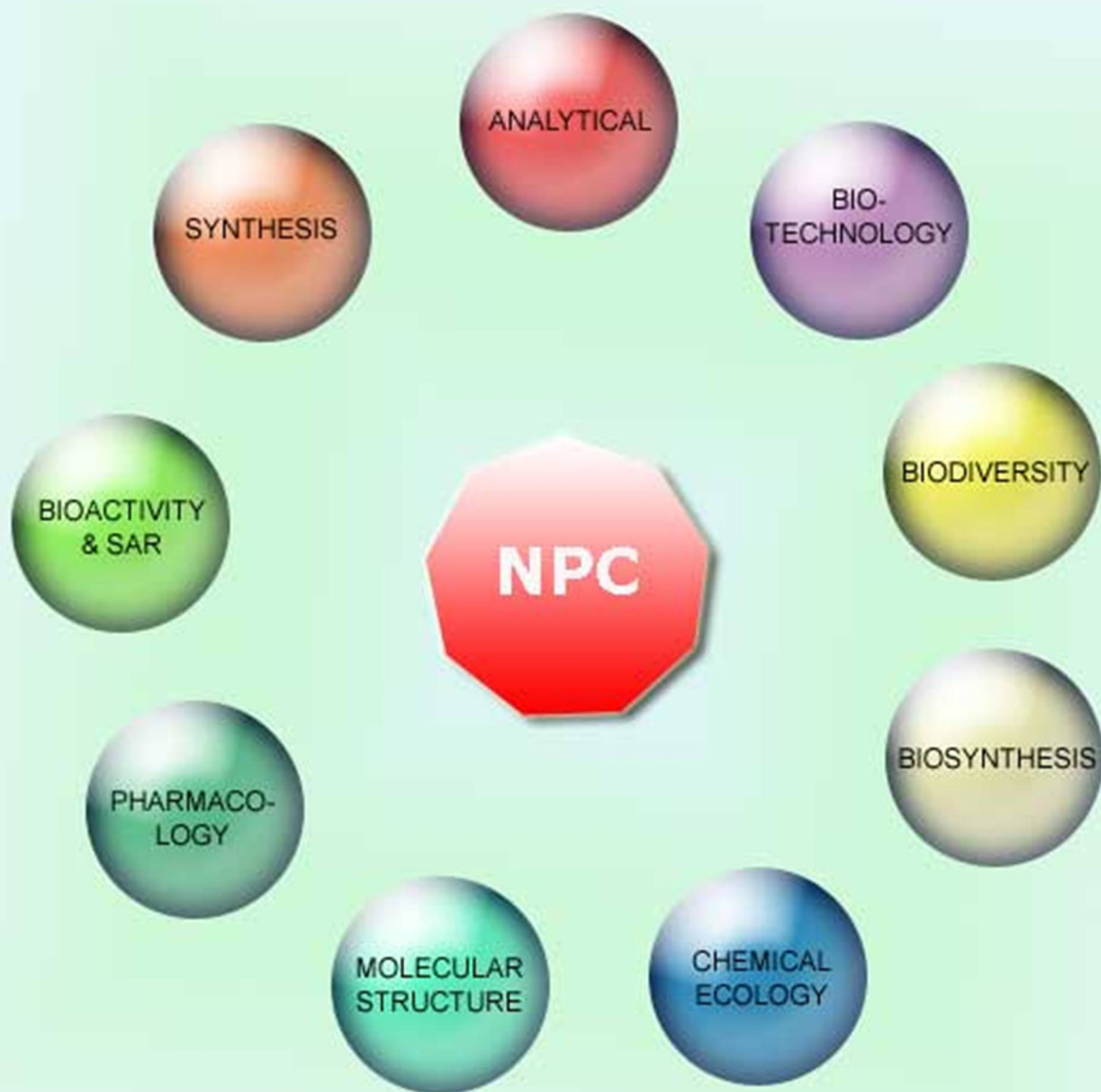


NATURAL PRODUCT COMMUNICATIONS

An International Journal for Communications and Reviews Covering all
Aspects of Natural Products Research



Volume 8. Issue 1. Pages 1-146. 2013
ISSN 1934-578X (printed); ISSN 1555-9475 (online)
www.naturalproduct.us

EDITOR-IN-CHIEF**DR. PAWAN K AGRAWAL**

Natural Product Inc.
7963, Anderson Park Lane,
Westerville, Ohio 43081, USA
agrawal@naturalproduct.us

EDITORS**PROFESSOR ALEJANDRO F. BARRERO**

Department of Organic Chemistry,
University of Granada,
Campus de Fuente Nueva, s/n, 18071, Granada, Spain
afbarre@ugr.es

PROFESSOR ALESSANDRA BRACA

Dipartimento di Chimica Bioorganica e Biofarmacia,
Università di Pisa,
via Bonanno 33, 56126 Pisa, Italy
braca@farm.unipi.it

PROFESSOR DEAN GUO

State Key Laboratory of Natural and Biomimetic Drugs,
School of Pharmaceutical Sciences,
Peking University,
Beijing 100083, China
gda5958@163.com

PROFESSOR YOSHIHIRO MIMAKI

School of Pharmacy,
Tokyo University of Pharmacy and Life Sciences,
Horinouchi 1432-1, Hachioji, Tokyo 192-0392, Japan
mimakiy@ps.toyaku.ac.jp

PROFESSOR STEPHEN G. PYNE

Department of Chemistry
University of Wollongong
Wollongong, New South Wales, 2522, Australia
spyne@uow.edu.au

PROFESSOR MANFRED G. REINECKE

Department of Chemistry,
Texas Christian University,
Forts Worth, TX 76129, USA
m.reinecke@tcu.edu

PROFESSOR WILLIAM N. SETZER

Department of Chemistry
The University of Alabama in Huntsville
Huntsville, AL 35809, USA
wsetzer@chemistry.uah.edu

PROFESSOR YASUHIRO TEZUKA

Institute of Natural Medicine
Institute of Natural Medicine, University of Toyama,
2630-Sugitani, Toyama 930-0194, Japan
tezuka@inm.u-toyama.ac.jp

PROFESSOR DAVID E. THURSTON

Department of Pharmaceutical and Biological Chemistry,
The School of Pharmacy,
University of London, 29-39 Brunswick Square,
London WC1N 1AX, UK
david.thurston@pharmacy.ac.uk

HONORARY EDITOR**PROFESSOR GERALD BLUNDEN**

The School of Pharmacy & Biomedical Sciences,
University of Portsmouth,
Portsmouth, PO1 2DT U.K.
axuf64@dsl.pipex.com

ADVISORY BOARD

Prof. Berhanu M. Abegaz
Gaborone, Botswana

Prof. Viqar Uddin Ahmad
Karachi, Pakistan

Prof. Øyvind M. Andersen
Bergen, Norway

Prof. Giovanni Appendino
Novara, Italy

Prof. Yoshinori Asakawa
Tokushima, Japan

Prof. Lee Banting
Portsmouth, U.K.

Prof. Julie Banerji
Kolkata, India

Prof. Anna R. Bilia
Florence, Italy

Prof. Maurizio Bruno
Palermo, Italy

Prof. César A. N. Catalán
Tucumán, Argentina

Prof. Josep Coll
Barcelona, Spain

Prof. Geoffrey Cordell
Chicago, IL, USA

Prof. Ana Cristina Figueiredo
Lisbon, Portugal

Prof. Cristina Gracia-Viguera
Murcia, Spain

Prof. Duvvuru Gunasekar
Tirupati, India

Prof. Kurt Hostettmann
Lausanne, Switzerland

Prof. Martin A. Iglesias Arteaga
Mexico, D. F., Mexico

Prof. Leopold Jirovetz
Vienna, Austria

Prof. Vladimir I Kalinin
Vladivostok, Russia

Prof. Niel A. Koorbanally
Durban, South Africa

Prof. Karsten Krohn
Paderborn, Germany

Prof. Chiaki Kuroda
Tokyo, Japan

Prof. Hartmut Laatsch
Gottingen, Germany

Prof. Marie Lacaille-Dubois
Dijon, France

Prof. Shoei-Sheng Lee
Taipei, Taiwan

Prof. Francisco Macias
Cadiz, Spain

Prof. Imre Mathe
Szeged, Hungary

Prof. Ermino Murano
Trieste, Italy

Prof. M. Soledade C. Pedras
Saskatoon, Canada

Prof. Luc Pieters
Antwerp, Belgium

Prof. Peter Proksch
Düsseldorf, Germany

Prof. Phila Raharivelomanana
Tahiti, French Polynesia

Prof. Luca Rastrelli
Fisciano, Italy

Prof. Monique Simmonds
Richmond, UK

Dr. Bikram Singh
Palampur, India

Prof. John L. Sorensen
Manitoba, Canada

Prof. Valentin Stonik
Vladivostok, Russia

Prof. Winston F. Tinto
Barbados, West Indies

Prof. Sylvia Urban
Melbourne, Australia

Prof. Karen Valant-Vetschera
Vienna, Austria

INFORMATION FOR AUTHORS

Full details of how to submit a manuscript for publication in Natural Product Communications are given in Information for Authors on our Web site <http://www.naturalproduct.us>.

Authors may reproduce/republish portions of their published contribution without seeking permission from NPC, provided that any such republication is accompanied by an acknowledgment (original citation)-Reproduced by permission of Natural Product Communications. Any unauthorized reproduction, transmission or storage may result in either civil or criminal liability.

The publication of each of the articles contained herein is protected by copyright. Except as allowed under national "fair use" laws, copying is not permitted by any means or for any purpose, such as for distribution to any third party (whether by sale, loan, gift, or otherwise); as agent (express or implied) of any third party; for purposes of advertising or promotion; or to create collective or derivative works. Such permission requests, or other inquiries, should be addressed to the Natural Product Inc. (NPI). A photocopy license is available from the NPI for institutional subscribers that need to make multiple copies of single articles for internal study or research purposes.

To Subscribe: Natural Product Communications is a journal published monthly. 2013 subscription price: US\$2,395 (Print, ISSN# 1934-578X); US\$2,395 (Web edition, ISSN# 1555-9475); US\$2,795 (Print + single site online); US\$595 (Personal online). Orders should be addressed to Subscription Department, Natural Product Communications, Natural Product Inc., 7963 Anderson Park Lane, Westerville, Ohio 43081, USA. Subscriptions are renewed on an annual basis. Claims for nonreceipt of issues will be honored if made within three months of publication of the issue. All issues are dispatched by airmail throughout the world, excluding the USA and Canada.

Volatile Compound Formation During Argan Kernel Roasting

Hanae El Monfalouti^{a,b}, Zoubida Charrouf^{a,*}, Manuela Giordano^c, Dominique Guillaume^b, Badreddine Kartah^a, Hicham Harhar^a, Saïd Gharby^a, Clément Denhez^b and Giuseppe Zeppa^c

^aFaculté des Sciences, Université Mohammed V-Agdal, Laboratoire de Chimie des Plantes, BP 1014, Rabat, Morocco

^bUFR Medicine-Pharmacy, Med Chem Department, CNRS-UMR6229, Université de Reims Champagne-Ardenne, 51 rue Cognacq Jay, 51100 Reims, France

^cDepartment of Valorization and Exploitation of Agroforestry Resources, Food Microbiology and Technology Sector, University of Turin, Via Leonardo da Vinci, 44 – 10095 Grugliasco, Italy.

zcharrouf@menara.ma

Received: July 25th, 2012; Accepted: August 31th, 2012

Virgin edible argan oil is prepared by cold-pressing argan kernels previously roasted at 110°C for up to 25 minutes. The concentration of 40 volatile compounds in virgin edible argan oil was determined as a function of argan kernel roasting time. Most of the volatile compounds begin to be formed after 15 to 25 minutes of roasting. This suggests that a strictly controlled roasting time should allow the modulation of argan oil taste and thus satisfy different types of consumers. This could be of major importance considering the present booming use of edible argan oil.

Keywords: Argan oil, GC/MS, Flavor variation, Aroma variation.

Argan oil, the basic ingredient of the Amazigh diet [1], has become a major player in the competitive virgin oil kingdom. This is due to its unique taste and numerous nutritional and pharmacological properties [2,3]. Argan oil is prepared by extraction with a mechanical press after the argan kernels have been roasted at 110°C for the appropriate time [4]. During roasting, a hazelnut like-aroma is developed, and this is transferred along with the oil during extraction. However, if kernel roasting is prolonged over 25 minutes, the resulting oil presents an unpleasant taste, then a burning taste, and is rejected by consumers [5]. A large number of chemical compounds of different classes, such as aldehydes, hydrocarbons, ketones, and furans participate in the argan oil final aroma [6]. Most of these compounds are produced by oxidation of fatty acids after enzymatic reactions occurring in the presence of oxygen. C₆ and C₅ volatile compounds, which come from primary or secondary lipoxygenase pathways, respectively, are particularly well known to participate actively in the edible oil aroma [7]. Prolonged storage of the argan fruit also favors volatile compound formation [8]. However, as also in the case of olive oil, those latter are generally responsible for off-flavors [9]. Interestingly, the distinctive hazelnut aroma of argan oil is also likely to be due to pyrazines, formed from Maillard-type non-enzymatic reactions between reducing sugar and free amino acid during the roasting process [10], as frequently observed in many different types of thermally processed food [11, 12].

This paper intends to macroscopically characterize the kinetics of the volatile compound formation in argan kernels during the roasting time. Such study could permit the tuning of the argan oil aroma and possibly satisfy new types of consumers.

Already known volatile compounds isolated from argan oil belong to six major families: alcohols, aldehydes, ketones, esters, terpenes, and *N*-heterocycles [6]. Argan oil prepared from animal-processed fruit possesses additional volatile compounds [6], but because of its low quality [13], such oil was voluntarily excluded from this study.

However, the kinetics of the formation of all these families of compounds is still unknown. Therefore, we chose several volatile compounds belonging to each known family of argan oil volatiles and quantified them all along the roasting process. Ten alcohols, three aldehydes, four esters or lactones, three ketones, one terpene, and ten *N*-heterocycles were selected (Table 1). Additionally, four acid volatiles were also selected, together with five furans, even though their presence had not been previously reported.

Oxygen reacts with unsaturated fatty acids to yield hydroperoxides from which a large variety of volatile and non-volatile secondary products are formed. Elevated temperature greatly favors volatile compound formation through lipoxidation [14]. Aldehydes, acids, and esters result from carbon-carbon cleavage. Other derivatives result from more complex processes that may involve isomerization [14]. For example, Strecker degradation is a well-studied process that is known to afford aldehydes from amino-acids [15].

Acids play an important function in food taste. For example, valeric and hexanoic acids possess a cheesy and barnyard animal flavor, respectively. Whereas in argan oil the butanoic acid level remained unchanged over a roasting period of 35 minutes, the level of valeric, and hexanoic acids started to increase significantly after 20 minutes. Such an increase unambiguously established the occurrence of a process involving linoleic acid oxidation during this period. Among the alcohols, 1-pentanol, 1-heptanol, and 1-octanol, three primary alcohols known to result from secondary oxidation of oleic or linoleic acids by autoxidation [16], were the three volatiles whose content significantly increased after 20 minutes. Other alcohol levels remained stable, attesting to the lack of influence of roasting on either their formation or their fast involvement in subsequent reactions. Interestingly, aldehyde content also increased after 20 minutes of heating. The hexanal level increased particularly rapidly attesting to an oxidative process involving linoleic acid, consistent with the previously observed formation of 1-hexanol. Concerning benzaldehyde, which is likely to be a degradation product of the

Table 1: Quantified volatile compounds ($\mu\text{g}/\text{kg}$ of oil \pm SD) isolated in argan oil from kernels roasted for different times.

Compound	Ions (<i>m/z</i>)	Roasting time (min.)						p
		0	10	15	20	25	35	
Acids								
<i>i</i> -Butanoic	43, 73 ^q , 88	0.5 \pm 0.1	0.5 \pm 0.05	0.5 \pm 0.05	0.5 \pm 0.05	0.6 \pm 0.02	0.7 \pm 0.4	ns
Butanoic	60 ^q , 73	1.1 \pm 0.1 ^{ab}	1.1 \pm 0.2 ^{ab}	1.2 \pm 0.1 ^{abc}	1.6 \pm 0.2 ^{bcd}	1.9 \pm 0.6 ^{cd}	2.0 \pm 0.8 ^d	**
Valeric	60 ^q	0.5 \pm 0.1 ^a	0.5 \pm 0.04 ^a	0.4 \pm 0.02 ^a	2.1 \pm 0.5 ^c	1.6 \pm 0.6 ^{bc}	1.3 \pm 0.5 ^d	***
Hexanoic	73	2.4 \pm 0.2 ^a	1.9 \pm 0.1 ^a	1.9 \pm 0.1 ^a	7.3 \pm 2.1 ^b	6.7 \pm 2.5 ^b	6.8 \pm 3.3 ^b	**
Alcohols								
<i>i</i> -Butanol	43, 74 ^q	0.5 \pm 0.1 ^b	0.6 \pm 0.1 ^{bc}	0.7 \pm 0.1 ^b	0.5 \pm 0.1 ^b	0.3 \pm 0.1 ^a	0.25 \pm 0.05 ^a	***
1-Butanol	41, 56 ^q	1.2 \pm 0.1	1.3 \pm 0.1	1.0 \pm 0.02	1.6 \pm 0.22	1.4 \pm 0.05	1.6 \pm 0.63	ns
<i>i</i> -Pentanol	41, 55, 70 ^q	7.9 \pm 1.1 ^b	8.4 \pm 0.4 ^b	9.6 \pm 0.1 ^b	8.0 \pm 0.9 ^b	4.9 \pm 0.2 ^a	4.8 \pm 1.6 ^a	***
1-Pentanol	42, 55, 70 ^q	3.0 \pm 0.2 ^a	3.3 \pm 0.2 ^a	3.1 \pm 0.1 ^a	8.3 \pm 1 ^b	8.3 \pm 0.5 ^b	13.6 \pm 4.3 ^c	***
1-Hexanol	56 ^q , 69	25.9 \pm 2.4	20.8 \pm 1.1	21.6 \pm 2.1	20.8 \pm 2.6	19.5 \pm 2.1	20.5 \pm 6.1	ns
1-Heptanol	56, 70 ^q	0.54 \pm 0.03 ^a	0.4 \pm 0.01 ^a	0.5 \pm 0.06 ^a	1.1 \pm 0.1 ^b	1.7 \pm 0.2 ^c	2.2 \pm 0.7 ^c	**
2-Heptanol	45 ^q , 55, 83	2.5 \pm 0.2 ^b	1.5 \pm 0.05 ^a	1.3 \pm 0.2 ^a	1.4 \pm 0.2 ^a	1.1 \pm 0.1 ^a	1.3 \pm 0.4 ^a	***
2,3-Butanediol <i>d,l</i>	45 ^q	37 \pm 8	52.1 \pm 9.3	53.4 \pm 11.3	55.3 \pm 24.1	60.5 \pm 12.8	38.3 \pm 12.4	ns
2,3-Butanediol <i>meso</i>	45 ^q , 57	42.1 \pm 16.3	51.1 \pm 15.7	44.0 \pm 11.6	43.3 \pm 16.6	55.6 \pm 16.4	39.7 \pm 14.6	ns
1-Octanol	56 ^q , 69, 84	0.5 \pm 0.04 ^a	0.5 \pm 0.02 ^a	0.7 \pm 0.1 ^a	0.9 \pm 0.15 ^{ab}	1.4 \pm 0.3 ^{bc}	1.6 \pm 0.6 ^c	***
Aldehydes								
Hexanal	44, 56 ^q , 72	3.95 \pm 1 ^a	2.4 \pm 0.8 ^a	2.1 \pm 0.6 ^a	6.1 \pm 1.9 ^a	20.1 \pm 3.3 ^b	31.9 \pm 12.5 ^c	***
Nonanal	57 ^q	0.8 \pm 0.8 ^{ab}	0.2 \pm 0.02 ^a	0.2 \pm 0.02 ^a	0.6 \pm 0.13 ^a	1.7 \pm 0.5 ^b	2.8 \pm 1.4 ^c	***
Benzaldehyde	105 ^q	0.5 \pm 0.1 ^a	0.4 \pm 0.1 ^a	0.5 \pm 0.1 ^a	0.9 \pm 0.2 ^{ab}	1.6 \pm 0.2 ^{bc}	1.7 \pm 0.6 ^c	***
Esters, lactones								
Ethyl 2-methyl butanoate	57, 85, 102 ^q	0.4 \pm 0.05 ^c	0.2 \pm 0.01 ^b	0.1 \pm 0.02 ^a	0.2 \pm 0.02 ^{ab}	0.2 \pm 0.02 ^{ab}	0.2 \pm 0.06 ^a	***
<i>i</i> -Amylacetate	55, 70 ^q	2.1 \pm 1 ^{ab}	1.8 \pm 0.07 ^a	0.9 \pm 0.5 ^a	1.6 \pm 0.4 ^{bc}	1.6 \pm 0.1 ^c	1.1 \pm 0.5 ^c	**
γ -Butyrolactone	42, 56, 86 ^q	2.1 \pm 0.5 ^{ab}	1.4 \pm 0.2 ^a	1.5 \pm 0.04 ^a	3.2 \pm 0.6 ^{bc}	3.8 \pm 1.2 ^c	4.0 \pm 1.8 ^c	**
δ -Caprolactone	42, 70 ^q	0.1 \pm 0.01 ^a	0.09 \pm 0.01 ^{ab}	0.1 \pm 0.01 ^{ab}	0.3 \pm 0.04 ^{bc}	0.4 \pm 0.05 ^c	0.4 \pm 0.2 ^c	***
Ketones								
2-Heptanone	43, 58 ^q , 114	0.8 \pm 0.4 ^a	1.0 \pm 0.05 ^a	1.3 \pm 0.2 ^a	4.4 \pm 0.7 ^b	4.6 \pm 0.6 ^b	6.4 \pm 2.3 ^c	***
Acetoin	43, 45 ^q	6.5 \pm 1.1 ^{ab}	9.21 \pm 2.3 ^b	14.1 \pm 1.4 ^c	12.8 \pm 1.3 ^c	6.4 \pm 0.4 ^{ab}	6.5 \pm 3.4 ^{ab}	***
2-Undecanone	43, 58 ^q , 71	0.2 \pm 0.02 ^a	0.2 \pm 0.05 ^b	0.4 \pm 0.2 ^a	1.9 \pm 0.3 ^c	2.2 \pm 0.4 ^{ab}	3.2 \pm 1.2 ^{ab}	***
Terpene								
Limonene	68, 93 ^q , 121	1.1 \pm 0.1 ^b	0.5 \pm 0.03 ^a	0.5 \pm 0.08 ^a	0.8 \pm 0.1 ^a	0.8 \pm 0.1 ^a	0.55 \pm 0.4 ^b	**
N-Heterocycle								
1-Methyl-1 <i>H</i> -pyrrole	39, 53, 81 ^q	69.3 \pm 18.2 ^a	61.6 \pm 2.2 ^a	89.1 \pm 1.3 ^a	145.5 \pm 9.6 ^b	172.4 \pm 3.2 ^a	160.1 \pm 65.8 ^b	**
2-Methyl pyrazine	67, 94 ^q	3.2 \pm 0.25 ^a	0.8 \pm 0.07 ^a	7.4 \pm 0.5 ^a	52.3 \pm 6.4 ^b	134.7 \pm 61.0 ^{ab}	158.2 \pm 61.5 ^c	***
2,6-Dimethyl pyrazine	42, 81, 108 ^q	10.7 \pm 2.6 ^{ab}	1.5 \pm 0.1 ^a	17.7 \pm 1.3 ^{ab}	106.7 \pm 16.4 ^c	88.4 \pm 16 ^{bc}	261.1 \pm 110.3 ^d	**
2,3-Dimethyl pyrazine	67, 108 ^q	0.1 \pm 0.02 ^a	0.1 \pm 0.01 ^a	0.5 \pm 0.05 ^a	2.7 \pm 0.4 ^b	1.8 \pm 0.2 ^{ab}	8.8 \pm 3.1 ^c	**
2-Ethyl-5-methyl pyrazine	121, 122 ^q	1.8 \pm 0.5 ^a	0.06 \pm 0.01 ^a	1.4 \pm 0.2 ^a	5.4 \pm 0.6 ^a	4.9 \pm 0.9 ^a	23.4 \pm 8.6 ^c	***
2-Ethyl-6-methyl pyrazine	121 ^q , 122	-	0.05 \pm 0.08 ^a	2.9 \pm 0.15 ^a	15.2 \pm 2 ^b	15.4 \pm 2.7 ^b	42.5 \pm 16.8 ^c	***
Trimethyl pyrazine	42, 81, 122 ^q	1.1 \pm 0.2 ^a	0.2 \pm 0.02 ^a	3.4 \pm 0.3 ^{ab}	14.3 \pm 1.9 ^c	13.1 \pm 1.6 ^{bc}	39.8 \pm 14.6 ^d	***
2-Ethyl-3,5-dimethyl pyrazine	135 ^q	0.6 \pm 0.05 ^a	0.1 \pm 0.01 ^a	3.6 \pm 0.3 ^{ab}	10.9 \pm 1.6 ^{bc}	12.7 \pm 1.7 ^c	30.5 \pm 11.2 ^d	***
Pyrrole	39, 67 ^q	0.3 \pm 0.03 ^a	0.3 \pm 0.1 ^a	0.3 \pm 0.02 ^a	3.12 \pm 0.4 ^a	1.7 \pm 0.12 ^a	12.6 \pm 4.2 ^b	***
1 <i>H</i> -Pyrrole-2-carboxaldehyde	95 ^q	0.3 \pm 0.04 ^a	0.03 \pm 0.01 ^a	0.08 \pm 0.01 ^a	0.4 \pm 0.08 ^a	0.6 \pm 0.2 ^a	2.6 \pm 1.5 ^b	***
Furans								
2-Pentyl furan	53, 81 ^q , 138	9.4 \pm 1.1 ^a	4.9 \pm 0.3 ^a	6.4 \pm 0.8 ^a	10.9 \pm 1.1 ^a	13.5 \pm 2.5 ^{ab}	20.6 \pm 13.4 ^b	*
Furfural	96 ^q	2.3 \pm 0.2 ^a	0.2 \pm 0.3 ^a	1.1 \pm 0.08 ^a	19.3 \pm 2.9 ^a	12.9 \pm 2.1 ^a	84.9 \pm 33.8 ^b	***
2-Furanmethanol	55, 111 ^q , 126	-	0.8 \pm 0.1 ^a	1.1 \pm 0.04 ^a	2.8 \pm 0.3 ^b	2.9 \pm 0.5 ^b	14.0 \pm 6 ^c	***
2(5 <i>H</i>)-Furanone	55, 84 ^q	-	0.1 \pm 0.02 ^a	0.2 \pm 0.01 ^a	0.7 \pm 0.02 ^{ab}	0.9 \pm 0.36 ^b	1.98 \pm 0.9 ^c	***
Furaneol	85, 128 ^q	-	-	-	1.2 \pm 0.1 ^a	1.9 \pm 1.1 ^a	4.1 \pm 2.2 ^b	***

^q: Quantifier ion. Different letters in the same row at mean concentration values indicate significant differences ($p < 0.05$) as analyzed by Duncan test.

*: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$.

amino-acid phenylalanine following the Strecker degradation sequence [17]; its level also increased after 20 minutes. However, the slow rate of formation of benzaldehyde, compared with either hexanal or nonanal, suggests a moderate role for the Strecker degradation in the volatile formation in argan oil at 110°C. Among esters and lactones, ethyl 2-methylbutanoate, iso-amylacetate, γ -butyrolactone, and δ -caprolactone were easily quantified. The concentration of these four molecules decreased during the first ten minutes of heating, likely due to their high volatility. After 20 minutes of roasting, concentration of esters and lactones started to increase. Such a trend was particularly important for iso-amylacetate and γ -butyrolactone. Concentration of the former decreased after 35 minutes of heating, Ethyl 2-methyl butanoate and δ -caprolactone required a slightly longer heating period to accumulate. Ester and lactone formation necessitates two steps: first, alcohol formation, then its esterification with acid. Therefore, their high content in argan oil after 25 minutes of kernel roasting could be explained either by their inherent heat-induced formation or by the initial delay in producing the necessary alcohol and acid

derivatives. Like aldehydes, ketones are ultimate secondary lipidoxidation products [16]. The level of acetoin, a ketone known to contribute to the creamy and buttery aroma, peaked after 15 minutes of heating, then decreased to reach its initial low value after 25 minutes. Concerning the two other ketones quantified, levels of 2-heptanone and 2-undecanone consistently and significantly increased after 20 minutes of roasting. Limonene was the only terpene easy to quantify. Its concentration decreased rapidly after heating, likely due to degradation and/or heat-induced loss. Ten *N*-heterocyclic volatiles were analyzed. In oils prepared from roasted seeds, pyrazines are generally considered to occur in the course of the Maillard reaction [18, 19]. Very interestingly, most pyrazines are correlated with sensory attributes, such as roasty, nutty, and woody [20], the attributes looked for to describe quality argan oil [21]. All studied pyrazines started to accumulate after 15 min of heating. For pyrroles, another type of flavor compound eliciting a typical meat or roasted flavor, 20 minutes were necessary for their formation. Interestingly, it has been shown that for pumpkin seed oil, a roasting temperature higher than 100°C is necessary to

achieve a large production of *N*-heterocyclic compounds [20], whereas for perilla seed oil, the roasting temperature must be higher than 150°C. Our study provides evidence that the generally accepted optimum roasting time of 20-25 minutes for argan kernels [5] indeed corresponds to the time necessary to form those specific compounds that present the looked for flavor attributes.

Furans are commonly found volatiles in oilseed products [19]. They can result from two formation pathways: lipid peroxidation or carbohydrate degradation. Four furan derivatives were quantified. 2-Pentyl furan is derived from lipid peroxidation [22]. It is an important compound since it possesses flavor properties [23]. 2-Pentyl furan started to accumulate after 25 minutes of roasting. Once again, reduction in 2-pentyl furan concentration during the first 20 minutes of heating likely results from its high volatility. Levels of furanmethanol and furfural, which are formed by degradation of carbohydrates [24], increased rapidly after 15 minutes. Furaneol, that could not be detected in fresh kernels, appeared after 20 minutes of heating.

The results of our study clearly show that the roasting process of argan kernels is a major step to obtain the aroma of the final product. Roasting induces the formation of several compounds, including those from Strecker degradation, lipid peroxidation, and Maillard reaction. Because at 110°C the kinetic of formation of these compounds is different, it is reasonable to suggest that the use of appropriate roasting times should afford argan oils whose health benefits would be preserved, but presenting a variety of taste. Such produce is particularly looked for in the *haute cuisine* domain.

Experimental

Sample preparation: Argan fruit (*Argania spinosa* (L.) Skeels) was collected during the summer of 2010 in the Ait Baha area (Morocco). Harvested argan fruit was crushed and pulped. Nuts were broken to afford kernels, which were divided into 6 batches. The first was not roasted, but the 5 others were roasted at 110°C using a mechanical roaster whose temperature was controlled using a Testo 945 sensor/thermometer (Testo, Casablanca, Morocco), for 10, 15, 20, 25 and 35 min. Then, each batch was separately mechanically cold-pressed using Komet DD 85 G presses (IBG Monforts Oekotec GmbH, Mönchengladbach, Germany) to afford virgin argan oil.

SPME sampling conditions: Analysis was performed as described by Baccouri *et al.* [25]. Each oil sample was spiked with 4-methyl-2-pentanone (internal standard) to a final concentration of 6.7

µg/kg. Then 1.5 g was introduced into a 10 mL vial fitted with a silicone septum. The vial was immersed in a water bath at 40°C and the oily solution maintained under magnetic stirring. After 2 min, a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (50/30 µm, 2 cm long from Supelco Ltd., Bellefonte, PA) was exposed to the sample headspace for 30 min [35] and immediately desorbed for 2 min at 260°C in the gas chromatograph in splitless condition. All the analyses were performed in triplicate.

GC-MS analysis: GC/MS analysis was performed with a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu QP-2010 Plus quadrupole mass spectrometer (Shimadzu Corporation, Kyoto, Japan) and a DB-WAXETR capillary column (30m x 0.25 mm, 0.25 mm film thickness, (J&W Scientific Inc., Folsom, CA, USA). The temperature program started at 40°C for 10 min, and increased at a rate of 3°C min⁻¹ to 200°C and held for 5 min. The carrier gas used was He at a flow-rate of 1mL min⁻¹. The injection port temperature was 260°C, the ion source temperature 240°C, and the interface temperature 230°C. Detection was carried out by electron impact mass spectrometry in total ion current (TIC) mode, using an ionization energy of 70 eV. The mass acquisition range was *m/z* 33–330. The identification of volatile compounds was confirmed by injection of pure standards, and by comparison of their retention indices (a mixture of a homologous series of C₅-C₂₈ was used), MS data reported in the literature and in the database (<http://webbook.nist.gov/chemistry/>).

Compounds for which pure standards were not available were identified on the basis of mass spectra and retention indices available in the literature. The relative concentration (mg/kg⁻¹ of oil) of the identified compounds was calculated by relating the areas of the internal standard by means of the quantifier ion (*m/z* 100) to the areas of the characteristic ions (quantifier ions) of each compound.

Statistical analysis: Significant differences among different roasted oils were tested by the one-way analysis of variance and the Duncan test for mean comparison. Statistical analyses were performed using the software package Statistica version 7 (Stat-Soft, Tulsa, OK, USA).

Acknowledgments - We thank the Slow Food Foundation for Biodiversity, Piedmont Region, and Association Ibn Al Baytar for their financial support. We are also grateful to the women of the Tighanimine co-operative. This work was realized in the frame of the emergency program of Université Mohammed V-Agdal, Project N°SCH 15/09.

References

- [1] Charrouf Z, Guillaume D. (2010) Should the Amazigh diet (regular and moderate argan-oil consumption) have a beneficial impact on human health? *Critical Reviews in Food Science and Nutrition*, **50**, 473-477.
- [2] El Monfalouti H, Guillaume D, Denhez C, Charrouf Z. (2010) Therapeutic potential of argan oil-A review. *Journal of Pharmacy and Pharmacology*, **62**, 1669-1675.
- [3] Charrouf Z, Guillaume D. (1999) Ethnoeconomical, ethnomedical, and phytochemical study of *Argania spinosa* (L.) Skeels: A review. *Journal of Ethnopharmacology*, **67**, 7-14.
- [4] Charrouf Z, Guillaume D. (2008) Argan oil, functional food, and the sustainable development of the argan forest. *Natural Product Communications*, **3**, 283-288.
- [5] Harhar H, Gharby S, Kartah B, El Monfalouti H, Guillaume D, Charrouf Z. (2011) Influence of argan kernel roasting-time on virgin argan oil composition and oxidative stability. *Plants Food for Human Nutrition*, **66**, 163-168.
- [6] Charrouf Z, El Halima H, Mallia S, Licita G, Guillaume D. (2006) Influence of roasting and seed collection on argan oil odorant composition. *Natural Product Communications*, **1**, 399-404.
- [7] Angerosa F. (2002) Influence of volatile compounds on virgin olive oil quality evaluated by analytical approaches and sensor panels. *European Journal of Lipid Science and Technology*, **104**, 639-660.
- [8] Harhar H, Gharby S, Kartah B, El Monfalouti H, Charrouf Z, Guillaume D. (2010) Long argan fruit drying time is detrimental for argan oil quality. *Natural Product Communications*, **5**, 1799-1802.
- [9] Kalua CM, Allen MS, Bedgood DR, Bishop AG, Prenzler PD, Robards K. (2007) Olive oil volatile compounds, flavour development and quality: A critical review. *Food Chemistry*, **100**, 273-286.

- [10] Koehler PE, Odell GV. (1970) Factors affecting the formation of pyrazine compounds in sugar-amine reactions. *Journal of Agricultural and Food Chemistry*, **18**, 895-898.
- [11] Maga JA. (1982) Pyrazines in foods: an update. *CRC Critical Reviews in Food Science and Nutrition*, **16**, 1-48.
- [12] Shibamoto T, Akiyama T, Sakaguchi M, Enomoto Y, Massuda A. (1979) A study of pyrazine formation. *Journal of Agricultural and Food Chemistry*, **27**, 1027-1031.
- [13] Hilali M, Charrouf Z, El Aziz Souhli A, Hachimi L, Guillaume D. (2005) Influence of origin and extraction method on argan oil physico-chemical characteristics and composition. *Journal of Agricultural and Food Chemistry*, **53**, 2081-2087.
- [14] Frankel EN. (1980) Lipid oxidation. *Progress in Lipid Research*, **19**, 1-22.
- [15] Rizzi GP. (2008) The Strecker degradation of amino acids: newer avenues for flavor formation. *Food Reviews International*, **24**, 416-435.
- [16] Choe E, Min BD (2006) Mechanisms and factors for edible oil oxidation. *Comprehensive Reviews in Food Science and Food Safety*, **5**, 169-186.
- [17] Adamiec J, Rössner J, Velisek J, Cejpek K, Savel J. (2001) Minor Strecker degradation products of phenylalanine and phenylglycine. *European Food Research and Technology*, **212**, 135-140.
- [18] Maga J, Sizer CE. (1973) Pyrazines in foods. *CRC Critical Reviews in Food Technology*, **4**, 39-115.
- [19] Siegmund B, Murkovic M. (2004) Changes in chemical composition of pumpkin seeds during the roasting process for production of pumpkin seed oil (Part 2: volatile compounds). *Food Chemistry*, **84**, 367-374.
- [20] Baker GL, Cornell JA, Gorbet DW, O'Keefe SF, Sims CA, Talcott ST. (2003) Determination of pyrazine and flavor variations in peanut genotypes during roasting. *Journal of Food Science*, **68**, 394-400.
- [21] Matthäus B, Guillaume D, Gharby S, Haddad A, Harhar H, Charrouf Z. (2010) Effect of processing on the quality of edible argan oil, *Food Chemistry*, **120**, 426-432.
- [22] Frankel EN. (1982) Volatile lipid oxidation products. *Progress in Lipid Research*, **22**, 1-33.
- [23] Krishnamurthy RG, Smouse TH, Mookherjee BD, Reddy BR, Chang SS. (1967) Identification of 2-pentyl furan in fats and oils and its relationship to the reversion flavor of soybean oil. *Journal of Food Science*, **32**, 372-374.
- [24] Maga JA. (1979) Furans in foods. *CRC Critical Reviews in Food Science and Nutrition*, **4**, 39-115.
- [25] Baccouri O, Bendini A, Cerretani L, Guerfel M, Baccouri B, Lercker G, Zarrouk M, Daoud Ben Miled D. (2008) Comparative study on volatile compounds from Tunisian and Sicilian monovarietal virgin olive oils. *Food Chemistry*, **111**, 322-328.

Fusaodavinvin, a Novel Metabolite Containing Sulfur from the Endophytic Fungus <i>Fusarium sp.</i> (CTGU-ZL-34) Liang Zhang, Yanhui Liu, Zhangshuang Deng, Zhiyong Guo, Jianfeng Chen, Xuan Tu and Kun Zou	83
Summation Solute Hydrogen Bonding Acidity Values for Hydroxyl Substituted Flavones Determined by NMR Spectroscopy William L. Whaley, Ekua M. Okoso-amaa, Cody L. Womack, Anna Vladimirova, Laura B. Rogers, Margaret J. Risher and Michael H. Abraham	85
Phenolic Content and DPPH Radical Scavenging Activity of the Flowers and Leaves of <i>Trifolium repens</i> Agnieszka Kicel and Maria Wolbiś	99
Kenganthranol F, a new Anthranol from <i>Psorospermum aurantiacum</i> Gesquiere M. Tiani, Ishtiaq Ahmed, Karsten Krohn, Ivan R. Green and Augustin E. Nkengfack	103
Inhibition of <i>In Vitro</i> Leukotriene B₄ Biosynthesis in Human Neutrophil Granulocytes and Docking Studies of Natural Quinones Premysl Landa, Zsofia Kutil, Veronika Temml, Jan Malik, Ladislav Kokoska, Ute Widowitz, Marie Pribylova, Marcela Dvorakova, Petr Marsik, Daniela Schuster, Rudolf Bauer and Tomas Vanek	105
Effect of <i>Hypogymnia physodes</i> Extracts and their Depsidones on Micronucleus Distribution in Human Lymphocytes Igor Ž. Stojanović, Miroslava Stanković, Olga Jovanović, Goran Petrović, Andrija Šmelcerović and Gordana S. Stojanović	109
A New Lyoniresinol Derivative from <i>Smilax microphylla</i> Li-Sha Liu, Hui-Lian Huang, Rong-Hua Liu, Gang Ren, Feng Shao, Yao-Hui Ye and Tao Lin	113
Anti-metastatic Activities of Bibenzyls from <i>Dendrobium pulchellum</i> Pithi Chanvorachote, Akkarawut Kowitdamrong, Thidarat Ruanghirun, Boonchoo Sritularak, Chutichot Mungmee and Kittisak Likhitwitayawuid	115
Synthesis of 3,5,3',4'-Tetrahydroxy-trans-stilbene-4'-O-β-D-glucopyranoside by Glucosyltransferases from <i>Phytolacca americana</i> Tomoya Iwakiri, Hiroya Imai, Hiroki Hamada, Toru Nakayama and Shin-ichi Ozaki	119
Challenges of Curcumin Bioavailability: Novel Aerosol Remedies Parasuraman Aiya Subramani and Venkata R. Narala	121
Molecular Analysis of <i>Vitex</i> Species Using Candidate DNA Barcoding and PCR-RFLP of the <i>matK</i> Gene for Authentication of <i>Vitex glabrata</i> Waranyoo Phoolcharoen and Suchada Sukrong	125
Volatiles from <i>Syzygium paniculatum</i> Fruit Clara E. Quijano-Célis, Daniel Echeverri-Gil, Yinet Ruiz and Jorge A. Pino	129
Seasonal Variations in the Composition of the Essential Oils of Rosemary (<i>Rosmarinus officinalis</i>, Lamiaceae) Dmitar Lakušić, Mihailo Ristić, Violeta Slavkovska and Branislava Lakušić	131
Chemical Compositions and Antimicrobial and Antioxidant Activities of the Essential Oils from <i>Magnolia grandiflora</i>, <i>Chrysactinia mexicana</i>, and <i>Schinus molle</i> Found in Northeast Mexico Laura Guerra-Boone, Rocío Álvarez-Román, Ricardo Salazar-Aranda, Anabel Torres-Cirio, Verónica Mayela Rivas-Galindo, Noemí Waksman de Torres, Gloria María González González and Luis Alejandro Pérez-López	135
Chemical Composition and Biological Activities of the Essential Oil from <i>Calamintha nepeta</i> Plants from the Wild in Southern Italy Emilia Mancini, Laura De Martino, Hanna Malova and Vincenzo De Feo	139
Composition and <i>in-vitro</i> Cytotoxic Activities of the Leaf Essential Oil of <i>Beilschmiedia erythrophloia</i> from Taiwan Yu-Chang Su and Chen-Lung Ho	143

Natural Product Communications

2013

Volume 8, Number 1

Contents

Argan Tree Metabolites and Argan Oil (Guest Editor: Dom Guillaume)

<u>Original Paper</u>	<u>Page</u>
The Social and Environmental Context of Argan Oil Production Yann le Polain de Waroux	1
Climatic Conditions and Herbivory Effects on Morphological Plasticity of <i>Argania spinosa</i> Fatima Ain-Lhout, María Zunzunegui, Mari Cruz Díaz Barradas, Juan Jáuregui, Tarik Tagma and Said Boutaleb	5
Some Secrets of <i>Argania spinosa</i> Water Economy in a Semiarid Climate Mari Cruz Díaz Barradas, María Zunzunegui, Mari Paz Esquivias, Said Boutaleb, Javier Valera-Burgos, Tarek Tagma and Fátima Ain-Lhout	11
Germination Success and Seedling Development of <i>Argania spinosa</i> under Different Climatic Conditions and Browsing Intensity María Zunzunegui, Juan Jáuregui, Fatima Ain-Lhout, Said Boutaleb, Leonor Álvarez-Cansino and MariPaz Esquivias	15
Modeling of the Distribution of Heavy Metals and Trace Elements in Argan Forest Soil and Parts of Argan Tree Faez A. E. Mohammed, Rahma Behitou, Mohamed Boulmane, Ahmed Bouhaouss and Dominique Guillaume	21
Can Fruit-form be a Marker for Argan Oil Production? Saïd Gharby, Hicham Harhar, Badr Eddine Kartah, Hanae El Monfalouti, Clément Denhez, Miloudi Hilali, Dom Guillaume and Zoubida Charrouf	25
Chemical Changes in Extra Virgin Argan Oil after Thermal Treatment Saïd Gharby, Hicham Harhar, Badr Eddine Kartah, Dom Guillaume and Zoubida Charrouf	29
Volatile Compound Formation During Argan Kernel Roasting Hanae El Monfalouti, Zoubida Charrouf, Manuela Giordano, Dominique Guillaume, Badreddine Kartah, Hicham Harhar, Saïd Gharby, Clément Denhez and Giuseppe Zeppa	33
Quality Parameters for Cold Pressed Edible Argan Oils Bertrand Matthäus	37
Triterpenoids from <i>Argania spinosa</i>: 20 Years of Research Imane Chafchaouini-Moussaoui, Zoubida Charrouf and Dom Guillaume	43
Argan Oil-contained Antioxidants for Human Mitochondria Luis C. López, Carmen Cabrera-Vique, Carmen Venegas, Laura García-Corzo, Marta Luna-Sánchez, Darío Acuña-Castroviejo and Germaine Escames	47
Effect of Argan and Olive Oil Consumption on the Hormonal Profile of Androgens Among Healthy Adult Moroccan Men Abdelfettah Derouiche, Ali Jafri, Issam Driouch, Mohammed El Khasmi, Ahmed Adlouni, Nada Benajiba, Youssef Bamou, Rachid Saïle and Mohammed Benouhoud	51
Argan Oil and Postmenopausal Moroccan Women: Impact on the Vitamin E Profile Hanae El Monfalouti, Zoubida Charrouf, Asma El Hamdouchi, Hanane Labraimi, Imane Chafchaouini-Moussaoui, Badreddine Kartah, Khalid El Kari, Yahya Bensouda, Abdelfettah Derouich, Sylvie Dodin, Clément Denhez, Dom Guillaume and Hassan Agnaou	55

Microbial Transformations of Isophorone by <i>Alternaria alternata</i> and <i>Neurospora crassa</i> Ismail Kiran, Özge Özşen, Turgay Çelik, Semra İlhan, Bükay Yenice Gürsu and Fatih Demirci	59
Headspace, Solid-phase Micro-extraction, Gas Chromatographic-Mass Spectrometric Analysis of Terpenoids in the Latex of <i>Euphorbia</i> Species Asmita V. Patel, Stephen Sumner, H. Leslie Thompson, Gerald Blunden, David Wright, Liu Jun-feng and Zan Jun-feng	63
Trichodermaerin, a New Diterpenoid Lactone from the Marine Fungus <i>Trichoderma erinaceum</i> Associated with the Sea Star <i>Acanthaster planci</i> Zhong-Liang Xie, Hou-Jin Li, Lai-You Wang, Wan-Ling Liang, Wei Liu and Wen-Jian Lan	67
Chemical Composition and Biological Activities of Soldiers of the Brazilian Termite Species, <i>Nasutitermes macrocephalus</i> (Isoptera: Natutitermitinae) Márcia N. S. de la Cruz, Helvécio M. S. Júnior, Denilson F. Oliveira, Letícia V. Costa-Lotufo, Antonio G. Ferreira, Daniela S. Alviano and Claudia M. Rezende	69
Evaluation of the Quality of Chinese and Vietnamese Cassia Using LC-MS and Multivariate Analysis Ken Tanaka, Feng Li, Yasuhiro Tezuka, Shiro Watanabe, Nobuo Kawahara and Hiroaki Kida	75
Norcucurbitane Triterpenoids from the Fruits of <i>Momordica charantia</i> var. <i>abbreviata</i> Yun-Wen Liao, Chiy-Rong Chen, Jue-Liang Hsu, Yun-Sheng Lin, Hsueh-Ling Cheng, Wen-Ling Shih, Yueh-Hsiung Kuo and Chi-I Chang	79

Continued inside backcover