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REVIEWS

Onions: A Source of Unique Dietary Flavonoids

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Onion bulbs (*Allium cepa* L.) are among the richest sources of dietary flavonoids and contribute to a large extent to the overall intake of flavonoids. This review includes a compilation of the existing qualitative and quantitative information about flavonoids reported to occur in onion bulbs, including NMR spectroscopic evidence used for structural characterization. In addition, a summary is given to index onion cultivars according to their content of flavonoids measured as quercetin. Only compounds belonging to the flavonols, the anthocyanins, and the dihydroflavonols have been reported to occur in onion bulbs. Yellow onions contain 270–1187 mg of flavonols per kilogram of fresh weight (FW), whereas red onions contain 415–1917 mg of flavonols per kilogram of FW. Flavonols are the predominant pigments of onions. At least 25 different flavonols have been characterized, and quercetin derivatives are the most important ones in all onion cultivars. Their glycosyl moieties are almost exclusively glucose, which is mainly attached to the 4′, 3, and/or 7-positions of the aglycones. Quercetin 4′-glucoside and quercetin 3,4′-diglucoside are in most cases reported as the main flavonols in recent literature. Analogous derivatives of kaempferol and isorhamnetin have been identified as minor pigments. Recent reports indicate that the outer dry layers of onion bulbs contain oligomeric structures of quercetin in addition to condensation products of quercetin and protocatechuic acid. The anthocyanins of red onions are mainly cyanidin glucosides acylated with malonic acid or nonacylated. Some of these pigments facilitate unique structural features like 4′-glycosylation and unusual substitution patterns of sugar moieties. Altogether at least 25 different anthocyanins have been reported from red onions, including two novel 5-carboxypyranocyanidin-derivatives. The quantitative content of anthocyanins in some red onion cultivars has been reported to be approximately 10% of the total flavonoid content or 39–240 mg kg^{-1} FW. The dihydroflavonol taxifolin and its 3-, 7-, and 4′-glucosides have been identified in onions. Although the structural diversity of dihydroflavonols characterized from onions is restricted compared with the wide structural assortment of flavonols and anthocyanins identified, they may occur at high concentrations in some cultivars. From bulbs of the cultivar “Tropea”, 5.9 mg of taxifolin 7-glucoside and 98.1 mg of taxifolin have been isolated per kilogram of FW.

KEYWORDS: Onion; *Allium cepa*; flavonoids; flavonols; anthocyanins; dihydroflavonols; cultivars; quantitative content; NMR

INTRODUCTION

Onion (*Allium cepa* L.) is one of the most important vegetables worldwide with an estimated annual production of almost 47 million tons in year 2000 (http://faostat.fao.org). The main production areas are China, India, United States, Russia, Turkey, and Iran. Consumption per capita differs greatly between countries and areas, but a major trend seems to be that onion consumption is increasing worldwide. Onion has been recognized as an important source of valuable phytonutrients as flavonoids, fructo-oligosaccharides (FOS), and thiosulfinates and other sulphur compounds. Flavonoids continue to attract attention as potentially useful agents with implications for inflammation, cardiovascular diseases, and cancer (*1, 2*).

The common onion belongs to the family Alliaceae and is biennial, but in commercial production it is mainly grown as

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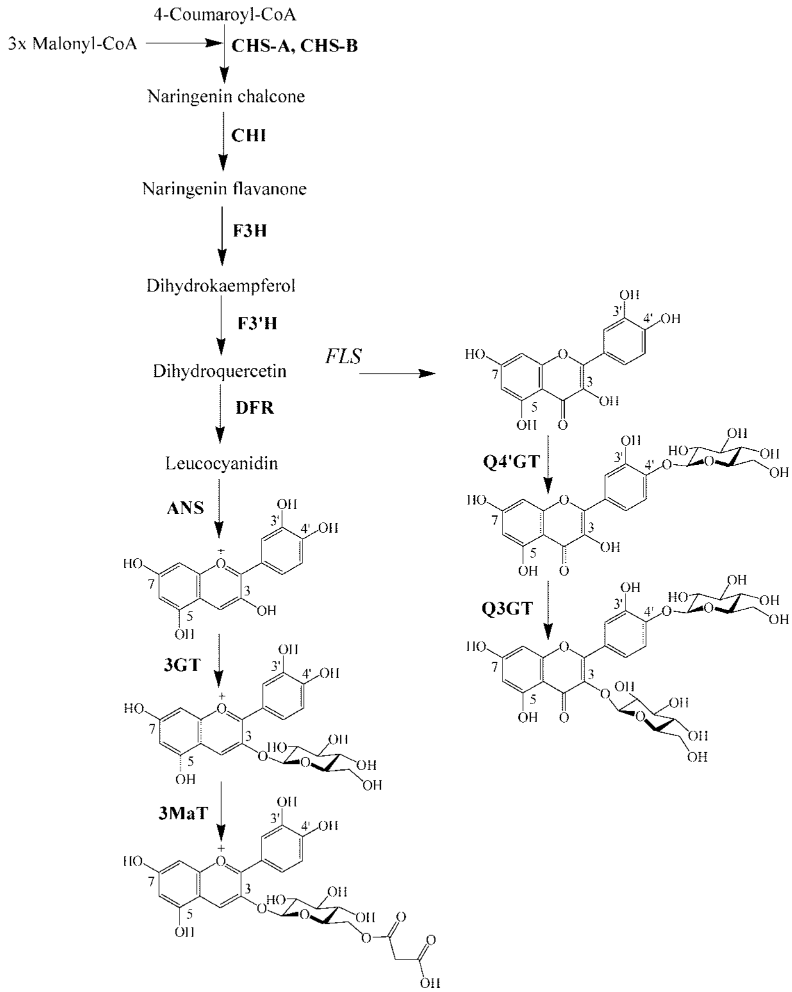


Figure 1. Putative flavonoid biosynthesis pathway in *A. cepa* adopted from Masuzaki and co-workers. CHS, chalcone synthase; CHI, chalcone isomerase; F3H, flavanone 3-hydroxylase; F3′H, flavonoid 3′-hydroxylase; DFR, dihydroflavonol 4-reductase; ANS, anthocyanidin synthase; 3GT, UDP glucose: flavonoid 3-*O*-glucosyltransferase; 3MaT, malonyl coenzyme-A:anthocyanidin 3-*O*-glucoside-6′′-*O*-malonyltransferase; FLS, flavonol synthase; Q4′GT, quercetin 4′-*O*-glucosyltransferase; Q3GT, quercetin 3-*O*-glucosyltransferase.

an annual. The bulb consists of the swollen base of the stem and several fleshy leaves or scales. Onions may differ greatly in bulb shape, color of the outer scales (yellow, red, white), pungency (from mild and sweet to very pungent), bulb storage life, and dry-matter content (*3*). Onions are grown in most climate zones around the world, from tropical to cool temperate climates. Transition from leaf growth to bulb formation depends both on temperature and on the day length adaptation of the cultivar, and cultivars are commonly divided into groups based on growing latitude. Content of potential health-promoting substances, like flavonoids, may also vary considerably between cultivars. This fact is often neglected in studies, which is why we have chosen to pay special attention to variations among cultivars in this review.

Flavonoids are present in all terrestrial plants and are found in all plant organs including flower, fruit, leaf, stem, and root. The distribution with respect to structural diversity and quantities may vary considerably within a plant. The compounds are of a mixed biosynthetic origin with one ring being shikimate-derived and the other being derived from the Krebs cycle (polyketide) (**Figure 1**) (*4, 5*). Significant progress has been made with respect to assignment of structural genes involved in the flavonoid biosynthesis of onions (*6, 7*). Takahama and Hirota have suggested that quercetin is formed by deglucosidation of its glucosides, followed by autoxidation to produce protocatechuic acid (*8*). Moreover, peroxidase in scales oxidize flavonols in the order quercetin ≫ quercetin 4′-glucoside > isoquercetin ≫ quercetin 3,4′-diglucoside, and moreover, the activity is higher in the outer than in the inner scales. This suggests an enzymatic formation of defence substances against infection in the dry skin from quercetin (*9*).

Even though onions are among the most important dietary sources of flavonoids (*10*), no review exists that contains a comprehensive compilation of the various flavonoid structures characterized from these sources. The existing reviews including qualitative flavonoid contents of onions are still relatively incomplete. In a preceding review (Herrmann, 1988) only ten different flavonols were included (*11*), or approximately 70% of the real number of pre-1988 published flavonol structures from onions. Most of the structures reported prior to 1988 were elucidated by means of thin-layer chromatography and UV-absorption spectroscopy in combination with the use of UV shift reagents and acidic or enzymatic hydrolysis. Few structures were supported with mass-spectral (MS) data or data from nuclear magnetic resonance (NMR) spectroscopic investigations.

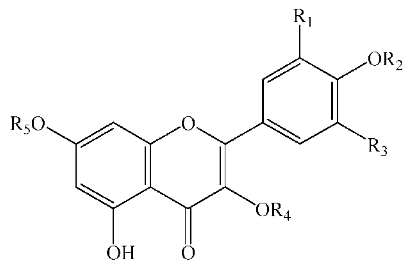
A more recent review (*12*) surveys different groups of compounds that have been reported from onions and garlic. With respect to flavonoids, only total hydrolyzed amounts of the three flavonol aglycones quercetin, kaempferol, and isorhamnetin have

Table 1. Flavonoids Reported To Occur in Bulbs of Onion (*Allium cepa* L.)

no.	flavonoids	refs
	Flavonols	
1	quercetin	*15–17, 21, 27, 29*
2	quercetin 4′-glucoside	*16, 17, 20, 21, 27–29, 34, 43, 46, 60, 65, 71, 98*
3	quercetin 3,4′-diglucoside	*21–29, 34, 60, 71, 98*
4	quercetin 7-glucoside	*26, 29, 67*
5	quercetin 7,4′-diglucoside	*21–24, 26–29, 39, 60, 67, 71*
6	quercetin 3-glucoside	*21, 26, 28, 29, 39, 60, 67, 71*
7	quercetin 3′-glucoside	*34*
8	quercetin 3,7-diglucoside	*29, 67, 93*
9	quercetin 3,7,4′-triglucoside	*27, 39*
10	quercetin 3-rhamnoside	*36*
11	quercetin 3-rutinoside	*33, 35*
12	kaempferol	*29, 31, 66, 99*
13	kaempferol 4′-glucoside	*26, 28, 29, 32*
14	kaempferol 3-glucoside	*28, 29, 37, 38*
15	kaempferol 7,4′-diglucoside	*29*
16	kaempferol 3,4′-diglucoside	*26, 67*
17	isorhamnetin 4′-glucoside	*26, 28, 33, 39, 60, 67, 98, 99*
18	isorhamnetin 3-glucoside	*34, 39*
19	isorhamnetin 3,4′-diglucoside	*26, 39, 67*
20	isorhamnetin	*33*
21	myricetin	*40, 41*
22	quercetin dimer	*43, 46*
23	4′-glucoside of quercetin dimer	*43, 46*
24	condensation products of quercetin and protocatechuic acid	*46*
25	quercetin trimer	*46*
	Anthocyanins	
26	cyanidin 3-glucoside	*21, 50–53, 56–60, 62, 100*
27	cyanidin 3-(3′′-glucosylglucoside) = cyanidin 3-laminariobioside	*21, 51–53, 56–59, 62, 63, 100*
28	cyanidin 3-(3′′-malonylglucoside)	*57, 58, 60, 62*
29	cyanidin 3-(6′′-malonylglucoside)	*56–59, 62, 63*
30	cyanidin 3-(3′′-glucosyl-6′′-malonylglucoside)	*56–59, 62, 63*
31	cyanidin 3-(3′′,6′′-dimalonylglucoside)	*57*
32	cyanidin 3-(dimalonyl)laminariobioside	*58*
33	cyanidin 3-(3′′-acetylglucoside)	*62*
34	cyanidin 3-(malonyl)(acetyl)glucoside	*62*
35	cyanidin 3,5-diglucoside	*57, 59*
36	cyanidin 3-(malonyl)-glucoside-5-glucoside	*62*
37	cyanidin 4′-glucoside	*59*
38	cyanidin 3,4′-diglucoside	*59*
39	cyanidin 3-(3′′-glucosyl-6′′-malonylglucoside)-4′-glucoside	*59*
40	cyanidin 7-(3′′-glucosyl-6′′-malonylglucoside)-4′-glucoside	*59*
41	peonidin 3-glucoside	*52, 58*
42	peonidin 3-(6′′-malonylglucoside)	*58, 59*
43	peonidin 3,5-diglucoside	*57*
44	peonidin 3-(6′′-malonylglucoside)-5-glucoside	*59*
45	delphinidin 3-glucoside	*63*
46	delphinidin 3-glucosylglucoside	*63*
47	petunidin glucoside	*63*
48	petunidin (glucosylglucoside)	*63*
49	5-carboxypyranocyanidin 3-glucoside	*61*
50	5-carboxypyranocyanidin 3-(6′′-malonylglucoside)	*61*
	Dihydroflavonols	
51	taxifolin 4′-glucoside	*27*
52	taxifolin	*65*
53	taxifolin 7-glucoside	*65*
54	taxifolin 3-glucoside	*60*

been measured from onions, according to that review. Despite the vast numbers of commercially important anthocyanin-containing onion cultivars, reviews including compilations of anthocyanins or any flavonoids other than flavonols are non-existent in previous literature.

Along with the continuous improvement in methods and instrumentation of isolation and structure determination of flavonoids, structural information with increasing levels of precision has become available on an increasing number of flavonoids. Among the more than 8000 known flavonoid structures, nearly half of them have been characterized during the last decade (*13*). In this review, a compilation of more than 50 flavonoids identified in pigmented scales of onions are included (**Table 1**). Approximately 70% of these compounds have been reported during the last 15 years. Among the 13 different main flavonoid classes, only compounds belonging to the flavonols, the anthocyanins, and to less extent the dihydroflavonols have been reported from onion bulbs. The majority of these structures have been confirmed through NMR investigations, and chemical shift values for both proton and carbon are reviewed. For the first time, an extended anthology of the numerous quantitative analyses of flavonols, and to some extent anthocyanins and dihydroflavonols, of onions, particularly



	R_1	R_2	R_3	R_4	R_5
1	OH	H	H	H	H
2	OH	Glc	H	H	H
3	OH	Glc	H	Glc	H
4	OH	H	H	H	Glc
5	OH	Glc	H	H	Glc
6	OH	H	H	Glc	H
7	OGlc	H	H	H	H
8	OH	H	H	Glc	Glc
9	OH	Glc	H	Glc	Glc
10	OH	H	H	Rha	H
11	OH	H	H	Rut	H
12	H	H	H	H	H
13	H	Glc	H	H	H
14	H	H	H	Glc	H
15	H	Glc	H	H	Glc
16	H	Glc	H	Glc	H
17	OCH_3	Glc	H	H	H
18	OCH_3	H	H	Glc	H
19	OCH_3	Glc	H	Glc	H
20	OCH_3	H	H	H	H
21	OH	H	OH	H	H

Figure 2. Structures of flavonols (**1** through **21**) reported to occur in bulbs of onions (*Allium cepa* L.). Abbreviations are as follows: glc = glucose, rut = rutinose, rha = rhamnose.

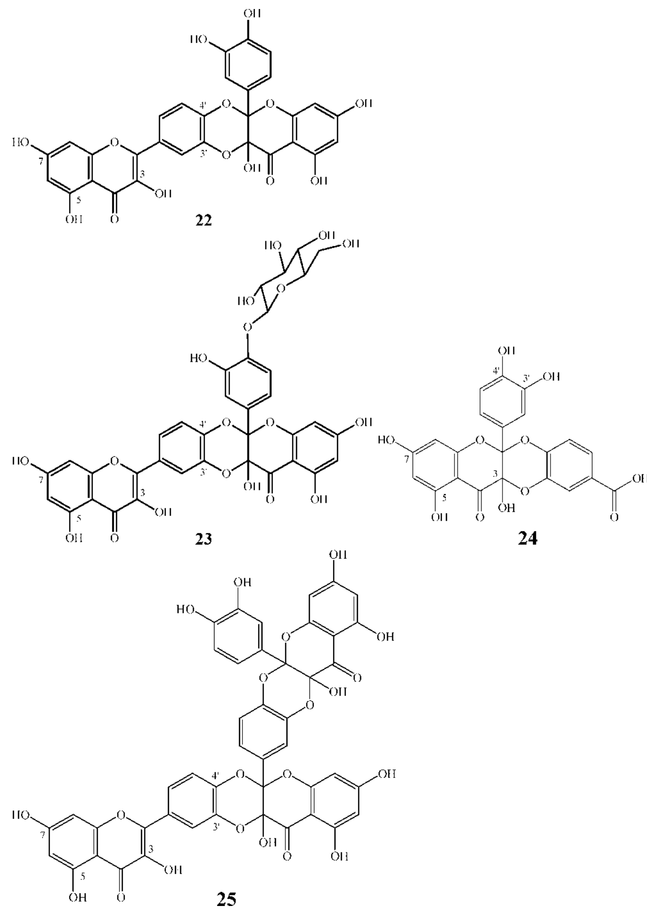
related to different cultivars, is included as one of the main objectives of this review.

FLAVONOLS OF ONIONS

From ancient times, dried pigmented scales of onions have been used to provide yellow coloration of textiles and Easter eggs (*14*). Flavonols are the main flavonoids of pigmented scales of onions. The main flavonols are based on quercetin (3,5,7,3′,4′-pentahydroxyflavone). The structural diversity of the minor flavonols of onions is extensive and includes derivatives of kaempferol, isorhamnetin, and possibly myricetin. Altogether at least 25 different flavonols have been characterized from onion bulbs (**Figures 2** and **3**, **Table 1**). The glycosyl unit(s) of these pigments has in most cases been identified as glucose.

Perkin and Hummel (1896) first reported the structure of quercetin, **1**, isolated from pigmented scales of onion bulbs (*15*). The presence of quercetin aglycone as one of the main flavonoids in some onion cultivars has been confirmed in later publications (*16, 17, 21, 27, 29*). One should however keep in mind that hydrolysis of quercetin glycosides might occur during sample preparation and analysis. The presence and amount of aglycone reported can therefore be an overestimate.

Herrmann (*16, 17*) identified another main flavonol of onions, namely, quercetin 4′-glucoside (spiraeoside, **2**) in addition to quercetin from pigmented scales of the cultivar "Braunschweiger Dunkelblutrote". The identification of quercetin 4′-glucoside was mainly based on comparison of the physiochemical and paper chromatographic properties with the same compound previously isolated from *Filipendula flos spirea* and its tetramethylated derivative (*18, 19*). Koeppen and van der Spuy (*20*) reported quercetin 4′-glucoside as the main flavonol in the cultivar "Australian Brown". They also tentatively indicated the presence of quercetin 5-glucoside and a quercetin 3-diglucoside. The latter two compounds have



22 23 24 25

Figure 3. Structures of flavonols (**22** through **25**)

not been identified in more recent studies of other onion cultivars. The third major flavonol, quercetin 3,4′-diglucoside, **3**, was reported at the same time in two independent papers. Brandwein (*21*) isolated quercetin 4′-glucoside and quercetin 3,4′-diglucoside in addition to the 7,4′-diglucoside, **5**, and the 3-glucoside, **6**, of quercetin from the cultivars "Southport Yellow Globe", "Southport White Globe", and "Southport Red Globe". The identifications were based on paper chromatography and UV-spectroscopy with shift reagents. Harborne (*22*) reported the 3,4′-diglucoside and the 7,4′-diglucoside of quercetin from an unspecified onion cultivar. These structures have been confirmed in later publications (*23–27*).

Tissut (*28*) reported on the occurrence of quercetin 3-glucoside (isoquercitrin, **6**), kaempferol 3-glucoside (astragalin, **14**), kaempferol 4′-glucoside, **13**, and isorhamnetin 4′-glucoside, **17**, as minor pigments. Panisset and Tissut (*29*) identified quercetin 3,7-diglucoside, **8**, from onion bulbs using cochromatography on TLC. A complete NMR spectroscopic assignment of the structure of this compound isolated from onions is lacking in previous literature and has been included in **Tables 2.1–3.2** (*30*). Using TLC, Panisset and Tissut also detected quercetin 7-glucoside, **4**, kaempferol, **12**, and kaempferol 7,4′-diglucoside, **15**, as minor pigments from the cultivars 447, 947, 935, Hyper, Hygro, Topaz, and Superba (*29*). Kaempferol had earlier been reported from the light pink Indian cultivar "Malwi" (*31*).The structures of the 4′-glucosides of kaempferol (*32*) and isorhamnetin (*33*) have more recently been confirmed by NMR spectroscopic studies (**Tables 2.1–3.2**). Omidiji (*34*) identified isorhamnetin 3-glucoside, **18**, and quercetin 3′-glucoside, **7**, as minor pigments in the cultivar "Red Creole", in addition to the main pigments quercetin 4′-glucoside and quercetin 3,4′-diglucoside. Tsushida and Suzuki (*26*) additionally identified

Table 2.1. ^{1}H NMR Spectral Data of Flavonoids from Onions Recorded in Various Solvents[a]

		chemical shift (ppm), multiplicity, coupling constant (Hz)									
no.	flavonols	OCH_3	6	7	8	2′	3′	4′	5′	6′	ref
13	kaempferol 4′-glc (D)		6.19, d, 2.0		6.45, d, 1.8	8.13, ‘d’, 9.0	7.18, ‘d’, 9.0		7.18, ‘d’, 9.0	8.13, ‘d’, 9.0	*32*
1	quercetin (M)		6.27		6.47	7.82			6.97	7.72	*27*
7	quercetin 3′-glc (D)		6.13, d, 2.0		6.37, d, 1.7	7.68, d, 2.5			7.23, d, 8.8	7.70, d, 2.5	*34*
2	quercetin 4′-glc (M)		6.25		6.44	7.81			7.35	7.75	*27*
8	quercetin 3,7-diglc (D)		6.42, d 1.9		6.75, d, 1.9	7.59, d, 2.3			6.85, d, 8.5	7.57, dd, 8.5, 2.3	*30*
3	quercetin 3,4′-diglc (D)		6.14		6.35	7.64			7.20	7.57	*27*
5	quercetin 7,4′-diglc (D)		6.42, d, 1.9		6.81, d, 1.9	7.74, d, 2.2			7.26, d, 8.6	7.64, dd, 8.6, 2.2	*30*
9	quercetin 3,7,4′-triglc (D)		6.43		6.80	7.67			7.21	7.62	*27*
20	isorhamnetin (D)	3.83, s	6.19, d, 1.4		6.47, d, 1.4	7.74, d, 1.3			6.93, d, 8.5	7.68, dd, 8.5, 1.3	*33*
18	isorhamnetin 3-glc (D)	3.83, s	6.15, d, 2.0		6.47, d, 1.8	7.67, d, 2.6			7.22, d, 8.0	7.70, d, 2.4	*34*
17	isorhamnetin 4′-glc	3.80, s	6.20, d, 2.2		6.50, d, 2.2	7.79, d, 2.4			7.25, d, 8.8	7.77, dd, 8.8, 2.4	*33*

		chemical shift (ppm), multiplicity, coupling constant (Hz)						
no.	dimeric flavonols	6	8	2′	3′	5′	6′	ref
22	quercetin dimer 4′-glc[b] (A)	6.27, d, 2.1	6.60, d, 2.1	7.92, d, 2.1		7.29, d, 8.8	8.02, dd, 8.8, 2.1	*43*

		chemical shift (ppm), multiplicity, coupling constant (Hz)						
no.	dimeric flavonols	6″	8″	2‴	3‴	5‴	6‴	ref
23	quercetin dimer 4′-glc[b] (A)	6.04, d, 1.7	6.11, d, 1.7 6.22, d, 1.7	7.37, d, 1.7 7.39, d, 1.7		7.17, d, 8.8	7.20, d, 8.8 7.21, d, 8.8	*43*

		chemical shift (ppm), multiplicity, coupling constant (Hz)								
no.	dihydroflavonols	2	3a	3b	6	8	2′	3′	5′	6′	ref
51	taxifolin 4′-glc (M)	5.08	4.59		6.02[c]	5.99[c]	7.14		7.33	7.06	*27*

		chemical shift (ppm), multiplicity, coupling constant (Hz)									
no.	anthocyanins	4/β	6	8	2′	3′ 4′	5′	6′	OCH_3	malonyl	ref
26	cy 3-glc (M/T5)	9.03	6.71	6.90	8.05		7.04	8.25			*57*
27	cy 3-(3″-glc-glc) (M/T5)	9.12	6.75	6.92	8.13		7.10	8.35			*57*
27	cy 3-(3″-glc-glc) (D/T10)	8.90, s	6.89, d, 2	6.70, d, 2	8.01, d, 2		7.02, d, 9	8.20, dd, 9, 2			*56*
29	cy 3-(6″-mal-glc) (M/T5)	8.99	6.74	6.95	8.07		7.08	8.33		3.44, s	*57*
30	cy 3-(3″-glc-6″-mal-glc) (D/T10)	8.82, s	6.89, s	6.72, s	7.98, d, 2		7.02, d, 9	8.20, dd, 9, 2		3.36, s	*56*
30	cy 3-(3″-glc-6″-mal-glc) (M/T5)	9.04	6.77	6.99	8.11		7.10	8.36		3.44, s	*57*
	cy 3-(3″-glc-6″-metmal-glc) (M/T5)	9.02, s	6.76, d, 1.8	6.98, d, 1.8	8.09, d, 2.3		7.09, d, 8.8	8.35, dd, 8.8, 2.3	3.69, s	3.54, s	*59*
35	cy 3,5-diglc (M/T5)	9.24, d, 0.9	7.16, d, 1.9	7.18, dd, 1.9, 0.9	8.17, d, 2.3		7.13, d, 8.8	8.44, dd, 8.8, 2.3			*59*
38	cy 3,4′-diglc (M/T5)	9.26, d, 0.9	6.78, d, 1.9	7.04, dd, 1.9, 0.9	8.16, d, 2.2		7.50, d, 8.7	8.35, dd, 8.7, 2.2			*59*
39	cy 3-(3″-glc-6″-mal-glc)-4′-glc (M/T5)	9.19 s (b)	6.80, d, 2.1	7.04, dd, 2.1, 0.9	8.16, d, 2.2		7.50, d, 8.8	8.32, dd, 8.8, 2.2			*59*
40	cy 7-(3″-glc-6″-mal-glc)-4′-glc (M/T5)	9.19, s	6.29, d, 2.1	6.37, d, 2.1	7.70, d, 2.2		7.37, d, 8.8	7.76, dd, 8.8, 2.2			*59*
42	pn 3-(6″-mal-glc) (M/T5)	9.06 s (b)	6.77, d, 1.8	7.01, dd, 1.8, 0.9	8.29, d, 2.2		7.14, d, 8.8	8.34, dd, 8.8, 2.2	4.11, s		*59*
44	pn 3-(6″-mal-glc)-5glc (M/T5)	9.08, d, 0.9	7.13, d, 2.0	7.23, dd, 2.0, 0.9	8.34, d, 2.3		7.18, d, 8.8	8.41, dd, 8.8, 2.3	4.12, s		*59*
50	5-Carboxypyranocyanidin 3-(6″-mal-glc) (D/T20)	7.92, s	7.16, d, 1.8	7.25, d, 1.8	7.88, d, 2.0		6.92, d, 8.7	8.00, dd, 8.7, 2.0			*61*

[a] (A) = acetone-d_6, (M) = CD_3OD; (M/T5) = CD_3OD-CF_3COOD 95:5; (D) = DMSO-d_6, (D/T10) = DMSO-d_6-CF_3COOD 90:10; (D/T20) = DMSO-d_6-CF_3COOD 80:20; (T) = CF_3COOD; glc = glucopyranose; mal = malonyl; s = singlet; d = doublet; ‘d’ = semi-doublet; dd = double doublet. [b] Mixture of two stereoisomers. [c] Assignments may be reversed.

isorhamnetin 4′-glucoside, quercetin 3-glucoside, and quercetin 7-glucoside as minor pigments, each accounting for more than 1% of the total flavonoid content, in addition to trace amounts of isorhamnetin 3,4′-diglucoside, **19**, kaempferol 3,4′-diglucoside, and

Table 2.2. ^{1}H NMR Spectral Data of Glycosyl Moieties of Flavonoid Glycosides from Onions Recorded in Various Solvents[a]

		chemical shift (ppm), multiplicity, coupling constant (Hz)						
no.	glycosyl moiety	H-1	H-2	H-3	H-4	H-5	H-6	ref
				Flavonols				
13	kaempferol 4′-glc (D)	4.98, d, 7.2	na	na	na	na	3.71, dd, 11.0, 3.7; 3.46, dd, 11.0, 3.7	*32*
7	quercetin 3′-glc (D)	4.83, d, 7.2	3.16–4.14, m	3.16–4.14, m	3.16–4.14, m	3.16–4.14, m	3.16–4.14, m	*34*
2	quercetin 4′-glc (M)	5.00	3.61	3.60	3.53	3.57	4.02 3.85	*27*
8	quercetin 3,7-diglc (D)	5.47, d, 7.4	3.22	3.21	3.06	3.07	3.56 3.30	*30*
8	quercetin 3,**7**-diglc (D)	5.08, d, 7.4	3.24	3.27	3.14	3.42	3.67 3.43	*30*
3	quercetin **3**,4′-diglc (D)	5.48	3.21	3.23	3.10	3.11	3.58 3.33	*27*
3	quercetin 3,**4′**-diglc (D)	4.85	3.34	3.32	3.21	3.39	3.72 3.50	*27*
5	quercetin **7**,4′-diglc (D)	5.08, d, 7.5	3.26, dd, 7.5, 9.3	3.29 *t* 9.3	3.18 *t* 9.3	3.46, m	3.71, dd, 11.7, 2.0; 3.48, dd, 11.7, 5.6	*30*
5	quercetin 7,**4′**-diglc (D)	4.85, d, 7.5	3.33, dd, 7.5, 9.2	3.31, t, 9.2	3.19, dd, 9.2, 9.6	3.38, ddd, 2.0, 6.3, 9.6	3.73, dd, 12.1, 2.0; 3.48, dd, 12.1, 6.3	*30*
9	quercetin **3**,7,4′-triglc (D)	5.51	3.19	3.22	3.03	3.07	3.54; 3.30	*27*
9	quercetin 3,**7**,4′-triglc (D)	4.87	3.23	3.26	3.12	3.37	3.69; 3.46	*27*
9	quercetin 3,7,**4′**-triglc (D)	5.09	3.31	3.26	3.16	3.41	3.69; 3.46	*27*
18	isorhamnetin 3-glc (D)	5.38, d, 6.8	3.25–4.15, m	3.25–4.15, m	3.25–4.15, m	3.25–4.15, m	3.25–4.15, m	*34*
				Dimeric Flavonols				
23	quercetin dimer 4′-glc[b] (A)	4.85, d, 7.4 4.86, d, 7.4	3.45–3.52, m	3.45–3.52, m	3.45–3.52, m	3.45–3.52, m	3.45–3.52, m	(*43*)
				Dihydroflavonols				
51	taxifolin 4′-glc (M)	4.91	3.60	3.52	3.50	3.56	3.99; 3.82	*27*
				Anthocyanins				
26	cy 3-glc (M/T5)	5.37	3.76	3.67	3.56	3.67	4.02; 3.83	*57*
27	cy **3-**(3″-glc-**glc**) (D/T10)	5.46, d, 8	3.73	3.51–3.59	3.40, t, 9	3.51–3.59	3.73; 3.51–3.59	*56*
27	cy 3-(**3″-glc**-glc) (D/T10)	4.38, d, 8	3.14, t, 8	3.24, t, 9	3.08, t, 9	3.38–3.44	3.73; 3.21–3.28	*56*
29	cy 3-(6″-mal-glc) (M/T5)	5.36	3.79	3.58	3.43	3.88	4.65; 4.37	*57*
30	cy **3-**(3″-glc-6″-mal-**glc**) (D/T10)	5.49, d, 8	3.76, t, 8	3.60, t, 9	3.42, br t, 8	3.42	4.46, d, 12; 4.16, dd, 12, 8	*56*
30	cy 3-(**3″-glc**-6″-mal-glc) (D/T10)	4.39, d, 8	3.14, t, 8	3.24, t, 9	3.08, t, 9	3.42	3.74, br s; 3.26, t, 9	*56*
30	cy **3-**(3″-glc-6″-mal-**glc**) (M/T5)	5.41	3.99	3.84	3.62	3.96	4.66; 4.38	*57*
30	cy 3-(**3″-glc**-6″-mal-glc) (M/T5)	4.71	3.43	3.54	3.38	3.46	4.00; 3.74	*57*
	cy **3-**(3″-glc-6″-metmal-**glc**) (M/T5)	5.43, d, 7.7	3.98, dd, 9.0, 7.7	3.84, t, 9.0	3.63, dd, 9.3, 9.0	3.95, ddd, 9.3, 7.0, 1.8	4.67, dd, 11.8, 1.8; 4.40, dd, 11.8, 7.0	*59*
	cy 3-(**3″-glc**-6″-metmal-glc) (M/T5)	4.71, d, 7.7	3.43, m	3.51, t, 9.1	3.39, m	3.47, ddd, 9.5, 6.8, 2.0	4.01, dd, 11.8, 2.0; 3.75, dd, 11.8, 6.8	*59*
35	cy **3glc**-5-glc (M/T5)	5.38, d, 7.9	3.78, dd, 9.3, 7.9	3.62, t, 9.3	3.49, t, 9.3	3.71, m	4.06, dd, 12.0, 2.2; 3.81, dd, 12.0, 6.0	*59*
35	cy 3glc-**5-glc** (M/T5)	5.25, d, 7.9	3.76, dd, 9.3, 7.9	3.64, m	3.54, t, 9.3	3.65, m	4.04, dd, 12.0, 2.2; 3.83, dd, 12.0, 5.8	*59*
38	cy **3-glc**-4′-glc (M/T5)	5.40, d, 7.8	3.75, dd, 9.2, 7.8	3.61, t, 9.2	3.51, m	3.64, m	4.00, dd, 12.0, 2.0; 3.79, dd, 12.0, 6.1	*59*
38	cy 3-glc-**4′-glc** (M/T5)	5.17, d, 7.8	3.69, dd, 9.2, 7.8	3.62, t, 9.2	3.53, t, 9.2	3.64, m	4.04, dd, 12.0, 2.1; 3.84, dd, 12.0, 5.7	*59*
39	cy **3-**(3″-glc-6″-mal-**glc**)-4′-glc (M/T5)	5.44, d, 7.7	3.98, m	3.84, m	3.65, m	3.96, m	4.68, dd, 12.1, 1.8; 4.39, dd, 12.1, 7.3	*59*
39	cy 3-(**3″-glc**-6″-mal-glc)-4′-glc (M/T5)	4.71, d, 7.7	3.44, m	3.39, m	3.51, m	3.47, m	4.01, dd, 12.1, 2.2; 3.75, m	*59*
39	cy 3-(3″-glc-6″-mal-glc)-**4′-glc** (M/T5)	5.17, d, 7.7	3.69, m	3.62, m	3.54, m	3.64, m	4.04, dd, 12.1, 1.8; 3.84, dd, 12.1, 3.0	*59*
40	cy **7-**(3″-glc-6″-mal-**glc**)-4′-glc (M/T5)	5.53, d, 7.7	3.55, m	3.69, m	3.52, m	3.67, m	4.49, dd, 12.1, 1.8; 4.35, dd, 12.1, 5.9	*59*
40	cy 7-(**3″-glc**-6″-mal-glc)-4′-glc (M/T5)	4.65, d, 7.7	3.38, m	3.49, m	3.39, m	3.43, m	3.98, m; 3.74, m	*59*
40	cy 7-(3″-glc-6″-mal-glc)-**4′-glc** (M/T5)	5.07, d, 7.7	3.66, m	3.62, m	3.54, m	3.65, m	4.03, m; 3.84, m	*59*
42	pn 3-(6″-mal-glc) (M/T5)	5.39, d, 7.7	3.75, m	3.64, t, 9.0	3.51, m	3.91, ddd, 9.5, 7.0, 2.0	4.63, dd, 11.8, 2.0; 4.39, dd, 11.8, 7.0	*59*
44	pn **3-**(6″-mal-**glc**)-5glc (M/T5)	5.53, d, 7.7	3.78, m	3.65, m	3.53, m	3.98, m	4.53, dd, 11.9, 2.3; 4.45, dd, 11.9, 7.2	*59*
44	pn 3-(6″-mal-glc)-**5glc** (M/T5)	5.29, d, 7.7	3.79, m	3.65, m	3.55, m	3.69, m	4.05, dd, 12.1, 2.3; 3.84, dd, 12.1, 6.5	*59*
50	5-carboxypyranocyanidin 3-(6″-mal-glc) (D/T20)	4.59, d, 7.7	3.49, t, 8.7	3.21, m	3.17, m	3.23, m	4.03, d b, 11.8; 3.94, dd, 11.8, 6.1	*61*

[a] cy = cyanidin; pn = peonidin; glc = glucopyranose; mal = malonyl; (M) = CD_3OD; (M/T5) = CD_3OD-CF_3COOD 95:5; (D) = DMSO-d_6, (D/T10) = DMSO-d_6-CF_3COOD 90:10; (T) = CF_3COOD, (A) = acetone-d_6; na = not assigned; d = doublet; 'd' = semi-doublet; dd = double doublet; t = triplet; ddd = double double doublet; m = multiplet. The parts in bold indicate the monosaccharide involved. [b] Mixture of two stereoisomers.

kaempferol 4′-glucoside. Quercetin 3-rutinoside (rutin, **11**) has been reported as a minor flavonoid in different onion cultivars (*33, 35*). Together with quercetin 3-rhamnoside, **10** (*36*), rutin is the only reported flavonoid from bulbs of onions containing a glycosyl unit other than glucose. Rodrigues and co-workers (*37*) reported kaempferol 3-glucoside, **14**, as a minor pigment from the cultivars "Póvoa White" and "Póvoa Red" using HPLC. The latter compound was recently isolated from onion sources and its structure confirmed by NMR spectroscopy (*38*). Fossen and co-workers (*27*) isolated quercetin 3,7,4′-triglucoside, **9**, in addition to quercetin,

Table 3.1. ^{13}C NMR Spectral Data of Flavonoids from Onions Recorded in Various Solvents[a]

no.	flavonols	2	3	4	5	6	7	8	9	10	1′	2′	3′	4′	5′	6′	ref
13	kaempferol 4′-glc (D)	145.91	136.3	176.05	160.69	98.33	164.32	93.6	156.27	103.02	124.41	129.13	116.11	158.44	116.11	129.13	*32*
1	quercetin (M)	148.00	137.21	177.33	162.50	99.25	165.34	94.40	158.22	104.52	124.15	115.99	148.75	146.21	116.22	121.67	*27*
1	quercetin (D)	146.83	135.75	175.86	160.75	98.21	163.89	93.38	156.16	103.04	121.98	115.10	145.08	147.72	115.63	120.01	*26*
6	quercetin 3-glc (D)	156.19	133.34	177.45	161.20	98.66	164.10	93.50	156.33	104.00	121.62	115.21	144.81	148.46	116.22	121.18	*26*
4	quercetin 7-glc (D)	147.58	136.06	176.01	160.36	99.88	162.68	94.26	155.72	104.66	121.05	115.37	145.06	147.90	115.57	120.05	*26*
2	quercetin 4′-glc (D)	146.78	136.41	176.05	160.72	98.26	164.06	93.52	156.25	103.11	125.12	115.07	146.36	145.92	115.84	119.54	*26*
2	quercetin 4′-glc (M)	148.04	137.89	177.36	162.47	99.31	165.66	94.47	158.19	104.54	127.60	116.49	147.83	146.79	117.62	121.26	*27*
8	quercetin 3,7-diglc (D)	155.95	133.56	177.59	160.85	99.71	162.79	94.31	156.80	105.60	121.62	115.17	144.81	148.61	116.44	121.05	*26*
3	quercetin 3,4′-diglc (D)	155.96	134.26	174.82	161.64	99.16	164.65	94.08	156.83	104.53	124.92	115.86	147.67	146.52	116.97	121.42	*27*
5	quercetin 7,4′-diglc (D)	147.06	136.88	176.37	160.46	98.96	162.94	94.45	155.97	104.86	125.12	115.46	146.74	146.48	115.96	119.77	*30*
9	quercetin 3,7,4′-triglc(D)	156.27	134.20	177.62	160.90	99.48	162.99	94.49	156.12	105.61	124.42	116.73	147.72	146.22	115.52	120.40	*27*

no.	dimeric flavonols	2	3	4	5	6	7	8	9	10	1′	2′	3′	4′	5′	6′	ref
23	quercetin dimer 4′-glc	145.4	137.6	176.8	162.3	99.3	165.4	94.7	157.9	104.2	127.1	117.1	142.9	141.8	118.1	120.6	*43*

no.	dimeric flavonols	2″	3″	4″	5″	6″	7″	8″	9″	10″	1‴	2‴	3‴	4‴	5‴	6‴	ref
23	quercetin dimer 4′-glc	101.3	92.4	188.6	165.0	98.3	170.2	97.6	160.6	100.6	127.1	117.2	148.0	147.5	117.6	120.6	*43*

no.	dihydroflavonols	2	3	4	5	6	7	8	9	10	1′	2′	3′	4′	5′	6′	ref
51	taxifolin 4′-glc (M)	85.55	73.70	198.22	168.69	97.39[b]	165.72	96.32[b]	164.35	102.19	133.96	116.57	147.22	148.37	118.51	120.70	*27*

no.	anthocyanins	2	3	4	5	6	7	8	9	10	1′	2′	3′	4′	5′	6′	OCH_3	ref
26	cyanidin 3-glc (M/T5)	163.91	145.57	136.68	159.25	103.45	170.55	95.17	157.58	113.32	121.16	118.39	147.34	155.77	117.46	128.25		*57*
35	cy 3,5-diglc	165.0	146.6	136.0	156.8	105.8	169.5	97.4	157.2	113.4	121.2	118.6	147.7	156.7	117.6	129.1		*59*
38	cy 3,4′-diglc	na	na	138.5	na	na	na	na	na	na	na	118.7	na	na	117.0	126.4		*59*
29	cyanidin 3-(6″-mal-glc) (M/T5)	164.30	145.55	136.69	159.70	103.43	170.49	95.26	157.71	113.23	121.18	118.37	147.44	155.86	117.39	128.47		*57*
30	cy 3-(3″-glc-6″-mal-glc) (M/T5)	164.58	145.55	137.00	na	103.4	173.54	na	na	113.20	121.23	118.50	147.46	155.94	117.33	128.48		*57*
	cy 3-(3″-glc-6″-metmal-glc) (M/T5)	164.61	145.50	136.93	159.10	103.48	170.50	95.31	157.77	113.24	121.19	118.48	147.57	155.95	117.32	128.51	52.86	*59*
39	cy 3-(3″-glc-6″-mal-glc)-4′-glc (M/T5)	163.3	145.3	141.6	158.5	na	na	na	na	na	123.9	119.2	148.6	152.8	117.2	127.8		*59*
40	cy 7-(3″-glc-6″-mal-glc)-4′-glc (M/T5)	na	na	139.1	na	101.7	na	101.2	na	na	na	118.5	na	na	117.0	124.3		*59*
42	pn 3-(6″-mal-glc) (M/T5)	164.32	145.54	137.34	159.20	103.40	170.54	95.50	157.91	113.52	121.09	115.28	149.59	156.62	117.65	129.04	56.91	*59*
44	pn 3-(6″-mal-glc)-5glc (M/T5)	na	na	na	na	105.4	na	97.5	na	na	na	115.3	na	na	117.8	na	57.1	*59*
50	carboxypyrcy 3-(6″-mal-glc) (D/T20)	165.01	135.25	109.79[b]	153.07	101.30	168.40	101.05	153.20	109.67[b]	120.33	118.5	146.14	153.89	116.89	126.52		*61*

no.	anthocyanins	COOH	α	β	1 Mal	2 Mal	3 Mal	ref
29	cyanidin 3-(6″-mal-glc) (M/T5)				166.65	na	170.19	*57*
30	cy 3-(3″-glc-6″-mal-glc) (M/T5)				168.59	na	170.88	*57*
	cy 3-(3″-glc-6″-metmal-glc) (M/T5)				168.15	41.70	168.76	*59*
42	pn 3-(6″-mal-glc) (M/T5)				168.59	na	168.76	*59*
50	carboxypyrcy 3-(6″-mal-glc) (D/T20)	160.52	154.46	106.8	167.03	na	168.28	*61*

[a] (A) = acetone-d_6, (M) = CD_3OD; (M/T5) = CD_3OD-CF_3COOD 95:5; (D) = DMSO-d_6, (D/T10) = DMSO-d_6-CF_3COOD 90:10; (D/T20) = DMSO-d_6-CF_3COOD 80:20; (T) = CF_3COOD; cy = cyanidin; pn = peonidin; glc = glucopyranose; mal = malonyl; carboxypyrcy = 5-carboxypryanocyanidin; na = not assigned. [b] Assignments may be reversed.

quercetin 4′-glucoside, and quercetin 3,4′-diglucoside from pigmented scales of the cultivar "Red Baron". The structure determinations were based on acid hydrolysis, chromatography (TLC and HPLC), and 2D homo- and heteronuclear NMR spectroscopic techniques. The same compounds were reported to occur in a southern Italian onion cultivar, in addition to minor amounts of

Table 3.2. ^{13}C NMR Spectral Data of Glycosyl Moieties of Flavonoid Glycosides from Onions Recorded in Various Solvents[a]

no.	glycosyl moiety	chemical shift (ppm) C-1	C-2	C-3	C-4	C-5	C-6	ref
	flavonols							
13	kaempferol 4′-glc (D)	99.93	73.17	76.6	69.61	77.12	60.6	*32*
6	quercetin 3-glc (D)	100.87	74.01	76.50	69.95	77.57	60.98	*26*
4	quercetin 7-glc (D)	98.76	73.13	76.13	69.56	77.15	60.61	*26*
2	quercetin 4′-glc (D)	101.38	72.28	75.96	69.80	77.29	60.73	*26*
2	quercetin 4′-glc (M)	103.42	74.82	77.54	71.32	78.36	62.44	*27*
8	quercetin 3,7-diglc (D)	100.68	74.05	76.49	69.92	77.61	60.94	*26*
8	quercetin 3,**7**-diglc (D)	99.30	73.08	76.39	69.56	77.14	60.60	*26*
3	quercetin **3**,4′-diglc (D)	101.23	74.55	76.66	70.36	77.92	61.36	*27*
3	quercetin 3,**4′**-diglc (D)	101.86	73.66	76.22	70.13	77.56	61.10	*27*
5	quercetin **7**,4′-diglc (D)	99.92	73.22	76.54	69.68	77.23	60.75	*30*
5	quercetin 7,**4′**-diglc (D)	101.54	73.39	76.04	69.96	77.41	60.86	*30*
9	quercetin **3**,7,4′-triglc (D)	100.69	74.19	76.49	70.19	77.76	61.46	*27*
9	quercetin 3,**7**,4′-triglc (D)	99.73	73.15	76.50	69.83	77.83	60.79	*27*
9	quercetin 3,7,**4′**-triglc (D)	101.56	73.55	76.49	69.88	77.19	61.04	*27*
		Dimeric Flavonols						
23	quercetin dimer 4′-glc[b] (A)	103.5, 103.4	74.6	77.3	71.0	78.0	62.4	*43*
		Dihydroflavonols						
51	taxifolin 4′-glc (M)	104.24	74.87	77.63	71.33	78.37	62.01	*27*
		Anthocyanins						
26	cy 3-glc (M/T5)	103.72	74.79	78.14	71.08	78.77	62.36	*57*
29	cy 3-(6″-mal-glc) (M/T5)	103.58	74.64	77.90	71.31	75.93	65.47	*57*
30	cy **3**-(3″-glc-6″-mal-**glc**) (M/T5)	103.34	73.91	87.56	69.98	75.60	65.44	*57*
30	cy 3-(**3″-glc**-6″-mal-glc) (M/T5)	105.14	75.46	77.89	71.61	78.29	62.64	*57*
	cy **3**-(3″-glc-6″-metmal-**glc**) (M/T5)	103.32	73.90	87.55	69.92	75.58	65.45	*59*
	cy 3-(**3″-glc**-6″-metmal-glc) (M/T5)	105.13	75.46	77.88	71.61	78.28	62.64	*59*
35	cy **3glc**-5-glc (M/T5)	104.6	74.7	78.3	71.4	79.0	62.7	*59*
35	cy 3glc-**5-glc** (M/T5)	102.7	74.6	78.1	71.2	78.6	62.6	*59*
38	cy **3-glc**-4′-glc (M/T5)	103.7	74.6	77.6	71.0	78.3	62.4	*59*
38	cy 3-glc-**4′-glc** (M/T5)	102.3	74.5	77.8	71.1	78.3	62.4	*59*
39	cy **3**-(3″-glc-6″-mal-**glc**)-4′-glc (M/T5)	103.3	74.2	87.5	70.0	75.6	65.5	*59*
39	cy 3-(**3″-glc**-6″-mal-glc)-4′-glc (M/T5)	104.8	75.5	78.0	71.2	78.2	62.7	*59*
39	cy 3-(3″-glc-6″-mal-glc)-**4′-glc** (M/T5)	102.4	74.9	77.9	71.2	78.1	62.5	*59*
40	cy **7**-(3″-glc-6″-mal-**glc**)-4′-glc (M/T5)	95.3	74.9	87.3	71.2	75.0	65.4	*59*
40	cy 7-(**3″-glc**-6″-mal-glc)-4′-glc (M/T5)	104.9	75.5	78.0	71.6	78.2	62.7	*59*
40	cy 7-(3″-glc-6″-mal-glc)-**4′-glc** (M/T5)	102.7	75.0	77.7	71.2	78.1	62.5	*59*
42	pn 3-(6″-mal-glc) (M/T5)	103.81	74.81	78.00	71.33	76.01	65.45	*59*
44	pn **3**-(6″-mal-**glc**)-5glc (M/T5)	102.6	74.7	78.1	71.5	75.7	65.6	*59*
44	pn 3-(6″-mal-glc)-**5glc** (M/T5)	102.8	74.7	78.1	71.3	78.5	62.8	*59*
50	5-carboxypyranocyanidin 3-(6″-mal-glc) (D/T20)	105.58	74.13	76.52	70.05	74.78	64.30	*61*

[a] glc = glucopyranose; mal = malonyl; (M) = CD_3OD; (M/T5) = CD_3OD-CF_3COOD 95:5; (D) = DMSO-d_6, (D/T10) = DMSO-d_6-CF_3COOD 90:10; (T) = CF_3COOD, (A) = acetone-d_6. The parts in bold indicate the monosaccharide involved. [b] Mixture of two stereoisomers.

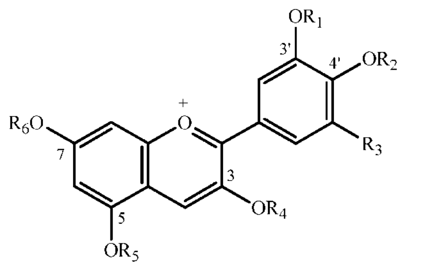
isorhamnetin 3,4′-diglucoside, **19**, and traces of isorhamnetin 3-glucoside, **18** (*39*). Glycosides of myricetin have hitherto not been detected in onions. However, after complete hydrolysis of a red onion extract, myricetin aglycone, **21**, has been preliminarily characterized (*40, 41*).

TLC and HPLC analyses, combined with hydrolytic treatment of flavonoid-containing extracts from onions, revealed the presence of kaempferol and quercetin glycosides substituted with sulphate and glucuronic acid (*42*). These pigments still await NMR spectroscopic and mass spectral characterization.

As a consequence of the significant improvements in methods and instrumentations used for separation and structure elucidation (*13*), especially during the last decade, complex dimeric and trimeric flavonoids isolated from onions have been reported (*43–46*). From the brownish, dry scales of onions, Furusawa and co-workers (*43*) isolated quercetin and quercetin 4′-glucoside together with novel isomeric quercetin dimers (**Figure 3**). These dimers were either glucosylated at the 4′-position, **23**, of one of the quercetin subunits or nonglucosylated, **22**. The compounds are found to interact with lipid bilayers and change the fluidity of liposomal membranes (*44, 45*). Such compounds have also been isolated by Ly and co-workers (*46*) who also indicated a trimeric and further dimeric flavonoid structures derived from quercetin, **25**, as well as condensation products of quercetin and protocatechuic acid, **24** (**Figure 3**).

ANTHOCYANINS OF ONIONS

The qualitative anthocyanin content of red onion cultivars includes a wide structural assortment including several unique flavonoid structures (**Figures 4** and **5**, **Table 1**). Vandevelde (*47*) first mentioned red onion as a rich source of anthocyanins. In an early survey, Robinson and Robinson (*48*) indicated that the red skins of cv. “Sutton’s Blood Red” contained a cyanidin derivative glycosylated with a bioside composed of an unidentified pentose and an unidentified hexose. Bate-Smith and co-workers suggested a cyanidin glucoside (*49*). Fouassin (*50*) reported the presence of three cyanidin derivatives in red onion including a cyanidin monoside and a cyanidin diglucoside. The identification of peonidin 3-arabinoside (*21*) could not be confirmed by Fuleki (*51, 52*) who, however, identified cyanidin 3-glucoside, **26**, as one of the main anthocyanins, in addition to minor amounts of peonidin 3-glucoside, **41**. Du and co-workers (*53*) identified a second major anthocyanin as cyanidin 3-(3″-glucosylglucoside) (also known as cyanidin 3-laminari-



	R_1	R_2	R_3	R_4	R_5	R_6
26	H	H	H	glc	H	H
27	H	H	H	lam	H	H
28	H	H	H	3''-malglc	H	H
29	H	H	H	6''-malglc	H	H
30	H	H	H	6''-mallam	H	H
31	H	H	H	3'',6''-di-malglc	H	H
32	H	H	H	di-mallam	H	H
33	H	H	H	3''-acglc	H	H
34	H	H	H	mal-acglc	H	H
35	H	H	H	glc	glc	H
36	H	H	H	malglc	glc	H
37	H	glc	H	H	H	H
38	H	glc	H	glc	H	H
39	H	glc	H	6''-mallam	H	H
40	H	glc	H	H	H	6''-mallam
41	CH_3	H	H	glc	H	H
42	CH_3	H	H	6''-malglc	H	H
43	CH_3	H	H	glc	glc	H
44	CH_3	H	H	6''-malglc	glc	H
45	H	H	OH	glc	H	H
46	H	H	OH	glcglc	H	H
47	CH_3	H	OH	glc	H	H
48	CH_3	H	OH	glcglc	H	H

Figure 4. Structures of anthocyanins (**26** through **48**) reported to occur in bulbs of onions (*Allium cepa* L.). Abbreviations are as follows: glc = glucose; lam = laminariobioside (3-glucosylglucoside); mal = malonyl; ac = acetoyl.

obioside, **27**). Moore and co-workers (*54, 55*) indicated the presence of significant amounts of anthocyanins acylated with aliphatic acids, however, without determining their identities. More recently, the main anthocyanins of several red onion cultivars have been identified as cyanidin 3-(6″-malonylglucoside), **29**, and cyanidin 3-(3″-glucosyl-6″-malonylglucoside), **30**, in addition to cyanidin 3-glucoside and cyanidin 3-(3″-glucosylglucoside), **27** (*56–59*). These anthocyanins are among the main pigments in all recently investigated cultivars. The identification of cyanidin 3-(3″-glucosylglucoside) as one of the main anthocyanins in Spanish red onion (*53*) could not be confirmed by Ferreres and co-workers (*60*), who reported the main anthocyanins of this cultivar to be the 3-glucoside, the 3-malonylglucoside, **28**, the 3-arabinoside, and the 3-malonylarabinoside of cyanidin. However, the latter two pigments are lacking NMR spectroscopic and mass spectral characterization.

Most of the anthocyanins reported to occur in various cultivars of red onion are cyanidin derivatives, although minor amounts of peonidin derivatives have been identified (**Table 1**) (*51, 52, 57, 58, 61, 62*). The cultivar “Tropea” seems to be exceptional due to a relatively high content of delphinidin derivatives (about 30 % of the total anthocyanin content) and the presence of petunidin derivatives (*63*). The cultivars Póvoa red and Póvoa white have been indicated to contain exclusively di- and monoglucosyl derivatives of delphinidin and petunidin (*37*); however, structural evidence for these compounds has not been presented. Among the pigments characterized by NMR spectroscopy and mass spectrometry, the glycosyl moiety of anthocyanins from red onions is restricted to glucose (**Tables 2.1–3.2**). The main anthocyanins of all cultivars investigated are exclusively glycosylated at the anthocyanidin 3-position. However, minor amounts of peonidin 3-(6″-malonylglucoside)-5-glucoside, **44** (*59*), and the 3,5-diglucosides of cyanidin, **35**, and peonidin, **43**, have been identified (*57*). The 4′-glucoside, **37**, the 3,4′-diglucoside, **38**, the 3-(3″-glucosyl-6″-malonylglucoside)-4′-glucoside, **39**, and the 7-(3″-glucosyl-6″-malonylglucoside)-4′-glucoside, **40**, of cyanidin that were recently characterized from pigmented scales of red onion (*59*) are the only anthocyanins with a glycosyl at the 4′-position (*13, 64*). Malonic acid is the main acyl moiety of acylated anthocyanins of red onion cultivars (*56–63*). According to the recent literature (*56–60*), anthocyanins acylated with malonic acid are the quantitatively most significant, and these pigments predominate the anthocyanin profiles of red onions. However, minor amounts of acetylated pigments have recently been detected by LC-MS analysis (*62*). Recently, Fossen and Andersen (*61*) characterized minor amounts of 5-carboxypyranocyanidin 3-glucoside, **49**, and 5-carboxypyranocyanidin 3-(6″-malonylglucoside), **50**, belonging to the group of pyranoanthocyanins that are regarded as particularly color-stable compared with analogous anthocyanidin glycosides (**Figure 5**).

DIHYDROFLAVONOLS

The dihydroflavonols identified in onions (**Figure 6**) are all based on taxifolin (3,5,7,3′,4′-pentahydroxyflavanone), **52**, which exhibits structural analogy to quercetin and cyanidin, that is, the predominant flavonol and anthocyanidin aglycones found in pigmented scales of onions. Ferreres and co-workers (*60*) identified taxifolin 3-glucoside, **54**, in Spanish red onion (cultivar “Morada de Amposta”). Fossen and co-workers (*27*) characterized the rare dihydroflavonol taxifolin 4′-glucoside, **51**, from pigmented scales of cv. “Red Baron”’ by the application of 1D and 2D NMR spectroscopy. Although the structural diversity of dihydroflavonoids characterized from onions is restricted compared with the wide structural assortment of flavonols and anthocyanins identified from the same source, they may occur at high concentrations in some cultivars (*65*). From bulbs of the cv. “Tropea”, which is cultivated in Southern Italy, Corea and co-workers (*65*) isolated 5.9 mg of taxifolin 7-glucoside, **53**, and 98.1 mg of taxifolin per kilogram of FW.

QUANTITATIVE AMOUNTS OF FLAVONOIDS IN ONION CULTIVARS

Particularly in the early literature, quercetin aglycone has been identified as one of the major pigments of several cultivars (*17, 66*). In “Carmen hybrid”, “Sweet Spanish Utah”, “Early Yellow Globe”, “Yellow Globe hybrid”, “Sweet Spanish hybrid”, “Red Hamburger”, and “Walla Walla”, 23%, 24%, 39%, 53%, 50%, 40%, and 51%, respectively, of the total quercetin content in onion skin was present as quercetin aglycone (*66*). Although there is some variation regarding the relative quantitative content of individual flavonols in different cultivars, quercetin 4′-glucoside and quercetin 3,4′-diglucoside have in most instances, in more recent literature, been identified as the main flavonols. These two pigments have been shown to account for more than 80–85% of the total flavonoid content in some yellow cultivars, with concentrations from 50 to 1300 and from 36 to 394 $mg \cdot kg^{-1}$ FW for quercetin 4′-glucoside and quercetin 3,4′-diglucoside, respectively (*26, 35, 37, 67–71*). Among the remaining flavonols, quercetin 3-glucoside, quercetin 7-glucoside, quercetin 7,4′-diglucoside, and isorhamnetin 4′-glucoside have each been recognized to account for more than 1% of the total flavonoid content (*26*). However, derivatives of kaempferol, isorhamnetin, and myricetin have been reported to comprise altogether 19% and 21% of the total flavonoid contents in

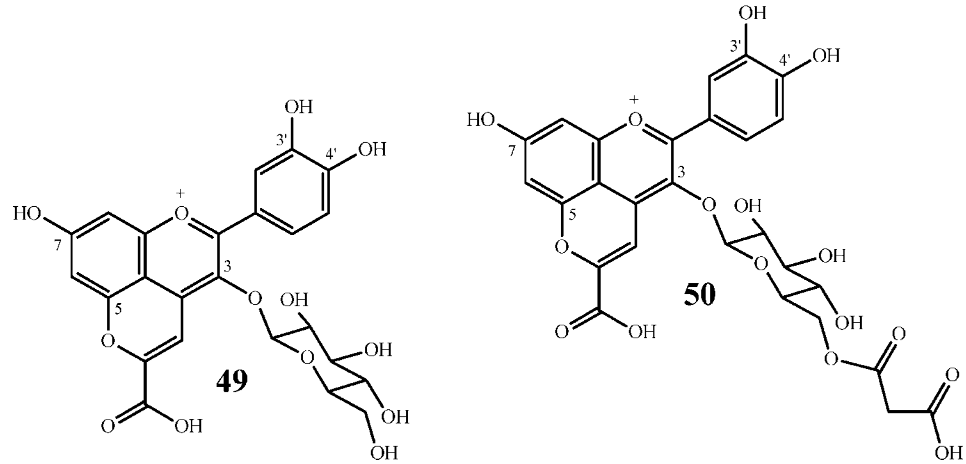
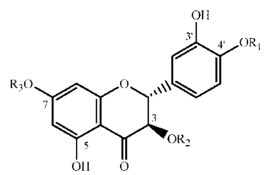


Figure 5. Structures of the 5-carboxypyranoanthocyanins **49** and **50**.



	R_1	R_2	R_3
51	Glc	H	H
52	H	H	H
53	H	H	Glc
54	H	Glc	H

Figure 6. Structures of dihydroflavonols (**51** through **54**) reported to occur in bulbs of onions (*Allium cepa* L.). Abbreviation glc = glucose.

hydrolyzed extracts of some red and yellow cultivars, respectively (http://www.nal.usda.gov/fnic/foodcomp/Data/Flav/Flav02-1.pdf). This indicates that the sum of several minor/trace pigments, whose individual concentrations may be too low to be isolated, seems to be quantitatively significant.

According to the USDA Database for the Flavonoid Content of Selected Food (http://www.nal.usda.gov/fnic/foodcomp/Data/Flav/Flav02-1.pdf), yellow onions contain 214 mg of quercetin, 50 mg of isorhamnetin, 6 mg of kaempferol, and 0.2 mg of myricetin per kilogram of FW. Some red onion cultivars have been found to contain 334 mg of quercetin, 43 mg of isorhamnetin, 11 mg of kaempferol, and 27 mg of myricetin per kilogram of FW. The maximum values reported for quercetin in yellow and red onion are 1187 and 1917 $mg \cdot kg^{-1}$ FW, respectively (*41, 66, 67, 69, 70, 72–86*). Determinations of absolute quantities of anthocyanins in red and pink onion cultivars are sparse in the literature. Rhodes and Price (*68*) reported that the anthocyanins of the red cultivar “Red baron” and the pink cultivar “Rose” comprised 9.2% and 0.7%, respectively, of the total flavonoid contents in the edible parts of the bulbs. The total flavonoid contents in “Red baron” and “Rose” were 803 and 711 $mg \cdot kg^{-1}$ FW, respectively, indicating that the corresponding anthocyanin contents of these two cultivars were 74 and 5 $mg \cdot kg^{-1}$ FW. According to Fossen and co-workers (*57*), the cultivar “Red Baron” contains 51% cyanidin 3-(6″-malonylglucoside), 22% cyanidin 3-(3″-glucosyl-6″-malonylglucoside), 3% cyanidin 3-(3″-glucosylglucoside), and 18% cyanidin 3-glucoside, respectively. Rodrigues and co-workers (*37*) reported that the anthocyanin content of the edible portions of “Póvoa white” and “Póvoa red” were 39.4 and 53.7 $mg \cdot kg^{-1}$ FW, respectively. The anthocyanin content in red onions, based on calculations of quantities of their anthocyanidins has been indicated to be 62–240 mg of cyanidin, 0–23 mg of delphinidin, and up to 12 mg of peonidin per kilogram of FW (*60, 63, 69, 87–90*). Donner and co-workers reported on the total content of anthocyanins in four cultivars of red onions (*58*). The one with the highest score, “Red Bone”, contained 219 mg of anthocyanins per 100 g of DW and cyanidin 3-malonylglucoside accounted for 39.4%, cyanidin 3-malonyllaminariobioside 23.5%, cyanidin 3-laminariobioside 17.8%, and cyanidin 3-glucoside 6.8% of the total anthocyanin content. Gennaro and co-workers reported delphinidin 3-glucosylglucoside to be the major pigment in the edible portion of “Tropea” (65 $mg \cdot kg^{-1}$ FW), whereas cyanidin 3-(6″-malonylglucoside) and cyanidin 3-(3″-glucosyl-6″-malonylglucoside) contributed to the overall anthocyanin concentration with 15 and 10 $mg \cdot kg^{-1}$ FW, respectively (*63*).

Determinations of flavonoid content are in most cases based upon analysis of liberated aglycones after hydrolysis of extracts. In some cases unhydrolyzed extracts have been analyzed on a molar basis, and the amounts of compounds bearing the same flavonoid skeleton have been summarized. It has been found that yellow and red onions are exceptional with respect to their high flavonol content (*91*). Outer dry skins contain 2.5–6.5% flavonols by weight with 67–86% being quercetin aglycone and only to a smaller extent quercetin 4′-glucoside. The epidermis is found to contain glucosides exclusively, mainly as the 4′-glucoside and the 3,4′-diglucoside of quercetin. Quercetin 4′-glucoside is believed to be formed first, whereas formation of quercetin 3,4′-diglucoside follows during storage, and their concentrations increase continuously. There appear to be no flavonols in the mesophyll. The flavonol concentration decreases from the outer to the inner scales with higher levels in the outer than in the inner epidermis (*9, 92*). In a study on the cultivar “Stuttgarter Riesen”, the total flavonol content increased during the growth season from 990 to 7900 $mg \cdot kg^{-1}$ DW (*92*). Quercetin derivatives comprised more than 90% of the total flavonol content.

Some authors point out the importance of location and genetic factors on the impact of quercetin content (*66, 93*). For instance, Okamoto and co-workers recently reported on the differences in quercetin content between long-day cultivars and short-day cultivars (*94*). The long-day cultivars of Rijnsburger type from Northern Europe and their close relatives contain higher concentrations of quercetin glucosides than those of Japanese and North American origins. Also variation within populations is an important factor as intraspecific differences regarding flavonoid contents have been detected in well-known species (*95*). In a screening program involving 75 onion cultivars grown in Texas, it was shown that location, growth stage, and soil type affected the total level of flavonols (*82*). Moreover, the

Table 4. Quantitative Flavonol Contents of Various Onion Cultivars Quantified as Milligrams of Quercetin per Kilogram of FW[a]

cultivar	contents	ref	cultivar	contents	ref
			Red		
Red Baron	930	69	Red Bone	117	83
Karmen	2549	35	Tropea	390	63
20356G	202	83	Tropea rossa	763	80
20355G	157	83	Rossa Lilia	487	80
Kadavan	153	83	Redwing	582	80
20354G	150	83	Morada de Amposta	943	60
4172	141	83			
			Pink		
Rose	719	69	20366G	128	83
20352G	158	83	20357G	118	83
			Yellow		
Sweet savannah	286	83	20249G	68	83
4128	286	83	20257G	56	83
XPH 6068	214	83	4145	54	83
XPH 6023	207	83	447	294	29
4101	179	83	947	365	29
4157	175	83	935	282	29
4122	159	83	Hyper	333	29
XPH 6022	157	83	Hygro	361	29
4144	153	83	Topaz	326	29
TG1015Y	150	83	Superba	228	29
XPH 6028	150	83	Rff	350	29
20275G	150	83	Nirvana	217	40
20277G	146	83	DPS 1032	524	40
4155	145	83	Yellow 2025	482	40
4018	141	83	King-Midas	133	40
TG502	140	83	SBO 133	122	40
Granex 33	139	83	Walla Walla	26	66
Granex 429	138	83	Carmen Hybrid	59	66
20270G	137	83	Sweet Spanish Hybrid	62	66
4143	137	83	Sweet Spanish Utah	61	66
4130	136	83	Yellow Globe Hybrid	25	66
4141	136	83	Early Yellow Globe	15	66
4120	135	83	Rijnsburger	814	69
20272G	128	83	Vsetana	1831	35
4143	126	83	Festival	526	80
4149	124	83	Tamara	617	80
Henry special	123	83	Daytona	933	80
4146	119	83	Dorata Density	979	80
4122	116	83	Castillo	786	80
20303G	111	83	Santana	749	80
20291G	110	83	Kitamiko	292	86
20274G	108	83	Toyohira	359	86
4127	107	83	Kitawase3	213	86
4124	105	83	Tsukisappu	366	86
0001	100	83	Superkitamomiji	367	86
20288G	98	83	CS3–12	331	86
20276G	96	83	Tsukiko22	436	86
20280G	95	83	2935A	396	86
TG502	95	83	K83211	398	86
20290G	94	83	Tamara	145	35
4135	93	83	Predator	158	35
20301G	87	83	RioRita	223	35
Rio Bravo	87	83	RNX 10968	276	35
20253G	85	83	Barito	251	96
20330G	81	83	Hyskin	234	96
Vidalia	80	83	Summit	221	96
20263G	77	83	MSU 826	276	97
20316G	76	83	MSU 2935	332	97
20338G	74	83	MSU 1459	394	97
20251G	74	83	MSU 1654	501	97
20305G	71	83	MSU 4921	608	97
20259G	70	83	MSU4535	1285	97
			White		
Albion	50	69	20304G	<1	83
20223G	1	83	20215G	<1	83
20319G	1	83	20221G	<1	83
20240G	<1	83	Ala	180	35
Contessa	<1	83	Gladstone	2	80
20234G	<1	83	Southport	3	80
4168	<1	83	White Hawk	1	80
20216G	<1	83			

[a] For comparison, flavonol content reported as quantities of flavonoid glycosides in the orginal publications have been converted to quantities of the corresponding aglycones.

Table 5. Quantitative Contents of Specific Flavonoid Structures (mg·kg^{-1} FW) in Different Onion Cultivars

cultivar	que 3,4′-diglc	rutin	que 4′-glc	que	ref
		Red			
Karmen[a]		157	32234	163	*35*
Pòvoa red	261		353	1	*37*
Red Baron	1375		394	9	*69*
Rose	1052		302	15	*69*
Red Baron[b]	1001		889	17	*70*
unspecific	410		350	20	*71*
Tropea Rossa	11	2	126	558	*80*
Rossa Lilia	33	3	352	58	*80*
Redwing	30	2	419	77	*80*
		Yellow			
Vsetana[a]		64	23283	56	*35*
Rijnsburger	1117		360	39	*69*
Cross Bow[b]	504		653	29	*70*
unspecific	170		130	10	*71*
Festival	43	2	374	56	*80*
Tamara	38	5	460	67	*80*
Daytona	41	6	713	112	*80*
Dorata Density	73	14	725	95	*80*
Castillo	51	9	611	65	*80*
Santana	49	6	547	92	*80*
Kitamiko27	263		254		*86*
Toyohira	266		355		*86*
Kitawase3	208		172		*86*
Tsukisappu	294		344		*86*
Superkitamomiji	297		343		*86*
CS3–12	276		304		*86*
Tsukiko22	412		364		*86*
2935A	290		392		*86*
K83211	356		347		*86*
Barito[c]	177		337		*96*
Hyskin[c]	180		334		*96*
Summit[c]	157		281		*96*
		White			
Ala[a]		15	265	1	*35*
Pòvoa white	109		147	0	*37*
Albion	50		36	3	*69*
Gladstone			1	1	*80*
Southport			2	1	*80*
White Hawk			1	1	*80*

[a] Reported as mg kg^{-1} DW. [b] Content expressed as quercetin. [c] Values from 2004 in the beginning of storage in autumn.

total quercetin content in yellow, pink, and red onions varied from 54 to 286 mg·kg^{-1} FW in different onion entries. The content of free quercetin in all these onion cultivars was low (<0.4 mg·kg^{-1}), with the exception of "20272-G" containing 12.5 mg·kg^{-1} FW quercetin. The highest levels of total quercetin were found in two yellow onion cultivars ("Sweet Savanna" and "4128") both containing 286 mg·kg^{-1} FW (*83*). The cultivars Nirvana, DPS 1032, Yellow 2025, King-Midas, and SBO 133 grown at Vidalia, Georgia, were analyzed for flavonoid content based on the aglycones as released upon acid hydrolysis. In these hydrolyzed extracts, quercetin was the major flavonol aglycone (77–463 mg·kg^{-1} FW) derived from all cultivars, followed by myricetin (28–41 mg·kg^{-1} FW). Minor quantities of kaempferol (11–20 mg·kg^{-1} FW) were also detected (*40*). Twelve cultivars of different colored onions (white, golden, and red) were evaluated for their flavonoid contents. The flavonoids were mainly made up of quercetin and isorhamnetin in the form of aglycones and glycosides. The highest amount of free quercetin was detected in the fresh bulbs of "Tropea rossa tonda" (557.8 mg·kg^{-1}) whereas the highest level of total flavonoids was found in "Dorata Density" (979.1 mg·kg^{-1}) (*80*).

On a world basis, an immense number of onion types, cultivars, and landraces exist. **Tables 4a**nd **5** display the reported flavonol content of a range of cultivars from several individual reports, grouped by color of the skin (red, pink, yellow, and white). Although there may be difficulties associated with comparing the values reported from different research groups, some major trends may still be extracted. Red cultivars generally contain quite high flavonoid quantities, while white cultivars contain very low amounts of flavonols. The largest group, the yellow cultivars, reveals the largest variation, as contents vary from very low to very high. The compilation of quantitative data presented in **Tables 4** and **5** indicates a great diversity in flavonoid content among the cultivars surveyed; hence, the world's genetic onion resources may represent a huge potential for utilization of flavonoid selection of targeted productions of onion cultivars that possess naturally high concentrations of flavonoids.

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