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SESQUITERPENE HYDROCARBONS FROM *LENTINUS LEPIDEUS*

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Key Word Index—*Lentinus lepideus*; Basidiomycetes; volatile metabolites; sesquiterpene hydrocarbons; fungal terpenoids.

Abstract—Several sesquiterpene hydrocarbons, mainly of the cadinane skeleton, have been identified in cultures of the brown rot fungus *Lentinus lepideus*. The main compounds are δ-cadinene, α- and γ-muurolene.

INTRODUCTION

Lentinus lepideus Fr. has been investigated in regard to the production of metabolites formed via the Shikimate Pathway [1]. Under suitable culture conditions, certain strains of this brown rot fungus produce not only volatile cinnamate derivatives, but also terpenes [2]. In the present paper, the identification of several sesquiterpene hydrocarbons from cultures of the strain FPRL 7B after cultivation on a defined synthetic medium containing *iso*-leucine as sole nitrogen source is reported. The main components are compounds with a cadinane structure. Though relatively widespread in the Plant Kingdom, these compounds are described for the first time as fungal metabolites.

RESULTS AND DISCUSSION

L. lepideus FRPL 7B was cultivated on a glucose–*iso*-leucine–mineral salt medium. The steam distillate mainly consisted of sesquiterpene hydrocarbons, oxygenated sesquiterpenes, and 2-methyl butan-1-ol obviously deriving from *iso*-leucine metabolism [3]. The sesquiterpene hydrocarbon fraction was separated by dry-CC using pentane as solvent [4].

More than 25 compounds were characterized as sesquiterpene hydrocarbons by their GC/MS data. The components with a quota of more than 1% of the total hydrocarbon fraction are listed in Table 1. The major compound was δ-cadinene (31.1%), followed by α-muurolene (21.2%) and γ-muurolene (14.9%). Other components with a cadinane structure were cadina-1,4-diene (1.6%) and calacorene (4.8%). As calacorene was present, peak 25 (7.1%) with m/z 202 $[M^+]$ was presumed to be calamenene. The literature data [5] for this compound, however, did not accord with those of peak 25. Besides sesquiterpenes of the cadinane typus, acyclic (*trans*-β-farnesene, 5.0%) and tricyclic (α-copaene, 1.9%) terpenes were identified.

With the exception of *trans*-β-farnesene, previously described as a metabolite of *Cronartium fusiforme* [6], these sesquiterpene hydrocarbons have been identified for the first time in fungi. The identification of the oxygenated sesquiterpenes will be the subject of a further communication.

Table 1. Sesquiterpene hydrocarbons from *L. lepideus*

Peak no.*	Compound	Means of identification§	% Hydrocarbon fraction
1	α-Copaene‡	MS, R_t	1.9
8	$C_{15}H_{24}$	MS	1.9
13	α-elemene?‡	MS	7.3
14	*Trans*-β-farnesene†	MS, R_t	5.0
15	γ-Muurolene‡	MS, R_t, IR	14.9
17	α-Muurolene‡	MS, R_t, IR	21.2
19	δ-Cadinene‡	MS, R_t, IR	31.1
20	Cadina-1,4-diene‡	MS, R_t	1.6
23	Calacorene‡	MS, R_t	4.8
25	$C_{15}H_{22}$	MS	7.1

*Order on Carbowax 20 M.

†Newly identified in *L. lepideus*.

‡Newly identified in fungi.

§MS: Mass spectral data identical with authentic material and literature data, respectively [5]; R_t: Retention time identical with authentic material on columns of different polarity; R_t identical; IR: IR spectral data identical with literature data [7].

EXPERIMENTAL

Cultivation. L. lepideus FPRL 7B (Forest Products Research Laboratory, Princes Risborough, U.K.) was cultivated on a defined synthetic medium containing glucose (2%), *iso*-leucine (0.15%), and mineral salts [3] for 90 days.

Identification of sesquiterpene hydrocarbons. The volatile metabolites were obtained by circulation steam distillation [8] in pentane. The hydrocarbon fraction was separated from the more polar components by modified dry-CC [4]. The identification resulted from GC/MS data by comparison with lit. data [5], and retention time comparison of R_t values, and comparison with commercial essential oils of well-known composition (e.g. copaiva balsam), respectively. Preparation of single components for IR by prep. TLC is described in ref. [3]; IR spectral data were compared with lit. data [7]. GC conditions are described in [9], using additionally capillary columns (Carbowax 20 M) of different lengths, and a computing integrator.

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REFERENCES

1. Sprecher, E. (1961) *Arch. Microbiol.* **38**, 299.
2. Sprecher, E. (1980) *Pharm. Ztg.* **125**, 1008.
3. Hanssen, H.-P. (1979) Dissertation, Hamburg.
4. Kubeczka, K.-H. (1973) *Chromatographia* **6**, 106.
5. Stenhagen, E., Abrahamsson, S. and McLafferty, F. W. (1976) *Registry of Mass Spectra Data.* Wiley & Sons, New York.
6. Laseter, J. L., Weete, J. D. and Walkinshaw, C. H. (1973) *Phytochemistry* **12**, 387.
7. Wenninger, J. A., Yates, R. L. and Dolinsky, M. (1967) *JAOAC* **50**, 1313.
8. Sprecher, E. (1963) *Dtsch. Apoth. Ztg.* **103**, 213.
9. Sprecher, E., Kubeczka, K.-H. and Ratschko, M. (1975) *Arch. Pharm.* **308**, 843.

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SESQUITERPENES AND NORSESQUITERPENES FROM *PECHUEL-LOESCHEA LEIBNITZIAE*[*]

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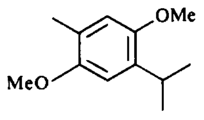
Key Word Index—*Pechuel-Loeschea leibnitziae*; Compositae; Inuleae; sesquiterpenes; guaiene derivative; norsequiterpenes; guaianolide.

Abstract—The aerial parts of *Pechuel-Loeschea leibnitziae* afforded, in addition to thymohydroquinone dimethyl ether, sitosterol and stigmasterol, xerantholide and its probable precursor, the 11,13-dihydro derivative methyl pechueloate and two norsequiterpenes, probably formed by degradation of the corresponding sesquiterpene acid. Two eudesmane derivatives were also isolated. The chemotaxonomy of *Pechuel-Loeschea* is discussed briefly.

INTRODUCTION

The monotypic genus *Pechuel-Loeschea* has not been investigated chemically. This genus was included in *Pluchea* [1], but was later maintained to be a separate genus [2, 3]. It was of interest, therefore, to see whether the chemistry supports a separation from *Pluchea* or not.



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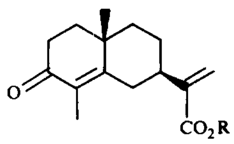

2a R = H

2b R = Me

RESULTS AND DISCUSSION

The roots of *P.-L. leibnitziae* (Kuntze) O. Hoffm. gave only thymohydroquinone dimethyl ether (**1**). Whilst the aerial parts afforded it as the main compound, stigmasterol, sitosterol, the acid **2a** [4], the corresponding methyl ester **2b** and the isomeric ester **3** were also produced. The structure of compound **3** followed from the ^{1}H NMR data (Table 1). The

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[*] Part 424 in the series "Naturally Occurring Terpene Derivatives". For Part 423 see Bohlmann, F., Jakupovic, J. and Vogel, W. (1982) *Phytochemistry* **21**, 1153.