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Cycloaddition reactions of conjugated dienoic carboxylic acids and esters with *N*-substituted maleimides and Schiff bases

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Sorbic acid and its esters were investigated as potential dienes in Diels–Alder reactions with *N*-substituted maleimides. The purpose was to characterise such Diels–Alder adducts by means of NMR, and to provide reference compounds to identify the formation of related products in model food systems. These reactions occur both in aqueous and non-aqueous systems and it is possible that the C=N bond of Schiff bases could act as a dienophile towards sorbic acid. In general, the ^1H chemical shifts for the olefinic protons, originally at C_3 and C_4 of sorbic acid, are to be found at δ 5.7–5.9 and 6.3–6.5, respectively in the adduct. Those at C_2, C_5 and C_6 are at δ 2.4–2.6, 3.4–4.2 and 1.4–1.5, respectively. All these values are characteristically different from the corresponding proton chemical shifts in sorbic acid. © 1997 Elsevier Science Ltd

INTRODUCTION

2,4-Hexadienoic acid (sorbic acid) has been widely used as a food preservative. This compound is very susceptible to nucleophilic attack as illustrated by its known reactivity towards sulphite ion, thiols and amines (Khandelwal & Wedzicha, 1990*a*,*b*, 1992; Wedzicha & Brook, 1989; Wedzicha & Zeb, 1990). The catalysed and uncatalysed reactions of butadiene and 2,3-dimethylbutadiene with methyl sorbate have been reported (Garrat & Wyatt, 1974) and indicate that, in the absence of catalyst, methyl sorbate behaves as a diene and butadiene as a dienophile; in the presence of catalyst their roles are reversed.

We wish to report the uncatalysed reactions of *N*-substituted maleimides and Schiff bases with sorbic acid and its esters. The purpose of this investigation is to characterise the spectroscopic properties of a wide range of cycloaddition products involving sorbic acid as a part of our investigation of its reactivity in foods.

MATERIALS AND METHODS

Sorbic acid, ethyl sorbate, *N*-ethyl-, *N*-methyl- and *N*-phenylmaleimide, maleic anhydride, 2,4-hexadien-1-ol (sorbyl alcohol), phenylglyoxal hydrate, *p*-toluenesulphonamide, boron trifluoride etherate were obtained from Aldrich (Gillingham, UK). Crotonylidene acetone (sorbyl ketone) was prepared by the published method (Meerwein, 1908).

Methyl, butyl and propyl sorbates were prepared as previously reported (Khandelwal & Wedzicha, 1990*b*). Methylenebisurethane and benzalbisurethane were prepared according to the method of Cava *et al.* (1965) and *N*-benzoylidene toluene-*p*-sulphonamide according to McKay and Proctor (1979).

ANALYSIS OF REACTION PRODUCTS

Reaction products isolated were subjected to microanalysis and identified by ^1H NMR (60 MHz), mass spectrometry and infrared spectroscopy. Structures of individual products are given in Fig. 1 and analytical data for each compound are as follows:

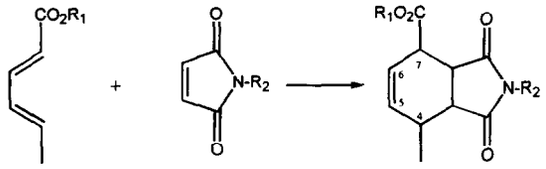
2-Methyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxoisoindoline-7-carboxylic acid methyl ester (from methyl sorbate and N*-methyl maleimide*) (structure 1)

Yield, 77%; colourless solid; m.p. 180–182°C (from MeOH); IR (KBr): 1770 sh, 1730, 1695 cm^{-1}; mass spectrum *m/e*: 237, 205, 177 (*m/e*–CO_2Me); $C_{12}H_{15}NO_4$ requires 237.0999. Found: 237.0998. ^1H NMR: δ 6.32 (dt, H-5, 1p, $J = 2.4$ Hz), 5.72 (dt, H-6, 1p, $J = 2.4$ Hz), 3.84 (S, OMe), 3.52–3.76 (m, H-4, lp), 3.0–3.24 (m, H-8 and H-9, 2p), 2.88 (S, NMe, 3P), 2.40 (b, H-7, 1p), 1.44

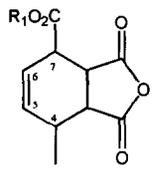
(d, CMe, $J = 7.2$ Hz). Anal. calcd. for $C_{12}H_{15}NO_4$: C, 60.65; H, 6.45; N, 5.80. Found: C, 60.70; H, 6.32; N, 5.90.

2-Ethyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid ethyl ester (from ethyl sorbate and N-methyl maleimide) (structure 2)

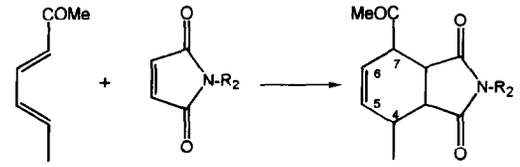
Yield, 78%; colourless solid; m.p. 148–150°C (from MeOH); IR (KBr): 1770 sh, 1730, 1695 cm^{-1}; mass spectrum *m/e* 251, 206, 177 ($-CO_2Et$); $C_{13}H_{17}NO_4$ requires 251.1155. Found: 251.1167. ^1H NMR: δ 6.32 (dt, H-5, 1p, $J = 2.4$ Hz), 5.80 (dt, H-6, 1p, $J = 2.4$ Hz), 4.26 (q, $J = 7$ Hz, 2p), 3.56–3.80 (m, H-4, 1p), 3.00–3.20 (m, H-8 and H-9, 2p), 2.88 (S, NMe), 2.44 (b, H-7, 1p), 1.42 (d, CMe, $J = 7$ Hz), 1.32 (q, $J = 7$ Hz, 3p). Anal. calcd. for $C_{13}H_{17}NO_4$: C, 62.35; H, 6.85; N, 5.45. Found: C, 62.15; H, 6.77; N, 5.58.



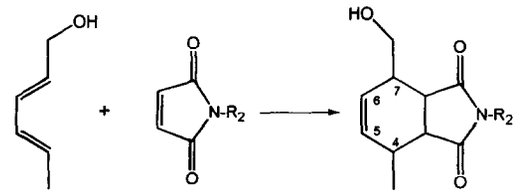
(1) R_1= Me R_2= Me
(2) R_1= Et R_2= Me
(3) R_1= Pr R_2= Me
(4) R_1= Bu R_2= Me
(5) R_1= H R_2= Me
(6) R_1= Me R_2= Ph
(7) R_1= Et R_2= Ph
(8) R_1= Pr R_2= Ph
(9) R_1= Bu R_2= Ph
(10) R_1= H R_2= Ph
(11) R_1= Me R_2= Et
(12) R_1= Et R_2= Et
(13) R_1= Pr R_2= Et
(14) R_1= Bu R_2= Et
(15) R_1= H R_2= Et
(16) R_1= hexyl R_2= Me
(17) R_1= heptyl R_2= Me
(18) R_1= isoamyl R_2= Me
(19) R_1= isoamyl R_2= Me



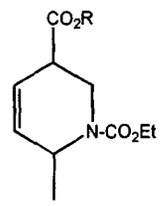
(20) R_1= Et
(21) R_1= Bu



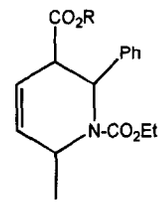
(22) R_2= Me
(23) R_2= Ph
(24) R_2= Et



(25) R_2= Me
(26) R_2= Ph
(27) R_2= Et



(28) R= Et
(29) R= Me



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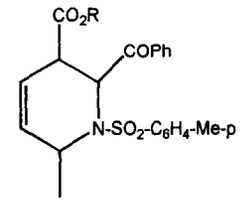


(31) R= Et
(32) R= Me

CH_2-$(NHCO_2Et)_2$ (33)

CH_2=NCO_2Et (34)

Ph-CH$(NHCOOEt)_2$ (35)

Ph-CH=N-COOEt (36)

PhCOCHO+H_2N-SO_2-C_6H_4-Me-p (37)

PhCO-CH=N-SO_2-C_6H_4-Me-p (38)

Fig. 1. Structure of Diels–Alder products synthesised in this investigation.

2-Methyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid propyl ester (from propyl sorbate and N-*methyl maleimide*) (structure 3)

Yield, 77%; colourless solid (from MeOH); m.p. 88–89°C; IR (KBr): 1765 sh, 1718, 1695 cm^{-1}; mass spectrum *m/e*: 265, 206 (*m/e*–$O(CH_2)_3$), 179 (*m/e*–$CO_2(CH_2)_2Me$). $C_{14}H_{19}NO_4$ requires 265.1311. Found: 265.1301. ^1H NMR: δ 6.32 (dt, H-5, 1p, $J = 2.4$ Hz), 5.72 (dt, H-6, 1p, $J = 2.4$ Hz), 4.20 (t, $J = 7.2$ Hz, 2p), 3.60–3.84 (m, H-4, lp), 3.00–3.28 (m, H-8 and H-9, 2p), 2.88 (S, NMe), 2.40 (b, H-7, 1p), 1.76 (q, $J = 7.2$ Hz, 2p), 1.44 (d, $J = 7.2$ Hz, 3p), 1.00 (t, $J = 7.00$ Hz, 3P). Anal. calcd. for $C_{14}H_{19}NO_4$: C, 63.15; H, 7.20; N, 5.10. Found: C, 63.39; H, 7.17; N, 5.28.

2-Ethyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid butyl ester (from butyl sorbate and N-*methylmaleimide)* (structure 4)

Yield, 78%; colourless solid (from MeOH); m.p. 79–80°C; IR (KBr): 1768 sh, 1725, 1695 cm^{-1}; mass spectrum *m/e*: 279, 206 (*m/e*–$O(CH_2)_3$), 179; $C_{15}H_{21}NO_4$ requires 279.1468. Found: 279.1461; ^1H NMR: δ 6.26 (dt, H-5, 1P, $J = 2.4$ Hz), 5.68 (dt, H-6, 1P, $J = 2.4$ Hz), 4.24 (t, $J = 7$ Hz, 2P), 3.60–3.80 (m, H-4, 1P), 3.0–3.24 (m, H-8 and H-9, 2P), 2.88 (S, NMe), 2.40 (b, H-7, 1P), 1.40–1.88 (incl. CMe, $J = 7$ Hz, 7P), 0.96 (t, $J = 7$ Hz, 3P). Anal. calcd. for $C_{15}H_{21}NO_4$: C, 64.30; H, 7.55; N, 5.00. Found: C, 64.52; H, 7.53; N, 5.02.

2-Methyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid (from sorbic acid and N-*methylmaleimide)* (structure 5)

Yield, 80%; colourless solid (from EtOH), m.p. 196–197°C; IR (KBr): 3480, 1760 sh, 1710, 1680 cm^{-1}; mass spectrum *m/e*: 223, 205, 177 (*m/e*–CO_2H); $C_{11}H_{13}NO_4$ requires 223.0812. Found: 223.1012. ^1H NMR: δ 6.28 (dt, H-5, 1P, $J = 2.4$ Hz), 5.72 (dt, H-6, 1P, $J = 2.4$ Hz), 3.72–3.96 (m, H-4,1P), 2.82 (S, NMe), 3.20–3.44 (m, H-8 and H-9, 2P), 2.44 (b H-7, 1P), 1.44 (d, OMe, $J = 7.2$ Hz, 3P). Anal. calcd. for $C_{11}H_{13}NO_4$: C, 59.05; H, 5.90; H, 6.20. Found: C, 59.19; H, 5.83; N, 6.28.

2-Phenyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid methyl ester (from methyl sorbate and N-*phenylmaleimide)* (structure 6)

Yield, 79%; colourless solid (from EtOH), m.p. 172–174°C; IR (KBr): 1768 sh, 1728, 1705 cm^{-1}; mass spectrum *m/e*: 299, 268, 239 (*m/e*–CO_2Me), 174. $C_{17}H_{17}NO_4$ requires 299.1156, Found: 299.1142. ^1H NMR: δ 7.0–7.44 (m, 5P), 6.40 (dt, H-5, 1P, $J = 2.4$ Hz), 5.80 (dt, H-6, 1P, $J = 2.4$ Hz), 3.80 (S, OMe), 3.70–3.94 (m, H-4, 1P), 3.04–3.32 (m, H-8 and H-9, 2P), 2.44 (b, H-7, 1P), 1.44 (d, OMe, $J = 7.2$ Hz). Anal. calcd. for $C_{17}H_{17}NO_4$: C, 68.05; H, 5.66; N, 4.60. Found: C, 68.23; H, 5.68; N, 4.68.

2-Phenyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid ethyl ester (from ethyl sorbate and N-*phenylmaleimide)* (structure 7)

Yield,79%; colourless solid (MeOH/ether), m.p. 127–128°C; IR (KBr): 1780 sh, 1730, 1705 cm^{-1}; mass spectrum *m/e*: 313, 268, 239 (*m/e*–CO_2Et), 174. $C_{18}H_{19}NO_4$ requires 313.1313. Found: 313.1298. ^1H NMR: δ 7.04–7.48 (m, 5P), 6.40 (dt, H-5, 1P, $J = 2.4$ Hz), 5.80 (dt, H-6, 1P, $J = 2.4$ Hz), 4.24 (q, $J = 7.2$ Hz, 2P), 3.72–3.96 (m, H-4, 1P), 3.08–3.40 (m, H-8 and H-9, 2P), 2.44 (b, H-7, 1P), 1.46 (d, CMe, $J = 7.2$ Hz), 1.32 (t, $J = 7.2$ Hz, 3P). Anal. calcd. for $C_{18}H_{19}NO_4$: C, 68.05; H, 5.66; N, 4.60. Found: C, 69.00; H, 6.07; N, 4.47.

2-Phenyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid propyl ester (from propyl sorbate and N-*phenylmaleimide)* (structure 8)

Yield, 79%; colourless solid (from aq. MeOH), m.p. 102–103°C; IR (KBr): 1775 sh, 1728, 1710 cm^{-1}; mass spectrum *m/e*: 327, 268, 241 (*m/e*–Pr), 174, 154. $C_{19}H_{21}NO_4$ requires 327.1469. Found: 327.1450. ^1H NMR: δ 7.0–7.48 (m, 5P), 6.40 (dt, H-5, 1P, $J = 2.4$ Hz), 5.76 (dt, H-5, 1P, $J = 2.4$ Hz), 4.16 (t, $J = 7$ Hz, 2P), 3.72–3.96 (m, H-4, 1p), 3.0–3.36 (m, H-8 and H-9, 2P), 2.48 (b, H-7, 1P), 1.80 (q, $J = 7.2$ Hz, 2P), 1.46 (d, CMe, $J = 7.2$ Hz), 0.96 (t, 3P, $J = 7.2$ Hz). Anal. calcd. for $C_{19}H_{21}NO_4$: C, 69.60; H, 6.45; N, 4.15. Found: C, 69.72; H, 6.42; N, 4.28.

2-Phenyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid butyl ester (from butyl sorbate and N-*phenylmaleimide)* (structure 9)

Yield, 76%; colourless solid (from aq. EtOH), m.p. 106–108°C; IR (KBr): 1775 sh, 1725, 1709 cm^{-1}; mass spectrum *m/e*: 341, 241. ^1H NMR: δ 7.04–7.52 (m, 5P), 6.44 (dt, H-5, 1P, $J = 2.4$ Hz), 5.88 (dt, H-6, 1P, $J = 2.4$ Hz), 4.24 (t, $J = 7.2$ Hz, 2P), 3.72–3.96 (m, H-4, 1P), 3.08–3.40 (m, H-8 and H-9, 2P), 2.48 (b, H-7, 1P), 1.20–1.80 (7P, contg. d at 1.44, $J = 7.2$ Hz), 0.96 t ($J = 7.2$ Hz, 3P). Anal. calcd. for $C_{20}H_{23}NO_4$: C, 70.38; H, 6.85; N, 4.00. Found: C, 70.38; H, 6.75; N, 4.11.

2-Phenyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid (from sorbic acid and N-*phenylmaleimide)* (structure 10)

Yield, 80%; colorless solid (from MeOH), m.p. 204–206°C; IR (KBr): 3260, 1750, 1695 cm^{-1}; mass spectrum *m/e*: 285, 267, 241 (*m/e*–CO_2H), 174; $C_{16}H_{15}NO_4$ requires 285.1000. Found: 285.0996. ^1H NMR: δ 8.10 (b, OH), 7.12–7.16 (m, 5P), 6.38 (dt, H-5, 1P, $J = 2.4$ Hz), 5.78 (dt, H-6, 1P, $J = 2.4$ Hz), 3.74–4.02 (m, H-4, 1P), 3.10–3.38 (m, H-8 and H-9, 2P), 2.46 (b, H-7, 1P), 1.42 (d, CMe, $J = 7.2$ Hz). Anal. calcd. for $C_{16}H_{15}NO_4$: C, 67.20; H, 5.25; N, 4.85. Found: C, 67.37; H, 5.26; N, 4.92.

2-Ethyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid methyl ester (from methyl sorbate and N-*ethylmaleimide)* (structure 11)

Yield, 78%; colourless solid (EtOH/ether), m.p. 107–108°C; IR (KBr): 1765 sh, 1725, 1695 cm^{-1}; mass spectrum *m/e*: 251, 219, 191 (*m/e*–CO2Me), 126. $C_{13}H_{17}NO_4$ requires 251.1125. Found: 251.1122. ^1H NMR: δ 6.28 (dt, H-5, 1P, $J = 2.4$ Hz), 5.72 (dt, H-6, 1P, $J = 2.4$ Hz), 3.84 (S, OMe), 2.44 (b, H-7, 1P), 3.44–3.72 (m, 3P), 3.0–3.32 (m, H-8 and H-9, 2P), 1.48 (d, CMe, $J = 7.2$ Hz), 1.08 (t, 3P, $J = 7.2$ Hz). Anal. calcd.

for $C_{13}H_{17}NO_4$: C, 62.20; H, 6.85; N, 5.55. Found: C, 62.15; H, 6.77; N, 5.58.

2-Ethyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid ethyl ester (from ethyl sorbate and N-*ethylmaleimide)* (structure 12)

Yield, 78%; colourless solid (from ether/petroleum ether 40/60°C), m.p. 115–116°C; IR (KBr): 1768 sh, 1728, 1695 cm^{-1}; mass spectrum *m/e*: 265, 220, 191 (*m/e*–CO_2Et). $C_{14}H_{19}NO_4$ requires 265.1313. Found: 265.1309. ^1H NMR: δ 6.32 (dt, H-5, 1P, $J = 2.4$ Hz), 5.70 (dt, H-6, 1P, $J = 2.4$ Hz), 4.30 (q, 2P, $J = 7.2$ Hz), 3.38–3.82 (m, 3P), 3.06–3.28 (m, H-8 and H-9, 2P), 2.46 (b, H-7, 1P), 1.42 (d, CMe, $J = 7.2$ Hz), 1.48 (t, $J = 7.2$ Hz, 3P), 1.08 (t, $J = 7.2$ Hz 3P). Anal. calcd. for $C_{14}H_{19}NO_4$: C, 63.10; H, 7.15; N, 5.25. Found: C, 63.39; H, 7.17; N, 5.28.

2-Ethyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid propyl ester (from propyl sorbate and N-*ethylmaleimide)* (structure 13)

Yield, 78%; colourless solid (from ether/petroleum ether 40/60°C), m.p. 95–96°C; IR (KBr): 1765 sh, 1730, 1692 cm^{-1}; mass spectrum *m/e*: 279, 220, 193 (*m/e*–Pr), 178, 154. $C_{15}H_{21}NO_4$ requires 279.1461. Found 279.1461. ^1H NMR: δ 6 40 (dt, H-5, 1P, $J = 2.4$ Hz) 5.76 (dt, H-5, 1P, J = 2.4 Hz), 4.20 (t, 7.2 Hz, 2P), 3.60–3.92 (m, 3P), 2.96–3.28 (m, H-8 and H-9, 2P), 2.42 (b, H-7, 1P), 1.88 (q, $J = 6$ Hz, 2P), 1.44 (d, $J = 7.2$ Hz, 3P), 1.04 (dq, $J = 4.8$ Hz, 6P). Anal. calcd. for $C_{15}H_{21}O_4$: C, 64.25; H, 7.55; N, 5.00. Found: C, 64.51; H, 7.53; N, 5.02.

2-Ethyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid butyl ester (from butyl sorbate and N-*ethylmaleimide)* (structure 14)

Yield, 78%; colourless solid (from hexane), m.p. 49–50°C; IR (KBr): 1765 sh, 1725 b, 1709 cm^{-1}; mass spectrum *m/e*: 293, 238, 220, 193 (*m/e*–Bu), 169, 126. $C_{16}H_{23}NO_4$ requires 293.1591. Found: 293.1595. ^1H NMR: δ 6.36 (dt, H-5, 1P, $J = 2.4$ Hz), 5.72 (dt, H-6, 1P, $J = 2.4$ Hz), 4.24 (t, $J = 7.2$ Hz, 2P), 3.52–3.80 (m, 3P), 3.00–3.40 (m, H8 and H-9, 2P), 2.48 (b, H-7, 1P), 1.72–1.28 (7P, contg. d at 1.44, $J = 7.2$ Hz), 1.04 (m, 6P). Anal. calcd. for $C_{16}H_{23}NO_4$: C, 65.15; H, 7.85; N, 4.60. Found: C, 65.53; H, 7.85; N, 4.78.

2-Ethyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid (from sorbic acid and N-*ethylmaleimide)* (structure 15)

Yield, 77%; colourless solid (from EtOH), m.p. 187–189°C; IR (KBr): 1778 sh, 1700 b cm^{-1}; mass spectrum *m/e*: 237, 219, 191 (*m/e*–CO_2H), 126. $C_{12}H_{15}NO_4$ requires 237.1000. Found: 237.0990. ^1H NMR: δ 6.28 (dt. H-5, 1P, $J = 2.4$ Hz), 5.72 (dt, H-6, 1P, $J = 2.4$ Hz), 3.44–3.84 (m, 4P), 3.04–3.32 (H-8 and H-9, 2P), 2.44 (b, H-7, 1P), 1.42 (d, CMe, $J = 7.2$ Hz), 1.08 (t, $J = 7.2$ Hz, 2P). Anal. calcd. for $C_{12}H_{15}NO_4$: C, 60.90; H, 6.40; N, 6.00. Found: C, 60.76; H, 6.33; N, 5.91.

2-Methyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid hexyl ester (from hexyl sorbate and N-*methylmaleimide)* (structure 16)

Yield, 95%; colourless needles (from aq. EtOH); m.p. 64–65°C; IR (KBr): 1768, 1728, 1695 cm^{-1}; mass spectrum *m/e*: 307, 179 (*m/e*–CO_2–hexyl), 112, 93, 77. ^1H NMR: δ 6.32 (dt, H-5, 1P, $J = 2.4$ Hz), 5.72 (dt, H-6, 1P, $J = 2.4$ Hz), 4.20 (t, $J = 7$ Hz, 2P), 3.44–3.66 (m, H-4, 1P), 2.88–3.16 (S with multiplet, 5P) 2.46 (b, H-7, 1P), 0.92–2.00 (m, 14 P). Anal. calcd. for $C_{17}H_{25}O_4$: C, 66.45; H, 8.14. Found: C, 66.40; H, 8.10.

2-Methyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid heptyl ester (from heptyl sorbate and N-*methylmaleimide)* (structure 17)

Yield, 95%; colourless needles (from aqueous ethanol); m.p. 58–60°C; IR (KBr): 1770, 1725, 1695 cm^{-1}; mass spectrum *m/e*: 322 (M + 1), 264, 224 (*m/e*–heptyl), 206, 179. ^1H NMR: 6.32 (dt, H-5, 1P, $J = 2.4$ Hz), 5.76 (dt, H-6, 1P, $J = 2.4$ Hz), 4.20 (t, $J = 7$ Hz, 2P), 3.48–3.80 (H-4, 1P), 2.88–3.24 (m, contg. S at 2.88 NMe and H-8 and H-9), 2.40 (b, H-7, 1P), 1.08–1.88 (m, 13P), 0.96 (t, 3P, CH_2–Me). Anal. calcd. for $C_{18}H_{27}NO_4$: C, 67.29; H, 8.41. Found: C, 67.20; H, 8.40.

2-Methyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid isoamyl ester (from isoamyl sorbate and N-*methylmaleimide)* (structure 18)

Yield, 94%; colourless needles (from aqueous ethanol); m.p. 101–102°C; IR (KBr): 1770, 1725, 1695 cm^{-1}; mass spectrum *m/e*: 294 (M + 1), 264, 224, 206, 179 (M + 1–$CO(CH_2)_2CHMe_2$), 112, 93, 71. ^1H NMR: × • ⊂δτ∴ ∇<∴ ∅Π∴ $J = 2.4$ Hz), 5.72 (dt, H-6, 1P, $J = 2.4$ Hz), 4.20 (t, $J = 7$ Hz, 2P), 3.48–3.72 (m, H-4, 1P), 2.88–3.20 (m, 5P), 2.40 (b, H-7, 1P), 1.40–1.84 (m, 6P), 0.96 (d, $J = 6$ Hz). Anal. calcd. for $C_{16}H_{23}NO_4$: C, 65.53; H, 7.85. Found: C, 65.30; H, 7.80.

2-Phenyl-2,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isoindoline-7-carboxylic acid isoamyl ester (from isoamyl sorbate and N-*methylmaleimide)* (structure 19)

Yield, 94%; colourless needles (from ethanol); m.p. 85–86°C; IR (KBr): 1775, 1728, 1710 cm^{-1}; mass spectrum *m/e*: 355, 241 (*m/e*–$CO_2(CH_2)_2CHMe_2$), 174, 119, 93. ^1H NMR: δ 7.04–7.60 (m, 5P, aromatics), 6.36 (dt, H-5, 1P, $J = 2.4$ Hz), 5.76 (dt, H-6, 1P, $J = 2.4$ Hz), 4.20 (t, $J = 7$ Hz, 2P), 3.60–3.92 (H-4, 1P), 2.92–3.32 (m, 2P, H-8 and H-9), 2.44 (b, H-7, 1P), 1.44–1.88 (m, $CHMe_2$, C–Me, CH_2, 6P), 1.04 (d, $J = 6$ Hz, 6P). Anal. calcd. for $C_{21}H_{25}NO_4$: C, 70.98; H, 70.04; N, 3.94. Found: C, 70.60; H, 7.20; N, 4.00.

Ethyl-1,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isobenzofuran-7-carboxylate (from ethyl sorbate and maleic anhydride) (structure 20)

Yield, 66%; colourless solid (from ethanol); m.p. 122–123°C; IR (KBr): 1770, 1725 cm^{-1}; mass spectrum *m/e*: 238, 166 (*m/e*–CO_2Et). ^1H NMR: δ 6.44 (dt, H-5, 1P, $J = 2.4$ Hz), 5.84 (dt, H-6, 1P, $J = 2.4$ Hz), 4.32 (q, $J = 7.2$ Hz, 2P), 3.92–4.20 (m, H-4, 1P), 3.08–3.60 (m, H-8 and H-9, 2P), 2.48 (b, H-7, 1P), 1.20–1.48 (superimposed d, $J = 7$ Hz and t, J = 7 Hz, 6P). Anal calcd. for $C_{12}H_{14}O_5$: C, 60.65; H, 5.95. Found: C, 60.50; H, 5.88.

Butyl-1,3,3a,4,7,7a-hexahydro-4-methyl-1,3-dioxo-isobenzofuran-7-carboxylate (from butyl sorbate and maleic anhydride) (structure 21)

Yield, 68%; colourless solid (from ether/petroleum ether 40–60°C); m.p. 88–89°C; IR (KBr): 1770, 1725 cm^{-1}; mass spectrum *m/e*: 266 (M + 1), 223, 211. $C_{14}H_{18}O_5$ requires 266.1152. Found: 266.134. ^1H NMR: × • > ° ⊂δτ˙.˙ ∇< ˙.˙ ∅Π˙.˙ *J* = 2.4 Hz), 5.88 (dt, H-6, 1P, *J* = 2.4 Hz), 4.32 (t, 6 Hz, 2P), 4.00–4.20 (m, H-4, 1P), 3.04–3.64 (m, H-8 and H-9, 2P), 2.56 (b, H-7, 1P), 1.40–1.96 (m with d at 1.44, *J* = 7.2 Hz, 7P), 1.08 (t, *J* = 6 Hz, 3P). Anal. calcd. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.77. Found: C, 63.39; H, 6.70.

2-Methyl-3,3a,4,7,7a-hexahydro-4-methyl-7-acetyl-1,3-dioxoisoindoline (from crotonylidene acetone amd N-*methylmaleimide)* (structure 22)

Yield, 97%; colourless solid (from ethanol), m.p. 154–156°C; IR (KBr): 1765, 1710, 1685 cm^{-1}; mass spectrum *m/e*: 221, 206, 179, 164. $C_{12}H_{15}NO_3$ requires 221.1050. Found: 221.1050. ^1H NMR: δ 6.32 (dt, H-5, 1P, *J* = 2.4 Hz), 5.72 (dt, H-6, 1P, *J* = 2.4 Hz), 3.62–3.84 (m, H-4, 1P), 2.92 (S, NMe), 3.0–3.28 (m, H-8 and H-9, 2P), 2.44 (S, with broad baseline, COMe, H-7, 4P), 1.44 (d, *J* = 7.2 Hz, 3P). Anal. calcd. for $C_{12}H_{15}NO_3$: C, 65.15; H, 6.79; N, 6.33. Found: C, 65.15; H, 6.85; N, 6.30.

2-Phenyl-3,3a,4,7,7a-hexahydro-4-methyl-7-acetyl-1,3-dioxoisoindoline (from crotonylidene acetone and N-*phenylmaleimide)* (structure 23)

Yield, 94%; colourless solid (from ethanol), m.p. 155–156°C; IR (KBr): 1768, 1710 b, 1685 cm^{-1}; mass spectrum *m/e*: 283, 241 (COMe), 212, 174. $C_{17}H_{17}NO_3$ requires 283.1207. Found: 283.1207. ^1H NMR: δ 7.0–7.60 (m, aromatics, 5P), 6.36 (dt, H-5, 1P, *J* = 2.4 Hz), 5.76 (dt, H-6, 1P, *J* = 2.4 Hz), 3.68–3.88 (m, H-4, 1P), 3.16–3.40 (m, H-8 and H-9, 2P), 2.44 (S with broad baseline COMe and H-7, 4P), 1.44 (d, *J* = 7.2 Hz, 3P). Anal. calcd. for $C_{17}H_{17}NO_3$: C, 72.08; H, 6.00; N, 4.95. Found: C, 72.00; H, 6.07; N, 4.90.

2-Ethyl-3,3a,4,7,7a-hexahydro-4-methyl-7-acetyl-1,3-dioxoisoindoline (from crotonylidene acetone and N-*ethylmaleimide)* (structure 24)

Yield, 97%; colourless solid (from aqueous methanol); m.p. 109–111°C; IR (KBr): 1760, 1705, 1685 cm^{-1}; mass spectrum *m/e*: 235, 193 (*m/e*–COMe). $C_{13}H_{17}NO_3$ requires 235.1207. Found: 235.1192. ^1H NMR: δ 6.32 (dt, H-5, 1P, *J* = 2.4 Hz), 5.72 (dt, H-6, 1P, *J* = 2.4 Hz), 3.64–3.84 (m, H-4, 1P), 3.44 (q, CH2, *J* = 7 Hz, 2P), 3.00–3.28 (m, H-8 and H-9, 2P), 2.42 (S with broad baseline, COMe and H-7, 4P), 1.44 (d, CMe, *J* = 7.2 Hz), 1.08 (t, *J* = 7 Hz, 3P). Anal. calcd. for $C_{13}H_{17}NO_3$: C, 66.38; H, 7.23; N, 5.95. Found: C, 66.40; H, 7.20; N, 6.00.

2-Methyl-3,3a,4,7,7a-hexahydro-4-methyl-7-hydroxymethyl-1,3-dioxo-isoindoline (from 2,4-hexadien-1-ol and N-*methylmaleimide)* (structure 25)

Yield, 90%; colourless solid (from benzene/hexane), m.p. 101–103°C; IR (KBr): 3380, 1685 b, 1765 cm^{-1}; mass spectrum *m/e*: 210 (M^+), 192, 179 (M^+-CH_2OH), 113. $C_{11}H_{15}NO_3$ requires 209.1051. Found: 209.1082. ^1H NMR: δ 5.72 (S, H-5 and H-6, 2P), 4.04 (d, CH_2, *J* = 7 Hz, 2P), 3.13–3.70 (m, 3P), 2.92 (S, NMe, 3P), 2.40–2.72 (m, 2P), 1.44 (d, *J* = 7 Hz, 3P). Anal. calcd. for $C_{11}H_{15}NO_3$: C, 63.15; H, 7.17; N, 6.70. Found: C, 63.10; H, 7.20; N, 6.78.

2-Phenyl-3,3a,4,7,7a-hexahydro-4-methyl-7- hydroxymethyl-1,3-dioxo-isoindoline (from 2,4-hexadien-1-ol and N-*phenylmaleimide)* (structure 26)

Yield, 81%; colourless solid (from benzene); m.p. 160–161°C; IR (KBr): 3495, 1760, 1685 cm^{-1}; mass spectrum *m/e*: 271, 241 (*m/e*–CH_2OH), 175. $C_{16}H_{17}NO_3$ requires 271.1207. Found: 271.1201. ^1H NMR: δ 7.04–7.48 (m, aromatics, 5p), 5.80 (S, 2P), 4.04 (d, *J* = 7.2 Hz, 2P), 3.00–3.64 (m, 3P), 2.44–2.72 (m, 2P), 1.44 (d, CMe, *J* = 7.2 Hz). Anal. calcd. for $C_{16}H_{17}NO_3$: C, 70.80; H, 6.27; N, 5.17. Found: C, 70.80; H, 6.33; N, 5.11.

2-Ethyl-3,3a,4,7,7a-hexahydro-4-methyl-7-hydroxymethyl-1,3-dioxo-isoindoline (from 2,4-hexadien-1-ol and N-*ethylmaleimide)* (structure 27)

Yield, 57%; colourless solid (from hexane); m.p. 59–60°C; IR (KBr): 3450, 1765, 1670 cm^{-1}; mass spectrum *m/e*: 224 (M^+), 193 (M^+-CH_2OH), 206, 127. ^1H NMR: δ 5.72 (S, H-5 and H-6, 2P), 4.04 (d, *J* = 7 Hz, 2P), 2.92–3.32 (m, 3P), 3.48 (q, *J* = 7 Hz, 2P), 2.40–2.72 (m, 2P), 1.10 (t, *J* = 7 Hz, 3P), 1.44 (d, CMe, *J* = 7.2 Hz) Anal. calcd. for $C_{12}H_{17}NO_3$: C, 64.57; H,7.62; N, 6.28. Found: C, 64.60; H, 7.60; N, 6.28.

1,3-(diethoxycarbonyl)-6-methyl-2,3,6-tetrahydropyridine (from ethyl sorbate and methylenebisurethane) (structure 28)

To a solution of methylenebisurethane (2.4 g) in anhydrous CH_2Cl_2 (50 ml) containing ethyl sorbate (1.6 g) was added boron trifluoride etherate (1 ml) and the resulting solution stirred for 20 h at room temperature and then refluxed for 6 h. Ice–water (50 cm^{-1}) was added and the organic phase separated, dried ($MgSO_4$) and evaporated to yield an viscous oil which was further purified by column chromatography (SiO_2), eluent being ether, to give the adduct (28) as a viscous oil (2.07 g, 75%). Mass spectrum *m/e*: 241, 226, 196, 168, 154, 140. $C_{12}H_{19}NO_4$ requires 241.1272. Found: 241.1271. IR (neat): 1730, 1700 cm^{-1}. ^1H NMR: δ 5.60–6.00 (m, 2P, olefinic), 4.00–4.60 (m, 6P), 2.90–3.20 (m, 2P), 1.20–1.40 (t, *J* = 7 Hz, 9H). Anal. calcd. for $C_{12}H_{19}NO_4$: C, 59.75; H, 7.88; N, 5.80. Found: C, 59.15; H, 7.50; N, 5.58.

1-(Ethoxycarbonyl)-3-methoxycarbonyl-6-methyl-2,3,6-tetrahydropyridine (from methyl sorbate and methylenebisurethane) (structure 29)

BF_3 etherate was added to a solution of methylenebisurethane (1.90 g) in benzene (50 ml). The mixture was heated to reflux and methyl sorbate (1.26 g) was added. The resulting mixture was allowed to reflux for 6 h before cooling to room temperature; ice–water was added, the organic layer dried ($MgSO_4$). Evaporation of the solvent gave a viscous oil, which was purified as mentioned above (adduct 29) as a viscous oil, yield 79%. Mass spectrum *m/e*: 228 (M^+), 212, 168, 154, 111.

$C_{11}H_{17}NO_4$ requires 227.1141. Found: 227.1145. IR (neat): 1730, 1700 cm^{-1}. ^1H NMR: δ 5.64–6.00 (m, olefinic, 2P), 3.90–4.56 (m, 4P), 3.68 (S, OMe, 3P), 2.92–3.40 (m, 2P), 1.12–1.36 (t, $J = 7$ Hz, 6P). Anal. calcd. for $C_{11}H_{17}NO_4$: C, 59.15; H,7.49; N, 6.17. Found: C, 59.15; H, 7.10; N, 6.20.

2-Phenyl-1,3-diethoxycarbonyl-6-methyl-2,3,6-tetrahydropyridine (from ethyl sorbate and benzalbisurethane) (structure 30)

To a solution of benzalbisurethane (2.60 g) in anhydrous CH_2Cl_2 (50 ml) containing ethyl sorbate (1.40 g) was added BF_3 etherate (1 ml) and the resulting dark solution was stirred at room temperature for 4 h, then refluxed for 4 h and worked-up in the usual manner as described earlier to give a pale yellow oil (0.98 g, 31%). Mass spectrum *m/e*: 317, 302, 272, 244, 178, 150. $C_{18}H_{23}NO_4$ requires 317.1630. Found: 317.1637. IR (neat): 1730, 1700 cm^{-1}. ^1H NMR: δ 7.04–7.40 (m, aromatics, 5P), 5.60–6.20 (m, olefinic and H6), 3.88–4.60 (m, 5P), 3.36–3.48 (m, 1P), 0.96–1.52 (7 peak multiplet, 9P). Anal. calcd. for $C_{18}H_{23}NO_4$: C, 68.13; H, 7.25; N, 4.42. Found: C, 67.80; H, 7.25; N, 4.65.

*2-Benzoyl-1 (toluene-*p*-sulphonamido)-3-ethoxycarbonyl-6-methyl-2,3,6-tetrahydropyridine (from ethyl sorbate and* N*-benzoylidene toluene-*p*-sulphonamide)* (structure 31)

Phenylglyoxal (1 g) and *p*-toluene sulphonamide (1 g) were heated at reflux in benzene (50 ml) for 0.25 h under Dean and Stark; ethyl sorbate (2.3 g) was added followed by BF3 etherate (2.3 g) and refluxed for 12 h, then worked-up as before to give a viscous oil which eventually solidified. Colourless solid (from ether/petroleum ether 40–60°C); yield, 28%; m.p. 167–169°C. IR (neat): 1732, 1690 cm^{-1}; mass spectrum *m/e*: 428 (M^+), 322 (M^+–COPh), 238, 171, 155, 105. ^1H NMR: δ 8.2–8.32 (m, 2H), 7.20–7.80 (m, 7H), 6.12–6.36 (m, olefinic), 5.32–5.62 (dt, 1P, $J = 2.4$ Hz), 4.00–4.44 (q with broadness, 3P), 2.88 (m, 1P), 2.44 (S, –Me, 3P), 1.20 (t, $J = 7$ Hz, 3P), 0.94 (d, $J = 7$ Hz, 3P). Anal. calcd. for $C_{23}H_{25}NSO_5$: C, 64.64; H, 5.85; N, 3.28. Found: C, 64.60; H, 5.85; N, 3.15.

*2-Benzoyl-1 (toluene-*p*-sulphonamido)-3-methoxycarbonyl-6-methyl-2,3,6-tetrahydropyrine (from methyl sorbate and* N*-benzoylidene toluene-*p*-sulphonamide)* (structure 32)

It was prepared as previously by using methyl sorbate. Yield, 15%; a viscous oil; IR (neat): 1732, 1690 cm^{-1}; mass spectrum *m/e*: 414 (M^+), 308 (M^+–COPh). ^1H NMR: δ 8.2–8.32 (m, 2P), 7.2–7.8 (m, 7P), 6.12–6.40 (m, olefinic, 2P), 5.40–5.70 (dt, 1P, $J = 2.4$ Hz), 4.40 (b, 1P), 3.66 (S, OMe, 3P), 2.88 (b, 1P), 2.44 (S, Me, 3P), 0.94 (d, $J = 7$ Hz, 3P). Anal. calcd. for $C_{22}H_{23}NSO_5$: C, 63.92; H, 5.57; N, 3.39. Found: C, 63.80; H, 5.70; N, 3.35.

RESULTS AND DISCUSSION

Diels–Alder reactions may be carried out in aqueous solutions (Breslow *et al.*, 1983; Chao-Jun Li, 1993) and they proceed efficiently with excellent regiochemical control. *N*-substituted maleimides were chosen initially to demonstrate the Diels–Alder reactivity of sorbic acid because they are known to be highly reactive in this type of reaction; they are stable and the products easily characterised. When reactions of the *N*-substituted maleimides with sorbic acid were carried out in aqueous solution, they gave adducts similar to those obtained using benzene and toluene as solvents. In general, products prepared in the organic solvents were much easier to work-up than in water, and most of them were prepared in this way for characterisation. The adducts (1–15) shown in Fig. 1 were prepared from sorbic acid and its esters in 77–80% yield by reaction with equimolar amounts of the *N*-substituted maleimides in ethanol, benzene or toluene at reflux temperature for 1 h, and the solid obtained after evaporation of the solvent was recrystallised from an appropriate solvent. It is evident that sorbic acid and its esters behave as the diene component of the Diels–Alder reaction. Crotonylidene acetone and 2,4-hexadien-1-ol (sorbyl alcohol) also gave cycloaddition adducts (22–24 and 25–27, respectively) by reaction with *N*-substituted maleimides in quantitative yield.

It was decided to investigate the reaction of sorbic acid with simple Schiff bases. In order to facilitate identification and reduce the number of ^1H signals to a minimum, Schiff bases of ethyl carbamate with formaldehyde and benzaldehyde were used. Methylenebisurethane (33) gives imine (34) in the presence of a catalytic quantity of BF_3 in Et_2O which gave cycloaddition adducts (28 and 29) with ethyl sorbate and methyl sorbate. Similarly benzalbisurethane (35) gave imine (36) which reacted with ethyl sorbate to give (30). Furthermore, *N*-tosylimine (38), was prepared from phenylglyoxal and toluene-*p*-sulphonamide as a structurally very different species and this undergoes

Table 1. ^1H chemical shifts for sorbic acid and its derivatives (Leraux & Vauthier, 1970). The group R is in this structure $CH_3CH=CH-CH=CHCOOR$. The hydrogen atoms are labelled so as to make the label numbers directly comparable with those of the Diels–Alder adducts in Table 2

Carbon atom	H-7	H-6	H-5	H-4	C–Me
R=H	5.81, d, $J = 16$ Hz	7.41 m	6.25 m	6.25 m	1.83, d, $J = 6$ Hz
R=Me	5.70, d, $J = 16$ Hz	7.15 m	6.20 m	6.20 m	1 85, d, $J = 6$ Hz
R=Et	5.68, d, $J = 16$ Hz	7.16 m	6.16 m	6.16 m	1.80, d, $J = 6$ Hz

cycloaddition with ethyl and methyl sorbate to form adducts (31 and 32).

The structures of the products isolated have been assigned on the basis of the analytical and spectroscopic data given above. ^1H NMR data for sorbic acid and its derivatives are summarised in Table 1, and the observed chemical shifts of ^1H-associated with the double bond are listed in Table 2.

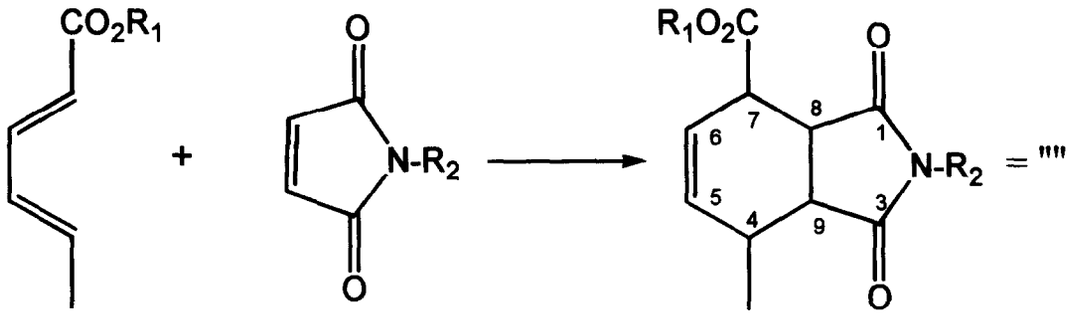
It is evident that the adducts of sorbic acid and its derivatives with *N*-alkylmaleimide show the carbon atoms associated with the double bond at δ 6.28–6.40 (H-5) and δ 5.72–5.80 (H-6). In spectra of sorbic acid and its derivatives, these carbon atoms are found at δ 6.16–6.25 (H-5) and δ 7.16–7.41 (H-6). The chemical shift of the C–Me in the adducts appears in the region of δ 1.42–1.48, whilst in sorbic acid and its esters, the C–Me group is at δ 1.80–1.86. The chemical shifts of the significant protons in the Diels–Alder adducts are, therefore, characteristically different from those of sorbic acid.

Whilst the ability of Schiff bases to act as dienophiles is well known (Weinreb & Staib, 1982), adducts (28–32) illustrate the ability of sorbic acid to act as the diene in this reaction. There has been speculation that sorbic acid interacts with intermediates in Maillard browning (Arya, 1980), although Wedzicha *et al.* (1991) showed that, on a short time-scale the behaviour of sorbic acid is probably only that of an acid–base catalyst.

Schiff bases are an important type of intermediate formed in the Maillard reaction and the fact that a Diels–Alder reaction between sorbic acid and Schiff bases is possible would indicate a potential reaction of sorbic acid with components of Maillard systems.

Overall, it is surprising that there has been no pub-

Table 2. ^{1}H Chemical shifts for Diels–Alder adducts of sorbic acid (and its derivatives) with *N*-alkyl and *N*-phenyl maleimides



Adduct	H-7	H-6	H-5	H-8 and H-9	H-4	C–Me
1	2.40 b	5.72 dt	6.32 dt	3.0–3.24 m	3.52–3.76 m	1.44 d
2	2.44 b	5.80 dt	6.32 dt	3.0–3.20 m	3.56–3.80 m	1.42 d
3	2.40 b	5.72 dt	6.32 dt	3.0–3.28 m	3.60–3.84 m	1.44 d
4	2.40 b	5.68 dt	6.26 dt	3.0–3.24 m	3.60–3.80 m	1.40 d
5	2.44 b	5.72 dt	6.28 dt	3.0–3.44 m	3.72–3.96 m	1.44 d
6	2.44 b	5.80 dt	6.40 dt	3.0–3.32 m	3.70–3.94 m	1.44 d
7	2.44 b	5.80 dt	6.40 dt	3.0–3.40 m	3.72–3.96 m	1.46 d
8	2.48 b	5.76 dt	6.40 dt	3.0–3.36 m	3.72–3.96 m	1.46 d
9	2.48 b	5.88 dt	6.44 dt	3.0–3.40 m	3.72–3.96 m	1.44 d
10	2.46 b	5.78 dt	6.38 dt	3.0–3.32 m	3.74–4.02 m	1.42 d
11	2.44 b	5.72 dt	6.28 dt	3.0–3.28 m	—	1.48 d
12	2.46 b	5.70 dt	6.32 dt	3.0–3.28 m	—	1.42 d
13	2.42 b	5.76 dt	6.40 dt	3.0–3.28 m	—	1.44 d
14	2.48 b	5.72 dt	6.36 dt	—	—	1.44 d
15	2.44 b	5.72 dt	6.28 dt	—	—	1.42 d
16	2.46 b	5.72 dt	6.32 dt	—	3.44–3.66 m	—
17	2.40 b	5.76 dt	6.32 dt	—	3.43–3.80 m	—
18	2.40 b	5.72 dt	6.32 dt	2.92–3.32 m	3.48–3.72 m	—
19	2.44 b	5.76 dt	6.36 dt	3.08–3.60 m	3.60–3.92 m	—
20	2.48 b	5.84 dt	6.44 dt	3.04–3.64 m	3.92–4.20 m	—
21	2.56 b	5.88 dt	6.48 dt	3.00–3.28 m	4.00–4.20 m	—
22	2.44 b	5.72 dt	6.32 dt	3.16–3.40 m	3.62–3.84 m	—
23		5.76 dt	6.36 dt	3.00–3.28 m	3.68–3.88 m	—
24		5.72 dt	6.32 dt	3.00–3.24 m	3.64–3.84 m	—
25		5.72 s		3.00–3.24 m	—	—
26		5.80 s		3.00–3.24 m	—	—
27		5.72 s			—	—

lished evidence of Diels–Alder reactions of sorbic acid in foods. The most obvious dienophile is the double bond of mono-unsaturated fatty acids; normally this bond is *cis* which is also the preferred arrangement for Diels–Alder reactions. In addition, sorbic acid is easily dissolved in triglyceride mixtures. Our own preliminary work on the reaction of methyl oleate with sorbic acid has given rise only to an intractible residue.

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