Phytochemistry, 1970, Vol. 9, pp. 1341 to 1343. Pergamon Press. Printed in England.

SESQUITERPENES—IDENTIFICATION OF DEHYDROGENATION PRODUCTS

NIELS H. ANDERSEN, MARK S. FALCONE* and DANIEL D. SYRDAL†

Department of Chemistry, University of Washington, Seattle, Washington 98105, U.S.A.

(*Received* 29 *July* 1969)

Abstract—Highly reproducible GLC retention data for common sesquiterpene dehydrogenation products are presented. The composition of the sesquiterpene portions of ginger oil, cade oil, celery seed oil, vetiver oil, technical guaiene, and the leaf oil of *Chamaecyparis nootkatensis* has been studied by small-scale dehydrogenation coupled with GLC analysis. The absence of eudalene from the mixture obtained from *C. nootkatensis* confirms our contention that the leaf oil contains (in contrast to the wood oil[1]) no selinenes or nootkatenes.[2]

INTRODUCTION

THE DEHYDROGENATION of sesquiterpenes from plant sources has long been an important step in ascertaining the carbon skeletons of these substances. The resulting naphthalenes and azulenes have generally been characterized as crystalline adducts, e.g. picrates and trinitrobenzene adducts. With the increased use of preparative GLC and TLC, new sesquiterpenes are often isolated in milligram quantities only. The usual dehydrogenation procedures and methods for isolation and identification cannot readily be extended to the small scale required. A previous report[3] indicated that these products are readily resolved by GLC; however, the relative retention data presented could not be reproduced adequately.‡ In this communication we present simple procedures for small-scale dehydrogenations together with self-consistent retention indices[5] for the commonly encountered products.

RESULTS

Sesquiterpene fractions of essential oils were dehydrogenated at 220–320° using both sulfur and selenium as dehydrogenating agents. The structures of the dehydrogenation products were confirmed by NMR spectroscopy. GLC retention data are collected in Table 1.

The following essential oil fractions were dehydrogenated: (*a*) cadinene fraction of oil of cade, (*b*) selinene fraction of celery seed oil (~90 per cent β-selinene), (*c*) sesquiterpene hydrocarbon fraction of ginger oil, (*d*) technical guaiene, (*e*) whole oil of vetiver (Reunion), and (*f*) sesquiterpene fraction of the leaf oil of *Chamaecyparis nootkatensis*.[2] Sample (*a*) and (*b*) afforded pure cadalene and eudalene respectively. Sample (*c*) afforded α-curcumene

* Undergraduate Honors Research Participant.

† National Science Foundation Predoctoral Fellow, 1968–1969.

‡ We have generally observed that literature relative retentions and even Kovats' indices obtained in the usual way[4] cannot be reproduced. The preceding communication[2] includes a comparison of literature data for monoterpenes with those obtained in our laboratories.

[1] H. ERDTMAN and T. NORIN, *Fortschr. Chem. organ. Naturstoffe* **24**, 206 (1966).
[2] N. H. ANDERSEN and D. D. SYRDAL, *Phytochem.* **9**, 1325 (1970).
[3] I. C. NIGAM and L. LEVI, *J. Chromatog.* **17**, 466 (1965).
[4] E. KOVATS, *Helv. Chim. Acta* **41**, 1915 (1958).
[5] N. H. ANDERSEN and M. S. FALCONE, *J. Chromatog.* **44**, 52 1969.

TABLE 1. GLC RETENTION DATA FOR SESQUITERPENE DEHYDROGENATION PRODUCTS

Standards	DEGS* 200°		Apiezon L 195°	
	RR†	I‡	RR†	I§
Acenaphthene	1·001	2634	0·529	1590·6
Fluorene	1·746	2837	0·806	1686·4
"Sesquiterpenes"	0·08–0·21		0·27–0·56	
α-Curcumene	0·201		0·354	1497·5
1,6-Dimethylnaphthalene‖	0·632	2465	0·499	1576·0
Eudalene	0·719	2512	0·624	1627·1
Cadalene	1·000	2633	1·000	1735·5
S-Guaiazulene	1·760	2840	1·550	1835·7
Chamazulene	1·793	2847	1·360	1805·8
Se-Guaiazulene	1·913	2870	1·675	1853·0
Vetivazulene	2·095	2904	1·775	1866·6

* Diethylene glycol succinate as stationary phase, retain aromatic and polar compounds strongly.
† ± 0·7%. ‡ ±2 units. § ±0·8 units.
‖ Assignment suggested by data in Ref. 3.

and cadalene. Sample (*d*) afforded guaiazulene (S- or S- + Se- depending on the dehydrogenating agent used) together with the small amounts of eudalene and very minor amounts of cadalene.

The Reunion vetiver oil sample (*e*) afforded eudalene, cadalene, 1,6-dimethylnaphthalene, S-guaiazulene, and vetivazulene in the ratio 54:26:11:5:4. The known constituents of this oil[6] account for the formation of eudalene and vetivazulene, but no known components can account for the formation of cadalene (and 1,6-dimethylnaphthalene, a cracking product of cadalene) and S-guaiazulene. A detailed study of this oil is in progress.

Sample (*f*) was included in this study in order to confirm the results presented in the preceding paper. In that paper we report a rather detailed analysis of the sesquiterpene hydrocarbon portion of this oil, in which we isolated fourteen sesquiterpenes, three of which remain unidentified.[2] However, no eudesmane (selinane) or nootkatane derivatives were isolated. This stands in sharp contrast to recent reports which indicate that nootkatene, nootkatone, and valencene are major constituents of the heartwood oil of this species.[1,7] GLC analysis of the leaf oil indicates that valencene and nootkatene¶ cannot be detected in the oil.[2] However, we were not able to eliminate the possibility that some of the minor components are eudesmane or nootkatane sesquiterpenes from the data available. Dehydrogenation of a representative sample of the sesquiterpene fraction produced a mixture of α-curcumene, 1,6-dimethylnaphthalene, cadalene, an unknown product (see Experimental) and no eudalene. As little as 0·15 per cent of eudalene could have been detected. We therefore conclude that *C. nootkatensis* leaf oil is, in fact, devoid of selinenes and nootkatenes.

EXPERIMENTAL

The GLC analytical methods used have been described in detail.[5] The retention indices are self-consistent (determined using aromatic compounds as standards).

¶ Nootkatene was isolated from Reunion vetiver oil, unpublished work.

[6] N. H. ANDERSEN, *Phytochem.* **9**, 145 (1970).
[7] W. D. MACLEOD, JR., *Tetrahedron Letters* 4779 (1965).

*Dehydrogenation Procedures**

Dehydrogenations with S (0·1 g) were performed in 3–10 volumes of triglyme at reflux for 2 hr. The reaction mixtures were diluted with light petroleum ether and washed repeatedly with water, 85% aq. H_3PO_4, water, 10% aq. NaOH, and saturated brine. The dried (Na_2SO_4) solutions were filtered through alumina (Woelm, basic, activity I–II) prior to examination by NMR and GLC. The azulenes were isolated from the phosphoric acid layers with petroleum ether after the addition of water.

Dehydrogenations with Se (0·5–2·0 g, large excess) were carried out at 260–320° for 30 min without added solvent. The petroleum ether soluble products were chromatographed on 10 g of alumina (Woelm, basic, activity I). The eluted material was examined by NMR and GLC. Blue fractions were further purified (for the isolation of azulenes) by repeated extraction and reisolation using petroleum ether and aqueous phosphoric acid.

Authentic Samples

S-Guaiazulene was supplied by Givaudan Corporation. Chamazulene was isolated from whole oil of chamomile (Hungarian) by repeated extraction with 85% aq. H_3PO_4 and reisolation with petroleum ether after the addition of water. The resulting concentrate afforded pure chamazulene (NMR, u.v.) after chromatography on basic alumina. α-Curcumene was isolated from the oil of *Curcuma aromatica*.

Dehydrogenation of Chamaecyparis nootkatensis *Sesquiterpenes*

The sesquiterpene fraction (0·03 g)† of the leaf oil of *C. nootkatensis*[2] was refluxed with S (0·01 g) in 5 ml of triglyme. After 4 hr, the reaction mixture was cooled and processed as above giving the dehydrogenation product mixture. GLC analysis (DEGS and Apiezon L columns) indicated minor amounts of unreacted sesquiterpenes and the following dehydrogenation products: α-curcumene (29,‡ 19%), 1,6-dimethylnaphthalene (10,‡ 5%), eudalene (<0·5, <0·15§%), cadalene (24, 26%), and an unknown component‖ (33, 40%).

Acknowledgements—The authors are grateful to Fritzsche Brothers, Inc. and Givaudan Corp. for samples of essential oils and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work (PRF No. 1586-G1).

* Written for a 0·25 g sample of sesquiterpene, applicable to 0·01–3 g scale.

† Made up from a variety of samples; GLC indicates that all components encountered are present in this sample.

‡ On the Apiezon-L column unreacted sesquiterpenes frequently coincide with these products thus vitiating this analysis.

§ Absolute maximum value. Eudalene occurs at RR (DEGS) 0·719. The product from *C. nootkatensis* contains a 1·6% impurity at RR (DEGS) 0·698. Co-injection with authentic eudalene indicated that as little as 0·15% (<10% relative to the impurity peak) could be detected as a distinct shoulder on the impurity peak at RR (DEGS) 0·698.

‖ RR (Apiezon-L) = 1·225, RR (DEGS) = 1·315.