Reflections of a Retired Flavorist Before He Forgets:

Raspberry

By James J. Broderick, River Edge, New Jersey

In the late 1930s when we first had an opportunity to evaluate flavors, the standard for raspberry was a Fritzsche Brothers (prior to acquisition of Dodge & Olcott, and they being acquired by Givaudan) flavor. It was dependent on ionones; was rather floral with essential oils and high in esters—isobutyl acetate seemed to predominate. Methyl sulfide was an important topnote.

In the late 1940s, after our military service and return to the industry, we were employed by Van Ameringen-Haebler (who later merged with Polak & Schwartz to form IFF) and was delighted to learn that they apparently had done some basic work on raspberry volatiles. We encouraged our superior, Dr. James McGlumphy, to publish and when he was asked to give a talk at the International Food Technologists (IFT) Convention on the volatiles of fruit,[1] he agreed if I would do the literature search for him. In this search, an article[2] by Coppens and Hoejenbos of PFW, Holland (since acquired by Hercules) was discovered. Their findings were remarkably similar to the alleged VAH staff work so Dr. McGlumphy had little new to report. Nevertheless, his talk was well received.

Some years later, we had the opportunity to discuss the Coppens and Hoejenbos work with Ernst Polak. He claimed the key components discovered were never disclosed, but the impetus for publishing was governmental concerns that were arising about the safety of flavoring ingredients and PFW's desire to show that these components were innocuous and similar to those found naturally.

Two problems developed for us shortly thereafter. We received a sample of the now famous Firmenich raspberry before it was introduced into this country, and unsuccessfully attempted to duplicate it for a number of years. We also had another project to develop a Raspberry WONF similar to the flavor in the then popular Hoffman beverage raspberry. Here again we were unsuccessful. However, our attempts at both these flavors were an invaluable learning process. The derivation of the uniquely U.S. category of WONF flavors is a story in itself. Suffice to say they were supposed to supply at least 50% of the flavor to the end product from extractives of the named fruit and the remainder from other natural extracts, essential oils, absolutes.

We were later told, but could not actually verify, that the original Coppens and Hoejenbos work had uncovered raspberry ketone (para hydroxy phenyl butanone) and that it had been held captive by PFW and used at a low level in their Raspberry WONF which was, in turn, part of the Hoffman raspberry flavor. Later Firmenich synthesized this key component, and its use at a much higher level was the secret to their famous raspberry. This information, when finally obtained, helped our morale as it explained, at least partially, our inability to match the two raspberry flavors.

In 1952 we went to work for Givaudan and requested Geneva to identify the Firmenich raspberry unknown and shortly thereafter received their results and a sample of raspberry ketone. The secret was out and not too long afterwards, raspberry ketone was commercially available and the Firmenich-type raspberry became the norm for the industry. We never learned what channel was used by the Firmenich technical people to uncover the identity of this key material.

In 1960 we decided to become a consultant. We had been fortunate to have one of the first commercial gas chromatographs but were unsuccessful convincing those in

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the industry of its potential. One of our principal clients, Bob Fries, authorized work on the volatiles of fruits. In our early work on raspberry,[3] two-in-one like peaks were spotted that we felt were indispensible. When trapped and forwarded to New York University for mass spectra data, compared to α- and β-ionone, they were found to be identical to α- and β-ionone. Although they had the same retention time as α- and β-ionone, we did not consider them. First of all, they did not smell like our α- and β-ionones. Secondly, there was an AOAC test for β-ionone in raspberry to detect adulteration. We learned, of course, that at that time commercial ionones were a mixture of ionones, and our α-ionone was 70% alpha and contained almost 30% beta plus other ionones and the AOAC test was insensitive to the level of ionone in raspberries.

As our work on raspberry volatiles continued, we isolated another unknown, which we felt was also the key to its flavor. It had the same retention time as nerol in a Carbowax 20M column and smelled somewhat similar. For years this was labeled our "nerol-like" unknown. A boric acid loop attached to our column and mass spectra showed it to be a terpene alcohol but when we gave up consulting, it was still unidentified (1965).

In 1967 we traveled to Australia and made the acquaintance of Dr. Keith Murray and his associate, Dr. Frank Whitfield of CSIRO Laboratories. Among other topics we discussed our "nerol-like" unknown, and Dr. Murray kindly offered to look at it if we supplied him with a sample. In a subsequent visit to Australia, we gave Dr. Murray the sample we had extracted and isolated from red raspberry essence produced in Kohnstamm's (since acquired by Universal Foods) own plant, just prior to our visit. They ran mass spectra and compared its mass numbers to data in their files. It was quickly identified as myrtenol. On our return home, we couldn't wait to add it to our raspberry flavors only to learn that at levels approaching its level in raspberries (approx. 1 ppm), it had little or no flavor effect. Things don't always work out as in the movies.

More recently the trend towards "natural" and the loose interpretation of "natural" has modified the standard for raspberry flavor. For example, the original Firmenich flavor contained important ingredients not yet considered or available in a "natural" form. Also the green notes, of importance to natural raspberry flavor, were not in that original flavor. As of this writing, we have not seen a natural raspberry ketone, but if and when it arrives, the target for raspberry will once again change.

References

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1. JH McGlumphy, *Food Technol*, **5**, 353 (1951)
2. A Coppens and L Hoejenbos, *Rec Trav Chim*, **58**, 675-679 (1939)
3. JJ Broderick, Paper presented at the FEMA Annual Convention (1962)