nerolidol [28]. The material produced from nerolidol should be the *cis*-isomer based on the work of Regan as quoted by Wenninger and in more recent work on the α-bisabolenes [29].

The substance from *S. undulata* designated as 'γ_1-cadinene?' deserves some comment. The retention indices on four different GLC phases corresponded within experimental error to those of authentic γ-cadinene [31]: the liverwort component could not be resolved from the authentic material by capillary GLC (15 m) on two phases. The NMR spectrum of the pure material met the usual criterion of 'superimposability' with that of the authentic sample. A CD comparison and a preliminary ORD comparison indicated the dextrorotatory form (**40**). Our expectation that liverwort essential oils display absolute stereochemical homogeneity, as observed in tracheophyte oils [11a], led us to pursue a more detailed examination. The spectral comparisons of the *Scapania* component and (+)-γ-cadinene [**40**] are collected in Table 2. The very minor NMR differences would be undetectable in the regular spectral trace, and may indeed be non-existent. The CD indicate, if the substances are identical, comparable optical purity; but the λ_2 band of the liverwort derived material appears to be shifted to higher energy. The greatest differences are in the ORD traces and these cannot (based on the CD) be the result of optical purity differences. Structure **40** is thus ruled out even though the NMR, CD, and GC data would normally constitute proof of identity; other γ-cadala-

Table 2. Spectral comparison of authentic γ-cadinene (ex. *Chamaecyparis nootkatensis* [31]) and 'γ-cadinene' from *Scapania undulata*

NMR ($CDCl_3$, 80 MHz)*	Authentic	*S. undulata*
vinyl-H	5.528, 4.640, 4.531	5.528, 4.634, 4.533
vinyl-Me	1.676	1.684
doublet-Me's (*J*, Hz)	0.928 (7.0), 0.741 (6.9)	0.926 (6.4), 0.738 (7.1)
CD (pentane)		
$\Delta\varepsilon(\lambda_1)$	+18 (203.5–4.0)	+17.8 (202.5)
couplet center	195–196	194
$\Delta\varepsilon(\lambda_2)$	−19 ± 2 (188–190)	−7 ± 2 (190)!
ORD ($CHCl_3$)†		
$[\alpha]_D$	+90 ± 5	+28 ± 5
$[\alpha]_{365}$	+340 ± 20	+112 ± 20
$[\alpha]_{300}$	+830 ± 40	+200 ± 40

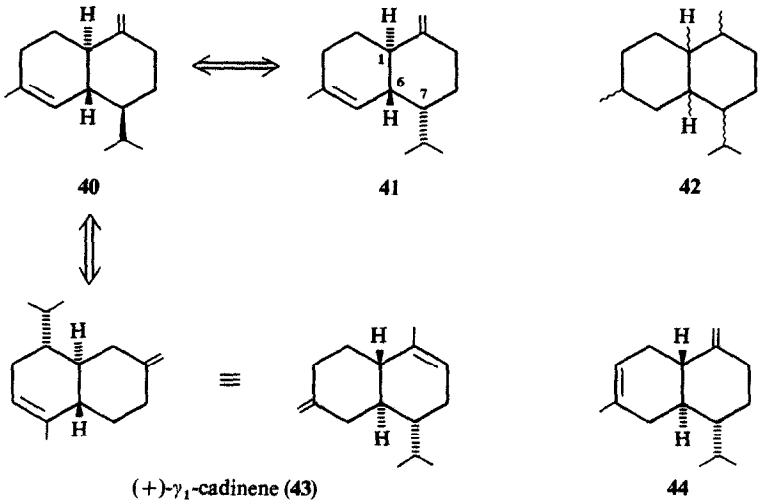
* FT–NMR data on dilute solutions (*ca* 20 mM). The shift data is a direct read-out, rather than from measurements from the spectral trace, in each case calibrated by the TMS to $CHCl_3$ measurement (7.220 ppm). † The lit. values for (+)-γ-cadinene are $[\alpha]_D = +18$–$153°$ ($CHCl_3$). We observed $[\alpha]_D = +95 \pm 2°$, $[\alpha]_{300} = +950 \pm 20°$ (CH_2Cl_2); and $[\alpha]_D = +113 \pm 4°$, $[\alpha]_{300} = +860 \pm 20°$ (pentane) [31]. The lit. value of +88° is from *Amorpha fruticosa* [32], that of +117° from *Pinus silvestris* [33].

dienes must be considered. Of these γ-muurolene and γ-amorphene have been isolated in these laboratories and are known to be distinguishable by GLC and spectral comparison. The substance (**41**), which would be designated (+)-γ-bulgarene,* is not reported in either enantiomeric form in the literature. Two other γ-type isomers are known: (−)-γ_1-cadinene [34, 35] and (−)-γ_2-cadinene (**44**) [36]. The latter is reported [37] to elute much earlier than γ-cadinene from an HB-2000 (Carbowax-like) GLC column. As can be seen from the structural drawings of **41** and **43** it is quite reasonable to expect a CD spectrum like that of (+)-γ-cadinene (**40**): the cyclohexene rings have comparable chirality [12]

Structure **41** differs from the others in the relative configuration at C-1,6,7 and should afford different diastereomers (**42**) upon hydrogenation. Fig. 1 shows the GLC traces from three hydrogenation experiments: A, authentic γ-cadinene alone; C, a 1:1 mixture of γ-cadinene and the 'γ-cadinene' from *S. undulata*; and B, the *S. uindulata* component alone. The near absence of muurolanes establishes that hydrogenation is occurring more rapidly than double bond migration and thus the *S. undulata* component must have the cadinane relative stereochemistry, i.e. structure **43**. A confirmation of this is seen in the acid-catalyzed rearrangements of (+)-γ_1-cadinene (see Experimental).

A particularly detailed examination (Table 6, Experimental) of the hydrocarbon portion of a longipinanol-producing *S. undulata* oil revealed two additional representatives of the germacrene–cadalane group: (−)-α-ylangene (**45**) and (−)-sativene (**47**). In the case of α-ylangene the assignment is based on GLC comparison with authentic material [38] and NMR data consistent with the reported values [39]. The absolute configuration follows from the CD, compare (−)-α-copaene (**46**) [40]. In the case of sativene, the absolute configuration is not securely established, but that shown (**47**) correlates with that established for the co-occurring ylangene and with regard to the camphene core of longifolene (**14**). A similar correlation in absolute stereo-

* The sign of rotation for this enantiomer is a prediction based on the chirality of the cyclohexene ring [12].



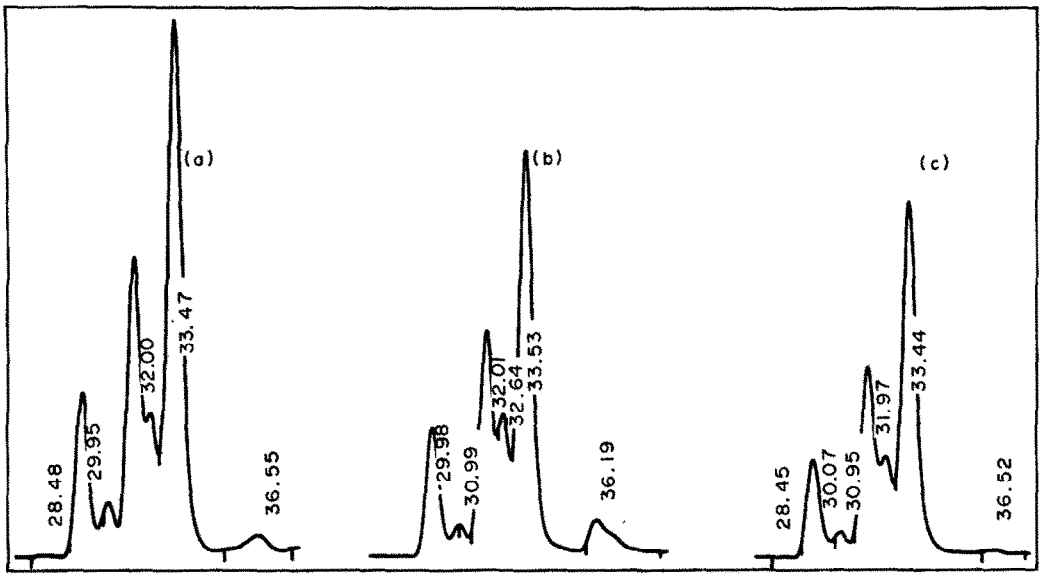


Fig. 1. GLC Traces of Cadalanes (**42**) on SF-96 (15 m × 3.2 mm) at 170°: a, from authentic γ-cadinene: b, from *S. undulata* γ_1-cadinene, c, from the 1:1 mixture. The three major peaks are cadinanes (stereochemistry at C-1, C-6, C-7).

chemistry between sativene- and longifolene-related compounds has been observed in fungi in, *Helminthosporium* species [41].

Three nominal selinenes (**48** → **50**) were also isolated. We view these rather as related to the germacrene–ylangene–sativene group. This can be seen by disconnecting bond *a* of structure **45** which affords structure **48** after H-loss.

The component responsible for *S. undulata* peak #4d, now accorded structure **48**, was identified as sibirene based on a NMR comparison [42] and GLC data [43]. Although siberene was first isolated (*Pinus sibirica*) in 1961 [44], its structure was not assigned until 1966 [42]. The assigned structure (**52a**), with a conjugated diene system, seems inconsistent with the observed low intensity, UV absorption (λ_{max} 246.nm, log ε 2.5, reported; (Our sample displays λ_{max} 245 nm, log ε 2.3), particularly in light of the already reported values for compound

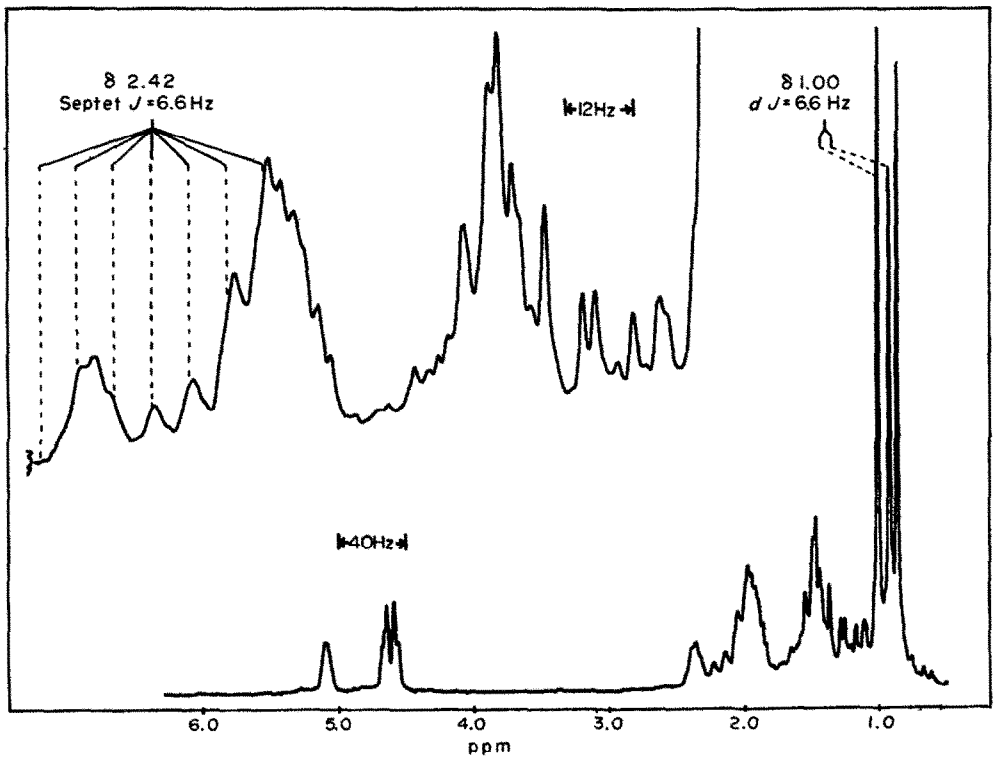
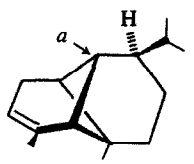
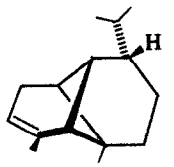


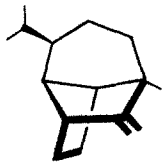
Fig. 2. The 80 MHz NMR spectrum of the component responsible for *S. undulata* peak #4d, sibirene (**48**).



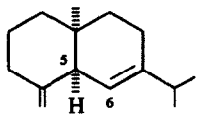
45
$\Delta\varepsilon_{209} = -1.4$



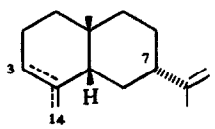
(−)-α-copaene (46)
$\Delta\varepsilon_{219} = -0.75$



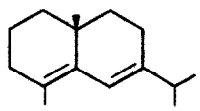
47



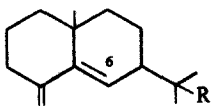
48*



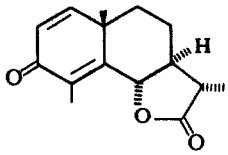
49 Δ^3
50 $\Delta^{4,14}$



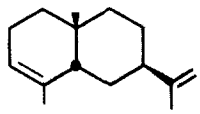
51



52a R = H
52b R = OH



53



54

52b (λ_{max} 240 nm, log ε 4.4) [45]. The 80 MHz NMR spectrum† of sibirene, presented in Fig. 2, is better interpreted with the homoconjugated structure (**48**). We note in particular the ratio of allyl- to non-allyl-H and the chemical shift of the cyclohexene hydrogen (δ 5.12 ppm). For structure **52a**, H-6 would be expected at 5.9–6.4 ppm due to a buttressed *peri*-effect (for detailed comparisons see ref. [18c]).

The selinene skeleton is confirmed by acid-catalyzed rearrangement to more familiar selinadienes (see Experimental). Confirmation of absolute configuration must await isolation of larger quantities of sibirene and CD comparison with appropriate model systems.

A *cis*-fused α-selinene diastereomer, designated (−)-α-helmiscapene‡ (**49**), was isolated in pure form [11b]. The NMR spectrum revealed an isopropenyl, a singlet-Me, and a —CH=CMe-unit and the selinene skeleton was confirmed by stirring α-helmiscapene with 3:3:1 *n*-heptane–HCO_2H–$MeSO_3H$ which afforded (+)-δ-selinene (**51**, λ_{max} 246 nm, ε = 19000, $\Delta\varepsilon$ = +15) identical by NMR, GLC, and CD to a sample prepared from authentic (−)-α-selinene or (+)-β-selinene.§

α-Helmiscapene was readily distinguished by GLC and NMR from both *trans*-fused diastereomers [4c] capable of yielding selinene **51**. Upon hydrogenation two tetrahydro derivatives, not obtainable from available selinenes, were isolated. With the *cis*-fusion established only structures **49** and **54** can rationalize the production of (+)-δ-selinene. A decision between these can be made based on the chiroptical properties observed for α-helmiscapene: $[\alpha]_D = -100°$, $\Delta\varepsilon_{198} = -16.5$. Assuming for each diastereomer, a strong preference for that conformer with the isopropenyl group in an equatorial position only structure **49** predicts a negative band for the olefin CD: note the model cyclohexene (**55**) [12]. The assignment has been confirmed by the synthesis of *cis*-α-selinene (**54**) via *cis* hydrogenation of santonin (**53**) and further transformations [11b].

Early fractions of γ-himachalene eluted from $AgNO_3$–SiO_2 columns contained a new substance indistinguishable from α-helmiscapene by GLC. Subtracting the resonances associated with γ-himachalene revealed proton resonances at 4.68 (*br. s*) and 0.88 (*s*) ppm in the integrated ratio of 4:3. The ^{13}C-NMR revealed,in addition to the fifteen signals associated with γ-himachalene, fifteen signals consistent with structure **50**, including sp^2 carbons at 150.62, 125.56, 108.18, and 108.09 ppm. The assignment was confirmed by hydrogenation which afforded the same *cis*-selinanes obtained from **49**.

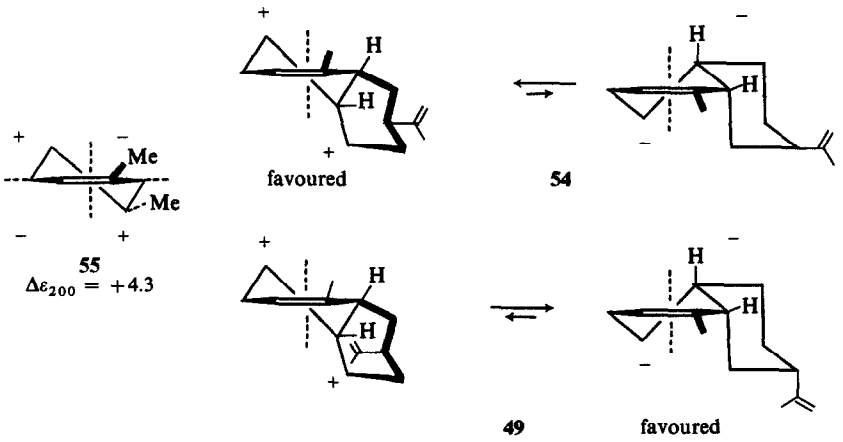
Two components were identified as β- and α-chamigrene (**35**) by GLC and NMR comparison with authentic samples [47]. Only in the case of α-chamigrene has the absolute configuration been established. A CD comparison of the liverwort derived material (**35**) and that from *Schisandia chinensis* [47, 48], (−)-α-chamigrene (**57**), revealed their antipodal relationship. The assignment of the spiro center in **57** follows from the report that (−)-thujopsene (**56**) affords (−)-α- and (−)-β-chamigrene (**57, 58**) on treatment with HCO_2H [49]. Hydrogenation

* The stereochemistry of sibirene (=**48**) has not been established. The enantiomer shown is chosen to correlate with ylangene structure **45**. *Ent*-**48** (like **49** → **50**) would be similarly related to (+)-α-copaene.

† It should be noted that the misassigned isopropyl doublet of ref. [42] has been corrected in a subsequent paper [46].

‡ The name follows from the isolation of the same substance from *Helminthosporium sativum* by Franz Dorn [41a]. Independent structure elucidations and spectral comparisons confirm identity [11b].

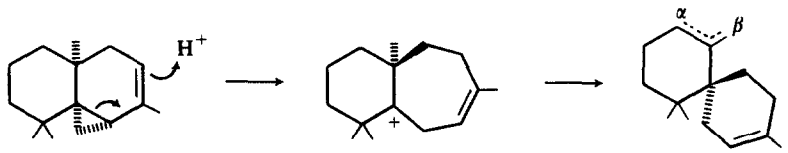
§ (−)-α-Selinene($[\alpha]_D = -6.9°$) is *trans*-fused and bears a 10β-Me and 7β-isopropenyl group and corresponds at all centers to (+)-β-selinene. There are however frequent literature references to this material as (+)-α-selinene due to incomplete separation of the β-isomer.



55
$\Delta\varepsilon_{200} = +4.3$

and acid rearrangement studies are detailed in the Experimental.

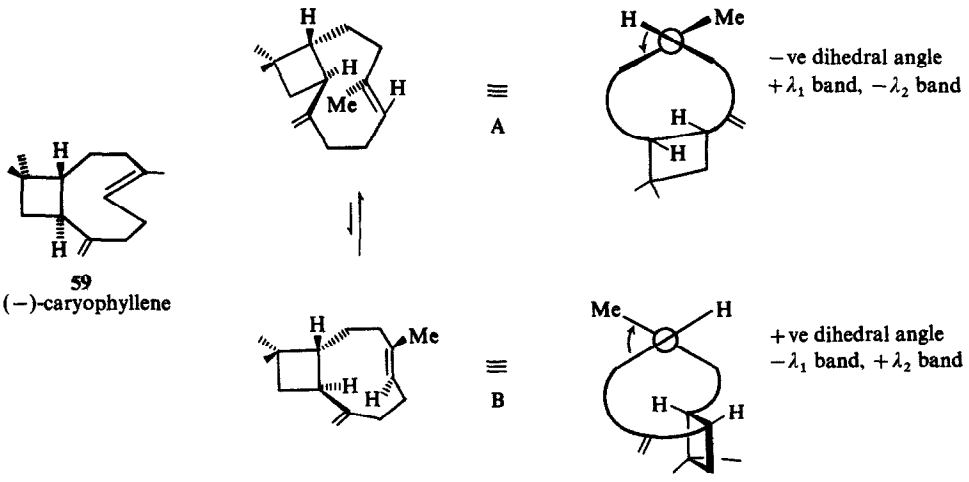
The component eluting immediately before β-farnesene proved to be caryophyllene by GLC and NMR comparison. Although the himachalenes and longifolene-related sesquiterpenes from this oil sample were all of the form antipodal to those obtained from tracheophyte oils this proved not to be the case with carophyllene. The sample derived from *S. undulata* proved to display the same positive olefin CD couplet observed for an authentic sample of $(-)_D$-caryophyllene (**59**)*: $\Delta\varepsilon_{218} = +15.1$, $\Delta\varepsilon_{202.5} = -10.5$. The 9-membered ring in caryophyllene is quite flexible and can adopt two conformations A and B by rotating about the single bonds so as to have the plane of the endocyclic double bond perpendicular to the cyclobutane ring [51].



56

57 α-form
58 β-form

The couplet bands observed in CD indicate that the olefin chiroptical activity is mainly due to the torsion effect [12] of the endocyclic double bond. As depicted in the figure below, conformer A predicts a positive λ_1 band, followed by a negative λ_2 one, whereas conformer B would have a reverse CD effect. The predictions along with the observations imply that conformer A is predominant at room temperature. The same conclusion was also reported by Warnhoff and Srinivasan in an NMR study of caryophyllene [52]†.



59
(−)-caryophyllene

* The absolute configuration of (−)-carophyllene depicted has been confirmed by X-ray crystallographic studies [50]. We use the designation $(-)_D$ to denote that the strong positive λ_1 CD band of caryophyllene is reflected in the ORD by positive rotation values below 360 nm.

† The question of interconversion of conformations A and B was considered in that report [52]. Since the CD effects are predicted to be different, a temperature-dependent CD study on caryophyllene may result in more information concerning the interconversion.

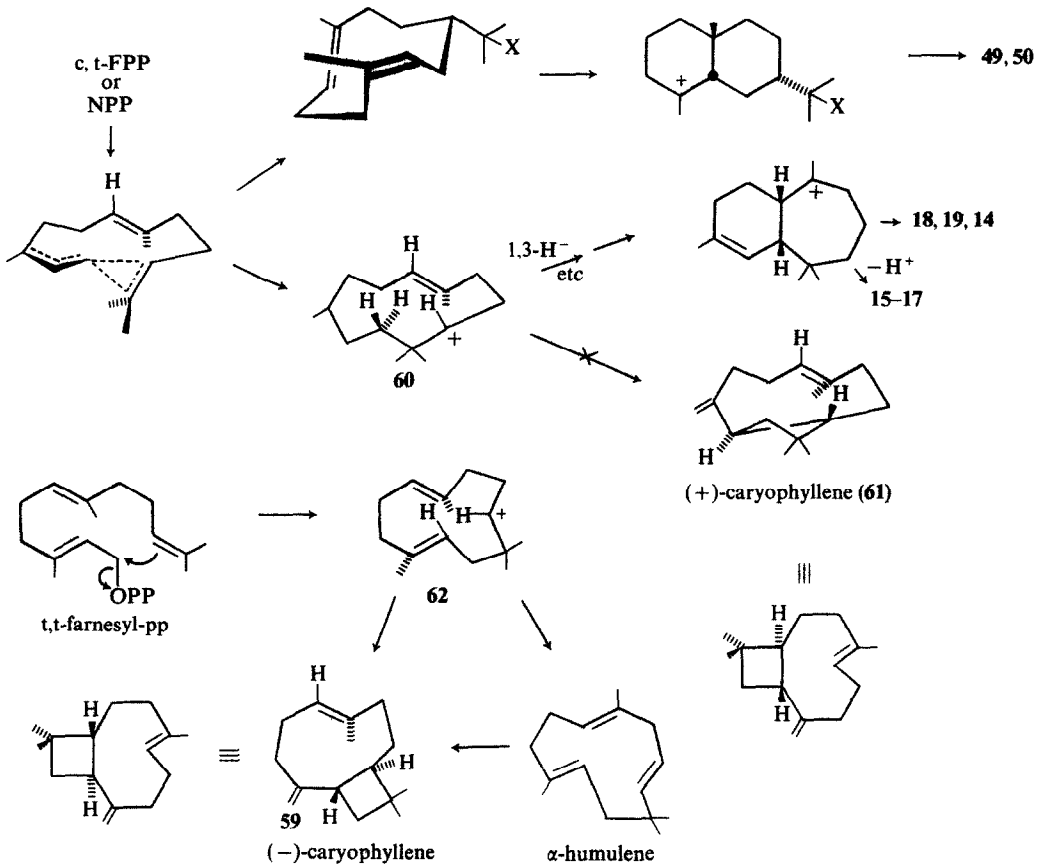
Caryophyllene is usually viewed as a biogenetic relative of the himachalene–longifolene group [53]. However the conformation of the *cis,trans*-humuladienyl cation (**60**) responsible for the enantiomeric himachalenes and longifolenes (found in this oil) would afford (+)-caryophyllene (**61**) [54]. Cation **60** is viewed as an intermediate derived from nerolidyl- or *cis,trans*-farnesyl-PP [11]. Cation **60** represents one of two possible collapses of the initial cyclization; the other, yielding a *cis*-germacrene, produces the observed steroechemistry of the helmiscapenes (**49**, **50**). We therefore suggest that, at least in this plant, caryophyllene (**59**) arises from t,t-FPP via cation **62**. The *in vitro* conversions of α-humulene to caryophyllene has been reported [55].

	A (35%)	*B* (65%)	**14** std.
I_A^{155}	1457	1464	1464
I_A^{190}	1490	1494	1494
I_B^{170}	1435	1445	1440
I_C^{150}	1601	1618	1620

The GLC data for A do not correspond well to any of the known sesquiterpenes. Product B virtually corresponds to longifolene (**14**)†.

DISCUSSION

Our results confirm preliminary suggestions that only



Four additional novel sesquiterpene hydrocarbons were isolated in pure enough form for spectral characterization. Of these only scapanene has been studied extensively (see Experimental for data on undulatene, asperene, and aequilobene).

Scapanene is a tricyclic sesquiterpene with a single exomethylene and three singlet-Me groups based on its NMR (Fig. 3) and mass spectral data ($C_{15}H_{24}$). On treatment with formic acid in *n*-decane, no transformation could be detected by GLC. Addition of CF_3CO_2H led to a rapid reaction producing two products *A* and *B* with the retention indices listed below.

enantiomeric sesquiterpenes are produced by liverworts and that certain new skeletons (anastreptene and barbatene) constitute taxonomic markers for the Jungermanniales. The list of the enantiomeric skeletons observes is now extended to include chamigrene, cadinene, ylangene and sativene, but not caryophyllene. Although the materials produced are enantiomeric to their tracheophyte counterparts, the thorough examination of the *Scapania* oils suggests that current biosynthetic mechanisms suggested for the tracheophytes, and now for fungi, hold in that several missing links (**17**, **19**, **37**, **45**, and **49**) in these proposals have now been found.

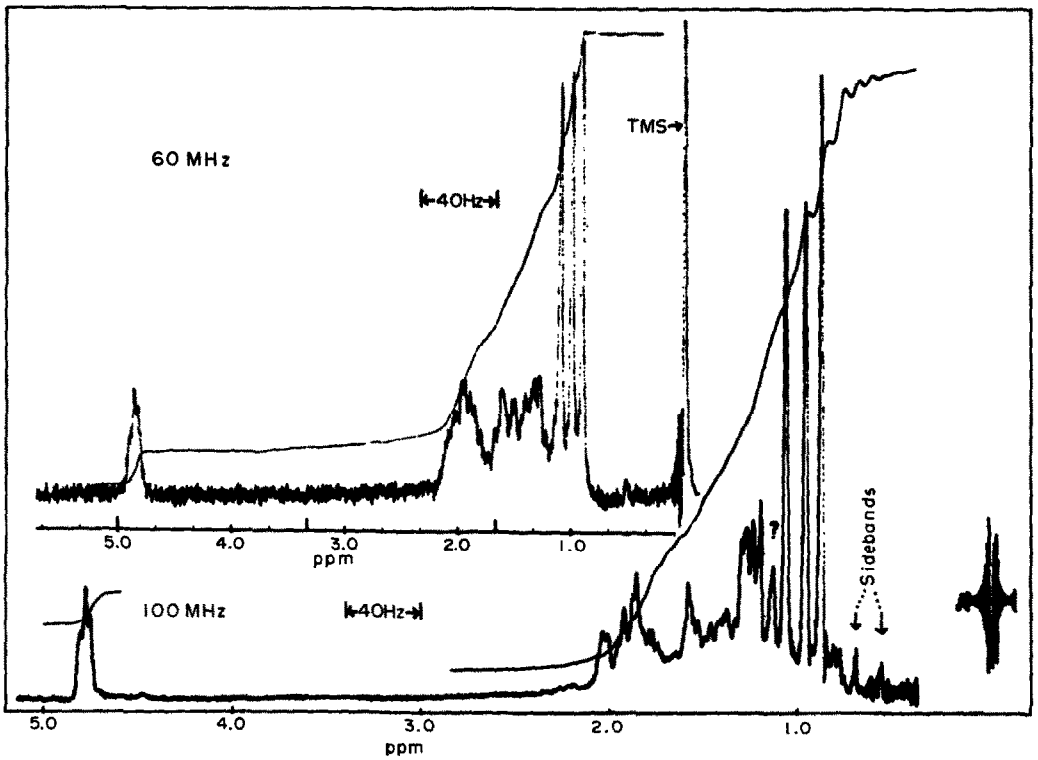
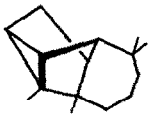


Fig. 3. The NMR spectra of scapanene.

†The NMR data for scapanene are not those expected for the one missing member of the family, 'isolongifolene' (ii) [47]. Note that longicyclene (i) was also detected in this oil.



i

ii

To facilitate further studies of sequiterpenes from liverworts we have collected the GLC retention data and physical constants for all well-defined substances observed in livewort essential oils to date. The hydrocarbons are collected in Table 3. The Table includes only substances that have been confirmed by spectroscopic data as well as GLC data. The oxygenated sesquitperenes are listed in Table 4.

EXPERIMENTAL

General methods. Our procedures for acid-catalyzed rearrangements, small-scale hydrogenations, column chromatography on argentic media, and preparative GLC are as in ref. [4d]. For gas chromatographic analyses we employ modified Kovats' indices obtained using α-copaene and γ-cadinene as standards [4d, 9]. Additional GLC phases employed in this work are: B, silicone SF-96; E, silicone SE-52. All relative retention data for oxygenated sesquiterpenes employ cedrol as the standard (*RR* = 1.00) either directly or indirectly. NMR spectra are for $CDCl_3$ unless otherwise stated with TMS set at $\delta = 0.00$. Spectra at 80 MHz were obtained in the FT mode on a Varian CFT-20 spectrometer with D-lock. High resolution mass spectral data (AEI-MS-9) were obtained by a computer controlled scan of masses for compound and a perfluoro standard. The computer reports masses for non-standard peaks to 0.0001 amu together with the best fitting formula, with error (in mmass) by comparison with five neighbouring standard peaks. Therefore our mass spectral data is reported as follows: mass (% of base peak, formula or other designation of peak identify, error in mmass). For rotatory data methods see the accompanying article [4e] and ref. [4d].

Plant materials and essential oil preparation. All essential oils were prepared by steam distillation of the Et_2O extract of dried powdered plant material. The plant collections, with the exception of some later *Scapania undulata* specimens (detailed below), have been described previously [1a, c, 19, 58] and voucher specimens are in the herbarium of S. H. The experimental work except for *Anastrepta orcadensis* and *Scapania undulata* consisted of GLC analyses and determination of spectra for substances isolated by preparative GLC. The results are presented in the text and Tables 1, 3, and 4.

The wide-spread natural occurrence of anastreptene. Besides the essential oils detailed in this report, we have also reexamined four *Barbilophozia* species, the original essential oils [4b] and newly isolated oils from more recent collections, and find that anastreptene is present in all the oil samples (4–31% of the hydrocarbon protion). Three collections of *Anastrepta orcadensis* (chemically distinct with respect to diterpenes) [19] each showed only two major components: anastreptene and β-barbatene Table 1).

Isolation of anastreptene from A. Orcadensis oil. A sample of oil (4.5 g) eluted from Al_2O_3 with hexane, which analyzed 38% anastreptene and 50% β-barbatene by GLC, was set aside at −20° with hexane. Crystalline anastreptene comes out slowly. Recrystallization from absolute EtOH afforded 380 mg (9%) of pure anastreptene: mp 91–93°; MS, *m/e* (%) 202.172 (P, $C_{15}H_{22}$, 55), 187 (42), 159 (100), 145 (53), 131 (65), and 105

Table 3. Physical constants for liverwort sesquiterpene hydrocarbons

	Retention data					
	I_A^{190}	I_B^{170}	I_C^{150}	I_D^{160}	$[\alpha]_D^*$	CD extrema* $\Delta\varepsilon(\lambda, nm)$
(+)-Anastreptene	1403	1391	1568	1726	+29°a, +32°p	+5.5 (215)
(−)-α-Longipinene	1423.5	1385	1524.5	~1652	−24°p, −33°c	+2.1 (204), +4 (188)!
(−)-α-Ylangene	1423.7	1396.1	1540	1653	n.d.	−1.4 (209), 3.2 (187)!
β-Elemene	1428.5	—	1608	—	n.d.	n.d.
β-Farnesene	1433.5	1449.5	1670	1818	0°	—
β-Bourbonene‡	1443.5	1411.7	1577	—	n.d.	n.d.
Sibirene	1457.7	1426.7	1594	—	n.d.	n.d.
(−)-Longicyclene	1458	1409?	1554.5	1684	n.d.	−ve @ 190
(−)-Sativene†	1462.5	1421	1575	~1736	−ve	−30 (196)
β-Ylangene‡	—	—	~1642	—	n.d.	n.d.
(−)-β-Longipinene	1474.5	1432.5	1612	—	−52°c	+9.78 (201)
Chiloscyphene-6	1479.5	—	1613	—	n.d.	n.d.
β-Diploalbicene	1480	—	1650	—	n.d.	+2.4 (208), −8.2 (190)!
(+)-Sinuene'	1482	1450.6	1646	—	+5°p	+4.7 (1.99), −1.7 (185)!
β-Cubebene‡	—	—	1651	—	n.d.	n.d.
(−)-Longifolene	1494	1440	1620	1802	−36°p, −47°c	−24 (198)
(−)-Caryophyllene	1479	1446	1638	1836	−ve	+15 (218), −11 (202)||||
(+)-α-Barbatene	1501	1440.5	1627.5	1812	+48°c, +70°p	+5.0 (201)
(−)-α-Helmiscapene	1502	1467	1683	—	−100°c	−16.5 (198)
β-Helmiscapene	1506	~1466	1686	—	n.d.	n.d.
α_2-Bisabolene	1512	1499	1737.5	—	n.d.	n.d.
(+)-α-Himachalene||	1519.5	1475.3	1683	1889	+230°p, +112°c	+15.1 (200)
(−)-Selina-4,11-diene	1519.5	—	1702	—	−23°p	+7.3 (216), −15 (193)
(+)-Scapanene	1522	1464.9	1664	1841	+6.5°p	−2.4 (200)
Aequilobene	1522	1483	1702.5	1893	n.d.	n.d.
(−)-β-Bisabolene	1522	1510	1731	1909.5	−83°p	−2.97 (205)
(+)-β-Chamigrene†	1559	1550	1737	—	n.d.	n.d.
(−)-β-Barbatene	1536	1473	1690	1902.5	−16°p, −14°c	+8.2 (197)
(+)-γ-Himachalene¶	1544	1498.5	1723	—	+14°p	+19.8 (218), −6 (200)!
α_1-Bisabolene	1547	1538?	1777	—	n.d.	n.d.
γ-Cuprenene‡	—	—	~1707	—	n.d.	n.d.
(−)-β-Himachalene†	1553.5	1517	1736	1752.5	−220°c	−15.7 (194)
(−)-β-Selinene†‡	1556	1507	1749	1958	−34°c	+4.4 (198)
(−)-α-Alaskene	1557	—	1748	1939	−78°p	−2.7 (213), +7.8 (192)
(+)-α-Selinene**	1557.5	1512.8	1750.5	—	+6.9°c	+3.9 (212), −5.4 (196)
(−)-δ-Cadinene	1562	1526	1771	1960	−60°p	+2.6 (213), −11 (190)
(−)-Cuparene††	1566	1516	1838	2090	−28°c	n.d.
(+)-Calamenene‡‡	1568	1524	1839	2087	n.d.	−0.4 (278), +12 (203)
(+)-γ_1-Cadinene	1574	1524	1778	—	+28°c	+17.8 (202), −7 (190)!
(+)-α-Chamigrene	1576	1523	1765	—	n.d.	+4.2 (204)§§
ar-Himachalene	1585.5	1542	1873	1915	n.d.	n.d.
(+)-β-Bazzanene	1590	1535.5	1789.5	2050	+48°c	+0.54 (214), −0.7 (200)
Undulatene	1616.5	1557	1812	—	n.d.	n.d.

* The solvent code for rotation data is that given with Table 4. All CD data is for pentane solutions. † No ORD data available, sign of rotation is assigned based on the absolute configuration of congeners. If ORD and CD data is quoted, it is taken from measurements of the same substance isolated from non-Hepaticae. ‡ Only spectroscopic confirmation is mass spectroscopy during GLC analysis. § Values as large as −52° have been reported [2f]. Determinations on the enantiomer from conifers confirm the values quoted. || Matsuo quotes +112°c for this material from *S. undulata* [2f]. The original report for the enantiomer is −192°c [57]; a subsequent one, −180°c [25]. ¶ Reported for the enantiomer as obtained from *Cedrus atlantica*, −29°c [25]. ** Literature rotatory values for α-selinene vary greatly, likely due to contamaination with β-selenine. We find that (+)-β-selinene ($[\alpha]_D$ = +34°p, from Celery seed oil) affords a pure sample of (−)-α-selinene ($[\alpha]_D$ = −6°c) on acid treatment followed by extensive chromatography on $AgNO_3$–SiO_2. †† Based on values for the enantiomers, rotations as high as −60° could be expected. ‡‡ Calamenene exists in a *cis* and *trans* form with differing ORD and CD constants but inseparable by chromatographic methods. The rotation at the D-line is opposite that of the lower energy CD band in both forms [18]. §§ Authentic (−)-α-chanrigrene [47] displays $\Delta\varepsilon_{203}$ = −3.5. |||| CD values are for the same substance from a non-liverwort source.

(47%); $[\alpha]_D$ = +29° (*c* 0.26, MeCN); UV-CD (MeCN) 190 (ε = 8,700, $\Delta\varepsilon$ ~ +4.5), 215 (ε = 4500, shoulder; $\Delta\varepsilon$ (max) = +5.5), 235 (ε = 2700, $\Delta\varepsilon$ = +2.2); IR (CCl_4) 3060 (vinyl-H), 3045 (cyclopropyl-H), 1640, (C=C), 1456, 1448, 1436, 1375, 1328, 1305, 1170, 1067, 1040, 1025, and 892 cm^{-1}; δ 0.24–0.72 (2-3H, cyclopropyl), 0.76 (3H, Me *s*), 0.99 (6H, *s*), 1.33 (1H, *d*, 6.5 Hz), 1.71 (vinyl-Me, *m*), and 5.18 ppm (1H, *m*). The noncrystalline portion of the oil and mother liquors from recrystallization were combined and chromatographed on 15% $AgNO_3/SiO_2$ using a hexane–C_6H_6 gradient. The first eluted component was anastreptene. Recrystallization afforded an additional 610 mg of pure anastreptene bringing the yield to 16%. The second eluted component was β-barbatene by NMR and IR comparison with authentic material [4b]. The last eluted component proved to be oxygenated (a terpene?): I_A^{190} = 1068, I_D^{160} = 1559; δ 0.9 (3H, *s*), 1.27 (*s*), 2.08 (*s*), 2.18 (*s*),

Table 4. Oxygenated sesquiterpenes of hepaticae*†

Compound (ref.)††	mp	RR_A^{200}	RR_C^{200}	$[\alpha]_D$‡	CD§
Albicanol [4d]	oil	1.75	~2.26	n.d.	n.d.
Drimenol [1b]	98°	2.05	2.87	−18°	n.d.
Diploalbicanol [4d]	47–48°	1.29	1.07	n.d.	n.d.
Acetoxydiplophyllin [4d]	92–95°	—	—	−132° m	+2.57 (266), −4.2 (231)
Diplophyllin [4d]	31–32.5°	—	—	−108°m	+2.9 (266), −4.6 (235)
Diplophyllolide-A [3d]	62–62°‖	—	—	−132°m	+2.0 (259), −13.5 (215)
Bazzanenol [15]	oil	n.d.	n.d.	+19°c	n.r.
Chiloscyphone [2g]	oil	n.r.	n.r.	−46°d	−0.82 (362), −13.9 (222)
Cyclocolorenone [2d, 71]	oil	n.r.	n.r.	+404°c	+0.15 (330)
δ-Cuparenol [2f]	oil	n.r.	n.r.	−73.5°c	n.r.
Gymnomitrol [6]	114–116°	1.16	n.d.	+7°c	n.d.
Myliol [3b]	110–111°	n.r.	n.r.	−20°c	n.r.
Dihydromyliol	77–78°	0.89	1.34	n.d.	n.d.
Maalioxide [2d]	66°	n.r.	n.r.	−34.5°c	n.d.
Pinguisone [3a]	63–63.5°	n.r.	n.r.	n.r.	UV max 292 nm
Norpinguisone [71, 73]	liq.	—	—	−27°c	n.r.
Deoxypinguisone [3a, 71]	oil	n.r.	n.r.	−27°c	n.r.
Nordeoxypinguisone [71, 73]	126–127°	—	—	+2°c	n.r.
Longiborneol	106–107°	0.96	1.07	−20°c, p** −32°m	
Longipinanol	82.5–83°	0.28¶ 0.35	—	−50°p	n.d.
4-Hydroxycalamenene	oil	1.35	n.d.	n.d.	n.d.
(+)-Frullanolide [7, 70]	76°	—	—	+114°c	−1.5 (265)
(−)-Frullanolide [7]	77°	—	—	−113°c	n.r.
(+)-Dihydrofrullanolide [70]	120–121°	—	—	+55°c	n.r.
(−)-Arbusculine-B [70]	85–86°	—	—	−35°c	n.r.
(+)-Eremofrullanolide [70]	82–82.5°	—	—	+9°c	n.r.
(+)-Dihydroeremofrullanolide [70]	70–71°	—	—	+108°c	n.r.
(+)-Oxyfrullanolide [70]	179–180°			+71°c	−1.6 (259)
(+)-*cis*-β-Cyclocostunolide [71]	75–76°			+38°	+0.9 (260)
Confertifolin [71]	133–134°	—	—	−43°c	n.r.
(−)-Tadeonal [73, 71]	57–58°	—	—	−130°c	n.r.
(−)-Cinnamolide [71] (+)-Dihydrocinnamolide [72]	125–126°	—	—	−31°c	n.r.

* Relative retention data reported using cedrol as a standard (RR = 1.00). Other suitable GLC standards are elemol (RR_A^{200} = 0.581, RR_C^{200} = 0.800, and RR_D^{205} = 0.808) or nerolidol (RR_A^{200} = 0.493, RR_C^{200} = 0.66). All GLC data is from our laboratories. † Whenever a substance has been isolated from liverworts in other laboratories as well, we report our mp, $[\alpha]_D$, etc values only if they concur with previous reports for that substance either from liverworts or for the enantiomer from Tracheophytes. When there is substantial disagreement both values are listed. ‡ The solvent employed is indicated by letter: (a) acetonitrile; (c) chloroform; (d) dioxane; (e) ethanol; (i) isooctane; (m) methanol; and (p) pentane. § CD measurements are for pentane solutions except for the lactones which are done in MeOH, units are $\Delta\varepsilon$ (λ, nm). ‖The mp recorded for the natural product. The synthetic enantiomer displays mp 81–82° [4d]. ¶ Decomposes to α- and β-longipinene on GLC. ** Svensson and Bendz report $[\alpha]_D = -14.5e°$ [8]. Matsuo reports −16.3°c [2f]. †† Present study. ‡‡ Unpublished work from this laboratory.

5.0–5.8 ppm (*m*, vinyl-H); IR ($CHCl_3$) 1738 (C=O), 1470, 1385, and 1260 cm^{-1}.

Hydroboration–oxidation of anastreptene. Anastreptene, 40 mg in 1 ml of THF, was treated with 0.67 ml of 1M BH_3-THF (3.3 eq.) for 2.5 hr with stirring. The reaction was maintained at near ambient temp. while 70 μl 3N aq. NaOH and 200 μl of 30% aq. H_2O_2 were added. Et_2O extraction after 2 hr and the addition of H_2O afforded 30 mg of oily product. The major zone from preparative TLC (SiO_2, 6% EtOAc in φH) was oxidized with excess CrO_3 in Py for 16 hr. After addition of H_2O, Et_2O extraction afforded 10 mg of ketone **22**: IR (film) 1743 cm^{-1}; δ 0.88, 1.03, 1.10 (3 Me *s*), 1.17 (Me, *d*), and 2.1–3.0 ppm (3H, m), identical to the spectrum of the myliol degradation product [3b, 59].

Reactions of β-bazzanene (from B. trilobata). (A) Hydrogenation of β-bazzanene (PtO_2, EtOAc) affords a mixture which was analyzed by GLC: 3%, I_B^{170} = 1489, I_A^{190} = 1569; 19% I_B^{170} = 1499, I_A^{190} 1610, monohydrogenated?; 43%, I_B^{170} = 1540.7, I_A^{190} = 1607; 26%, I_B^{170} = 1553, I_A^{190} = 1620.8. (B) Reaction in the two phase media, heptane–HCO_2H. A soln of β-bazzanene was treated with an equal vol. of HCO_2H at room temp. After 15 hr of stirring, GLC showed conversion to the following: I_A^{190} = 1391 (6%, I_B^{170} = 1350, I_C^{150} = 1453), I_A^{190} = 1498 (18%), and $I_A^{190} \simeq$ 1579 (53%). The latter two components were collected from a preparative column (phase A). The I_A^{190} = 1498 component displayed a single peak on phase C (I = 1641) but two on phase B (10% I = 1445, α-barbatene?; 86% I = 1460); the NMR spectrum showed: δ 5.3–5.45 (1-2H, vinyl-H), ~2.0 (~4H, allyl-H), 1.67 (3H, vinyl-Me), 1.20, 1.16, and 1.09 ppm (Me s). This component displayed only a very weak olefin CD spectrum: $\Delta\varepsilon_{215} = -0.26 \pm 0.15$. The I_A^{190} = 1579 component was 85% pure by GLC (I_B^{170} = 1532, I_C^{150} = 1771): δ 5.34 (2H, vinyl-H), 1.66–1.73 (1-2 vinyl-Me), 1.01 and 0.96 (*ca* 1.5H each, Me group(*s*)), and 0.85 ppm (Me, *s*). Hydrogenation of this product afforded bazzananes based on GLC analysis: 65% I_B^{170} = 1540, I_A^{190} = 1607; 14% I_A^{170} = 1551. (C) Reaction with *n*-decane/CF_3CO_2H. After 18 hr at room temp. a complex mixture resulted. GLC analysis on three phases allowed a correlation with the products derived from α-chamigrene, see Table 5.

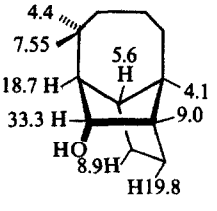
Separation of longiborneol from Scapania undulata *oil Tharandt/Dresden).* The total essential oil (10.8 g, obtained by

Table 5. CF_3CO_2H Reaction products of β-bazzanene and α-chamigrene (ex *S. undulata, vide infra*)

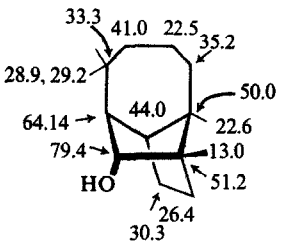
Component GLC Indices A, 190	B, 170	C, 150	Assignment	% from **26**	% from **35**
1389	1349.5	1447.5		1.6	0.8
1443.9	1429.5	1538		2.1	2.8
1470	1418.5	1570.5		2.0	3.5
1501.1	1446	1644		18	4
1516	1457	1642	isobarbatene	29	8
(1516)	1491	1709		7	6
(1516?)	~1475	1711		10	15
1567	1515	1838	cuparene (**5**)	9	5
1567	1525	1838	calamenene (**7**)	5	4
1584	1542	1874	ar-himachalene	2	35

steam distillation of the ether extract of dried plant material* was chromatographed on 250 g of SiO_2 using a hexane–C_6H_6 gradient. Pure hexane eluted 6.4 g of a mixture of sesquiterpene hydrocarbons (see below). Early C_6H_6-eluted fractions (2.8 g) crystallized as the solvent was removed. GLC analysis revealed 90+% longiborneol and the minor peaks for the longipinenes indicated the near absence of longipinanol (~6%). Recrystallization (MeCN) afforded pure (−)-longiborneol: mp 106–107°; δ 3.76 (1H, *d*, 5 Hz), 1.85 (*d*), 0.940 (2 Me *s*), 0.869 and 0.843 ppm (2 Me, *s*). An $Eu(FOD)_3$ shift study revealed the LIS data shown on the structure (**13b**). The ^{13}C-NMR spectrum **13c** could be assigned by reference to the assigned spectrum of borneol (**63**) [60].

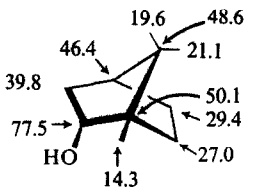
rotatory form on four GLC phases, negative trending CD at 190 nm; δ 0.957, 0.935, 0.867, and 0.783 ppm for four singlet Me resonances. (+)-*Scapanene* (unknown structure, peak 10a): IR (CCl_4) 3090, 1650, 890 (C=CH_2), 1395, 1375, 870, and 850 cm^{-1}; δ 4.84 (2H, ~*s*, C=CH_2), 1.12, 1.02, and 0.94 ppm (3 Me, *s*) see Fig. 3; $[\alpha]_{300}$ = +26° (*n*-C_5H_{12}); MS 204.1860 (21, $C_{15}H_{24}$ −1.6), 189.1644 (9, $C_{14}H_{21}$ +0.2), 161.1318 (15, $C_{12}H_{17}$ −1.0), 133.1066 (22, $C_{10}H_{13}$ +5.0), 119.0856 (24, C_9H_{11} −0.4), 109.1010 (28, C_8H_{13} −0.6), 57.0700 (84, C_4H_9 −0.4), and 43.0540 amu (100%, C_3H_7 −0.8 mmass). Acid rearrangement studies employed a 5% soln of this material in *n*-decane. (−)-α-*Longipinene* (**18**, peak 2b): see Table 3; $[\alpha]_{300}$ = −47° (*n*-C_5H_{12} ([46]; δ_{CCl_4} 5.16 (1H, *m*), 2.19, 20.2



13b



13c



63

On dissolution in HCO_2H and standing for 8 hr, longiborneol affords the formate: $[\alpha]_D$ = −22.4° (*n*-C_5H_{12}); δ 8.00 (1H, *s*, CHO), 4.50 ppm (1H, *d*), Oxidation, by treating an ethereal soln with a two-fold excess of aq. chromic acid, afforded after extraction and distillation (70°, 0.2 torr) (−)-longicamphor as a colorless oil: f.p. *ca* −8°, $[\alpha]_D$ = −36° (*n*-C_5H_{12}), $\Delta\varepsilon_{303}$ = −0.57 (*n*-C_5H_{12}); reported [2e]—$\Delta\varepsilon_{309}$ = −0.43 (MeOH), $[\alpha]_D$ = −1.8° ($CHCl_3$); reported for the enantiomer—$[\alpha]_D$ = +22° (EtOH) [61], $\Delta\varepsilon$ = +0.35 [62].

Sesquiterpene hydrocarbon components of longiborneol-yielding Scapania undulata.† The hydrocarbon fraction from the experiment above was chromatographed on a 50-fold column of 15% $AgNO_3$–Al_2O_3 eluting with a cyclohexane–C_6H_6 gradient. Like fractions were combined and the major pure components were isolated by preparative GLC. They were, in order of elution: (−)-*longicyclene* (*i* peak 4a): identical to authentic dextro-(3H, allyl-H), 1.63 (vinyl-Me), 0.90 (3H, Me *s*), and 0.83 ppm (6H, 2 Me *s*). (−)-*Longifolene* (**14**, peak 6b): see Table 3; $[\alpha]_{300}$ = −590° (*n*-C_5H_{12}); identical to previous samples by NMR, CD, and GLC. (+)-α-*Himachalene* (**15**, peak 9a): see Table 3; $[\alpha]_{300}$ = +1200° (*n*-C_5H_{12}); δ_{CCl_4} 5.40 (1H), 4.69 (2H), 2.78 (1H, *br.* d, allyl-H), 1.64 or 178 (vinyl-Me), 0.990 and 0.960 ppm (2 Me *s*, in $CDCl_3$ δ = 0.036 ppm). The CD was mirror-image related to that of an authentic specimen of the enantiomer [57]. For the hydrogenation of α-himachalene (PtO_2, EtOAc), see Table 7. Upon stirring an *n*-decane solution of α-himachalene with 9:1 HCO_2H–CF_3CO_2H an equilibrium between the double bond isomers was established: 52% α-, 5% γ-himachalene (see later), and 43% β-himachalene (I_A^{190} = 1554, I_B^{170} = 1517, I_C^{150} = 1736) [57]. The same (by GLC) mixture is obtained from authentic α- and β-himachalene [57] under these conditions. Further reaction, or treatment with 1:1 HCO_2H–CF_3CO_2H, affords aryl-himachalene (I_A^{190} = 1585, I_A^{170} = 1542, I_C^{130} = 1873). (−)-β-*Longipinene* (**19**, peak 5c): see Table 3; $[\alpha]_{300}$ = −40° (*n*-C_5H_{12}); δ_{CCl_4} 4.50 (2H, C=CH_2), 2.44 (center for two allyl-H), 1.97 (allyl-H), 1.52 (*br. s*, CH_2 groups), 0.896 (6H, 2 Me *s*), and 0.69 ppm (Me *s*); identical by NMR and IR to a sample prepared from the dehydration of totally synthetic *epi*-longipianol [21]. Reaction with *n*-decane–HCO_2H did *not* produce α-longipinene, rather β- and α-himachalene were formed in a 2:1 ratio. In 10:1 HCO_2H–CF_3CO_2H, β-longipinene affords the equilibrium mixture of the himachalenes previously encountered. Ozonolysis of β-longipinene afforded a

* Collected in August 1967 near Tharandt/Dresden, 300 m a.s., DDR. A 3.98 kg sample of dried material yielded 27 g (0.7%) of oil with a faint yellow coloration. A voucher specimen is in the herbarium of S.H., Halle-Neustadt.

† Entirely comparable results have been obtained with a specimen of the first *S. undulata* oil examined [1a] and three subsequent collections yielding longiborneol to the virtual exclusion of longipinanol, these include that collection which yielded scapanin [19].

cyclohexanone: IR $\nu_{C=O}$ 1715, 1410 cm^{-1}; δ_{CCl_4} 2.18–2.60 (3H, α to carbonyl), 0.92, 0.90, and 0.80 ppm (3 Me *s*). (−)-*β-barbatene* (2, peak 11a): see Table 3; $[\alpha]_{300} = -48°$ (n-C_5H_{12}); NMR, IR, CD, and GLC behaviour identical to that of previously isolated specimens. (+)-*γ-himachalene* (17, peak 12d): see Table 3; $[\alpha]_{300} = +157°$ (n-C_5H_{12}); δ5.57 and 5.49 (1H each, vinyl-H), 1.67 (vinyl-Me), 1.00 and 0.95 ppm (2 Me *s*), superimposable with that of the enantiometric substance [24]; ^{13}C-NMR ($CDCl_3$) δ 138.11, 134,06, 125.56, 124.68, 47.54, 43.20, 39.54, 36.60, 30.42, 29.47, 29.09, 26.16, 25.33, 24.33 and 23.78 ppm; MS 204.1876 (55, $C_{15}H_{24}$ + 0.0), 147.1162 (47, $C_{11}H_{15}$ −1.0), 133.1022 (65, $C_{10}H_{13}$ +0.6), 119, 0860 (61, C_9H_{11} +0.0), 95.0860 (47, C_7H_{11} +0.0), 93.0702, C_7H_9 −0.2), 91.0548 (88, C_7H_7 +0.0), 81.0710 (53, C_6H_9 +0.6), and 79.0556 amu (68, C_6H_7 +0.8 mmass). Hydrogenation (PtO_2, EtOAc) results are collected in Table 7. Upon reaction in *n*-decane–HCO_2H–CF_3CO_2H, γ-himachalene yields α- and β-himachalene as judged by GLC analyses.

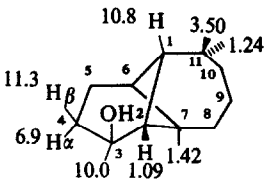
The fractions containing γ-himachalene also contained a later eluting material. A sample obtained by preparative GLC gave an NMR consistent with the α-bisabolene structure. GLC analysis reveals that this is the presumed *trans* isomer encountered in the next section. It is interesting to note that this isomer of α-bisabolene elutes with or after γ-himachalene from $AgNO_3$–Al_2O_3, but before from $AgNO_3$–SiO_2.

Sesquiterpene consitituents of Scapania undulata, *samples from longipinanol-producing races*: crystalline *distillate*. Later steam distillation fractions from a Thuringer Wald sample of *Scapania undulata* crystallized in part. The collected crystals (mp 63–65°) showed three peaks on GLC analysis (phase A, 190°): α-longipinene (~55%, $RR_A^{190} = 0.28$. β-longipinene (~20%, $RR_A^{190} = 0.35$), and longiborneol (~25%, $RR_A^{190} = 0.94$). Preparative GLC allowed collection of each major peak for an NMR confirmation of structure assignments. TLC showed two poorly resolved spots: R_f (5% EtOAc–φH, SiO_2) 0.67 (red coloration, minor) and 0.63 (brown, major); R_f ($CHCl_3$, SiO_2) 0.41 (brown, major), and 0.46 (red, minor). Authentic longiborneol gave a red coloration and ran with the minor component in both systems.

(*A*) *Oxidation of the mixture*. The crystalline sample (118 mg) was oxidized with CrO_3 (0.5 g) in 10 ml of Py for 23 hr at room temp. affording, after the usual work-up, 115 mg of an oily mixture. GLC analysis (phase A, 190°) shows: α-longipinene (~50%, RR = 0.28), β-longipinene (~15%, RR = 0.35), and longicamphor (~30%, RR = 0.80); TLC R_f ($CHCl_3$, SiO_2) 0.73 (longicamphor), and 0.41 (tertiary alcohol). Column chromatography on silica (5% EtOAc–φH) afforded a sample of alcohol 37, mp 81–82.5° as the second eluted component.

(*B*) *Acetylation*. The crystalline mixture (28 mg) was treated with 0.5 ml of Ac_2O in 2 ml of Py at room temp. for 20 hr. The product displayed the usual GLC peaks for α- and β-longipinene and one for longibornyl acetate ($RR_A^{190} = 0.92$); TLC ($CHCl_3$, SiO_2) R_f 0.79 (longibornyl acetate) and 0.41 (tertiary alcohol).

Separation of longiborneol and longipinanol. The crystalline mixture (660 mg) was chromatographed on a 1.5 cm × 60 cm column of SilicAR CC-7 using 5% EtOAc in C_6H_6. Initial fractions were combined affording 120 mg of longiborneol (18%) identical to authentic material. After that, 110 mg (17%) of a 1:1 mixture of alcohols was eluted. The final fractions yielded 430 mg (65%) of the crystalline alcohol, longipinanol (37), (mp 82.5–83°, from MeOH–H_2O): $[\alpha]_D = -50$, $[\alpha]_{300} = -296°$ (*c* 0.22 n-C_5H_{12}); IR (nujol) 3370 (OH), 1385, 1368, 1165, 1098, 900, 979, 962, 920 and 885 cm^{-1}; δ0.90 (3H, *s*, Me), 0,91 (6H, *s*, Me), 1.35 (3H, *s*, MeCOH), and 1.85 (OH), 1.8–1.95 ppm (5H). Sublimation (80°, 0.1 torr) afforded an analytic sample, mp 82.5–83.0°: MS *m/e* (%, 70 eV) 222 (P, $C_{15}H_{26}O$, 0.6%), 207 (P-15, 10%), 204 (P-18, 13%), 189 (25%), 175 (7%), 161 (38%), 133 (44%), 119 (75%), and 109 (base), in another MS run the molecular formula was confirmed for the 222 peak ($C_{15}H_{26}O$, 7% of base). A $Eu(FOD)_3$ shifted NMR spectral study was done by sequential addition of $Eu(FOD)_3$ up to 0.6 equivalents. Plots of δ vs equiv. of $Eu(FOD)_3$, linear to 0.45 equivalents, were used to obtain LIS values extrapolated to expectation values at 1.0 equivalents of $Eu(FOD)_3$. These are shown below together with coupling data which was revealed in the expanded spectrum. The ^{13}C-NMR signals can be assigned using the longiborneol data (above) for analogy for the cycloheptyl portion and recent data on pinane derivatives [63].



$J_{4\alpha,4\beta} = 16.0$, $^3J_{4\alpha} = 5.0, 10.7$
$^3J_{4\beta} = 4.7, 12.0$, $J_{2,6} = 5$

^{13}C-resonances (ppm)
quartets: 25.7 (C-7Me), 27.1 and 28.6 (C-11Me), 31.2 (C-3Me).
triplets: 21.7 (C-9), 27.8 (C-5), 32.5 (C-8), 39.3 (C-4), 42.55 (C-10).
doublets: 39.9 (C-6), 52.3 and 52.8 (C-1 and C-2)
singlets: 32.1 (C-11), 39.7 (C-7), 76.7 (C-3)

A similar $Eu(FOD)_3$ complexation experiment in CCl_4 was followed by CD spectroscopy. A sharp positive band was induced at 525 nm, $[\theta]_{Eu} = +10$ ($\rho = 0.4$), indicating an *S* configuration at the hydroxyl center. [64].

Dehydration of longipinanol. Longipinanol (32 mg) was dehydrated with $SOCl_2$ (0.15 ml) in 1 ml dry Py at ~0° for 15 min. The reaction mixture was poured into 15 ml of ice-cold $NaHCO_3$ soln and extracted with Et_2O, the extract was washed with H_2O, $CuSO_4$ soln, and H_2O; and then dried. Evaporation gave 23 mg of oily product which was shown to be the mixture of one major and three minor hydrocarbons. TLC showed the complete dehydration of longipinol occurred. The major hydrocarbon was identified as α-longipinene and one of the minor hydrocarbons as β-longipinene by NMR comparisons of purified sample on preparative GLC (phase C, 190°). The α-longipinene sample obtained displayed a CD spectrum ($\Delta\varepsilon_{206.5} = +3.17$) with a Cotton effect of the same sign as that of authentic (−)-α-longipinene.

The hydrocarbon components of longipinanol yielding Scapania undulata. A sample (5.78 g) of the early steam distillate from a Thuringian Wald sample of this species [65] was freed of alcohols by elution through SiO_2 with hexane. The 4.8 g sample of hydrocarbon was chromatographed repeatedly on 15% $AgNO_3$–SiO_2 using cyclohexene–EtOAc gradients. Each fraction was analyzed on three GLC phases (A, B, C) revealing the order of elution and % composition for the hydrocarbon portion of the oil [66] shown in Table 6. Components isolated for the first time in this run are listed below. See also Table 3.

Component 7, (−)-α-*ylangene* (45). See Table 3, δ 5.25 (1H), 1.65 (vinyl-Me), 0.85 (6H, *d*, 7 Hz), 0.785 ppm (Me, *s*), consistent with reported values [39].

Component 8, *sativene* (47). Isolated only in 24% purity by GLC, but the NMR does show the expected characteristic resonances [67]: δ 4.75, 4.45 (C=CH_2), 1.05 (Me, *s*), 0.90 and 0.85 ppm (2 Me, *d*).

Component 12, (+)-α-*chamigrene* (35). See Table 3, δ 5.43 and 5.33 (2 vinyl-H, *br. s.*), 1.65 and 1.63 (3H each, 2 vinyl-Me), 0.880 and 0.831 ppm (2 Me, *s*)*; MS 204.1872 (55, $C_{15}H_{24}$ −0.4), 136.1182 (100, $C_{10}H_{16}$ −6.8), 121.1004 (62, C_9H_{13} −1.2), 93.0708 (68, C_7H_9 +0.4), and 91.0546 amu (89, C_7H_7 −0.2 mmass).* Hydrogenation (PtO_2, EtOAc) of a sample afforded a mixture, by GLC: 57% $I_B^{170} = 1536$ ($I_A^{190} = 1608$), 22% $I_B^{170} = 1548$ ($I_A^{190} = 1620$?), 3% $I_B^{170} = 1489$ ($I_A^{190} = 1567$). Component #12 reacts sluggishly with *n*-decane–HCO_2H yielding *ar*-himachalene (based on GLC indices on 2 phases). In *n*-decane–CF_3CO_2H there is produced, in addition to *ar*-himachalene (35%), the materials observed on acid treatment of β-bazzanene; see Table 5.

Component 17, *sibirene* (48). δ 5.11 (1H), 4.68 and 4.60 (2H, C=CH_2), 1.00 (6H, *d*, 6.8 Hz), and 0.90 ppm (Me *s*), see Fig. 2; MS 204.1858 (61, $C_{15}H_{24}$ −1.8), 189.1616 (34, $C_{14}H_{21}$ −2.6),

* Consistent with literature reports [48].

Table 6. *S. Undulata* hydrocarbons, elution order from $AgNO_3$–SiO_2

Component #	Peak designation (Table 1)	%	I_A^{190}	I_B^{170}	I_C^{150}	Assignment
1	4a	1.2	1460.3	1409	1560	longicyclene†
2*	5a	<0.03	1477.6	1424.5	1582.4	isolongifolene?‡
3*	7aa	0.7	1502.4	1444	1629.1	unknown
4	10a	7.1	1523	1465	1664	scapanene†
5	2b	23.8	1424	1384.4	1523	α-longipinene†
6	6b	26.6	1495	1440	1622	longifolene†
7	2c	2.4	1424	1397.2	1523	α-ylangene
8	4c	0.1	1462	1424.5	1577	sativene
9	5b	0.4	1475	1424.5	1598	unknown
10	7a	0.1	1500	1440.5	1623	(α-barbatene)‡
11*	9a	2.4	1521.3	1476	1684	α-himachalene†
12*	15a	1.2	1573	1523	1765.3	α-chamigrene
13	5c	1.7	1474	1430	1612.2	β-longipinene†
14*	7b	0.4	1504.2	1498.4	1769.5	unknown
15*	9b	0.3	1521.2	1485.5	1743	unknown
16	11a	2.9	1536.3	1476	1692.6	β-barbatene†
17	4d	0.6	1457.7	1427	1593.5	sibirene
18	18	0.5	1616	1557.2	1812	undulatene
19*	9c	0.5	1520	1483.2	1709	aequilobene§
20*	11b	0.3	1540	1493	1727	unknown
21*	17	0.1	1594	1544.5	1805	asperene§
22	14	0.2	1558.5	1500	1737	β-chamigrene
23	7c	1.3	1504	1467	1683	α-helmiscapene
24*	8a	1.9	1511.6	1499.3	1738	*trans*-α-bisabolene
25*	12c	1.1	1549	1538.3	1779	*cis*-α-bisabolene
26*	15b	1.2	1573	1524	1779	γ_1-cadinene
27	7d	1.6	1504.3	1465.1	1685	β-helmiscapene
28	12d	6.7	1547	1499	1726	γ-himachalene†
29	5d	0.5	1479	1446	1637.7	caryophyllene
30	3	0.3	1433	1449.4	1669.5	β-farnesene

* Elute at nearly the same rate from the column. † Components with this designation were obtained pure and were identical to those obtained previously, see Table 3. ‡ Fits only by GLC data, NMR data on this fraction not definitive. § Identity with material from other *Scapania* species based on GLC only.

161.1272 (100, $C_{12}H_{17}$ −5.6), 119.0862 (50, C_9H_{11} +0.2), 105.0728 amu (82%, C_8H_9 +2.4 mmass). The UV spectrum revealed a single weak peak and end absorption, λ_{max} (ε): 245 (200), 210 nm (3900, end). Acid treatment (HCO_2H–$MeSO_3H$, *n*-heptane) of sibirene for 15 hr resulted in a mixture of selinenes: selina-3(4),6(7)-diene ($I_A^{190°}$ = 1514.3, 5%), δ-selinene (I_A^{190} = 1524, 15.5%), α- and/or β-selinene (I_A^{190} = 1561.2, 27.4%), 10-*epi*-α-selinene ($I_A^{190°}$ = 1579.1' 15%), and two other components (I_A^{190} = 1497, 10% and I_A^{190} = 1586.5, 27%).

Component 18, undulatene. A 70% pure sample was isolated—δ 5.31 (2H, vinyl-H, *m*), 1.60 and 1.73 (vinyl-Me's), 0.83 (Me, *d*, 5.5 Hz), and 0.58 ppm (Me, *s*); MS 204.1868 (49, $C_{15}H_{24}$ −0.8), 176.1572 (33, $C_{13}H_{20}$ +0.8), 161.1320 (19, $C_{12}H_{17}$ −0.8), 136.1238 74, $C_{10}H_{16}$ −1.2), 121.1020 (100, C_9H_{13} +0.4), and 109.1012 amu (31%, C_8H_{13} −0.4 mmass). The even mass fragments suggest retro-Diels–Alder fragments of spiro-fused ring systems [68].

Component 19, aequilobene. A 60% pure sample was isolated—δ 5.2 (1 vinyl-H), 4.7 (C=CH_2), 1.65 (vinyl-Me), and 0.9–1.1 ppm (Me signals), a —CH=CMe— unit is suggested.

Component 21, asperene. A 70% pure sample was isolated—δ 5.58 and 5.38 (2 vinyl-H), 1.66 and 1.41 (2 vinyl-Me), 0.89 (Me, *d*, 6.7), and 0.78 ppm (Me, *d*, 6.9 Hz). The last two signals suggest an isopropyl group.

* R. L. Yates (Food and Drug Administration) has provided us with an account of A. F. Regan's NMR studies and his basis for assigning the *cis/trans* stereochemistry to the α-bisabolenes. We find our isomers to have such similar NMR data that we cannot readily distinguish them in that way.

Component 22, β-chamigrene (ent-**58**). An 80% pure sample was isolated—δ 5.26 (1H, *br. s*) 4.90 and 4.55 (C=CH_2), 1.55 (vinyl-Me), 0.86 and 0.81 ppm (2 Me, *s*), corresponding to that of an authentic sample [47].

Component 23, (−)-α-helmiscapene (**49**). See Table 3; $[\alpha]_{365}$ = −385°; δ 5.25 (1H), 4.68 (2H), 1.72 and 1.68 (2 vinyl-Me), and 0.89 ppm (Me, *s*); MS 204.1922 (70, $C_{15}H_{24}$ +4.6) 189.1640 (59, $C_{14}H_{21}$ −0.2) 107.0858 (65, C_8H_{11} −0.2), 93.0712 (74, C_7H_9 +0.8), 81.0726 (62, C_6H_9 +2.2), and 41.0376 amu (100%, C_3H_5 −1.4 mmass). Hydrogenation (PtO_2, EtOAc) afforded three major components, see Table 7. The third component (21%) was a monohydrogenated material (I_A^{190} = 1496, I_B^{170} = 1458).

Component 24, α-bisabolene. (*Trans*-isomer*, see Discussion MS 204.1888 (60, $C_{15}H_{24}$ +1.2, 189.1628 (7, $C_{14}H_{21}$ −1.4), 133.1026 (17, $C_{10}H_{13}$ +1.0), 121.1050 (33, C_9H_{13} + 3.4), 109.1008 (28, C_8H_{13} −0.8), 93.0706 (100, C_7H_9 +0.2), and 41.0394 amu (54%, C_3H_5 +0.4 mmass); δ 5.40 (1H, *br. s*), 5.065 (2H, *t*), 2.68 (2H, =CH—CH_2—CH=, *t*, 7.4 Hz), ~1.95 (CH_2 envelope), 1.65 and 1.60–1.61 ppm (vinyl-Me signals), essentially superimposable to that of the minor nerolidol cyclization product in HCO_2H [69] and perfectly superimposable to that of the synthetic material [29].

Component 25, α-bisabolene. (*Cis*-isomer*): δ 5.37 (1H, *br. s*), 5.09 (2H, broadened *t*), 2.66 (2H, =CH—CH_2—CH=, *t*), ~1.935 (CH_2 envelope), 1.67 and 1.61 ppm (vinyl-Me signals), identical by GLC and NMR to the major α-bisabolene isomer from the cyclization of nerolidol in HCO_2H [18, 69].

Component 26, (+)-γ_1-cadinene (**43**). MS 204.1904 (45, $C_{15}H_{24}$ +2.8), 161.1418 (100, $C_{12}H_{17}$ +9.0), 147.1190 (24, $C_{11}H_{15}$ +1.8), 133.0980 (29, $C_{10}H_{13}$ −3.6), 105.0704 (57, C_8H_9),

Table 7. Hydrogenation of selinenes and himachalenes

Compound hydrogenated	% Prod.	I_A^{190}	I_B^{170}
β-Selinene	19	1520.6	1472.6
	81	1559.4	1510.4
10-*epi*-α-Selinene	4	1522.1	1471.1
	19	1534	1484
	77	1559.7	1508.7
α-Helmiscapene (**49**)	11	1511.4	1469.4
	89	1551.5	1497.1
β-Helmiscapene (**50**, 35%)	10	1512.1	1468.5
	25	1551.7	1497.6
+ γ-Himachalene (**17**, 65%)	33	1541.2	1488
	5	1570	
	16	1580	1518.4
γ-Himachalene (**17**)	51	1540.5	1488.3
	11	1570.4	1509
	14	1580?	1513
	25	1580	1518.6
α-Himachalene (**15**)	56	1541.8	1488.4
	9	1471.7	1509
	9	1582?	1514.5
	13	1582	1518.2

93.0702 (47, C_7H_9 −0.2), and 41.0414 amu (62%, C_3H_5 +2.4 mmass); see Table 2 for an NMR and rotary data comparison with authentic (+)-γ-cadinene [31]. The hydrogenations of component 26, authentic γ-cadinene, and a 1:1 mixture of the two materials are given in Fig. 1. Acid treatment of authentic γ-cadinene and component #26 were performed separately under the same conditions (anhy-HCO_2H, *n*-decane, 24 hr). Essentially two products were detected by GLC from both reactions: δ-cadinene (I_C^{150} = 1772.7, 62%), and β_1-cadinene (I_C^{150} = 1800.5, 23%). Addition of 3 drops of $MeSO_3H$ resulted in further transformations:

from γ-cad, %	from #26 %	I_A^{190}	I_C^{150}	Assignment
9.7	6.7	1538	1733.6	10-*epi*-zonarene
8.2	9.2	1557	1914.5?	
40.0	34.1	1569	1840.4	calamenene
12.4	28.4	1589	1894.2	calcorene
3.9	3.1	1605.6	1956.1?	
25.7	27.4	1624	1942.1?	

Component 27, β-helmiscapene (**50**). Isolated in 35% pure form in a mixture with γ-himachalene from the repeated $AgNO_3$-impregnated column chromatography—δ 4.68 (4H, C=CH_2, *br*, *s*) and 0.88 ppm (Me, *s*); ^{13}C-NMR ($CDCl_3$) δ 150.62, 125.56, 108.18, 108.09, 52.67, 45.74, 41.00, 34.21, 33.81, 29.89, 29.09, 28.01, 27.27, 23.33, 21.03, and 29.78 or 22.69 or 33.81 ppm. Hydrogenation (PtO_2, EtOAc) apparently yielded two tetrahydro derivatives, after the himachalane contribution is subtracted, see Table 7.

Component 29, (−)-α-caryophyllene (**59**). $\Delta\varepsilon_{217.5} = +5.8$, $\Delta\varepsilon_{202} = -6.9$;* δ 5.4 (vinyl-H), 4.95 and 4.85 (2H, C=CH_2), 1.6 (vinyl-Me), and 0.99 ppm (2 Me, *s*), identical to that of an authentic sample (for CD see Table 3) displaying ORD ($CHCl_3$) $[\alpha]_D = -12.2$ (lit. $[\alpha]_D$ ($CHCl_3$) = −14.02 [34]) $[\alpha]_{363} = -2.4$, $[\alpha]_{360} = 0$, $[\alpha]_{325} = +35.2°$.

Component 30, β-farnesene. δ 4.97 (4H, 2 C=CH_2), 1.66–1.59 ppm (vinyl-Me's), consistent with that of an authentic sample [69].

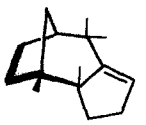
* The low Δε value probably reflects low purity (non-chiral impurities) rather than low optical purity. The CD curve was superimposable to that of the authentic material.

Acknowledgements—The PDP-12 computer and software for the computer controlled exact mass analyses were obtained by NSF funding (#GP-18433). This program of sesquiterpene structure elucidation is supported by the National Institutes of Health (GM-18143). N.H.A. acknowledges support from a Career Development Award (NIH) and a Dreyfus Teacher–Scholar Award.

REFERENCES

1. (a) Huneck, S. and Klein, E. (1967) *Phytochemistry* **6**, 383; (b) Huneck, S. (1967) *Z. Naturforschg.* **22b**, 462; (c) Huneck, S., Grolle, R. and Vevle, O. (1972) *J. Hattori Bot. Lab.* **36**, 93.
2. (a) Matsuo, A. (1971) *Tetrahedron* **27**, 2757; (b) Matsuo, A., Nakayama, M. and Hayashi, S. (1973) *Bull. Chem. Soc. (Japan)* **46**, 1010; (c) Matsuo, A., Nozaki, H., Nakayama, M., Kushi, Y., Hayashi, S. and Kamijo, N. (1975) *Tetrahedron Letters* 241 and refs. therein; (d) Matsuo, A., Nakayama, M., Sato, S., Nakamoto, T., Uto, S. and Hayashi, S. (1974) *Experientia* **30**, 321; (e) Matsuo, A., Nakayama, M. and Hayashi, S. (1973) *Chem. Letters*, 769; (f) Matsuo, A., Nakayama, M. and Hayashi, S. (1972) *Chem. Letters*, 341; Matsuo, A., Nakayama, M., Maeda, T., Noda, Y. and Hayashi, S. (1975) *Phytochemistry* **14**, 1037; (g) Matsuo, A. (1972) *Tetrahedron* **28**, 1203.
3. (a) Benešová, V., Samek, Z., Herout, V. and Šorm, F. (1969) *Collection Czech. Chem. Commun.* **34**, 582; (b) Benešová, V., Sedmera, P., Herout, V. and Šorm, F. (1971) *Tetrahedron Letters* 2679; (1973) *Collection Czech. Chem. Commun.* **38**, 1084; (c) Benešová, V., Herout, V. and Šorm, F. (1969) *Collection Czech. Chem. Commun.* **34**, 1810; (d) Benešová, V., Samek, Z. and Vašíčkova, S. (1975) *Collection Czech. Chem.* Commun. **40**, 1966.
4. (a) Andersen, N. H. and Huneck, S. (1973) *Phytochemistry* **12**, 1818; (b) Andersen, N. H., Costin, C. R. Kramer, C. M. Jr., Ohta, Y. and Huneck, S. (1973) *Phytochemistry* **12**, 2709; (c) Andersen, N. H., Shunk, B. and Costin, C. R. (1973) *Experientia* **29**, 645; (d) Ohta, Y., Andersen, N. H. and Liu, C.-B. (1977) *Tetrahedron* **33**, 617; (e) Andersen, N. H., Ohta, Y., Liu, C.-B., Kramer, C. M., Allison, K., and Huneck, S. (1977) *Phytochemistry* **16**, 1727.
5. Huneck, S. (1969) *J. Hattori Bot. Lab.* **32**, 1; *Misc. Bryol. et Lichenol.* **5**, 49; (1972) *J. Hattori Bot. Lab.* **36**, 1.
6. Connolly, J. D., Harding, A. E. and Thornton, I. M. S. (1972) *Chem. Commun.* 1320.
7. See note in proof (with J. C. Muller) in Knoche, H., Ourisson, G., Perold, G. W., Fousseraeu, J. and Maleville, J. (1969) *Science* **166**, 239.
8. Svensson, L. and Bendz, G. (1972) *Phytochemistry* **11**, 1172.
9. Andersen, N. H. and Falcone, M. S. (1969) *J. Chromatogr.* **44**, 52.
10. Matsuo, A., Nozaki, H., Nakayama, M., Kushi, Y., Hayashi, S., Kamijo, N., Benesova, V. and Herout, V. (1976) *J. Chem. Soc. Chem. Comm.* 1006.
11. (a) The biogenetic rationales and biomimetic interconversions have been presented: Andersen, N. H., Ohta, Y. and Syrdal, D. D. (1977) in *Bioorganic Chemistry* (van Tamelen, E. E., ed.). Vol. 2, chap. 1. Academic Press, New York; (b) Dorn, F., P., Bernasconi, P., Winter, R. E. K., Arigoni, D., Tseng, C.-L.W., Liu, C.-B., Dasher, W. E. and Andersen, N. H. (1977) manuscript in preparation.
12. Andersen, N. H., Costin, C. R. and Shaw, J. R. (1974) *J. Am. Chem. Soc.* **96**, 603; Andersen, N. H., Costin, C. R., Syrdal, D. D. and Svedberg, D. P. (1973) *ibid* **95**, 2049.
13. Nozoe, S. and Machida, Y. (1970) *Tetrahedton Letters* 2671.
14. Dr. Y. Asakawa (with J. C. Muller) independently concluded that the bazzanene structure was incorrect and Prof. Yamakawa (at the *Symposium on the Chemistry of Terpenes, Essential Oils and Aromatics*, Japan, Oct. 1975) has also arrived at a trichodiene-like structure assignment. Personal communication from Y. Asakawa.
15. Hayashi, S. and Matsuo, A. (1970) *Experientia* **26**, 347.
16. Evans, R. and Hanson, J. R. (1976) *J. Chem. Soc. Perkin I* 326; (1975) *Chem. Commun.* 231

17. Nakanishi, K. (1974) in *Natural Products Chemistry*, Vol. 1, p. 35. Academic Press, New York.
18. Andersen, N. H., Syrdal, D. D. and Graham, C. (1972) *Tetrahedron Letters* 903.
18(b). The structure of isobarbatene is now established as **iii**. The



iii

details of the structure proof appear in the Ph.D. thesis of C.-L. W. Tseng [18c].
18(c). Tseng, C.-L. W. (1976) Studies on Sesquiterpene Constituents of Liverworts, Ph.D. Thesis, University of Washington.
19. Huneck, S. and Overton, K. H. (1971) *Phytochemistry* **10**, 3279.
20. Huneck, S. (1972). Unpublished work on the diterpene constituents of various races of *Scapania undulata*.
21. Miyashita, M. and Yoshikoshi, A. (1974) *J. Am. Chem. Soc.* **96**, 1917.
22. Moore, A., Andersen, N. H. and Bottino, B. J. (1976) manuscript in preparation; see for a preliminary account: Andersen, N. H., Bottino, B. J. and Smith, S. E. (1972) *Chem. Commun.* 1193.
23. Plattier, M. and Teisseire, P. (1971) communicated at the *Fifth International Congress on Essential Oils* at Sao Paulo.
24. Plattier, M. and Teisseire, P. (1974) *Recherches* **19**, 131; Plattier ,M., Rouillier, P. and Teisseire, P. (1974) *ibid.* 145.
25. Tabacchi, R., Garnero, J. and Buil, P. (1974) *Helv. Chim. Acta* **57**, 849.
26. Regan, A. F. and Andrews, R. R. (1967) *J. Chromatog.* **31**, 209; Nigam, I. C. and Levi, L. (1966) *J. Chromatog.* **23**, 217; (1968) *ibid* **34**, 85.
27 (b) Wenninger, J. A. and Yates, R. L. (1970) *J. AOAC* **53**, 949; (b) (1969) *ibid* **52**, 1155.
28. Andersen, N. H. and Syrdal, D. D. (1972) *Tetrahedton Letters* 2455.
29. Giraudi, E., Plattier, M. and Teisseire, P. (1974) *Recherches* **19**, 205.
30. Unpublished work of A. F. Regan as quoted by Wenninger [27b].
31. Andersen, N. H. and Syrdal, D. D. (1970) *Phytochemistry* **9**, 1325.
32. Motl, O., Romanuk, M. and Herout, V. (1966) *Collection Czech. Chem. Commun.* **31**, 2025.
33. Westfelt, L. (1966) *Acta Chem. Scand.* **20**, 2841.
34. Irie, T., Yamamoto, K. and Masamune, T. (1964) *Bull. Chem. Soc. (Japan)* **37**, 1053; Ghatgey, B.-B., Razdan, R.-K. and Bhattacharyya, S. C. (1956) *Perfumery Essent. Oil Rec.* **47**, 157.
35. Herout, V. and Sykora, V. (1958) *Tetrahedron* **4**, 246.
36. (a) Burk, L. A. and Soffer, M. D. (1971) *Tetrahedron Letters* 4367; (b) Kartha, C. C., Kalsi, P. S., Shaligram, A. M., Chakravarti, K. K. and Bhattacharyya, S. C. (1963) *Tetrahedron* **19**, 241; (c) Trivedi, G. K., Chakravarti, K. K. and Bhattacharyya, S. C. (1971) *Ind. J. Chem.* **9**, 1049.
37. Sakai, T., Yoshihara, K. and Hirose, Y. (1968) *Bull. Chem. Soc. (Japan)* **41**, 1945.
38. Authentic α-ylangene was a gift from Prof. Y. Hirose (The Inst. of Food Chem., Osaka, Japan).
39. Hiroi, M. (1967) *Bull. Chem. Soc. (Japan)* **40**, 1003.
40. A comparison of the CD spectra of α-longipinene, α-copaene, and α-pinene has been published: Andersen, N. H. and Ohta, Y. (1974) *J. Chem. Soc. Chem. Commun.* 730.
41. (a) Dorn, F. (1975) Ph.D. Thesis, E.T.H. Zurich; (b) Dorn, F., Bernasconi, P. and Arigoni, D. (1975) *Chimia* **29**, 24 and refs. therein; (c) Arigoni, D. (1975) *Pure Appl. Chem.* **141**, 219.
42. Pentagova, V. A., Kashtanova, N. K., Rezvukhin, A. I. and Kolipova, E. I. (1966) *Khim Prir. Soed.* **2**, 239; in translation—*Chem. Natur. Cpds.* **2**, 193.
43. Sibirene first came to our attention from retention index data derived from Zavarin's work on *Pinus edulis* [Snajberk, K. and Zavarin, E. (1975) *Phytochemistry* **14**, 2025.]. Professor Zavarin sent an IR spectrum of this material.
44. Pyntagova, V. A., Motl, O. and Herout, V. (1961) *Collection Czech. Chem. Commun.* **26**, 1362.
45. Ayer, W. A. and Taylor, W. I. (1955) *J. Chem. Soc.* 3027.
46. Dubovenko, Zh. V., Babkin, V. A. and Pentagova, V. A. (1969) *Izv. Sib. Otd. Adak. Nauk SSSR, Ser Khim. Nauk* (4), 108.
47. β-Chamigrene was supplied by Dr. A. Yoshikoshi (Chem. Res. Inst. of Non-Aqueous Solutions, Tohoku University, Sendai, Japan). Y. Ohta supplied a sample of α-chamigrene and appropriate spectra on returning to the Inst. of Food Chen, Osaka, Japan.
48. Ohta, Y. and Hirose, Y. (1968) *Tetrahedron Letters* 2483.
49. Daeniker, H. U., Hochstetler, A. R., Kaiser, K. and Kitchens, G. C. (1972) *J. Org. Chem.* **37**, 1; Itô, S., Yatagai, J., Endo, K. and Kodama, M. (1971) *Tetrahedron Letters* 1153.
50. Robertson, J. M. and Todd, G. (1953) *Chem. Ind.* 437; Hawley, C. M., Ferguson, G. and Robertson, J. M. (1968) *J. Chem. Soc. (B)* 1255.
51. Aebi, A., Barton, D. H. R., Burgstahler, A. W. and Lindsay, A. S. (1954) *J. Chem. Soc.* 4659.
52. Warnhoff, E. W. and Srinivason, V. (1973) *Can. J. Chem.* **51**, 3955.
53. See for example: Parker, W., Roberts, J. S. and Ramage, R. (1967) *Quart. Rev.* **21**, 331. In higher plants (−)-carophyllene frequently co-occurs with (+)-longifolene [see *Selected Constants: Sesquiterpenoids*, Pergamon Press, Oxford.] Ourisson, G., Munavalli, S. and Ehret, C. (1966).
54. The (+) form of caryophyllene is reported as a natural product, but is uncommon: Pigulevskii. G. V. and Barovkov, A. V. (1963) *J. Appl. Chem.* **36**, 884.
55. Greenwood, J. M., Solomon, M. D., Sutherland, J. K. and Torre, A. (1968) *J. Chem. Soc. (C)* 3004.
56. Not the compound (**20**) usually called isolongifolene; rather the '*iso*' rearrangement product in analogy to the sativene series: McMurry, J. E. (1971) *J. Org. Chem.* **36**, 2826.
57. We thank S. Dev for authentic samples of α-, β-, and aryl-himachalene: Joseph, T. C. and Dev, S. (1968) *Tetrahedron* **24**, 3809, 3841, 3853.
58. Huneck, S. and Klein, E. (1970) *J. Hattori Bot. Lab.* **33**, 1.
59. The spectrum was kindly provided by Drs. Benesova and Herout.
60. Lipmaa, E., Pehk, T., Paasivirta, J., Belikova, N. and Plate, A. (1970) *Org. Mag. Resonance* **2**, 581. The assignments have been confirmed by LIS studies: Hawkes, G. E., Leibfritz, D., Roberts, D. W. and Roberts, J. D. (1973) *J. Am. Chem. Soc.* **95**, 1659.
61. Data from S. Gould and D. Arigoni, ETH-Zurich, personal communication.
62. From the ORD data: Jacob, G., Ourisson, G. and Rassat, A. (1959) *Bull. Soc. Chim. France* 1374.
63. Himmele, W. and Siegel, H. (1976) *Tetrahedron Letters* 907.
64. Andersen, N. H., Bottino, B. J. and Moore, A. (1974) *J. Am. Chem. Soc.* **96**, 603.
65. A non-scapanin producing race [19, 20]. Two distinct samples have been examined.
66. The initial GLC assay of the sample, prior to longipinanol removal, was: 13% α-longipinene, 2% longicyclene (+ sativene), 21% β-longipinene, 14% α-himachalene + scapanene + α-bisabolene, 4–5% β-barbatene, and 8% γ-himachalene.
67. We wish to thank E. Piers (University of British Columbia) for supplying the sample of sativene which was used for GLC and spectral comparison.
68. Andersen, N. H. and Syrdal, D. D. (1970) *Tetrahedron Letters* 2277; Marshall, J. A., Brady, S. F. and Andersen, N. H. (1974) *Prog. Chem. Nat. Prods.* **31**, 283.

69. Syrdal, D. D. (1971) Ph.D. Thesis, University of Washington.
70. Asakawa, Y., Muller, J.-C., Ourisson, G., Foussereau, J. and Ducombs, G. (1976) *Bull. Soc. Chim. France* 1465.
71. Asakawa, Y. and Aratani, T. (1976) *Bull. Soc. Chim. France* 1469.
72. Huneck, S. and Schreiber, K. (1975) *J. Hatt. Bot. Lab.* **39**, 215.
73. Asakawa, Y., Toyota, M., Uemoto, M. and Aratani, T. (1976) *Phytochemistry* **15**, 1929.