95 (10), 81 (12), 67 (50), 41 (18); IR 1680 cm^{-1}, ^{13}C NMR (100 MHz, $CDCl_3$) δ 13 0 (Me), 21 5 (Me), 22 8 (CH_2-2′), 24 0 (Me), 25.5 (Me), 28 3 (CH-4), 41.3 (C-6), 45.7 (CH_2-5), 138 2 (C-2), 147.7 (CH-3), 204.4 (C-1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (3H, *t*, $J = 7.5$ Hz, $\underline{Me}$ CH_2-2), 1 07, 1.09 (both 3H, *s*, 2x Me-6), 1.09(3H, *d*, $J = 7\ 1$ Hz, Me-4), 1 51 (1H, *dd*, $J_{gem} = 13\ 3$ Hz, $J_{4,5} = 11.0$ Hz, H_{ax}-5), 1.76 (1H, *ddd*, $J_{gem} = 13.0$ Hz, $J_{4,5} = 4.8$ Hz, $J_{3,5} = 1\ 8$ Hz, H_{equ}-5), 2.15 (1H, *dqdd*, $J_{gem} = 15\ 0$ Hz, $J_{2',2''} = 7\ 5$ Hz, $J_{2',4} = 2.0$ Hz, $J_{2',3} = 1\ 3$ Hz, MeC$\underline{H}$H-2), 2.19 (1H, *dqdd*, $J_{gem} = 15.0$ Hz, $J_{2',2''} = 7.5$ Hz, $J_{2',4} = 2\ 2$ Hz, $J_{2',3} = 1\ 4$ Hz, MeCH$\underline{H}$-2), 2 59(1H, *m*, H-4), 6 36 (1H, *m*, H-3)

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A *NOR-SECO*-AROMADENDRANE FROM THE LIVERWORT *MYLIA TAYLORII*

LESLIE J HARRISON* and HANS BECKER

Pharmakognosie und Analytische Phytochemie, Universitat des Saarlandes, D-6600 Saarbrucken, F R G

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Key Word Index—*Mylia taylorii*; Hepaticae, liverworts, sesquiterpenoids, *nor-seco*-aromadendrane, 2-*nor*-1,3-epoxy-1,10-*seco*-aromadendra-1(5),3-dien-10-one

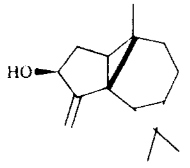
Abstract—A novel *nor-seco*-aromadendrane, 2-*nor*-1,3-epoxy-1,10-*seco*-aromadendra-1(5),3-dien-10-one, was obtained from *Mylia taylorii* It was identified by spectroscopic methods and chemical correlation with a known compound

INTRODUCTION

The liverwort *Mylia taylorii* (Hook) Gray is a rich source of unusual sesquiterpenoids. Some are derived from the aromadendrane skeleton, either by further cyclization (myliol (**1**) [1] and dihydromylione A (**2**) [2]) or by ring cleavage {taylorione (**3**) [3]}. Two further sesquiterpenoids, myltaylenol (**4**) [4] and cyclomultaylenol (**5**) [5], have also been reported, as well as a diterpenoid, (15*S*,16*S*)-2β,16-epoxyverrucosan-16-ol (**6**) [6]. We now report on the isolation from *M taylorii* of a novel *nor-seco*-aromadendrane (**7**).

RESULTS AND DISCUSSION

Mylia taylorii was collected in the Bavarian Alps. The ether extract was separated by vacuum liquid chromatography [7] over silica gel and afforded compounds **1**–**3** which were identified by comparison of their spectroscopic properties with literature values or by comparison with authentic samples. HPLC of an early column fraction yielded a novel *nor-seco*-aromadendrane, (**7**), $C_{14}H_{20}O_2$ (*m/z* 220 1458), $[\alpha]_D$ $-25\ 8$ ($CHCl_3$, *c* 2.89) $\nu_{max}^{CCl_4}$ 1726 cm^{-1}. The ^{1}H and ^{13}C NMR spectra contain resonances characteristic of a 3,4-disubstituted furan [δ_H 7.13 (*quin*, $J = 1.2$ Hz, H-3) and 7 08 (1H, *t*, $J = 1\ 2$ Hz, H-1); δ_C 121.62 (*s*), 121.91 (*s*), 138 72 (*d*), and 138.80 (*d*)], a methyl ketone [δ_H 2.22 (*s*, H_3-15), δ_C 29 00 (*q*) and 208.52 (*s*)], a vinyl methyl [δ_H 1.94 (*d*, $J = 1.0$ Hz, H_3-14); δ_C 8.28 (*q*)], a cyclopropane ring [δ_H 1 32 (*dd*, $J = 1.2$ and 8.8 Hz, H-6) and 0.82 (*dt*, $J = 6\ 0$ and 8.8 Hz, H-7), δ_C 19.20 (*s*), 21 75 (*d*), and 27.75 (*d*)], two tertiary methyl groups [δ_H 1 17 and 0.89 (each *s*, H_3-12 and H_3-13); δ_C 15 73 (*q*) and 29.81 (*q*)] and two methylene groups [δ_H 2.46 (*t*, $J = 7.6$ Hz, H_2-9), 1.75 and 1.48 (each *m*, H_2-8); δ_C 20.36 (*t*) and 43.89 (*t*)] The ^{1}H NMR spectrum is very similar to that of taylorione (**3**), except that the signals of the exomethylene cyclopentene have been replaced by those of a methyl furan This suggested that the compound is 2-*nor*-1,3-epoxy-1,10-*seco*-aromadendra-1(5),3-dien-10-one (**7**). A small allylic coupling of 1 2 Hz between H-6 and H-1 supports this structure Ozonolysis of **7** afforded the



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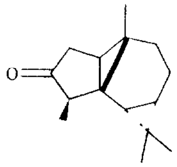

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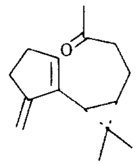

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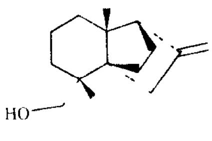

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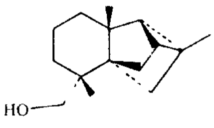

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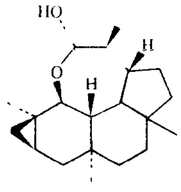

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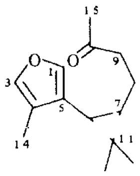

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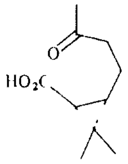

8

known carboxylic acid **8** which was identical with the same compound obtained by ozonolysis of taylorione Therefore, **7** has the absolute configuration shown

EXPERIMENTAL

Optical rotations: $CHCl_3$, NMR 400 MHz (^{1}H) or 100 5 MHz (^{13}C), $CDCl_3$ relative to $CHCl_3$ at δ_H 7 25 or $CDCl_3$ at δ_C 77.00 ^{13}C multiplicities were determined using the DEPT pulse sequence Kieselgel 60 HR (Merck) was used for vacuum liquid chromatography (VLC) and HPLC was carried out using a Lichrosorb 5 μ silica column (25 × 0 4 cm) Petrol refers to the fraction boiling in the range 40–60° Organic solns were dried over Na_2SO_4

M taylorii was collected in the Bavarian Alps in August 1987 Contaminating plant material was removed and the air-dried material was ground The resulting powder (3 4 kg) was extracted with Et_2O (12 l) to afford a crude extract This was partitioned between petrol and 90% aq MeOH to give two portions The MeOH-soluble portion (12 8 g) was subjected to VLC using a gradient of EtOAc in petrol A crystalline fraction was recrystallized from petrol at −10° to give *myliol* (**1**) (1 2 g), identical with an authentic sample The petrol-soluble portion (9 3 g) was chromatographed in a similar manner to give, in order of elution, the *nor-seco*-aromadendrane (**7**) which was further purified by HPLC (2% EtOAc–hexane) to give an oil (37 mg), *m/z* 220 1458 ($C_{14}H_{20}O_2$ requires *m/z* 220 1463), UV λ_{max}^{MeOH} nm (log ε) 214 (3 67), IR $\nu_{max}^{CCl_4}$ cm^{-1} 2950, 2930, 2895, 2870, 1726, 1459, 1390, 1380, 1362, 1165, 1148, 1055, ^{1}H NMR and ^{13}C NMR see Discussion, EIMS 70 eV, *m/z* (rel int) 220 $[M]^+$ (22), 205 $[M - Me]^+$ (9), 177 $[M - Me - CO]^+$ (19), 162 (20), 149 (45), 147 (22), 91 (37), 43 (100), *taylorione* (**3**) (1 05 g), identical with an authentic sample, and dihydromylione A (**2**) (25 mg), ^{1}H NMR δ_H 2 62 (2H, *m*), 2 21 (1H, *d*, *J* = 19 1 Hz), 1 35 (1H, *d*, *J* = 6 5 Hz), 1 15 (*d*, *J* = 7 1 Hz, H_3-14), 1 08 (3H, *s*), 1 02 (3H, *s*), 0 87 (3H, *s*) and 0 62 (*q*, *J* = 8 9 Hz, H-7)

Ozonolysis of **7** A soln of the *nor-seco*-aromadendrane (20 mg) in EtOAc (30 ml) was cooled to −20° and a stream of ozonized O_2 was passed through the soln until a blue colour persisted The soln was kept at −20° for a further hr after which it was evapd The ozonide was decomposed by refluxing for 1 hr with H_2O containing a few drops of 30% H_2O_2 Extraction with EtOAc gave the crude product which was purified by CC over silica gel (MeOH–$CHCl_3$, 1 49) to give the carboxylic-acid **8** (12 mg), $[\alpha]_D$ −22 3 ($CHCl_3$, *c* 0 1) [lit [3] −20 6], identical with an authentic sample produced by ozonolysis of taylorione

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