

3,6-Dimethyl Octan-3-ol

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3,6-Dimethyl octan-3-ol (AR-1) possesses a mild, sweet linalool type odor, almost identical to that of its structural isomer tetrahydrolinalool. The organoleptic impressions of both products are so close that it is difficult to differentiate between them. Batch to batch variation of the two alcohols display more organoleptic difference than the basic note of the individual products. Moreover, the storage stability of both these materials is so high that prime grade productions made by various processes show little variation when comparing samples of recent production versus material produced twenty years ago. Recent production samples show a clean impression, while material produced by the processes used in the 1960's and 1970's often displayed sour, burned or dimethylol notes.

AR-1 is solely a fragrance material and its use is especially desirable in aggressive media. This alcohol holds it

own far better than linalool in high surface area applications, high and low pH, and strong oxidation systems. Significant quantities have been used in soap and detergent formulations because of its fresh impression and superior stability.

Natural Sources

Although AR-1 has a terpenoid structure, with the prime isoprene unit identical to tetrahydrolinalool, the secondary isoprene unit is reversed. Thus, AR-1's isoprene units are joined head to head versus the normal head to tail linkage found in most naturally occurring terpenoid materials. There are no reports of AR-1 being found in nature.

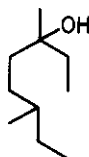
History

AR-1 began its commercial life some forty years ago in

3,6-Dimethyl Octan-3-ol

Mwt 158
CAS 151-19-9

C₁₀H₂₂O
FEMA-GRAS not listed



Classification:

A saturated terpenoid tertiary alcohol not found in nature.

Additional Names:

dimethyl octanol
APROL 100
AR-1

Physical Data:^{1,2}

Appearance: Clear, colorless liquid
Specific Gravity: 20/20°C 0.8366
Refractive Index: 1.4370 (20°C)
Boiling Point: 202.2°C at 760 mmHg
130-132°C at 100 mmHg
Solubility: H₂O (20°C) 11.7% by wt., soluble in ethanol, DEP, organic esters, mineral oil, chlorinated solvents, hydrocarbons and Cellosolve.

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the Central Research Laboratories of Air Reduction Chemical Co. in Murry Hill, N.J. Its designation as AR-1 resulted from its appearance as a by-product in a chemical reaction, and the observation that it had a pleasant odor. This led to a semi-formal research program to determine what aroma chemicals could be produced by Airco's acetylene chemistry. A list of candidates was developed and 3,6-dimethyl octan-3-ol was first on the list; hence (A)ir (R)eduction.¹

The history of its commercial life is of interest not only because AR-1 could have been a most important aroma chemical (if synthetic linalool had not been available from the vitamin intermediate process) but also as its development reflects the changes which occurred over the last 40 years in organic chemistry.

The organic chemists trained prior to the 1950's were largely schooled in the Edisonian or Imperial school of chemistry. They memorized reactions and ran experiments to see what would happen. Few of these chemists had any real theoretical understanding of what was happening or how the reaction conditions affected the outcome of the reaction.

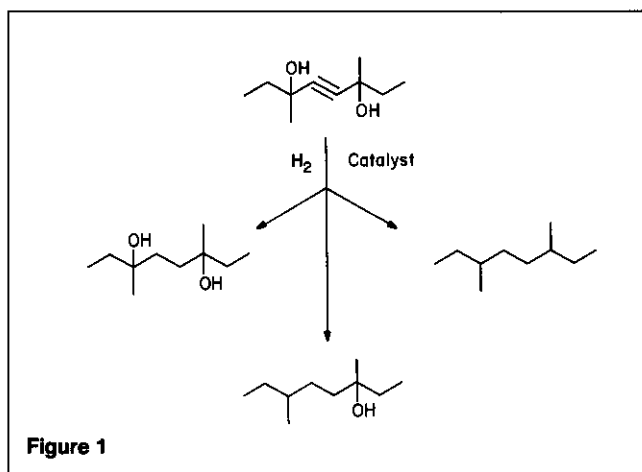
From about 1950 on, more and more organic chemists leaving the universities were armed with a basic understanding of reaction mechanisms and physical chemical principles. Thus, a schism developed between the older school of chemists (who often would have made better alchemists than scientists) and the theoretical group of "young turks". The practical day to day approach to chemistry and the antagonism of the two schools of thought were to affect the development of AR-1.

As the consumer goods market of the late 1940's and 1950's grew, the need for aroma chemicals outstripped the capacity of many natural sources. In particular, the demand for linalool caused many flavor and fragrance houses to seek synthetic routes to linalool or alternate synthetic products. Synthetic linalool from the vitamin process stream would not commercially appear on the market until about 1957.

Air Reduction's involvement in the aroma chemical area was purely accidental. One of Airco's chemists synthesized 3,6-dimethyl octan-3-ol in 1949, but the product remained buried in the lab not books until 1954.

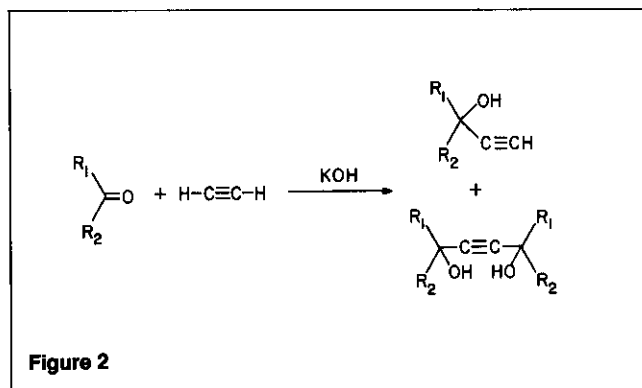
A research chemist, Sidney Gister, was assigned the task of hydrogenating the acetylenic diol, 3,6-dimethyl-4-octyn-3,6-diol to the saturated analogue so it could be evaluated for its surfactant properties. To Gister's constant frustration, the hydrogenation only yielded 50% of the diol and 50% by-products: The alcohol 3,6-dimethyl octan-3-ol and the analogous hydrocarbon (Figure 1). Gister tried every catalyst he could lay his hands on, but the reaction could not be suppressed. However, as he worked up his reaction product, he obtained fractions of the alcohol which possessed a very pleasant odor.

Airco was in a very key position in those days as they began offering chemicals which no other firm produced and which were the key raw materials for the production



of Vitamins A and E. Their chemistry centered on the Favorskii³ low pressure ethynylation of ketones to acetylenic alcohols and diols. (Figure 2). The products generated found uses as vitamin intermediates, aroma chemicals and intermediate to them, surfactants and corrosion inhibitors.

If acetone were used as the feed stock, then methyl butynol and dimethyl hexyndiol were the resulting products. Methyl butynol soon became the commercial feed stock for Hoffmann-La Roche's vitamin A process and hence linalool. Dimethyl hexyndiol could be hydrogenated to the saturated diol, Dimethyl hexandiol, which became the critical raw material for the new musk "Versalide" being offered by Givaudan. Thus Airco's sales force had very active contact in the F+F area and sought to expand their sales by offering other aroma chemicals. Airco's aroma chemical program was born and AR-1 was its first thrust.



The group leader in this effort was Dr. Robert Tedeschi, who reviewed the problem of uncontrolled by-product production of AR-1 and decided that the residual acid present in the hydrogenation catalyst was the culprit. Experiments using small amounts of KOH to adjust the pH of the system proved both frustrating and fruitful. The combination of noble metal catalyst and KOH, however, not only suppressed the production of AR-1,⁴ but stopped the hydrogenation of acetylenic alcohol and diol head in their tracks at the olefinic stage.

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The Tedeschi catalyst was born, which allowed a superior control of the hydrogenation of methyl butynol to methyl butenol, the intermediate necessary for linalool and vitamin A production and production of prenyl alcohol.^{5,6}

Their contracts in the F+F industry resulted in FD+O developing specialties based on AR-1, while their customer for methyl butynol and dimethyl hexanediol (Hoffmann La Roche-Givaudan) developed their products using synthetic linalool. Still unable to control the reaction, the commercial production of AR-1 began in 1957, as significant sales volumes were being generated with Fritzsche, D+O where it was being used for the production of the specialty "Lavol". Lavol sales were growing in the soap and detergent area.

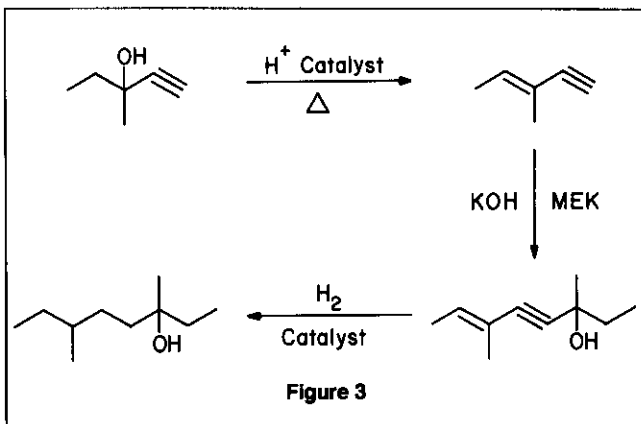
The AR-1 reaction finally was adjusted enough so that 50% yields were possible. However, the by-product diol found no commercial use and the hydrocarbon was worthless (it did make a good barbecue starting fluid and was great for cleaning Austin Healey parts!).

As demand grew, the erratic yields and increasing raw material costs began pressuring Airco to develop a better process, but their chemists from the old school insisted that the original method could not be improved on.

By 1970, Airco had made the decision to sell the division, so active research was put on hold. Air products and Chemicals purchased the chemical division from Air Reduction Co. in 1972 and quickly decided that something had to be done to improve yields and organoleptic quality.

The older school of chemists who controlled Airco's research never could see the woods for the trees. However, one engineer, Ernest Wiegleb, ignored them and resorted to some "naive" paper and graphite chemistry. Based on rough yield and production cost estimates, he proposed the following reactions for the synthesis of AR-1 (Figure 3):

Wiegleb's proposal stirred up a hornet's nest. The "They tried it at Murray Hill and it didn't work" group



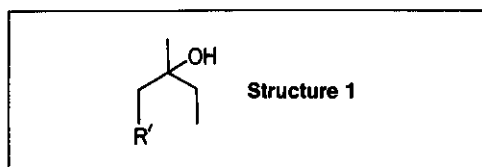
maintained that the enyn proposed would not react and even if it did, it could not be separated from the "polar" solvent used in the reaction—diisopropyl ether (IPE).

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The older chemists started mumbling such vaguely understood phrases as "polar solvents", "acetylene complexes" and "synergism". One of Wiegleb's young turk colleagues viewed IPE as a non-polar solvent and irreverently used the envn as the solvent for the KOH and stirred in the MEK. Yields of 95% resulted and reactor loadings increased six-fold. A new process was born.

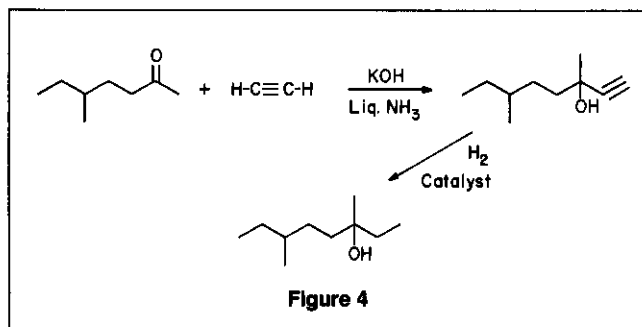
This new AR-1 process reduced costs and gave the product a new lease on life just as the raw material shortage of 1973-74 occurred which reduced the availability of linalool. Sales of AR-1 leaped and the customer base went from 6 firms to 54 in just 30 days. The escalating prices for linalool forced more than one fragrance compounder to use AR-1 in place of linalool or in combination. Moreover, the new process allowed the synthesis of a multitude of new alcohols that had never been synthesized before. Air Products explored them and their derivatives under the tradename APROL.

Many of these new materials furnished important structural insight into the organoleptic changes that occur in C₈-C₁₂ terpene alcohols with structural changes and demonstrated that the key determinant for a linalool floral odor was the basic structure of the prime isoprene unit coupled with a secondary (R') unit (Structure I). The secondary unit's structure was relatively unimportant to the alcohol's odor classification.^{7,8}



By 1976, Air Products' aroma chemical business looked bright, but trouble was ahead. Versalide was soon found to have safety problems and Air Products saw a loss of \$1.5 Mi of sales during a 2-week period in 1977. Soon after, sales of ethylacetylene dropped off and the company's management decided that they did not belong in the aroma chemical business. The Middlesex, N.J. plant was to be closed and AR-1 production ceased. When FD+O was informed of the decision, BASF quickly developed a new route to synthesize AR-1. After a difficult period of process changes to match the organoleptic profile, BASF was successful in supplying the product from their Ludwigshaven, Germany facilities. Analysis of their current production indicates they are employing the following route for its synthesis (Figure 4):

Thus is the history of 3,6-dimethyl octan-3-ol and its chemical evolution over forty years of changes in the flavor and fragrance industry. One wonders what might have been the fate of AR-1 if synthetic linalool had not been made available from the vitamin intermediate stream.



World Consumption

AR-1 or APROL 100 consumption reached levels of 500,000 lbs worldwide by 1977. This figure also includes about 20,000 lbs of consumption as the acetate ester (APROL 102).

Consumption in the U.S. was about 400,000 lbs with the remaining 100,000 lbs being used in Europe and Japan.

It is estimated that current worldwide usage is about 100,000 lbs both as the alcohol and esters, and is declining due to the price differential of THL and AR-1.

Pricing

AR-1's chief rival in usage is linalool and tetrahydro linalool. Thus, it is not surprising to see a strong price relationship between the three products and usage volumes.

During the period 1970 to 1980, AR-1 was priced relatively competitively versus linalool and far lower than THL. AR-1 prices began to rise as Air Products exited the market and reached the levels of tetrahydro linalool 1986. Since 1989, THL prices have been more competitive and, hence, favor its use as a replacement for AR-1 in both new and established formulas.

References

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1. Airco Chemicals and Plastics, Technical Bulletin A-4, (1965)
2. Air Products and Chemicals, Acetylenic Chemicals Division Data Sheet A-4, (1974)
3. A Favorskii, *J Russ Physikchem Ges* **37** (1905) 643 *Reaktionen der Organischen Chemie*, H Krauch and W Kunz. Dr Alfred Huethig Verlag, Heidelberg (1966)
4. R J Tedeschi, *JOC* **27** 2308 (1962)
5. R J Tedeschi and G S Clark, Selective Semihydrogenation of Tertiary Ethynyl carbinols in the presence of Base, *JOC* **27** 4323 (1962)
6. R J Tedeschi, G S Clark and W F Tiedge, Continuous Allylic Isomerization of Tertiary Vinyl Carbinols to Compounds of Varied Odors, *J Agr Food Chem* **19**(6), (1971)
7. G S Clark and V J Grande, A Study of Odor variation with structural change in C₉-C₁₁, aliphatic alcohols, VIth International Congress of Essential Oils (1974)
8. G S Clark and V J Grande, A Study of Odor Variation with structural change in C₈-C₁₂ Aliphatic Alcohols, 18th Annual Symposium of the American Soc. of Perfumers (1975)