EXPERIMENTAL

The air-dried aerial parts (300 g) (voucher RMK 8429) were extracted with Et_2O–petrol (1:2) and the resulting extract was separated first by CC and further by repeated TLC (Si gel). The less polar fractions afforded 100 mg germacrene D, 30 mg caryophyllene and 20 mg bicyclogermacrene, followed by 20 mg **1**. The polar fractions could be separated only after esterification with CH_2N_2. Finally, 15 mg **2b**, 3 mg **3b–5b** (*ca* 2:3:1), 3 mg **6b**, 3 mg **7b**, 1 mg **8b** and 1 mg **9b** were obtained (sepn with Et_2O–petrol, 1:3, several times).

Methyl-2β-acetoxy-δ-cadinene-15-oate (**2b**). Colourless oil, IR $\nu_{\max}^{CCl_4}$, cm^{-1}: 1730, 1245 (OAc), 1720, 1645 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 306.183 $[M]^+$ (0.7) ($C_{18}H_{26}O_4$), 246 $[M-AcOH]^+$ (21), 215 $[246-{}^{\cdot}OMe]^+$ (7), 203 $[246-{}^{\cdot}CHMe_2]^+$ (42), 187 $[215-CO]^+$ (61), 176 $[246-H_2C{=}CHCHMe_2]^+$ (RAD, 100), 145 $[176-{}^{\cdot}OMe]^+$ (38);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{-16 \quad -17 \quad -21 \quad -36}\ (c = 1.4, CHCl_3).$$

Methyl-2β-isovaleryloxy-2-methylbutyryloxy and isobutyryloxy-δ-cadinene-15-oate (**3b–5b**). Not separated. Oily mixture, IR $\nu_{\max}^{CCl_4}$, cm^{-1}: 1730 (CO_2R), 1645 ($C{=}C$); MS *m/z* (rel. int.): 348.230 $[M]^+$ (0.4) ($C_{21}H_{32}O_4$), 334 $[M]^+$ (0.1) ($C_{20}H_{30}O_4$), 246–162 $[M-RCO_2H]^+$(24) ($C_{16}H_{22}O_6$), 203 $[246-{}^{\cdot}CHMe_2]^+$ (41), 187 $[246-{}^{\cdot}OMe, CO]^+$ (81), 176 $[246-H_2C{=}CHCHMe_2]^+$ (100), 85 $[RCO]^+$ (5), 71 $[RCO]^+$ (4).

Methyl-13-hydroxy-δ-cadinene-15-oate (**7b**). Colourless oil, IR $\nu_{\max}^{CCl_4}$, cm^{-1}: 3620 (OH), 1715, 1640 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 264.173 $[M]^+$ (37), 246 $[M-H_2O]^+$ (28), 232 $[M-MeOH]^+$ (100), 205 $[M-{}^{\cdot}CH(Me)CH_2OH]^+$ (53), 203 $[205-H_2]^+$ (70);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{-116 \quad -122 \quad -139 \quad -248}\ (c = 0.3, CHCl_3).$$

Methyl-7α-hydroxy-calamenene-15-oate (**8b**). Colourless oil, IR $\nu_{\max}^{CCl_4}$, cm^{-1}: 3620 (OH), 1730 (CO_2R); MS *m/z* (rel. int.): 262.157 $[M]^+$ (3) ($C_{16}H_{22}O_3$), 244 $[M-H_2O]^+$, (51), 201 $[244-{}^{\cdot}CHMe_2]^+$ (100), 169 $[201-MeOH]^+$, (28), 142 $[201-{}^{\cdot}CO_2Me]^+$ (44); $[\alpha]_D = +65^\circ$ ($c = 0.1$, $CHCl_3$).

1 mg **8b** in 2 ml C_6H_6 was heated with 2 mg *p*-TS acid for 1 hr at 70°. TLC afforded **10**; ^1H NMR see Table 1.

Methyl-7β-hydroxy-calamenene-15-oate (**9b**). Colourless oil, IR $\nu_{\max}^{CCl_4}$, cm^{-1}: 3620 (OH), 1730 (CO_2R); MS identical with that of **8b**. 1 mg **9b** with *p*-TS also afforded **10**, colourless oil, MS *m/z* (rel. int.): 244.146 $[M]^+$ ($C_{16}H_{20}O_2$), 201 $[M-{}^{\cdot}CHMe_2]^+$ (81), 169 $[201-MeOH]^+$ (43), 142 $[201-{}^{\cdot}CO_2Me]^+$ (100).

Acknowledgements—We thank Dr. D. Breedlove, California Academy of Science, San Francisco, for identification of the plant material and the Deutsche Forschungsgemeinschaft for financial support.

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Phytochemistry, Vol. 21, No. 12, pp. 2984–2985, 1982.
Printed in Great Britain.

0031-9422/82/122984-02$03.00/0
Pergamon Press Ltd.

TWO SINAPYL ALCOHOL DERIVATIVES FROM BERGAMOT ESSENTIAL OIL

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(*Revised received* 5 *March* 1982)

Key Word Index—*Citrus bergamia*; Rutaceae; sesquiterpenes; coumarin; sinapyl alcohol.

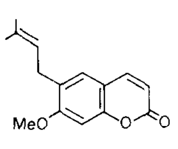
Abstract—Together with T-cadinol, β-eudesmol, farnesol, sitosterol and suberosin, two derivatives of sinapyl alcohol have been identified in the less volatile fraction of Bergamot oil.

INTRODUCTION

Bergamot oil, widely used in perfumery, is obtained by cold pressing the peel of the Bergamot fruit (*Citrus bergamia* Risso); two comprehensive reviews concerned with the chemical composition of this oil have been published recently [1, 2].

RESULTS AND DISCUSSION

In the course of our work on the less volatile components of Bergamot oil, we have shown the presence of three sesquiterpene alcohols: T-cadinol, β-eudesmol and farnesol (GC/MS) and have isolated sitosterol, suberosin (**1**), 3-(3, 4, 5-trimethoxy-



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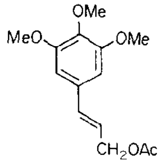

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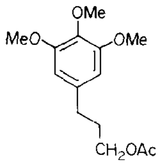

3

phenyl)propenal acetate (**2**) and 3-(3, 4, 5-trimethoxyphenyl)propanol acetate (**3**), all components not reported in the literature as constituents of Bergamot oil.

The two latter are sinapyl alcohol derivatives and to our knowledge have been isolated for the first time from a natural source. A glycoside of sinapyl alcohol has been isolated from *Magnolia grandiflora* [3]. Compound **3** has been prepared from 3, 4, 5-trimethoxycinnamic acid [3]. The structures of compounds **2** and **3** have been confirmed by synthesis.

EXPERIMENTAL

The less volatile part (5% wt of the oil) of Bergamot oil obtained after distillation of the volatile fraction (93% wt of the oil) under red. pres. followed by separation of most of the coumarins and furocoumarins (2% wt of the oil, by pptation in petrol at 0°), was fractionated by chromatography on a Si gel column. A GC/MS study of the fraction eluted by Et_2O–petrol (15 : 85) showed the presence of T-cadinol, β-eudesmol and farnesol (in ratios less than 0.01%wt of the oil). From the fraction eluted with Et_2O–petrol (2 : 3) we could isolate and identify sitosterol (mp 141–142°, TLC, HPLC, MS, ^{1}H NMR, IR) [4] and suberosin (mp 80–82°, HPLC, MS, ^{1}H NMR, IR) [5, 6]. These two compounds represent 0.1 and 0.055% wt of the oil

From the fraction eluted with Et_2O–petrol (1 : 1) compounds **2** and **3** were obtained by prep. HPLC. **3** was identical with a known [3] compound (^{1}H NMR, IR). Together, **2** and **3** represent *ca* 0.025% wt of the oil.

Methylation of sinapic acid [Me_2SO_4, $CHCl_3$, triethylbenzylammonium chloride, aq. NaOH (45%); reflux, 5 hr], followed by reduction ($LiAlH_4$, Et_2O; reflux, 2 hr) and acetylation (Ac_2O, pyridine; room temp., 2 hr) furnished a product identical in all respects (HPLC, TLC, ^{1}H NMR, IR, MS) with natural **2**. Hydrogenation of synthetic **2** (Pd/C 5%, EtOH; room temp., 3.5 hr) led to a product identical with compound **3**.

3-(3, 4, 5-*Trimethoxyphenyl)propenal acetate* (**2**). Colourless oil. Prep. HPLC (PE 3B, pump: PE, injector: Rheodyne; detector PE LC 75: UV λ_{max} 254 nm; Lichrosorb Si 60, 5 μm, column (250 × 10.5 mm); eluent: $CHCl_3$–hexane (5 : 95 → 2 : 3 in 80 min); 5 ml/min, 0.8 MPa. EIMS 70 eV, *m/z* (rel. int.): 266 $[M]^+$ (100) ($C_{14}H_{18}O_5$); 223 $[M-COMe_3]^+$ (11); 206 $[M-AcOH]^+$ (58); 191 $[206-Me]^+$ (15); 176 $[206-CH_2O]^+$ (96); 149 $[176-OH]^+$ (35). IR ν_{max}^{film} cm^{-1}: 2840 (νMe of –OMe); 1740 (C=O ester); 1650 (C=C); 1590, 1510 (C=C aromatic); 1240 (C–O–acetate); 960 (γCH double bond *trans*); 845, 780 (γCH aromatic ring). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.09 [3H, s, ($C\underline{H}_3COO$–)]; 3.84 [3H, s, (–$OC\underline{H}_3$)], 3.86 [2 × 3H, 2*s*, 2 × (–$OC\underline{H}_3$)], 4.71 [2H, d, (MeCOO–$C\underline{H}_2$–CH=CH–); 6.18 [1H, *dt*, *J* = 15 and 5.5 Hz) and 6.56 [1H, *d*, *J* = 15 Hz (–C$\underline{H}$=C$\underline{H}$–), 6.60 [2H, *s*, (2 aromatic protons)].

Acknowledgements—We are indebted to Dr. A. Galfré and Mr. A. Morello for HPLC analysis, and to Mr. M. Achard, Mrs. M. L'Official and Dr. P. Witz for ^{1}H NMR, IR and MS measurements.

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