organic layer was subjected to CC on silica gel eluting with $CHCl_3$. Fractions containing **1** were subjected to repeated preparative TLC using cyclohexane–$CH_2Cl_2$ (1:4) to afford yellow needles of **1** (5 mg, 0.00006%), mp 205–206°; UV $\lambda_{max}^{MeOH}$ nm ($\log \varepsilon$): 215 (4.42), 230sh (4.16), 254 (4.38), 344 (3.66) and 370sh (3.63) nm; UV $\lambda_{max}^{MeOH+OH^-}$ nm ($\log \varepsilon$): 204 (4.68), 225 (4.37), 240sh (4.18), 272 (4.29), 344 (3.51) and 435 (3.75); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3270, 1750, 1640, 1505 and 1485; $^1$H NMR ($CDCl_3$, 400 MHz), (TMS): $\delta$7.90 (*d*, $J = 8.2$ Hz, 1H, H-7), 7.38 (*d*, $J = 8.2$ Hz, 1H, H-6), 5.96 (*s*, 1H, OH, $D_2O$ exch, C-12 OH), 3.47 (*sept*, $J = 6.9$ Hz, 1H, H-15), 2.79 (*s*, 3H, H-20) and 1.34 (*d*, $J = 6.9$ Hz, 6H, H-16 and H-17); MS (electron impact, 70 eV) *m/z* (rel. int.): 242 $[M]^+$ (96), 227 (100), 213 (27), 199 (9), 184 (6), 171 (12), 171 (12), 155 (9), 141 (21), 129 (38) and 115 (30); HRMS 242.0938 for $C_{15}H_{14}O_3$, cal. 242.0932.

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# PHLOROACYLPHENONES IN THE ESSENTIAL OIL OF *THRYPTOMENE SAXICOLA*

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**Key Word Index**—*Thryptomene saxicola*; Myrtaceae; essential oil; phloroacylphenones; *O*-isobaeckeol.

**Abstract**—The essential oil of *Thryptomene saxicola* is shown to contain α-pinene, 1,8-cineole, α-terpineol, globulol, *O*-isobaeckeol and its homologue.

## INTRODUCTION

The genus *Thryptomene* is endemic to Australia and consists of *ca* 25 species [1] most of which are restricted to the south-west and Eremean provinces of Western Australia [2]. Previous work on Thryptomene had been restricted to the detection and isolation of sesquiterpenes. Thus the essential oil of *T. kochi* has been shown to contain aromadendrene and globulol [3, 4]. The presence of the latter in *T. australis* Endl and *T. stenocalyx* F.v.M. has also been established [4]. As part of a screening programme of essential oils from Western Australian plants, we had the opportunity of analysing the essential oil of a sample of *T. saxicola* (A. Cunn.) Schau which from preliminary examination appeared to contain two aromatic compounds. These have been characterized as *O*-isobaeckeol (**1**) and its homologue (**2**).

## RESULTS AND DISCUSSION

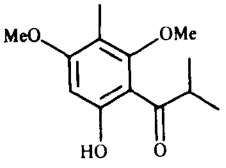
Steam distillation of the leaves and terminal branches of the plant yielded a yellow oil (1.5%) which on distillation afforded fractions of α-pinene (57%), a mixture (12%) of α-pinene, cineole, α-terpineol and five unidentified sesquiterpene hydrocarbons. A third fraction (20%) contained three compounds. Separation by chromatography on basic alumina gave globulol and another compound to which the structure of *O*-isobaeckeol (**1**) was assigned on the following evidence.

Interpretation of the spectral data indicated that the compound ($[M]^+$ 238) contained a pentasubstituted benzene with two methoxyls, a methyl, a hydrogen bonded hydroxyl ($\delta_H$ 13.14) and an isobutanoyl group as substituents. These features are consistent with the compound being baeckeol (**3**). However, comparison of their

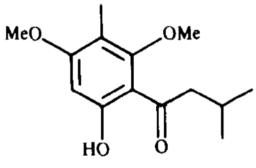
Table 1. Carbon chemical shifts of baeckeol (**3**) and *O*-isobaeckeol (**1**)

| C | **3** | **1** | C | **3** | **1** |
|---|---|---|---|---|---|
| 1 | 210.54 | 210.75 | 4′ | 163.07$^c$ | 164.10 |
| 2 | 39.60 | 38.40 | 5′ | 85.79 | 107.51$^b$ |
| 3 | 19.29 | 19.58 | 6′ | 163.99$^c$ | 164.06 |
| 2-Me | 19.29 | 19.58 | Ar-Me | 7.24* | 8.50 |
| 1′ | 105.85$^a$ | 107.51$^b$ | OMe | 55.38 | 62.02 |
| 2′ | 160.89 | 160.14 | OMe | 55.38 | 55.83 |
| 3′ | 104.86$^a$ | 95.76 | | | |

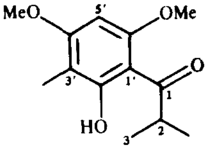
$^{a-c}$Values with identical superscript may be interchanged.
*Assigned by selective decoupling of methyl protons.



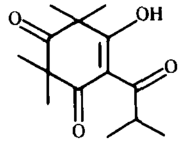
**1**



**2**



**3**



**4**

$^{13}$C NMR spectra (Table 1) and $^1$H NMR spectra showed significant differences. In particular the carbon of the aromatic methyl in **3** at $\delta_C$ 7.24 appears at lower field ($\delta_C$ 8.50) in **1** as does the unsubstituted aromatic carbon ($\delta_C$ 85.79 in **3**; $\delta_C$ 95.76 in **1**). This suggests the orientation of substitutents for the compounded to be that shown in **1** which is named *O*-isobaeckeol. This compound has been prepared [5] but has not been found to occur naturally before.

Crude fractions of **1** were shown by GC-MS to contain trace amounts of another compound at longer $R_t$. The mass spectrum showed an $[M]^+$ at $m/z$ 252, otherwise it was indistinguishable from that of **1**, suggesting it to be a homologue probably with an isopentanoyl side chain (**2**). The presence of **2** is not unexpected given the occurrence of leptospermone (**4**) and its homologue, flavesone in species of the Myrtaceae. It has also been suggested that the homologue of baeckeol might be a natural product [6].

## EXPERIMENTAL

General experimental details have been described elsewhere [7].

*Isolation of* O-*isobaeckeol* (**1**) *from* Thryptomene saxicola. Leaves and terminal branches (750 g) of the air-dried plant, obtained from Australian Flower Farms, Coorow, Western Australia, were steam distilled for 7 hr to give a yellow oil (12 ml). GC analysis (HP Ultra-1 column, cross-linked methyl silicon gum, 0.02 mm × 50 m WCOT) of the crude essential oil showed the following composition: α-pinene (60%), 1,8-cineole (7.5%), α-terpineol (6%), five unidentified sesquiterpene hydrocarbons (11%), globulol (6%), *O*-isobaeckeol (3.5%) and its homologue (trace). Distillation (< 140°C, 15 mm) yielded a colourless oil (3.4 g) whose $^1$H NMR and mass spectra were identical with those of authentic α-pinene. The residue (2.5 g) was separated into three fractions by Kügelrohr distillation (250°, 15 mm) which by GC-MS were shown to contain the following: Fraction 1 (150 mg) α-pinene, 1,8-cineole, α-terpineol and five sesquiterpene hydrocarbons ($[M]^+$ $m/z$ 204); fraction 2 (528 mg) contained all the components of the undistilled sample; fraction 3 (411 mg)—mainly globulol, *O*-isobaeckeol (**1**) and the homologue (**2**). GC-MS (X-linked Me-silicone gum, 0.31 mm × 25 m WCOT capillary 100–250° at 4°/min) of fraction 3 showed two peaks at $R_t > 20$ min. The major one at $R_t$ 22 min was shown to be **1** and the minor one at $R_t$ 23.9 min gave the following MS $m/z$ (rel. int.) 252 $[M]^+$ (9), 195 (100), 180 (3), 152 (7), 151 (2), 109 (2), 69 (2). Chromatography of fraction 3 on basic alumina (act. I; 10 g) and elution with 10% $CH_2Cl_2$: petrol yielded **1** (100 mg) as an oil, $R_t$ 0.6 ($CH_2Cl_2$; silica gel), $\nu_{max}$ ($CHCl_3$) 1625–1610 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$13.14 (1H, *br s*, OH), 6.25 (1H, *s*, H-3′), 3.84 (3H, *s*, $OCH_3$), 3.82 (1H, *septet*, $J = 6.8$ Hz, H-2), 3.71 (3H, *s*, OMe), 2.06 (3H, *s*, 5′-Me), 1.18 (6H, *d*, $J = 6.7$ Hz, 2-Me and $H_3$-3); $^{13}$C NMR (75.5 MHz, $CDCl_3$): see Table 1. MS (EI), $m/z$ (rel. int.): 238 $[M]^+$ (11), 195 (100), 180 (3), 152 (9), 151 (2), 69 (2), 43 (2). Elution with $CH_2Cl_2$ afforded fractions of a single compound (150 mg), $R_f$ 0.2 ($CH_2Cl_2$, silica gel) whose $^1$H, $^{13}$C NMR, mass spectra and GC $R_t$ were identical with those of an authentic sample of globulol.

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