International Journal of Agriculture Innovations and Research
Volume 5, Issue 4, ISSN (Online) 2319-1473
Manuscript Processing Details (dd/mm/yyyy) :
Received: 19/11/2016 | Accepted on : 25/11/2016 | Published : 05/01/2017

# Mouldy, Mutzu, Earthy Off-odour Compounds in 'Golden Delicious' Apple Fruit Skin

**K. Kaack**
Department of Food Sciences, Aarhus University, Kirstinebjergvej 10, 5792 Aarslev, Denmark.
Corresponding author email id: karl.kaack@kalnet.dk

*Abstract* – **The two major products from autoxidation of α-farnesene in cool stored apple fruit skin were conjugated trienols 2,6,10-trimethyldodeca-2,7(E), 9(E), 11-tetraen-6-ol, and 6-droperoxy 2,6,19-tr-methyl-dodeca-2,7(E), 9(E),11-tetra-ene-conjuga-ted compounds have a very distinctive smelling ketone 6-methyl-5-heptene-2-one that are produced by cleavage of the 6-7 bond of α-farnesene. The complete transfer of α-farnesene from the apple surface to the air is a very convincing step in development of off-flavour in apples. The final oxidation product of the temperature-dependent autoxidation of conjugated trienols in apples was the ketone 6-methyl-5-heptene-2-one without hydrogen making it impossible to be oxidized.**

*Keywords* – **Farnesene Mouldy, Musty, Earthy, Odour.**

## I. Introduction

The odour of 'Golden Delicious' were previously associated with a mouldy, musty and earthy off-odour as in this research were two endoperoxides occurring with molecular weights 236 and 252, in the two apple cultivars respectively, as described previously [1] Anet 1972 [2] Spicer et al. 1993; [3] Rowan et al. 1995, [4] Rowan et al. 2001). In the literature it has been reported that 1-octen-3-one found in apple juice processed from the apple cultivars 'Golden Delicious' and 'Fuji' apples have a strong metallic mushroom-like odour [5] (Glindemann et al. 2006) [19]. Besides have other aroma compounds including 2-methyl-1-penten-3-one, hexanal, (E)-2-heptenal, 6-methyl-5-hepten-2-one and (E)-2octenal contribute to this off-odour [1] Anet, 1972; [6] Hashizume et al. 2007).

In the period beginning in the mid-sixties and ending in the early nineties the flavour of 'Golden Delicious' apples from cool and controlled atmosphere (CA) storage were described as mouldy, musty, earthy without fresh apple fruit aroma [1] Anet 1972. At that time increased research were conducted into the causes of scald, which was a problem for apple fruit growers, because the apple fruit quality was seriously damaged by this illness in most Western countries. Therefore increased research in the effects of the storage conditions on the sensory quality characteristics and the possibilities for determination of the significantly differences in quality properties such as size, aroma compounds, colour, firmness, soluble solids, acidity, starch index and Streif index [20] (Rowan, 2010). Already in 1969 [2] Spicer et al. 1993 showed that autoxidation of α-farnesene in apple fruit resulted in formation of a conjugated triene, a hydroperoxide and a large amount of ketones with low mole weight. Later on [3] Rowan et al 1995 showed that the content of α-farnesene in apple wax increased to a maximum after 95 days of cool storage and decreased thereafter for up to 120 days. The apple cultivars 'Granny Smith', 'Red Delicious' and 'Gala' produced 6-methyl-5-heptene-2-one, 1-octen-3-one with a-mushroom-like odour, which increased during apple fruit maturation and contributed to occurrence of a mouldy, musty, earthy off-odour at low oxygen concentration during storage at low temperatures, as found previously [4] [5] [6]. The hydrocarbon α-farnesene present in the apple fruit skin rapidly auto oxidizes very easily at 1°C to (E,E) -1.5-dimethyl -1- (4- methylpent - 3 - enylhepta - 2, 4, 6-trieny-hydroperoxide and (E,E)-4-(1-hydroperoxy-1-methylethyl) -1-methyl - 1 - 4 - methylhexa-1, 3, 5 - triphenyl) tetra-methylene- peroxide [2] Spicer et al. 1993. And a few years later described [2] Spicer et al. 1993 an oxidation chain from α-farnesene to ketones encompassing 6- methyl- 5- hepten- 2-one, methylheptan -2 -one, methyloctan-2-one, and 2, 6, 10-trimethyldodecan-6-l. Later on confirmed [7] Rowan et al. (1972) that autoxidation of α-farnesene resulted in farnesyl hydroperoxide, a trienol, endoperoxide and that a cleavage of the C6-C7 bonding in α-farnesene resulted in heavy bursts of this instinctive smelling ketone 6-methyl-5-hepten-2-one [2] Spicer et al., 1993. And therefore the aim of this research was to identify the organic compounds causing the mouldy, mutzy and earthy off-odour of apples.

## II. Materials and Methods

Apple trees of the cultivar 'Golden Delicious' on rootstock M9 were established in 1989 at the location 10° 27' (E) and 55° 18' (N), on sandy loam (JB6) rich in phosphorous and calcium. The planting distance was 3.75 x 1.75 m, and the trees were fertilised annually using 100 kg $ha^{-1}$ potassium in early spring and 50 kg $ha^{-1}$ nitrogen in late spring. Plant protection was carried out according to recommendations for integrated production. Thinning of flowers was carried out using ammonium thiosulphate at flowering and hand thinning of fruitlets. Apples with 60-80 mm in diameter were harvested at the optimum maturity for storage in controlled atmosphere (CA) with 11.5-13.0 g $100^{-1}$ soluble solids, firmness 7-8 kg $m^{-2}$ (N), starch index 6-7 and Streif index 0.09-0.12 according to normal praxis as described previously [9] (Kaack and Bertelsen, 2004). Each experimental treatment included storage of 10 net sacks with 25 apples (8 kg) in a common cool storage room and another 10 sacks with 25 apples were stored in drums with controlled atmosphere storage drums with 3 % CO2 and 3 % O2 at 1 °C for 6 months. Apples from all treatments were matured at 20 °C for five days before sensory evaluation, extraction, chemical and physical analysis and identification by combined gas chromatography and mass spectrometry (GC-MS).

### 2.2 *Sensory Evaluation*

All sixteen panel members of age 18-32 year were previously trained intensively in evaluation of the sensory characteristics of at least six different raw or processed strawberries, black currants, gooseberry, raspberry, elderberry, apples and at least six raw or processed vegetables encompassing peas, carrot, maize, spinach, cucumber and spinach for three to ten years using a sensory scale with increasing points from 1 to 10 points regarding mouldy mutzu and earthy off flavour. The four technicians involved in determination of apple fruit sensory characteristics participated also in sorting of stored apples in two groups with a low and a high level of mouldy, mutzu and earthy odour. The samples with the highest content of volatiles were separated and identified using GC-MS. Samples with the highest contents of these volatiles were separated and identified quantified gas chromatography in order to determine the characteristic odour of each separated compound. Separation of the volatile odour components by GC-MS required 60 min in four replicates by four panel members make the total time for these sniffing analysis up to 16 hours.

### 2.3 *Extraction*

Four times twenty five 'Golden Delicious' apples were kept in 500 ml ether for 3 min until sampling of 50 µl apple extract that was transferred to a white paper filter for evaporation of the ether in one to two minutes. The paper was evaluated for a low or high level of mouldy, musty, earthy off-odour on shift by four intensively trained members of the sensory panel. Extracts from apples with a high level of mouldy, musty, earthy off-odour were collected in one sample and used for identification of the organic compounds causing mouldy, mutzu and earthy off odour. The ether was removed using an evaporator and 1 g of the samples was dissolved in ether and transferred to a 2 x 20-cm column with a mixture of silica acid (Fluka, Ramsey & Patterson, Buchs, Schwitzerland) and aluminium oxide (Merck, Darmstadt, Germany). The components of interest were eluted using pentane (Bie & Berntsen, Rødovre, Denmark). The free fatty acids were then removed from the eluate by extraction using 8 % $Na_2CO_3$ (Merck, Darmstadt, Germany) dissolved in water, and the long chain hydrocarbons were precipitated using acetone.

### 2.4 *GC-MS*

The extracted compounds were separated using a gas chromatograph (Pye Unicam Model 64, Cambridge, UK) equipped with an integrator (Hewlett-Packard 3370, Palo Alto, California, USA) and a 2.5-m stainless steel column 2 mm in diameter packed with 3 % OV-1 on diatomite CQ. Nitrogen was applied as carrier gas (15 ml $min^{-1}$), and the velocities of hydrogen and air gas were 25 ml $min^{-1}$ and 250 ml $min^{-1}$, respectively. The injector and detector temperatures were 130 and 300°C, respectively, and the oven temperature increased from 150 °C (1 min); 150-215 °C (1°C• 10 min-1); and then 215-300(2°C• min-1) 300°C (10 min) by separation of the extracted compounds. A Varian Saturn 2000 ion trap mass spectrometer (Varian, Walnut Creek, California, USA) operated at an ionisation potential of 70 eV and interfaced to a 3400 CX GC using the column described above for the production of mass spectre.

### 2.6 *Statistical Analyses*

The statistical analyses were carried out using a Statgraphics Statistical Package version 4 (Statistical Graphics Corporation, Rockville, USA), and averages were separated using different letters ($P < 0.05$).

## III. Results

The odour of 'Golden Delicious' were previously associated with a mouldy, musty and earthy off-odour as in this research were two endoperoxides with molecular weights 236 and 252, in the two apple cultivars respectively, as described previously [1]Anet 1972 [2] Spicer et al. 1993; [3]Rowan et al. 1995, [15] 2001). In the literature it has been reported that 1-octen-3-one found in apple juice processed from the apple cultivars 'Golden Delicious' and 'Fuji' apples has a strong metallic mushroom-like odour Besides have other aroma compounds including 2-methyl-1-penten-3-one, hexanal, (E)-2-heptenal, 6-methyl-5-hepten-2-one and (E)-2octenal contributed to off-odour [1] (Anet, 1972; [6]Hashizume et al. 2007). The data obtained by GC-MS analyses showed presence of the extraction liquid pentane peak and six peaks with unknown compounds for the extraction compound pentane with retention time 7.0 min occurrence.

The GC-MS table showing that the major oxidation occur by breaking of the C6-C7 bonding resulting in a burst of 6-methyl-5-heptene-2-one that are an end compound contributing significantly to the mouldy, musty earthy odour of 'Golden Delicious' from cool storage and controlled storage with controlled air composition. The hydrocarbon α-farnesene rapidly auto oxidizes at 1° to two conjugated two conjugated trienyl hydroperoxides including (E,E)-1.5-dimethyl-1-(4-methoxypent-3-enylhepta-2,4,6-trienyl hydroperoxide, with some of the (E,Z) isomer and a mixture of the erythro and threo (E;E)-4-(1-hydroperoxy-1-methylethyl)-1-methyl-1-(4methylhexa-1, 3,5-triphenyl) tetramethylene peroxide [7] (Anet, 1966). These compounds results in α-farnesene and conjugated trienes. At that time had [1] Anet 1972 collected knowledge to describe an oxidation chain from α-farnesene to ketones including 6-methyl-5-hepten-2-one,methylheptan-2-one, ethyloctan-2-one, and 2,6,10-trimethyl-dode-can-6-ol [1]Anet 1972). Later on confirmed []Rowan et al. (1972) that autoxidation of α-farnesene resulted in farnesyl hydroperoxide, a trienol and an endoperoxide. The GC-MS table shows that the major oxidation occur by breaking of the C6-C7 bonding resulting in a burst of 6-methyl-5-heptene-2-one that are an end compound contributing significantly to the mouldy, musty earthy odour of 'Golden Delicious' from cool and storage with controlled air composition. Occurrence of 6-methyl-5-heptene-2-one may interact with other volatiles and may thereby promote a new aroma notes. Such interactions may result in various combinations with other volatiles resulting in important interactions and different odours and therefore are 6-methyl-5-hepten-2-one not the only compound that contribute to the apple odour. Synthesis of aroma compounds in the apple skin may be a member of a large or small group of aroma compounds. The aroma

compounds in non-mature apples because the aroma composition in apple fruit skin changes significantly during the maturation phases. Apple fruit odour compounds are produced in the outmost apple fruit cell layers and may diffuses outwards to the apple surface that are covered with waxy cuticula containing long chain hydrocarbons, fatty acid esters, ketones and alcohols and other very volatile compounds [that are soluble in the waxes. Therefore was ether used by extraction of the aroma compounds. A combination of gas chromatography and mass spectrometry (GC-MS) was used for determination of the chemical structures of the compounds with mouldy, musty or earthy odour. The data showed that the compound eluted after 61.2 minutes resulted in an 87 per cent reduction of the total emission of constituents with mole weights 204, 161, 123, 119, 107, 93, 79, 69 and 55 corresponding to α-farnesene [7]. These data from GC-MS analyses correspond to GC-MS data previously published [4][7][8] [4, 7, 8]). Data for the compound eluted after 40.0 minutes with an area of 7 per cent included peaks 220, 202, 159, 147, 133, 119, 107, 105, 95, 93, 91, 79, 69, 55, 43 and 41, documenting that this compound were 2,6,10-trimethyldodeca-2,7E,9E,11-tetraen-6-ol. The presence of its Z isomer 2,7E,9Z,11, found by [4], was confirmed, as described by other researchers [8,9]. Deposition of 2, 6, 10-trimethyldo-deca-2,7E,9E,11-tetraen-6-ol and the Z-isomer 2,7E,9Z,11 occurred in the proportion 9:1 [4]. The percentages of peaks 236, 219, 218, 202, 159,147, 121, 119, 105, 93, 91, 81, 69, 55, 43 and 41 showed that the presence of 6-hydroperoxy-2,6,10-trimethyldodeca-2,7E,9E,11-tetraen-6-ol, which was previously found in the skin of the five apple cultivars 'Red Delicious', 'Fuji', 'Gala', 'Golden Delicious' and 'Granny Smith' [8, 24], did not occur in the 'Golden Delicious' apples used in this research. A low concentration of farnesols in the apple fruit skin was expected, because they are based on mono-epoxidation of α-farnesene, which is rather rare ([8,11,18]). Further analysis of extracts from the skin of 'Golden Delicious' apples led to identification of 6.7-epoxy-3,7,11trimethyldodeca-1,3E,10E-triene with the characteristic peaks 220, 205, 204, 189, 161, 159, 147, 145, 133, 123, 121, 120, 119, 107, 105, 95, 94, 91, 81, 79, 69 and 55, as previously described by [8] and eluted from the GC column after 30.5 minutes, making up an area of 2 per cent. The last compounds found in 'Golden Delicious' apples used for this research were two endero-peroxides with molecular weights 236 and 252, respectively, which, as described by [4, 8], were eluted after 28.1 minutes with an area of 1 per cent. Further documentation of the presence of these compounds does not appear to be available. The end product of autoxidation was 6-methyl-5-hepten-2-one [10], which may increase during the first part of storage and then deceases [18]. The odour of 'Golden Delicious' were previously associated with a mouldy, musty and earthy off-odour as in this research were two endoperoxides occurring with molecular weights 236 and 252, in the two apple cultivars respectively, as described previously [1] Anet 1972; [2]Spicer et al. 1993; [3] Rowan et al. 1995, [15]. In the literature it has been reported that 1-octen-3-one found in apple juice processed from the apple cultivars 'Golden Delicious' and 'Fuji' apples had a strong metallic mushroom-like odour [5] (Glindemann et al. 2006) [19]. Besides may other aroma compounds including 2-methyl-1-penten-3-one, hexanal, (E)-2-heptenal, 6-methyl-5-hepten-2-one and (E)-2octenal contribute significantly to this this off-odour [1] Anet, 1972; [6]Hashizume et al. 2007).

## IV. Discussion

During the storage period the apples accumulated α-farnesene and conjugated trienes progressively in the fruit skin, as previously found [6]). It has previously been shown that 6-methyl-7-heptane-2-one is the final product of oxidation of trienols [2, 6]. In accordance with this research, farnesols were the major autoxidation products in 'Golden Delicious' apple skin, as previously found [10] and the final oxidation product in these apples was 6-methyl-5-hepten-2-one [4,6,8], which is produced through cleavage of the C6-C7 bond of α-farnesene [6,11]. The odour of α-farnesene has been characterised as green and herbaceous [12], and the most important oxidation product was 3,7,11-trimethyldodeca-1,3(E),5(E)10-tetraene-7-ol, described as having a pleasant citrus odour [13], whereas 6-methyl-5-heptene-2-one was described as having a distinctive mouldy, musty and earthy odour [11]. Organic compounds with mouldy, musty and earthy odours have been identified as ketones and include 1-octen-3-ol, 3-octanone, 3-octanone, 1-octen-one, 1-octen-3-one and 6-methyl-5-hepten-2-one [14]. Based on this it can be concluded that 6-methyl-5-hepten-2-one results in the off-odour of apple fruits. The increasing retention time and decreasing oxidation levels for the identified hydroperoxides are in agreement with the data previously presented by [5][7]. The presence of the endoperoxy hydroperoxides represents the highest level of oxidation in the apple peel, and their chemical structure has been confirmed by previous research [4][7][8][15]. The changes in apple fruit characteristics, such as decreasing firmness and acidity and increasing levels of soluble solids during CA and cool storage, as described above, occur when the plant hormone ethylene initiates and promotes natural fruit development through fast increases in ripening and senescence [16]. These changes are associated with degradation of starches and pectins, increasing levels of energy molecules, precursors for aroma compounds and several hydrolytic enzymes [17]. A combination of gas chromatography and mass spectrometry (GC-MS) was used for determination of the chemical structures of compounds with mouldy, musty or earthy odour. This showed that the compound eluted after 61.2 minutes resulted in a 87 per cent reduction of the total emission of constituents with mole weights 204, 161, 123, 119, 107, 93, 79, 69 and 55 corresponding to α-farnesene [7]. These data from GC-MS analyses correspond to GC-MS data previously published [4][7][8]. Data for the compound eluted after 40.0 minutes with an area of 7 per cent included peaks 220, 202, 159, 147, 133, 119, 107, 105, 95, 93, 91, 79, 69, 55, 43 and 41, documenting that this compound was 2,6,10-trimethyldodeca-2,7E,9E,11-tetraen-6-ol. The presence of its Z isomer 2,7E,9Z, 11, found by [4],

was confirmed, as described by other researchers [8,9]. Deposition of 2, 6, 10-trimethyldodeca-2, 7E, 9E, 11-tetraen-6-ol and its Z isomer 2,7E,9Z,11 occurred in the proportion 9:1[4]. The relative percentages of peaks 236, 219, 218, 202, 159, 147, 121, 119, 105, 93, 91, 81, 69, 55, 43 and 41 showed that the presence of 6-hydroperoxy-2,6,10-trimethyldodeca-2,7E,9E,11-tetraen-6-ol, which was previously found in the skin of the five apple cultivars 'Red Delicious', 'Fuji', 'Gala', 'Golden Delicious' and 'Granny Smith' [8], did not occur in the 'Golden Delicious' apples used in this research. A low concentration of farnesols in the apple fruit skin was expected, because they are based on mono-epoxidation of α-farnesene, which is rather rare ([8][11][18]. Further analysis of extracts from the skin of 'Golden Delicious' apples led to the identification of 6.7-epoxy-3,7,11trimethyldodeca-1,3E,10E-triene with the characteristic peaks 220, 205, 204, 189, 161, 159, 147, 145, 133, 123, 121, 120, 119, 107, 105, 95, 94, 91, 81, 79, 69 and 55, as previously described [8] and eluted from the GC column after 30.5 minutes, making up an area of 2 per cent. The last compounds found in 'Golden Delicious' apples used for this research were two endero-peroxides with molecular weights 236 and 252, respectively, which, as described by [4], [8], were eluted after 28.1 minutes with an area of 1 per cent.

## V. Conclusion

Mouldy, musty, earthy odour compounds occurring in apples after non-controlled CA and cool storage were identified as the autoxidation products of farnesene (3,7,11-trimethyldodecane1,3(E,)6(E)-10-tetraene), including 2,6,10-trimethyldodeca-2,7E,9E,11-tetra-en-6-ol, 2,7E,9Z,11a, 6.7-epoxy-3,7,11trimethyldodeca-1,3E,10E-triene and two 6-endero-hydroperoxy-2,6,10-trimethyldodeca-2,7E,9-tetraenes with 6-methyl-5-hepten-2-one as the major compound with the characteristic mouldy, musty and earthy odour.

## Annexure (Tables)

Table 1. Quality characteristics of 'Golden Delicious' after storage for five months at 1°C (n = 4).

| Storage | Weight loss w/w% | Stiffness factor *$10^{-6}$, hz | Soluble solids, w/w % | Acidity, w/w % | Off-flavour, point |
|---|---|---|---|---|---|
| Cool storage, 3°C | 5.77a | 22.4ab | 11.4b | 0.16c | 8b |
| CA-storage, 3 % $CO_2/O_2$ | 3.01 | 14.8b | 13.1a | 0.25a | 10a |
| Exsiccator 760 mm Hg | 0.39c | 22.4ab | 11.9ab | 0.22a | 0c |
| Exsiccator 100 mm Hg | 0.40c | 31.2a | 12.1ab | 0.25a | 0c |

Points: 0 = no off flavour, 10 = very strong off-odour

Table 2. Effects of treatments on quality characteristics Quality characteristics after storage. Off flavour 0-10 none and very starch.

| Storage | Air shift L $min^{-1}$ | Pressure mm Hg | Weight loss, w/w% | Stiffness f*$10^{-6}$ $hz^{-1}$ | Sol/sol g 100 $g^{-1}$ | Dry matter g 100 $g^{-1}$ | Acidity g 100 $g^{-1}$ | Off flavour point | Ascorbic mg 100 $g^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cool | None | none | 6.22a | 12.8 | 15.9ab | 17.0a | 0.42a | 10a | 6.7ab |
| CA | " | " | 3.69b | 24.3b | 15.1a | 17.3a | 0.35a | 8b | 0.6c |
| Exsiccator | 15 min | 760 | 0.98d | 31.3a | 14.5b | 17.1a | 0.41a | 0d | 6.0ab |
| " | " | 380 | 2.00c | 29.5a | 14.3b | 16.9a | 0.41a | 0d | 8.5a |
| " | " | 280 | 1.07cd | 1.30cd | 12.1c | 17.0a | 0.42a | 0.42a | 6.7ab |
| " | " | 100 | 1.07cd | 1.07cd | 14.4b | 16.8a | 0.44a | 0.44a | |

Table 3 Compounds identified and quantified by GC-MC analysis of the purified extracts from 'Golden Delicious' peel extracts (n = 4).

| Conpound | Peak, no | M+ | Retention time, min | Height, mm | Width, mm | Area, $mm^2$ | Area, % |
|---|---|---|---|---|---|---|---|
| Enderoperoxy-hydroperoxide | 2 | 268 | 30.5 | 3.5 | 1.5 | 2.6 | 0.8 |
| Trienyl hydroperoxide | 3 | 268 | 33.9 | 99.0 | 2.5 | 123.8 | 36.3 |
| 2,6,101-Trimethyldodeca-2,7(E),9(Z),11-tetraen-6-ol | 4 | 220 | 39.8 | 2.8 | 4.0 | 5.6 | 1.6 |
| 2,6,101-Trimethyldodeca-2,7(E),9(E),11-tetraen-6-ol | 5 | 220 | 53.7 | 19.7 | 4.0 | 39.4 | 11.5 |
| α-farnesene (3,7,11-trimethyldodecane 1,3(E,)6(E)-10- tetraene) | 6 | 204 | 61.2 | 82.5 | 4.0 | 165.0 | 48.3 |

Table 4 Mass spectre of compounds identified in apple fruit tissue (n = 24).

| Weight | M | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | alfa-farnesene | | | | | | | | | | |
| " | 189 | 175 | 159 | 161 | 147 | 145 | 135 | 133 | 107 | 119 | 79 | 105 | 93 | 91 | 79 | 77 | 65 | 55 | 41 |
| " | 15 | 14 | 18 | 14 | 14 | 14 | 14 | 14 | 28 | 14 | 44 | 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 |
| Lost | $CH_3$ | $CH_2$ | $H_20$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $2CH_2$ | $CH_2$ | $(CH_3)_2$ $+H_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ |
| | | | | | | | | | α-farnesol | | | | | | | | | | |
| " | 220 | 205 | 189 | 175 | 161 | 159 | 147 | 145 | 135 | 133 | 123 | 119 | 107 | 105 | 93 | 91 | 79 | 69 | 55 |
| " | 205 | 189 | 175 | 161 | 147 | 135 | 133 | 131 | 107 | 119 | 79 | 105 | 93 | 91 | 79 | 77 | 65 | 55 | 41 |
| " | 15 | 16 | 14 | 14 | 14 | 14 | 14 | 14 | 28 | 14 | 44 | 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 |
| Lost | $CH_3$ | O | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $(CH_3)_2$ + $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ |
| | | | | | | | | | Hydroperoxide | | | | | | | | | | |
| Weight | 236 | 204 | 189 | 175 | 161 | 147 | 135 | 135 | 121 | 119 | 107 | 105 | 93 | 93 | 93 | 91 | 91 | 77 | 69 | 55 |
| " | 204 | 189 | 175 | 161 | 147 | 135 | 121 | 119 | 107 | 107 | 93 | 91 | 79 | 77 | 69 | 77 | 69 | 63 | 55 | 41 |
| " | 32 | 15 | 14 | 14 | 14 | 12 | 16 | 14 | 14 | 14 | 14 | 14 | 16 | 14 | 16 | 14 | 14 | 14 | 14 | 14 |
| " | 20 | $CH_3$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | O | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | O | O | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_2$ |
| Ketone | 126 | 111 | 108 | 69 | 35 | 43 | 41 | | | | | | | | | | | | |

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