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THYMOL DERIVATIVES FROM *POROPHYLLUM RIEDELII**

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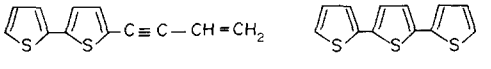
Key Word Index—*Porophyllum riedelii*; Compositae; monoterpenes; thymol derivatives.

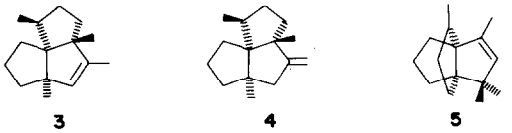
Abstract—In addition to known compounds, *Porophyllum riedelii* afforded three new 2-methoxythymol derivatives.

The genus *Porophyllum* (Compositae), originally had been regarded as a member of the tribes Helenieae and Tagetae, tribes now regarded as part of the Heliantheae [1]; taxonomic data [1] as well as the chemistry [2, 3] indicate that *Porophyllum* should be placed in the subtribe Pectidinae.

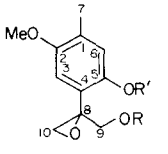
We now have studied the constituents of a further species, *Porophyllum riedelii* Baker. The aerial parts afforded the thiophene derivatives **1** and **2** typical for the genera of subtribe Pectidinae [2–4], the hydrocarbons **3** [4], **4** [6] and **5** [7] and the thymol derivatives **6–9**. The ^{1}H NMR spectrum of the di-isobutyrate **6** was identical with that of an authentic sample [3, 8]. The ^{1}H NMR spectral data of **7** (Table 1) were close to those of **6**; however, the chemical shifts of H-9 and H-10 were slightly different due to the deshielding effect of the unsaturated ester groups. The ^{1}H NMR spectra of **8** and **9** (Table 1), which could not be completely separated, again were close to that of **6**. The relative position of the two ester groups



1 **2**



3 **4** **5**



	6	7	8	9
R	*i*Bu	Tigl	Tigl	*i*Bu
R′	*i*Bu	Tigl	*i*Bu	Tigl

Table 1. ^{1}H NMR spectral data of **7–9** (400 MHz, TMS as int. standard)

	7	8	9
H-3	6.93 *s*	6.91 *s*	6.92 *s*
H-6	6.85 *br s*	6.80 *br s*	6.85 *br s*
H-7	2.18 *br s*	2.18 *br s*	2.19 *br s*
H-9	4.62 *d*	4.60 *d*	4.64 *d*
H-9′	4.22 *d*	4.26 *d*	4.12 *d*
H-10	3.03 *d*	3.05 *d*	3.01 *d*
H-10′	2.82 *d*	2.81 *d*	2.80 *d*
OTigl	7.09 *qq*	6.83 *qq*	7.10 *qq*
	1.93 *dq*	1.78 *dq*	1.94 *dq*
	1.87 *dq*	1.76 *dq*	1.87 *dq*
	6.81 *qq*	—	—
	1.77 *dq*	—	—
	1.75 *dq*	—	—
O*i*Bu	—	2.80 *qq*	2.50 *qq*
	—	1.28 *d*	1.09 *d*
	—	—	1.07 *d*
OMe	3.83 *s*	3.82 *s*	3.83 *s*

J (Hz): 6, 7 ~ 1; 9, 9′ = 12.5; 10, 10′ = 5.5; OTigl: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5; O*i*Bu: 2′, 3′ = 2′, 4′ = 7.

clearly followed from the chemical shifts of the ester signals which were at a lower field as in a phenolic ester. The assignment of the remaining signals in the spectrum of the mixture was possible since partial separation led to unequal amounts of the two compounds. The mass spectra of **7–9** further supported the structures of these thymol derivatives.

The aerial parts afforded squalene, caryophyllene, germacrene D, bicyclogermacrene, **1** and **2**. The chemistry agreed closely with that of the species investigated previously. Thiophenes and methoxythymol derivatives may be characteristic for this genus.

EXPERIMENTAL

The air-dried plant material, collected in Brazil, province Minas Gerais (voucher RMK 8525, deposited in the U.S. National Herbarium, Washington) was extracted with Et_2O–petrol (1:2), and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). In the case of **1–5**, $AgNO_3$-coated Si gel

*Part 469 in the series "Naturally Occurring Terpene Derivatives". For Part 468 see Tsankova, E. and Bohlmann, F. (1983) *Phytochemistry* **22** (in press).

was used, while **6**–**9** were separated using Et_2O–petrol (1:10, five developments). The roots (100 g) afforded 5 mg **1**, 10 mg **2**, 3 mg **3**, 2 mg **4**, 1 mg **5**, 2 mg **6**, 2 mg **7**, 3 mg **8** and 3 mg **9**, while the aerial parts (210 mg) gave 30 mg squalene, 3 mg caryophyllene, 5 mg germacrene D, 2 mg bicyclogermacrene, 2 mg **1** and 1 mg **2**.

2-Methoxy-9-tigloyloxy-8, 10-epoxythymol tiglate (**7**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (PhOCOC=C), 1710 (C=CCO$_2$R), 1650 (C=C); MS *m/z* (rel. int.): 374.173 $[M]^+$ (2) ($C_{21}H_{26}O_6$), 274 $[M-RCO_2H]^+$ (2), 192 $[274-O=C=C(Me)CH=CH_2]^+$ (14), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (71).

2-Methoxy-9-(tigloyloxy and isobutyryloxy)-8,10-epoxythymol (isobutyrate and tiglate, respectively) (**8** *and* **9**). Inseparable colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (PhOCOR), 1735 (PhOCOC=C), 1715 (C=CCO$_2$R), 1650 (C=C); MS *m/z* (rel. int.): 362.173 $[M]^+$ (6) ($C_{20}H_{26}O_6$), 274 $[M-C_3H_7CO_2H]^+$ (5), 262 $[M-C_4H_7CO_2H]^+$ (8), 192 $[274-O=C(Me)CH=CH_2]^+$ and $[262-O=C-CMe_2]^+$ (78), 83 $[C_4H_7CO]^+$ (100), 71 $[C_3H_7CO]^+$ (20), 55 $[83-CO]^+$ (60).

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6′-*p*-HYDROXYBENZOYLMUSSAENOSIDIC ACID–AN IRIDOID GLUCOSIDE FROM *VITEX NEGUNDO**

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Key Word Index—*Vitex negundo*; Verbenaceae; iridoid; 6′-*p*-hydroxybenzoylmussaenosidic acid; ^{13}C NMR.

Abstract—Further chromatography of an ethanolic extract of *Vitex negundo* resulted in the isolation of another new iridoid glucoside which was characterized as 6′-*p*-hydroxybenzoylmussaenosidic acid.

In a previous communication [1], we reported on the isolation and characterization of a new iridoid, 2′-*p*-hydroxybenzolymussaenosidic acid (**1b**), from the ethanolic extract of the leaves of *Vitex negundo* L. We now report on the characterization of another minor iridoid from the same extract, which has been assigned the structure 6′-*p*-hydroxybenzoylmussaenosidic acid (**1a**).

Compound **1a** was isolated as a viscous solid. Its mass spectrum showed $[M]^+$ at 496, which corresponded to the molecular formula $C_{23}H_{28}O_{12}$. As in the case of **1b**, hydrolysis of **1a** resulted in the formation of *p*-hydroxybenzoic acid. The ^1H NMR spectrum of **1a** in DMSO-d_6 displayed signals at δ1.20 (3H) for a C-8 methyl group. A C-3 proton was located at δ7.40 as a sharp singlet and four protons of the aromatic moiety were observed as an AA′BB′ pattern at δ6.93 and 7.90 (J = 8.5 Hz), respectively. Other signals were located at the usual positions.

Acetylation at room temperature resulted in the formation of the tetra-acetate **2**, mp 91–92°. ^1H NMR signals for three acetate methyls were observed at δ1.93–2.10. A fourth signal appeared at δ2.33 and was assigned to the aromatic acetoxyl methyl. This clearly indicated that the *p*-hydroxybenzoyl moiety was attached to the glucose part of the molecule.

Methylation of **2** with diazomethane gave the methyl ester **3** as a viscous mass. The signal for a carbomethoxy group appeared at δ3.73. Alkaline hydrolysis of **1a** again resulted in the formation of two compounds. One of them

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