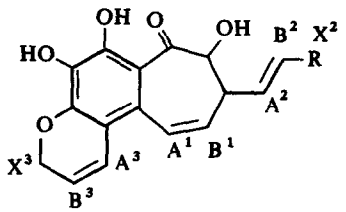
Tableau 1. Valeur des déplacements chimiques (δ ppm/TMS) et des constantes de couplage (Hz) des constituants de *Fomes fomentarius* dans DMSO-D_6 (100 MHz)

	A^1	B^1	A^3	B^3	X^3	A^2	B^2	X^2
Fomentariol (1)	7,74	7,10	6,66	5,96	4,24	7,16	6,62	4,24
	13	13	16–1,5	16–5	5–1,5	16–1,5	16–5	5–1,5
	d	*d*	*dt*	*dt*	*dd*	*dt*	*dt*	*dd*
Dehydrofomentariol (2)	7,68	7,07	6,66	5,97	4,21	8,17	6,91	9,77
	13	13	16–1,5	16–5	5–1,5	16	16–7,5	7,5
	d	*d*	*dt*	*dt*	*dd*	*d*	*dd*	*d*
Anhydrofomentatiol (3)	7,67	7,16	7,16	6,04	4,87	7,16	6,62	4,23
	13	13	10	10–3	3	16	16–5	5
	d	*m*	*m*	*dt*	*d*	*m*	*dt*	*d*
Anhydrodehydrofomentariol (4)	7,59	7,12	7,12	6,04	4,89	8,16	6,88	9,77
	13	13	10	10–3	3	16	16–7,3	7,3
	d	*d*	*d*	*dt*	*d*	*d*	*dd*	*d*

l'ADF. Enfin l'un de nous a obtenu l'ADF par déshydratation de 2 en présence d'acide tosylique dans THF, à chaud.



3 R = CH_2OH: Anhydrofomentariol
4 R = CHO: Anhydrodéhydrofomentatiol

PARTIE EXPERIMENTALE

Anhydrodéhydrofomentariol (4). UV-vis.: λ_{max} dioxane (log ε): 242 (4, 18), 305 ép (4, 39), 340 (4, 60), 400 ép (3, 94), 488 (3, 44) nm; SM (70 eV-175°): *m/e* 312 (M^+, 100%), *tr.* 312, 0631 calc. pour $C_{17}H_{12}O_6$: 312,06338), 283 (M-29, 20%), 266 (16%), 255 (13%), 237 (9%), 101 (18%).

Anhydrodéhydrofomentariol TMSi. Préparé par action du BSTFA à 1% de TMCS sur une solution pyridinique de 4. SM (70 eV-175°): *m/e* à 528 (M^+: 312 + 3 TMSi, 5%), 513 (M-15, 100%), 499 (2%), 485 (22%), 441 (5%), 425 (5%), 441 (2%), 395 (3%), 379 (2%), 367 (2%), 341 (2%), 323 (2%), 147 (17%), 75 (57%), 73 (100%).

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EUGENYL ISOVALERATE AND ISOEUGENYL ISOVALERATE IN THE ESSENTIAL OIL OF *VALERIAN* ROOT

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Key Word Index—*Valeriana officinalis*; Valerianaceae; essential oil; eugenyl isovalerate; isoeugenyl isovalerate.

The essential oil (43.0 g) of *Valerian* roots, obtained by steam distillation, was submitted to column chromatography on Si gel using petrol (bp < 40°) with an increasing percentage of Et_2O (0 → 100%) as the eluting solvent. Fraction 5 (petrol–Et_2O, 9:1) contained about 1.6 g of material which was investigated by GC–MS.

Bornylacetate and valeranone were present as the main constituents in this fraction. Two other GLC peaks were observed, both with MS molecular ions at *m/e* 248 and a base peak of 164 indicating that they may be eugenol and isoeugenol. Only two other fragments at *m/e* 191 (1%) and *m/e* 248 (2%) were present in both MS.

Because of the presence of isovaleric esters in the essential oil of *Valerian* [1] both eugenyl isovalerate

and isoeugenyl isovalerate were prepared by means of the thionyl chloride method [2]. These esters showed, after purification, the same MS and GLC R_t values as those of the compounds in fraction 5. The MS of synthesised eugenyl valerate and isoeugenyl valerate did not show great differences from those of the isovalerates but the fragment at *m/e* 191 could not be observed in these spectra. The GLC R_t values were also different. The NMR-spectra of the isovalerates showed a doublet at δ 2.4 (J = 1.5 Hz) for $Me_2CH.\underline{CH_2}—COOR$, whereas the valerates showed a triplet at δ 2.5 (J = 7 Hz) for $Me—CH_2—CH_2.\underline{CH_2}.COOR$. The IR-spectra of the isovalerates showed a double band at 1185–1200 cm^{-1}; the valerates one band at 1200 cm^{-1}.

The distinction between the eugenyl- and isoeugenyl esters could be easily made with the aid of NMR- and IR-spectral data (see Experimental). The presence of eugenol has been reported in the essential oil of *Valeriana officinalis* L. var. *angustifolia* Mig [3]. Eugenyl isovalerate and isoeugenyl isovalerate recently have been reported in *Felicia* species [4].

EXPERIMENTAL

Isolation of the essential oil. 7300 g of *Valerian* root (air dried) was submitted to steam distillation according to ref. [5]. Yield 48.3 g (0.66%). 43.0 g of the essential oil was submitted to chromatography on a Si gel column (100 × 4 cm) using petrol (bp < 40°) containing an increasing percentage of Et_2O (0 → 100%). Twenty fractions of about 250 ml were collected. Fraction 5 was investigated by GLC using a 2 m × 2 mm column of Carbowax 20 M on chromosorb W HP 100–200 mesh; temp. 80–200° (4°/min); flow 25 ml N_2/min; FID. R_t bornylacetate (17% normalization method) 950 sec, valeranone (32%) 1810 sec, eugenyl isovalerate (3%) 2200 sec and isoeugenyl isovalerate (5%) 2580 sec. R_t eugenyl valerate 2290 sec and isoeugenyl valerate 2850 sec.

GC-MS. GC-MS was performed on a Finnigan 3300 quadrupole computerized system under the above gaschromatographic conditions. Electron energy 70 eV; scan speed 2 sec/scan; ion source 200°.

Spectral data. Eugenyl isovalerate. MS 248 (M^+), 191, 166, 165, 164 (100), 163, 149, 137, 133, 132, 131, 121, 104, 103, 91, 85, 77, 65, 57, 55, 51, 43, 41, 39. NMR, 60 MHz, CCl_4: δ 1,1 (6H, *d*, J = 6 Hz); ~1,9 (1H, *m*) 2,4 (2H, *d*, J = 1,5); 3,3 (2H, *d*, J = 7 Hz); 3,7 (3H, *s*); 5,1 (2H, *d*, J = 14 Hz); ~6,0 (1H, *m*); 6,7 (3H, arom.). IR ν_{max}^{NaCl} cm^{-1}: 910, 990, 1185–1200 (double band), 1640. Isoeugenyl isovalerate. MS: 248 (M^+), 191, 166, 165, 164 (100), 163, 149, 137, 133, 132, 131, 121, 104, 103, 91, 85, 77, 65, 57, 55, 51, 43, 41, 39. NMR: δ 1,1 (6H, *d*, J = 6 Hz); 1,8 (3H, *d*, J = 5 Hz); 1,9 (1H, *m*); 2,4 (2H, *d*, J = 15 Hz); 3,7 (3H, *s*); 5,5–6,4 (2H, *m*); 6,7 (3H, arom). IR ν_{max}^{NaCl} cm^{-1}: 960, 1185–1200 (double band). Eugenyl valerate. MS: 248 (M^+), 166, 165, 164 (100), 163, 149, 137, 133, 132, 131, 121, 104, 103, 91, 85, 77, 65, 57, 55, 51, 43, 41, 39. NMR: δ = 0,9 (3H, *t*, J = 6 Hz); 1,6 (4H, *m*); 2,5 (2H, *t*, J = 7 Hz); 3,3 (2H, *d*, J = 6 Hz); 3,7 (3H, *s*); 5,1 (2H, *d*, J = 14 Hz); ~6,0 (1H, *m*); 6,7 (3H, arom). IR ν_{max}^{NaCl} cm^{-1}: 910, 990, 1200, 1640. Isoeugenyl valerate. MS: 248 (M^+), 166, 165, 164 (100), 163, 149, 137, 133, 132, 131, 121, 104, 103, 91, 85, 77, 65, 57, 55, 51, 43, 41, 39. NMR: δ = 0,9 (3H, *t*, J = 6 Hz); 1,6 (4H, *m*); 1,8 (3H, *d*, J = 5 Hz); 2,5 (2H, *t*, J = 7 Hz); 3,7 (3H, *s*); 5,5–6,4 (2H, *m*); 6,8 (3H arom). IR ν_{max}^{NaCl} cm^{-1}: 960, 1200.

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EIN NEUES THYMOL-DERIVAT AUS *CALLILEPIS LAUREOLA*

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Key Word Index—*Callilepis laureola*; Compositae; new thymol derivative.

Die Wurzeln der in Südafrika heimischen *Callilepis laureola* DC. sind sehr toxisch, sie werden jedoch auch in der Volksmedizin als Wurmmittel sowie gegen verschiedene andere Krankheiten benutzt. Die Inhaltsstoffe der Wurzelknollen sind jedoch noch nicht untersucht worden. Neben dem weitverbreiteten Pentainen **1** [1] isoliert man praktisch als einzigen wesentlichen Inhaltsstoff einen Aldehyd der Summerformel $C_{20}H_{26}O_6$. Das ^{1}H-NMR-Spektrum bei 270 MHz läßt sofort erkennen, daß es sich um ein Epoxid handelt, das neben einer Aldehyd-Gruppe zwei Esterreste enthält, bei denen es sich um Isovaleriansäureesterreste handeln muß. Alle Daten sind nur vereinbar mit der Konstitution **2**. Während Thymolepoxide bei Compositen sehr verbreitet sind [2], haben wir bisher erst einen Aldehyd isoliert [2]. Weiterhin handelt es sich stets um Phenolisobutyrate. Insofern ist **2** doch ein neuartiger Typ. Die pharmakologische Prüfung diese Substanz ist noch nicht abgeschlossen.

Die Untersuchung weiterer Arten muß zeigen, ob Verbindungen vom Typ **2** für die Gattung charakteristisch sind.

EXPERIMENTELLES

IR: Beckman IR 9 in CCl_4; ^{1}H-NMR. Bruker WH 270, δ-