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DIESTERS OF 2-(*E*-3-METHYLOXIRANYL)HYDROQUINONE FROM *PIMPINELLA DIVERSIFOLIA*

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Key Word Index—*Pimpinella diversifolia*; Apiaceae; 1,2,4-trisubstituted benzenes; ^{1}H NMR spectra.

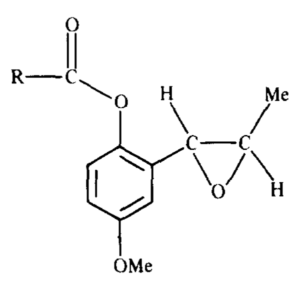
Abstract—Three minor components of the essential oil from roots of *Pimpinella diversifolia*, gathered in the Kumaun Region of India, have been identified, primarily on the basis of their ^{1}H NMR spectra, as the mixed angelate-isobutyrate esters and the diangelate ester of 2-(*E*-3-methyloxiranyl)hydroquinone.

INTRODUCTION

The (+)-*Z*-2-methyl-2-butenoate (angelate) and (+)-isobutyrate esters of 4-methoxy-2-(*E*-3-methyloxiranyl) phenol (**1a** and **1b**) are the major constituents of the essential oil from roots of pre-flowering *Pimpinella diversifolia* DC. gathered in the Kumaun Region of India [1]. Examination of the oil by GC-MS showed the presence of three minor components with longer R_ts than those of **1a** and **1b** and with relatively simple fragmentation patterns that indicated they were not terpenes. We describe here the isolation of these components and their identification as the previously unreported 1-angelyloxy-2-(*E*-3-methyloxiranyl)-4-isobutyryloxybenzene (**2a**), 1-isobutyryloxy-2-(*E*-3-methyloxiranyl)-4-angelyloxybenzene (**2b**) and 1,4-diangelyoxy-2-(*E*-3-methyloxiranyl)benzene (**2c**).

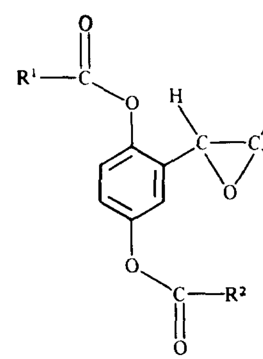
RESULTS AND DISCUSSION

Compounds **2a–c** were isolated as colourless oils in mg quantities by a modification of the chromatographic methods used to isolate **1a** and **1b**. The ^{1}H NMR spectra of **2a–c** are strikingly similar to those of **1a** and **1b**. Their signals at lowest field (δ6.95–7.11) show that the compounds are 1,4-trisubstituted benzenes [2], and their signals at δ3.60 ($J = 2.0$ Hz), 2.92 or 2.93, and *ca* 1.4 show the presence of an *E*-3-methyloxiranyl group [3]. Signals at about δ6.3 (1H) and between δ2.1 and 2.0 (6H) characteristic of the angelyloxy part [4] are seen in the spectra of **2a** and **2b**, and two closely spaced sets of these signals (14H total) are seen in the spectrum of **2c**. The spectra of **2a** and **2b** also have signals characteristic of the $CHMe_2$ part of an isobutyryl group. The *gem*-dimethyl



1

a R = C(Me)$\overset{Z}{=}$CHMe
b R = $CHMe_2$



2

a R^1 = C(Me)$\overset{Z}{=}$CHMe, R^2 = $CHMe_2$
b R^1 = $CHMe_2$, R^2 = C(Me)$\overset{Z}{=}$CHMe
c R^1 = R^2 = C(Me)$\overset{Z}{=}$CHMe

signal in the spectrum of **2a** is a doublet at δ1.29. In the spectrum of **2b**, as in that of **1b**, the *gem*-dimethyl signal consists of two doublets at *ca* δ1.34 separated by <0.01 ppm by the influence of one or both chiral centres of the 3-methyloxiranyl group [5], which must be *ortho* to the isobutyryloxy group.

The essential oil used for this study was from roots of plants gathered in the flowering stage rather than the pre-flowering stage. It was notably richer in **1a** and **1b** (54 and 21% compared with 37 and 15%) as well as **2a** (0.8%), **2b** (3.6%) and **2c** (1.2%), but their relative amounts were similar.

EXPERIMENTAL

Isolation of **2a–c**. *Pimpinella diversifolia* in the flowering stage, was gathered in Sept. from the same location and the essential oil was obtained as described earlier. Compounds **2a–c** were obtained together by CC (silica gel, hexane–Et_2O) of the essential oil and separated by HPLC on a 10-μ Porasil column using hexane–Et_2O (17:3) as the mobile phase. From 2.42 g of the essential oil were obtained 1–3 mg of **2a–c** as colourless oils. The purity of the samples was >90% as determined by GC using a Varian 3700 GC equipped with a CDS 111 microprocessor, an FID and a 30-m J&W fused silica capillary column coated with DB-5. R_ts observed for **2a–c** were 70.4, 71.4 and 78.6 min under conditions that gave R_ts of 57.3 and 50.5 min for **1a** and **1b**.

1-*Angelyloxy*-2-(E-3-*methyloxiranyl*)-4-*isobutyryloxybenzene* (**2a**). HREIMS (probe) 70 eV, *m/z* (rel. int., BP 83) 318.1469 $[C_{18}H_{22}O_5]^+$ (8.4), 248.1031 $[C_{14}H_{16}O_4]^+$ (8.2), 236.1044 $[C_{13}H_{16}O_4]^+$ (54.6), 166.0635 $[C_9H_{10}O_3]^+$ (29.8), 148.0528 $[C_9H_8O_2]^+$ (4.10) [$C_{18}H_{22}O_5$ requires: 318.1467]. ^{1}H NMR (360 MHz, $CDCl_3$): δ7.10 (*d*, $J = 8.7$ Hz, H-6), 7.00 (*dd*, $J = 8.7$, 2.7 Hz, H-5), 6.95 (*d*, $J = 2.7$ Hz, H-3), 6.30 (*qq*, $J = 7.1$, 1.6 Hz, H-3′), 3.60 (*d*, $J = 2.0$ Hz, H-1″), 2.93 (*qd*, $J = 5.1$, 2.0 Hz, H-3″), 2.77 (*septet*, $J = 7.0$ Hz, $\underline{H}CMe_2$), 2.09 (*dq*, $J = 7.2$, 1.6 Hz, H_3-4′), 2.06 (app *p*, $J = 1.6$ Hz, Me-2′), 1.39 (*d*, $J = 5.1$ Hz, Me-3″) and 1.29 (*d*, $J = 7.0$ Hz, $HC\underline{Me_2}$).

1-*Isobutyryloxy*-2-(E-3-*methyloxiranyl*)-4-*angelyloxybenzene* (**2b**). HREIMS (probe) 70 eV, *m/z* (rel. int., BP 83) 318.1481 $[C_{18}H_{22}O_5]^+$ (11.5), 248.1020 $[C_{14}H_{16}O_4]^+$ (10.1), 236.1043 $[C_{13}H_{16}O_4]^+$ (59.8), 166.0639 $[C_9H_{10}O_3]^+$ (40.6), 148.0528 $[C_9H_8O_2]^+$ (49.7) [$C_{18}H_{22}O_5$ requires: 318.1467]. ^{1}H NMR (360 MHz, $CDCl_3$): δ7.05 (app *d*, $J = 1.6$ Hz, H-5 and H-6), 6.97 (app *t*, $J_{app} = 1.6$ Hz, H-3) 6.25 (*qq*, $J = 7.0$, 1.6 Hz, H-3′), 3.60 (*d*, $J = 2.0$ Hz, H-1″), 2.92 (*q*, *d*, $J = 5.1$, 2.0 Hz, H-3″), 2.86 (septet, $J = 7.0$ Hz, $C\underline{H}Me_2$), 2.06 (*dq*, $J = 7.1$, 1.4 Hz, H_3-4′), 2.01 (*m*, Me-2′), 1.42 (*d*, $J = 5.1$ Hz, Me-3″), 1.335 (*d*, $J = 7.0$ Hz, $\underline{Me}$CHMe) and 1.330 (*d*, $J = 7.0$ Hz, MeCH$\underline{Me}$).

1,4-*Diangelyloxy*-2-(E-3-*methyloxiranyl*)*benzene* (**2c**). HREIMS (probe) 70 eV, *m/z* (rel. int., BP 83) 330.1469 $[C_{19}H_{22}O_5]^+$ (9.8), 248.1049 $[C_{14}H_{16}O_4]^+$ (45.3), 230.0943 $[C_{14}H_{14}O_3]^+$ (7.8), 166.0639 $[C_9H_{10}O_3]^+$ (3.1), 148.0515 $[C_9H_8O_2]^+$ (23.4) [$C_{19}H_{22}O_5$ requires: 330.1467]. ^{1}H NMR (360 MHz, $CDCl_3$): δ7.11 (*d*, $J = 8.7$ Hz, H-6), 7.05 (*dd*, $J = 8.7$, 2.7 Hz, H-5), 6.99 (*d*, $J = 2.7$ Hz, H-3), 6.30 (*qq*, $J = 7.0$, 1.6 Hz, H-3′), 6.24 (*qq*, $J = 7.0$, 1.6 Hz, H-3‴), 3.60 (*d*, $J = 2.0$ Hz, H-1″), 2.93 (*qd*, $J = 5.1$, 2.0 Hz, H-3″), 2.09–2.02 ($C_{4'}$-H_3, H_3-4‴ Me-2′, Me-2‴) and 1.39 (*d*, $J = 5.1$ Hz, Me-3″).

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