Biotransformations of Terpenes by Fungi from Amazonian *Citrus* Plants

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The biotransformations of (*RS*)-linalool (**1**), (*S*)-citronellal (**2**), and sabinene (**3**) with fungi isolated from the epicarp of fruits of *Citrus* genus of the Amazonian forest (*i.e.*, *C. limon*, *C. aurantifolia*, *C. aurantium*, and *C. paradisiaca*) are reported. The more active strains have been characterized, and they belong to the genus *Penicillium* and *Fusarium.* Different biotransformation products have been obtained depending on fungi and substrates. (*RS*)-Linalool (**1**) afforded the (*E*)- and (*Z*)-furanlinalool oxides (**7** and **8**, resp.; 39 and 37% yield, resp.) with *Fusarium* sp. (1D2), 6-methylhept-5-en-2-one (**4**; 49%) with *F. fujikuroi*, and 1-methyl-1-(4-methypentyl)oxiranemethanol (**6**; 42%) with *F. concentricum*. (*S*)-Citronellal (**2**) gave (*S*)-citronellol (**12**; 36–76%) and (*S*)-citronellic acid (**11**; 5–43%) with *Fusarium* species, while diastereoisomeric *p*-menthane-3,8-diols **13** and **14** (20 and 50% yield, resp.) were obtained as main products with *Penicillium paxilli*. Finally, both *Fusarium* species and *P. paxilli* biotransformed sabinene (**3**) to give mainly 4-terpineol (**19**; 23–56%), and (*Z*)- and (*E*)-sabinene hydrates (**17** (3–21%) and **18** (11–17%), resp.).

1. Introduction. – Terpenes are secondary metabolites of plants and are produced both for the defence against microorganisms and insects, and for their pollinator-attractive properties [1]. In mammals, terpenes are involved in stabilizing cell membrane, in metabolic pathways, and they act as regulators in some enzymatic reactions [2]. In particular, mono- and sesquiterpenes are the major constituents of essential oils and are widely used in the perfumery industry. Moreover, terpenes are good starting materials for the synthesis of fine chemicals [3], and, in particular, they are employed to produce flavorings [4][5]. On the other hand, the application of terpenes as fragrances and flavors depends on the absolute configuration of the compounds, since the enantiomers present different organoleptic properties. In this field, the biotransformations allow the regio- and stereoselective production of compounds under mild conditions [2][6].

The use of microorganisms in terpene biotransformations is relatively recent. Various fungal and bacterial strains have been employed in order to obtain new fragrances, and new strains are continuously selected based on their ability to biotransform terpenes [6]. While various microbial and plant cells are able to biotransform linalool (*i.e.*, *Aspergillus niger* [7–9], *Botrytis cinerea* [9], *Corynespora cassicola* [9], *Diplodia gossipina* [10], *Debaryomyces* sp. [11], *Kluyveromyces* sp. [11], and *Pichia* sp. [11]) and citronellal (*i.e.*, *Saccharomyces cerevisiae* [12][13], *Pseudo-*

monas aeruginosa [14], *Rhodotorula minuta* [15], *Petroselinum crispum* [16], and *Solanum aviculare* [17]), the biotransformations of sabinene have not been studied.

Since these terpenes are significantly present in the essential oils obtained from the leaves of the plants of *Citrus* genus that are used in cosmetology, their possible biotransformations could be applied successively to the essential oils in order to improve their properties.

In this article, the isolation of 33 fungi (*Table 1*) from the epicarp of fruits of *Citrus* genus (*i.e.*, *C. limon*, *C. aurantifolia*, *C. aurantium*, and *C. paradisiaca*) harvested from three Achuar communities[1]) (*i.e.*, Wasakentsa, Pumpuentsa, and Sewastian) of the Amazonian forest (Ecuador, Province of Morona-Santiago), and their activities to biotransform (*RS*)-linalool (**1**), (*S*)-citronellal (**2**), and sabinene (**3**) are reported.

Table 1. *Fungi from Fruits of* Citrus *Genus of the Amazonian Forest* (Ecuador)

Plant	Origin	Fruit	Fungi
Citrus aurantifolia	Pumpuentsa	1A	1A5
		2A	2A2, 2A17
	Wasakentsa	1B	1B5, 1B7, 1B13, 1B14, 1B18, 1B20, 1B23, 1B24
		2B	2B4
Citrus limon	Wasakentsa	1C	1C3, 1C4, 1C5, 1C19, 1C21, 1C22
Citrus paradisiaca	Wasakentsa	1D	1D2, 1D4, 1D6
		2D	2D1, 2D2, 2D4, 2D7, 2D10, 2D15, 2D17
Citrus aurantium	Sewastian	1F	1F1, 1F2, 1F5, 1F6, 1F9

2. Results and Discussion. – 2.1. *Biotranformation Screening of Linalool* (**1**). The biotransformation screening with fungi was carried out on analytical scale adding the substrate (1 g l^{-1}) to the cultures grown at 28–30° for 5 d. The reaction mixtures were analyzed by GC-FID, and the products were characterized by GC/MS. The results obtained with linalool (**1**) are compiled in *Table 2* and *Scheme 1*.

Only eleven fungi were able to biotransform linalool (**1**). Some strains (*i.e.*, 1B14, 1B24, 1C21, and 2D7) afforded 6-methylhept-5-en-2-one (**4**; 4–62%), obtained by a loss of vinyl moiety, but only the strain 1B14 gave its reduction product 6-methylhept-5-en-2-ol (**5**; 8%). The heptenone **4** has been reported to be obtained by biotransformation with *B. cinerea* [18][19], while the heptenol **5** has not been previously detected.

The other fungi produced a mixture of (*E*)-furanlinalool oxide (**7**; 10–49%), (*Z*)-furanlinalool oxide (**8**; 8–46%), (*E*)-pyranlinalool oxide (**9**; 1–16%), and (*Z*)-pyranlinalool oxide (**10**; 1–2%) in variable amounts. A similar distribution of products have been obtained with *Aspergillus* strains [8]. In GC-FID spectra, however, traces (<1%) of their precursor (*i.e.*, 6,7-epoxylinalool) [7] were present. Together with the

[1]) The Achuar territory represents one of the last primary forests that connect the Andes with the Amazon forests of Peru and Brazil.

Table 2. *Screening of Biotransformation of (*RS*)-Linalool* (**1**) *with Fungi* (analytical scale)

Fungi	Biotransformation products, yield [%][a])							
	1	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1B14	30	62	8					
1B24	71	29						
1C5	17			29	36		16	2
1C21	92	8						
1D2	2				49	46	1	2
1D4	2				46	45	3	4
1D15	55			45				
2D7	–	4		2	47	45	1	1
1F1	80				10	8	1	1
1F2	41			2	29	25	1	2
1F9	78			22				

[a]) Yields obtained from GC-FID.

mixture of rearranged compounds **7**–**10**, some fungi (*i.e.*, 2D7, 1F2, 1C5, and 1F9) furnished the 1-methyl-1-(4-methylpentyl)oxiranemethanol (**6**; 2–45%), which was, however, the only product obtained with the fungus 1D15 (45%).

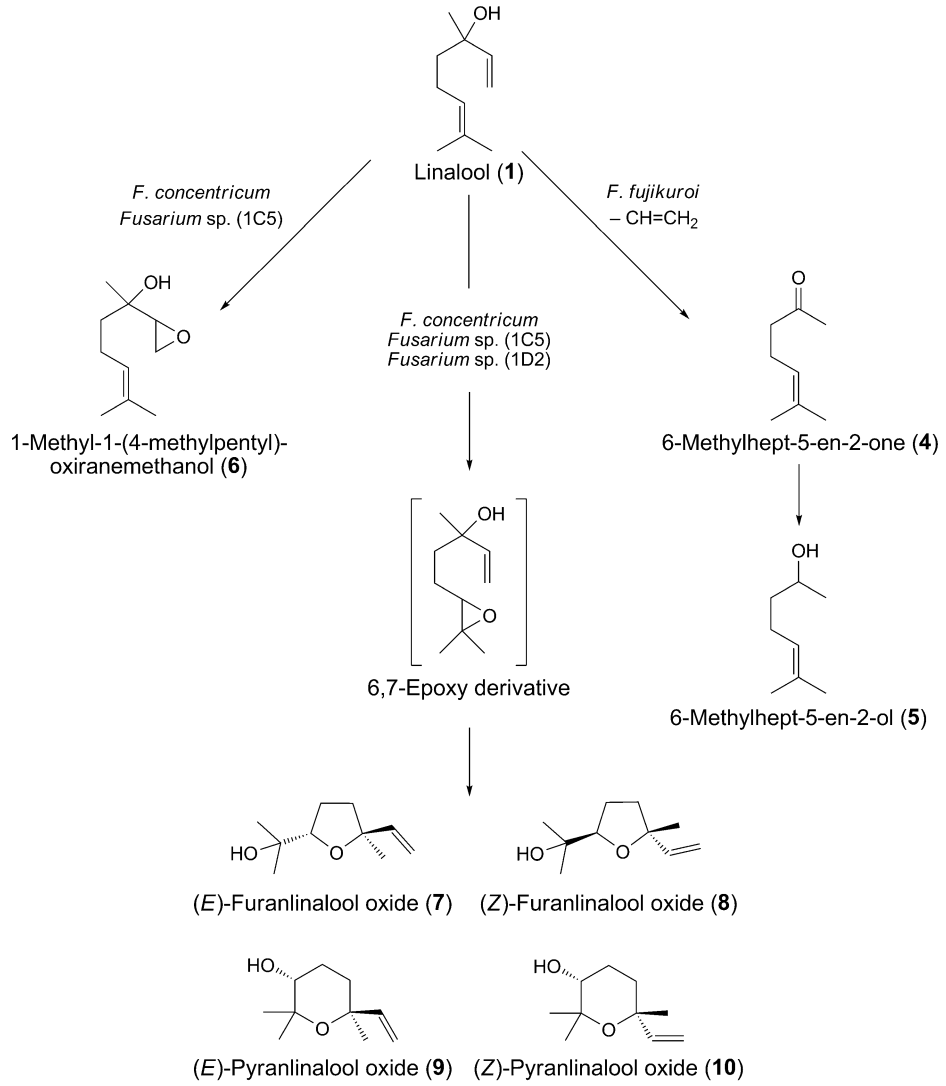
2.1. *Biotranformation Screening of (*S*)-Citronellal* (**2**). Almost all the strains showed a high aptitude to biotransform (*S*)-citronellal (**2**; *Table 3* and *Scheme 2*).

Almost all strains produced the reduction product (*S*)-citronellol (**12**) in high yields (>50%) and, in some cases, in quantitative yields (*i.e.*, 2A17, 1B20, and 2D15) as previously observed with various microorganisms [12][13][20][21], germinating wheat seed [22], and tissue cultures of *Petrosellinum crispum* [16]. Many strains gave also the oxidation product (*S*)-citronellic acid (**11**), although in lower yields (4–62%). On the other hand, the strain 1D6 produced the mixture of the diastereoisomers (1*S*,3*S*,4*S*)-*p*-menthane-3,8-diol (**13**; 25%) and (1*S*,3*R*,4*S*)-*p*-menthane-3,8-diol (**14**; 62%) obtained by ring closure and subsequent addition of H_2O. The yields of compounds **13** and **14** are very remarkable when compared with those obtained with *Solanum aviculare* [17]. Both compounds **13** and **14** were also obtained with other strains (*i.e.*, 1B18, 1B24, 2B4, 1C3, 1C22, 1C4, 1D4, 2D1, and 2D4) in variable yields (5–25% and 5–60%, resp.). Also (1*S*,3*S*,4*R*)-isopulegol (**15**; 1%) and (1*S*,3*R*,4*R*)-isopulegol (**16**; 2–13%) were obtained as minor products by ring closure and proton exchange. The strains 2D4 and 1D4 gave the best yields of the isopulegol **16** (12 and 13%, resp.). A similar behaviour was reported with *Solanum aviculare* [17].

2.3. *Biotranformation Screening of Sabinene* (**3**). Only nine strains gave biotransformation products with sabinene (**3**; *Table 4* and *Scheme 3*).

In all cases, 4-terpineol (**19**; 3–74% yield) was the main product, with poor yields of (*Z*)-sabinene hydrate (**17**; 1–3%) and (*E*)-sabinene hydrate (**18**; 1–5%). The most interesting strain was 1C22 that, together with high yield of **19** (74%) and low yield of **17** (3%) and **18** (2%), furnished traces of other metabolites such as (*Z*)-*p*-menth-2-en-1-ol (**21**; 1%), (*E*)-*p*-menth-2-en-1-ol (**22**; 1%), and α-terpineol (**20**; 1%). All of the products were obtained by an initial protonation of the C=C bond to give a *Thuile*

Scheme 1. *Biotransformation Products of* (RS)*-Linalool* (**1**)



carbocation **A** that is in equilibrium with the terpinen-4-yl cation **B**, the α-terpinyl cation **C**, and finally with the phellandrenyl cation **D**. All carbocations, upon addition of H_2O, give the biotransformation products **17**–**22**. This proposed mechanism for the biotransformations was observed in biosynthetic pathways [23][24].

2.4. *Identification of Fungi.* The fungi 1B14, 1C5, 1C22, 1D2, and 2D15 have been chosen as representatives of the phenotypes isolated from different origins and as producers of different biotransformation products. They have been identified by *CBS* as belonging to *Fusarium* and *Penicillium* genera (*Table 5*).

Table 3. *Screening of Biotransformation of (*S*)-Citronellal* (**2**) *with Fungi* (analytical scale)

Fungi	Biotransformation products, yield [%][a])						
	2	**11**	**12**	**13**	**14**	**15**	**16**
2A17	–		100				
1B5	–	36	64				
1B13	1	16	83				
1B14	–	55	45				
1B18	1	7	57	8	25		2
1B20	–		100				
1B23	–	62	38				
1B24	1		63	5	31		
2B4	3	15	40	15	27		
1C3	–		51	12	35		2
1C4	–	4	23	19	50		4
1C5	–	22	69		9		
1C19	–	16	84				
1C21	2	12	86				
1C22	–		10	25	60	1	4
1D2	–	16	84				
1D4	–		11	21	55		13
1D6	11			25	62		2
1D15	–		100				
2D1	10	28	2	11	45		4
2D2	17		68		7		8
2D4	2		11	20	53	2	12
2D7	23		43		34		
2D10	1	11	81		5		2
2D17	26		74				
1F1	1	24	75				
1F2	3	19	74				4
1F9	17	11	72				

[a]) Yields obtained from GC-FID.

In particular the fungi 1C5 and 1D2, identified as *Fusarium* sp., are new species although very close to *F. concolor* REINKING, showing an identical ribosomal ITS but with different EF (elongation factor 1α) sequence.

2.5. *Biotransformation of Terpenes* **1**–**3** *with* Penicillium *and* Fusarium *sp.* The biotransformations of (*RS*)-linalool (**1**), (*S*)-citronellal (**2**), and sabinene (**3**) were repeated on preparative scale with the selected and identified fungi, and the products were isolated by chromatography and characterized (GC/MS, and ^{1}H- and ^{13}C-NMR).

The biotransformation of linalool (**1**) with *F. fujikuroi* gave 6-methylhept-5-en-2-one (**4**; 49%) and 6-methylhept-5-en-2-ol (**5**; 10%; *Table 6*), arising from the degradation of C(1)–C(2) chain ($\rightarrow$**4**) and the subsequent reduction of CO function ($\rightarrow$**5**) (*Scheme 1*). The other *Fusarium* species, however, afforded oxidation products. The 1,2-epoxy derivative **6** was obtained in appreciable yield (42%, with *F. concentricum* and 22% with *Fusarium* sp. (1C5)), while the 6,7-epoxy derivative has been described as the intermediate through which the biotransformations of linalool

Scheme 2. *Biotransformation Products of (*S*)-Citronellal* (**2**)

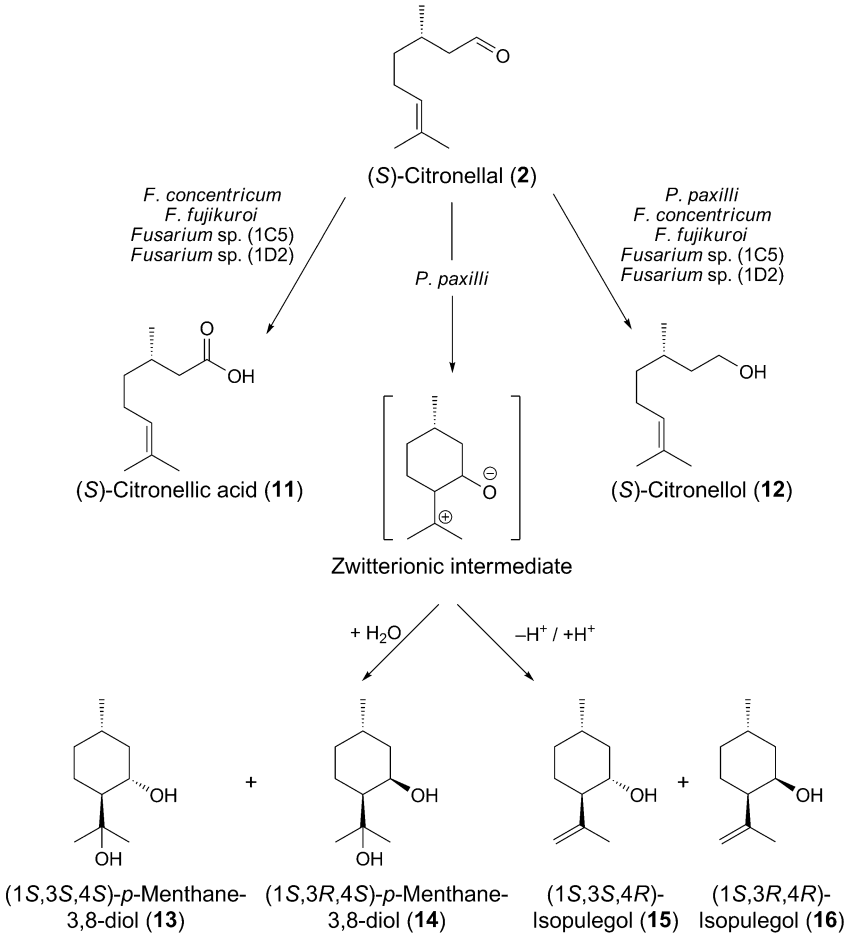
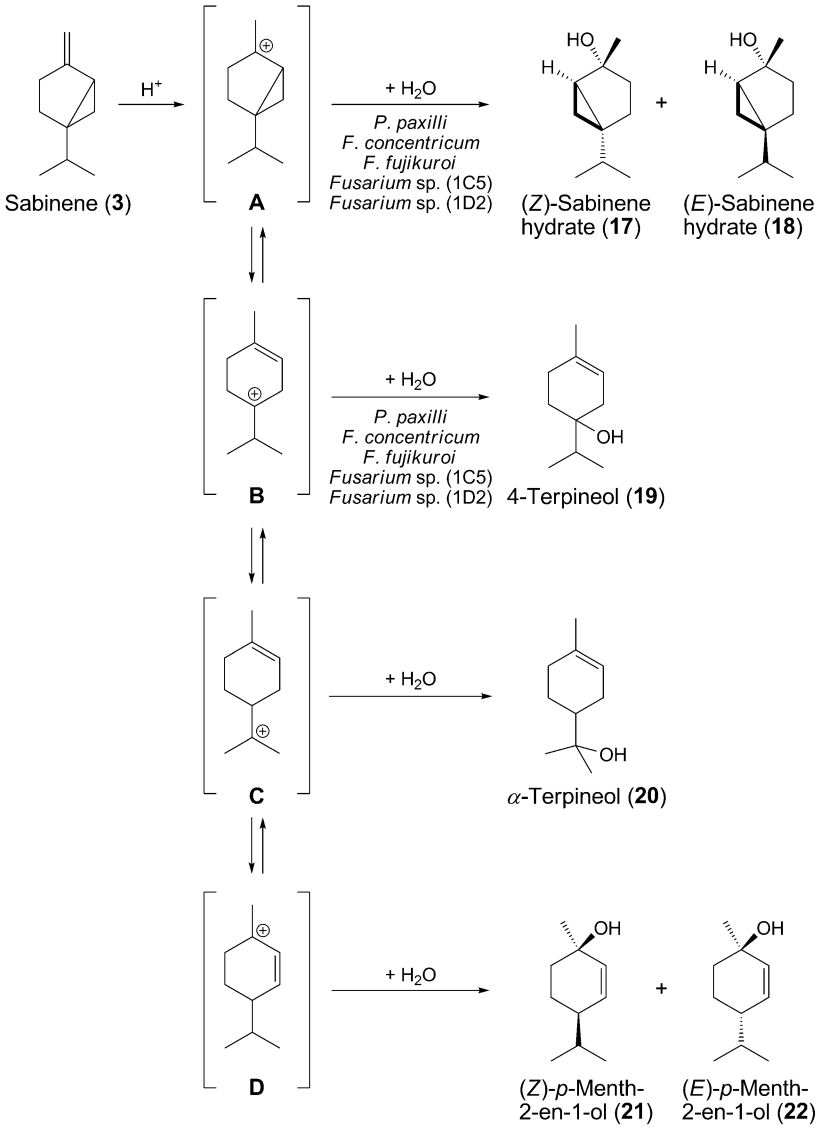


Table 4. *Screening of Biotransformation of Sabinene* (**3**) *with Fungi* (analytical scale)

Fungi	Biotransformation products, yield [%][a])						
	3	**17**	**18**	**19**	**20**	**21**	**22**
1B14	86	3	2	9			
1B24	81	3	3	13			
1C5	77	3	3	17			
1C22	18	3	2	74	1	1	1
1D2	82	3	5	10			
1D6	95		1	3		1	
2D1	85	1	1	13			
2D4	89	2	2	7			
2D7	86	1	1	12			

[a]) Yields obtained from GC-FID.

Scheme 3. *Biotransformation Products of Sabinene* (**3**)



can afford the diasteroisomeric furan- and pyranlinalool oxides **7**–**10** [7–9]. In our case, *Fusarium sp.* (1C5) gave (*E*)-furanlinalool oxide (**7**; 32%), lower amounts of (*E*)-pyranlinalool oxide (**9**; 12%), and traces of (*Z*)-pyranlinalool oxide (**10**; 1%), while *Fusarium sp.* (1D2) produced practically equimolar amounts of **7** (39%) and (*Z*)-furanlinalool oxide (**8**; 37%). The different behavior of the 1C5 and 1D2 strains confirmed their different identity. As observed on analytical scale, no biotransforma-

Table 5. CBS[a]) *Characterization of Fungi*

Fungus	Plant	Identification
1B14	*Citrus latifolia*[b])	*Fusarium fujikuroi* NIRENBERG
1C5	*Citrus limon*[b])	*Fusarium* sp.[c])
1C22	*Citrus limon*[b])	*Penicillium paxilli* BALNIER
1D2	*Citrus paradisiaca*[b])	*Fusarium* sp.[d])
2D15	*Citrus paradisiaca*[b])	*Fusarium concentricum* NIRENBERG & O'DONNELL

[a]) *Central Bureau voor Schimmelcultures*, Utrecht, The Netherlands. [b]) From Wasakentsa. [c]) Close to *Fusarium concolor* REINKING. [d]) Close to *Fusarium concolor* REINKING. This strain is identical to strain 1C5 with regard to the nucleotide sequence of the ribosomal ITS but somewhat different in the EF (elongation factor 1α) sequence.

Table 6. *Biotransformations of Terpenes* **1**–**3** *with* Penicillium *and* Fusarium *Strains*

Fungi	Terpene	Products (yields [%])						
P. paxilli	**1**							
F. fujikuroi	**1**	**4** (49)	**5** (10)					
F. concentricum	**1**			**6** (42)				
Fusarium sp. (1C5)	**1**			**6** (22)	**7** (32)		**9** (12)	**10** (2)
Fusarium sp. (1D2)	**1**				**7** (39)	**8** (37)		
P. paxilli	**2**		**12**(10)	**13** (20)	**14** (50)	**15** (2)	**16** (5)	
F. fujikuroi	**2**	**11** (43)	**12** (36)					
F. concentricum	**2**	**11** (5)	**12** (76)					
Fusarium sp. (1C5)	**2**	**11** (22)	**12** (38)					
Fusarium sp. (1D2)	**2**	**11** (7)	**12** (71)					
P. paxilli	**3**	**17** (3)	**18** (13)	**19** (56)				
F. fujikuroi	**3**	**17** (14)	**18** (11)	**19** (23)				
F. concentricum	**3**	**17** (21)	**18** (17)	**19** (30)				
Fusarium sp. (1C5)	**3**	**17** (15)	**18** (12)	**19** (38)				
Fusarium sp. (1D2)	**3**	**17** (16)	**18** (13)	**19** (35)				

tion of linalool (**1**) was obtained with *Penicillium paxilli* that showed, on the contrary, a good activity towards (*S*)-citronellal (**2**) affording the diasteroisomeric (1*S*,3*S*,4*S*)-*p*-menthane-3,8-diol (**13**; 20%) and (1*S*,3*R*,4*S*)-*p*-menthane-3,8-diol (**14**; 50%), and traces of (1*S*,3*S*,4*R*)-isopulegol (**15**; 2%), and (1*S*,3*R*,4*R*)-isopulegol (**16**; 5%; *Table 6* and *Scheme 2*). These compounds derived from the same cyclic zwitterionic intermediate originating from the nucleophilic attack of the C=C bond on the aldehydic function. The zwitterionic intermediate gave the diols **13** and **14** through H_2O addition and the isopulegols **15** and **16** through prototropic rearrangement [17]. Finally, all *Fusarium* strains both reduced and oxidized the aldehydic function to give (*S*)-citronellol **12** (36–76%) and (*S*)-citronellic acid **11** (5–43%), respectively.

On the other hand, while various studies regarding the biotransformation of linalool [7–11] and citronellal [12–17] have been reported, biotransformations of sabinene were not studied. In this field, *Fusarium* and *Penicillium* strains followed a common pathway (*Table 6* and *Scheme 3*).

In particular both *P. paxilli* and *Fusarium* strains gave as main product the 4-terpineol **19** (23–56%). Other products, obtained in appreciable yields, were the diasteroisomeric (*Z*)-and (*E*)-sabinene hydrates, **17** (14–21%) and **18** (11–17%), respectively.

3. Conclusions. – Various fungi from the Amazonian forest were tested to biotransform linalool, citronellal, and sabinene. This screening has identified some strains belonging to *Fusarium* and *Penicillium* genera able to biotransform these terpenes to various products. Two *Fusarium* strains are new although very similar to *F. concolor* REINKING. While various microrganisms have been employed in biotrasformation of linalool and citronellal, this is the first example of biotranformation of sabinene to 4-terpineol and (*E*)- and (*Z*)-sabinene hydrate in appreciable yields.

Experimental Part

General. (*RS*)-Linalool (*Fluka*), (–)-(*S*)-citronellal (*Aldrich*), and sabinene (*Extrasynthese*) are commercially available. Various culture media have been used: PDA (potato-dextrose agar; potato extract, 4 g l^{-1}; glucose, 20 g l^{-1}; agar, 15 g l^{-1}), PDB (potato-dextrose broth; potato extract, 4 g l^{-1}; glucose, 20 g, l^{-1}), and *Saboraud* broth (trypton, 5 g l^{-1}; pepton, 5 g l^{-1}; glucose, 20 g l^{-1}).

Isolation of Fungi. The fungi were isolated from the epicarp of the fruits of *Citrus* genus harvested from three Achuar communities (*i.e.*, Wasakentsa, Pumpuentsa, and Sewastian) of the Amazonian forest (Ecuador, Province of Morona-Santiago). The fruits were cut in two, and 4.0-cm^2 segments were cut to separate flavedo and albedo in order to sample inside and outside the epicarp. The samples were put on four *Petri* dishes containing PDA and chloramphenicol (200 mg l^{-1}), incubated at 30° for 48 h. Thirty-three strains of fungi were isolated and numbered (*Table 1*).

GC and GC/MS Analysis. GC Analyses were performed on a *ThermoQuest GC-Trace* gas chromatograph equipped with a FID detector and a *Varian FactorFour VF-5ms* poly-5% phenyl-95%-dimethyl-siloxane-bonded phase column (30 m × 0.25 mm; film thickness, 0.15 μm). Operating conditions were as follows: injector temp., 300°; FID temp., 300°; He, carrier gas (flow rate, 1 ml/min and split ratio, 1:5); oven temp., 55–90° (1°/min), 90–250° (20°/min). The percentage composition of chemical constituents was computed by the normalization method from the GC peak areas, without using correction factors.

The GC analysis of the mixture of *(*RS*)-linalool* (**1**) displayed the following retention times (t_R [min]): *6-methylhept-5-en-2-one* (**4**), 12.22; *6-methylhept-5-en-2-ol* (**5**), 12.78; *(*E*)-furanlinalool oxide* (**7**), 18.86; *(*Z*)-furanlinalool oxide* (**8**), 20.37; *1-methyl-1-(4-methylpentyl)oxiranemethanol* (**6**), 20.48; **1**, 21.86; *(*E*)-pyranlinalool oxide* (**9**), 28.9; *(Z)-pyranlinalool oxide* (**10**), 29.65. The analysis of the mixture of (*S*)-citronellal (**2**) led to the following t_R values [min]: *(1*S*,3*S*,4*R*)-isopulegol* (**15**), 26.49; *(1*S*,3*R*,4*R*)-isopulegol* (**16**), 27.45; **2**, 27.18; *(*S*)-citronellol* (**12**), 35.60; *(*S*)-citronellic acid* (**11**), 38.48; *(1*S*,3*S*,4*S*)*-p-*menthane-3,8-diol* (**13**), 38.12; *(1*S*,3*R*,4*S*)*-p-*menthane-3,8-diol* (**14**), 38.74. The analysis of mixture of *sabinene* (**3**) exhibited the following t_R values [min]: **3**, 11.26; *(*Z*)-sabinene hydrate* (**17**), 18.85; *(*E*)-sabinene hydrate* (**18**), 21.77; *(*Z*)-*p-*menth-2-en-1-ol* (**21**), 24.03; *(*E*)-*p-*menth-2-en-1-ol* (**22**), 25.95; *4-terpineol* (**19**), 30.00; *α-terpineol* (**20**), 31.72.

GC/MS Analyses were performed on a *Varian GC-3800* gas chromatograph equipped with a *Varian MS-4000* mass spectrometer using electron impact (EI), and hooked to *NIST* and *Abreg* libraries. The compounds were identified by comparing their GC t_R values, *Kováts* indices (*KI* values), and the MS fragmentation pattern with those of pure standards, or by matching the MS fragmentation patterns and *KI* values with those in the above mentioned mass-spectra libraries and those in the literature [25]. The GC conditions were the same as reported for GC analysis, and the same column was used. The MS conditions were as follows: ionization voltage, 70 eV; emission current, 10 μAmp; scan rate, 1 scan/s; mass range, *m*/*z* 40–500; trap temp., 150°, transfer line temp., 300°. A mixture of aliphatic hydrocarbons

(C_8–C_{24}) in hexane (*Sigma–Aldrich*) was injected, under the above temp. program, to calculate the retention indices [26].

Screening of Biotransformation of Terpenes **1**–**3** *with Fungi on Anal. Scale. General Procedure.* Sterilized *Saboraud* medium (20 ml) was inoculated with a mycelium portion of the isolated fungi on PDA medium. The mixture was incubated for 5 d at 28–30° and 80 rpm. The selected substrate (200 µl; the soln. was prepared dissolving 0.1 g of substrate in 1 ml of DMSO) was added to the resulting suspension of grown cells, and the incubation was continued for 5 d. Aliquots (1 ml) were withdrawn and centrifuged to remove the cells (5000 rpm; 10 min). The supernatant was extracted with Et_2O (1 ml), dried (Na_2SO_4), and analyzed by GC and GC/MS. The yields of biotransformation of **1** (*Table 2*), **2** (*Table 3*), and **3** (*Table 4*) were calculated by GC-FID, and the biotransformations products were characterized by GC/MS.

Identification of Fungi. The identification of fungi was performed by *CBS* (*Centraal Bureau voor Schimmelcultures*) Fungal Biodiversity Centre, Utrecht, The Netherlands. Five strains were selected on basis of the biotransformations of **1**, **2**, and **3**: 1B14, 1C5, 1C22, 1D6, and 2D15. The results are compiled in *Table 5*.

Biotranformations of Terpenes **1**–**3** *with Fungi. General Procedure.* The biotransformations were carried out as previously described. Sterilized *Saboraud* medium (200 ml) was inoculated with a mycelium portion obtained from the culture of the fungi identified by *CBS*. The mixture was incubated for 5 d at 28° and 80 rpm. To the resulting suspension of grown cells, a soln. of selected terpene (0.2 g) in DMSO (2 ml) was added. After 5 d incubation, the mixture was centrifuged (5000 rpm; 10 min), the supernatant was extracted with Et_2O (3×5 ml), dried (Na_2SO_4), and the solvent was removed under vacuum (bath at r.t.) to obtain the crude mixture (0.17–0.19 g (85–95%) for **1** and **2**, 0.11–0.12 g (55–60%) for **3**).

For **1**, the crude mixture was subjected to prep. TLC (hexane/Et_2O 1:1), and the products were characterized by GC/MS analysis and NMR spectra, compared with those of authentic samples. In particular the furanlinalool oxides **6** and **7**, and the pyranlinalool oxides **9** and **10** were prepared according to the method described by *Winterhalter* [27]. The structures of 6-methylhept-5-en-2-one (**4**) and its alcohol **5** in crude extracts were determined by comparison with commercial standards (*Sigma–Aldrich*). The other compounds were identified in GC/MS with the methods reported in *Exper. Part* and references therein.

For **2**, the mixture was separated by prep. TLC (petroleum ether (PE)/AcOEt 5:2) to obtain (1*S*,3*R*,4*S*)-*p*-menthane-3,8-diol (**14**) and (1*S*,3*S*,4*S*)-*p*-menthane-3,8-diol (**13**), characterized by NMR spectra and comparison of their GC/MS data with those of the authentic samples prepared according to the method reported in [17][28]. The minor products were identified only by GC/MS. The structure of (*S*)-citronellic acid (**11**) and (*S*)-citronellol (**12**) was confirmed by GC/MS of the reference standards, prepared by oxidation and reduction of (*S*)-citronellal, resp.

For **3**, 4-terpineol (**19**) and α-terpineol (**20**), their GC/MS data were compared with those of the authentic samples (*Sigma–Aldrich*). The other compounds were identified in GC/MS with the method reported in the *Exper. Part* and references therein.

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