Precision Constant Temperature Bath and Circulating System.

REFERENCES

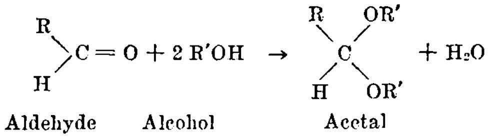
1. Haller, A. Compt. rend. *143*, 803 (1906).
2. Elsdon, G. D. Analyst *38*, 8 (1913).
3. Lepkovsky, S. L., Feskov, G. V., and Evans, H. M. J. Am. Chem. Soc. *58*, 978 (1936).
4. Longenecker, H. E. J. Biol. Chem. *130*, 167 (1939).
5. Althouse, P. M. A Thesis, The Penna. State College (1940).
6. Armstrong, E. F., Allan, J., and Moore, C. W. J. Soc. Chem. Ind. *44*, 63T (1925).
7. Oyler, J. R. A Thesis, The Penna. State College (1940).
8. Wyman, F. W., and Barkenbus, C. Ind. Eng. Chem., Anal. Ed. *12*, 658 (1940).
9. Althouse, P. M. A Thesis, The Penna. State College (1943).
10. Mattil, K. F., and Longenecker, H. E. Oil and Soap *21*, 16 (1944).
11. Bauer, S. T. Oil and Soap *23*, 1 (1946).
12. Tildon, L. W., and Taylor, J. K. J. Res. of the N.B.S. *20*, 449 (1938).

Ketals

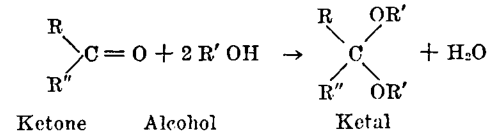
R. W. MONCRIEFF
563 Scott Hall Road, Leeds 7, England

Structure

KETALS are ketone acetals. Just as an acetal is formed by the addition of an aldehyde to an alcohol, so is a ketal formed by adding a ketone to an alcohol.



$$\mathrm{R(H)C{=}O + 2\,R'OH \rightarrow R(H)C(OR')_2 + H_2O}$$



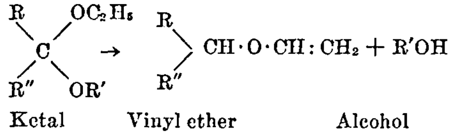
$$\mathrm{R(R'')C{=}O + 2\,R'OH \rightarrow R(R'')C(OR')_2 + H_2O}$$

It will be seen that the acetals constitute a special form of the ketals in which one of the substituent groups is a hydrogen atom. The acetals are important in perfumery and have already been described in considerable detail in Soap Perfumery & Cosmetics, June and July, 1945. One of the main reasons for the importance of the acetals is that they provide a means of using the valuable aldehydic perfume constituents without their attendant defects of liability to oxidation and decomposition. In a similar way some of the ketals have found use in perfumery, but they have not yet attained anything approaching the importance of acetals and I think the reason for this is partly that the ketones as a class are so much more stable than the aldehydes. Whereas the danger of the aldehydes decomposing, especially on exposure to the atmosphere, is very great, the ketones are reasonably stable. Consequently whilst some sort of protection is necessary for the aldehydes, and this protection is very conveniently afforded by acetal formation, yet the ketones are stable enough as a rule not to require protection and as a result the development of the ketals has lagged behind that of the acetals.

There are, however, special cases where the protection of the ketone is desirable, and there are other cases where the conversion of a ketone to a ketal is accompanied by a change of odour, which may be desirable, and in some cases, indeed, the ketal may have a *nuance* not otherwise obtainable.

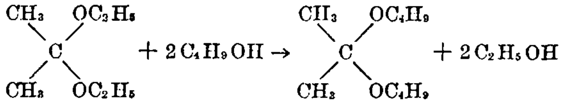
Properties

As a general rule ketals are colourless liquids with characteristic odours. Acetone dimethyl acetal $(CH_3)_2C(OCH_3)_2$ boils at 83°C. and the corresponding ketal from acetone and ethyl alcohol which is acetone diethyl acetal $(CH_3)_2C(OC_2H_5)_2$ boils at 114°C. They lose alcohol when heated and form vinyl ethers



$$\mathrm{R(R'')C(OC_2H_5)(OR') \rightarrow R(R'')CH{\cdot}O{\cdot}CH{:}CH_2 + R'OH}$$

When ketals of the lower alcohols are boiled with alcohols of greater molecular weight exchange of alkyl groups takes place

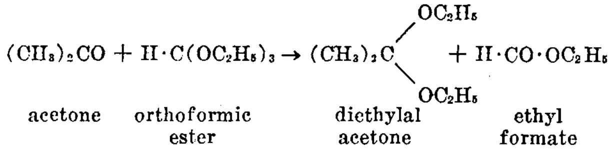


$$\mathrm{(CH_3)_2C(OC_2H_5)_2 + 2\,C_4H_9OH \rightarrow (CH_3)_2C(OC_4H_9)_2 + 2\,C_2H_5OH}$$

Monomeric ketals will react with polyvinyl alcohol in the presence of a catalyst such as sulphuric acid and in a substantially anhydrous solvent such as methanol to give polyvinyl ketals (1).

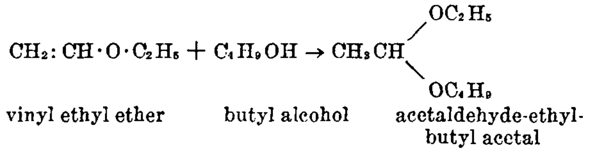
Preparation

1. Ketals may be prepared by reacting ketones with orthoformic esters in the presence of alcohols. Small quantities of anhydrous acids are necessary to promote the reaction



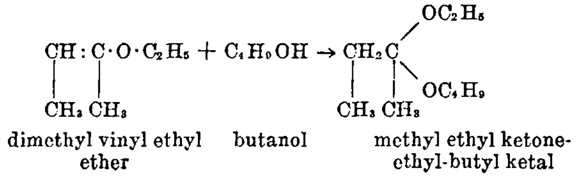
$$\mathrm{(CH_3)_2CO + H{\cdot}C(OC_2H_5)_3 \rightarrow (CH_3)_2C(OC_2H_5)_2 + H{\cdot}CO{\cdot}OC_2H_5}$$

2. Although British Patent 352,474 (2) is concerned primarily with the formation of acetals by the addition of alcohols to vinyl ethers, the possibility is envisaged in the specification of preparing ketals by the addition of alcohols to substituted vinyl ethers. Whilst vinyl ethyl ether and butanol react to give an acetal known as acetaldehyde-ethyl-normal-butyl acetal



$$\mathrm{CH_2{:}CH{\cdot}O{\cdot}C_2H_5 + C_4H_9OH \rightarrow CH_3CH(OC_2H_5)(OC_4H_9)}$$

dimethyl vinyl ethyl ether would react with butanol to give a ketal



$$\mathrm{CH(CH_3){:}C(CH_3){\cdot}O{\cdot}C_2H_5 + C_4H_9OH \rightarrow CH_2(CH_3)C(CH_3)(OC_2H_5)(OC_4H_9)}$$

It is possible that this method may prove of practical importance in the future. In practice a small quantity of concentrated sulphuric acid is added to the alcohol and the vinyl ether is then allowed to flow in while stirring, the temperature being kept below 30°C. When the conversion is completed, a little potassium carbonate is added, the liquid is decanted off and distilled. In the case of the acetals, yields vary from 50 to 85 per cent. An accelerator less active than sulphuric acid may, if desired, be used; glacial acetic acid is suggested but in this case a higher temperature and pressure are required to stimulate the reaction. The preparation of vinyl ethers which are used in this process is described in British Patent 332,605 from the sodium alcoholate and vinyl chloride.

3. A third method of preparing ketals is by reacting acetylenes with alcohols in the presence of mercuric oxide or boron trifluoride as a catalyst. In some cases trichloracetic acid may also be used as a catalyst.

Inasmuch as a substituted acetylene is a dehydration product of a ketone, the third method is basically the same as the first. Thus

$$CH_3CO\ CH_3 - H_2O \rightarrow CH_3C{:}CH$$

acetone methyl acetylene

4. Substances which are presumably ketals are made by condensing a cyclic ketone with a polyhydric alcohol. For example dextrose may be condensed with cyclohexanone or cane sugar with methyl cyclohexanone as described in British Patent 385,139 (3).

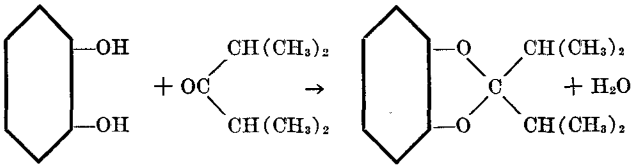
Application in Perfumery

Until recently ketals have not been employed in perfumery but certain dihydric alcohols and ketones have been found to give ketals suitable for use in perfumes. Not all of these do, for the condensation product from pyrocatechol and acetone has been described (4) as having an odour resembling that of the aromatic hydrocarbons. But Weissenborn (5) has shown that when the ketone residue contains from 6 to 9 carbon atoms the condensation products with pyrocatechol are attractive odorants. If the ketone is too simple, i.e. if it contains fewer than 6 carbon atoms, the pleasant odoriferous characteristics do not develop in the condensation product with pyrocatechol and if, on the other hand, the ketone possesses more than 9 carbon atoms, the condensation product is of such a high molecular weight that it is practically inodorous. To comply with this specification of from 6 to 9 carbon atoms limits the choice of ketones in practice to the following:

(1)	Dipropyl ketone	$C_3H_7\cdot CO\cdot C_3H_7$
(2)	Diisopropyl ketone	$(CH_3)_2CH\cdot CO\cdot CH(CH_3)_2$
(3)	Dibutyl ketone	$C_4H_9CO\cdot C_4H_9$
(4)	Diisobutyl ketone	$(CH_3)_2CHCH_2CO\cdot CH_2CH(CH_3)_2$
(5)	Methyl butyl ketone	$CH_3COC_4H_9$
(6)	Methyl amyl ketone	$CH_3COC_5H_{11}$

The ketals from the symmetrical ketones (1), (2), (3), and (4) resemble, in odour, natural geranium or rose oil, whereas ketals from the unsymmetrical ketones (5) and (6) are suitable for compounding jasmin mixtures. It may be noted that the ketal from methyl amyl ketone, which is the best for jasmine perfumes, has in common with jasmin aldehyde (α-amyl cinnamic aldehyde) the possession of an amyl group.

The ketal from pyrocatechol and diisopropyl ketone



pyrocatechol diisopropyl ketone diisopropyl pyrocatechol ketal

is particularly suitable for incorporation in geranium or rose perfumes. The following recipes illustrate its use:

ARTIFICIAL GERANIUM OIL

	Parts
Diisopropyl pyrocatechol ketal	25
Phenyl ethyl alcohol	15
Geraniol	41
Diphenyl ether	4
Citronellol R	15

ROSE

	Parts
Diisopropyl pyrocatechol ketal	6
Phenyl ethyl alcohol	30
Geraniol	25
Citronellol R	22
Nerol	5
Methyl ionone	4
Phenyl acetic acid (10%)	4
Phenyl acetaldehyde (10%)	2
Nonyl aldehyde (10%)	2

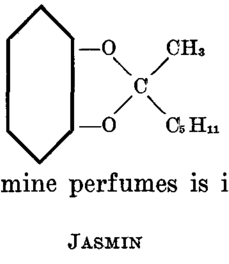
The ketal from pyrocatechol and diisobutyl ketone, which is a 9 carbon atom ketone, is particularly suitable for honey perfumes as the following formulation shows.

HONEY

	Parts
Diisobutyl pyrocatechol ketal	75
Genuine rose oil (1%)	15
Methyl ionone	6
Phenyl acetic acid (10%)	3
Acetophenone	1

The high percentage (75) of the ketal in this formulation is noteworthy.

The unsymmetrical ketal from methyl amyl ketone and pyrocatechol has the formula

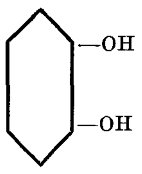


and its use in jasmine perfumes is illustrated in the following formula

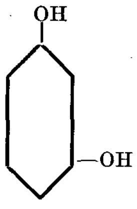
JASMIN

	Parts
Methyl amyl pyrocatechol ketal	6
Jasmin aldehyde	20
Benzyl acetate	30
Linalool	10
Benzyl salicylate	10
Cinnamic alcohol	3
Hydroxycitronellal	6
Linalyl acetate	3
Indol (10%)	5
Phenyl ethyl alcohol	2
β-Acetonaphthone	5

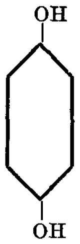
It may well be that such compounds will prove of considerable value to the perfumer. In particular, research would appear to be well worth-while to investigate the odours of ketals made from other dihydric phenols, resorcinol and hydroquinone, and also from orcinol



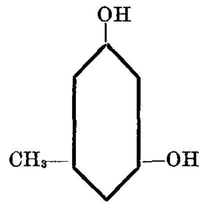
pyrocatechol



resorcinol

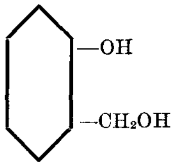


hydroquinone



orcinol

It is unlikely that the trihydric phenols such as phloroglucinol would give ketals similar in configuration and complexity to those from pyrocatechol but it would be a simple and interesting experiment to condense phloroglucinol with diisopropyl ketone and see what the odoriferous properties of the product offer. Saligenin



which is at one and the same time a phenol and an alcohol is another body which, condensed with diisopropyl ketone, might offer unusual possibilities. It would indeed seem that in the ketals, the perfumers are confronted with a field which is wide, probably fertile and almost completely unexplored.

REFERENCES

1. U. S. Patent 2,341,306 (to du Pont de Nemours & Co.).
2. British Patent 352,474, I. G. Farbenindustrie A. G. (1931).
3. British Patent 385,139, I. G. Farbenindustrie A. G. (1932).
4. *Rec. Trav. Chim. Pays. Bas.*, 1935, p. 998.
5. A. Weissenborn. U. S. Patent 2,169,984 (to Winthrop Chemical Co. Inc.) (1939).

The Flavor Problem of Soybean Oil.

I. A Test of the Water Washing-Citric Acid Refining Technique

HERBERT J. DUTTON, HELEN A. MOSER, and JOHN C. COWAN
Northern Regional Research Laboratory,[1] Peoria, Illinois

DURING the past 12 years soybean oil production has risen from an inconspicuous place among edible and industrial oils to one of major importance and from less than 50 million pounds per year to 1,300 million pounds per year. The scarcity of other food oils during the late war was responsible for much of this expansion. However, edible soybean oil does not have the flavor stability of the oils it has replaced. It is the opinion in the edible oil industry that unless the flavor stability is substantially improved, considerable contraction in production, processing, and consumption of soybeans may result. It has been pointed out that the solution of this problem will benefit agriculture, industry, and the public (1, 2).

Studies of the relationships of phospholipids to flavor stability were initially undertaken at the Northern Regional Research Laboratory because recent investigations had indicated that phospholipids were responsible for flavor instability of dehydrated eggs (3). Additional impetus and direction were given in the reports of Warren H. Goss of this Laboratory who, on behalf of the Technical Industrial Intelligence Committee, recently conducted an investigation of the German oilseed industry (4, 5). These accounts stated that the German oil refiners consider "lecithin" responsible for flavor instability. "Lecithin" was reportedly removed by two successive water washings of freshly extracted soybean oil prior to alkali refining. Traces of lecithin which remained were thought to be inactivated by the introduction of citric acid (0.01%) during deodorization.

In the laboratory-scale experiments to be described, a crude, degummed, extracted soybean oil was given an additional water washing. This sample and the original sample were given identical refining and deodorization processing with the exception that 0.01% citric acid was added to the washed sample during deodorization. The chemical and organoleptic evaluations of the samples during storage indicate that washing, followed by the prescribed treatment with citric acid, effects a significant increase in flavor stability.

Materials and Methods

The crude soybean oil on which the refining experiments were conducted was extracted by a plant in which the equipment is identical with that used in a number of German oil mills. During production of the oil operators of the plant exercised care to avoid heating the oil excessively during any step of the process. However, there is evidence that any extracted oil which had been stripped of solvent at comparatively low temperatures would have been satisfactory for this experiment. "Lecithin" was removed according to normal degumming practice by passing the oil, containing a small amount of water, through two successive centrifuges. The water was obtained by the condensation of the direct steam used in the scrubbing section of the still. German practice includes an additional water washing between the centrifugings. The equivalent of this additional washing was carried out in our Laboratory as follows: 10% of water was sprayed into the crude oil at 65° C. with

---

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.