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GAS CHROMATOGRAPHY IN DEVELOPING THE PRODUCTION OF CITRAL FROM GERANIOL

S. BÉKÁSSY, J. HEISZMAN and J. PETRÓ

Institute for Organic Chemical Technology, Technical University, Budapest (Hungary)

SUMMARY

In technology the optimal conditions of industrial processes must be determined. Gas chromatography is a method that can be used very advantageously in solving this problem and also even in supervision and control of the process. Production of citral from geraniol was used as an example to illustrate how gas chromatography plays an essential part in the development of this technology.

INTRODUCTION

The science of technology deals with the development of new rational manufacturing processes and with the improvement of existing processes. The task of the process engineer is the determination of optimal process conditions. Processes in chemical engineering are determined by natural (chemical, physicochemical, physical) laws and by economic requirements. For the adequate economic development of technological processes, the course of the reaction, the effect of parameters influencing the reaction and the efficiency of various operations must be known. The following of individual steps and the supervision of the operation and, based on these, the planning of the control or possible automation of the process require appropriate methods of analysis.

Gas chromatography (GC) is of obvious use in the following of several processes. It is a rapid and sensitive method, it can be used automatically for quantitative evaluation, it is particularly adapted for the analysis of multicomponent systems and used on-line, as process chromatography, it is particularly useful for the direct supervision and control of continuous processes and also of batch processes.

An example will be presented in which GC analysis and results played part in each phase of the development of the technology, beginning from the testing of the raw materials up to the quality control of the end product.

EXPERIMENTAL AND RESULTS

Development of a process for the preparation of citral from geraniol (Fig. 1) was required which could also be realized on an industrial scale. Citral, the principal aroma substance of lemon oil, is an important basic substance in the cosmetics and

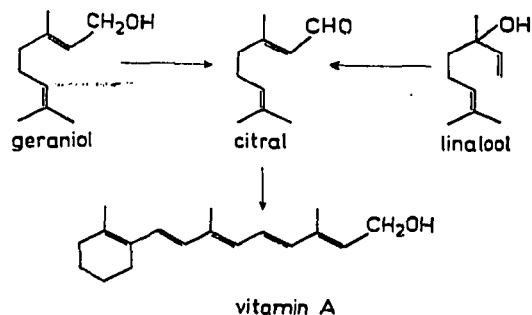


Fig. 1. Scheme for the preparation and application of citral.

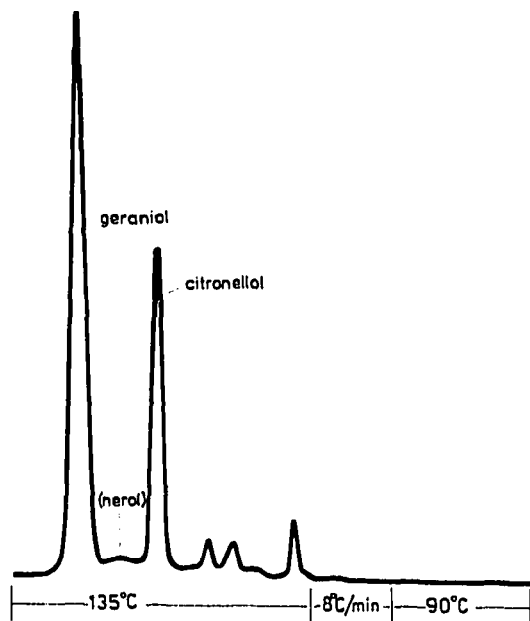


Fig. 2. Chromatogram of geraniol raw material. Column: 1.2 m \times 5 mm (I.D.), 15% PEG-1500 on Celite. Temperature: 90° for 10 min and after that, programmed (from 90°) to 135° at a rate of 8°/min. Detector: flame ionization. Hydrogen carrier gas flow-rate: 80 ml/min.

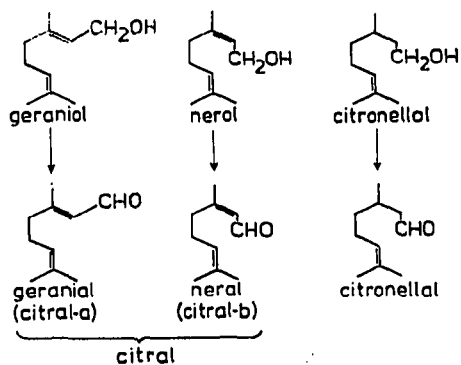


Fig. 3. Oxidation products of geraniol and related compounds.

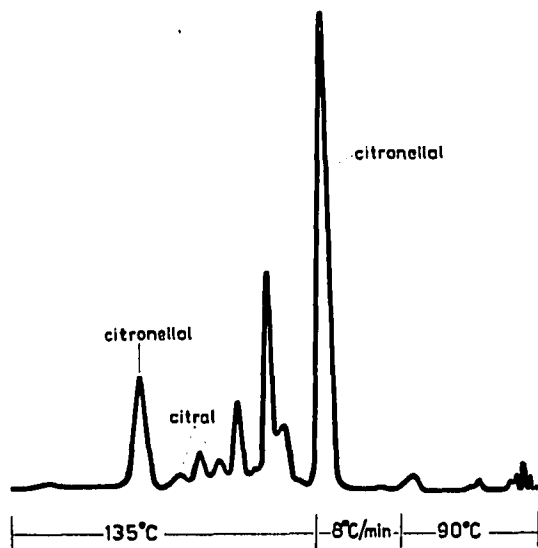


Fig. 4. Product of dehydrogenation over a copper chromite catalyst. For conditions, see the legend to Fig. 2.

perfumery industry and, in addition, it is used as an α,β -unsaturated aldehyde in a steadily widening field for syntheses in the organic chemical industry, *e.g.* as the starting material of vitamin A synthesis.

Geraniol is also used directly in the perfumery industry, and raw material of this kind was obtained for our experiments. The gas chromatogram of the substance is shown in Fig. 2. In addition to several smaller peaks, two main components appear on the chromatogram. After preparative GC separation, they were unequivocally identified on the basis of their IR spectra¹. Geraniol corresponds to the last peak of the chromatogram, and thus constitutes about 50% of the raw material. The other main component is citronellol (Fig. 3).

The structure of citronellol is similar to that of geraniol, *i.e.* one of the double

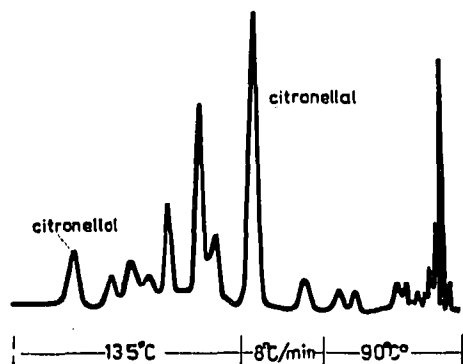


Fig. 5. Product of dehydrogenation over a copper chromite catalyst with an admixture of 3% air. For conditions, see the legend to Fig. 2.

TABLE I
SOME IMPORTANT DATA ON THE CHEMICAL OXIDATION METHODS

Oxidizing agent	Solvent	Temperature (°C)	Time of reaction (h)	Molar oxidant to geraniol ratio	Conversion of geraniol (%)	Yield (%)
$K_2Cr_2O_7$ + H_2SO_4 and/or CH_3COOH	Water or benzene	80–105	0.75	2.5:1	95	90
Pyridine + CrO_3 MnO_2	Pyridine	20	25	8:1	~100	~100
	<i>n</i> -Hexane or petroleum ether (b.p. 40–70°)	20	120	20:1	90–98	85
$Ni(OH)_3$	Benzene	80	3	5:1	90	90
<i>tert.</i> -Butyl chromate	Petroleum ether (b.p. 40–70°)	20	24	7:1	98	60

bonds is saturated. On oxidation, citronellal is formed, which is an interfering component in citral, used in the perfumery industry or for organic synthesis. According to data in the literature², geraniol of plant origin contains citronellol, and its separation is cumbersome.

In geraniol prepared synthetically, nerol is the accompanying component instead of citronellol. Nerol is the geometrical isomer of geraniol. On oxidation, this too yields an α,β -unsaturated aldehyde, *viz.* neral. This aldehyde is also present in natural citral and can be used for every purpose in the same way as geraniol.

Chemical and economic evaluations of the available processes suggested that only chemical oxidation or vapour-phase catalytic dehydrogenation were feasible.

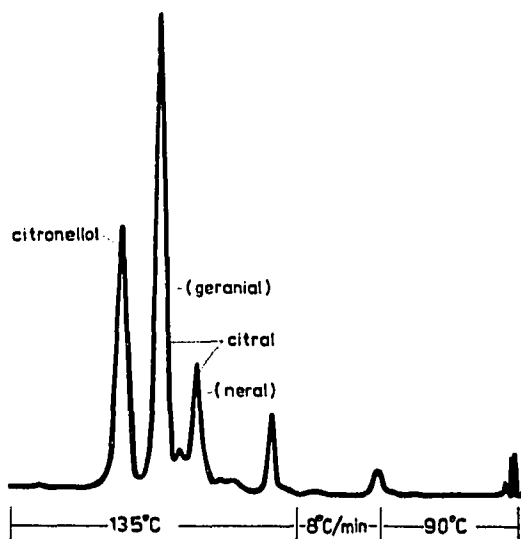


Fig. 6. Product of oxidation with MnO_2 . For conditions, see the legend to Fig. 2.

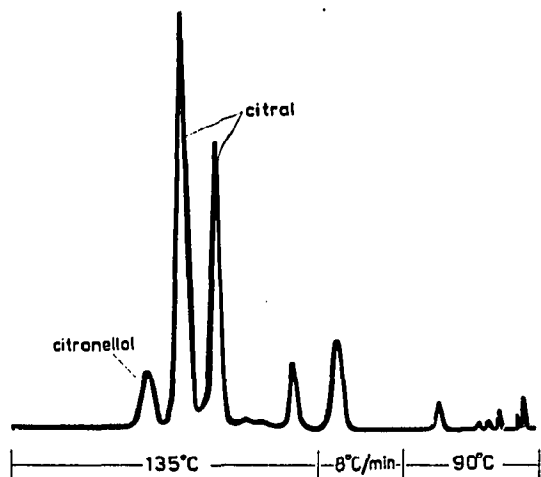


Fig. 7. Product of oxidation with a pyridine-CrO₃ complex. For conditions, see the legend to Fig. 2.

We tried to achieve dehydrogenation at 200–280° over a copper chromite catalyst in a continuous reactor using a technology developed earlier for a similar alcohol dehydrogenation³. In the mixture leaving the reactor only a small proportion of geraniol was present (Fig. 4). However, the expected citral (geranial) was formed only in small quantities, while the main product was a new component, which was identified as citronellal. Under more vigorous experimental conditions, the citronellol content of the raw material also decreased considerably. From this, too, citronellal was formed.

Thus, hydrogen liberated on dehydrogenation immediately saturates the neighbouring double bond^{4,5}. In the presence of hydrogen acceptors the dehydrogenation can probably be carried out, but afterwards the additive has to be separated, because even traces of it make the product unusable in the perfumery industry. We tried to use air as hydrogen acceptor, but without success, because already on the admixture of 2–5% of air strong splitting and oxidation occurred, and in the first section of the chromatogram the peaks of many new compounds appeared (Fig. 5).

Various chemical oxidations were extensively studied⁶. Some important para-

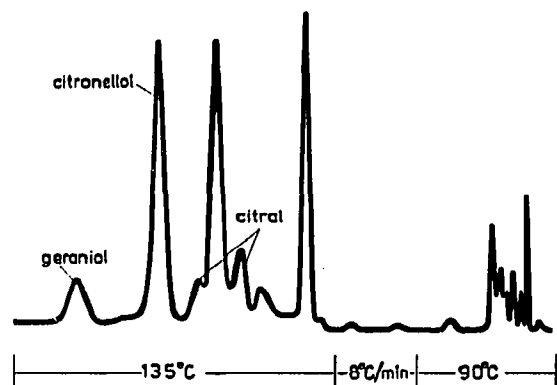


Fig. 8. Product of oxidation with K₂Cr₂O₇ and sulphuric acid. For conditions, see the legend to Fig. 2.

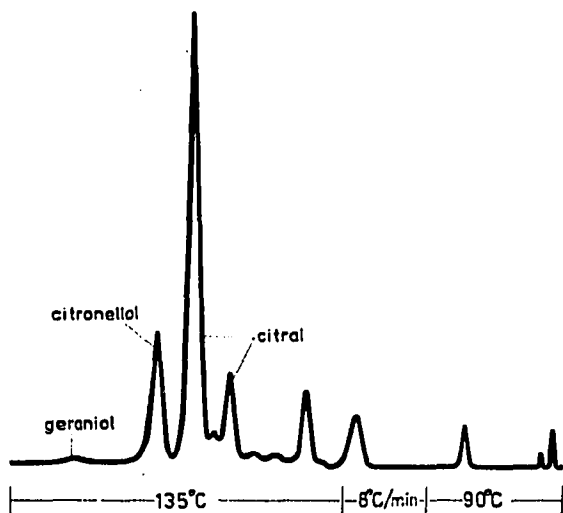


Fig. 9. Product of oxidation with $K_2Cr_2O_7$ and glacial acetic acid. For conditions, see the legend to Fig. 2.

meters of the various processes are shown in Table I. Yield and conversion data, calculated on the basis of the GC analysis of the raw products, relative to the geraniol content of the raw material, are also given.

Without going into technological details, we would like to present here only the results which seem to be the best, each illustrated by a chromatogram. Oxidation with MnO_2 (Fig. 6) is easy to perform, but proceeds only with a high excess of oxidant, and takes a very long time. Good results were obtained with a pyridine- CrO_3 complex (Fig. 7), but the process involves a rather high fire hazard, great volumes must be handled and large quantities of substances are used up.

Oxidation with $K_2Cr_2O_7$ can be realized in different ways⁷. The reaction mix-

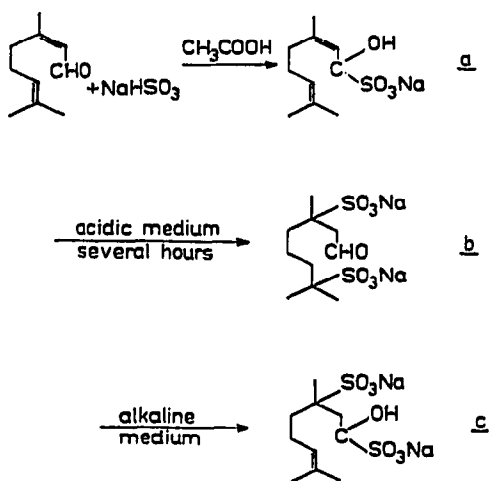


Fig. 10. Possible ways of $NaHSO_3$ addition by citral.

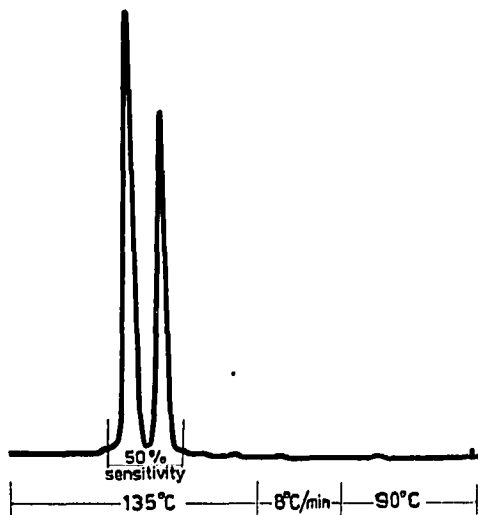


Fig. 11. Citral prepared and purified in-house. For conditions, see the legend to Fig. 2.

ture can be acidified with sulphuric acid or glacial acetic acid. When sulphuric acid is used (whether in aqueous or in benzene solution), a substantial part of the geraniol remains unconverted and a relatively small amount of citral and several other by-products are formed (Fig. 8). Reactions in the solvent glacial acetic acid–benzene were found to be considerably more advantageous (Fig. 9).

On the basis of an economic comparison of the reactions mentioned, oxidation with $K_2Cr_2O_7$ and glacial acetic acid was chosen. The optimal parameters of the reaction, the effect of a deviation from these and the mode of processing were determined on the basis of the quantitative GC analysis of the products.

As mentioned already in Experimental and results, only about half of the raw material obtained for the experiments was geraniol, while the other half was unusable or

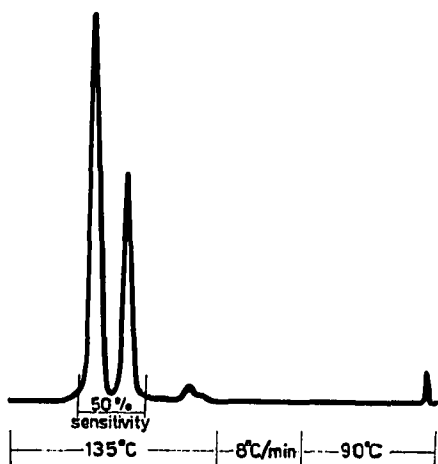


Fig. 12. Citral from the firm Givaudan. For conditions, see the legend to Fig. 2.

even detrimental from the aspect of the required target product. This made purification of raw product necessary, in order that citral should meet the quality specifications. The required purity cannot be attained by rectification, so that a method had to be found which is selective for citral and also makes possible its separation from citronellal. Addition of NaHSO_3 to aldehydes proved to be suitable for this purpose. From the adduct, the aldehyde can be easily recovered. Depending on the circumstances, this reaction results in different products^{8,9} (Fig. 10). In alkaline medium, between 5° and 10°, a disulphonate soluble in water is formed, from which citral can be liberated (from the disulphonate formed in acidic medium (b) citral cannot be liberated).

In the purification step, 80–85% of the citral contained in the raw product is recovered. The chromatogram of such a purified substance is shown in Fig. 11. For comparison, the chromatogram of a citral of suitable quality, a product of Givaudan (Geneva, Switzerland) is shown (Fig. 12).

CONCLUSION

The process developed by us gives substantially higher yields and selectivity than reported so far in the literature. The product must be purified, primarily on account of contaminants of the raw material. By purification, a product containing more than 96% of citral can be prepared.

On the basis of our results, the technological design for a plant of 6 tons' annual capacity has been prepared. When the plant has been built, GC will play a role in process control.

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