Grasas y Aceites Vol. 54. Fasc. 4 (2003), 335-338

335

# INVESTIGACIÓN

# Study of the composition of pyracantha crenulata roem seed, oil and meal

By Olinda E. Quiroga, Soledad M. Bou, Carlos I. Sarlingo and Susana M. Nolasco\*

Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires, Avda. del Valle 5737, B7400JWI-Olavarría, Argentina, Tel/Fax: 54-02284-451055/56, e-mail: snolasco@fio.unicen.edu.ar.

#### RESUMEN

#### Estudio de la composición química de la semilla, harina y aceite seminal de *Pyracantha crenulata Roem.*

Semillas de *Pyracantha crenulata* Roem, provenientes de frutos cosechados en Olavarría (provincia de Buenos Aires, Argentina) se trataron con hexano (soxhlet) obteniéndose el aceite crudo (rendimiento: 5,5 %) y la harina residual de extracción. Las características fisicoquímicas del aceite crudo fueron: índice de refracción: 1,4770 (a 25°C); índice de iodo: 121; índice de saponificación: 203; insaponificable: 7,4%, índice de peróxidos (mEq/kg) 8,7. Se determinó la composición acidica del aceite por cromatografía gasliquido. Los ácidos grasos mayoritarios fueron: ácido linoleico (61,1%), ácido oleico (17,3%) y ácido palmítico (17,4%). La harina residual de extracción contenia baja proporción de

La harina residual de extracción contenía baja proporción de proteina cruda (13% b.s), considerable contenido de fibra cruda; y un valor de fibra detergente neutra relativamente alto, lo que concuerda con la muy baja digestibilidad observada. Se informan valores de cenizas, minerales e hidratos de carbono.

PALABRAS-CLAVE: Aceite - Ácidos grasos (composición en) - Composición química - Harina - Pyracantha crenulata Roem - Semilla.

#### SUMMARY

# Study of the composition of *Pyracantha crenulata Roem* seed, oil and meal.

Seeds from *Pyracantha crenulata* Roem, harvested in Olavarría (Buenos Aires, Argentine) were defatted with hexane, obtaining raw oil with a yield of 5.5 % dry basis. The physicochemical characteristics of crude oil were: refractive index: 1.4770 (at 25°C), iodine value: 121; saponification index: 203, unsaponifiable matter: 7.4 %, peroxide value: 8.7. The fatty acid composition of seed oil was studied by gas-liquid chromatography. Major fatty acids of seed oil were: linoleic (61.1 %), oleic (17.3 %) and palmitic acid (17.4 %). The residual seed meal contained low level of crude protein

The residual seed meal contained low level of crude protein (13%, dry basis), considerable content of crude fiber and a relativity high value of neutral detergent fiber, that matching with the low digestibility observed. Metals, ash, sugar and polysaccharides contents are reported.

KEY-WORDS: Chemical composition - Fatty acid (composition in) - Meal - Oil - Pyracantha crenulata Roem - Seed.

### 1. INTRODUCTION

Pyracantha crenulata Roem is a 1 to 3 metre highly ramified and prickly bush. Some of its characteristics are: 5 cm length alternate oblong leaves, shrewdly jogged and brilliant on their superior side, white flowers and orange colour fruit. It belongs to the family *Rosaceae*, from which many fruits (naturally or processed) are used for food, such as plums, apricots or hit-rose. This kind of plant comes from China and it is widely used as an ornamental plant (Cabrera, 1963; Dinitri, 1987).

Studies about fruit composition of the *Pyracantha* genus have been carried out (Maskey and Shah, 1982; Deng *et al.*, 1990; Wong *et al.*, 1992; Quiroga *et al.*, 1994) and information referred to crude oil extraction characteristics has been obtained (Suzuki *et al.*, 1973; Mitsushashi *et al.*, 1977; Endo *et al.*, 1983), but data available on extracted meal composition is scanty (Wiese *et al.*, 1995). An exhaustive survey of the literature reveals that no information is available on the characteristics and chemical composition of seed of *P. crenulata Roem.* 

Due to the wide distribution in Argentina, it was considered of interest to perform a study on the general chemical composition of this seed species so as to contribute with data that determine its possible utilisation. The present investigation was carried out to determinate the physical and chemical characteristics of seeds, oil and meal of *P. crenulata Roem.* 

#### 2. EXPERIMENTAL

Seeds of ripe fruits harvested in Olavarría (Buenos Aires province, Argentine, crop 2000) were manually separated and their size, mean weight and moisture content were determined. The seeds were ground, and the lipid fraction was extracted with n-hexane (Soxhlet). The remaining solvent was removed from the residual meal (40-50°C, vacuum).

#### 2.1. Lipid fraction examination

The physical and chemical characteristics of the lipid fractions were determined according to the following methods: refractive index (Abbe refractometer, 25°C);

Grasas y Aceites

viscosity and specific gravity (Rodenbush *et al.*, 1999); combustion heat (Bertman, 1997); saponification value method 920.160 (AOAC, 1990); unsaponifiable matter, method Ca 6b- 53 (AOCS, 1998); iodine value of the unsaponifiable (Rosenmund); Acid value, method Ca 5a-40 (AOCS, 1998); peroxide value, method 2501 (IUPAC, 1992). The iodine value of the total fatty acid was calculated from its percentage composition obtained from CGL, method Cd 1c- 85 (AOCS, 1998).

Fatty acid composition was assessed by gas chromatography-mass spectrometry (GC/MS) of the methyl esters of the total acids, free of the unsaponifiable fraction, obtained by esterification with methanol containing 1.5 % H<sub>2</sub>SO<sub>4</sub> (Hilditch and Williams, 1964). A GC-MS Hewlett Packard (gas chromatograph 5890-mass spectrometer 5972) was employed. The GC was equipped with a SPB-5 capillary column (30 m x 0.25 mm, 2.5  $\mu$ m film thickness). The oven temperature was programmed from 70°C to 290°C with a 10°C/min increase. The injector temperature was 280°C. The carrier gas was helium at a flow rate of 30 mL/min. Methyl esters of fatty acid were identified by comparison with the retention times and mass spectrums of standards.

The presence of conjugated polyunsaturated acids was investigated spectrophotometrically according to method Cd-758 (AOCS, 1998).

The methyl esters were examined by infrared (IR) absorption as a liquid film on a FTIR Nicolet Magna System 550 spectrometer.

#### 2.2. Residual meal examination

The following characteristics were determined according to the AOAC (1990) methods, except where otherwise noted: moisture content, method Ba 2a--38 (AOCS, 1998); ash, method Ba 5a-49 (AOCS, 1998); reducing and non-reducing sugars (methods 925.05 and 925.11); hydrolyzable carbohydrates (methods 920.40 and 925.11); crude fiber (method 926.09); total nitrogen (Kjeldahl), method 959.04c; urease activity, method Ba 9-58 (AOCS, 1998); total phosphorus, method Ca 12-55 (AOCS, 1998); calcium (method 927.02); Cu, Zn, Mg and Na (atomic absorption: Osborne and Voogt, 1978); dry mass and organic matter digestibility (Tilley and Terry, 1963); neutral detergent fiber (NDF), acid detergent fiber (ADF), lignin, cellulose and silica (Goering and Van Soest, 1970).

The following data are triplicate averages expressed on dry basis (d.b.).

#### 3. RESULTS AND DISCUSSION

Physical and chemical characteristics and composition of *P. crenulata Roem* are shown in Table I and II.

Table I		
Physical and chemical Characteristics of Pyracant- ha crenulata Roem.		
Fruit and seed		

FRUIT	
Color	orange
Туре	berry
Length (mm)	$\textbf{6.2} \pm \textbf{0.685}$
Thickness (mm)	7.8 ± 1.081
Number of seeds/ fruit	5
SEED	
Color	brownie black
Number of seeds/g	315
Length (mm)	$2.68 \pm 0.319$
Thickness (mm)	$1.38 \pm 0.148$
Oil (%)	$5.5\pm0.526$
Moisture (%)	$9.4\pm0.725$

Table I shows a high value in the number of seeds per gram, thus implying that the seed size is very small, as corroborated by data about these seed dimensions.

Seed moisture content was relatively high (10.4%) yielding 5.5 % (d.b.) of a limpid yellow oil at room temperature, by extraction with hexane. Oil yield is quite low but similar to those reported for *P. angustifolia* (Endo *et al.*, 1983) and *P. atalantoides* (Wiese *et al.*, 1995).

The high level of unsaponifiable fraction and the high saponification value suggest a low concentration of acids with a high molecular weight (Table II). However, the unsaponifiable matter (%) was smaller than the value reported by Endo *et al.* (1983) for *P. angustifolia* and by Wiese *et al.* (1995) for *P. atalantoides* (20.5% and 12 %, respectively).

Some parameters indicating either the oil quality or its deterioration such as the peroxide value and

#### Table II Physical and chemical Characteristics of Pyracantha crenulata Roem. Seed lipid fraction

Colour	yellow
lodine value	121
Peroxide value	8.7
Acid value	2.5
Saponification value (mg KOH/g )	203
Unsaponifiable matter (%)	7.4
lodine value of unsaponifiable	56.7
Refractive index (25°C)	1.4770
Viscosity (cp ; 25°C)	57.94
Specific gravity (15°C)	0.9205
Combustion heat (cal/g)	9.402

Table III Pyracantha crenulata Roem : fatty acid composition

Fatty acids	% of total fatty acids
14:0	0.7
16:0	17.4
16:1	0.5
18:0	2.2
18:1	17.3
18:2	61.1
20:0	0.8
Total saturated acids	21.1
Total non saturated acids	78.9

acid value resulted relatively low, the latter indicating low lipase activity.

The results of the fatty acid composition expressed in methyl ester percentages are shown in Table III.

The iodine value was calculated in base to this composition (Table II). It indicated that the oil was of the semidrying type. Major components were linoleic, palmitic and oleic acids, in that order. The high linoleic acid value (61.1 %) was similar to those found in safflower and sunflower oils (Gustone et al, 1994). This percentage was considerably greater than the values reported by Endo et al. (1983) and Suzuki et al. (1973) for P. angustifolia (45.2% and 22.5%, respectively). The content of linoleic acid is highly interesting due to its nutritional importance (essential fatty acid). The percentage of saturated acids was 21.1%, mostly consisting of palmitic acid. But the content of palmitic acid was less than the 23.7% and 37.4% reported by Endo et al. (1983) and Suzuki et al. (1973, respectively, for P. angustifolia. The arachidic acid (only acid with more than 18 carbon atoms detected) was present in small amounts (0.8%).

Ultraviolet spectrophotometric analysis disclosed a low proportion of conjugated triene ( $C_3 = 0.11\%$ ), and neither conjugated diene nor tetraene was detected.

IR spectra showed a bond at 3435 cm<sup>1</sup>, indicative of the presence of the hydroxyl group. Bonds at 914-847 cm<sup>1</sup> relative to the probable presence of the epoxy groups were detected as well.

In spite of having a fatty acid composition with characteristics similar to sunflower oil, the *P* crenulata Roem oil yield is quite lower, showing the seed as a poor lipid source for industrial application.

Table IV lists the results achieved from the analysis of the meal.

*P. crenulata* meal had higher contents of fiber (34.4%), particularly cellulose, and lowers content of

Table IV Chemical Composition of *Pyracantha crenulata Roem.* Seed Meal

Dry matter (%)	85.5-92
Ash (%)	5.2
Crude protein (N x 6,25) (%)	13.0
Crude fiber (%)	34.4
Reducing sugars % (as glucose)	0.7
Non reducing sugars % (as sucrose)	1.1
Hydrolyzable carbohydrates % (as starch)	12.0
Urease activity	Undetected
Organic matter (%)	93.1
Neutral detergent fiber (NDF)	61.0
Acid detergent fiber (ADF)	41.7
Lignin	8.5
Cellulose	32.6
Silica	traces
Dry matter digestibility	23.4
Organic matter digestibility	19.5
Digestible energy	0.7
Total phosphorus (%)	0.03
Calcium (%)	0.13
Copper (p.p.m.)	24.00
Zinc (p.p.m.)	77.45
Magnesium (p.p.m.)	1273.86
Sodium (p.p.m.)	2957.02

Except dry matter and digestible energy, all the results are expressed on a dry basis.

protein (13 % d.b.) and ash (5.2 %d.b.). The carbohydrate concentration was very low for both reducing and non-reducing sugar with an important concentration in hydrolyzable carbohydrates. Our values for *P. crenulata* are similar to data on carbohydrate concentration for *P. atalantoides* meal reported by Wiese *et al.* (1995).

The analysis of the ash showed a significant (>1000 ppm) concentration of sodium, calcium and magnesium. Copper, zinc and phosphorus ranged from 24 to 300 ppm (Table IV) The low concentration of phosphorus determined that the Ca/P ratio was greater than that one required for an adequate absorption in infants and adults (1,5:1 and 1:1, respectively; Llyod *et al.*, 1982).

As regards to animal feeding, although the protein content of the meal showed a value considered adequate for a good ruminant functioning, the crude fiber content and the cellular wall membrane content (NDF) was considerably high, concordant with the low digestibility observed. These results indicated that meal would be useful only for animal maintenance or for increasing their weight slightly (Aello and Di Marco, 1997).

We believe that these preliminary findings will prove useful for further studies on *P. crenulata Roem* seed, particularly regarding the aminoacid composition of seed proteins and its potentially toxic components. *P. crenulata Roem* belongs to a genus where most members produce hydrogen cyanide. This toxin is found mainly in the leaves and seed, usually in small quantity. In small doses, hydrogen cyanide has been shown to stimulate respiration and improve digestion. However, in excess it can cause respiratory failure and even death (Plants For A Future and Ken Fern, 1992-2002).

# ACKNOWLEDGEMENTS

This research work was supported by the "Universidad Nacional del Centro de la Provincia de Buenos Aires (Argentina)" and the Commission of Scientific Investigation of Buenos Aires Province. The authors thank Agr. Engineer Carlos D'Alfonso (Agronomy Faculty, U.N.C, Azul, Argentina) for the sample identification.

# REFERENCES

- Aello, M.; Di Marco O. (1997) Curso de Nutrición Animal Facultad de Ciencias Agrarias, Universidad Nacional de Mar del Plata, Argentina.
- AOAC (1990) Official Methods of Analysis of the
- Association, of Official Analytical Chemists, Ed. W. Horwitz, 14<sup>th</sup>. edition, Washington, D.C. AOCS (1998) Official and Tentative Methods of the American Oil Chemists' Society, 5<sup>th</sup> edition, Chicago, Illinois
- Bertman, S.H. (1997) Chem. Technol. (Dordrecht) 1.101 citado por Sipos, E.F.; Szuhaj, B.F., Aceites y Grasas, 27: 193-199
- Cabrera, A. L. (1963) Flora de la Provincia de Buenos Aires, Colección Científica I.N.T.A. (Instituto Nacional
- de Tecnología Agropecuaria), Buenos Aires. Deng, Rufu; Wang, Sangen; Li, Guarong, (1990) Nutrients in fruit of wild fire thorn, Yngyang Xuebad, 12 (1), 79-83.
- iitri, M. J. (1972) Enciclopedia de Agricultura y Jardinería, Ed. ACME, Buenos Aires, Vol I, pp. Dimitri M 433-435.
- Endo, Setsuko; Jos, Setsuko; Yamagata, Noriko; Ohtsuji, Takashi; Mitsushashi, Tatsuo (1983) Fatty Acids and Sterols in the Seed Oils of *Rosaceae*, Bulletin of Tokyo Gakugei
- Goering, H.R.; Van Soest, PJ. (1970) Forage fiber analysis, Agriculture Handbook N<sup>o</sup> 379, Agriculture Research Service, USDA, Washington D.C..

- Gustone, F.D.; Harwood, J.L. and Pady, F.B. (1994) The Lipid Handbook, 2<sup>nd</sup> edition Chapman & Hall . London.
   Hilditch, T.P.; Williams, P.N. (1964) The Chemical Constitution of Natural Fat, 4<sup>th</sup> edition, Chapman &
- Hall, London, p.688. IUPAC (1992) Standard Methods for the Analysis of Oils, Fats and Derivates, 7<sup>th</sup> edition, C. Paquot y A.S. Hautfenne (Ed.) International Union of Pure and Applied Chemistry, Blackwell Scientific Publications

- Applied Chemistry, Blackwell Scientific Publications Inc., Oxford.
  Llyod L.E.; Mc Donald B.E.; Crampton E.W. (1982) Fundamentos de Nutrición, Ed. Acribia, Zaragoza.
  Maskey, K.; Shah, B.B. (1982) Sugar in some Nepalese edible wild fruits, J. Nepal Chem. Soc. 2, 23-30.
  Mitsushashi, Tatsuo; Ohtake, Yukiko; Nishio, Akiko; Yamamoto, Yoshiya; Sugai, Hiroko; Endo, Setsuko (1977) The seed oils from four species of *Rosaceae*, Tokyo Gakugei Daigaku Kiyo, Dai-4-Sb, 29, 120-124.
  Osborne, D.R.; Vooget (1978) Análisis de los nutrientes de los alimentos, Ed. Acribia, Zaragoza.
  Plants for a Future and Ken Fern (1992-2002) Plants For A Future Species Database, England.
- Future Species Database, England.
- Quiroga, O.E.; Wiese, B.; Vigo, M.S.; Nolasco, S.M. (1994)
   Composición química de los frutos de *Pyracantha* atalantoides y Cotoneaster glaucophylla (Rosaceas), Alimentos, VI Congreso Argentino de Ciencia y Tecnología de Alimentos, 419-421.
   Rodenbush, C.M.; Hsieh, F.H.; Viswanath, D.S. (1999)
   Donsity and Viscositu of Vacatable Oils. L. Amor. Oils
- Density and Viscosity of Vegetable Oils, J. Amer. Oil Chemists' Soc., 76 (12) 1415 1419. Suzuki, S.; Satoh, J.Y.; Hagitani, A. (1973) Petrol soluble
- constituents of the seeds of Pyracantha angustifolia,
- Phytochemistry, 12, p.1193.
   Tilley, J.H.A.; Terry, R.A.A. (1963) Two-stage technique for the *in vitro* digestion of forage crops, J. Brit. Grassld. Soc., 18, 104-111.
- Wiese, B.; Quiroga, O.E.; Vigo, M.S.; Nolasco, S.M. (1995) Estudio sobre semilla de *Pyracantha atalantoides* (Hance): aceite crudo de extracción y harina residual, Revista COPAQUI, 15, 818-825.
- Wong, J.; Liao, D.; Li, Q.; Wang, Z. (1992) Chemical constituents and function of *Pyracantha Roemer* pigments, Shipin Kexue, 152, 4-6.

Recibido: Septiembre 2002 Aceptado: Febrero 2003

# 338