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THREE NEW OXYGENATED CADINANES FROM *BACCHARIS* SPECIES

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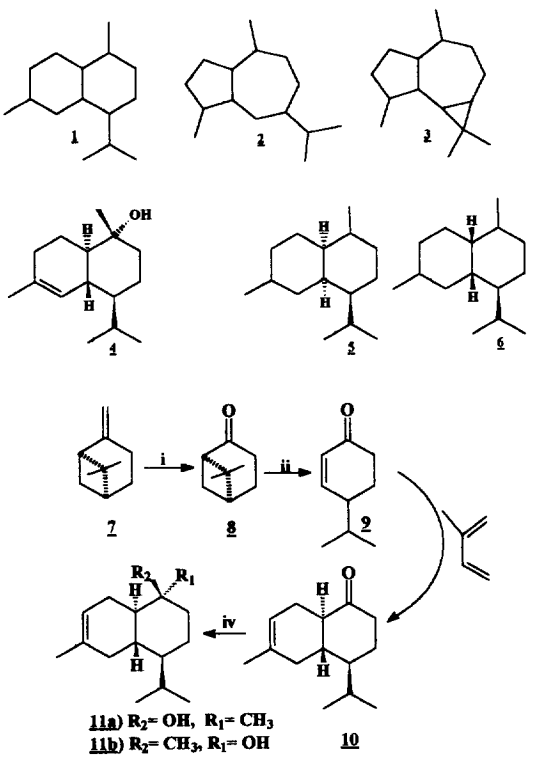
Key Word Index—*Baccharis platipoda*, *Baccharis tridentata*, *Baccharis myriocephala*; Compositae; essential oils, novel cadinanes.

Abstract—Synthesis of several (±)-[4S-(4β,4aβ,8aα)]-1,6-dimethyl-4-(1methylethyl)-1,2,3,4,5,8,8a-octahydro-1-naphthalenol derivatives (cadinanol derivatives) provided the necessary evidence for the identification of three novel cadinane derivatives [(±)-[1S-(1β, 4β, 4aβ, 8aα)]-1,6-dimethyl-4-(1-methylethyl)-1,2,3,4,4a,5,8,8a-octahydro-1-naphthalenol **11a**, (±)-[1S-(1β, 4β, 4aβ, 4aβ, 6α, 7α, 8aα)]-6, 7-epoxide-1,6-dimethyl-4-(1-methylethyl)-1,2,3,4,4a,5,6,7,8,8a-decahydro-1-naphthalenol **14** and (±)-[1S-(1β,4β,4aβ,6β,8aα)]-1,6-dimethyl-4-(1-methylethyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,6-naphthalenediol **15**] detected, in the essential oils of, *B. platipoda*. Compound **14** was also detected in *B. tridentata*. The synthetic compounds were characterized by one and two dimensional ^{1}H and ^{13}C NMR. The identification was obtained by coinjection of the oils with the synthetic standards and fragmentation pattern comparison.

INTRODUCTION

Characterization of some sesquiterpenes possessing either the cadinane **1** (bicyclo[4.4.0]decane), guaiane **2** (bicyclo[5.3.0]decane) or aromadendrane **3** (tricyclo[6.3.0.0^{2,4}]undecane) skeletons cannot be achieved on the sole basis of their the fragmentation pattern due to their similarities i.e., they present the same major fragments with no significant abundance differences [1, 2].

During our study of the *Baccharis* essential oils we have detected several unknown oxygenated sesquiterpenes possessing mass spectra compatible with alcohol derivatives of **1**, **2** or **3**. The presence of derivatives possessing the aromadendrane skeleton was confirmed making use of isolated, commercial and synthetic standards [3, 4]. The isolation of α-cadinol **4** [5] from *B. dracunculifolia* (characterized by ^{1}H, and ^{13}C NMR) was taken as indicative of the presence of other derivatives in the *Baccharis* essential oil. As previously cited, the identification of these compounds would only be possible by standard co-injection due to the minute amount in the oil or the limited availability of the oil itself. This led us to the synthesis of several oxygenated cadinane derivatives and to the search for these standards among the essential oil constituents of seven *Baccharis* (*B. caprariaefolia* DC, female and male, *B. dracunculifolia* DC male and female, *B. erioclada* DC



Scheme 1. Reagents (yield): i, $RuCl_3$, $3H_2O$, $NaIO_4$ (67.6%); ii, $AlCl_3$ (87.5%); iii, $AlCl_3$, isoprene (25.7%; iv, MeLi or MeMgBr (33% **11a** and 12% **11b**).

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male and female, *B. myriocephala* DC, *B. platipoda* DC, *B. tridentata* Vahl and *B. vincaefolia*). Three novel products were thus detected and a fourth was suggested.

RESULTS AND DISCUSSION

Synthesis of standards

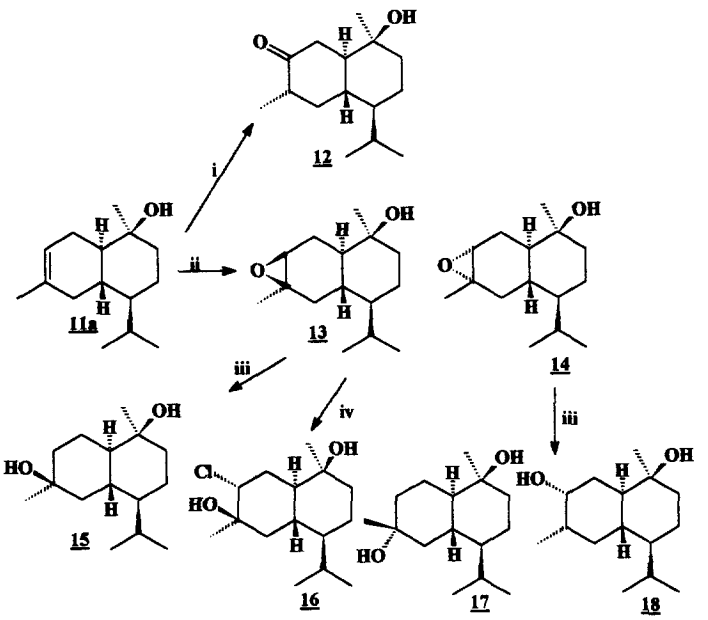
Our synthetic route did not take into consideration the muurolane **5** and amorphane **6** derivatives which are also included in the cadinane group [6].

As depicted in Scheme 1, the key feature in our synthetic program was to obtain cadinane derivatives containing one or two oxygens which were not previously reported, using an easily accessible methodology. A search in the literature revealed that the desired key intermediate, *trans*-octalone **10**, was readily available through a Diels-Alder reaction between isoprene and (±) cryptone **9** [7]. (+)–Nopinone **8**, (±) cryptone **9** starting material, was obtained using (−) β-pinene **7** and $KMnO_4$ [8], ozone or $RuCl_3.3H_2O$ [9]. Ozone is most efficient but our equipment was not appropriate to large scale reactions; ruthenium trichloride oxidation was efficient but rather expensive. Permanganate oxidation was most used in large scale reactions, mainly because in one reaction we could produce three intermediates of interest in our laboratory, including nopinone **8** [8]. Alkylation of **10** furnished (±)-axial-cadinol **11a** and (±) equatorial-cadinol **11b** (MeLi 45% yield, BrMgMe 87% yield) in a 3:1 ratio, respectively which were characterized by ^1H and ^{13}C NMR. The relative stereochemistry at carbon-1 was inferred based on the resonance of the C-1 methyl group, 28.4 ppm for the equatorial methyl and axial hydroxyl groups, compound **11a** (major component), and 21.3 ppm for the axial methyl and equatorial hydroxyl groups, compound **11b** (minor component) [10]. Formation of **11a** as a major diastereomer is expected, based on the preferred equatorial approach of alkyl lithium or alkyl magnesium bromides, nucleophiles larger than hydrides [11].

Taking into consideration that the compounds detected in the essential oils showed molecular ions and mass spectra consistent with cadinane derivatives containing two oxygen functions axial-cadinol **11a** was treated with MCPBA leading to (±)-ketol **12** and under milder conditions (MCPBA–$NaHCO_3$ [12]) to the epoxides **13** and **14** in a 1:1 ratio (40% yield). Epoxide **13** was treated with $LiAlH_4$ yielding the diol **15** (92% yield). Epoxide **14** had a completely different behaviour and produced compounds **17** and **18** in a 1.7:1 ratio. The lack of regioselectivity in the epoxide **14** opening can be ascribed to the competition between the favored *trans*-diaxial opening (formation of diol **18**), which involves a nucleophilic attack at the quaternary carbon of the epoxide (with more steric hindrance but a chair conformation transition state) and the hydride attack to the tertiary position (formation of diol **17**) which involves a higher energy transition state (skew boat). Compound **16** was produced in a dehydration [13] of **13**. The available amount of **13** did not allow any further investigation.

Identification of new cadinanes in Baccharis *essential oils*

The standards were co-injected with *B. caprariaefolia* DC female and male, *B. dracunculifolia* DC



Scheme 2. Reagents (yield): i, McPBA (11%); ii, MCPBA, $NaHCO_3$ (40% of a 1:1 mixture); iii, $LiAlH_4$ (92% for **15** and 88% for **17** and **18**); iv, $SOCl_2$, py.

male and female, *B. erioclada* DC male and female, *B. myriocephala* DC, *B. platipoda* DC, *B. tridentata* Vahl and *B. vincaefolia* essential oils and the compounds **11a**, **14** and **15** co-eluted with components in *B. platipoda*; compound **14** was also detected in *B. tridentata*.

Comparison of the mass spectra of the standards and with those of the oil components indicated that they were identical (Fig. 1). The molecular ion was not present in compound **19**, **11a**, **14** and **15**, and this fact was assigned to the loss of H_2O for **19**, **14** and **11a** and loss of H_2O and CH_3 for **15**. The same behaviour was observed in the natural products present in the essential oils. The molecular ions could be detected when the standard mass spectra were obtained using a solid probe.

It should be mentioned that α-cadinol **4**, isolated in our laboratory from commercial *B. dracunculifolia* essential oil has a different fragmentation pattern than that reported by Hayashi *et al.* [1].

In our case the structure was confirmed by ^{13}C NMR data, when compared with those reported by Sanz and Marco [5]. We have detected an additional cadinane, in *B. tridentata* and *B. myriocephala*, showing an almost identical fragmentation pattern to axial-cadinol **11a** but with a smaller retention index. The differences in RI and fragmentation patterns of **11a** and the unknown cadinol were compatible with those between **11b** and α-cadinol **4** (Fig. 1) Based on the above observations we suggested structure **19**. A search in the literature revealed that **19** is the T-cadinol [6] but the relative abundance of their major fragments (mainly 161 (50%), 119 (100%) and 105 (65%) for **19** and 161 (100), 119 (not mentioned) and 105 (19%) for T-cadinol [14]) are not compatible. We are now obtaining an authentic T-cadinol sample to clarify this matter. Finally the full assignment of the carbons and protons of the synthetic standards was obtained by one- and two-dimensional ^1H and ^{13}C NMR are given in the experimental data. Spectrometric discussions will be published elsewhere.

CONCLUSIONS

This work has confirmed that with a little synthetic work we can identify minor essential oil components, and in our case it has enabled the identification of 3 novel cadinols, (±)-[1S-(1β,4β,4aβ,8aα)]-1,6-dimethyl-5-(1-methylethyl)-1,2,3,4,4a,5,8,8a-octahydro-1-naphthalenol **11a**, (±)-[1S-(1β,4β,4aβ,6α,7α,8aα)]-6,7-epoxide-1,6-dimethyl-4-(1-methylethyl)-1,2,3,4,4a,5,6,7,8,8a-decahydro-1-naphthalenol **14** and (±)-[1S-(1β,4β,4aβ,6β,8aα)]-1,6-dimethyl-4-(1-methylethyl)-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,6-naphthalenediol **15**, minor components of *B. platipoda* essential oil. Compound **14** was also detected in *B. tridentata*. We believe that the synthesis of oxygen containing derivatives of the hydrocarbons present in an essential oil can lead to the identification of several new sesquiterpenes.

EXPERIMENTAL

Mps were recorded with a Kofler hot plate set up in a microscope Thermopan model (C. Reichert Optische Werke A G). FT-IR Spectra were taken on a Perkin Elmer 298 spectrophotometer. ^1H NMR spectra were recorded with a Bruker AC 300P (300 MHz) or a GEMINI 300 (300 MHz, Varian) spectrometer. $CDCl_3$ was used as the solvent, with Me_4Si (TMS) as internal standard. ^{13}C NMR spectra were obtained with a Bruker AC 300 P (75.4 MHz) or a GEMINI 300 (75.4 MHz, Varian) spectrometer. $CDCl_3$ (77.0 ppm) was used as internal standard. The number of hydrogens attached to the carbon atoms were obtained from the DEPT-135 spectra (Distortionless Enhancement by Polarization Transfer): CH_3/CH (+), CH_2 (−), C_{quat} (absent), DEPT-90 spectra (CH). 2-D NMR spectroscopy was performed with standard COSY (H-H correlation) and HETCOR (C-H correlation) pulse sequence. Mass spectra were determined with a Varian MAT 731. GC was effected on a HP chromatograph, VCD 5890A model, equipped with a flame ionization detector. A J&W Scientific DB-5 fused silica capillary column (30 m × 0.25 mm × 0.25 μm) was used at a H_2 flow rate of 30 ml min^{-1}. Column temp. was programmed from 105° to 280° (2° min^{-1}). The retention indices were calculated coinjecting the oil sample with a hydrocarbon mixture (nC_{10}–nC_{30}) and applying the Van der Dool and Kratz equation [15]. GC-MS analyses were carried out using HP 5890 MSD system, equipped with a J&W DB-5 capillary column (30 m × 0.25 mm × 0.25 μm), He was used as the carrier gas. The column temp. program was: 55°-20°/min-120°-1.5°/min-150°-20°/min-200°. All air-sensitive reactions were carried out under argon. The citation 'dried and evapd' implies that the soln was dried over Na_2SO_4 and the solvent was evapd under red. pres. Voucher specimens and plant descriptions were cited in ref [4].

(+)-*Nopinone* **8**. To a stirred soln of (−)-β-pinene **7** (5.0 g, 35 mmol) in MeCN (150 ml), CCl_4 (150 ml) and H_2O (220 ml) small portions of $NaIO_4$ (30.8 g, 144 mmol) and $RuCl_3.3H_2O$ (94 mg, 3.6 mmol) were added. The reaction was further stirred at room temp. for 2 hr and then partitioned between sat. $NaHCO_3$ soln. and Et_2O. The solvent was evapd and the residue dissolved in a small amount of hexane and filtered over celite and active charcoal. The filtrate was dried and evapd. The crude product was distilled under red. pres. (70°) to give (+)-nopinone **8** (3.38 g, 67.6%) as a yellow oil: IR (film): 1720–^1H NMR (300 MHz, CCl_4, TMS): δ 0.85 (3H, *s*), 1.33 (3H, *s*) – ^{13}C NMR (75.4 MHz, CCl_4, TMS): δ 21.32 (C-5), 21.93 (C-9), 25.04 (C-9), 25.89 (C-8), 32.10 (C-6), 40.44 (C-4), 40.81 (C-3), 57.24 (C-2), 209.69 (C-1). EI-MS (probe), 70 eV, *m/z* (rel. int.): 138 $[M]^+$ (21), 123 (12), 120 (3), 110 (6), 109 (2), 95 (29), 83 (100), 82 (12), 79 (6), 67 (17), 55 (43), 43 (11), 41 (33).

(±)-*Cryptone* **9**. To a stirred soln of (+)-nopinone **8** (3.2 g, 23 mmol) in CH_2Cl_2, freshly sublimed $AlCl_3$ was added at 0°. After 1.5 hr the reaction was extracted

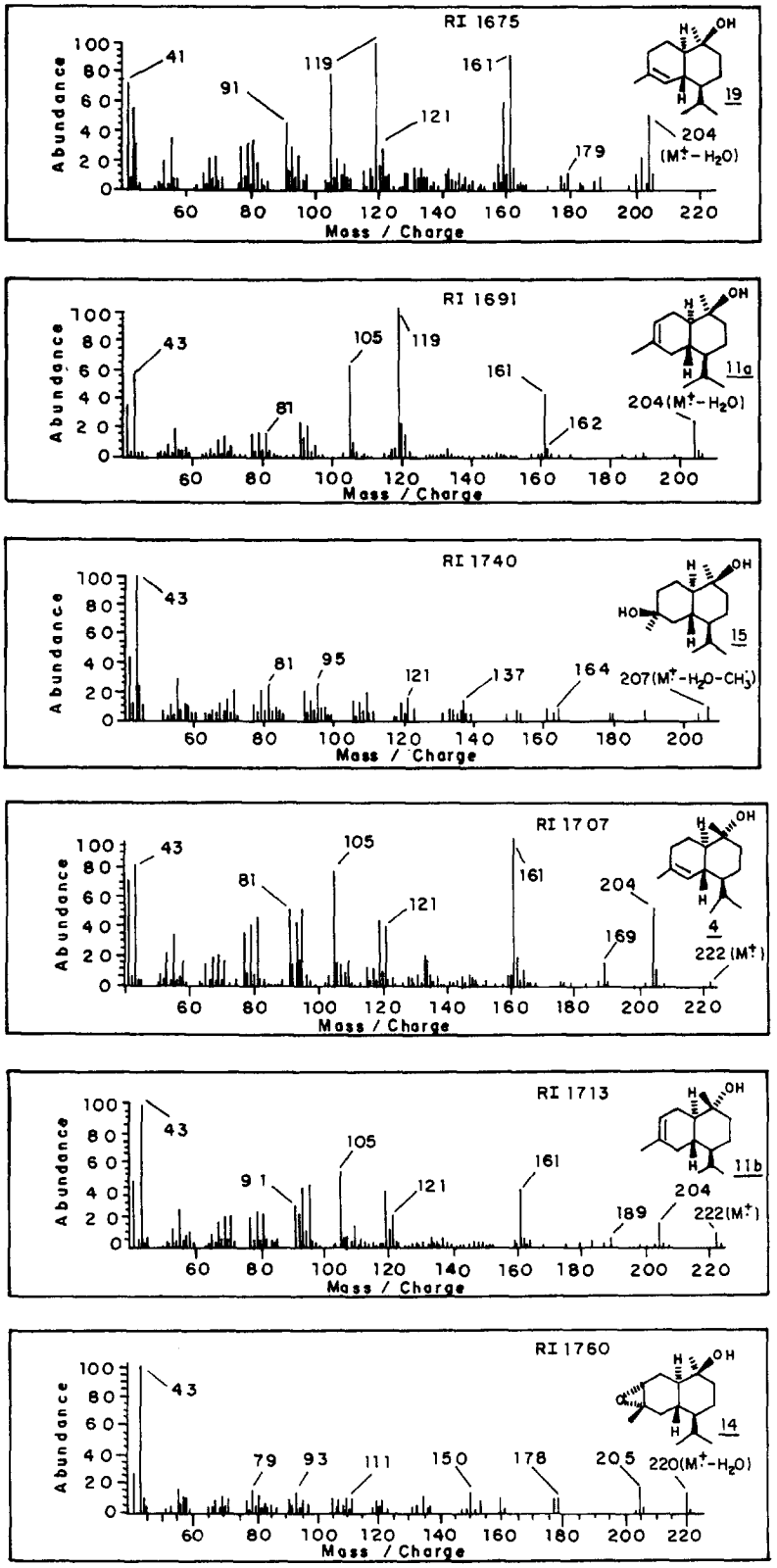


Fig. 1. Mass spectra and retention indices of synthethic and natural cadinols present in *Baccharis* essential oils.

with Et_2O. The organic layer was dried and evapd. The crude product was distilled under red. pres. (125°) to give (±) cryptone **9** (2.8 g, 87.5%) as a yellow oil. IR (film): ν (cm^{-1}) 1168 – ^1H NMR (300 MHz, CCl_4, TMS): δ 0.97 (3H, *d*, J = 6.8 Hz, H-9), 0.98 (3H, *d*, J = 6.8 Hz, H-8), 5.90 (1H, *dd*, J = 10.5; 3 Hz, H-2), 6.74 (1H, *dt*, J = 10.5; 2.6 Hz, H-3) – ^{13}C NMR (75.4 MHz, CCl_4, TMS): δ 19.39 (C-9), 19.54 (C-8), 25.16 (C-5), 31.43 (C-7), 36.86 (C-6), 42.25 (C-4), 130.01 (C-2), 150.95 (C-3), 195.64 (C-1). GC-MS 70 eV, *m/z* (rel. int.): 138 $[M]^+$ (27), 123 (4), 120 (3), 110 (4), 97 (11), 96 (100), 95 (58), 81 (21), 67 (20), 55 (13), 43 (58), 41 (37).

(±)-*trans-Octalone* **10**. To a stirred soln of (±) cryptone **9** (1.4 g, 10 mmol) in dry toluene (9 ml) under argon, a suspension of anhydrous $AlCl_3$ (333 mg, 2.5 mmol) in dry toluene (55 ml) was added. After the complexation time (40 min) a soln of isoprene **5** (10.2 g, 0.15 mmol) in dry toluene (22 ml) was added, the flask was closed and stirred for a further 5 hr at 60°. The resulting soln was cooled, poured over ice water and extracted with Et_2O. The organic layer was washed (10% aq. $NaHCO_3$), dried and evapd. The crude product was purified by medium pres. column chromatography (hexane–EtOAc, 99:1) to give (±)-*trans*-octalone **10** (0.4 g, 20%) as a clear yellow oil: IR (film): ν (cm^{-1}) 1712 – ^1H NMR (300 MHz, $CDCl_3$): δ 0.75 (3H, *d*, J = 6.9 Hz, H-2′), 0.99 (3H, *d*, J = 6.9 Hz, Me-C1′), 1.65 (3H, *s*, Me-C6), 5.40 (1H, *bs*, H-7) – ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS): δ 14.93 (C-2′), 21.74 (Me-C1′), 23.37 (Me-C6), 24.78 (C-8), 25.12 (C-3), 26.15 (C-1′), 36.01 (C-5), 41.45 (C-2), 41.80 (C-4a), 47.76 (C-4), 49.36 (C-8a), 119.79 (C-7), 132.20 (C-6), 212.56 (C-1). GC-MS, 70 eV, *m/z* (rel. int.): 206 $[M]^+$ (100), 163 (37), 145 (97), 136 (24), 121 (64), 115 (55), 105 (28), 93 (50), 77 (40), 71 (33), 67 (40), 55 (59), 43 (98).

(±)-[1*S*-(1β,4β,4aβ,8aα)]-1,6-*Dimethyl*-4-(1-*methylethyl*)-1,2,3,4,4*a*,5,8,8*a*-*octahydro*-1-*naphthalenol* **11***a* *and* (±)-[1*S*-(1α,4β,4aβ,8aα)]-1,6-*dimethyl*-4-(1-*methylethyl*)-1,2,3,4,4*a*,5,8,8*a*-*octahydro*-1-*naphthalenol* **11***b*. *Method A*: To a stirred soln of (±)-*trans*-octalone **10** (237 mg, 1.15 mmol) in THF (5 ml), MeLi (0.96 ml, 1.72 mmol) in THF was added at −78°. After 15 min, a NH_4Cl soln was added dropwise. The resulting mixture was extracted with Et_2O and the organic layer was dried and evapd. The crude product was purified by column chromatography using gradient elution hexane–AcOEt (9:1) to give (±) axial-cadinol **11a** (85 mg, 33%) as an oil and (±) equatorial-cadinol **11b** (30 mg, 12%) as a solid. *Method B*: To a stirred soln of (±)-*trans*-octalone **10** (138 mg; 0.7 mmol) in THF (10 ml), a soln of 1.4 M vinylmagnesium bromide (2 ml, 2.8 mmol) was added at room temp. After 30 min a NH_4Cl soln was added dropwise. The resulting soln was extracted with Et_2O, dried and evapd to give (±) axial-cadinol axial **11a** and (±) equatorial-cadinol **11b** (134 mg, 87.3%) in a 3:1 (GC) ratio. (±) axial-cadinol **11a**: IR (film): ν (cm^{-1}) 3447, 1633 – ^1H NMR (300 MHz, $CDCl_3$, TMS); δ 0.77 (3H, *d*, J = 6.9 Hz, H-2′), 092 (3H, *d*, J = 6.9 Hz, Me-C1′), 1.64 (3H, *bs*, Me-C6), 1.17 (3H, *s*, Me-C1), 5.40 (1H, *bs*, H-7) – ^{13}C NMR (75.4 MHz, $CDCl_3$); δ 15.05 (C-2′), 18.69 (C-3), 21.52 (Me-C1′), 23.34 (Me-C6), 25.14 (C-8), 26.10 (C-1′), 28.40 (Me-C1′), 34.39 (C-4a), 35.47 (C-5), 40.19 (C-2), 45.31 (C-8a), 48.75 (C-4), 70.28 (C-1), 120.30 (C-7), 132.58 (C-6) – GC-MS (R_t 23.806 min, R_i = 1691), *m/z* (rel. int.); 222 (absent) $[M]^+$, 204 (24) $[M - H_2O]^+$, 183 (2), 161 (45), 133 (6), 119 (100), 105 (63), 91 (22), 81 (15), 69 (12), 55 (19), 43 (57). (±) cadinol equatorial **11b**: IR (film): ν (cm^{-1}) 3447, 1654 – ^1H NMR (300 MHz, $CDCl_3$): δ 0.77 (3H, *d*, J = 6.9 Hz, H-2′), 0.94 (3H, *d*, J = 6.9 Hz, Me-C1′), 1.12 (3H, *s*, Me-C1), 1.65 (3H, *s*, Me-C6), 1.99 (1H, *m*, H-1), 5.42 (1H, *dd*, J = 3.75; 1.5 Hz, H-8) – ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS): δ 15.00 (C-2′), 21.15 (C-3), 21.31 (Me-C1), 21.64 (Me-C1′), 23.27 (Me-C6), 25.12 (C-8), 25.99 (C-1′), 36.33 (C-5), 36.43 (C-4a), 42.30 (C-2), 47.67 (C-8a), 49.19 (C-4), 72.76 (C-1), 120.24 (C-7), 132.55 (C-6 – CG-MS (R_t 25.592 min, *Ri* = 1713), 70 eV, *m/z* (rel. int.): 222 $[M]^+$ (10), 204 (15), 189 (4), 161 (36), 133 (6), 119 (37), 105 (50), 95 (42), 79 (25), 71 (20), 55 (23), 43 (100).

(±) [1*S*-(1β,4β,4aβ,6β,7β,8aα)]-6,7-*Epoxide*-1,6-*dimethyl*-4-(1-*methylethyl*)-1,2,3,4,4a,5,6,7,8,8a-*decahydro*-1-*naphthalenol* **13** *and* (±) [1*S*-(1β,4β,4aβ,6α,7α,8aα)]-6,7-*epoxide*-1,6-*dimethyl*-4-(1-*methylethyl*) 1,2,3,4,4*a*,5,6,7,8,8*a*-*Decahydro*-1-*naphthalenol* **14**. To a stirred soln of (±) cadinol axial **11a** (148 mg; 0.669 mmol), 80% MCPBA (115 mg; 0.669 mmol) and $NaHCO_3$ (134 mg; 1.60 mmol) in CH_2Cl_2 (10 ml) was added at room temp. for 0.5 hr. The mixt. was partitioned between CH_2Cl_2 and 10% aq. Na_2SO_3. The organic layer was washed (10% $NaHCO_3$ and brine), dried and evapd. The crude product was purified by column chromatography using $CHCl_3$–AcOEt (9:1) as eluent to give (±) 6α,7α-epoxide **13** (15.28 mg; R_f 0.57, $CHCl_3$ – EtOAc, 8:2) and (±) 6β,7β-epoxide **14** (25.61 mg; R_f 0.45, $CHCl_3$—EtOAc, 8:2) with total yield 40% (±)-,6β,7β-epoxide **14**: ^1H NMR (300 MHz, $CDCl_3$): δ 0.74 (3H, *d*, J = 6.9 Hz, H-2′), 0.83 (3H, *d*, J = 6.9 Hz, Me-C1′), 1.12 (3H, *s*, Me-C1), 1.30 (3H, *s*, Me-C6), 3.03 (1H, *d*, J = 5.13 Hz, H-7 – ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 15.03 (C-2′), 18.58 (C-3), 21.45 (Me-C1′), 23.05 (Me-C-6), 24.04 (C-8), 25.89 (C-1′), 28.04 (Me-C1), 31.53 (C-4a), 35.09 (C-5), 40.08 (C-2), 44.64 (C-4), 48.04 (C-8a), 57.66 (C-6), 59.10 (C-7), 69.88 (C-1) – GC-MS (R_t 32.207 min, *Ri* = 1760), *m/z* (rel. int.); 238 $[M]^+$ (2), 220 (13), 205 (16), 195 (6), 177 (16), 153 (20), 135 (13), 107 (14), 105 (10), 93 (20), 81 (13), 71 (15), 55 (16), 43 (100). (±) 6α,7α-epoxide **13**: Mp (uncorr.): 143–149° – ^1H NMR (300 MHz, $CDCl_3$): δ 0.75 (3H, *d*, J = 6.9 Hz, H-2′), 0.89 (3H, *d*, J = 6.9 Hz, Me-C1′), 1.17 (3H, *s*, Me-C1), 1.31 (3H, *s*, Me-C6), 3.08 (1H, *bs*, H-7) – ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.97 (C-2′, 18.49 (C-3), 21.52 (Me-C1′), 24.74 (Me-C6), 25.54 (C-8), 25.99 (C-1′), 28.53 (Me-C1), 34.19 (C-5), 40.39 (C-2), 40.51 (C-4), 48.65

(C-8a), 57.05 (C-6), 60.64 (C-7), 70.29 (C-1) – GC-MS (R_t 31.280 min), 70 eV, *m/z* (rel. int.): 238 (1) $[M]^+$, 220 (13), 205 (23), 191 (12), 177 (16), 153 (2), 135 (13), 119 (10), 107 (14), 93 (18), 81 (16), 55 (17), 43 (100).

(±) [1*S*-(1β, 4β, 4aβ, 6α, 8aα)]-1,6-*Dimethyl*-4-(1-*methylethyl*)-7-*oxo*-1,2,3,4,4*a*,5,6,7,8,8*a*-*decahydro*-1-*naphthalenol* **12**. A stirred soln of (±) cadinol axial **11a** (78 mg; 0.35 mmol) and 80% MCPBA (88 mg; 0.40 mmol) in CH_2Cl_2 (6 ml) was left 3 hr at room temp. The mixture was partitioned between CH_2Cl_2 and 10% aq. Na_2SO_3. The organic layer was washed (brine), dried and evapd. The crude product was purified by silica column chromatography eluted with hexane-EtOAc (9:1) yielding (±)-cetol **9** (9 mg, 11%): IR (film): ν (cm^{-1}) 3440, 1701 – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.82 (3H, *d*, *J* = 6.9 Hz, H2′), 0.92 (3H, *d*, *J* = 6.9 Hz, Me-C1′), 1.02 (3H, *d*, *J* = 6.4 Hz, Me-C6), 1.15 (3H, *s*, Me-C1), 2.03 (1H, *m*, H-1′) – ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS): δ 14.31 (Me-C6), 15.03 (C-2′), 18.92 (C-3), 21.70 (Me-C1′), 26.61 (C-1′), 28.29 (Me-C1), 38.08 (C-4a), 39.16 (C-5), 40.40 (C-2), 41.18 (C-8), 44.20 (C-6), 47.23 (C-4), 52.18 (C-8a), 70.57 (C-1), 214.44 (C-7) – GC-MS (R_t 31.911 min), 70 eV, *m/z* (rel. int.): 238 $[M]^+$ (2), 220 (13), 205 (17), 191 (4), 177 (16), 159 (15), 150 (10), 135 (14), 119 (16), 105 (14), 93 (21), 81 (15), 69 (12), 55 (27), 43 (100).

(±)-[1*S*-(1β, 4β, 4aβ, 6α, 8aα)]-1,6-*Dimethyl*-4-(1-*methylethyl*)-1,2,3,4,4*a*,5,6,7,8,8*a*-*decahydro*-1,6-*naphthalenediol* **15**. To a stirred soln of (±) 6β, 7β-epoxide **13** (14 mg; 0.063 mmol) in Et_2O (8 ml), $LiAlH_4$ (12 mg) was added in small portions and left at room temp. for 1 hr. The excess of $LiAlH_4$ was destroyed with small amount of $MgSO_4$ paste. The resulting soln was filtered and evapd to give (±) 1β, 6β-diol **15** (14 mg, 92%): Mp (uncorr.) 118–129° – ^1H NMR (300 MHz, $CDCl_3$): δ 0.75 (3H, *d*, *J* = 7.1 Hz, H-2′), 0.89 (3H, *d*, *J* = 7.1 Hz, Me-C1′), 1.19 (3H, *s*, Me-C1), 1.21 (3H, *s*, Me-C6), 1.95 (1H, *m*, H-1′) – ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.91 (C-2′), 19.15 (C-2), 20.72 (C-8), 21.71 (Me-C1′), 25.86 (C-1′), 28.55 (Me-C1), 31.31 (Me-C6), 33.81 (C-4a), 38.18 (C-5), 40.41 (C-2), 42.11 (C-7), 47.68 (C-4), 49.67 (C-8a), 69.26 (C-7), 70.59 (C-1) – GC-MS (R_t 30.069 min, *Ri* = 1740), *m/z* (rel. int.): 240 (absent) $[M]^-$, 225 (5), 222 (5), 207 (21), 204 (36), 189 (19), 161 (89), 137 (17), 119 (47), 109 (16), 105 (73), 93 (47), 81 (37), 77 (23), 69 (20), 55 (32), 43 (100).

(±)[1*S*-(1β,4β,4aβ,6α,8aα)]-1,6-*Dimethyl*-4-(1-*methylethyl*)-1,2,3,4,4*a*,5,6,7,8,8*a*-*decahydro*-1,6-*naphthalenediol* **17**. To a stirred soln of (±)6α, 7α-epoxide **14** (10 mg; 0.042 mmol) in Et_2O (8 ml), $LiAlH_4$ (7 mg) was added and left at room temp. for 1 hr. The excess of $LiAlH_4$ was destroyed with small amount of $MgSO_4$ paste. The resulting soln was filtered and evapd to give a mixture of two diols **17** e **18** (9 mg, 88%): GC-MS (R_t = 31.811 min) 70 eV, *m/z* (rel. int.): 207 (19), 204 (25), 161 (53), 133 (13), 119 (44), 105 (70), 91 (42), 81 (38), 77 (26), 55 (24), 43 (100); (R_t = 34.301 min) 70 eV, *m/z* (rel. intl): 225 (30), 207 (27), 188 (20), 171 (10), 161 (26), 119 (39), 105 (30), 91 (24), 69 (21), 55 (43), 44 (100), 43 (80).

(±) [1*S*-(1β,4β,4aβ,6β,8aα)]-7-*Chloro*-1,6-*dimethyl*-4-(1-*methylethyl*)-1,2,3,4,4*a*,5,6,7,8,8*a*-*decahydro*-1,6-*naphthalenediol* **16**. A soln of (±)-6β, 7β-epoxide **13** (13 mg; 0.055 mmol) in pyridine (1 ml) was added slowly $SOCl_2$ (0.083 mmol, 6 μl) with stirring at 0° for 5 hr. The resulting soln was partitioned between CH_2Cl_2 (10 ml) and 10% aq. $CuSO_4$. The organic layer was dried and evapd. The crude product was purified by column chromatography using gradient elution $CHCl_3$–EtOAc (9:1) to give (±)-7α-chloro-1β,4β-diol **16** (4 mg, 25%): Mp (uncorr.) 139–150°-IR (KBr): ν (cm^{-1}) 3455, 800 – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.75 (3H, *d*, *J* = 6.9 Hz, H-2′), 0.90 (3H, *d*, *J* = 6.9 Hz, Me-C1′), 1.18 (3H, *s*, Me-C1), 1.35 (3H, *s*, Me-C6), 1.96 (1H, *m*, H-1′), 4.04 (1H, H-7) – ^{13}C NMR (75.4 MHz, $CDCl_3$, TMS): δ 15.03 (C-2′), 19.39 (C3), 21.42 (Me-C1′), 26.02 (C-1′), 28.53 (Me-C1), 29.00 (Me-C6), 29.54 (C87), 33.46 (C-4a), 36.26 (C-5), 40.78 (C-2), 42.82 (C-8a), 47.30 (C-4), 65.49 (C-7), 70.75 (C-1), 72.22 (C-6) – GC-MS: R_t 30.114 min, 70 eV, *m/z* (rel. int.): 239 (0.15), 238 (0.65), 220 (41), 205 (47), 177 (25), 150 (32), 107 (14), 93 (20), 79 (14), 55 (17), 43 (100); GC-MS (R_t 40.198 min), 70 eV, *m/z* (rel. int.): 276 (0.35), 274 $[M]^+$ (0.89), 261 (6.8), 259 (18), 243 (3.7), 241 (9), 238 (4), 205 (10), 162 (21), 159 (28), 119 (16), 93 (19), 71 (22), 55 (17), 43 (100).

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