Pergamon

Wat. Res. Vol. 31, No. 5, pp. 1243–1246, 1997
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Printed in Great Britain
0043-1354/97 $17.00 + 0.00

PII: S0043-1354(96)00330-2

TECHNICAL NOTE

DEHYDRATION PRODUCTS OF 2-METHYLISOBORNEOL

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(Received February 1996; accepted in revised form November 1996)

Abstract—2-Methylenebornane and 2-methyl-2-bornene have previously been identified as dehydration or degradation products of 2-methylisoborneol (MIB), a compound responsible for taste and odour problems in various water environments. Previously, the identification of these products has been based on mass spectral analysis only. The dehydration of MIB under a variety of conditions was reinvestigated and the products fully characterised by ^{1}H and ^{13}C n.m.r. and GC-MS. Comparison of EI mass spectra of the dehydration products of MIB with those published previously indicate that earlier assignments of MIB dehydration products are incorrect. © 1997 Elsevier Science Ltd

Key words—2-methylisoborneol, MIB, dehydration products, mass spectra

INTRODUCTION

2-Methylisoborneol (MIB) (1; Fig. 1) a secondary metabolite of certain actinomycetes and cyanobacteria, has been identified as a major contributor to off-flavours in aquatic environments (Wnorowski, 1992). In the course of our investigations of MIB adsorption by powdered activated carbons for water treatment, we had occasion to dehydrate this tertiary alcohol.

Martin *et al.* (1988a, b), in studies of off-flavours in channel catfish, identified 2-methyl-2-bornene (2M2B) (2) and 2-methylenebornane (2MB) (3; Fig. 1) as dehydration products of MIB in the fish flesh. These workers reported the preparation of "authentic samples" of 2M2B and 2MB by dehydration of MIB using thionyl chloride and pyridine. The identification of the dehydration products was based on mass spectral analysis. Earlier, Lapalme *et al.* (1979) reported that the same reaction gave a 2:1 mixture of 2MB:2M2B, although the latter product was not characterised. Recently, Mills *et al.* (1993), in another study of off-flavours in channel catfish, also dehydrated MIB with thionyl chloride and pyridine. They used mass spectra to identify 2MB and 2M2B as the major products.

Sumitomo (1992), in a study of gravel filters for the removal of MIB from drinking water, reported biodegradation of MIB by the bacteria *Pseudomonas fluorescens* isolated from filter sludge. Analysis by GC-MS indicated that biodegradation resulted in dehydration of MIB to give the alkenes 2MB and 2M2B and the rearranged alkene 1-methylcamphene (1MC) (4; Fig. 1).

While examining the dehydration of MIB with thionyl chloride, we noted some anomalies with the results described above. A study of the dehydration of MIB was therefore undertaken and the products identified using ^{1}H and ^{13}C n.m.r. and GC-MS to unequivocally establish the structures of the products. The results of this investigation are reported here.

MATERIALS AND METHODS

GC analyses were conducted using a Hewlett Packard 5890 Series II gas chromatograph equipped with a BP5 (SGE; 25 m × 0.22 mm × 0.25 μm) capillary column operated isothermally at 70°C, the injector at 200°C and FID at 280°C with helium carrier gas. GC-MS analyses were carried out using a Hewlett Packard 5890 Series II gas chromatograph equipped with an HP 5971 MSD, EI source at 70 eV, and a BP1 (SGE; 25 m × 0.22 mm × 0.25 μm) capillary column operated as above with hydrogen carrier gas. ^{1}H and ^{13}C n.m.r. were recorded on a Varian Gemini 200 NMR Spectrometer at 200 and 50 MHz, respectively. (±)-2-Methylisoborneol was synthesised from racemic camphor using the method of Wood and Snoeyink (1977).

Dehydration of MIB

(a) Using $SOCl_2$*/pyridine*. MIB was treated with thionyl chloride and pyridine according to the procedures of Lapalme *et al.* (1979) and Martin *et al.* (1988a, b). GC-FID analysis of the product showed that essentially only three compounds were present in the mixture. GC-MS, ^{1}H and ^{13}C n.m.r. analysis identified the compounds as 2-methyl-2-bornene (2) (12%), 2-methylenebornane (3) (68%) and 1-methylcamphene (4) (20%).

2-*Methyl*-2-*bornene* (2): ^{1}H n.m.r. δ ($CDCl_3$) 0.77, (6H, s, $2 \times CH_3$); 0.93, (3H, s, CH_3); 1.60 (3H, br s, allylic CH_3); 2.17, (1H, br t, J 4 Hz); 5.51, (1H, m, vinylic H). ^{13}C n.m.r.

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δ ($CDCl_3$) 11.34, 13.37, 19.62, 19.87, 26.21, 31.05, 51.36, 54.05, 56.01, 127.58, 145.38. *m/z* 150 (M^+, 34%) 135 (61), 122 (33), 107 (100), 105 (14), 93 (27), 79 (16), 77 (15).

2-*Methylenebornane* (3): ^1H n.m.r. δ ($CDCl_3$) 0.75, (3H, s, $C(8)H_3$); 0.88, (3H, s, $C(10)H_3$); 0.91 (3H, s, $C(9)H_3$); 2.38, (1H, br d, *J* 16 Hz, C(3) exo H); 4.63, (1H, m, exocyclic CH_2); 4.68, (1H, m, exocyclic CH_2). ^{13}C n.m.r. δ ($CDCl_3$) 12.52, 18.96, 19.62, 28.01, 35.16, 37.02, 44.72, 47.24, 51.48, 101.03, 159.41. *m/z* 150 (M^+, 24%), 135 (42), 121 (23), 108 (22), 107 (100), 106 (14), 105 (15), 95 (38), 94 (52), 93 (59), 91 (44), 79 (67).

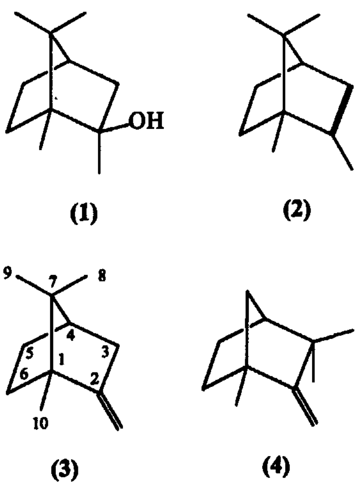
1-*Methylcamphene* (4): ^1H n.m.r. δ ($CDCl_3$) 1.01, (3H, s, CH_3); 1.06, (3H, s, CH_3); 1.17 (3H, s, CH_3); 4.53, (1H, br s, exocyclic CH_2); 4.60, (1H, br s, exocyclic CH_2). ^{13}C n.m.r. δ ($CDCl_3$) 18.40, 25.52, 26.21, 29.61, 35.60, 42.84, 44.33, 47.39, 49.97, 97.01, 169.27. *m/z* 150 (M^+, 15%), 121 (17), 108 (13), 107 (100), 93 (17), 91 (16), 69 (11).

(*b*) *Using* H_2SO_4. Two drops of H_2SO_4 (conc.) were added to ethyl acetate (2 ml), and two drops of this solution were added to MIB (1 mg) dissolved in ethyl acetate (2 ml). The mixture was heated for 0.5 h at 75°C. GC analysis of the reaction mixture showed the products were 2-methyl-2-bornene (2) (3%), 2-methylenebornane (3) (46%) and 1-methylcamphene (4) (51%).

(*c*) *Elimination of methyl xanthate (Chugaev reaction).* (±)-MIB (500 mg, 3 mmol) and sodium hydride (60% dispersion in oil (350 mg, 9 mmol)) were refluxed under nitrogen in THF (25 ml) for 5 h. The reaction mixture was cooled to room temperature and carbon disulphide (2.5 ml, 41.6 mmol) was added and the reaction stirred for 18 h. Methyl iodide (2.5 ml, 40 mmol) was added and stirring continued for a further 18 h. Water (50 ml) was added and the solution extracted with dichloromethane (3 × 10 ml). After drying and concentrating the extracts, followed by chromatography over silica eluted with petroleum spirit (b.p. 30–35°C), 380 mg (85%) of a mixture of three alkenes were obtained. GC-MS, ^1H and ^{13}C n.m.r. analysis showed that the mixture contained 2-methyl-2-bornene (2) (50%), 2-methylenebornane (3) (49%) and 1-methylcamphene (4) (1%).

RESULTS AND DISCUSSION

Dehydration of MIB with thionyl chloride in pyridine was carried out following the method used by earlier workers (Lapalme *et al.*, 1979; Martin *et al.*, 1988a, b) to obtain a mixture of 2MB and 2M2B. Analysis of the product by GC-FID indicated the presence of three compounds in the ratio 12:20:68. Analysis of the three-component mixture by ^1H and ^{13}C n.m.r. and comparison with data published for individual compounds (Burgstahler *et al.*, 1976; Lapalme *et al.*, 1979; Takai *et al.*, 1980; Grover *et al.*, 1975; Morris *et al.*, 1975; Walter *et al.*, 1983; Werstiuk *et al.*, 1972), indicated that the three compounds were 2M2B, 1MC and 2MB, respectively. Integration of the vinylic region in the ^1H n.m.r. spectrum confirmed this product ratio (entry 1, Table 1).



(1) **(2)** **(3)** **(4)**

Fig. 1. Structures of 2-methylisoborneol (MIB) (1), 2-methyl-2-bornene (2M2B) (2), 2-methylenebornane (2MB) (3) and 1-methylcamphene (1MC) (4).

Table 1. Product ratios for the dehydration of MIB

	Product (relative %)					
	GC-FID			^1H n.m.r.		
Dehydration method	2M2B (2)	2MB (3)	1MC (4)	2M2B (2)	2MB (3)	1MC (4)
$SOCl_2$/pyridine	12	68	20	12	69	19
H_2SO_4	3	46	51	–	–	–
Chugaev	49	49	2	50	49	1

The dehydration of MIB under acidic conditions was also investigated. Treatment of MIB with sulphuric acid gave an approximately 1:1 mixture of 2MB and 1MC, with only a trace of 2M2B (entry 2, Table 1). It is probable that these conditions most closely resemble the conditions under which MIB would undergo dehydration in natural water environments, where mild acid catalysis could lead to dehydration of the very acid-labile MIB. These results suggest that under such conditions, 2MB and the rearranged camphene 1MC would be the major products of MIB dehydration.

In an attempt to obtain 2MB and 2M2B without the rearranged product 1MC, the dehydration of MIB was carried out by elimination of the corresponding methyl xanthate. The methyl xanthate of MIB could not be isolated, as it readily undergoes elimination at room temperature, to give a 1:1 mixture of 2MB and 2M2B with less than 2% rearrangement (entry 3, Table 1).

The EI mass spectra of the three alkenes (2M2B, 1MC and 2MB) obtained from the dehydration of MIB with thionyl chloride and pyridine are shown in Fig. 2. Comparison of these spectra with those reported by Martin *et al.* (1988b) clearly shows that the two major alkenes these workers obtained on dehydration of MIB with thionyl chloride and pyridine were 2MB and 1MC, and not 2MB and 2M2B as reported. This also indicates that the dehydration products of MIB found in channel catfish (Martin *et al.*, 1988a, b; Mills *et al.*, 1993) were 2MB and the rearranged camphene 1MC. These results highlight the problems associated with making structural assignments of very similar compounds based on mass spectra only.

While the three major dehydration products of

MIB could be unambiguously identified by ^{1}H and ^{13}C n.m.r., they do in fact also give unique fragmentation patterns in their EI mass spectra. In particular, 2M2B which contains an endocyclic double bond gives a characteristic fragment ion at *m/z* 122, while 2MB and 1MC, which both have an exocyclic methylene group, do not give this ion with any significant intensity. It can be postulated that the ion at *m/z* 122 for the endocyclic alkene arises from a *retro*-Diels–Alder fragmentation (McLafferty *et al.*, 1993) of the molecular ion. In the case of 2M2B, this fragmentation will lead to a radical ion which may be drawn as shown in structure (5) (Fig. 3), where both the charge and the unpaired electron are stabilised.

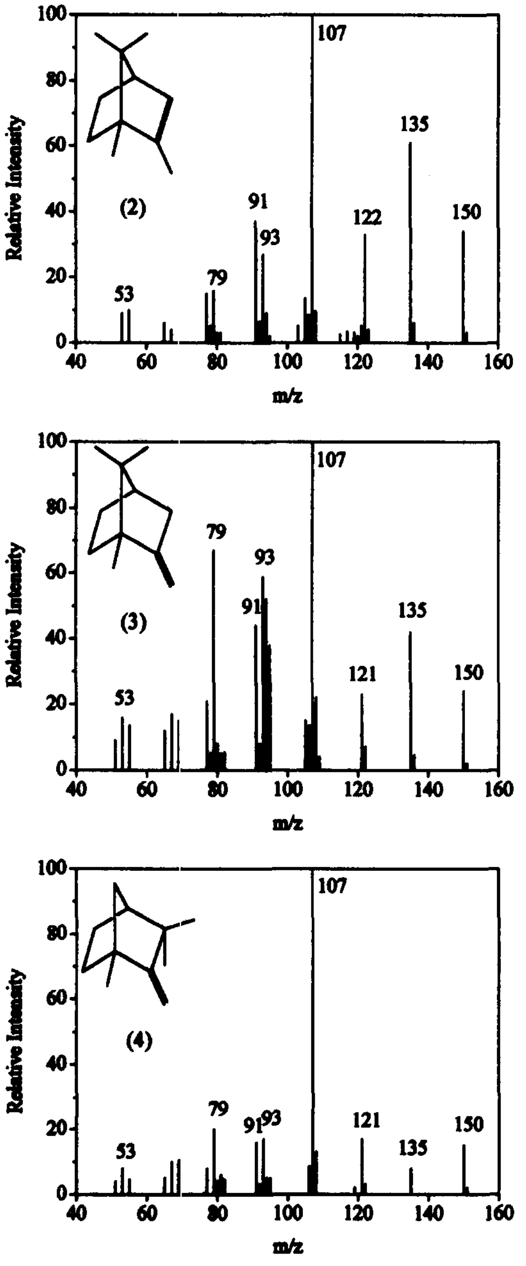


Fig. 2. EI mass spectra of the dehydration products of MIB.

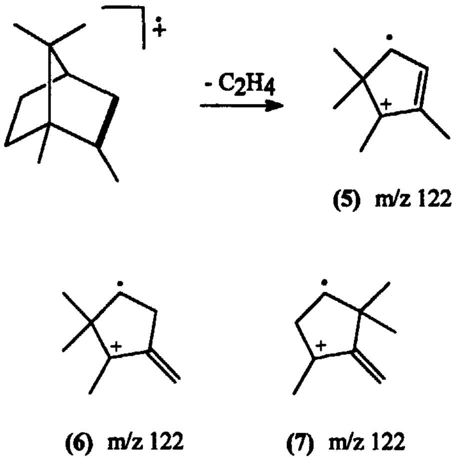


Fig. 3. Possible EI fragmentation ions for 2M2B (5), 2MB (6) and 1MC (7).

The corresponding fragmentation for 2MB and 1MC would yield radical ions of the type (6) and (7), respectively (Fig. 3). These radical ions would not be expected to be as stable as (5) and probably further fragment to give ions at *m/z* 121 and 107. As a result, the EI spectra of 2MB and 1MC do not show any significant ion intensity at *m/z* 122.

CONCLUSIONS

The dehydration of MIB has been investigated. ^{1}H and ^{13}C n.m.r. and GC-MS analyses have shown that the major products from dehydration using thionyl chloride and pyridine are 2MB (3) and 1MC (4), with only a minor amount of the endocyclic alkene 2M2B (2). Dehydration under acidic conditions also produced 2MB and 1MC as the major products, with only trace amounts of 2M2B. However, dehydration by elimination of the methyl xanthate of MIB gave a 1:1 mixture of 2M2B and 2MB, with very little (<2%) rearranged product (1MC). Comparison of the EI mass spectra of these compounds with those reported previously (Martin *et al.*, 1988b) indicated that the earlier assignment of 2MB and 2M2B as the sole products of MIB dehydration with thionyl chloride and pyridine was incorrect. As a result, the dehydration products of MIB identified in natural water environments by these and other workers (Mills *et al.*, 1993; Sumitomo, 1992), based solely on mass spectra, were also incorrectly identified. However, EI mass spectra can be used to distinguish the endocyclic alkene 2M2B from the exocyclic alkenes 2MB and 1MC, by the presence of an ion at *m/z* 122 for the former compound which is absent in the spectra of the latter compounds.

Acknowledgements—The authors wish to thank the Australian Research Council for funding in part of this work and the Australian Water Quality Centre–SA Water for kindly providing GC-MS analyses.

REFERENCES

Burgstahler A. W., Boger D. L. and Naik N. C. (1976) Synthesis and chiroptical properties of some asymmetric planar cisoid dienes. *Tetrahedron* **32,** 309–315.

Grover S. H. and Stothers J. B. (1975) ^{13}C nuclear magnetic resonance studies. 47. ^{13}C spectra of some *exo*-methylenecycloalkanes and -norbornanes. *Can. J. Chem.* **53,** 589–595.

Lapalme R., Borschberg H.-B., Soucy P. and Deslongchamps P. (1979) Thermal decomposition of ozonides. A complementary method to the Baeyer–Villiger oxidation of hindered ketones. *Can. J. Chem.* **57,** 305–312.

McLafferty F. W. and Turecek F. (1993) *Interpretation of Mass Spectra*, 4th Edn, p. 69. University Science Books, Mill Valley, CA.

Martin J. F., Bennett L. W. and Graham W. H. (1988a) Off-flavor in the channel catfish (*Ictalurus punctatus*) due to 2-methylisoborneol and its dehydration products. *Wat. Sci. Technol.* **20,** 99–105.

Martin J. F., Fisher T. H. and Bennett L. W. (1988b) Musty odor in chronically off-flavoured channel catfish: isolation of 2-methylenebornane and 2-methyl-2-bornene. *J. Agric. Food Chem.* **36,** 1257–1260.

Mills O. E., Chung S.-Y. and Johnsen P. B. (1993) Dehydration products of 2-methylisoborneol are not responsible for off-flavor in the channel catfish. *J. Agric. Food Chem.* **41,** 1690–1692.

Morris D. G. and Murray A. M. (1975) ^{13}C chemical shifts of 1-substituted camphenes. *J. Chem. Soc. Perkin II* **6,** 539–541.

Sumitomo H. (1992) Biodegradation of 2-methylisoborneol by gravel sand filtration. *Wat. Sci. Technol.* **25,** 191–198.

Takai K., Hotta Y., Oshima K. and Nozaki H. (1980) Wittig-type reaction of dimetallated carbodianion species as produced by zinc reduction of gem-polyhalogen compounds in the presence of Lewis acids. *Bull. Chem. Soc. Jpn* **53,** 1698–1702.

Walter S. R., Marshall J. L., McDaniel C. R. Jr, Canada E. D. Jr, and Barfield M. (1983) Experimental and theoretical studies of ^{13}C–^{13}C coupling constants. 1. Conformational and substituent dependencies of long-range coupling constants $^{4}J(^{13}C–^{13}C)$. *J. Am. Chem. Soc.* **105,** 4185–4190.

Werstiuk N. H., Taillefer R., Bell R. A. and Sayer B. G. (1972) ^{13}C chemical shifts of highly substituted bicyclo[2.2.1]heptanes. *Can. J. Chem.* **50,** 2146–2149.

Wnorowski A. (1992) Tastes and odours in the aquatic environment: A review. *Water SA* **18,** 203–214.

Wood N. F. and Snoeyink V. L. (1977) 2-Methylisoborneol, improved synthesis and a quantitative GC method for trace concentrations producing odor in water. *J. Chromatogr.* **132,** 405–420.