PERKIN 1

Facile access to optically active ring C aromatic diterpene derivatives from manool. Highly efficient syntheses of (+)-12-methyl-7-oxo-podocarpa-8,11,13-triene-13-carboxylic acid, (+)-13-methyl-7-oxopodocarpa-8,11,13-triene-12-carboxylic acid and (+)-nimbiol

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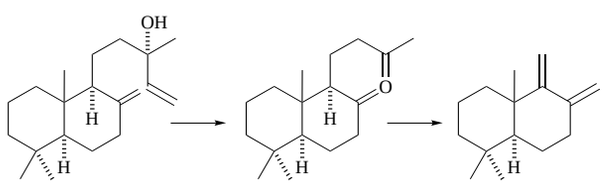
The extension of our recently developed strategy using the key intermediate 2, obtainable in two steps (52% overall yield) from manool 1, to the synthesis of naturally occurring ring C aromatic diterpene derivatives provides in three steps (+)-12-methyl-7-oxopodocarpa-8,11,13-triene-13-carboxylic acid 4b and its isomer 6b, and in seven steps (+)-nimbiol 11b, in good overall yields. This synthesis discloses that the structure 4b assigned to margolone isolated from *Azadirachta indica* A. Juss is incorrect and needs to be reinvestigated.

Introduction

We have recently developed a highly efficient, short route to the synthesis of naturally occurring, biologically active drimane-type sesquiterpenes,[1] (+)-confertifolin, (+)-isodrimenin, (+)-euryfuran and (−)-warburganal,[2] and also bicyclofarnesane-type sesquiterpenes, (+)-albicanol and (+)-bicyclofarnesol.[3] In all these syntheses, the diene **2**,[4] obtained in two steps (52% overall yield) (Scheme 1) from commercially available manool

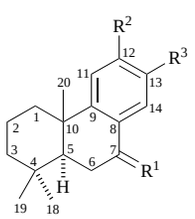


1 **2**

Scheme 1

1, has been used as a common key intermediate. This paper aims to demonstrate another utility of this diene for the synthesis of optically active ring C aromatic diterpene derivatives,[5] such as compounds **4b, 6b** and **11b**.

Because of its wide range of therapeutic and pesticidal properties, the study of the constituents of *Azadirachta indica* A. Juss (Meliaceae), commonly known as neem, has attracted much interest among natural product chemists during the past two decades.[6,7] A series of new terpenoidal constituents have been isolated from the various parts of neem. The tricyclic diterpenoid margolone was one of them and its chemical structure has been assigned the structure **4b** on the basis of spectroscopic evidence. This compound appears to be interesting from a biogenetic point of view since it possesses carbon substituents at both C-12 and C-13 in the podocarpane skeleton.



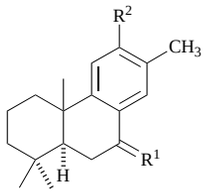
3 $R^1 = H_2$, $R^2 = CH_3$, $R^3 = CO_2CH_3$
4a $R^1 = O$, $R^2 = CH_3$, $R^3 = CO_2CH_3$
4b $R^1 = O$, $R^2 = CH_3$, $R^3 = CO_2H$
5 $R^1 = H_2$, $R^2 = CO_2CH_3$, $R^3 = CH_3$
6a $R^1 = O$, $R^2 = CO_2CH_3$, $R^3 = CH_3$
6b $R^1 = O$, $R^2 = CO_2H$, $R^3 = CH_3$

Results and discussion

Diels–Alder reaction of the diene **2** with methyl but-2-ynoate was carried out by heating the neat mixture in a sealed tube. No reaction took place below 160 °C. Above 180 °C, however, reaction was accompanied by a considerable degree of pyrolytic aromatization[8] and the major products were not the diene adducts but ring C aromatic compounds. At 214 °C almost quantitative aromatization occurred and a mixture of two isomeric products **3** and **5** (ratio of 3 : 2) was obtained in 80% yield. These two compounds were separated by medium pressure liquid chromatography over silica gel and their structures were differentiated by means of 2D NMR ^1H and ^{13}C single and multiple bond correlation studies.[5] The less polar product was assigned the structure **5** and the other more polar isomer, the structure **3**, which appeared to be that required for the synthesis of margolone. On benzylic oxidation with *tert*-butyl hydroperoxide and chromium hexacarbonyl[9] compound **3** afforded the 7-oxo-derivative **4a** (80% yield). Subsequent alkaline hydrolysis led to the desired compound **4b** (100% yield). When, however, the physical and spectroscopic properties of this synthetic compound **4b** were compared with those[6] reported for natural margolone, some significant discrepancies[5] were observed between them. We report here that the structure published for margolone is not correct and needs to be reinvestigated. The diterpene having the structure **4b** cannot be coloured yellow as reported with UV λ_{max} 360 and 383 nm. Probably the isolated compound was impure and needs to be properly characterised.

Benzylic oxidation of the isomeric compound **5** with *tert*-butyl hydroperoxide and pyridinium dichromate[10] afforded the other ring C aromatic diterpene **6a** (78% yield). Subsequent alkaline hydrolysis led to compound **6b** (100% yield).

Nimbiol was isolated from the trunk bark of *Melia azadirachta* Linn. (syn. *Azadirachta indica* Juss) and was shown to possess the structure **11b**.[11] Two independent groups of chemists[12] previously synthesised this diterpene from podocarpic acid. In our synthesis compound **6b**, one of the



7 $R^1 = H_2$, $R^2 = CH_2OH$
8 $R^1 = H_2$, $R^2 = CHO$
9 $R^1 = H_2$, $R^2 = OCHO$
10a $R^1 = H_2$, $R^2 = OH$
10b $R^1 = H_2$, $R^2 = OAc$
11a $R^1 = O$, $R^2 = OAc$
11b $R^1 = O$, $R^2 = OH$

intermediates obtained earlier, was employed as a convenient precursor.

Reduction of compound **5** with lithium aluminium hydride afforded the alcohol **7** (94% yield). Oxidation of alcohol **7** with tetra-*n*-propylammonium perruthenate and *N*-methylmorpholine *N*-oxide[13] gave the aldehyde **8** (94%). Baeyer–Villiger oxidation[14] of the aldehyde **8** was effected by heating with *m*-chloroperoxybenzoic acid in methylene chloride at refluxing temperature for 24 h. The resulting formate **9** (64% yield) was hydrolysed with methanolic potassium hydroxide to the phenol **10a** (96% yield). Acetylation of the phenol **10a** with acetic anhydride in pyridine afforded the acetate **10b** (90% yield) which was then oxidised with *tert*-butyl hydroperoxide and pyridinium dichromate[10] to give the 7-oxo derivative **11a** (74% yield). Subsequent alkaline hydrolysis afforded compound **11b**, identical with natural (+)-nimbiol[11,12] (100% yield).

The importance of the diene **2** as a key precursor in this synthesis has now been well demonstrated. Our strategy using the diene **2** as a building block will continue to find wide application in the synthesis of many other similar naturally occurring ring C aromatic diterpenes.

Experimental

Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded with a Nicolet 5DXC FT-IR spectrometer. UV spectra were determined with a UV–VIS Milton Roy 3000 array instrument. NMR spectra were obtained for solutions in $CDCl_3$ on a Bruker AM 300 spectrometer. *J* Values are given in Hz. The assignments of carbon signals were made by means of 2D NMR ^1H and ^{13}C single bond and multiple bond correlation studies. Mass spectra were determined on a Kratos MS 25 RFA spectrometer at 70 eV using a direct inlet system. Rotations were measured in chloroform solutions at 25 °C with a Zeiss '0.01' polarimeter. For column chromatography, silica gel 60 (Merck, 70–230 mesh) was used. Thin layer chromatograms were prepared on silica gel G or silica gel GF_{254} 60 (Merck) and the spots were observed by exposure to iodine vapour or UV light. All organic extracts were dried over anhydrous sodium sulfate and evaporated under reduced pressure below 60 °C. Ether refers to diethyl ether.

Diels–Alder reaction of the diene 2 with methyl but-2-ynoate

A mixture of the diene **2** (0.512 g, 0.25 mmol) and methyl but-2-ynoate (0.247 g, 0.25 mmol) was heated in a sealed tube at 250 °C for 24 h. The reaction mixture was chromatographed over silica gel and elution with 2% ether in hexane afforded in 80% yield a mixture of compounds **3** and **5** as a yellow oil, as evidenced by the ^1H NMR spectrum. The mixture of these two compounds was chromatographed over a 1 : 1 mixture of silica gel Merck 60 (230–400 mesh) and TLC silica gel without binder under medium pressure. Elution was effected with 2% ethylacetate in hexane, the less polar fractions consisted of *compound* **5** (0.11 g, 20%) as an oil; δ_H(300 MHz) 1.39 (1H, m, 1α-H), 2.32 (1H, br d, *J* 12.5, 1β-H), 1.62 (2H, m, 2-H), 1.24 (1H, m, 3-H), 1.48 (1H, br d, *J* 13.5, 3-H), 1.27 (1H, dd, *J* 12.3, 2.6), 1.72 (1H, m, 6-H), 1.87 (1H, m, 6-H), 2.49 (3H, $ArCH_3$), 2.84 (2H, m, 7-H), 7.81 (1H, s, 11-H), 6.88 (1H, s, 14-H), 3.80 (3H, s, OCH_3), 0.93 (3H, s, 18-CH_3), 0.91 (3H, s, 19-CH_3), 1.15 (3H, s, 20-CH_3); δ_C(75.45 MHz) 38.77 (C-1), 19.13 (C-2), 41.56 (C-3), 33.37 (C-4), 50.26 (C-5), 18.72 (C-6), 30.17 (C-7), 140.02 (C-8), 147.72 (C-9), 37.41 (C-10), 127.02 (C-11), 126.64 (C-12), 136.66 (C-13), 132.18 (C-14), 21.22 ($ArCH_3$), 168.21 (C=O), 51.50 (OCH_3), 33.21 (C-18), 21.53 (C-19) and 24.74 (C-20) (Found: M^+, 300.2102. $C_{20}H_{28}O_2$ requires 300.2089).

The more polar fraction afforded *compound* **3** (0.17 g, 30%) as an oil; δ_H(300 MHz) 1.37 (1H, m, 1α-H), 2.29 (1H, br d, *J* 10.5, 1β-H), 1.64 (2H, m, 2-H), 1.23 (1H, m, 3-H), 1.47 (1H, br d, *J* 13.5, 3-H), 1.28 (1H, dd, *J* 12.8, 3.8, 5-H), 1.74 (1H, m, 6-H), 1.87 (1H, m, 6-H), 2.85 (2H, m, 7-H), 7.09 (1H, s, 11-H), 7.62 (1H, s, 14-H), 2.54 (3H, s, $ArCH_3$), 3.84 (3H, s, OCH_3), 0.94 (3H, s, 18-CH_3), 0.92 (3H, s, 19-CH_3) and 1.16 (3H, s, 20-CH_3); δ_C(75.45 MHz) 38.52 (C-1), 19.12 (C-2), 41.52 (C-3), 33.42 (C-4), 50.05 (C-5), 18.88 (C-6), 36.65 (C-7), 132.58 (C-8), 154.31 (C-9), 37.87 (C-10), 127.58 (C-11), 137.04 (C-12), 126.25 (C-13), 131.39 (C-14), 21.55 ($ArCH_3$), 167.99 (C=O), 51.40 (OCH_3), 33.18 (C-18), 21.13 (C-19) and 24.47 (C-20) (Found: M^+, 300.2095. $C_{20}H_{28}O_2$ requires 300.2089).

Benzylic oxidation of compound 3

To a stirred solution of compound **3** (70 mg, 0.23 mmol) in benzene (4 ml) and Celite (0.2 g) was added pyridinium dichromate (0.351 g, 0.93 mmol) followed by the addition of *tert*-butyl hydroperoxide (0.5 ml, 5.21 mmol) at 10 °C. After 15 min at 10 °C, the reaction mixture was stirred for 24 h at room temperature. The excess reagents were decomposed by addition of methanol and the reaction mixture was filtered through a pad of Celite by eluting with hexane. The eluate was evaporated *in vacuo* to dryness. The crude product thus obtained was purified by chromatography over silica gel in hexane–ether to afford *compound* **4a** (57 mg, 78%) as colourless crystals, mp 99–100 °C; λ_{max}(EtOH)/nm 229 (log ε 4.5),† 256 (4.11) and 310 (3.27); ν_{max}/cm^{-1} 3400 (OH), 1719 (ester C=O) and 1678 (C=O); δ_H(300 MHz) 0.90 (3H, s, 18-CH_3), 0.96 (3H, s, 19-CH_3), 1.20 (3H, s, 20-CH_3), 2.60 (3H, s, $ArCH_3$), 3.84 (3H, s, OCH_3), 7.19 (1H, s, 11-H) and 8.50 (1H, s, 14-H) (Found: C, 76.37; H, 8.31. $C_{20}H_{26}O_3$ requires C, 76.40; H, 8.34%).

Hydrolysis of compound 4a

Compound **4a** (50 mg, 0.15 mmol) was treated with 10% methanolic potassium hydroxide (10 ml) at room temperature for 24 h. The solution was then acidified with hydrochloric acid, diluted with water, and then extracted with ether. The ether extract was dried and evaporated to afford *compound* **4b** (46 mg, 98%) as colourless crystals, mp 254–255 °C; $[\alpha]_D$ 10 (*c* 6.4); λ_{max}(MeOH)/nm 224, 263 and 320; ν_{max}(KBr)/cm^{-1} 3475 (OH) and 1686 (COOH and CO); *m/z* 300 (M^+, 40%), 285 ($M^+ - CH_3$, 100), 217 (75), 128 (40) and 69 (65); δ_H(300 MHz) 0.91 (3H, s, 19-CH_3), 0.97 (3H, s, 18-CH_3), 1.22 (3H, s, 20-CH_3), 1.28 (1H, m, 3-H), 1.50 (1H, m, 3-H), 1.53 (1H, m, 1α-H), 1.69 (2H, br m, 2-H), 1.82 (1H, dd, *J* 12.9, 4.2, 5-H), 2.32 (1H, br d, *J* 12.7, 1β-H), 2.61 (1H, dd, *J* 18.5, 12.9, 6β-H), 2.65 (3H, s, $ArCH_3$), 2.73 (1H, dd, *J* 18.5, 4.2, 6α-H), 7.23 (1H, s, 11-H) and 8.65 (1H, s, 14-H) (Found: C, 75.67; H, 8.26. $C_{19}H_{24}O_3$ requires C, 75.97; H, 8.05%).

Benzylic oxidation of compound 5

Treatment of compound **5** (0.122 g) in the same way as described for compound **3** afforded compound **6a** (0.100 g, 78%), mp 134–135 °C; δ_H(300 MHz) 0.90 (3H, s, 18-Me), 0.97 (3H, s, 19-Me), 1.20 (3H, s, 20-Me), 2.52 (3H, ArMe), 3.88 (3H, s, OMe), 7.81 (1H, s, 11-H) and 7.83 (1H, s, 14-H) (Found: M^+, 314.1845. $C_{20}H_{26}O_3$ requires 314.1881).

Hydrolysis of compound 6a

Compound **6a** (100 mg) was hydrolysed in the same way described for compound **4a**. Compound **6b** (93 mg, 98%) was

† ε Values are given in units of $dm^3\ mol^{-1}\ cm^{-1}$.

obtained as colourless crystals, mp 198–200 °C; $[\alpha]_D$ 18 (*c* 3.1); λ_{max}(MeOH)/nm 210, 266 and 320 (shoulder); ν_{max}(KBr)/cm^{-1} 3387 (OH) and 1686 (COOH and CO); *m/z* 300 (M^+, 40%), 285 ($M^+ - CH_3$, 80), 217 (70), 203 (60) and 69 (100); δ_H(300 MHz) 0.92 (1H, s, 18-CH_3), 0.98 (1H, s, 19-CH_3), 1.23 (1H, s, 20-CH_3), 1.28 (1H, dd, *J* 13.2, 4.5, 3-H), 1.51 (1H, br m, 3-H), 1.56 (1H, m, 1α-H), 1.71 (2H, br m, 2-H), 1.84 (1H, dd, *J* 13.2, 4.5, 5-H), 2.38 (1H, br d, *J* 12.5, 1β-H), 2.60 (3H, s, ArCH_3), 2.64 (1H, dd, *J* 18.4, 13.2, 6β-H), 2.75 (1H, dd, *J* 18.4, 4.5, 6α-H), 7.85 (1H, s, 14-H) and 8.02 (1H, s, 11-H); δ_C(75.45 MHz) 37.87 (C-1), 18.75 (C-2), 41.28 (C-3), 33.28 (C-4), 49.28 (C-5), 36.24 (C-6), 199.35 (C-7), 133.30 (C-8), 153.30 (C-9), 37.90 (C-10), 127.21 (C-11), 133.11 (C-12), 138.29 (C-13), 130.28 (C-14), 21.30 (ArCH_3), 171.98 (CO), 32.50 (C-18), 21.24 (C-19) and 23.37 (C-20) (Found: C, 75.86; H, 8.25. $C_{19}H_{24}O_3$ requires C, 75.97; H, 8.05%).

Lithium aluminium hydride reduction of compound 5

A solution of **5** (200 mg, 0.66 mmol) in ether (20 ml) was stirred with lithium aluminium hydride (200 mg, 5.26 mmol) under nitrogen at room temperature for 24 h. The excess reagent was decomposed with water and after addition of 30% aqueous potassium hydroxide the product was extracted with ether. Evaporation of the ether extract and subsequent purification with hexane–ether over silica gel yielded compound **7** (142 mg, 94%) as an oil; ν_{max}(liquid film)/cm^{-1} 3374 (OH) and 1719 (C=O); *m/z* 272 (M^+, 40%), 257 ($M^+ - CH_3$, 80), 69 (80) and 41 (100); δ_H(300 MHz) 0.90 (3H, s, 18-CH_3), 0.92 (3H, s, 19-CH_3), 1.23 (3H, s, 20-CH_3), 1.30–1.70 (2H, m, 1-H; 2H, br m, 2-H; 2H, m, 3-H), 1.73 (1H, dd, *J* 12.7, 6.3, 5-H), 1.82 (1H, dd, *J* 7.1, 3.3, 6-H), 1.88 (1H, dd, *J* 7.1, 3.3, 6-H), 2.27 (3H, s, ArCH_3), 2.78 (1H, m, *J* 18.0, 10.9, 7.1, 7-H), 2.88 (1H, dd, *J* 18.0, 7.1, 7-H), 4.62 (2H, s, CH_2OH), 6.85 (1H, s, 14-H) and 7.19 (1H, s, 11-H); δ_C(75.45 MHz) 38.89 (C-1), 19.24 (C-2), 41.68 (C-3), 33.40 (C-4), 50.51 (C-5), 18.02 (C-6), 29.66 (C-7), 135.93 (C-8), 147.97 (C-9), 37.91 (C-10), 124.11 (C-11), 132.94 (C-12), 134.89 (C-13), 130.95 (C-14), 33.28 (C-18), 21.57 (C-19), 24.82 (C-20), 18.97 (ArCH_3) and 63.87 (CH_2OH).

Oxidation of compound 7 with tetra-*n*-propylammonium perruthenate

Compound **7** (152 mg, 0.55 mmol) was dissolved in dichloromethane (5 ml) containing both 4 Å molecular sieves (0.279 g, 0.55 mmol) and *N*-methylmorpholine *N*-oxide (98 mg, 0.83 mmol). After stirring the mixture for 5 min, tetra-*n*-propylammonium perrutherate (10 mg, 0.02 mmol) was added and the reaction followed by TLC until complete. The reaction mixture was filtered through silica gel and elution with hexane afforded compound **8** (140 mg, 94%) as an oil; δ_H(300 MHz) 0.91 (3H, s, 18-CH_3), 0.93 (3H, s, 19-CH_3), 1.16 (3H, s, 20-CH_3), 1.20–1.26 (2H, m, 3-H), 1.30 (1H, m, 5-H), 1.74 (1H, m, 6-H), 1.40 (1H, m, 1β-H), 1.65 (2H, br m, 2-H), 1.87 (1H, m, 6-H), 2.35 (1H, m, 1α-H), 2.55 (3H, s, ArCH_3), 7.66 (1H, s, 11-H), 2.83–2.92 (2H, m, 7-H), 6.89 (1H, s, 14-H) and 10.14 (1H, s, CHO); δ_C(75.45 MHz) 38.71 (C-1), 19.10 (C-2), 41.56 (C-3), 33.41 (C-4), 50.19 (C-5), 18.67 (C-6), 30.47 (C-7), 142.35 (C-8), 148.54 (C-9), 37.51 (C-10), 128.86 (C-11), 132.17 (C-12), 136.95 (C-13), 132.31 (C-14), 33.20 (C-18), 21.55 (C-19), 24.76 (C-20), 18.89 (ArCH_3) and 192.73 (CHO).

Baeyer–Villiger oxidation of compound 8

Compound **8** (66 mg, 0.24 mmol) in dichloromethane (10 ml) was heated under reflux with *m*-chloroperoxybenzoic acid (0.127 g, 0.73 mmol) for 24 h. The reaction mixture was filtered through silica gel and evaporation of the solvent afforded compound **9** as an oil (45 mg, 64%); δ_H 0.96 (3H, s, 19-CH_3), 0.89 (3H, s, 18-CH_3), 1.16 (3H, s, 20-CH_3), 2.10 (3H, s, ArCH_3), 6.85 (1H, s, 11-H), 6.89 (1H, s, 14-H) and 8.26 (1H, s, OCHO); *m/z* 286 (M^+, 10%), 271 ($M^+ - CH_3$, 20), 258 (40), 243 (40), 69 (80) and 43 (100).

Hydrolysis of compound 9

Compound **9** (0.138 g) was hydrolysed with 10% methanolic potassium hydroxide (30 ml). Usual work-up afforded compound **10a** as an oil (0.119 g, 96%); δ_H(300 MHz) 0.89 (3H, s, 18-CH_3), 0.91 (3H, s, 19-CH_3), 1.14 (3H, s, 20-CH_3), 1.30–1.79 (6H, m, 1-, 2-, 3-H), 1.72 (1H, m, 5-H), 1.80–1.84 (2H, m, 6-H), 2.15 (3H, s, ArCH_3), 2.71–2.81 (2H, m, 7-H), 4.55 (1H, br s, OH), 6.65 (1H, s, 14-H) and 6.77 (1H, s, 11-H); δ_C(75.45 MHz) 38.89 (C-1), 19.27 (C-2), 41.64 (C-3), 33.39 (C-4), 50.39 (C-5), 19.11 (C-6), 29.45 (C-7), 120.75 (C-8), 149.22 (C-9), 37.53 (C-10), 110.57 (C-11), 151.68 (C-12), 127.17 (C-13), 131.19 (C-14), 33.25 (C-18), 21.56 (C-19), 24.73 (C-20) and 15.19 (ArCH_3); *m/z* 258 (M^+, 60%), 243 ($M^+ - CH_3$, 60), 121 (40), 69 (100) and 41 (90).

Acetylation of compound 10a

Compound **10a** (130 mg) was treated with pyridine (15 ml) and acetic anhydride (15 ml) and the solution was refluxed for 3 h. After addition of water the product was extracted with ether and chromatographed in hexane–ether over silica gel. Compound **10b** (135 mg, 90%) was obtained; δ_H(300 MHz) 0.91 (3H, s, 18-CH_3), 0.97 (3H, s, 19-CH_3), 1.23 (3H, s, 20-CH_3), 2.15 (3H, s, ArCH_3), 2.31 (3H, s, OAc), 6.97 and 6.98 (1H each, s, 11-H, 14-H).

Benzylic oxidation of compound 10b

Benzylic oxidation of compound **10b** (100 mg) in the same manner as described for compound **5b**, afforded compound **11a** (80 mg, 74%); δ_H(300 MHz) 0.91 (3H, s, 18-CH_3), 0.97 (3H, s, 19-CH_3), 1.23 (3H, s, 20-CH_3), 2.15 (3H, s, ArCH_3), 2.31 (3H, s, OAc), 6.98 (1H, s, 11-H) and 7.87 (1H, s, 14H).

Hydrolysis of compound 11a

Compound **11a** (70 mg) was hydrolysed with 10% methanolic potassium hydroxide (5 ml). After usual work-up compound **11b**, mp 235 °C, was obtained (70 mg, 100%); $[\alpha]_D$ 32 (*c* 1.7); δ_H(300 MHz) 0.89 (3H, s, 18-CH_3), 0.95 (3H, s, 19-CH_3), 1.17 (3H, s, 20-CH_3), 1.49 (1H, m, 1α-H), 1.82 (1H, dd, *J* 12.9, 4.7, 5-H), 2.14 (1H, m, 1β-H), 2.16 (3H, s, ArCH_3), 2.54 (1H, dd, *J* 18.2, 12.9, 6β-H), 2.66 (1H, dd, *J* 18.2, 4.7, 6α-H), 5.86 (1H, br s, OH), 6.75 (1H, s, 11-H) and 7.81 (1H, s, 14-H); δ_C(75.45 MHz) 37.91 (C-1), 18.93 (C-2), 41.38 (C-3), 33.33 (C-4), 49.61 (C-5), 36.03 (C-6), 199.34 (C-7), 127.53 (C-8), 157.22 (C-9), 37.10 (C-10), 109.62 (C-11), 160.01 (C-12), 124.02 (C-13), 130.80 (C-14), 32.62 (C-18), 21.42 (C-19), 23.20 (C-20) and 15.35 (ArCH_3); *m/z* 272 (M^+, 100%), 257 ($M^+ - CH_3$, 90), 183 (70), 175 (60), 69 (50) and 41 (60) (Found: C, 79.21; H, 8.67. $C_{18}H_{24}O_2$ requires C, 79.37; H, 8.88%).

Acknowledgements

We thank M. Sc. M. Gómez, Ing. P. Hernández, and Dr F. Vargas for the measurements of the NMR, IR and UV spectra.

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Paper 7/08795K
Received 8*th December* 1997
Accepted 29*th January* 1998