Phytochemistry, 1974, Vol. 13, pp. 1183 to 1185. Pergamon Press. Printed in England.

BICYCLOSESQUIPHELLANDRENE AND 1-EPIBICYCLOSESQUIPHELLANDRENE: TWO NEW DIENES BASED ON THE CADALENE SKELETON*

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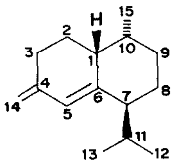
(*Received* 18 *September* 1973)

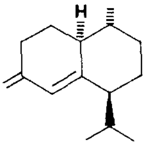
Key Word Index—*Piper cubeba*; Piperaceae; *Ocimum basilicum*; Labiatae; essential oils; sesquiterpenes; cadinadienes; bicyclosesquiphellandrene, 1-epibicyclosesquiphellandrene.

Abstract—Two new sesquiterpene hydrocarbons, bicyclosesquiphellandrene and 1-epibicyclosesquiphellandrene have been isolated from *Piper cubeba* oil and *Ocimum basilicum* oil respectively. Their structures were elucidated spectroscopically and their stereochemistry by acid rearrangement and hydrogenation studies.

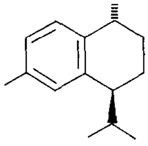
THE SESQUITERPENE hydrocarbon contents of the essential oils of both *Piper cubeba* L.[1–3] and *Ocimum basilicum* L.[4] have been studied in some detail. In a recent paper,[5] we mentioned the isolation of a cadina-4(14),5-diene from the oil of *Piper cubeba*. More recently, we found its epimer naturally occurring in the oil of *Ocimum basilicum*; consequently, we would like to report on the structural elucidation of both epimers. The nomenclatural problems pertaining to dienes based on the cadalane skeleton prompt us to propose the use of the semi-trivial names bicyclosesquiphellandrene and 1-epibicyclosesquiphellandrene for 1-β(H), 7α(H), 10β(H)-cadina-4(14),5-diene and 1α(H), 7α(H),10β(H)-cadina-4(14),5-diene respectively.



(1) Bicyclo-sesquiphellandrene



(2) 1-epi Bicyclo-sesquiphellandrene



(3) Calamenene

Bicyclosesquiphellandrene(1) isolated from *P. cubeba* and 1-epibicyclosesquiphellandrene(2) isolated from *O. basilicum* are very labile to acids. They also oxidize readily to calamenene(3). These facts plus their low concentration in essential oils (0·5% maximum in above two oils) could account for them being so elusive. Structures **1** and **2** were

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* Part XI in the series "Essential Oils and Their Constituents." For Part X see (1972) *Flavour Industry* **3**, 467.

[1] RAZDAN, R. K. and BHATTACHARYYA, S. (1955) *Perfum. Essent. Oil Rec.* **46**, 8.

[2] VONASEK, F., HEROUT, V. and SORM, F. (1960) *Coll. Czech. Chem. Commun.* **25**, 919.

[3] OHTA, Y., SAKAI, T. and HIROSE, Y. (1966) *Tetrahedron Letters* 6365.

[4] LAWRENCE, B. M., TERHUNE, S. J. and HOGG, J. W. (1971) *Flavour Industry* **2**, 173.

[5] ANDERSEN, N. H., SYRDAL, D. D., LAWRENCE, B. M., TERHUNE, S. J. and HOGG, J. W. (1973) *Phytochemistry* **12**, 827.

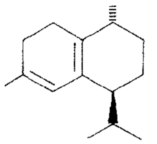
assigned to bicyclosesquiphellandrene and 1-epibicyclosesquiphellandrene respectively based on their NMR, UV and IR data (Table 1).

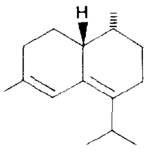
TABLE 1. SPECTRAL CHARACTERISTICS OF BICYCLOSESQUIPHELLANDRENE (**1**) AND ITS EPIMER (**2**)

	1				**2**		
NMR	δ	#H	J (cps)	Inference	δ	#H	J (Hz)
	0·67	3(*d*)	5·5	$\underline{CH_3}-CH-$	0·77	3(*d*)	7
	0·78 0·84	6(2*d*)	6	$(\underline{CH_3})_2-CH$	0·93 0·98	6(2*d*)	6
	4·58	2(*bs*)		$\underline{CH_2}=C-$	4·55 4·62	2(2*s*)	
	5·85	1(*s*)		$=C-\underline{H}C=C-$	5·92	1(*s*)	
UV	239 nm E_{max} = 11 300			Trisubstituted diene 2 Exocyclic double bonds			
IR	6·12, 6·25μ			Conjugated exocyclic diene*	6·15, 6·26 μm		

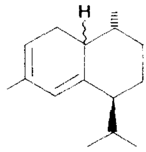
* Similar to β-phellandrene.

Under mild acid conditions, **1** produced diene **4**, zonarene(**5**) and calamenene(**3**), while under the same conditions **2** produced diene **4**, diene **6**, epizonarene **7** and calamenene. Also, when **1**, δ-cadinene (**8**), cubenene (**9**) and α-muurolene (**10**) are fully hydrogenated one product (alkane **11**) common to all four was isolated. This common alkane must have, therefore, the stereochemistry shown in structure **11** and **1** must also have this same stereochemistry at the 1, 7 and 10 positions. On hydrogenation of **2**, one product (dissimilar to **11**) isolated was the same as a hydrogenation product from δ-cadinene and cubenene. This confirms the stereochemistry at the 7 and 10 positions.

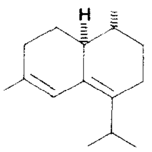

(**4**)



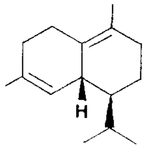
(**5**) Zonarene



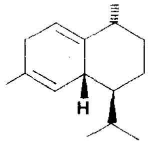
(**6**)



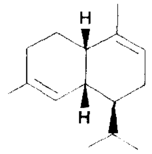
(**7**) 10-epi Zonarene



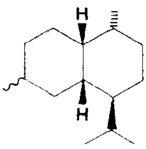
(**8**) δ-Cadinene



(**9**) Cubenene



(**10**) α-Muurolene



(**11**)

A second hydrogenation product was isolated from **2** which was the same as a hydrogenation product from *epi*-zonarene which confirms the stereochemistry at the 1 and 10 positions. Thus with this and the previous evidence the stereochemistry of **II** is established.

EXPERIMENTAL

The methods used for hydrogenation[6] and isolation[7] have been described previously. All identifications were made by IR and confirmed by GC retention times. The NMR spectra were run on 1% solutions in CCl_4 on a Varian Aerograph 60 MHz spectrometer (**1**) or VA 220 MHz (**2**).

Acid rearrangements. Bicyclosesquiphellandrene (**1**) was heated for 1 hr at 50° in 0·012 N.HCl–80% aq. dioxan to give diene **4** (80%), zonarene (**5**) (10%), calamenene **3** (5%) with 5% of unreacted starting material. Under similar conditions, 1-epibicyclosesquiphellandrene (**2**) produced 10-epizonarene (**7**) (36%), diene (**4**) (23%), diene (**6**) (21%), calamenene (**3**) (6%) with 14% of unreacted starting material.

[6] LAWRENCE, B. M. and HOGG, J. W. (1968) *Perfum. Essent. Oil Rec.* **59**, 515.

[7] LAWRENCE, B. M. (1971) *Can. Inst. Food Technol. J.* **4**, A44.