

# The effect of citric acid in lime mash on the composition of lime oil

J. K. B. A. ATA

Food Research Institute, P.O. Box M.20, Accra, Ghana

## SUMMARY

Production of essential oils from lime mash is becoming a big industry in West Africa. However, owing to lack of distillation facilities, the lime mash is shipped to European countries where the essential oils are then distilled. An investigation into the effect of naturally present citric acid in lime mash on the final lime oil distillate quality, has shown that the citric acid is an important factor in causing a major change in the chemical constitution of the lime oil during distillation. This change is manifested by loss of colour and flavour reminiscent of natural lime oil.

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## Introduction

The essential oil of lime is used very much in the perfumery, cosmetics and food industries.

The older methods of obtaining lime oil involved the expression of the oil from the fruit, but modern methods use distillation of the lime mash, which is obtained as a by-product after the removal of the lime juice cordial.

However, the sources of lime are very remote from the places of lime oil manufacture, and the transport of raw materials over long distances as lime mash usually results in much chemical transformation of the constituents, which vitally affect the final product quality in colour and odour.

In finding out the differences between the qualities of expressed lime oil and distilled lime

## RÉSUMÉ

ATA, J. K. B. A.: *Les effets de l'acide citrique de la purée de citrons sur la composition de l'essence de citrons.* La production d'huile essentielle à partir de citrons broyés est en train de devenir une industrie importante en Afrique occidentale. Cependant, en raison de l'absence de distilleries, la purée de citrons est expédiée à certains pays d'Europe où l'essence est distillée. Des recherches sur l'effet de l'acide citrique existant naturellement dans la purée de citrons, sur la qualité finale de l'essence après distillation, ont montré que cet acide citrique est un facteur important des changements de constitution chimique qui se produisent pendant la distillation. Ces changements se manifestent par la perte de couleur et de parfum rappelant l'essence naturelle de citron.

oil, Guenther & Langenau (1943) and Slater (1961) suggested that the distillation made the difference, and the contribution of citric acid was only mentioned. Slater (1961) also showed that the distilled oil of lime showed marked deviations especially in the loss of ciroptene, 5, 7-dimethoxy coumarin. Slater & Watkins (1964) established a distinct difference in aroma and flavour between natural (cold pressed) lime oil and distilled lime oil; the natural oil had a more delicate flavour and aroma than the latter. Their work showed that this change was probably derived from the hydrocarbon fraction of the original lime oil by heating under acidic conditions. The aim of this work was, therefore, to show whether the naturally present citric acid in the mash was a contributory factor to this change.

## Materials and methods

### *Preparation of sample*

Some limes of the Dominican type were carefully washed in water and macerated whole in a sterile Waring blender; a little quantity of distilled water was added to get a perfect mash. The mash was transferred into sterile conical flasks fitted with cotton-wool plugs and rubber band. These were kept at room temperature (20-24 °C) for varying periods of 1, 2 and 3 months. The mash was then steam distilled using the British Pharmacopoeia (1958) apparatus for the determination of volatile oils.

The essential oil fraction was tapped off and corked tightly in a sample tube. A second batch of limes of the same origin was peeled carefully by hand to avoid contact of the peel with the internal juice, rich in citric acid. The peels were placed in acetone, in a screw cap jar for 5 days and the acetone-extract was concentrated using a vacuum rotary evaporator (100 rpm and temperature of 35 °C). The oil was then re-extracted from the crude water containing acetone-essential oil concentrate with diethyl-ether. The extract was placed in the flask of the B.P. apparatus for the determination of volatile oils and vacuum was applied to it to evaporate the ether. (By this method, contact with oxygen was kept at a minimum.) The crude oil was then steam-distilled with about 500 cm<sup>3</sup> of water using the same apparatus. The oil was then dried over anhydrous sodium sulphate and kept for thin layer chromatographic analysis. A third batch of limes was carefully peeled by hand and the fresh peel steam distilled using the B.P. apparatus for volatile oils. The oils were dried over anhydrous sodium sulphate and kept for analysis.

### *Thin layer chromatostrips*

The chromatostrips were prepared by the method of Miller & Kirchner (1953). 19 g of kieselguhr HF 254 was mixed with 1 g of plaster of Paris and made into a thin paste with 36 cm<sup>3</sup> of water with slight warming and with a further addition of 2-3 cm<sup>3</sup> of water to form a thin paste to spread on the glass strips. A uniform coating (0.02 cm thick) was made on glass plates (20.32 cm × 10.16 cm) which were dried at 105 °C for 15 min, and then kept in a desiccator containing

sodium hydroxide pellets. Using micro-pipettes, 2 cm<sup>3</sup> of sample was spotted and the plate run in a solvent of 15% ethyl acetate in hexane in a tank, saturated with the solvent. The chromatostrips were developed by spraying with freshly prepared 1% vanilin in concentrated sulphuric acid. Other sprays such as concentrated sulphuric acid, 5% vanilin in 30% of 85% phosphoric acid in methanol, orthoanisidine and a dilute solution of flourescein in water followed by exposure over bromine vapour were used for specific identification of some components as suggested by Kirchner, Miller & Keller (1951).

### *Gas chromatograph*

The gas chromatographic technique used was a modification of the method used by Green (1957). 10% w/w polyethylene glycol adipate (PEGA) on 100-200 mesh embacel in a 1.22 cm × 0.63 cm column was used. A pye-argon gas chromatogram with a detector and strontium 90 radioactive source was used. Sample size was 0.025 cm<sup>3</sup>, with gas flow rate of 38 cm<sup>3</sup> per minute and column temperature of 135 °C.

### *Identification of thin layer chromatograph spots*

For this, 4 cm<sup>3</sup> of sample was spotted. The position of spots was identified by viewing the plate under ultra-violet light. The spots were scrapped into a test tube and dissolved in a small volume of di-ethyl ether (40-60). As the kieselguhr settled, the ether layer was decanted and concentrated. 0.1 cm<sup>3</sup> of the concentrated sample was injected into the gas chromatogram. Reference samples of constituents of essential oils were also spotted for purposes of identification.

## Results

The thin layer chromatostrips of the lime mash distillate after 1, 2 and 3 months storage of the mash prior to distillation, showed seven distinct spots in each distillate. The chromatostrips of the distillate also after 6 months storage of the distillate showed the same number of spots (Fig. 1). Fig. 2 shows the thin layer chromatospots of lime peel acetone extract distillate and Fig. 3 and Fig. 4 show a comparison of the thin layer chromatospots of lime mash and lime peel distillates. Fig. 5 shows thin layer chromatospots of lime mash and



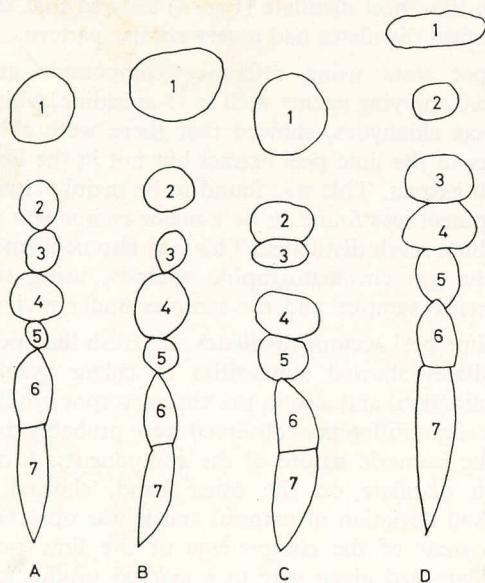


Fig. 1. Thin layer chromatostrips of lime mash distillate after various periods of storage of mash and distillate (A, after 1 month's storage; B, after 2 months' storage; C, after 2 months' storage, spotted 30 days later; D, after 3 months' storage).

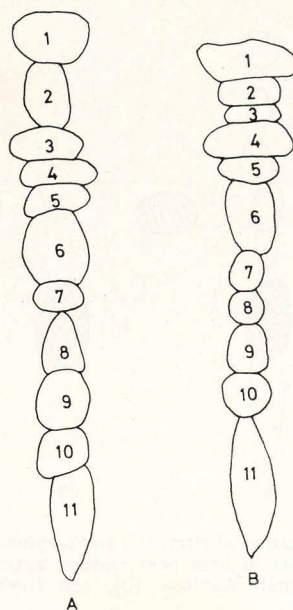


Fig. 2. Chromatospots of lime peel acetone extract distillate (A and B, lime peel acetone extract spotted immediately and after 1 month respectively).

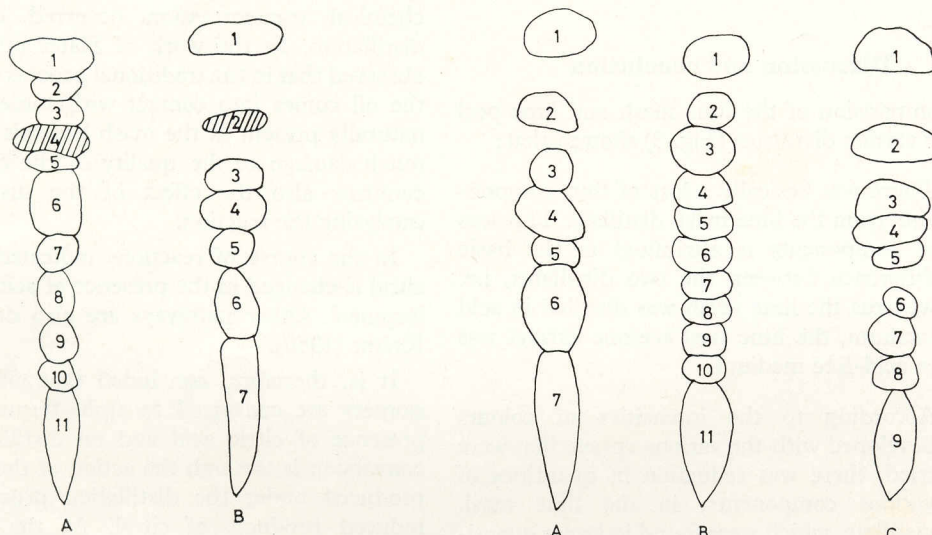


Fig. 3. A comparison of the chromatospots of the lime mash distillate and lime peel acetone extract distillate (A, lime peel acetone extract distillate; B, lime mash distillate).

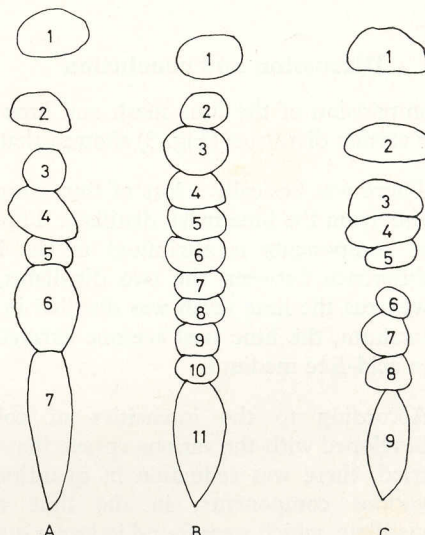


Fig. 4. A comparison of the chromatospots of lime mash distillate (A), lime peel acetone extract distillate (B) and fresh lime peel distillate (C).

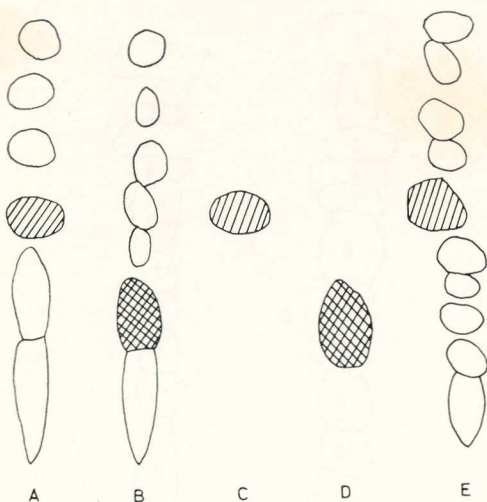


Fig. 5. Identification of citral (C) and terpineol (D) in the chromatospots of lime peel acetone extract distillate (A), lime mash distillate (B), and fresh lime peel distillate (E).

lime peel distillates and of reference compounds which were used to identify the difference in the two samples.

### Discussion and conclusion

A comparison of the lime mash and lime peel acetone extract distillates (Fig. 3) showed that:

- (a) There was basically a loss of four components from the lime mash distillate. This loss of components is attributed to the basic difference between the two distillates, i.e. whereas the lime mash was distilled in acid medium, the lime peel acetone extract was in acid-free medium.
- (b) According to the intensities of colours developed with the various sprays that were tried, there was reduction in quantities of various components, in the lime mash distillate, which were found in larger quantities in the lime peel acetone extract distillate.

A comparison of the chromatospots of lime mash distillate, lime peel acetone extract distillate and

fresh lime peel distillate (Fig. 4) showed that the lime peel distillates had a very similar pattern.

Spot tests using reference compounds and special spraying agents such as *O*-anisidine, which detects aldehydes, showed that there were aldehydes in the lime peel extract but not in the lime mash extract. This was found to be mainly citral. Terpineol was found to be a major component in the lime mash distillates. This was also confirmed in the gas chromatographic analysis, using the reference samples and the samples under review.

Lime peel acetone distillates and fresh lime peel distillates showed similarities in colour (visual examination) and also in the chromatospot profile. The slight differences observed were probably due to the isomeric nature of the components. Lime mash distillate on the other hand, showed a marked deviation in pattern, and it was observed that most of the components of the lime peel distillate had given way to a marked production of terpineol. The fact that the prolonged storage of the mash did not affect the quality of the distillate suggests that the chemical transformation does not occur prior to distillation. Similarly, the fact that distillates, spotted 30 days and more after distillation did not show any difference from spots of fresh distillates would confirm that the chemical transformation occurred during the distillation. In the work of Slater (1961) it was observed that in the traditional process of pressing, the oil comes into contact with some citric acid naturally present in the mash but this did not do much damage to the quality of the oil and this confirms also the effect of the distillation in catalysing the reaction.

In the course of reactions indicated in Fig. 6, citral is changed in the presence of acids to alpha-terpineol. Other pathways are also described by Karrer (1950).

It is, therefore, concluded that citral and its isomers are converted to alpha-terpineol in the presence of citric acid and on distillation. This conversion is through the action of the anhydride produced under the distillation process on the reduced products of citral. As the distillation process is essential for obtaining lime oil, the prevention of the contact of the naturally present citric acid of lime with lime oil would go a long way to producing a better quality lime oil.

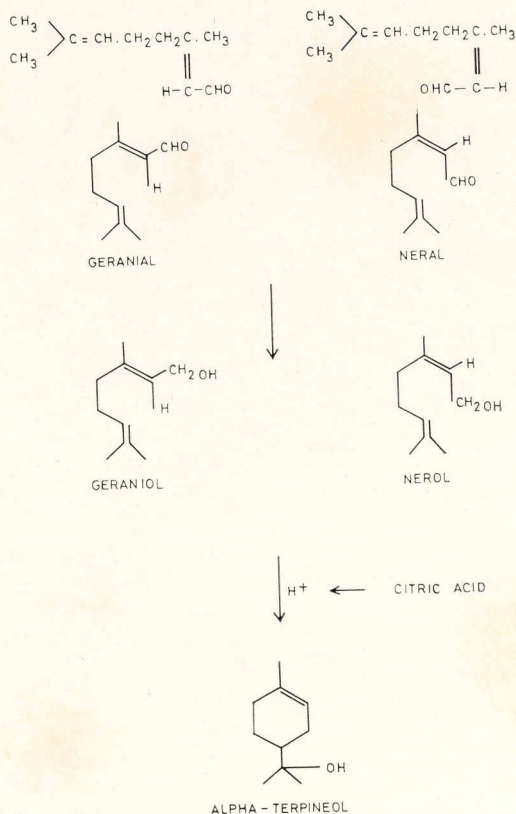


Fig. 6. Pathways for the conversion of citral to terpineol.

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