1 Hz each, H-5, H-8), MS m/z (rel. int) 282.0890 $[M]^+$ (100) (Calc for $C_{17}H_{14}O_4$ 282.0890), 267 $[M-Me]^+$ (20), 254 $[M-CO]^+$ (60), 253 $[M-CHO]^+$ (44), 239 $[254-Me]^+$ (24), 211 $[239-CO]^+$ (12), 210 $[239-CHO]^+$ (13), 57 (98)

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ANGUSTIFOLENONE, A KETONE FROM *BACKHOUSIA ANGUSTIFOLIA*

JOSEPH J. BROPHY, JOHN R. CLARKSON* and CHRISTOPHER J R FOOKES†

Department of Organic Chemistry, University of New South Wales, P O Box 1, Kensington, N S W, 2033, Australia, *Department of Primary Industries, P O Box 1054, Mareeba, Queensland, 4880, Australia, †C.S I R O, Division of Fuel Technology, Private Mail Bag 7, Menai, N S W 2234, Australia

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Key Word Index—*Backhousia angustifolia*, Myrtaceae; cyclohexenone, NMR GC/MS

Abstract—Angustifolenone, 2-ethyl-4,6,6-trimethylcyclohex-2-ene-1-one, has been identified in 25% yield from the steam volatile leaf oil of *Backhousia angustifolia*

INTRODUCTION

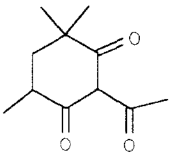
Backhousia angustifolia F Muell. is a shrub or small tree reaching 6–8 m in height. The species is endemic to Queensland where it occurs in depauperate rainforests mainly in central and south-eastern areas of the state, between Blackdown Tableland and the Bunya Mountains. Two disjunct populations have been recorded north of this range, one in the Eungella area west of Mackay and the other near Wando Vale, *ca* 75 km south of Greenvale. A southern outlying occurrence south west of Stanthorpe at present referred to as *B. angustifolia* may prove on further study to warrant recognition as a distinct taxon.

Backhousia angustifolia was first investigated by Penfold in 1923 [1]. He isolated the two β-triketones angustione (**1**) and dehydroangustione (**2**), and in some cases the chromone angustifolionol (**3**), together with some monoterpenes, from the steam volatile leaf oil. The structures of the two β-triketones were finally elucidated by Birch [2, 3], and proved by synthesis [4, 5], while the structure of the chromone was also deduced by Birch *et al.* [6] Some years later Cannon and Corbett demonstrated the existence of physiological forms in this species [7]

RESULTS AND DISCUSSION

During an investigation of tropical oil bearing Australian plants we found that the leaf oil from several specimens of *Backhousia angustifolia* contained, as well as the two β-triketones, **1** and **2**, a significant amount of 1,8-cineole and *ca* 25% of a compound of M_r 166. This compound had GLC Linear Retention indices (LRI) of 1422 on FFAP and 1157 on OV1 respectively. To facilitate identification, the compound was isolated by preparative GLC

^{13}C NMR spectroscopy, using the DEPT procedure, revealed a carbonyl (δ 204.4) plus olefinic CH and C



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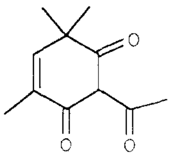

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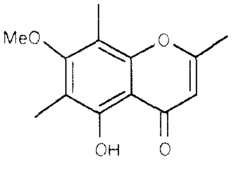

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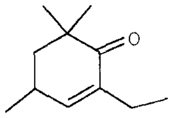

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resonances whose chemical shifts (δ 147.7 and 138.2 respectively) suggested a 2-substituted cyclohexenone partial structure. Additional signals from four aliphatic methyls, two methylenes, a methine and a quaternary carbon indicated an emperical formula of $C_{11}H_{18}O$, consistent with the observed M_r. Accurate mass measurement on the molecular ion gave a value of 166.1352, ($C_{11}H_{18}O$ requires 166.1352). The IR spectrum showed absorption at $1680\ cm^{-1}$, consistent with an α,β-unsaturated cyclohexenone derivative. The compound was optically active with $[\alpha]_D^{15}$ +74°, though allowing for the fact that the asymmetric centre is at an easily enolisable position, the real value may be larger.

Complete identification was obtained from the 400 MHz ^1H NMR spectrum which indicated a $CH_2CH(Me)CH{=}C(CO)CH_2Me$ fragment, plus two methyls which appeared as singlets. The only structure compatible with the above data is 2-ethyl-4,6,6-trimethylcyclohex-2-ene-1-one (**4**), for which we propose the trivial name angustifolenone.

The magnitude of the coupling constant between H-4 and one of the protons at C-5 ($J = 11.0$ Hz) shows that, as expected, the methyl substituent at C-4 adopts a pseudo-equatorial configuration in solution. This is confirmed by the large homo-allylic coupling between H-4 and the C-2 methylene protons ($J = 2.0$ and 2.2 Hz) and the relatively small vicinal coupling to H-3 ($J = 2.3$ Hz), which indicate that H-4 is close to perpendicular to the plane of the enone system. The absolute configuration of angustifolenone has not been determined.

It is noteworthy that angustifolenone (**4**) has the same carbon skeleton as angustione (**1**) and dehydroangustione (**2**). This would seem to imply a common biogenetic precursor for these three compounds.

Cannon and Corbett had distinguished what they considered to be three physiological forms of *B. angustifolia* [7]. One form contained both dehydroangustione and angustifolionol, the second form containing only dehydroangustione, while the third form contained angustione and angustifolionol. It would now appear that yet another form of this species occurs in which both angustione and dehydroangustione occur together with angustifolenone. In these present samples there was no evidence for the presence of angustifolionol.

EXPERIMENTAL

Voucher material. The identity of material used in this study is vouched by a herbarium specimen lodged with the Queensland Herbarium, Meiers Road, Indooroopilly (J. R. Clarkson 7371, 20 Oct 1987, BRI 357361).

Collection of plant material and isolation of volatile oil. The species often occurs in almost monospecific stands. The strong phenolic odour of the crushed leaves readily serves to identify the plant in the field.

Leaf material used in this study was obtained from a recently discovered population on Eight Mile Mountain *ca* 20 km south west of Dimbulah (17° 16′ S, 144° 57′ E). This is the most northerly known occurrence of the species. Leaves and terminal branchlets were transported to Kensington within 24 hr of collection and were steam distilled with cohobation (16 hr), giving an oil with a 'burnt' smell in *ca* 0.5% yield.

Analysis of the oil and identification of the constituents. The oil was analysed by GC/MS on either FFAP or OV1 columns as described elsewhere [8] using a Milton Roy CI10 electronic integrator to determine percentages of the components. Compounds were identified by comparison of their mass spectra with those of authentic materials as well as coinjection on two columns with known standards. Compounds detected in the oil were α-pinene (0.4–4%), 1,8-cineole (35–37%), α-terpineol (2–3%), angustione (**1**) (6–10%), MS *m/z* (rel. int.) 196 (30), 181 (5), 154 (35), 140 (100), 126 (10), 112 (70), 69 (25), 43 (45), dehydroangustione (**2**) (15–37%), MS *m/z* (rel. int.) 194 (95), 179 (70), 166 (15), 161 (20), 151 (22) 123 (18), 110 (100), 95 (83), 81 (40), 67 (80), 43 (70), angustifolenone (**4**) (13–25%), $[\alpha]_D^{15} = 74°$. MS *m/z* (rel. int.) 166.1352 (15), 151.1118 (3), 123 (8), 110.0726 (100), 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