

GASCHROMATOGRAPHIC AND MASSPECTROMETRIC INVESTIGATION ON COCONUT-LIQUOR (MALIBU)

HİNDİSTANÇEVİZİ LİKÖRLERİNDE (MALİBU) GAZKROMATOĞRAFİK VE MASSPEKTROMETRİK ARAŞTIRMALAR

Ismail YAVAŞ¹, Adolf RAPP²

1) Ankara University Agricultural Faculty Food Engineering Department Ankara/TURKEY

2) Karlsruhe University Institut for Food Chemistry D-76128 Karlsruhe/GERMANY

SUMMARY: In different coconut-liquors (Malibu) 30 varieties of components were investigated by the gaschromatographic method. Among these, benzyl alcohol, benzaldehyde, benzodioxole-5-carboxaldehyde (piperonal), vanillin, 4-hydroxynonanoic acid lactone, 5-hydroxydecanoic acid lactone etc. were determined by using the gaschromatographic and massspectrometric methods. In respect of aromatic components in Malibu samples, only quantitative differences were found in the separate investigation.

ÖZET: Çeşitli hindistancevizi likörlerinde (Malibu) gazkromatografik olarak 30 farklı komponent tayin edilmiştir. Bunlardan benzil alkol, benzaldehid, benzodioksol-5-karboksaldehid (piperonal), vanillin, 4-hidroksinonanoik asit lakton, 5-hidroksidekanoik asit lakton vb. gazkromatografik ve masspektrometrik olarak saptanmıştır. Tek tek araştırılan "Malibu" örnekleri arasında aroma komponentleri yönünden yalnız nicel farklılıklar olduğu belirlenmiştir.

INTRODUCTION

The coconut (*Cocos nucifera*) is the main plant of the tropical regions, its fruit called by the same name. The tree reaches a height of nearly 25-30 meters. The leaves at the top of the trunk form a beautiful crown. The nuts are 30-35 centimeters long and 15-20 centimeters in diameter. The shape of the nut is ellipsoides and flat peel covers the nuts. The nuts weigh nearly 1.8 kg and contain 300-500 ml milky liquid inside the white seeds.

The seed of the coconut palm is the biggest seed in the world. A new plant sprouts from one of the three eyes of the coconut after the nut has fallen on the ground. The coconut gives fruit 3-6 years after plantation and continues to give fruits for 60 years. One palm gives 40-50 fruits. The yield of 1000 square meters is 9 to 11 metric tons and produces 0.6 to 1.5 ton of copra (ARGON, 1941).

The coconut is grown around the Equator. The motherland of the coconut is South-East Asia and went to other places by sea. The fruit can float or is carried to tropical lands all over world by people. The coconut fruit is valuable for human nutrition. The fruit contains 3.8 % protein, 3.6 % crude fat and 3.7 % carbohydrate (KESKİN, 1959). In the case of the soft fruit period, the fruit can be eaten. After maturation the fleshy part of the fruit is eaten, after grinding on top of rice. Another eating style is cooking it with spices and vegetables.

Some countries produce vegetable oil from the fleshy part of the coconut. This oil is used not only for cooking but also in lighting, cosmetic cream, wax and soap production. Copra, dried coconut, is the main export product. At the same time copra is the animal feeding material after the oil has been removed by pressing. Another use is fertizing of the land.

Dessicated coconut is used in the patisserie and biscuit industries. Coconut milk which is produced by pressing is used for producing different types of food products. The most suitable harvesting period of the coconut is the time when the nuts drops from the trees. In this case the fruit gives a great amount of oil and top quality copra. Copra contains nearly 64 to 66 % oil which is dried in the sun.

In the Pacific islands people produce a kind of sweet pulp from the flower bud. This pulp is used for drinking directly or for fermentation by using the strain of *Saccharomyces vordermanni* and *Monillia javanica* which gives a unique aromatic component to this pulp (GROSSMAN, 1943). The alcoholic beverage which contains 7 % alcohol, is distilled after 3 weeks and named *arrak* (DAHM, 1952). "Arrak" is clear and light yellow and has the odor and taste of rum. Arrak is also used with sugar beet molasses (DOBISLAW, 1954). On the other hand in Sri-Lanka and India palm wine is produced from the Toddy palm *Caryota urens* flowers. In Malaysia the Nipa palm (*Nypa fruticans*) tree can help to produce a kind

of drink which contains 17 % sugar. In Nigeria, *Raphia palm* (*Raphia vinifera* and *Raphia hookeri*) tree pulp is used for wine production and gives 5 % alcohol (HERRMANN, 1983).

Alcohol products produced from coconut are mixed with Jamaica rum for preparation of good drinks and send to the market for consuming. This product is named "Malibu" and is used as a subject for research.

Malibu is the alcoholic beverage mixed with Jamaica rum, coconut extract and natural aromatic components. In this research various aromatic components of Malibu samples (Producers: Twelve Islands Shipping Company Ltd., 1 York Gate, London NW 1) have been analysed by using gaschromatographic and massspectrometric methods for determining aromatic components.

MATERIAL AND METHODS

Material

The research was performed in "Bundesanstalt für Züchtungsforschung and Kulturpflanzen, Institut für Rebenzüchtung Geilweilerhof, D-76833 Siebeldingen"/Germany.

The samples are 6 different types of Malibu liquor bought from local markets in Germany and whose features are shown in Table 1.

Table 1. Information on labels of the product used in the experiment

| Samples | Statements | Alcohol of amount |
|----------|--|-------------------|
| Malibu-1 | Tropical Coconut laced with light Jamaican Rum | 24 % vol |
| Malibu-2 | Tropical Coconut laced with light Jamaican Rum | 28 % vol |
| Malibu-3 | Tropical Coconut laced with light Jamaican Rum | 24 % vol |
| Malibu-4 | Tropical Coconut laced with light Carribbean Ron | 24 % vol |
| Malibu-5 | Tropical Coconut laced with light Jamaican Rum | 24 % vol |
| Malibu-6 | Tropical Coconut laced with light Jamaican Rum | 28 % vol |

Method

4 ml samples are diluted 1:1 with distilled water and add 1 μ l standard solution (2,6-dimethyl-5-hepten-2-ol in ethanol) and prepared according to RAPP et al. (1994). Aroma extraction is made using the method described below:

- Column: 60 m DB-5, diameter 0.32 mm, film thickness 1 μ m,
- Temperature programme: 50-180°C, 5°C/min,
- Carrier gas: Hydrogen,
- Split: 1:25

After determining the aromatic components in the extracted samples by using gaschromatographic and massspectrometric methods, the retention times of those components were compared with the standard sample.

RESULTS AND DISCUSSION

In the Malibu (coconut-liquor) samples 30 different aroma components were determined with the gaschromatographic method (Figure 1 and Table 2). In addition to gaschromatographic and massspectrometric identification methods, benzaldehyde, benzyl alcohol, 3-methyl-butanol-1, 2-methyl-butanol-1, vanillin, benzodioxole-5-carboxaldehyde (piperonal) and a large amount of γ and δ -lactone were found. In a test special coconut components called γ -decalactone (= 4-hydroxydecanoic acid lactone), δ -decalactone (= 5-hydroxydecanoic acid lactone) or γ -undecalactone (= 4-hydroxyundecalactone) were determined (Table 3) were as 4-hydroxynonanoic acid lactone (γ -nonalactone) were not determined (MAARSE et al., 1989). Up to the present, benzyl alcohol, benzaldehyde, vanillin and benzodioxole-5-carboxaldehyde (piperonal) have not been found in coconut-liquor (MAARSE et al., 1989).

Table 2. The volatile components of coconut liquors (Malibu)

| Peak No | Relative peak height comparing standard | | | | | |
|---------|---|------|------|------|------|------|
| | M-1 | M-2 | M-3 | M-4 | M-5 | M-6 |
| 1 | 18 | 80 | 62 | 36 | 35 | 38 |
| 2 | - | - | - | - | 8.3 | 0.8 |
| 3 | 5.2 | 2.6 | 4.1 | 1.0 | 7.4 | 1.4 |
| 4 | 0.8 | 0.2 | 0.2 | 0.2 | 1.9 | 0.2 |
| 5 | 0.2 | 0.4 | 0.4 | 0.2 | 3.3 | 0.5 |
| 6 | 13.3 | 2.1 | 3.7 | 1.6 | 5.0 | 2.9 |
| 7 | 100 | 100 | 100 | 100 | 100 | 100 |
| 8 | 969 | 964 | 807 | 965 | 1928 | 824 |
| 9 | 2.7 | 6.1 | 2.4 | 10.9 | 1.0 | 1.4 |
| 10 | 0.9 | - | - | - | 7.1 | - |
| 11 | 17.3 | 42.5 | 16.9 | 9.8 | 20.0 | 10.4 |
| 12 | 7.6 | 20.0 | 8.1 | 5.9 | 6.0 | 4.5 |
| 13 | 6.4 | 5.6 | 6.0 | 9.8 | 13.8 | 7.4 |
| 14 | 2.4 | 2.8 | 0.7 | 0.5 | 6.9 | 1.3 |
| 15 | 757 | 789 | 747 | 706 | 1178 | 688 |
| 16 | 3.0 | 2.8 | 8.4 | 6.4 | 5.2 | 11.5 |
| 17 | 21.5 | 56.5 | 19.0 | 63.8 | 8.8 | 33.6 |
| 18 | 0.6 | 0.7 | 0.8 | 1.6 | 0.8 | 1.3 |
| 19 | 77 | 70 | 54 | 86 | 223 | 76 |
| 20 | 7.9 | 4.0 | 10.1 | 4.5 | 15.0 | 17.0 |
| 21 | 20 | 13 | 19 | 14 | 37 | 40 |
| 22 | 0.2 | 0.2 | 1.4 | 0.2 | 0.2 | 1.4 |
| 23 | 5.3 | 11.2 | 5.2 | 3.8 | 4.8 | 2.7 |
| 24 | 1.7 | 2.1 | 2.2 | 2.1 | 3.9 | 3.0 |
| 25 | 7.3 | 14.0 | 6.4 | 22.4 | 25.5 | 12.3 |
| 26 | 6.7 | 5.3 | 5.5 | 4.0 | 14.0 | 13.1 |
| 27 | 3.0 | 3.5 | 4.6 | 5.5 | 10.2 | 6.7 |
| 28 | 3.3 | 5.6 | 3.6 | 4.7 | 11.4 | 3.7 |
| 29 | 0.9 | 1.4 | 20.7 | 0.7 | 1.9 | 22.9 |
| 30 | 1.2 | 2.5 | 1.2 | 0.9 | 1.2 | 0.7 |

M: Malibu

Most of the research samples contain very small amounts of fermentation components are none at all. For instance 3-methyl-butanol-1, 2-methyl-butanol-1, butyric acid ethylester (ethyl butyrate) were found at a detectable level, where as 2-phenylethanol, lactic acid ethylester; caproic-, caprylic- and capric acid ethylester were not determined even in very small amounts. In the main coconut-liquor, volatile aromatic components were 4-hydroxynonanoic acid lactone (γ -nonalactone), vanillin and benzyl alcohol.

In the research samples, only quantitative differences in aroma components were found (Figure 1 and Table 2). As shown in Table 2, the coconut-liquor samples show big differences in the peaks; number 6 (benzaldehyde), number 8 (benzyl alcohol), number 10, 11 and 15 (4-hydroxynonanoic acid lactone), number 17 (lactone) and number 19 (vanillin), 25 (5-hydroxydecanoic acid lactone). Especially in the sample "Malibu-5" large differences in the aromatic components are shown compared to other samples.

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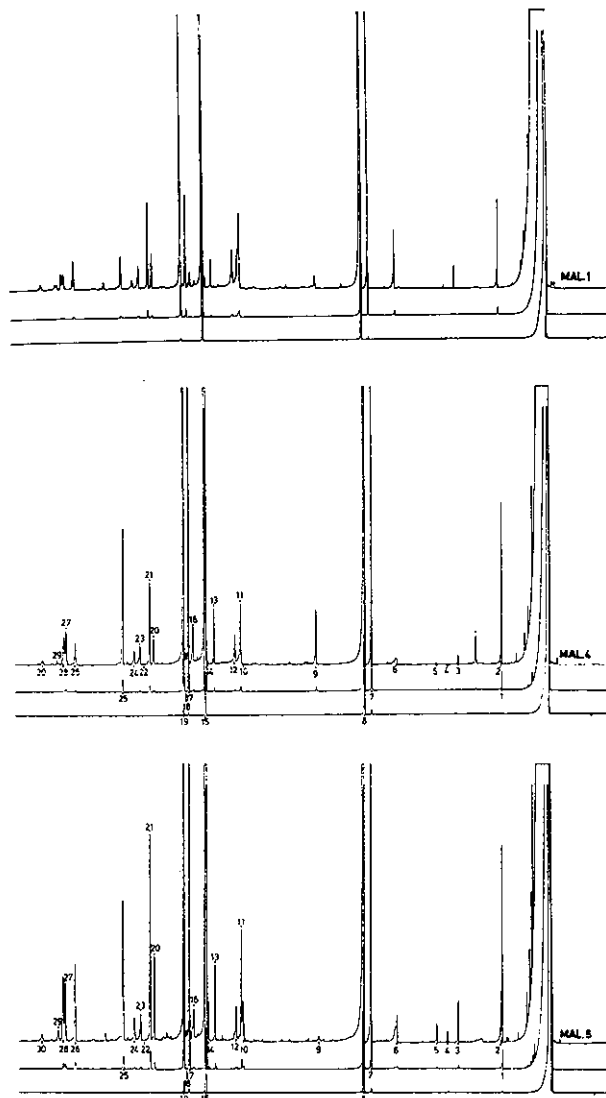


Figure 1. Aromatic components of various Malibu samples (60 m DB-5; 50°C-180°C, 5°C/min)

Table 3. The aromatic component of Malibu by using GC/MS

| Peak Number | Relative Ret. Time (Std= 100) | MS Results | Aroma components |
|-------------|-------------------------------|---|--|
| 1 | 24 | <u>55</u> , 70, 73, 42, 87 | 3-Methyl-butanol-1 |
| 2 | 25 | <u>57</u> , 41, 87 | 2-Methyl-butanol-1 |
| 3 | 44 | <u>43</u> , 59, 101 | 4-Hydroxy-4-methyl-2-pentanone |
| 4 | 50 | <u>41</u> , 46, 85, 57, 94 | |
| 5 | 61 | <u>57</u> , 41, 95, 87 | |
| 6 | 78 | <u>105</u> , 106, 77, 51, 79 | Benzaldehyde |
| 7 | 100 | <u>109</u> , 59, 41, 69, 81, 124 | 2,6-Dimethyl-5-hepten-2-ol (Std) |
| 8 | 108 | <u>79</u> , 77, 108, 107, 51, 65 | Benzyl alcohol |
| 9 | 132 | <u>126</u> , 43, 71, 55, 97 | Lactone |
| 11 | 148 | <u>59</u> , 41, 85, 79, 65, 108 | |
| 12 | 205 | <u>149</u> , 150, 121, 63, 91 | Benzodioxole-5-carboxaldehyde (Piperonal) |
| 15 | 220 | <u>85</u> , 55, 56, 41, 86, 114, 128 | γ -Nonalactone (4-Hydroxynonanoic acid lactone) |
| 16 | 222 | <u>100</u> , 55, 41, 85, 148, 113 | (Lactone) |
| 17 | 224 | <u>99</u> , 120, 43, 55, 71, 91 | (Lactone) |
| 18 | 226 | <u>99</u> , 71, 42, 55, 114 | Lactone (4-Hydroxy-3-methyl-nonanoic acid lactone) |
| 19 | 232 | <u>152</u> , 151, 81, 109, 123, 137, 53 | Vanillin |
| 21 | 244 | <u>137</u> , 166, 109, 81 | Ethyl vanillin (3-Ethoxy-4-hydroxy benzaldehyde) |
| 22 | 248 | <u>85</u> , 102, 55, 131, 71 | 4-Hydroxydecanoic acid lactone |
| 23 | 250 | <u>99</u> , 88, 71, 55, 41, 116 | Lactone |
| 24 | 251 | <u>97</u> , 68, 41, 108, 55, 69 | Lactone |
| 25 | 257 | <u>99</u> , 71, 42, 55, 114, 152, 170 | 5-Hydroxydecanoic acid lactone |
| 27 | 276 | <u>132</u> , 131, 160, 104, 51, 77 | 7-methyl-benzopyran-2-one |
| 28 | 279 | <u>85</u> , 41, 55, 69, 71, 56, 128, 148, 166 | 4-Hydroxyundecanoic acid lactone |
| 29 | 309 | <u>117</u> , 97, 68, 41, 69, 43, 118 | |

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