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FORMATION OF ACETALS IN RUM : A KINETIC STUDY

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SUMMARY

From time to time in literature, references on the importance of acetals as aroma compounds in rum and other alcoholic beverages are to be found. Most of these references are of qualitative nature, rarely concentrations are mentioned. For that reason, we developed a specific and sensitive photometrical method of determination and compared it with gas chromatographic data.

As the formation of acetals is an equilibrium reaction, one should think to find the aldehyde acetal contents in a distinctive relation to the percentage of alcohol in rum. In contrast to this hypothesis, again and again we found deviations from calculated data.

Therefore, we were forced to gain some more information about the kinetics of that reaction. It could be shown that the velocity of the formation of acetals depends mainly on the formation of semi-acetals which turn into acetals with high speed.

Using the known equilibrium constants of several acetals, we calculated their contents in rum and determined their sensoric threshold. Due to these results, we are inclined to point out that many of the acetals are without any importance for the aroma of rum and a great deal of them reported in literature are artificial products.

Any one dealing with the aroma of spirits, will often find the information in the pertinent, even old literature, that the group of acetals is of prominent importance for the flavour. Apart from other components, more than fifty different acetals have been identified among the aroma components of rum. The acetals can be well identified by gas chromatography. But they are very unstable and special precautionary steps must be taken if at least partial destruction during the GC separation shall be avoided. For this reason, chemical methods appear more suitable for quantitative determination.

A method utilizing the reaction of aldehydes with bisulfite has been published by GUYMON and CROWELL (1963). Such titration methods reach a sensitivity of approximatively 10-20 p.p.m. and unfortunately are too unspecific, because they cover all aldehydes. Therefore we developed a photometric method of determination,

based on the reaction of sodium nitroprusside and piperidine in alkaline environment. We investigated rums and other spirits by means of this method. This resulted in acetal contents, which we primarily found to be unexplainable. This shall be explained by the table 1.

TABLE I

Content of acetal in rum

	Alcohol Vol (%)	pH	Aldehyde (µg/l)		Combined (%)
			Total	Alcohol combined	
Martinique rum 3 years old	45	5.4	72	12	17
West-Indies rum unaged	45	6.2	89	34	36
Jamaica rum about 2 years old	75	5.2	275	129	47
Jamaica rum, blended unaged	45	5.3	27	9	32

According to the law of mass action, the proportion of combined aldehyde should be in a fixed relation with respect to the alcohol content. From the ascertained values, I selected 3 rums of 45 p. 100 of alcohol. The acetal contents range between 17 and 36 p. 100. Only the Jamaican rum of 75 p. 100 has a higher acetal content, viz. 47 p. 100. The blend produced therefrom, however, has 32 p. 100 of acetal only.

The pH too is not suitable for clarifying the conditions. The Martinique rum and the Jamaican rum have similar pHs, while the acetal proportions are completely different (17 or 47 p. 100). The West Indies rum has the highest pH, while the p. 100 ranges in the medium field.

This brief discussion should explain why we thought it to be advisable to deal with the equilibrium situation of acetalization and with the kinetics of reaction.

PEYNAUD and MAURIE (1938) published equilibrium data of acetal and aldehyde as a function of the alcohol contents already in 1938. They are in good agreement with our results.

The abscissa of the figure 1 shows the alcohol contents in p. 100 by volume while the ordinate shows the proportion of combined aldehyde from the total aldehyde content in p. 100. The circles indicate the acetal proportions determined. Calculation of the equilibrium constant for a medium alcohol content of 50 p. 100 results in a value of 0.111. These calculated values take the path indicated by the full-line curve in the figure.

The test values are below the law of mass action for high alcohol contents and are higher for lower contents. The assumption that the adjustment of equilibrium has not been entirely achieved in the experiments could be rejected by our own tests. We observed that a relatively good conformity with the law of mass action occurred when the square was omitted with the alcohol concentration. This however would mean that exclusively semi-acetal would be formed. This would be a complete

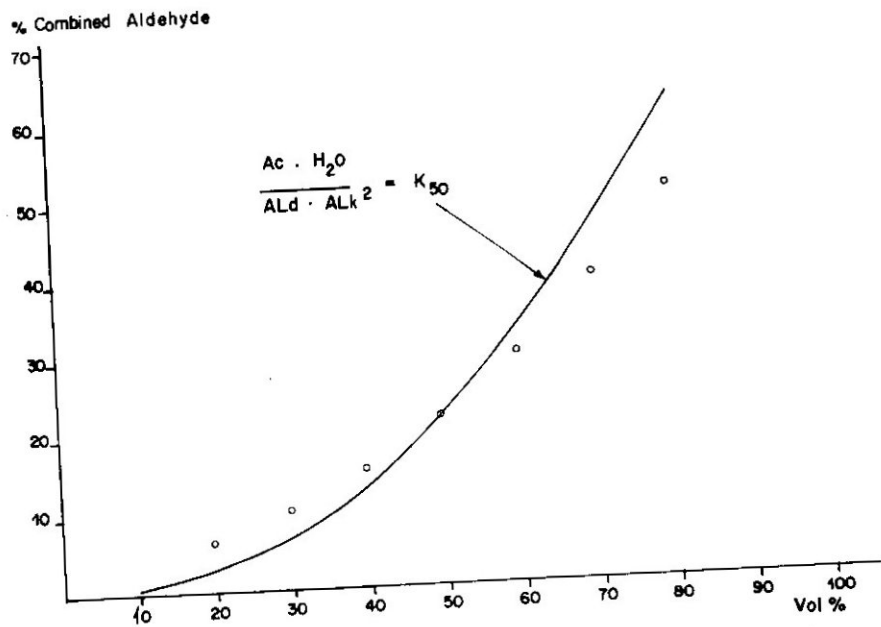


FIG. 1. Proportion of combined aldehyde at different concentration of alcohol

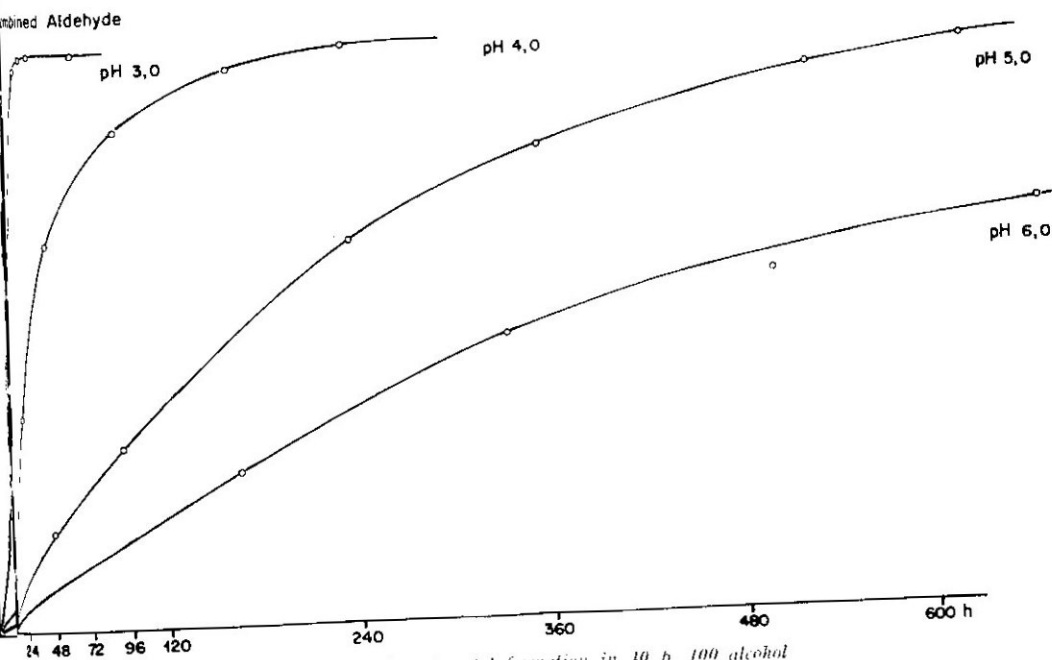
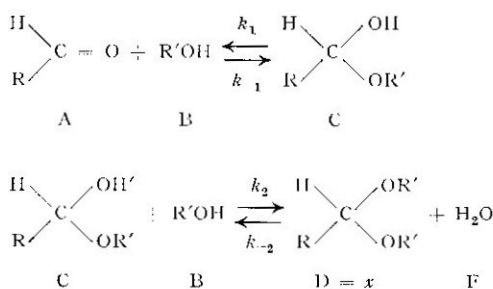


FIG. 2. Kinetics of acetal formation in 10 p. 100 alcohol

contradiction with respect to the hitherto results: so far only full acetals were found in alcoholic beverages. In this situation we made tests with respect to the time sequence of acetal formation as a function of pH so as to analyse the kinetics of reaction. The tests were principally made in 40 p. 100 alcohol-water mixtures, and the aldehyde quantity amounted to approx. 1 mol per litre (fig. 2). The abscissa shows the time in hours. The ordinate indicates the p. 100 proportion of the combined aldehyde from the total aldehyde contents. Independently from the pH, the acetal content asymptotically heads for a final value of 14.9 p. 100. However, the speed at which this value is attained widely depends upon the concentration of hydrogen ions. At pH 3.0, it takes approximately 1.5 days, at pH 2.0 it takes 2.5 hours only, so that the path can not be represented in this illustration. At pH 4.0, the reaction takes approximately 12 days, at pH 5.0 it takes one month and at pH 6.0 it takes approximately 3 months.

According to the generally applied formulation, first semiacetal is formed from aldehyde and alcohol and then the full acetal is formed from said semi-acetal with elimination of 1 mol of water (table 2).

TABLE 2

Reactions of acetals formation

$$\frac{dx}{dt} = k_1 B(A - x) - k_{-2} Fx$$

$$\text{with } \frac{dx}{dt} = 0$$

$$\frac{k_1}{k_{-2}} = \frac{x \cdot F}{(A - x) \cdot B} = K$$

As the semi-acetal cannot be analysed, it must be concluded that the reaction velocity constant k_1 is relatively small as compared with k_2 so that the semi-acetal formed, immediately will be consumed by further reaction to full acetal, so k_1 is the velocity limiting constant for formation of the full acetal. On the other hand, in the hydrolysis of the full acetal there must be k_{-2} much smaller than k_{-1} so that in this

case k_{-2} is the constant limiting the decomposition and the formed semi-acetal will be converted into alcohol and aldehyde by rapid decomposition.

When the concentrations of the reacting materials are designated by the capital letters A B ... and the quantity converted is called x , D equal x will occur under the condition that no measurable quantities of semi-acetal shall be produced. This relatively simple differential equation results from the general rules of kinetics. In the equation, the conversion of alcohol and water need not be considered, because x is so small as compared with B and F under test conditions that it can be neglected.

So we get for equilibrium condition this term :

$$\frac{k_1}{k_{-2}} = \frac{x \cdot F}{(A - x)B} \quad \text{with} \quad \frac{k_1}{k_{-2}} = K.$$

It can be seen that the alcohol B appears without square in the law of mass action, which was already indicated earlier. Thus this can be explained by the fact that only the first alcohol molecule converted into the semi-acetal is important for the equilibrium in view of the small size of k_1 .

For showing that this kinetic make-up is in line with the test results, the equation was integrated after substitution with :

$$m = \frac{K_1 B \cdot A}{k_1 B + k_{-2} F}.$$

After separation of the variable, the formula is obtained :

$$t = \frac{1}{k_1 B + k_{-2} F} \quad l_n \frac{m}{m - x}.$$

This is the equation of a line.

When drawing this term $l_n \frac{m}{m - x}$ against t in a system of coordinates, the test values should result in a line of the inclination $\frac{1}{k_1 B + k_{-2} F}$ so that the constant of reaction velocity can be ascertained therefrom.

In addition it should be noted that the difficulty that m contains the unknown RV constant can be overcome by developing the reciprocal value of m in such a manner that the ratio of the RV constant will appear therein. This can be substituted by K.

The figure 3 shows the test results previously discussed on the basis of curves. In this type of illustration, actually straight lines result so that it will be justified to indicate : the assumption that only traces of semi-acetals are generated is correct.

In this case, too, the dependence of the RV upon the pH can be seen well from the inclination of the straight line.

After description of the influence of the pH, it shall now be discussed at which position the H ions influence the reaction. It can be seen from the tests that ions are necessary for forming the diethyl acetal. It is the general opinion that acid catalysts are not necessary for forming semi-acetals. Thus, it should be possible to produce analysable quantities of semi-acetal by mixing equimolar quantities of absolute alcohol and aldehyde because this will exclude the further reaction to full acetals.

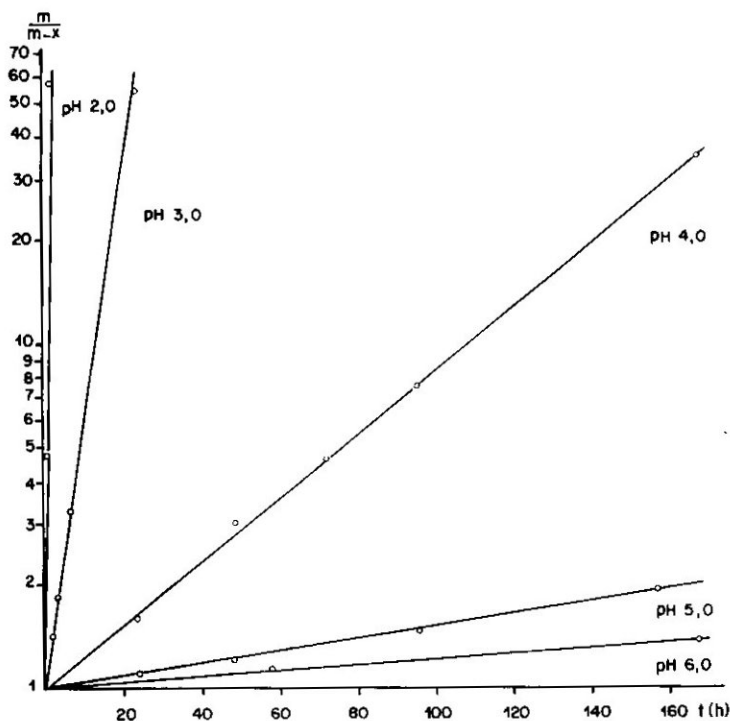


FIG. 3. Adjustment of the data to the theory of acetals formation

The first chromatogram shows the mixture of aldehyde and alcohol containing a trace of water which is not converted even after 24 hours. Beside this is indicated the 20 mm gas-chromatogram after one drop of *n*/10 hydrochloric acid was added, to 50 ml of mixture. Diethyl acetal and a new peak were generated, which has never been shown, as far as I know. Only the semi-acetal can be concerned and we made an identification by mass-spectrometry. The semi- and full-acetal peak increased after three hours from addition of acid. Fourteen hours later, the semi-acetal only is a relatively small peak and one day later it disappears completely. It can be concluded from this attitude that H⁺ ions are necessary already for forming semi-acetal. As it is also known that those aldehydes, showing a tendency towards hydrate formation, can be acetalized easily, we think that the reaction scheme of table 3 is obvious.

Hydrate protonized complex explains why semi-acetal cannot be found in spirits.

Reactions in conjunction with ionisation generally can be assumed to be rapid so that the velocity will be limited by the mentioned constants k_1 and k_{-2} .

Now let us revert to the samples of table 1 containing unexplainable acetal contents.

The first four columns of table 4 indicate previous shown contents without any modification. The fifth column shows the values calculated in line with the law of mass action (without the square with the alcohol).

TABLE 3

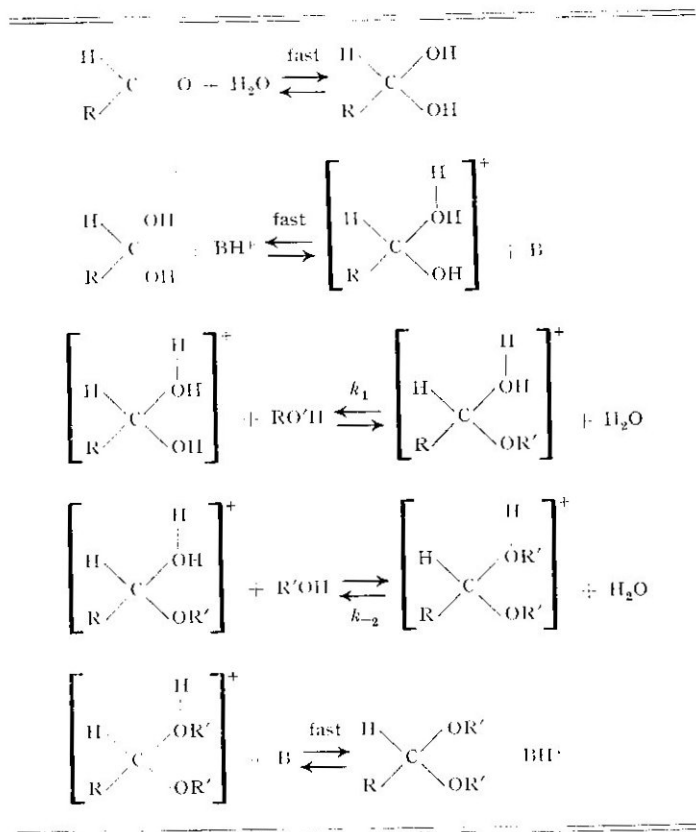
Reactions of acetals formation involving hydrate protonised aldehyde

TABLE 4

Calculated content of acetals in rum

	Aldehyde mg/l alcohol				
	Vol (%)	pH	Total	Combined found	Calculated
Martinique rum 3 years old	55	5.4	72	12	13
West-Indies rum unblended	55	6.2	89	34	16
Jamaica rum about 2 years old	75	4.2	275	129	123
Jamaica rum, blended unblended	55	5.3	27	9	5

First of all, let us consider the two stored rums, *i.e.* the Martinique and Jamaican rum. The balance was adjusted relatively exactly. On the other hand, the two non-stored rums show approximatively twice the quantity of acetal as compared with the calculation. This can be explained by the fact that the Martinique rum imported to Germany had a high alcohol percentage and had no longer been stored after reduction of the percentage to 45 p. 100 by volume. As has been shown, the balance adjustment at pH 6.2 takes more than half a year. The same applies to the Jamaican rum blend.

A further factor can be added: we could ascertain that materials extracted from wood have a strong retarding effect upon the speed of reaction. The effective principle probably is due to polyphenolic OH groups. Experiments with alcohol-water mixtures with addition of tannine or gallic acid showed such retarding effect.

Principally one can say: subject to sufficient time of storage, there will be the balance between aldehyde, alcohol, water and acetal provided that the pH will not exceed 7-8. The time required for this process moreover depends on the other materials contained.

Finally, I would like to discuss other acetals apart from acetaldehyde-diethyl acetal. The literature dealing with identification of certain acetals is very small. This is in some contradiction to the importance which is attributed to this group of materials with respect to the flavour of rum and other spirits in general. In any event, there are some reports by which such acetals in rum have been determined by the gas-chromatographic methods. One publication is by MAARSE and ten NOEVER de BRAUW (1966), which indicates 16 acetals among a total of 100 substances partially identified in rum aroma. In another publication, LIEBIG, KOENIG and BAYER (1970) identified more than 200 compounds and 45 acetals. These are acetals of acetaldehyde, propionaldehyde, butyr- and *i*-valeraldehyde with ethanol, propanol, *i*- and *n*-butanol as well as amyl alcohols from fermentation. The major proportion is in the form of mixtures, *i.e.* they contain various alcohol components.

To provide an image on the importance of these acetals, we produced some of them, we ascertained the sensory thresholds and we checked the literature to find equilibrium constants.

In the table 5 we have listed some acetals, about which, on the one hand,

TABLE 5

Equilibrium constant of acetals

	K	Aldehyde (mg/l)	
		Total	Combined
1,1-diäthoxy-äthan	0,9	100	15
1,1-diäthoxy-propan	1,0	0,8	0,16
1,1-diäthoxy- <i>i</i> butan	0,57	12	1,3
1,1-diäthoxy- <i>i</i> -pentan	0,63	10	1,2
1,1-diisopentoxy-äthan	10,9	100	0,35

equilibrium constants were found and about the aldehydes of which quantitative information was found in the literature. The highest quantities known to us are indicated in column 2. In column 3, you find the calculated acetal quantities occurring in equilibrium condition. Contents range between 0.16 and 1.3 mg/litre for the ethanol-containing acetals—apart from acetaldehydediethylacetal. As an example for « non-ethanol » acetals, acetaldehyde di-isoamyl acetal was chosen because, apart from ethanol, amyl-alcohol is the alcohol compound of which the largest quantities occur and this acetal in addition has the highest equilibrium constant ever determined. Nevertheless, only 0.35 p. 100 of the aldehyde are in the form of acetal. The reason for this is that the amyl alcohol in spirits is facing a water content higher by a factor of 1 000, which displaces the balance nearly total towards the free aldehyde.

In addition, let us consider in table 6 some sensory threshold values of acetals and let us assume the values determined in water for comparison purposes, and we shall see that practically only acetaldehyd di-ethyl acetal attains a concentration ranging above the threshold value. The higher acetals have thresholds which are above the possible concentrations by the factor of 30 — particularly with respect to the acetaldehyd di-isoamyl acetal. Only for exemplification purposes, additionally 3 thresholds in 40 p. 100 alcohol are indicated. They are higher by 10-80 times! So we come to the conclusion that most of the hitherto identified acetals are without importance for the flavour of rum.

TABLE 6
Sensory threshold of acetals

	Acetal in water (mg/l)	Acetal in alcohol (mg/l) 40 Vol (‰)	Aldehyde in water (mg/l)
1,1-diäthoxy-äthan	0,1	8	0,2
1,1-diäthoxy-propan	0,4		0,2
1,1-diäthoxy-butan	1		0,05
1,1-diäthoxy-isobutan	2	80	0,1
1,1-diäthoxy-pentan	2		0,2
1,1-diäthoxy-isopentan	3		0,2
1,1-diäthoxy-hexan	4		0,05
1,1-diisopentoxy-äthan	8	80	0,2

However, when the concentrations of higher acetals are so small — how could the authors determine and identify the substances by gas chromatography? Considering the working methods, these publications again and again indicate that extracts were produced before the gas-chromatographic separation. Such extracts, however, have to be dried prior to distillation of the solvent. This means that the hydrolytic influence of water on the equilibrium is eliminated in the extract. Furthermore, the relation between higher alcohols and aldehydes is widely displaced and as such extracts mostly react strongly acid, the reaction velocity of acetalization is considerable. Therefore, I am very sceptical with respect to those analyses and I think that these acetals are artefacts to a wide extent.

RÉSUMÉ

FORMATION D'ACÉTALS DANS LE RHUM : ÉTUDE CINÉTIQUE

On trouve de temps en temps dans la littérature des références relatives à l'importance des acétals en tant que composés aromatiques du rhum et d'autres boissons alcoolisées. La plupart de ces références concernent des études qualitatives, les concentrations sont rarement mentionnées. C'est pourquoi nous avons mis au point une méthode de détermination par photométrie spécifique et sensible et comparé les résultats obtenus avec ceux livrés par la chromatographie en phase gazeuse.

Comme la formation d'acétals est une réaction d'équilibre, on pourrait croire que la teneur en acétaldéhyde présente une relation particulière avec le pourcentage d'alcool dans le rhum. Contrairement à cette hypothèse nous avons toujours trouvé des déviations par rapport aux données calculées.

Nous avons donc été amenés à nous renseigner un peu plus sur la cinétique de cette réaction. Il a été démontré que la vitesse de formation des acétals est essentiellement fonction de la formation des semi-acétals qui se transforment très vite en acétals.

En se fondant sur la connaissance des constantes d'équilibre de plusieurs acétals, nous avons calculé leurs teneurs dans le rhum et déterminé leur seuil gustatif. En fonction de ces résultats, nous sommes tentés de conclure que bien des acétals n'ont aucune importance pour l'arôme du rhum et qu'un grand nombre d'entre eux, cités dans la littérature, sont des produits artificiels.

RESUMEN

LA FORMACIÓN DE ACETALES EN EL RON : ESTUDIO CINÉTICO

Se encuentra de cuando en cuando, en la literatura especializada, diversas referencias relativas a la importancia de los acetales, a título de componentes aromáticos del ron y otras bebidas alcoholizadas. La mayor parte de estas referencias se refieren a estudios cualitativos, ya que las concentraciones son mencionadas en contados casos. Por este motivo hemos puesto a punto un método de determinación por fotometría específica y sensible, y comparado los resultados obtenidos con aquellos proporcionados por la cromatografía en fase gaseosa.

Dado que la formación de acetatos es una formación de equilibrio, podría creerse que el contenido de acetaldehído presenta una relación particular con el porcentaje de alcohol en el ron. Contrariamente a esta hipótesis, hemos encontrado siempre desviaciones en relación con los datos calculados.

Nos hemos visto conducidos a informarnos con mayor precisión acerca de la cinética de esta reacción. Se ha demostrado que la velocidad de formación de los acetales depende principalmente de la formación de los semiacetales, que, con suma rapidez, se transforman en acetales.

Fundándose en el conocimiento de las constantes de equilibrio de varios acetales, hemos calculado sus contenidos en el ron y determinado su umbral gustativo. En función de estos resultados, tenemos tendencia a concluir que numerosos acetales no presentan ninguna importancia para el aroma del ron y que un gran número de los mismos, mencionados en la literatura especializada, no son otra cosa sino productos artificiales.

RIASSUNTO

FORMAZIONE DI ACETALI NEL RUM : STUDIO CINETICO

Di tanto in tanto si trovano nella letteratura delle considerazioni sull'importanza degli acetali quali composti aromatici del rum e di altre bevande alcoliche. La maggior parte di queste considerazioni riguardano degli studi qualitativi giacchè le concentrazioni sono raramente indi-

cate. E' per questo motivo che abbiamo messo a punto un metodo di determinazione mediante fotometria specifica e sensibile e abbiamo confrontato i risultati ottenuti con quelli dati dalla gas-cromatografia.

Poichè la formazione di acetali è una reazione d'equilibrio, si potrebbe credere che il tenore di acetaldeide presenta una relazione particolare con la percentuale di alcool nel rum. Contrariamente a questa ipotesi, abbiamo sempre trovato delle differenze rispetto ai dati calcolati.

E' cos' dunque che siamo stati portati ad approfondire la cinetica di questa reazione. E' stato dimostrato che la velocità di formazione degli acetali dipende essenzialmente dalla formazione di semiacetali che si trasformano in brevissimo tempo in acetali.

Basandoci sulla conoscenza delle costanti di equilibrio di diversi acetali, abbiamo calcolato i loro tenori nel rum e determinato la loro soglia gustativa. Alla luce di questi risultati, siamo tentati di concludere che molti acetali non hanno alcuna importanza per quanto riguarda l'aroma del rum e che un gran numero di essi, citati nella letteratura, sono dei prodotti artificiali.

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