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Polyphenols in the Waste Water Produced during the Hydrodistillation of 'Narcea Roses' Cultivated in the Cibea River Valley (Northern Spain)

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Abstract: The 'Narcea rose' is a recently described yet ancient rose cultivar of interest to the perfume industry. Given its excellent adaptation to the conditions of the place where it was rediscovered, the possibilities of its horticultural/industrial production have been under examination for some time. The hydrodistillation process produces a red-to-brownish mixture of water and rose petals that could contain compounds that could be used in other industrial procedures. Their recovery and further utilization would reduce disposal costs and improve the sustainability of relevant industries. This work reports the quantification, by high-performance liquid chromatography (HPLC–MS) and quadrupole time of flight Q-TOF analyses, of the polyphenol content in the waste water. This waste was found to contain high concentrations of quercetin, gallic acid and ellagic acid, as well as smaller concentrations of kaempferol and its derivatives, all of which can influence plant, human and animal health.

Keywords: ancient cultivated rose; hydrodistillation; waste water; zero waste; flavonoids; quercetin; health

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1. Introduction

The 'Narcea rose' is an ancient rose cultivar that was recently rediscovered in a private garden in the Cibea River Valley (situated in Cangas del Narcea, among the Cantabrian Mountains of Asturias, northern Spain) [1]. Botanical and genetic studies have shown it to be a natural hybrid of *Rosa gallica* and *Rosa centifolia*—and indeed it has characteristics of both. However, it has red-purple petals [1], quite different to the light-pink-coloured petals of the parental species. The Narcea rose is very well adapted to the mountainous area in which it was found, where winters are very cold and solar radiation is variable depending on altitude and orography. It blooms most intensely and with maximum scent production in May. Interestingly, it appears to be little affected by disease and shows good horticultural behaviour.

In recent years, the perfume industry has demonstrated growing interest in the use of natural raw materials from sustainably produced crops. In addition, there is much interest in their environmentally friendly transformation and production with zero waste, or at least waste that can be recycled. In this regard, several papers have been published showing the possible health-related [2,3] and animal feed [4] uses of the wastes produced during the hydrodistillation of *R. damascena*.

The intensity and persistence of the aroma of rose essential oils is influenced by different factors, including rose variety [5,6], the moment of petal collection, soil type and the

cultivation practices to which the plants were subject [7–10]. Similarly, the polyphenol and antioxidant contents of rose petals are strongly influenced by environmental, geographic and edaphic factors [3,11].

The perfume industry uses two extraction techniques for rose materials: solvent extraction and hydrodistillation. Solvent extraction gives rise to a solid known as 'rose concrete' that, after treatment with alcohol to eliminate paraffins and other waxes, generates an intensely scented liquid known as 'absolute'. The waste generated in this process consists of left-over rose petals impregnated with solvent but which still show their characteristic colour (red, pink or purple, etc.). Solvent extraction is much quicker and more efficient, but it requires more complex installations for the safe storage of the solvents needed. Further, it produces more contaminating wastes that require proper disposal. Fortunately, solvent extraction has been much improved in recent years, and to a large extent the solvents used can be recovered and reused. Hydrodistillation, in contrast, uses no chemical contaminants, although it does require a greater energy input. After 5–7 h of treatment, which provides essential oils and rose water, a red-to-brownish waste (depending on the rose variety used) is generated, composed only of water and petals. During hydrodistillation, volatile aromatic compounds are extracted in the rising vapour of water and lipid droplets. Condensation in the still's serpentine coil produces two fractions: essential oil and rose water. The polyphenols in the petals, given their water-soluble nature, remain in the waste water left at the end of the process. In fact, some of these give the water its colour.

The leaves, flowers and fruits of certain members of *Rosaceae* have a long medicinal and culinary history [3,12]. The hips of some species have been used for the treatment of colds and influenza, inflammation and chronic pain [13], and in cosmetic preparations for the skin [14,15]. Many of the medicinal properties of the genus *Rosa* lie in the high concentrations of polyphenols found in different tissues and organs [16,17]. Studies on the composition of *Rosa rose* hips [13,14,18,19] have shown that these organs are rich in bioactive compounds, such as ascorbic acid, antioxidants and polyphenols such as anthocyanins and flavonols. *Rosa* leaves [20,21] and preparations made from the petals [3,17,22–24] also contain polyphenols, especially anthocyanins (cyanidins and peonidins) and flavonoids (kaempferol, quercetin, procyanidins and proanthocyanidins). Göktürk-Baydar and Baydar [25], who analysed the extracts of *R. damascena* green leaves and flowers (fresh and withered), reported catechin and epicatechin to be the most abundant flavonols in the leaves, and gallic acid (phenolic acid) to be the most abundant in the petals. The polyphenol content of *R. gallica* petals explains the historic medicinal use of this species [20,23,24,26,27].

Polyphenols are secondary plant metabolites with a wide range of structures and functions which possess at least one aromatic ring to which is bound one or more hydroxyl groups. They are classed (and subclassed) depending on the number of phenolic rings they possess and the structural elements these contain. Some are physiologically indispensable [28]; others have roles in the response to light or water stimulus and stress, etc. [29]. Since polyphenols accumulate in certain plant tissues, they may act as micronutrients in the human diet, while their biochemical activities, for example, as antioxidants, anti-inflammatory agents, anticancer compounds and antimutagenic agents [18,24,30], have an influence on human health [31–34].

Studies have shown the beneficial effects of flavonols in animal and plant health. The procyanidins, in particular, have been ascribed antifungal, antimicrobial and bactericidal properties. It is believed that their bactericidal effect is greater against Gram-positive bacteria, since the external membrane of these organisms lies close to the cytoplasmic membrane [35,36]. Different authors [37–39] have indicated that they can be used as feed additives for ruminants; flavonoids improve the production of volatile fatty acids and reduce concentrations of ammonia and methane in the rumen. They also have a positive effect on fermentation (antibiotic effect) and acidosis in the rumen, as well as on bloating.

The aim of the present work was to determine whether certain polyphenols of interest are present in the waste water produced during the hydrodistillation of Narcea roses and thereby provide further evidence of the potential industrial uses of this variety.

2. Materials and Methods

2.1. Plant Material and Cultivation Conditions

The plant material used in this work was obtained from red-purple flowers from different Narcea rose plants (Figure 1), all cultivated in the same plot (altitude 535 m) in the Cibea River Valley (mean annual temperature 12.39 °C, mean absolute maximum temperature 28.21 °C, mean absolute minimum temperature 1.32 °C, annual rainfall 1217.15 mm). The soil in this plot is a highly acidic loam with a moderate organic matter content and with high available phosphate, medium assimilable potassium and mid-range exchangeable magnesium values. Its ion exchange complex ratio is Ca:Mg:K = 70:14:16.

Figure 1. A Narcea rose in flower.

2.2. Collection and Transport of Rose Flowers

Complete rose flowers (on 5 cm stems) were cut on 13 May 2020 from their bushes early in the morning. The stems were stuck in water-soaked phenolic floral foam and the samples were placed in a plastic-lined polystyrene box with a sealable lid. On the evening of the same day, the samples were transported by car to the laboratory, where the next day they were subjected to hydrodistillation.

2.3. Hydrodistillation and the Waste Water Produced

One-hundred-and-fifty grams of rose petals and 450 mL of distilled water were placed in a compact Behr-KOL 2 apparatus with a 1000 mL capacity flask (Figure 2). Two hydrodistillations were performed: one lasting 3 h and the other lasting 4 h. When complete, the remaining contents of the flasks (water and rose petals) were filtered to separate the petals from the now reddish waste water (Figure 3). Waste waters from 3 h and 4 h distillations were then pooled in 500 mL flasks (in a single bottle), allowed to cool to room temperature and then stored in a refrigerator at 4 °C. One week later (21 May) these samples were sent to the *Instituto de Ciencia y Tecnología de Alimentos y Nutrición* (ICTAN) for analysis.

Figure 2. Hydrodistillation apparatus with flask charged with petals.

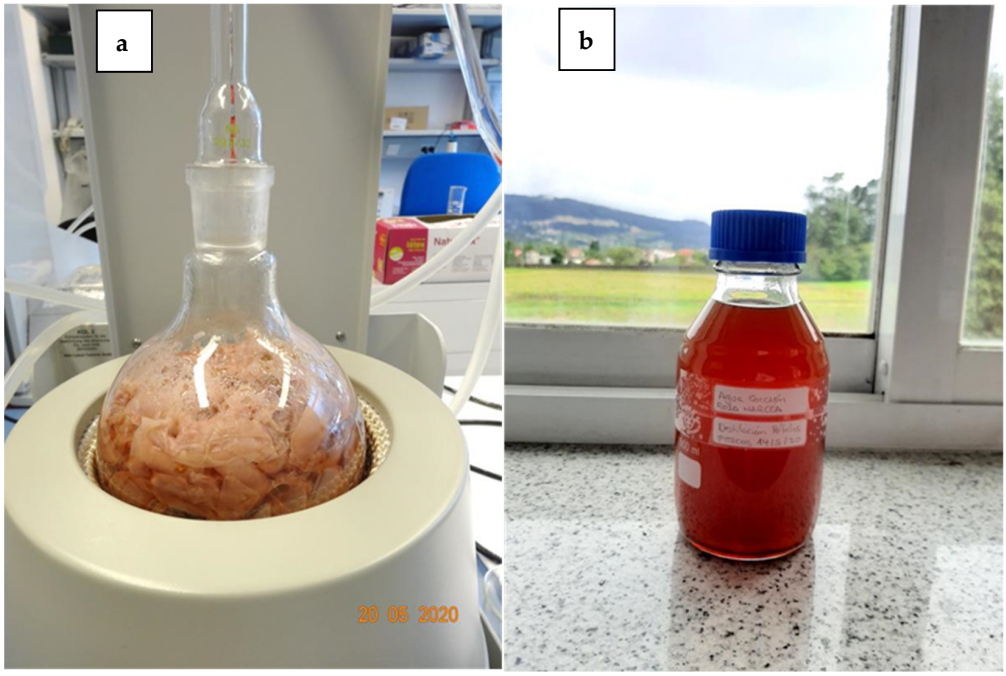

Figure 3. (**a**) Flask containing petals and water-view during hydrodistillation. (**b**) Flask containing waste water from the hydrodistillation process.

2.4. Waste Water Analysis

Upon arrival at the ICTAN (22 May), the samples were frozen at −80 °C until analysis. After thawing, the samples were analysed without further dilution or processing to determine the contents of bioactive flavonoids most commonly cited for *Rosa* leaves and fruits, i.e., cyanidin, kaempferol and quercetin, as well as their derivatives. Flavonols common in plants, including catechin and the Procyanidin B1 (PB1) dimer, were also searched for, as

were non-flavonoid polyphenols, such as benzoic acid and its derivatives gallic acid and ellagic acid.

Polyphenols were analysed by high performance liquid chromatography–quadrupole time-of-flight mass spectrometry (HPLC–MS Q-TOF). The HPLC–MS Q-TOF system involved an Agilent 1200 series HPLC equipped with an Agilent ZORBAX Eclipse XDB-C18 column (Santa Clara, CA, USA) (4.6 mm × 150 mm × 5 µm) at 40 °C. The mobile phase consisted of water containing 1% formic acid (A) and acetonitrile with 1% formic acid (B). The elution gradient was 5% B at 0 min, 15% B at 20 min, 30% B at 30 min, 50% B at 35 min, 5% at 37 min and 5% at 40 min. The flow rate was 1 mL/min.

Compound identification/quantification was performed by MS and MS/MS Q-TOF acquisition (2 GHz, low mass range (1700 *m/z*), negative polarity, drying gas 10 L 350 °C, sheath gas 11 L 350 °C, nebulizer 45 psi, cap voltage 4000 V, fragment or voltage 150 V). A collision energy of 20 V was used for all MS/MS experiments. Data capture and analysis were performed using the Data Analysis B. 05.01 and Qualitative Analysis B. 07.00 routines of the MassHunter Workstation software (Agilent Technologies, Waldbroon, Germany).

Identification and Quantification

The majority of the compounds that appeared in the HPLC chromatogram were identified from their exact mass and fragmentation patterns. They were quantified by making use of the negative polarity signal, extracting the (M-H) (the predomination) for each compound. The quantification patterns used were those of:

- Cyanidin-glucoside (for the derivatives of cyanidin);
- Kaempferol-glucoside (for the derivatives of kaempferol); and
- Quercetin-glucoside (for the derivatives of quercetin and other less abundant compounds).

3. Results

Table 1 shows the majority of compounds identified and quantified, along with their (M-H) values. The quantification pattern for quercetin-glucoside matched one of the compounds identified, confirming its identity.

The most common compounds were quercetin and its derivatives (Figure 4), plus gallic acid and ellagic acid. Among the quercetin derivatives, the most abundant was quercetin-glucoside (quercetin-3-O glucoside), quercetin-rhamnoside and quercetin-galactoside. Kaempferol-rhamnoside and kaempferol-galactoside were also detected.

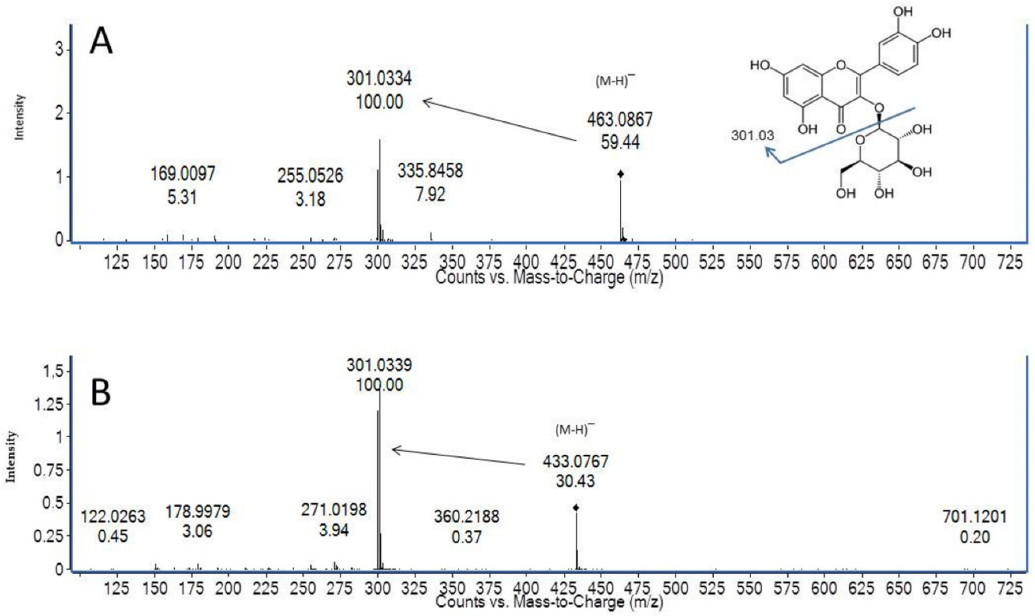

Figure 4. MS/MS spectra typical fragments for Quercetin-hexoside (Quercetin-3-O-Glucoside) (**A**) and Quercetin-pentoside (**B**).

Table 1. Phenolic compounds identified in the waste water of Narcea rose hydrodistillations.

ANTHOCYANINS	M-H	Formula	Score%	MS/MS	Fragment Identity	TR min	Means (μg/g)	S.D
CYANIDIN-DIGLUCOSIDE	**609.1461**	**$C_{27}H_{31}O_{16}$**	**97.9**	285	Cyanidin	**6.9**	13.45	3.01
FLAVONOLS [1]	**M-H**	**Formula**	**Score%**	**MS/MS**	**Fragment identity**	**TR min**	**Means (μg/g)**	**S.D**
KAEMPFEROL	**285.0405**	**$C_{15}H_{10}O_6$**	**97.6**			**34.2**	13.76	2.53
KAEMPFEROL-PENTOSIDE	**417.0827**	**$C_{20}H_{18}O_{10}$**	**97.9**	285	Kaempferol	**27.6**	13.76	0.70
KAEMPFEROL-PENTOSIDE	**417.0827**	**$C_{20}H_{18}O_{10}$**	**96.9**	285	Kaempferol	**28.2**	37.99	1.88
KAEMPFEROL-RHAMNOSIDE	**431.0984**	**$C_{21}H_{20}O_{10}$**	**96.4**	285	Kaempferol	**28.8**	52.04	5,90
KAEMPFEROL-HEXOSIDE (GALACTOSIDE)	**447.0933**	**$C_{21}H_{20}O_{11}$**	**98.9**	285	Kaempferol	**25.7**	21.81	1.24
KAEMPFEROL-RUTINOSIDE	**593.1301**	**$C_{30}H_{26}O_{13}$**	**99.2**	285	Kaempferol	**31.9**	15.34	2.46
TOTAL KAEMPFEROL DERIVATIVES							**154.70**	**14.71**
QUERCETIN	**301.0354**	**$C_{15}H_{10}O_7$**	**96.6**			**31.3**	73,84	12.28
QUERCETIN-PENTOSIDE	**433.0776**	**$C_{20}H_{18}O_{11}$**	**94.8**	301	Quercetin	**25.1**	50.73	4.40
QUERCETIN-PENTOSIDE	**433.0776**	**$C_{20}H_{18}O_{11}$**	**99.2**	301	Quercetin	**25.5**	12.14	1.18
QUERCETIN-PENTOSIDE	**433.0776**	**$C_{20}H_{18}O_{11}$**	**96.2**	301	Quercetin	**26.1**	155.96	5.25
QUERCETIN-RHAMNOSIDE	**447.0933**	**$C_{21}H_{20}O_{11}$**	**99.7**	301	Quercetin	**26.6**	216.53	11.60
QUERCETIN-HEXOSIDE (GALACTOSIDE)	**463.0882**	**$C_{21}H_{20}O_{12}$**	**99.6**	301	Quercetin	**23.7**	239.84	7.24
QUERCETIN-3-O-GLUCOSIDE	**463.0882**	**$C_{21}H_{20}O_{12}$**	**99.1**	301	Quercetin	**24.3**	260.11	9.73
QUERCETIN-HEXOSIDE-RHAMNOSIDE	**609.1250**	**$C_{30}H_{26}O_{14}$**	**97.9**	301	Quercetin	**30.2**	40.91	5.14
QUERCETIN-RUTINOSIDE	**609.1461**	**$C_{27}H_{30}O_{16}$**	**97.7**	301	Quercetin	**23.7**	126.84	0.98
TOTAL QUERCETIN DERIVATIVES							**1176.90**	**45.52**
FLAVANOLS AND PHENOLICS ACID	**M-H**	**Formula**	**Score%**	**MS/MS**	**Fragment identity**	**TR min**	**Means (μg/g)**	**S.D**
CATEQUIN	**289.0718**	**$C_{15}H_{14}O_6$**	**97.8**			**9.7**	39.82	1.35
PROCYANIDIN B1	**577.1351**	**$C_{30}H_{26}O_{12}$**	**94.9**			**8.1**	12.54	0.62
ELLAGIC ACID	**300.9990**	**$C_{14}H_6O_8$**	**98.6**			**22.9**	406.29	23.74
DERIVATIVE ELLAGIC ACID	**425.0150**	**$C_{20}H_{10}O_{11}$**	**97.4**	300	Ellagic acid	**27.7**	250.21	32.95
GALIC ACID	**169.0142**	**$C_7H_6O_5$**	**81.1**			**2.9**	726.96	23.47
TOTAL FLAVANOLS AND PHENOLICS ACID							**1435.82**	**82.13**
TOTAL μg/g sample							**2780.87**	**145.37**

[M-H]: Exact mass of the isotopes of an element; Formula: refers to neutral molecule; Score: Percentage of reliability of proposed formula according to exact mass and isotopic distribution; MS/MS: Majority fragment in MS/MS fragmentation confirmed to be derived from one of the compounds; TR: Retention time; S.D.: Standard deviation. [1] Quercetin derivatives eluted over three retention times and thus considered different isomers.

The quercetin-3-O-glucoside eluted at Rt = 24.3 was confirmed by a pure standard. The presence of a hexose in the molecule was confirmed by the loss of a mass of 162.05 in the first case (Figure 4A), while the presence of a pentose in the molecule (Figure 4B) was confirmed by a loss of 132.04. The fragment obtained with a mass of 301.03 confirmed the presence of quercetin in both cases.

4. Discussion

Several authors have analysed the polyphenols in the petals of different rose species, with particular interest in anthocyanins, these pigment compounds being responsible for the red-to-purple petal hues of many rose types. In addition, these compounds have also been reported in *R. gallica* and *R. centifolia* to show anti-inflammatory [38] and antimutagenic properties [24], respectively.

Cunja et al. [20] studied the anthocyanins and flavonoids in the leaves and petals of different species of *Rosa* and reported a clear correlation between anthocyanin content and colour. The cyanidins (along with smaller quantities of peonidins and pelargonidins) were reported to be the most abundant anthocyanins in species with pink flowers.

The Narcea rose has red-purple petals, and cyanidins were the most abundant anthocyanins in the waste water produced during the present hydrodistillation experiments—a finding in agreement with that reported by Cunja et al. [20] for *R. damascena*. It may be this compound that confers the red colour upon this waste water (Figure 3), even though it is not the most abundant polyphenol. Ge and Ma [40], who studied the concentration of anthocyanins in edible roses from Yunnan (China), reported cyaniding-diglucoside to be the most abundant anthocyanin (making up 95% of all such compounds) and proposed these roses as a source of natural pigments for the food industry.

Our data reveal flavonoids in greater quantities than the anthocyanins. These are important bioactive compounds. Several authors report flavonols, especially derivatives of quercetin and kaempferol, to be present in different species of rose [17,20,23]; the bactericidal and antiviral properties of these compounds have been examined in several recent studies [17,41,42]. Other authors have confirmed the importance of these compounds in animal health and concluded that the incorporation of flavonoids into milk and meat products could provide a way of increasing their consumption along with the health benefits they are associated with (especially for people with low levels of flavonoids in their diet).

High concentrations of gallic and ellagic acids have been reported in the hips of other roses [17,43]. Fascella et al. [19], who studied the hips of four rose species, reported the most abundant polyphenols to be derivatives of catechin and galloyls (such as ellagic acid). Other authors indicate that ellagic acid has an important antitumoral effect [44–48].

Like green tea, grapes, red berries, pomegranates, apples and pears, roses (and in particular their leaves) are rich in flavan-3-ols (catechins, epicatechins and proanthocyanidins) [17,30]. However, in the waste water studied here, catechin and Procyanidin B1 (PB1) were detected only in small amounts. It may be that they were degradate in the distillation compared to quercetin, kaempferol and their derivatives. This might be explained by the fact that flavonols, being very polar, are left in the vapour. Moreover, since they are thermosensitive, they become hydrolysed during the hydrodistillation process. Other authors have reported high concentrations of these compounds in the petals of *R. damascena* and other rose species [20,23,49], while Göktürk-Baydar and Baydar [25] indicated catechin and epicatechin to be the most abundant phenolic compounds in the leaves of this species. In the present work, the low concentration of these compounds in the waste water might reflect a varietal characteristic. Forthcoming analyses of these compounds in fresh petals should throw light on this. It might be that the time that elapsed between the collection of the present flowers and their analysis affected the results obtained [50]. Some authors [9,51,52] indicate that roses need to be collected early in the morning and, if possible, subjected to hydrodistillation immediately, in situ, if their aromatic compounds are to be examined (during transport the flowers deteriorate and lose some of their volatile aromatic compounds). Over longer collection-to-analysis times, it may be that polyphenols

are lost, too, explaining the present near-absence of flavanol-3-ols. (Logistically, however, it was impossible to analyse the present samples sooner after their collection.) Finally, the very small amounts of these compounds detected in the present samples might be a reflection of the latter's treatment in the laboratory. All were stored at 4 °C for some days before being frozen at −80 °C. The effects of handling should be thoroughly studied if the waste water produced in hydrodistillation is to be used to obtain compounds of interest.

Schmitzer et al. [27] report that the concentration of phenolic compounds in petals varies over the development of the flower and that buds contain many more quercetin derivatives, catechins and much more gallic acid than do flowers in later stages of development. Indeed, they indicate that there may be up to six times as much gallic acid in buds then in open flowers. However, the quantity and quality of oils in the petals reaches a maximum when the flowers are completely open [10].

In other crops, such as grapevine [53–55], the polyphenol content of the leaves is strongly influenced by climatic and other environmental factors, such as temperature, rainfall, altitude, soil type, crop management, fertilizer availability and collection time [56]. Petkova et al. [3] reported higher phenol and total flavonoid concentrations in water extracts from organically cultivated roses, while Ginova et al. [11] reported total polyphenols and oxidative activity to be higher with altitude. All these factors will need to be studied if oils and rose water of maximum quality are to be extracted from the Narcea rose and the best use is to be made of its hydrodistillation and other wastes.

5. Conclusions

In conclusion, the present work shows that waste water produced during the hydrodistillation of Narcea rose petals is rich in quercetin and its derivatives, gallic and ellagic acids. Among the quercetin derivatives, the most abundant was quercetin-glucoside, quercetin-rhamnoside and quercetin-galactoside. Kaempferol-rhamnoside and kaempferol-galactoside were also detected. According to reports in the literature, many of these compounds have antioxidant and other properties beneficial to health. The high concentration of these compounds in this waste water render it suitable as a raw material for developing nutraceutical, pharmacological, animal feed and even human and plant health products. However, one of the best applications could be dermocosmetic production, which could benefit from the water and the compounds inside. Protocols need to be developed to take advantage of this polyphenol-rich water.

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References

1. Martínez, M.C.; Santiago, J.L.; Boso, S.; Gago, P.; Álvarez-Acero, I.; De Vega, M.E.; Martínez-Bartolomé, M.; Álvarez-Nogal, R.; Molíst, P.; Caser, M.; et al. Narcea-an unknown, ancient cultivated rose variety from northern Spain. *Hortic. Res.* **2020**, *7*, 44. [CrossRef] [PubMed]
2. Wedler, J.; Weston, A.; Rausenberger, J.; Butterweck, V. In vitro modulation of inflammatory target gene expression by a polyphenol-enriched fraction of rose oil distillation waste water. *Fitoterapia* **2016**, *114*, 56–62. [CrossRef] [PubMed]
3. Petkova, D.; Mihaylova, D.; Denev, P.; Krastanov, A. Antioxidant activity of some edible flowers water extracts from Bulgaria. *Bull. UASVM Food Sci. Tech.* **2020**, *77*, 54–61. [CrossRef]
4. Dragoev, S.; Vlahova-Vangelova, D.; Balev, D.; Bozhilov, D.; Dagnon, S. Valorization of waste by-products of rose oil production as feedstuff phytonutrients. *Bulg. J. Agric. Sci.* **2021**, *27*, 209–219.
5. Saint-Lary, K.; Roy, C.; Paris, J.P.; Martin, J.F.; Thomas, O.P.; Fernandez, X. Metabolomics as a tool for the authentication of rose extracts used in flavour and fragrance area. *Metabolomics* **2016**, *12*, 49. [CrossRef]
6. Xiao, Z.; Luo, J.; Niu, Y.; Wu, M. Characterization of key aroma compounds from different rose essential oils using gas chromatography-mass spectrometry, gas chromatography-olfactometry and partial least squares regression. *Nat. Prod. Res.* **2018**, *32*, 1567–1572. [CrossRef]
7. Baydar, H.; Göktürk Baydar, N. The effects of harvest date, fermentation duration and Tween 20 treatment on essential oil content and composition of industrial oil rose (*Rosa damascena* Mill.). *Ind. Crops Prod.* **2005**, *21*, 251–255. [CrossRef]
8. Yassa, N.; Masoomi, F.; Rouhani Rankouhi, S.; Hadjiakhoondi, A. Chemical composition and antioxidant activity of the extract and essential oil of *Rosa damascena* from Iran, population of Guilan. *Daru J. Pharmac. Sci.* **2009**, *17*, 175–180.
9. Kovacheva, N.; Rusanov, K.; Atanassov, I. Industrial Cultivation of Oil Bearing Rose and Rose Oil Production in Bulgaria during the 21st Century, Directions and Challenges. Biotechnology & Biotechnological Equipment. *Biotechnol. Equip.* **2010**, *24*, 1793–1798.
10. Sharma, S.; Kumar, R. Influence of harvesting stage and distillation time of Damask rose (*Rosa damascena* Mill.) flowers of essential oil content and composition in the Western Himalayas. *J. Essent. Oil Bear. Plants* **2018**, *21*, 92–102. [CrossRef]
11. Ginova, A.; Mihalev, K.; Kondakova, V. Antioxidant capacity of petals and leaves from different rose (*Rosa damascena* mill.) plantations in Bulgaria. *Int. J. Pure Appl. Biosci.* **2013**, *1*, 38–43.
12. Pires, T.C.S.P.; Barros, L.; Santos-Buelga, C.; Ferreir, I.C.F.R. Edible flowers: Emerging components in the diet. *Trends Food Sci. Tech.* **2019**, *9*, 244–258. [CrossRef]
13. Ercişli, S.; Eşitken, A. Fruit characteristics of native rose hip (*Rosa* spp.) selections from the Erzurum province of Turkey. *N. Z. J. Crop Hortic. Sci.* **2004**, *32*, 51–53. [CrossRef]
14. Zhang, G.Q.; Huang, X.D.; Wang, H.; Leung, A.K.N.; Chan, C.L.; Fong, D.W.F.; Yub, Z.L. Anti-inflammatory and analgesic effects of the ethanol extract of *Rosa multiflora* Thunb. hips. *J. Ethnopharmacol.* **2008**, *118*, 290–294. [CrossRef] [PubMed]
15. Lee, M.H.; Nam, T.G.; Lee, I.; Shin, E.J.; Han, A.R.; Lee, P.; Lee, S.Y.; Lim, T.G. Skin anti-inflammatory activity of rose petal extract (*Rosa gallica*) through reduction of MAPK signaling pathway. *Food Sci. Nutr.* **2018**, *6*, 2560–2567. [CrossRef]
16. Guimaraes, R.; Barros, L.; Duenas, M.; Carvalho, A.M.; Queiroz, M.J.R.P.; Santos-Buelga, C.; CFR-Ferreira, I. Characterisation of phenolic compounds in wild fruits from Northeastern Portugal. *Food Chem.* **2013**, *141*, 3721–3730. [CrossRef]
17. Cendrowski, A.; Krasniewska, K.; Przybyl, J.L.; Zielinska, A.; Kalisz, S. Antibacterial and antioxidant activity of extracts from rose fruits (*Rosa rugosa*). *Molecules* **2020**, *25*, 1365. [CrossRef]
18. Nadpal, J.D.; Lesjak, M.M.; Mrkonjic, Z.O.; Majkic, T.M.; Cetojevic-Simin, D.D.; Mimica-Dukic, N.M.; Beara, I.N. Phytochemical composition and in vitro functional properties of three wild rose hips and their traditional preserves. *Food Chem.* **2018**, *241*, 290–300. [CrossRef]
19. Fascella, G.; D'Angiolillo, F.; Mammano, M.M.; Amenta, M.; Romeo, F.V. Bioactive compounds and antioxidant activity of four rose hip species from spontaneous Sicilian flora. *Food. Chem.* **2019**, *289*, 56–64. [CrossRef]
20. Cunja, V.; Mikulic-Petkovsek, M.; Stampar, F.; Schmitzer, V. Compound identification of selected Rose species and cultivars: An insight to petal and leaf phenolic profiles. *J. Amer. Soc. Hort. Sci.* **2014**, *139*, 157–166. [CrossRef]
21. D´Angiolillo, F.; Mammano, M.M.; Fascella, G. Pigments, polyphenols and antioxidant activity of leaf extracts from four wild rose species grown in Sicily. *Not. Bot. Horti Agrobot. Cluj-Napoca* **2018**, *46*, 402–409. [CrossRef]
22. Vinokur, Y.; Rodov, V.; Reznick, N.; Goldman, G.; Horev, B.; Umiel, N. Rose petal tea as an antioxidant-rich beverage: Cultivar effects. *J. Food Sci.* **2006**, *71*, S42–S47. [CrossRef]
23. Kumar, N.; Bhandari, P.; Singh, B.; Bari, S.S. Antioxidant activity and ultra-performance LC-electrospray ionization–quadrupole time-of-flight mass spectrometry for phenolics-based fingerprinting of rose species: *Rosa damascena*, *Rosa bourboniana* and *Rosa brunonii*. *Food Chem. Toxicol.* **2009**, *47*, 361–367. [CrossRef]
24. Kumar, S.; Gautam, S.; Sharma, A. Identification of antimutagenic properties of anthocyanins and other polyphenols from Rose (*Rosa centifolia*) petals and tea. *J. Food Sci.* **2013**, *78*, H948–H954. [CrossRef] [PubMed]
25. Göktürk-Baydar, N.; Baydar, H. Phenolic compounds, antiradical activity and antioxidant capacity of oil-bearing rose (*Rosa damascena* Mill.) extracts. *Ind. Crops Prod.* **2013**, *41*, 375–380. [CrossRef]
26. Boskabady, M.H.; Shafei, M.N.; Saberi, Z.; Amini, S. Pharmacological effects of *Rosa damascena*. *Iran. J. Basic Med. Sci.* **2011**, *14*, 295–307.
27. Schmitzer, V.; Veberic, R.; Osterc, G.; Stampar, F. Color and phenolic content changes during flower development in groundcover rose. *J. Amer. Soc. Hort. Sci.* **2010**, *135*, 195–202. [CrossRef]

28. Duthie, G.G.; Gardner, P.T.; Kyle, J.A. Plant polyphenols: Are they the new magic bullet? *Proc. Nutr. Soc.* **2003**, *62*, 599–603. [CrossRef]
29. Aubert, C.; Chalot, G. Chemical composition, bioactive com-pounds, and volatiles of six table grape varieties (*Vitis vinifera* L.). *Food Chem.* **2018**, *240*, 524–533. [CrossRef]
30. Rasouli, H.; Farzaei, M.H.; Khodarahmi, R. Polyphenols and their benefits: A review. *Int. J. Food Prop.* **2017**, *20*, 1700–1741. [CrossRef]
31. El Gharras, H. Polyphenols: Food sources, properties and applications—A review. *Int. J. Food Sci. Tech.* **2009**, *44*, 2512–2518. [CrossRef]
32. Quideau, S.; Deffieux, D.; Douat-Casassus, C.; Pouysegu, L. Plant polyphenols: Chemical properties, biological activities, and synthesis. *Angew. Chem. Int. Ed.* **2011**, *50*, 586–621. [CrossRef] [PubMed]
33. De la Cerda Carrasco, A.; López Solís, R.; Nuñez Kalasic, H.; Peña Neira, A.; Obreque Slier, E. Phenolic composition and antioxidant capacity of pomaces from four grape varieties (*Vitis vinifera* L.). *J. Sci. Food Agric.* **2015**, *95*, 1521–1527. [CrossRef]
34. Galanakis, C.M.; Food Waste Recovery Group (Eds.) *Polyphenols: Properties, Recovery, and Applications*; Woodhead Publishing: Vienna, Austria, 2018; 456p.
35. Ikigai, H.; Nakae, T.; Hara, Y.; Shimamura, T. Bactericidal catechins damage the lipid bilayer. *Biochim. Biophys. Acta (BBA)-Biomembr.* **1993**, *1147*, 132–136. [CrossRef]
36. Chung, K.T.; Wong, T.I.; Wei, C.I.; Huang, Y.W.; Li, Y. Tannins and human healt. *Crit. Rev. Food Sci. Nutr.* **1998**, *38*, 421–464. [CrossRef] [PubMed]
37. Zhang, J.; Shi, H.; Wang, Y.; Li, S.; Cao, Z.; Ji, S.; He, Y.; Zhang, H. Effect of dietary forage to concentrate ratios on dynamic profile changes and interactions of ruminal microbiota and metabolites in Holstein heifers. *Front. Microbiol.* **2017**, *8*, 2206. [CrossRef] [PubMed]
38. Lee, S.H.Y.; Humphries, D.J.; Cockman, D.A.; Givens, D.I.; Spencer, J.P.E. Accumulation of citrus flavanones in bobine milk following citrus pulp incorporation into the diet of dairy cows. *EC Nutr.* **2017**, *7*, 143–154.
39. Kalantar, M. The importance of flavonoids in ruminant nutrition. *Arch. Anim. Husb. Dairy Sci.* **2018**, *1*, 1–4. [CrossRef]
40. Ge, Q.; Ma, X. Composition and antioxidant activity of anthocyanins isolated from Yunnan edible rose (An Ning). *Food Sci. Hum. Wellness* **2013**, *2*, 68–74. [CrossRef]
41. Zakaryan, H.; Arabyan, E.; Oo, A.; Zandi, K. Flavonoids: Promising natural compounds against viral infections. *Arch. Virol.* **2017**, *162*, 2539–2551. [CrossRef]
42. Alvarez-Martinez, F.J.; Barrajon-Catalan, E.; Encinar, J.A.; Rodriguez-Diaz, J.C.; Micol, V. Antimicrobial capacity of plant polyphenols against gram-positive bacteria: A comprehensive review. *Curr. Med. Chem.* **2020**, *27*, 2576–2606. [CrossRef] [PubMed]
43. Stanila, A.; Diaconeasa, Z.; Roman, I.; Sima, N.; Maniutiu, D.; Roman, A.; Sima, R. Extraction and characterization of phenolic compounds from rose hip (*Rosa canina* L.) using liquid chromatography coupled with electrospray ionization—Mass spectrometry. *Not. Bot. Horti. Agrobo.* **2015**, *3*, 349–354. [CrossRef]
44. Chen, Y.C.; Chien, L.H.; Huang, B.M.; Chia, Y.C. Toona sinensis (aqueous leaf extracts) induces apoptosis through the generation of ROS and activation of intrinsic apoptotic pathways in human renal carcinoma cells. *J. Funct. Foods* **2014**, *7*, 362–372. [CrossRef]
45. Fontana, A.R.M.; Antoniolli, A.; Bottini, R. Grape pomace as a sustainable source of bioactive compounds: Extraction, characterization, and biotechnological applications of phenolics. *J. Agric. Food Chem.* **2013**, *61*, 8987–9003. [CrossRef]
46. Kampa, M.; Theodoropoulou, K.M.; Mavromati, F.; Pelekanou, V.; Notas, G.; Lagoudaki, E.D.; Nifli, A.P.; Morel-Salmi, C.; Stathopoulos, E.N.; Vercauteren, J.; et al. Novel oligomeric proanthocyanidin derivatives interact with membrane androgen sites and induce regression of hormone-independent prostate cancer. *J. Pharmacol. Exp. Ther.* **2011**, *337*, 24–32. [CrossRef]
47. Katiyar, S.K.; Athar, M. Grape seeds: Ripe for cancer chemoprevention. *Cancer Prev. Res.* **2013**, *6*, 617–621. [CrossRef]
48. Lachman, J.; Hejtmankova, A.; Hejtmankova, K.; Hornickova, S.; Pivec, V.; Skala, O.; Dedina, M.; Pribyl, J. Towards complex utilisation of winemaking residues: Characterisation of grape seeds by total phenols, tocols and essential elements content as a by-product of winemaking. *Ind. Crops Prod.* **2013**, *49*, 445–453. [CrossRef]
49. Velioglu, Y.S.; Mazza, G. Characterization of flavonoids in petals of *Rosa damascena* by HPLC and spectral analysis. *J. Agric. Food Chem.* **1991**, *39*, 463–467. [CrossRef]
50. Santiago, J.L.; Gago, P.; Boso, S.; Álvarez-Acero, I.; Martínez-Bartolomé, M.; Martínez, M.C. Polyphenol content of the petals of the 'Rosa Narcea' cultivated in the mountains of Asturias (northern Spain). IV International Symposium on woody ornamentals of the temperate zone. 3–4 March 2021 online symposium. *Acta Hortic.* **2021**, *133*, 233–238. [CrossRef]
51. Mihailova, J.; Atanasova, R.; Tsvetkova, B.A. Direct gas chromatography of essential oil in the separate parts of the flower of the Kazanlik rose (*Rosa damascena* Mill. f. trigintipetala Dieck.). In Proceedings of the 7th International Congress of Essential Oils, Kyoto, Japan, 7–11 October 1977; pp. 219–221.
52. Bayrak, A.; Akgul, A. Volatile oil composition of Turkish rose (*Rosa damascena*). *J. Sci. Food Agric.* **1994**, *64*, 441–448. [CrossRef]
53. Poudel, P.; Tamura, H.; Kataoka, I.; Mochiola, R. Phenolic compounds and antioxidant activities of skins and seeds of five wild grapes and two hybrids native to Japan. *J. Food Compos. Anal.* **2008**, *21*, 622–625. [CrossRef]
54. Martínez de Toda, F.; Ramos, M.C. Variability in grape composition and phenology of 'Tempranillo' in zones located at different elevations and with differences in the climatic conditions. *Vitis* **2019**, *58*, 131–139.

55. Gutiérrez-Gamboa, G.; Romanazzi, G.; Garde-Cerdán, T.; Pérez-Álvarez, E.P. A review of the use of biostimulants in the vineyard for improved grape and wine quality: Effects on prevention of grapevine diseases. *J. Sci. Food Agric.* **2019**, *99*, 1001–1009. [CrossRef] [PubMed]
56. Koczka, N.; Stefanovits-Banyai, E.; Ombodi, A. Total polyphenol content and antioxidant capacity of rosehips of some *Rosa* species. *Medicines* **2018**, *5*, 84. [CrossRef]