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A new method for the estimation of olive oil healthfulness

Evangelia Karkoula, Eleni Melliou, and Prokopios Magiatis

- **A growing body of evidence suggests that the healthfulness of olive oils could be classified based on their content of oleocanthal, oleacein, and related secoiridoids. However, such compounds are difficult to measure because they react with the water or methanol used during the mobile phase of liquid chromatography.**
- **Recently, a new method allowing olive oil polyphenols to be extracted without the use of reacting solvent was developed, making it possible to measure oleocanthal and oleacein levels directly by quantitative ^{1}H nuclear magnetic resonance (NMR) in $CDCl_3$ at 600 MHz and 800 MHz.**
- **Measurements of 300 olive oil samples using this method revealed wide variations in the concentrations of these healthful compounds among extra virgin olive oils.**

Several epidemiological studies have shown that the traditional Mediterranean diet is associated with a lower incidence of atherosclerosis, cardiovascular disease, neurodegenerative diseases, and certain kinds of cancer. These appreciable health-promoting properties have been partially correlated with the regular consumption of extra virgin olive oil as the principal source of fat. Olive oil is the most famous agricultural product in the Mediterranean, with a history as old as that region's civilization. Olive fruits and olive oil not only are delicious but also have been considered as medicines since ancient times.

Dioscorides (*ca.* 40–90 CE) and several other ancient doctors claimed that olive oil and other olive-related products had numerous therapeutic applications. In his monumental work "De Materia Medica," which is the basis of modern pharmacology and pharmacopoeia, Dioscorides clearly stated that olive oil from specific varieties—particularly early-harvested extra virgin olive oil—has anti-inflammatory activities. Ancient recipes described in incredible detail how olive oil could be used as remedies against conditions such as headache and toothache, clear indications of *in vivo* anti-inflammatory activity. Yet, according to descriptions in ancient manuscripts, not all olive oils display such properties. We were intrigued and decided to investigate whether that could be true and why.

In 2005 Beauchamp and co-workers reported in the journal *Nature* that olive oil contains a chemical compound called oleocanthal, which is responsible for the pungency of some olive oils and which has a very strong anti-inflammatory activity with ibuprofen-like cyclooxygenase (COX-1 and COX-2)-inhibiting activity. This may explain the therapeutic properties of virgin olive oil, since inflammation plays a significant role in the development of numerous chronic diseases, such as cardiovascular disease, as well as in certain kinds of cancer.

In addition, recent research has demonstrated that oleocanthal is a promising therapeutic agent for the treatment of inflammatory degenerative joint diseases. Moreover, oleocanthal can be a potentially useful agent for the development of new treatments for neurodegenerative tauopathies (diseases associated with the pathological aggregation of tau protein in the human brain), such as Alzheimer's disease, or as an agent against *Helicobacter pylori*, which is linked to a majority of peptic ulcers and to some types of gastric cancer. Oleocanthal also exhibits biological properties that can control skin aging and a growing body of evidence suggests that it could be used to treat damaged skin or to reduce a variety of disorders that arise from metabolic syndrome.

Another compound with a similar structure that is related to the bitter taste of some olive oils is the dialdehydic form of decarboxymethyl oleuropein aglycone, known as oleacein. This compound has shown activities similar to those of oleocanthal, but the former has also displayed significant anti-breast cancer properties. Most importantly, oleacein also has potent antioxidant activities, even better than those of hydroxytyrosol, another active compound found in table olives and olive oil. Oleacein can additionally protect low density lipoprotein from oxidation, a health claim already recognized by European Union legislation.

Modern findings about oleocanthal and oleacein and their potential health effects that confirmed the ancient reports prompted us to assume that several varieties of olive oils could be classified on the basis of their content of secoiridoids, such as oleocanthal, oleacein, and related compounds. Toward this end, we investigated the levels of oleocanthal and its related analog oleacein in a large number of Greek and California olive oils of monovarietal origin in relation with the variety, the geographic origin, and the time of harvest. To achieve this target, we recognized the need to develop a new, fast, and accurate analytical method that can circumvent a previously known analytical problem for the oleocanthal and oleacein measurement.

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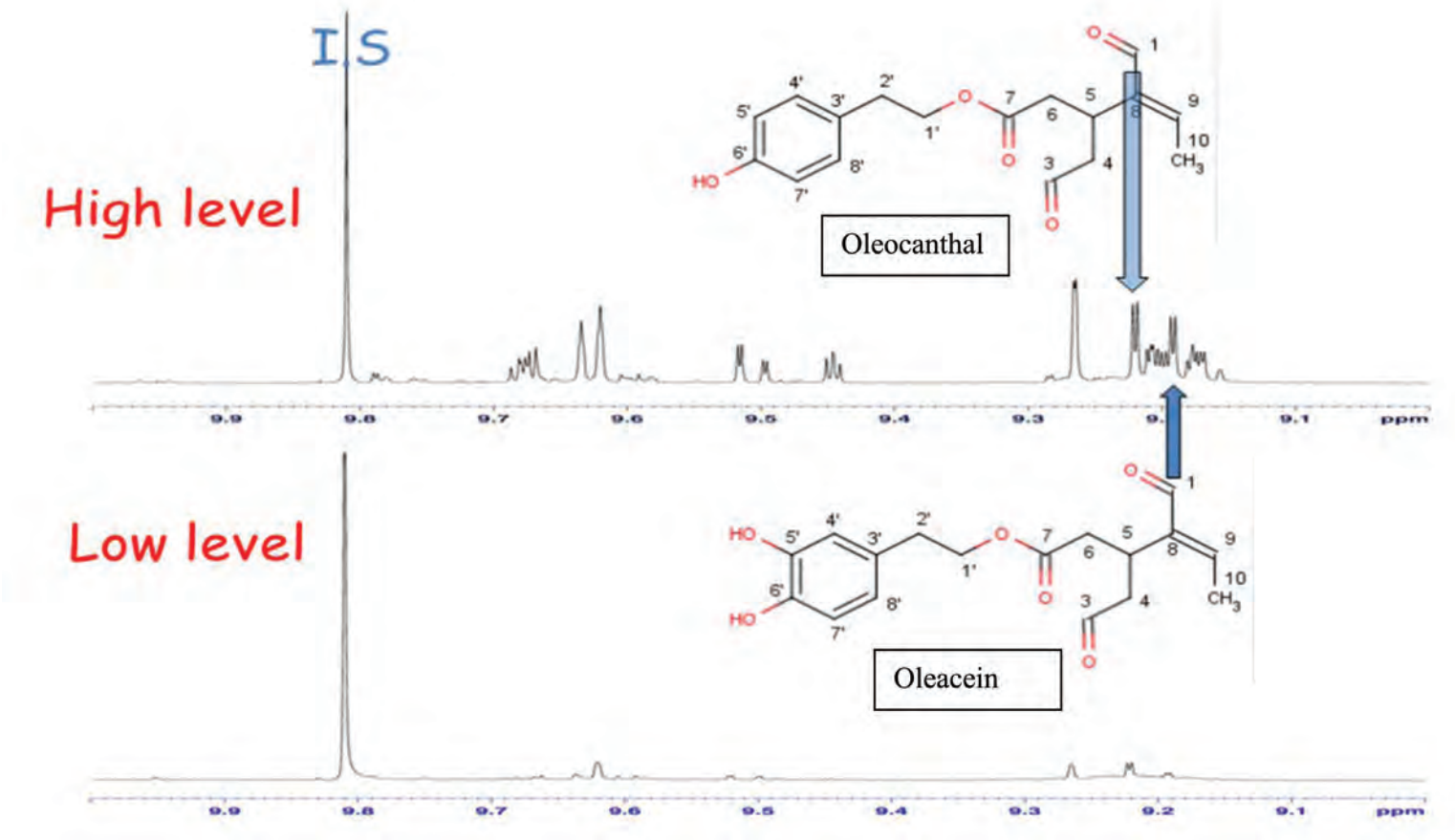

FIG. 1. Example of two ^{1}H nuclear magnetic resonance spectra of extra virgin olive oils presenting high and low levels of oleocanthal and oleacein. The arrows denote the peaks that are used for the quantification of each compound (IS: internal standard).

INFORMATION

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That problem arises because both compounds react rapidly with the water or methanol commonly used in the mobile phase of liquid chromatography, leading to broadened or multiple peaks. This reactivity necessitates the use of derivatization reactions.

For this reason, we developed methods to extract olive oil polyphenols without using any reacting solvent and to measure oleocanthal and oleacein levels directly by quantitative ^{1}H-NMR in $CDCl_3$ at 600 MHz and 800 MHz (Fig. 1).

The methods were applied in the study of over 300 olive oil samples. One of the main findings was a highly important variation in the concentrations of oleocanthal and oleacein among the studied extra virgin olive oil samples. The concentrations of both compounds ranged from non detectable to over 500 mg/kg, respectively, and their sum from 0 mg/kg to over 750 mg/kg.

It is important to note that according to the definition established by European Union legislation all the studied samples were considered as extra virgin olive oils. However, the observed important variation of the concentration of the bioactive polyphenolic secoiridoids revealed the need for a new type of classification especially related to possible health claims of

those compounds. For this reason we propose a new index, D1, as the sum of the concentrations of oleocanthal and oleacein.

GREEK OIL SAMPLES

The highest concentrations of oleocanthal and oleacein among the Greek samples were recorded in olive oil samples produced from the Koroneiki cultivar. However, a portion of olive oil samples coming from cv Koroneiki showed significantly low concentrations (Fig. 2). This result in most cases could be attributed either to very late harvest (fully ripe fruit) or to high temperature during malaxation or both.

We also found that there was a group of olive varieties that, independent of geographic origin, harvest time (early or late), or olive mill-related parameters, produced olive oil containing both compounds in low levels (mean value D1 = 49 mg/mg). The olive oil produced by those varieties is traditionally preferred for confectionary owing to its lower sensation of bitterness and pungency. Our findings confirmed their lower content of oleocanthal and oleacein, which are related with those specific organoleptic properties.

Another observation was that the ratio between oleocanthal and oleacein (index D2 = oleacein/oleocanthal) seems to be dependent on the olive tree variety, probably due to genetic reasons, and independent of the olive mill procedure.

We also discovered a positive correlation of oleocanthal and oleacein concentration with the early time of harvest. It is noteworthy that the highest D1 index (750 mg/kg) was recorded for a sample from Koroneiki variety (Antiparos Island) produced in late October 2012. Similarly, the second- and third-highest D1 indexes were recorded for early-harvested (early November) Koroneiki variety from Messini. The same variety from the same olive grove collected after two months and processed in the same olive mill under the same conditions afforded an olive oil with D1 index at 87 mg/kg.

CALIFORNIA OIL SAMPLES

Similarly to the Greek samples, significant differences were also observed for the California olive oil samples. Samples from seven different varieties were studied, and big differences were recorded. For example, the highest variability in D1 index was found for Taggiasca, Leccino and Barouni cultivars, ranging from 45 to 275 to 406 mg/kg, respectively.

Although we measured only two compounds bearing aldehyde groups, the NMR spectrum in the range 9.1–9.8 ppm seems to present a unique recognition pattern especially characteristic for some olive oil varieties. The ^{1}H-NMR spectrum not only

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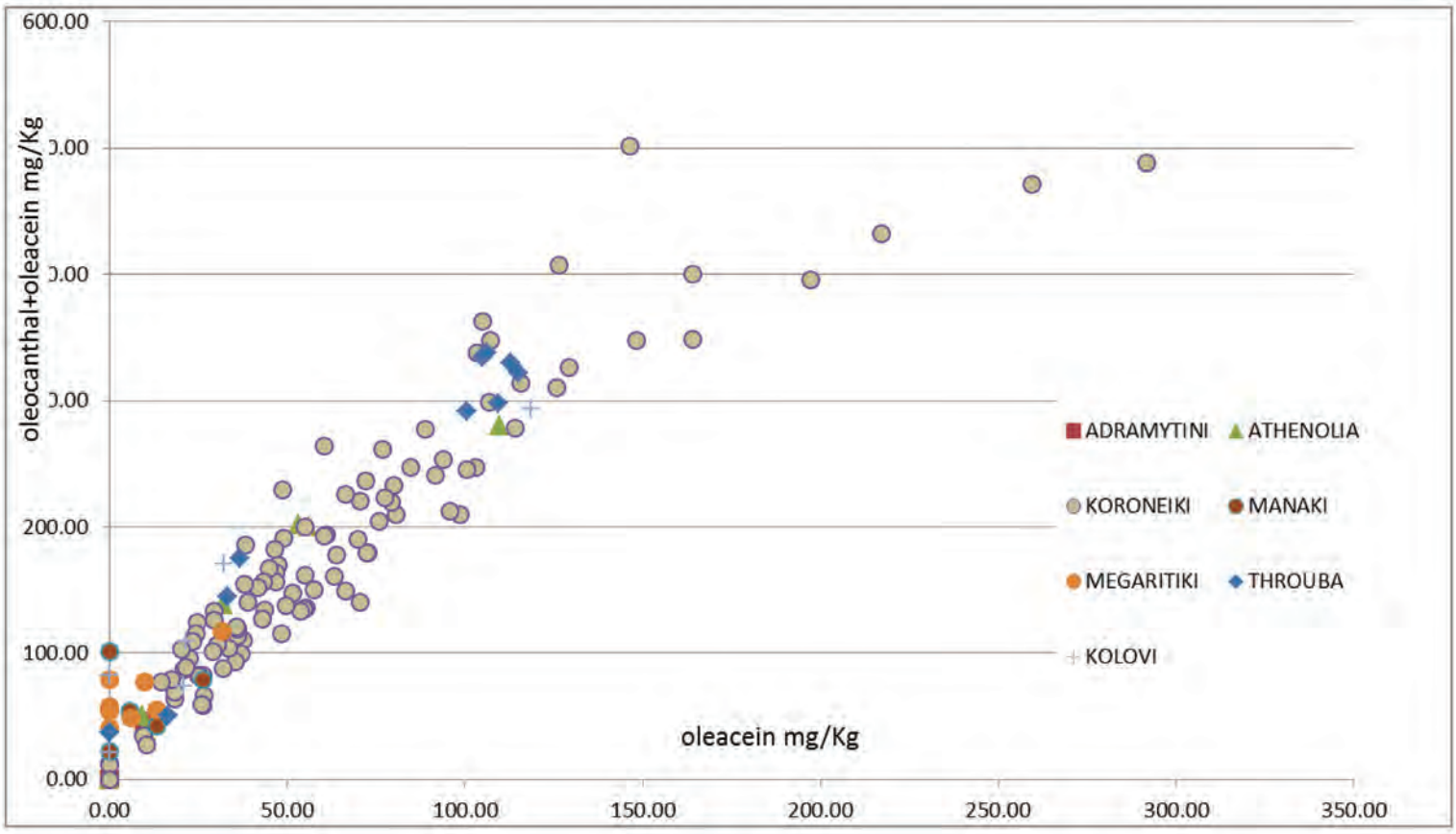

FIG. 2. Diagram showing the wide variability of oleocanthal and oleacein content among the several varieties studied.

offers a method for quantitation but also offers a tool for variety recognition but this finding needs further elaboration.

While there is need for more extensive study, based on our observations the new index for the characterization of extra virgin olive oils—a combination of D1 = oleocanthal + oleacein level with the D2 = oleocanthal/oleacein molar ratio—can be very useful for the estimation of the healthfulness of an olive oil and can be understood easily by consumers.

INDEXES D1 AND D2 IN PERSPECTIVE

In confirming the ancient observations, it was obvious that the oils can be categorized according to their content of bioactive compounds. The new indexes D1 and D2 reflect such significant differences among the olive oils that although the oils may belong to the official category of extra virgin olive oil, a new subcategory of "super" olive oils with high D1 and D2 can be established. It has to be clear that those indexes mainly concern the support of health claims and are more specific than the total polyphenols (expressed as gallic acid equivalent) related to antioxidant activity.

It is also noteworthy that in preliminary studies the indexes D1 and D2 can predict the pungent and bitter taste of an olive oil. In most cases the highest "healthfulness" is related with increased pungency and bitterness, which are organoleptic properties that are highly appreciated by olive oil experts.

[FAST FACTS]

Mayonnaise is said to be the invention of the French chef of the Duke de Richelieu in 1756. While the Duke was defeating the British at Port Mahon, his chef was creating a victory feast that included a sauce made of cream and eggs. When the chef realized that there was no cream in the kitchen, he improvised, substituting olive oil for the cream. A new culinary masterpiece was born, and the chef named it "Mahonnaise" in honor of the Duke's victory. (Copied from http://www.bestfoods.com/home/about)

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