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Oxidation of unsaturated monoterpenes with hydrogen peroxide catalysed by manganese(III) porphyrin complexes

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Abstract

Oxidation of (+)-3-carene (**1**), nerol (**2**) and geraniol (**3**) by hydrogen peroxide in the presence of catalytic amounts of several manganese(III) porphyrin complexes with electron withdrawing and electron donating groups was examined. The reactions were carried out at room temperature in acetonitrile, using aqueous hydrogen peroxide as oxidant and ammonium acetate as co-catalyst.

The oxidation reactions of 3-carene (**1**) showed high conversion of the substrate with all metalloporphyrins tested and four major products were identified and characterised, namely α-3,4-epoxycarane (**7**), β-3,4-epoxycarane (**8**), 3-caren-5-one (**9**) and 3-carene-2,5-dione (**10**). Nerol (**2**) oxidation reactions gave rise to 2,3-epoxynerol (**11**), 6,7-epoxynerol (**12**) and 2,3,6,7-diepoxynerol (**13**). In the case of geraniol (**3**), besides 2,3-epoxygeraniol (**14**), 6,7-epoxygeraniol (**15**) and 2,3,6,7-diepoxygeraniol (**16**), the oxidation reactions afforded 6,7-epoxygeranial (**17**). The terminal 6,7 double bond of nerol and geraniol was preferentially epoxidised. The regioselectivity induced by different porphyrins was investigated.

Keywords: Manganese(III); Porphyrins; Epoxidation; Hydrogen peroxide; Monoterpenes; Geraniol; Nerol; (+)-3-Carene

1. Introduction

The use of metalloporphyrins as catalysts in oxidation reactions, like epoxidation of olefins and hydroxylation of saturated hydrocarbons, has been largely documented during the last decade [1–7]. Most of the studies have been focused on the relationship between porphyrin structure and the corresponding catalytic efficiency. Only in the last few years the emphasis has been put on the promising applications of such catalytic systems [8–14].

Terpenes are one of the most abundant groups of cheap natural products, which can be transformed into novel and more valuable compounds [15]. Their epoxides often serve as starting materials for the synthesis of fragrances, flavours and therapeutically active substances [16]. We have already described the oxidation of 1,8-cineole, methyl dehydroabietate and other terpenes with hydrogen peroxide catalysed by manganese(III) porphyrin complexes [13,14]. Following this line of research, we now report the results obtained in the oxidation of 3-carene (**1**), nerol (**2**)

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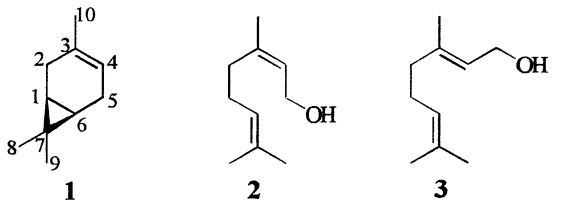
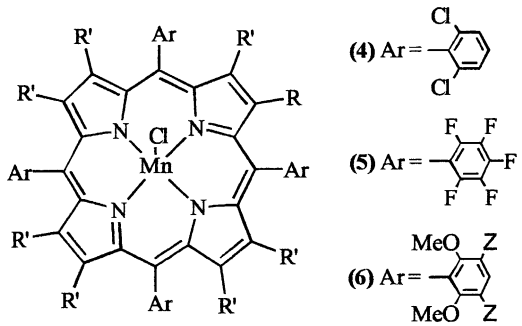


Scheme 1.

and geraniol (**3**) (Scheme 1) with hydrogen peroxide, catalysed by manganese(III) porphyrin complexes (**4–6**) (Fig. 1). The porphyrin complexes selected for these studies bear the following structural features: (i) electron-withdrawing substituents either in the phenyl groups, **4a** and **5a** or the related compounds, **4b** and **5b**, having also a nitro substituent at a β-peripheral position; (ii) electron-donating substituents at the 2,6-positions of the phenyl groups, **6a**; (iii) electron-donating substituents at the phenyl groups' 2,6-positions and also electron-withdrawing ones at all β-positions.

It is known that a considerable robustness is given to the macrocycles by bulky substituents at the 2,6-positions of the phenyl rings or other electron-withdrawing groups at the β-positions [17]. In particular, the tetra-*meso*-2,6-dimethoxyporphyrin has shown a good robustness in catalytic oxidation processes [18]. The choice for the porphyrins used in this work took into consideration such facts about the macrocycle catalytic behaviour, i.e. the presence of electron-withdrawing or electron-donating groups, or other groups with both types of effects, in the same molecule has been considered in order to look for the best catalyst for the oxidation of each substrate.



(4a)	Mn(TDCPP)Cl	R=R'=H	
(4b)	Mn(β-NO_2TDCPP)Cl	R=NO_2	R'=H
(5a)	Mn(TF_5PP)Cl	R=R'=H	
(5b)	Mn(β-NO_2TF_5PP)Cl	R=NO_2	R'=H
(6a)	Mn(TDMPP)Cl	R=R'=H	Z=H
(6b)	Mn(Cl_{16}TDMPP)Cl	R=R'=Cl	Z=Cl

Fig. 1. Manganese(III) porphyrin complexes used in this study.

The combination of manganese(III) complexes of porphyrins with H_2O_2, an inexpensive and readily available oxidant, which gives water as the only by-product, requires the presence of a co-catalyst. This is used to facilitate the desired heterolytic cleavage of H_2O_2 and also to stabilise the active species Mn(V) = O [1,4,6,19]. Based on literature data [20] and on our previous results [13,14], we have chosen ammonium acetate as the co-catalyst to be used in this work.

2. Results and discussion

2.1. Catalysts synthesis

The free bases of metalloporphyrins **4–6** were prepared according to known procedures [21–23]. Metallation of the free bases leading to the formation of complexes **4–6** was performed with $MnCl_2$ according to conventional methods [22,24].

2.2. Oxidation of substrates

The oxidation reactions were carried out in acetonitrile at room temperature with addition of H_2O_2 in the presence of the manganese(III) porphyrin catalyst and ammonium acetate as co-catalyst. In the oxidation of 3-carene (**1**) the addition of H_2O_2 was stopped when a complete conversion of the substrate was observed or when its conversion was not going further on. In the oxidation of substrates **2** and **3** the reaction mixtures were monitored at two different reaction times: at 30 min, when the highest selectivity for the major reaction products (**12** and **15**, respectively) was found and after 120 min, the time necessary for an almost complete conversion of the substrates with the most active catalyst **4a**.

Table 1
(+)-3-Carene oxidation with H_2O_2 catalysed by Mn(III) porphyrins **4–6**[a]

Catalyst	*t* (h)	Conversion[b]	Selectivity				
			7	**8**	**9**	**10**	**7/8**[c]
No catalyst	22	0	0	0	0	0	–
Mn(TDCPP)Cl (**4a**)	1.5	100	24	13	10	1	1.8
Mn(β-NO_2TDCPP)Cl (**4b**)	1.5	100	19	11	12	1	1.7
Mn(TF_5PP)Cl (**5a**)	3.5	100	43	17	6	1	2.5
Mn(β-NO_2TF_5PP)Cl (**5b**)	5.5	81	47	4	7	1	11.7
Mn(TDMPP)Cl (**6a**)	5.0	99	44	0.1	21	1	440
Mn(Cl_{16}TDMPP)Cl (**6b**)	6.0	85	33	6	13	0.2	5.5

[a] Reaction conditions: the substrate (**1**) (0.3 mmol), the catalyst (5 μmol) and ammonium acetate (70 μmol) were dissolved in acetonitrile (1.5 ml) and stirred at room temperature. Aqueous hydrogen peroxide (30% w/w) diluted in acetonitrile (1:10) was added to the reaction mixture in 0.2 ml aliquots every 30 min.

[b] Conversion of 3-carene, based on gas chromatographic peak areas.

[c] Ratio of isomers α (**7**) and β (**8**).

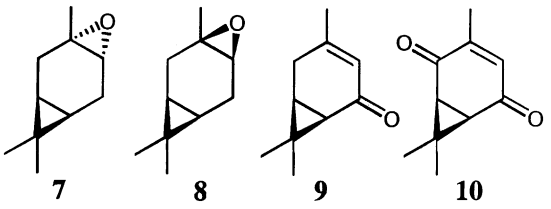
2.2.1. Oxidation of 3-carene

The GC analysis of the reaction mixtures of 3-carene (**1**) showed in all cases an almost complete conversion of the substrate (Table 1) and four major products (**7–10**) were identified (Scheme 2).

Fractionation of this reaction mixture by preparative TLC on silica gel afforded a clean separation of three major fractions. The less polar one (higher Rf) was shown by GC–MS to be constituted by two compounds, both with molecular ions at *m/z* 152 (which corresponds to the addition of one oxygen atom to 3-carene) in their mass spectra. These results and the fact that no signals of olefinic protons or carbons were observed in the ^{1}H and ^{13}C NMR spectra of this fraction prompted us to consider these compounds as α-(**7**) and β-(**8**) epoxides of 3-carene. The major component was identified as the α-epoxide (**7**) by comparison of its GC–MS behaviour and NMR profile with those of an authentic sample obtained from the treatment of 3-carene with *m*-chloroperbenzoic acid and with published data [25]. The analysis of the ^{1}H, ^{13}C, 2D COSY (^{1}H/^{1}H) and HETCOR (^{1}H/^{13}C) NMR experiments confirmed the assignment of all proton and carbon resonances of the α-epoxide (**7**). The close proximities of protons found in the NOESY spectrum of compound (**7**) (Fig. 2) unequivocally prove that it is the α-epoxide.

The minor component was identified as the β-epoxide (**8**) by comparison of its GC–MS behaviour and NMR profile with those of an authentic sample prepared by treatment of 3-carene with *N*-bromosuccinimide; the corresponding bromohydrin was then treated with potassium *t*-butoxide to yield the desired β-epoxide [26]. The assignment of the ^{1}H and ^{13}C of the β-epoxide (**8**) was made by comparison with the α-epoxide spectroscopic data and also on HETCOR (^{1}H/^{13}C) and COSY(^{1}H/^{13}C) experiments.

The second and third fractions isolated by preparative chromatography have shown to be pure



Scheme 2.

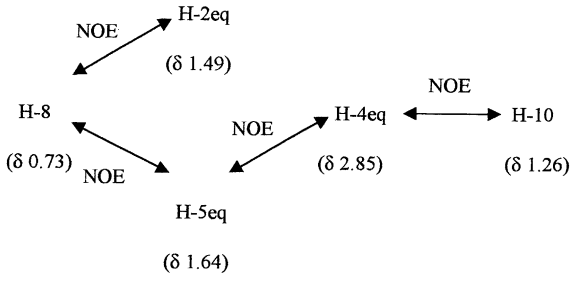


Fig. 2. Important NOE cross peaks found in the NOESY spectrum of α-3,4-epoxycarane (**7**).

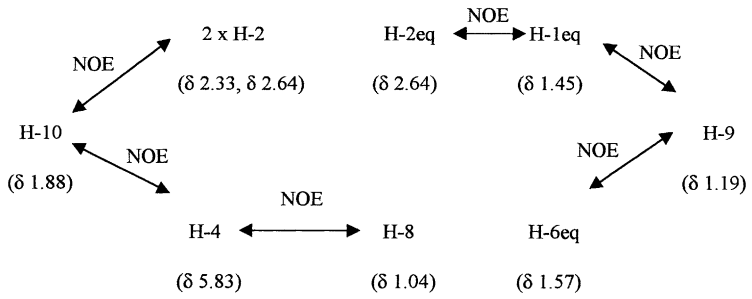


Fig. 3. Important NOE cross peaks found in the NOESY spectrum of 3-caren-5-one (**9**).

compounds and were identified by mass spectrometry and NMR spectroscopy [25], respectively, as 3-caren-5-one (**9**) and 3-carene-2,5-dione (**10**). The proton and carbon resonance assignments were confirmed by a detailed analysis of the ^{1}H, ^{13}C, COSY, NOESY and HETCOR NMR spectra of these compounds. The NOESY spectrum of 3-caren-5-one (**9**) was particularly important for the establishment of its structure and the most important results are shown in Fig. 3.

From Table 1, it can be seen that all catalysts used led to high conversion (80–100%) of 3-carene (**1**); the catalysts **4a** and **4b** gave rise to a complete conversion of the substrate with shorter reaction times, although a greater loss of selectivity for α-3,4-epoxycarane (**7**) was observed with porphyrins **4a** and **4b** (Fig. 4). The results obtained also show that the major product of 3-carene (**1**) oxidation is always the α-epoxide (**7**), generally followed by the β-epoxide (**8**), the allylic ketone (**9**) and, in minor amounts, the diketone (**10**).

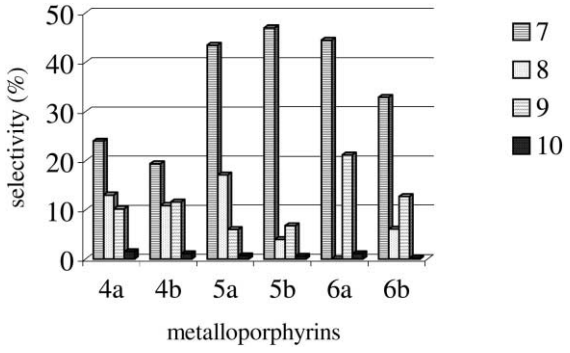


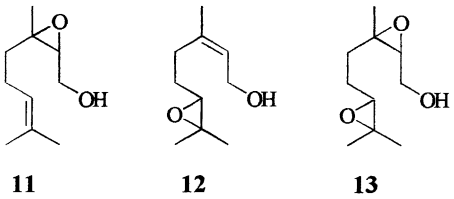
Fig. 4. Oxidation of (+)-3-carene with H_2O_2 catalysed by Mn(III) porphyrins **4**–**6**. Reaction conditions as described in Table 1.

The formation of the β-epoxide (**8**) might be somehow unexpected considering the work of Meunier et al. [27] where the α-epoxide was the only one detected in oxidative reactions with Mn(TPP)OAc as catalyst; however in a trial essay carried out with Mn(TPP)Cl and H_2O_2 as oxidant, under the same reaction conditions used in our studies, we were able to detect the formation of both the α- and β-epoxides, although the latter in minor amounts.

In the present studies the ratio between α- and β-epoxides (**7**/**8**) seems to be dependent on the nature of the porphyrin structure. In one case (**5b**) the presence of a nitro group in a β-position tend to increase their selectivity towards the epoxidation of **1** from the more accessible α-face. However, it is noteworthy that the highest α/β ratio was observed with porphyrin **6a**, with bulky electron-donating methoxy groups in the *meso*-phenyl rings. This fact might be probably due to the steric hindrance put by such substituents in relation with the stereochemistry of the cyclopropane moiety of 3-carene [17].

2.3. Oxidation of nerol and geraniol

The GC–MS analysis of nerol (**2**) reaction mixtures showed that this oxidative transformation catalysed by various metalloporphyrins gave rise to 2,3-epoxynerol (**11**), 6,7-epoxynerol (**12**) and 2,3,6,7-diepoxynerol (**13**) (as a mixture of two diastereomers). These products (Scheme 3) were identified by considering GC–MS and NMR results, by comparison with available analytical data [28] and also by comparison with spectroscopic data obtained with an authentic sample of 6,7-epoxynerol (**12**), prepared by treatment of nerol (**2**) with *m*-chloroperbenzoic acid.



Scheme 3.

One of the main features of the ^{1}H NMR spectra of the epoxides **11**–**13** are the proton resonances of the oxirane rings (H-2 at δ 2.97 ppm for **11** and δ 2.98–3.05 ppm for **13**; H-6 at δ 2.74 ppm for **12** and δ 2.74–2.81 ppm for **13**. In the case of **13**, one can conclude that it is a mixture of diastereomers because there is a duplication of ^{13}C NMR signals (e.g. six methyl groups instead of three), the typical resonances of proton oxirane ring are present and no vinylic resonances are observed. The conversions obtained in catalytic oxidation of nerol (**2**) after 30 and 120 min of reaction are illustrated in Fig. 5.

We can observe an increase of nerol (**2**) conversion with time, obtaining very high percentages of conversion after 120 min of reaction with catalysts **4a**, **4b** and **5a**. The major product after 30 min of reaction is always the 6,7-epoxide (**12**) (selectivity between 61 and 76%), followed by the 2,3-epoxide (**11**) (selectivity between 19 and 39%). Since after 30 min the amount of diepoxide strongly increases, one can consider, therefore, that this reaction time (30 min) is the ideal to stop the reaction in order to obtain the best selectivity for 6,7-epoxide (**12**) (Fig. 6).

After 120 min of reaction and considering the porphyrins showing higher conversions, the diepoxide

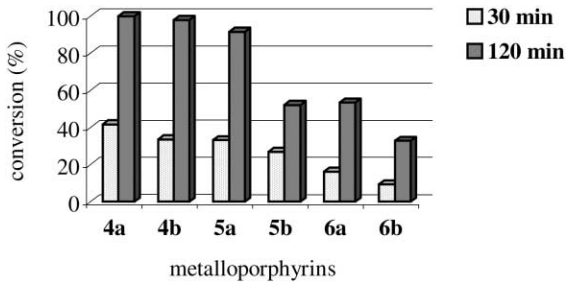


Fig. 5. Oxidation of nerol (**2**) with H_2O_2 catalysed by Mn(III) porphyrins **4**–**6**. Conversion obtained after 30 min and 120 min of reaction. Reaction conditions: the substrate (**2**) (0.3 mmol), the catalyst (5 μmol) and ammonium acetate (70 μmol) were dissolved in acetonitrile (1.5 ml) and stirred at room temperature. Aqueous hydrogen peroxide (30% w/w) diluted in acetonitrile (1:10) was added to the reaction mixture in 0.2 ml aliquots every 30 min.

(**13**) and the monoepoxide (**12**) are the major products. With porphyrins (**5b**), (**6a**) and (**6b**), which show only moderate conversions at this time of reaction, compound (**12**) is still the major product followed by the monoepoxide (**11**) (Fig. 7).

In the case of geraniol (**3**), besides the epoxides (**14**), (**15**) and (**16**), the oxidation reactions afforded the 6,7-epoxygeranial (**17**) (Scheme 4). These products were also identified by considering GC–MS and NMR results and by comparison with available analytical data [28–30]. As referred above for the mono and diepoxynerol derivatives, the ^{1}H NMR data of compounds **14**–**17** allowed us to conclude on the presence of oxirane rings (H-2 at δ 2.98 ppm for **14** and δ 3.01 ppm for **16**; H-6 at δ 2.73 ppm for **15**, δ 2.75 ppm for **16** and δ 2.73 ppm for **17**). In the case of 6,7-epoxygeranial (**17**) the typical aldehyde

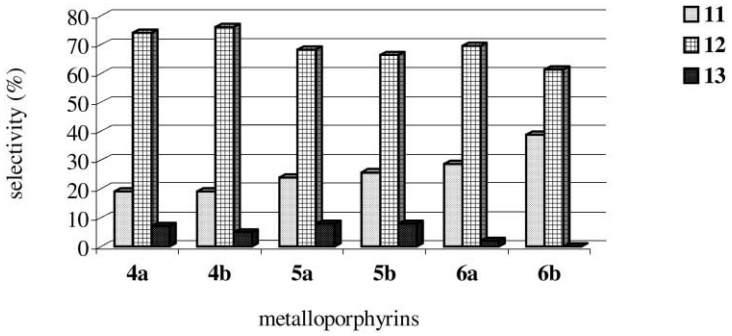


Fig. 6. Oxidation of nerol (**2**) with H_2O_2 catalysed by Mn(III) porphyrins **4**–**6** after 30 min of reaction.

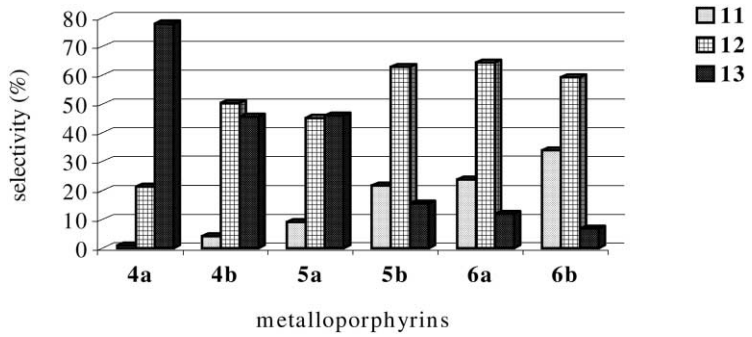
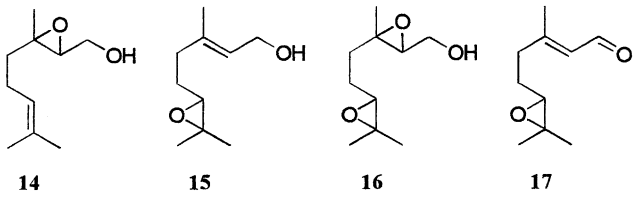


Fig. 7. Oxidation of nerol (**2**) with H_2O_2 catalysed by Mn(III) porphyrins **4–6** after 120 min of reaction.



Scheme 4.

resonance (H-1) appears at δ 10.01 ppm as a doublet, due to the coupling with the vinylic proton H-2.

Fig. 8 shows the results obtained in the oxidation of geraniol (**3**) and we can conclude that, in terms of conversion, the catalysts tested show a similar trend with both substrates **2** and **3**. As for nerol (**2**), the epoxidation of **3** preferentially occurs at the 6,7 double bond, which has higher HOMO coefficients than 2,3 double bond [31], affording 6,7-epoxygeraniol (**15**) as the major product, at low to moderate conversions (after 30 min, Fig. 9). The total conversion and the formation of the 2,3,6,7-diepoxygeraniol (**16**) after 120 min (Fig. 10) have better values with catalysts **4a**, **4b** and **5a**. The formation of **17** is probably related with the stereochemistry around the 2,3-double bond of geraniol. Apparently the C-1 centre is less protected and so more susceptible to oxidation in the case of geraniol.

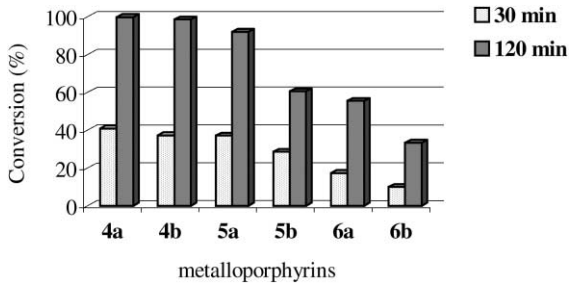


Fig. 8. Oxidation of geraniol (**3**) with H_2O_2 catalysed by metalloporphyrins **4–6**. Conversion obtained after 30 and 120 min of reaction. Reaction conditions: the substrate **3** (0.3 mmol), the catalyst (5 μmol) and ammonium acetate (70 μmol) were dissolved in acetonitrile (1.5 ml) and stirred at room temperature. Aqueous hydrogen peroxide (30% w/w) diluted in acetonitrile (1:10) was added to the reaction mixture in 0.2 ml aliquots every 30 min.

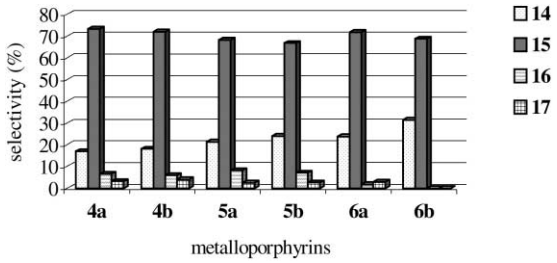


Fig. 9. Oxidation of geraniol (**3**) with H_2O_2 catalysed by Mn(III) porphyrins **4–6** after 30 min of reaction.

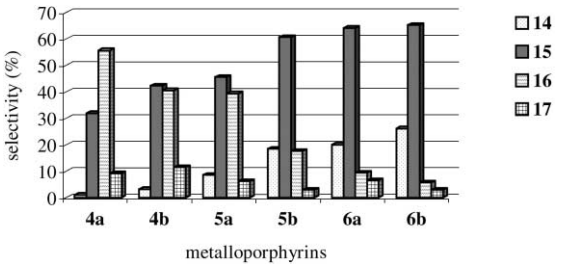


Fig. 10. Oxidation of geraniol (**3**) with H_2O_2 catalysed by Mn(III) porphyrins **4**–**6** after 120 min of reaction.

At high conversions of nerol and geraniol, the mixtures obtained have the diepoxide as one of the most abundant product. At moderate conversions of these substrates, however, production of diepoxide is considerably reduced and the 6,7-epoxide is the major product; this result is in agreement with earlier findings [29,32]. The figures for product distribution suggest that the diepoxide is being formed in consecutive monoepoxidation processes.

3. Experimental

3.1. General details

^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ solutions, using a Bruker AMX 300 at 300.13 and 75.47 MHz, respectively. The chemical shifts are expressed in δ (ppm) values relative to tetramethylsilane (TMS) as internal reference. Preparative thin layer chromatography (TLC) was carried out on silica gel plates (Riedel silica gel 60 DGF_{254}). Column chromatography was also performed on silica gel (Merck silica gel 60, 70–230 mesh). Mass spectra were obtained using a VG Autospec Q mass spectrometer. GC–MS analysis were performed using a Hewlett Packard 5890 gas chromatograph equipped with a Hewlett Packard MSD 5970 Series II using helium as the carrier gas (35 cm/s). GC–FID was performed using a Varian Star 3400CX chromatograph and hydrogen as the carrier gas (55 cm/s). In both cases fused silica Supelco capillary columns SPB-5 (30 m × 0.25 mm i.d.; 0.25 μm film thickness) were used. The chromatographic conditions were as follows: initial temperature, 60°C (reactions with 3-carene) and 100°C (reactions with nerol and geraniol); temperature rate, 5°C/min; final temperature, 220°C; injector temperature, 220°C; detector temperature, 230°C. Aliquots were withdrawn from the reaction mixture and injected directly into the injector. The percentages of each compound in the reaction mixtures were estimated directly from the corresponding peak areas.

Hydrogen peroxide (30 wt.% solution in water) was purchased from Riedel de Haën and (+)-3-carene, geraniol and nerol were purchased from Aldrich. All other chemicals and solvents used herein were obtained from commercial sources and used as received or distilled and dried using standard procedures. Light petroleum was the fraction of bp 40–60°C.

3.2. General oxidation procedure

In a typical experiment, the substrate **1**–**3** (0.3 mmol), the catalyst (5 μmol) and ammonium acetate (70 μmol) were dissolved in acetonitrile (1.5 ml) and stirred at room temperature. Aqueous hydrogen peroxide (30% w/w) diluted in acetonitrile (1:10) was added to the reaction mixture in 0.2 ml aliquots every 30 min. The reaction was followed by GC analysis and stopped when a complete conversion of the substrate was observed or when the product yields remained constant after two successive GC analysis. The reaction mixture was then poured into water and extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulphate and concentrated in the rotary evaporator. The mixtures were separated by preparative thin layer chromatography on silica gel, eluting with a mixture of ethyl acetate: dichloromethane (20:80) for the purification of geraniol (**2**) and nerol (**3**) oxidation products, or with a mixture of dichloromethane:light petroleum (1:1) for 3-carene (**1**) oxidation products.

3.2.1. α-3,4-Epoxycarane (*7*)

^{1}H NMR δ: 0.45 (ddd, 1H, H-1eq, J = 2.2, 8.9 and 9.1 Hz), 0.53 (ddd, 1H, H-6eq, J = 2.3, 8.9 and 9.1 Hz), 0.73 (s, 3H, H-8), 1.01 (s, 3H, H-9), 1.26 (s, 3H, H-10), 1.49 (dd, 1H, H-2eq, J = 2.2 and 16.2 Hz), 1.64 (dt, 1H, H-5eq, J = 2.3 and 16.4 Hz), 2.15 (dd, 1H, H-2ax, J = 9.1 and 16.2 Hz), 2.30 (ddd, 1H, H-5ax, J = 1.9, 8.9 and 16.4 Hz), 2.85 (t, 1H, H-4, J = 1.9 Hz). ^{13}C NMR δ: 13.8 (C-1), 14.6 (C-8), 15.9 (C-6), 16.0 (C-7), 19.1 (C-5), 23.1 (C-10), 23.3

(C-2), 27.7 (C-9), 56.1 (C-3), 58.3 (C-4). MS (EI) *m/z* (relative intensity %): 152 ($M^{+\bullet}$, 2), 137 (42), 109 (62), 91 (24), 81 (45), 67 (82), 43 (100), 39 (56).

*3.2.2. β-3,4-Epoxycarane (**8**)*

^{1}H NMR δ: 0.51–0.57 (m, 2H, H-1,6), 0.92 (s, 3H, H-8), 0.96 (s, 3H, H-9), 1.36 (s, 3H, H-10), 1.77 (2d, 2H, H-5,2, $J = 16.2$ Hz), 2.06 (dd, 1H, H-2, $J = 9.1$ and 16.4 Hz), 2.22-2.31 (m, 1H, H-5), 2.85 (d, 1H, H-4, $J = 5.4$ Hz). ^{13}C NMR δ: 14.7 (C-8), 17.3 (C-6), 17.5 (C-7), 18.2 (C-1), 19.7 (C-5), 23.8 (C-2), 24.7 (C-10), 29.1 (C-9), 55.9 (C-3), 58.2 (C-4). MS(EI) *m/z* (relative intensity %): 152 ($M^{+\bullet}$, 14), 137 (42), 109 (77), 94 (65), 91 (38), 81 (69), 79 (100), 67 (92), 55 (45), 43 (91), 39 (54).

*3.2.3. 3-Caren-5-one (**9**)*

^{1}H NMR δ: 1.04 (s, 3H, H-8), 1.19 (s, 3H, H-9), 1.26 (s, 3H, H-10), 1.45 (t, 1H, H-1eq, $J = 7.9$ Hz), 1.57 (d, 1H, H-6eq, $J = 7.9$ Hz), 2.33 (d, 1H, H-2ax, $J = 20.8$ Hz), 2.64 (dd, 1H, H-2eq, $J = 7.9$ and 20.8 Hz), 5.83 (s broad, 1H, H-4). ^{13}C NMR δ: 14.4 (C-8), 22.5 (C-7), 23.7 (C-10), 25.8 (C-1), 27.8 (C-2), 28.4 (C-9), 32.8 (C-6), 126.4 (C-4), 158.9 (C-3), 196.7 (C-5). MS (EI) *m/z* (relative intensity %): 150 ($M^{+\bullet}$, 100), 135 (41), 107 (93), 95 (26), 91 (76), 79 (54), 67 (32), 39 (74).

*3.2.4. 3-Carene-2,5-dione (**10**)*

^{1}H NMR δ: 1.32 and 1.33 (2s, 2 × 3 H, H-8,9), 1.98 (s, 3H, H-10), 2.31–2.36 (m, 2H, H-1,6), 6.51 (q, 1H, H-4, $J = 1.4$ Hz). ^{13}C NMR δ: 15.2 (C-8), 16.0 (C-10), 28.4 (C-9), 33.4 (C-7), 38.7 and 39.6 (C-1,6), 137.4 (C-4), 149.8 (C-3), 194.2 (C-2), 194.8 (C-5). MS (EI) *m/z* (relative intensity %) 164 ($M^{+\bullet}$, 56), 149 (100), 136 (29), 121 (47), 93 (53), 77 (49), 67 (38), 44 (58), 39 (87).

*3.2.5. 2,3-Epoxynerol (**11**)*

^{1}H NMR δ: 1.35 (s, 3H, H-10), 1.48 (ddd, 1H, H-5, $J = 7.2$, 9.7 and 13.8 Hz), 1.62–1.75 (m, 1H, H-5), 1.62 and 1.69 (2s, 2 × 3H, H-8,9), 1.99–2.19 (m, 2H, H-4), 2.97 (dd, 1H, H-2, $J = 4.3$ and 6.9 Hz), 3.66 (dd, 1H, H-1, $J = 6.9$ and 12.1 Hz), 3.82 (dd, 1H, H-1, $J = 4.3$ and 12.1 Hz), 5.10 (tq, 1H, H-6, $J = 1.3$ and 7.2 Hz). ^{13}C NMR δ: 17.6 and 25.6 (C-8,9), 22.1 (C-10), 24.1 (C-5), 33.1 (C-4), 61.2 (C-1), 61.5 (C-3), 64.2 (C-2), 123.2 (C-6), 132.5 (C-7). MS (EI) *m/z* (relative intensity %) 170 ($M^{+\bullet}$, 1), 155 (2), 127 (3), 109 (35), 95 (15), 82 (33), 69 (57), 41 (100).

*3.2.6. 6,7-Epoxynerol (**12**)*

^{1}H NMR δ: 1.31 and 1.28 (2s, 2 × 3H, H-8,9), 1.52–1.81 (m, 2H, H-5), 1.78 (s broad, 3H, H-10), 2.18–2.34 (m, 2H, H-4), 2.74 (dd, 1H, H-6, $J = 5.1$ and 7.7 Hz), 4.07–4.21 (m, 2H, H-1), 5.52 (t, 1H, H-2, $J = 7.2$ Hz). ^{13}C NMR δ: 18.8 and 24.8 (C-8,9), 23.3 (C-10), 26.9 (C-5), 28.4 (C-4), 58.8 (C-1), 58.9 (C-7), 63.8 (C-6), 125.2 (C-2), 138.9 (C-3). MS (EI) *m/z* (relative intensity %) 170 ($M^{+\bullet}$, 3), 167 (13), 153 (34), 143 (66), 135 (11), 125 (41), 110 (63), 81 (89), 71 (93), 59 (100).

*3.2.7. 2,3,6,7-Diepoxynerol (**13**)*

^{1}H NMR δ: 1.295, 1.304, 1.328, 1.34 and 1.37 (6s, H-8,9,10), 1.54–1.87 (m, H-4,5), 2.74–2.81 (m, H-6), 2.98–3.05 (m, H-2), 3.76 (d broad, H-1, $J = 3.9$ Hz). ^{13}C NMR δ: 18.5, 18.6, 22.0, 24.6, 24.7 and 28.9 (C-5,8,9,10), 29.0 and 29.8 (C-4), 59.1, 59.5, 60.5, 60.6, 60.7 and 61.2 (C-1,3,7), 63.4, 63.88, 63.91 and 64.3 (C-2,6). MS (EI) *m/z* (relative intensity) 186 ($M^{+\bullet}$, 1), 173 (4), 167 (8), 155 (5), 149 (12), 143 (54), 125 (40), 111 (59), 97 (55), 85 (93) 71 (96) 59 (100).

*3.2.8. 2,3-Epoxygeraniol (**14**)*

^{1}H NMR δ: 1.30 (s, 3H, H-10), 1.28–1.32 and 1.42–1.52 (2m, 2H, H-5), 1.61 (s, 3H, H-8), 1.68 (d, 3H, H-9, $J = 1.2$ Hz), 2.04–2.12 (m, 2H, H-4), 2.98 (dd, 1H, H-2, $J = 4.1$ and 6.9 Hz), 3.66 (dd, 1H, H-1, $J = 6.9$ and 12.2 Hz), 3.82 (dd, 1H, H-1, $J = 4.1$ and 12.2 Hz), 5.08 (tq, 1H, H-6, $J = 1.2$ and 6.4 Hz). ^{13}C NMR δ: 16.6 (C-10), 17.5, 23.6 and 25.6, (C-5,8,9), 38.4 (C-4), 61.2 (C-3), 61.3 (C-1), 63.1 (C-2), 123.2 (C-6), 132.0 (C-7). MS (EI) *m/z* (relative intensity %) 170 ($M^{+\bullet}$, 0.5), 152 (2), 137 (2), 109 (51), 95 (22), 82 (34), 67 (61), 55 (33), 41 (100).

*3.2.9. 6,7-Epoxygeraniol (**15**)*

^{1}H NMR δ: 1.24–1.35 and 1.73–1.80 (2m, 2H, H-5), 1.31 and 1.35 (2s, 2 × 3 H, H-8,9), 1.73 (s, 3H, H-10), 2.06–2.34 (m, 2H, H-4), 2.73 (s broad, 1H, H-6), 4.23 (s broad, 2H, H-1), 5.49 (s broad, 1H, H-2). ^{13}C NMR δ: 16.2 (C-10), 18.7, 24.8 and 27.1 (C-5,8,9), 36.3 (C-4), 58.6 (C-1), 59.4 (C-7), 64.1 (C-6), 124.2 (C-2), 138.8 (C-3). MS (EI) *m/z* (relative intensity %) 170

($M^{+\bullet}$ 1), 152 (1), 137 (5), 109 (17), 97 (22), 81 (75), 71 (52), 59 (95), 41 (100).

*3.2.10. 2,3,6,7-Diepoxygeraniol (**16**)*

^{1}H NMR δ: 1.25, 1.29, 1.297, 1.302, 1.33 and 1.34 (6s, H-8,9,10), 1.21–1.33 and 1.53–1.90 (2m, H-4,5), 2.75 (s broad, 1H, H-6), 3.01 (s broad, H-2), 3.73–3.82 (m, H-1). ^{13}C NMR δ: 16.3 and 16.9 (C-10), 18.6, 18.7, 24.5, 24.8, 29.6 and 29.7 (C-5,8,9), 35.1 and 36.2 (C-4), 60.7, 61.3, 62.4, 62.9, 63.3, 63.8, 64.3 and 64.4 (C-1,2,3,6,7). MS (EI) *m/z* (relative intensity %) 186 ($M^{+\bullet}$, 1), 155 (2), 125 (5), 111 (15), 84 (47), 71 (37), 59 (30), 43 (100).

*3.2.11. 6,7-Epoxygeranial (**17**)*

^{1}H NMR δ: 1.29 and 1.33 (2s, 2 × 3 H, H-8,9), 1.71 (s, 3H, H-10), 1.25-1.32 and 1.65-1.75 (2m, 2H, H-5), 2.14–2.25 and 2.31–2.43 (2m, 2H, H-4), 2.73 (s broad, 1H, H-6), 5.92 (d, 1H, H-2, $J = 7.4$ Hz), 10.01 (t, 1H, H-1, $J = 7.4$ Hz). MS (EI) *m/z* (relative intensity %) 168 ($M^{+\bullet}$, 1), 153 (2), 125 (6), 109 (8), 97 (34), 81 (91), 67 (23), 59 (100), 41 (85).

4. Conclusion

In the presence of catalytic amounts of manganese(III) porphyrin complexes, hydrogen peroxide is a good source of an oxygen atom for monoterpene epoxidation in homogeneous conditions. This catalytic method of epoxidation occurs in mild conditions and the use of a versatile, cheap and environmental friendly oxidant should probably make it useful among catalytic methods for performing oxidations.

The oxidation reactions of 3-carene (**1**) showed an almost complete conversion of the substrate in all cases and four major products **7–10** were identified and characterised. Most of the catalysts used led to almost 100% conversion of 3-carene (**1**) with exception of porphyrins **5b** and **6b** which gave conversions above 80%. Catalysts **4a** and **4b** allow a complete conversion of the substrate with shorter reaction times, although a greater loss of selectivity for α-3,4-epoxycarane was observed with these porphyrins.

Nerol (**2**) oxidation reactions gave rise to 2,3-epoxynerol (**11**), 6,7-epoxynerol (**12**) and 2,3,6,7-diepoxynerol (**13**) (as a mixture of two diastereomers). In the case of geraniol (**3**), besides 2,3-epoxygeraniol (**14**), 6,7-epoxygeraniol (**15**) and 2,3,6,7-diepoxygeraniol (**16**), the oxidation reactions afforded the 6,7-epoxygeranial (**17**). The terminal 6,7 double bond of nerol and geraniol is preferentially epoxidised. Although both the 2,3 and 6,7 double bonds are trisubstituted, the nucleophilicity of the 2,3 double bond is significantly lowered by the inductive electron-accepting effect of the hydroxyl group. The regioisomeric product distribution presumably depends on the relative nucleophilicity of the two double bonds.

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