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Saponins and Flavonoids of *Allium triquetrum*

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A phytochemical investigation of the flowers and bulbs of *Allium triquetrum* has been undertaken, leading to the isolation of five new furostanol saponins, triquetrosides A1/A2 (**1a**/**1b**), B (**3**), and C1/C2 (**4a**/**4b**), from the flowers, along with ascalonisides A1/A2 (**6a**/**6b**). The 22-*O*-methyl derivatives of triquetrosides A1/A2 (**2a** and **2b**) and C1/C2 (**5a** and **5b**) were also isolated, but they are considered extraction artifacts. Large amounts of seven kaempferol glycosides, of which one (**7**) has a new structure, were also isolated from both flowers and bulbs. The structures of the new compounds were determined by spectral and chemical methods.

The family Alliaceae, comprising 600 species in 30 genera, is widely distributed throughout the world and belongs to the order Liliales. The largest and most important representative genus is *Allium* L., the 450 species of which are widely distributed in the northern hemisphere. Some of the more strongly flavored *Allium* species have culinary and medicinal uses. Since early times, garlic and onion have been an important part of the diet. Evidence of garlic and onions used as food is found in paintings inside the Egyptian pyramids (3200−2800 B.C.) and in the words of the Greek writer Herodotus (484−435 B.C.), "people working at the pyramid of Giza have eaten onions and garlic for a total cost of 1600 silver talents". Moreover, there is evidence that the athletes of the Olympic games in Greece and the legionaries of ancient Rome used garlic and onion as tonics and stimulants.[1] Onion (*Allium cepa* L.), chives (*Allium schoenoprasum* L.), shallots (*Allium ascalonicum* Hort.), and leeks (*Allium porrum* L.) are very widely grown for culinary purposes. Several other species are cultivated for their attractive flowers, such as wild garlic (*Allium ursinum* L.) and *Allium neapolitanum* Cyr. *Allium triquetrum* L. is a very early blooming species and grows vigorously in cultivations. It is characterized by green striped, white, pendulous flowers looking like small lilies. It possesses several vernacular names (e.g., triangle onion, triangular-stalked garlic, three-cornered leek), which refer to different taxa. The plant is used in Italy as a main ingredient in salads and soups, because of its mild taste similar to onion.

As part of our ongoing studies of the chemistry of *Allium* species,[2,3] we have investigated *A. triquetrum*, which has not been studied before phytochemically. Examination of the MeOH extract of the flowers revealed the presence of high concentrations of saponins, as major metabolites, and we have isolated five new furostanol saponins, named triquetrosides A1/A2 (**1a**/**1b**), B (**3**), and C1/C2 (**4a**/**4b**), together with ascalonisides A1/A2 (**6a**/**6b**), previously isolated from shallot, *A. ascalonicum*.[4] Four *O*-methyl derivatives (**2a**, **2b**, **5a**, and **5b**), which are considered extraction artifacts, have also been found. In addition, high concentrations of kaempferol glycosides were also found in both the flowers and bulbs of *A. triquetrum*. One of these compounds (**7**) is new.

Results and Discussion

Flowers and bulbs of *Allium triquetrum* were briefly air-dried and separately exhaustively extracted with solvents

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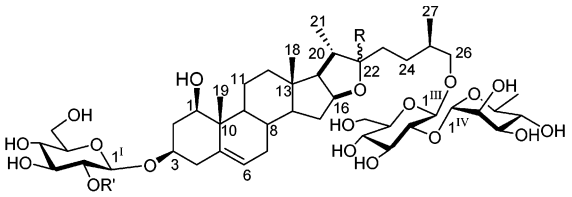
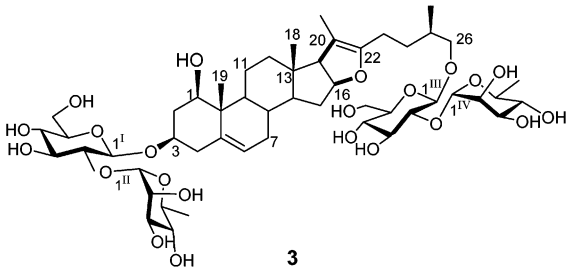


1a	R = α-OH	R' = α-L-Rha^{II}	**1b**	R =β-OH	R' =α-L-Rha^{II}
2a	R = α-OCH$_3$	R' = α-L-Rha	**2b**	R =β-OCH$_3$	R' =α-L-Rha
4a	R = α-OH	R' = H	**4b**	R =β-OH	R' =H
5a	R = α-OCH$_3$	R' = H	**5b**	R =β-OCH$_3$	R' =H



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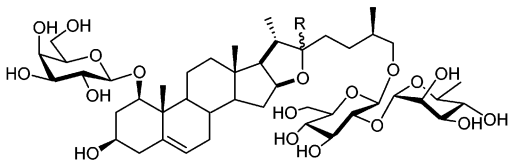
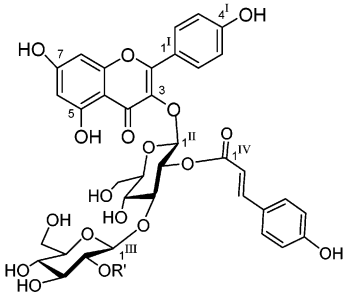


6a R = α-OH **6b** R = β-OH



7

of increasing polarity (Experimental Section). The MeOH extracts were partitioned between butanol and water, and the butanol-soluble portions were separated by sequential chromatographic techniques, affording from the flowers, as major metabolites, furostanol saponins (total saponin content 46 mg/kg) and flavonoids (total flavonoid concentration 319 mg/kg). The bulbs contained analogous concentrations of flavonoids, whereas saponins were present in traces.

Triquetroside A1 (**1a**) represented the most abundant saponin in *A. triquetrum* flowers, being 31.5% of the saponin fraction. Its HRFABMS exhibited a quasimolecular ion peak at *m/z* 1061.5136 [M − H]$^-$, corresponding to the molecular formula $C_{51}H_{81}O_{23}$. The ^{1}H NMR spectrum of **1a** (CD_3OD, Tables 1 and 3) exhibited signals for six distinct methyl groups (two singlets and four doublets), some overlapping signals between δ 1.1 and 2.4, and a number of signals from δ 3.1 and 5.2, due to protons linked to oxygen-bearing carbons. A broad doublet at δ 5.55 was ascribable to a proton on a sp^2 carbon. This series of signals clearly indicated a triterpene glycoside structure for compound **1a**. This was further confirmed by the presence in the ^{13}C NMR spectrum (CD_3OD, Tables 2 and 3) of four anomeric carbons (δ 102.9, 105.3, 107.1, 104.0), indicating the tetrasaccharide nature of the sugar portion. In addition, the presence of a hemiacetal carbon singlet at δ 114.1 suggested a furostane skeleton for the aglycon of **1a**.[5]

Although the ^{1}H NMR spectrum of **1a** contained several overlapping signals, the combined analysis of the 2D COSY and HOHAHA spectra allowed the detection of seven distinct spin systems, with three of them belonging to the aglycon moiety and the remaining four due to the four monosaccharide units present. For the aglycon moiety, the first spin system included the protons of ring A (C-1 to C-4), the second one started from C-6 of ring B and extended to the protonated carbons of ring E, and the third spin system included the protons of the side chain (C-23 to C-26), thus completing the aglycon moiety. An HMBC experiment was used to interconnect the partial structures; the key correlations are reported in Figure 1.

When the stereochemistry of the aglycon moiety was considered, in the ^{1}H NMR spectrum of **1a** the signals of H-1 and H-3 were overlapped with signals of the sugar portion. However, inspection of the 1D subspectra in the 2D HOHAHA experiment allowed the observation of the coupling constants of these protons, indicating the relative stereochemistry of carbons C-1 and C-3. In particular, H-1 (δ 3.26) resonated as a double doublet (J = 7.5 and 2.5 Hz), whereas H-3 (δ 3.49) appeared as a multiplet with two large (axial−axial) and two small (axial−equatorial) coupling constants. These data indicated the axial position for both H-1 and H-3. The 25*R* stereochemistry was deduced by the resonances of protons and carbons at positions C-25, C-26, and C-27 and by the $^3J_{HH}$ values between H-25 and H-26, in comparison with literature data.[6] ROESY correlations (Figure 1) of H-11/ H$_3$-19, H-11/ H$_3$-18, H-9/H-14, H-14/H-16, H-16/H-17, and H-17/ H$_3$-21 completed the relative stereochemistry of **1a**, indicating the usual furostane ring junctions with rings B/C *trans*, C/D *trans*, D/E *cis*, and C-20α.[4,5] On the basis of these data, and assuming that the aglycon possesses the same absolute configuration found in all furostanes isolated to date, the stereochemistry of the aglycon chiral centers (except for C-22, see below) could be assigned as in the structure shown for **1a**.

The first step in the analysis of the saccharide part of the molecule of **1a** was the association of the four anomeric carbons resonating at δ_C 107.1, 102.9, 105.3, and 104.0 with the relevant anomeric proton signals (δ_H 4.21, 4.47, 4.82, and 5.19, respectively), through the HSQC experiment. The nature of each monosaccharide and their sequence were determined by combined analysis of the COSY, HOHAHA, ROESY, HSQC, and HMBC spectra. Starting from the anomeric proton of each sugar unit, all the proton signals within each spin system were delineated using the COSY spectrum with the aid of a HOHAHA spectrum. Once the proton assignments had been made, each proton was correlated to the relative carbon through the cross-peaks observed in the HSQC spectrum. Hence, when the anomeric proton at δ 4.47 (H-1^I) was used as a starting point, a sequence of four oxymethines and one oxymethylene (Table 3) was identified from the above-mentioned spectra. The large coupling constants, observed in the 2D HOHAHA subspectrum for all the oxymethines, indicated their axial−axial relationship and defined this sugar as a β-glucopyranose. This residue was linked to the C-3 of the aglycon,

Table 1. ^{1}H NMR Data in CD_3OD of the Aglycon Portions of Triquetroside A1 (**1a**), A2 (**1b**), B (**3**), C1 (**4a**), and C2 (**4b**)

position	**1a** δ_H (int., mult., *J* in Hz)	**1b** δ_H (int., mult., *J* in Hz)	**3** δ_H (int., mult., *J* in Hz)	**4a** δ_H (int., mult., *J* in Hz)	**4b** δ_H (int., mult., *J* in Hz)
1	3.26[a]	3.26[a]	3.26[a]	3.25[a]	3.25[a]
2a	2.06[a]	2.04[a]	2.06[a]	2.05[a]	2.03[a]
2b	1.71[a]	1.71[a]	1.71[a]	1.70[a]	1.70[a]
3	3.49[a]	3.48[a]	3.49[a]	3.49[a]	3.48[a]
4a	2.38 (1H,dd,11.5,7.3)	2.37 (1H,dd,11.5,7.3)	2.40[a]	2.36 (1H,dd,11.5,7.3)	2.36 (1H,dd,11.5,7.3)
4b	2.25 (1H,dd,11.5,3.5)	2.26 (1H,dd,11.5,3.5)	2.25[a]	2.24 (1H,dd,11.5,3.5)	2.24 (1H,dd,11.5,3.5)
6	5.55 (1H,bd,3.2)	5.55 (1H,bd,3.2)	5.50 (1H,bd,3.2)	5.55 (1H,bd,3.2)	5.55 (1H,bd,3.2)
7a	1.96[a]	1.96[a]	1.96[a]	1.96[a]	1.96[a]
7b	1.95[a]	1.95[a]	1.95[a]	1.95[a]	1.95[a]
8	1.54 (1H,m)	1.54 (1H, m)	1.54[a]	1.52 (1H, m)	1.52 (1H,m)
9	1.12[a]	1.12[a]	1.12[a]	1.12[a]	1.12[a]
11a	2.26 (1H,dd,10.5,2.5)	2.26 (1H,dd,10.5,2.5)	2.26 (1H,dd,10.5,2.5)	2.26 (1H,dd,10.5,2.5)	2.26 (1H,dd,10.5,2.5)
11b	1.53 (1H,m)	1.53 (1H,m)	1.52 (1H,m)	1.53 (1H,m)	1.53 (1H,m)
12a	1.71[a]	1.71[a]	1.71[a]	1.72[a]	1.72[a]
12b	1.20[a]	1.20[a]	1.20[a]	1.20[a]	1.20[a]
14	1.18 (1H,m)	1.18 (1H,m)	1.14 (1H,m)	1.18 (1H,m)	1.18 (1H,m)
15a	1.95[a]	1.95[a]	1.98[a]	1.95[a]	1.95[a]
15b	1.25[a]	1.25[a]	1.25[a]	1.25[a]	1.25[a]
16	4.53 (1H,q,5.5)	4.33 (1H,q,5.5)	4.59 (1H,q,5.5)	4.53 (1H,q,5.5)	4.33 (1H,q, 5.5)
17	1.74[a]	1.69[a]	2.43 (1H,d,5.5)	1.74[a]	1.69[a]
18	0.81 (3H,s)	0.81 (3H,s)	0.83 (3H,s)	0.81 (3H,s)	0.81 (3H,s)
19	1.02 (3H,s)	1.02 (3H,s)	1.02 (3H,s)	1.02 (3H,s)	1.02 (3H,s)
20	2.06[a]	2.06[a]		2.04[a]	2.04[a]
21	0.98 (3H,d,6.6)	0.95 (3H,d,6.6)	1.88 (3H,s)	0.98 (3H,d,6.6)	0.96 (3H,d,6.6)
23a	1.73[a]	1.73[a]	2.19[a]	1.73[a]	1.73[a]
23b	1.62[a]	1.62[a]	2.14[a]	1.62[a]	1.62[a]
24a	1.32[a]	1.32[a]	1.65 (1H,m)	1.32[a]	1.32[a]
24b	1.30[a]	1.31[a]	1.53[a]	1.31[a]	1.31[a]
25	1.72 (1H,m)	1.72 (1H,m)	1.72 (1H,m)	1.72 (1H,m)	1.72 (1H,m)
26a	3.82 (1H,dd,9.5, 3.9)	3.82 (1H,dd, 9.5,3.9)	3.81 (1H,dd,9.5,3.9)	3.82 (1H,dd,9.5,3.9)	3.82 (1H,dd,9.5,3.9)
26b	3.32[a]	3.32[a]	3.33[a]	3.32[a]	3.32[a]
27	0.94 (3H,d,6.6)	0.94 (3H,d,6.6)	0.92 (3H,d,6.6)	0.95 (3H,d,6.6)	0.95 (3H,d,6.6)

[a] Overlapped with other signals.

Table 2. ^{13}C NMR Data in CD_3OD of the Aglycon Portions of **1a**, **1b**, **3**, **4a**, and **4b**

position	**1a** δ_C (mult.)	**1b** δ_C (mult.)	**3** δ_C (mult.)	**4a** δ_C (mult.)	**4b** δ_C (mult.)
1	74.0 (CH)	74.0 (CH)	74.0 (CH)	74.1 (CH)	74.1 (CH)
2	43.4 (CH_2)	43.4 (CH_2)	43.4 (CH_2)	43.2 (CH_2)	43.2 (CH_2)
3	82.3 (CH)	82.3 (CH)	82.4 (CH)	82.3 (CH)	82.3 (CH)
4	42.0 (CH_2)	42.0 (CH_2)	41.9 (CH_2)	42.1 (CH_2)	42.1 (CH_2)
5	143.7 (C)	143.7 (C)	143.5 (C)	143.7 (C)	143.7 (C)
6	128.6 (CH)	128.5 (CH)	128.4 (CH)	128.5 (CH)	128.5 (CH)
7	35.1 (CH_2)	35.0 (CH_2)	35.1 (CH_2)	35.1 (CH_2)	35.0 (CH_2)
8	36.1 (CH)	36.1 (CH)	36.1 (CH)	36.0 (CH)	36.0 (CH)
9	54.6 (CH)	54.6 (CH)	54.8 (CH)	54.6 (CH)	54.6 (CH)
10	44.5 (C)	44.5 (C)	44.4 (C)	44.5 (C)	44.5 (C)
11	27.2 (CH_2)	27.2 (CH_2)	27.3 (CH_2)	27.3 (CH_2)	27.3 (CH_2)
12	43.4 (CH_2)	43.2 (CH_2)	43.6 (CH_2)	43.4 (CH_2)	43.2 (CH_2)
13	46.8 (C)	46.8 (C)	48.8 (C)	46.7 (C)	46.7 (C)
14	60.0 (CH)	60.0 (CH)	58.4 (CH)	60.2 (CH)	60.2 (CH)
15	35.3 (CH_2)	35.3 (CH_2)	33.9 (CH_2)	35.3 (CH_2)	35.3 (CH_2)
16	84.5 (CH)	84.6 (CH)	86.8 (CH)	84.5 (CH)	84.6 (CH)
17	66.6 (CH)	67.7 (CH)	67.7 (CH)	66.7 (CH)	67.9 (CH)
18	19.3 (CH_3)	19.5 (CH_3)	17.6 (CH_3)	19.3 (CH_3)	19.5 (CH_3)
19	16.0 (CH_3)	16.0 (CH_3)	16.1 (CH_3)	16.0 (CH_3)	16.0 (CH_3)
20	43.2 (CH)	43.0 (CH)	105.4 (CH)	43.2 (CH)	43.0 (CH)
21	18.3 (CH_3)	18.5 (CH_3)	14.3 (CH_3)	18.3 (CH_3)	18.5 (CH_3)
22	114.1 (C)	117.2 (C)	154.8 (C)	114.0 (C)	117.3 (C)
23	39.2 (CH_2)	39.0 (CH_2)	37.0 (CH_2)	39.2 (CH_2)	39.0 (CH_2)
24	32.9 (CH_2)	32.7 (CH_2)	26.5 (CH_2)	32.9 (CH_2)	32.7 (CH_2)
25	37.7 (CH)	37.1 (CH)	36.5 (CH)	37.7 (CH)	37.1 (CH)
26	74.8 (CH_2)	74.6 (CH_2)	74.5 (CH_2)	74.8 (CH_2)	74.6 (CH_2)
27	19.7 (CH_3)	19.7 (CH_3)	19.7 (CH_3)	19.5 (CH_3)	19.5 (CH_3)

as indicated by the HMBC correlation peak (Figure 1) between the anomeric proton H-1^I and the downfield shifted (δ 82.3) C-3 signal. The HMBC cross-peaks of H-2^I (δ 3.48) with the anomeric carbon at δ 105.3 (C-1^{II}) and of C-2^I (δ 82.5) with H-1^{II} (δ 4.82) identified position 2 of the glucose unit as being involved in the glycosidic linkage. This was also confirmed by the ROESY cross-peak (Figure 1) of H-2^I (δ 3.48) with H-1^{II} (δ 4.82). The spin system starting from this last proton extended to four oxymethines and one methyl group (Table 3). This sugar moiety was identified as a rhamnopyranose due to the axial−axial couplings H-3^{II}/H-4^{II} and H-4^{II}/H-5^{II} and the axial−equatorial relationship between H-2^{II} and H-3^{II}. In accordance with data reported in the literature,[7,8] the α-anomeric

Table 3. ^{1}H and ^{13}C NMR Data in CD_3OD of the Sugar Portion of **1a**/**1b**/**3** (data extracted from **1a**) and **4a**/**4b** (data extracted from **4a**)

	1a		**4a**	
position	δ_H (int., mult., *J* in Hz)	δ_C (mult.)	δ_H (int., mult., *J* in Hz)	δ_C (mult.)
1^I	4.47 (1H,d,7.5)	102.9 (CH)	4.49 (1H,d,7.5)	103.5 (CH)
2^I	3.48 (1H,t,7.5)	82.5 (CH)	3.40 (1H,t,7.5)	76.2 (CH)
3^I	3.38[a]	76.2 (CH)	3.39[a]	77.7 (CH)
4^I	3.78 (1H,dd,6.8,6.5)	78.4 (CH)	3.78 (1H,dd,6.8,6.5)	78.4 (CH)
5^I	3.28 (1H,m)	74.4 (CH)	3.29 (1H,m)	74.4 (CH)
6^Ia	3.63 (1H,bd,11.5)	64.3 (CH_2)	3.64 (1H,bd,11.5)	64.5 (CH_2)
6^Ib	3.78 (1H,bd,11.5)		3.78 (1H,bd,11.5)	
1^{II}	4.82 (1H,bs)	105.3 (CH)		
2^{II}	3.89 (1H,bs)	73.0 (CH)		
3^{II}	3.60 (1H,d,6.5)	74.6 (CH)		
4^{II}	3.36 (1H,dd,6.5,6.0)	78.7 (CH)		
5^{II}	3.90[a]	74.5 (CH)		
6^{II}	1.24 (3H,d,6.6)	20.2 (CH_3)		
1^{III}	4.21 (1H,d,7.5)	107.1 (CH)	4.21 (1H,d,7.5)	107.1 (CH)
2^{III}	3.19 (1H,t,7.5)	77.5 (CH)	3.19 (1H,t,7.5)	77.5 (CH)
3^{III}	3.36[a]	74.6 (CH)	3.36[a]	74.6 (CH)
4^{III}	3.24 (1H,dd,7.0,6.4)	74.2 (CH)	3.24 (1H,dd,7.0,6.4)	74.2 (CH)
5^{III}	3.30 (1H,m)	78.5 (CH)	3.30 (1H,m)	78.5 (CH)
6^{III}a	3.64 (1H,bd,11.5)	65.2 (CH_2)	3.64 (1H,bd,11.5)	65.2 (CH_2)
6^{III}b	3.84 (1H,bd,11.5)		3.84 (1H,bd,11.5)	
1^{IV}	5.19 (1H,bs)	104.0 (CH)	5.19 (1H,bs)	104.0 (CH)
2^{IV}	3.91 (1H,bs)	73.1 (CH)	3.91 (1H,bs)	73.1 (CH)
3^{IV}	3.62 (1H,d,6.5)	74.5 (CH)	3.62 (1H,d,6.5)	74.5 (CH)
4^{IV}	3.38 (1H,dd,6.5,6.0)	78.7 (CH)	3.38 (1H,dd,6.5,6.0)	78.7 (CH)
5^{IV}	4.09[a]	74.5 (CH)	4.09[a]	74.5 (CH)
6^{IV}	1.23 (3H,d,6.6)	20.2 (CH_3)	1.23 (3H,d,6.6)	20.2 (CH_3)

[a] Overlapped with other signals.

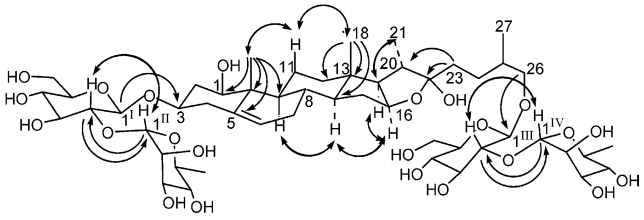


Figure 1. Selected HMBC (H→C) and ROESY (H↔H) NMR correlations observed for compound **1a**.

configuration of this sugar was judged by the chemical shifts of C-3^{II} (δ 74.6) and C-5^{II} (δ 74.5).

Starting from the anomeric proton at δ 4.21 (H-1^{III}), four oxymethines and one oxymethylene group were identified in sequence (Table 3). The sugar moiety was identified as β-glucopyranose due to the large coupling constants observed for all protons, thus indicating their axial−axial relationships. This residue was located at C-26 because of the HMBC correlations (Figure 1) between H_2-26 with the carbon of this glucose unit resonating at δ 107.1 (C-1^{III}). HMBC correlations (Figure 1) of C-2 ^{III}/H-1^{IIII} and of C-1^{IV}/H-2^{III} and the ROESY correlation of H-1^{IV}/H-2^{III} indicated position 2 of the glucose as the linkage site of the fourth monosaccharide unit. This last sugar was identified as a further α-rhamnopyranose, based on the previous arguments as those used for the characterization of the other α-rhamnopyranose unit.

To confirm the nature of the sugar residues and to identify their absolute configuration, acid hydrolysis with 1 N HCl was performed next on **1a**, followed by trimethylsilylation and GC analysis on a chiral column in comparison with both series of glucose and rhamnose, used as standards. By this procedure, the sugar residues were identified as D-glucose and L-rhamnose, respectively. This same procedure was applied to all the new isolated compounds in the present investigation.

All of this evidence defined the stereostructure of triquetroside A1 (**1a**) as furost-5(6)-en-1β,22α-diol 3β-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl] 26-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranoside].

Triquetroside A2 (**1b**) showed the same molecular formula as **1a** from its HRFABMS data. Analysis of the ^{1}H and ^{13}C NMR spectra of **1b** (Tables 1−3), aided by 2D NMR experiments, revealed the same gross structure as that of **1a**. Hence, we supposed that these molecules differ only in the stereochemistry of one or more carbon atoms. The carbon was identified as the hemiacetal carbon C-22, considering that both compounds **1a** and **1b**, after being kept overnight in aqueous solution at room temperature, gave the same mixture (about 40% of **1a** and 60% of **1b**). Accordingly, the ^{1}H and ^{13}C NMR spectra of triquetrosides A1 (**1a**) and A2 (**1b**) differed only in the resonances of the atoms located near C-22. We have tentatively assigned the 22α orientation to triquetroside A1 (**1a**) and the 22β orientation to triquetroside A2 (**1b**), respectively, on the basis of the ^{1}H NMR resonances of H_3-21 and H-16 being shifted slightly downfield (H_3-21 was at δ 0.98 instead of 0.95; H-16 was at δ 4.53 instead of 4.33) in triquetroside A1 (**1a**), suggesting that, most likely, they are deshielded by the *cis*-oriented OH-22 group.

Triquetroside B (**3**) was characterized on the basis of its close similarities with triquetrosides A1 (**1a**) and A2 (**1b**). The HRFABMS indicated the molecular formula of **3** as $C_{51}H_{79}O_{22}$, which differed from **1a**/**1b** in being 18 amu less. The NMR profile of **3** (Tables 1−3) also showed a strict analogy with those of **1a**/**1b**, especially for the midfield region of the ^{1}H NMR spectra that were superimposable on each other, suggesting the same sugar portions in each molecule. Differences in the ^{1}H NMR spectrum of **3** (Tables 1−3) were observed in the lack of a signal due to H-20 and the low-field shift of the following signals: H_3-21 (from δ 0.98 in **1a** to 1.88 in **3**), H-17 (from δ 1.74 to 2.43); H-16 (from δ 4.53−4.33 to 4.59); and H_2-23 (from δ 1.73 and 1.62 to 2.19 and 2.14). In an analogous fashion, the ^{13}C NMR resonances (Tables 1−3) of **3** differed from those of **1a**/**1b** only in the signals of C-20 (δ 43.2/43.0) and C-22 (δ 114.1/117.2), which were replaced by two sp^2 signals at δ 105.4

and 154.8, respectively. All these data indicated the structure of **3** to be furost-5(6),20(22)-dien-1β-ol 3β-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl] 26-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranoside].

The structure elucidation of triquetroside C1 (**4a**), present in minor amounts, was aided by comparison with the MS and NMR data obtained for triquetroside A1 (**1a**). The HRFABMS gave the molecular formula of $C_{45}H_{71}O_{19}$. The presence of three sugars in **4a** was apparent from three anomeric ^{1}H NMR signals at δ 4.21, 4.49, and 5.19, associated with the relevant signals in the ^{13}C NMR spectrum (δ 107.1, 103.5, 104.0, respectively) using the HSQC spectrum. Comparison of the molecular formula and of the ^{1}H and ^{13}C NMR spectra of **4a** (assigned by 2D NMR spectroscopy and reported in Tables 1−3) with analogous data obtained for **1a** showed the lack of one α-rhamnose unit. In particular, the resonances of the aglycon and of the sugars attached to C-26 appeared almost the same as those of **1a**, whereas slight modifications were detected among the resonances of the β-glucose linked at C-3 due to the absence of any glycosylation shift in the ^{13}C NMR spectrum. Consequently, the structure of triquetroside C1 (**4a)** was formulated as furost-5(6)-en-1β,22α-diol 3β-*O*-β-D-glucopyranosyl 26-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranoside].

Mass spectrometric analysis of triquetroside C2 (**4b**) indicated the same molecular formula as that of **4a**. By analogy, the NMR profile (Tables 1−3) revealed the same structure for both compounds, indicating that the difference was limited to the stereochemistry of a chiral carbon. As observed for **1a**/**1b**, the two compounds **4a**/**4b** were in equilibrium if left in solution overnight. Therefore, the structure of **4b** was postulated as the C-22 epimer of **4a**. The assignments of the ^{1}H and ^{13}C NMR spectra, obtained through 2D NMR spectra, are reported in Tables 1−3. On the basis of the same arguments applied for **1a**/**1b**, we have assigned tentatively the configurations 22α to **4a** and 22β to **4b**, respectively.

The ^{1}H and ^{13}C NMR resonances of **2a/2b** and **5a/5b** appeared superimposable to those obtained for **1a/1b** and **4a/4b**, respectively, with the exception of an additional methoxy group signal in each spectrum of **2a/2b** and **5a/5b** [^{1}H NMR δ 3.12 (3H, s); ^{13}C NMR δ 47.2]. Compounds **2a/2b** and **5a/5b** were identified as the 22-*O*-methyl derivatives of **1a/1b** and **4a/4b**, respectively, and considered as secondary products formed from the corresponding 22-hydroxyfurostanosides during the extraction of the plant in methanol. This was confirmed by repeating the extraction procedure in acetone and observing the absence of **2a/2b** and **5a/5b** in the extract. Therefore, we have not characterized them further.

Along with these compounds we have isolated the trisaccharide saponins, ascalonisides A1/A2 (**6a**/**6b**), recently reported by our group from *A. ascalonicum* Hort.[4] This finding is interesting from a chemotaxonomic point of view since this species is closely related to onion. As recently reported by Harmatha,[9] the saponins of *Allium* species are mostly concentrated in flowers where they are efficient regulators in plant−insect chemical interactions. As expected, we have found high concentrations of saponins in flowers and only traces in the bulbs.

The same flavonoids were found in both the flowers and bulbs of *A. triquetrum*. The chemical structures of the known compounds were identified by comparison of UV, FABMS, and ^{1}H and ^{13}C NMR data with those reported in the literature. Therefore we have characterized the flavonoids as kaempferol 3-*O*-(2-*O*-*trans*-*p*-coumaroyl)glucoside,[10,11] kaempferol 3-*O*-(2-*O*-*trans*-*p*-feruloyl)glucoside,[10,11] kaempferol 3-*O*-glucoside,[12] kaempferol 3-*O*-rutinoside,[12] kaempferol 7-*O*-glucoside,[12] and 8-hydroxykaempferol 8-*O*-glucoside.[13]

Table 4. ^{13}C and ^{1}H NMR Data in CD_3OD of **7**

position	δ_C (mult.)	δ_H (int., mult., *J* in Hz)
2	158.8 (C)	
3	134.0 (C)	
4	179.0 (C)	
5	161.6 (C)	
6	101.2 (CH)	6.18 (1H,d,1.9)
7	163.4 (C)	
8	96.2 (CH)	6.38 (1H,d,1.9)
9	158.3 (C)	
10	105.1 (C)	
1^{I}	123.1 (C)	
$2^{I}-6^{I}$	132.2 (CH)	8.07 (2H,d,9.0)
$3^{I}-5^{I}$	116.0 (CH)	6.91 (2H,d,9.0)
4^{I}	161.2 (C)	
1^{II}	99.8 (CH)	5.62 (1H,d,7.5)
2^{II}	73.6 (CH)	5.09 (1H,dd,7.5,8.6)
3^{II}	84.7 (CH)	3.52 (1H,t,8.6)
4^{II}	69.8 (CH)	3.78 (1H,t,8.6)
5^{II}	78.2 (CH)	3.68[a]
6^{II}a	62.3 (CH_2)	3.62 (1H,dd,5.6,12.0)
6^{II}b		3.70[a]
1^{III}	105.0 (CH)	4.22 (1H,d,7.5)
2^{III}	74.7 (CH)	3.12 (1H,dd,7.5,8.6)
3^{III}	77.7 (CH)	3.24 (1H,t,8.6)
4^{III}	71.3 (CH)	3.28 (1H,t,8.6)
5^{III}	78.2 (CH)	3.10 (1H,ddd,8.6,5.5,2.1)
6^{III}a	62.5 (CH_2)	3.69[a]
6^{III}b		4.02 (1H,dd,2.1,11.9)
1^{IV}	126.9 (C)	
$2^{IV}-6IV$	131.4 (CH)	7.50 (2H,d,8.5)
$3^{IV}-5IV$	117.0 (CH)	6.83 (2H,d,8.5)
4^{IV}	162.0 (C)	
7^{IV}	147.6 (CH)	7.70 (1H,d,16.0)
8^{IV}	114.6 (CH)	6.41 (1H,d,16.0)
9^{IV}	168.3 (C)	

[a] Overlapped with other signals.

The new compound, **7**, isolated as a yellow powder, gave in the negative-ion HRFABMS a pseudomolecular ion peak at *m*/*z* 755.1807 [M − H]$^-$, consistent with the formula $C_{36}H_{35}O_{18}$. Its UV spectrum exhibited the characteristic bands of a kaempferol derivative, substituted at position C-3, as indicated by the bathochromic shift on addition of diagnostic reagents[14] (Experimental Section). The ^{1}H and ^{13}C NMR spectra (Table 4) confirmed this structural observation and also indicated that two sugars and a coumaroyl subunit accounted for the remaining atoms implied by the molecular formula of **7**. Analysis of the NMR spectra was aided by the interpretation of the 2D HSQC and HMBC data, exhibiting $^1J_{CH}$ and $^{2,3}J_{CH}$ connections, respectively. In particular, the ^{1}H NMR spectrum showed the typical pairs of doublets due to a *trans*-*p*-coumaroyl residue, the first one (δ 7.70 and 6.41) with a coupling of 16 Hz, due to a *trans*-olefinic double bond, and the second (δ 7.50 and 6.83) with a coupling of 8.5 Hz, caused by the four ring protons.

With regard to the sugar portions of **7**, two anomeric proton signals at δ 4.22 and 5.62 were identified in the ^{1}H NMR spectrum and associated with the relevant anomeric carbon (δ 105.0 and 99.8, respectively) through the 2D HSQC spectrum. The large coupling constants of the anomeric protons (Table 4) indicated a β-configuration for both monosaccharide units. Starting from the anomeric proton at δ 5.62, analysis of the COSY and HOHAHA spectra allowed the identification, in sequence, of four oxymethine groups and one oxymethylene group (Table 4). The sugar moiety was identified as β-glucopyranose on the

basis of the large couplings observed for all the oxymethine protons, implying their axial position. Moreover, the downfield shift of H-2^{II} (δ 5.09) appeared in accordance with an acylation at this position, thus suggesting the *trans-p*-coumaroyl linkage site. HMBC correlation peaks of H-1^{II} (δ 5.62) with C-3 (δ 134.0) and of H-2^{II} (δ 5.09) with C-1^{IV} (δ 126.9) indicated the linkage site of this β-glucose at the C-3 of the aglycon and confirmed position C-2 of the glucose as the acylation site. Finally, a HMBC cross-peak of C-3^{II} (δ 84.7) with H-1^{III} (δ 4.22) indicated the linkage site of the terminal sugar that was identified as β-glucopyranose on the basis of the large value of the vicinal coupling constants interrelating all the oxymethine protons, arranged in sequence through COSY and HOHAHA NMR experiments. Compound **7** was therefore identified as kaempferol 3-*O*-[2-*O*-(*trans-p*-coumaroyl)-3-*O*-β-D-glucopyranosyl]-β-D-glucopyranoside (**7**).

In vitro and in vivo pharmacological tests have shown that the flavonoids of garlic and onion exhibit antioxidative (DNA protective)[15] and cancer chemopreventive activities.[16] The high concentration of flavonols found in our samples, resembling the high levels usually recorded in onion species compared to other dietary plants,[4,17,18] makes *A. triquetrum* a potentially good source of phytoconstituents useful for cancer chemoprevention.

Experimental Section

General Experimental Procedures. Optical rotations were determined on a Perkin-Elmer 192 polarimeter equipped with a sodium lamp (589 nm) and 10 cm microcell. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively, on a Bruker AMX-500 spectrometer. Chemical shifts were referred to the residual solvent signal (CD_3OD: δ_H 3.34, δ_C 49.0). The multiplicities of ^{13}C NMR resonances were determined by DEPT experiments. ^{1}H connectivities were determined using COSY and HOHAHA experiments; the 2D HOHAHA experiments were performed in the phase-sensitive mode (TPPI) using the MLEV-17 (mixing time 125 ms) sequence. One-bond heteronuclear ^{1}H−^{13}C connectivities were determined with a 2D HSQC[19] pulse sequence with an interpulse delay set for $^1J_{CH}$ of 130 Hz. Two- and three-bond heteronuclear ^{1}H−^{13}C connectivities were determined with 2D HMBC experiments, optimized for $^{2-3}J_{CH}$ of 8 Hz. Nuclear Overhauser effect (NOE) measurements were performed by 2D ROESY experiments. Low- and high-resolution FAB mass spectra (glycerol matrix) were measured on a Prospect Fisons mass spectrometer. Medium-pressure liquid chromatography (MPLC) was performed on a Büchi 861 apparatus using LiChroprep RP-18 (40−63 μm) columns. HPLC in isocratic mode was performed on a Varian apparatus equipped with an RI-3 refractive index detector using Waters columns [semipreparative μ-Bondapack C_{18} column (30 cm × 7.8 mm, i.d.) and analytical μ-Bondapack C_{18} column (30 cm × 3.9 mm, i.d.)].

Plant Material. Wild samples of *Allium triquetrum* L., bulbs and flowers, were collected in the Vesuvius area, near Naples, Italy, in March 2000 (bulbs) and March 2002 (flowers), and identified by Prof. Vincenzo De Feo (Università di Salerno) and Dr. Riccardo Motti (Università di Napoli Federico II). Voucher specimens (No. 2000AT1 for bulbs and No. 2002AT2 for flowers) have been deposited at the Dipartimento di Scienze e Tecnologie Agroalimentari, Ambientali e Microbiologiche, Campobasso.

Extraction and Isolation. The bulbs (350 g dry weight) were air-dried under a controlled temperature (22 °C), without exposure to light. They were chopped and then exhaustively extracted at room temperature with the following solvents in order: hexane, $CHCl_3$, $CHCl_3$−MeOH (9:1), and MeOH. Each solvent extraction was conducted for 1 day and was repeated four times using 500 mL of solvent, under stirring. The MeOH extract (25 g) was partitioned between BuOH and water, and the organic layer was then filtered and concentrated in vacuo to afford a crude extract (16 g), which was chromatographed by MPLC on a RP-18 column using a linear gradient from H_2O to MeOH. Fractions eluted with H_2O−MeOH (4:6; 53.9 mg), H_2O−MeOH (3:7; 35.3 mg), and H_2O−MeOH (2:8; 30.5 mg) contained flavonoids in high concentrations. Fraction 1 (H_2O−MeOH, 4:6) yielded the known kaempferol 3-*O*-rutinoside (53.9 mg). Fraction 2 (H_2O−MeOH, 3:7) was further purified by HPLC on a C_{18} column with a mobile phase of H_2O−MeOH (1:1), affording known compounds kaempferol 7-*O*-glucoside (17.1 mg), kaempferol 3-*O*-(2-*O*-*trans-p*-feruloyl)glucoside (7.0 mg), 8-hydroxykaempferol 8-*O*-glucoside (7.6 mg), and kaempferol 3-*O*-glucoside (3.6 mg). Fraction 3 (H_2O−MeOH, 2:8) was further purified by HPLC on a C_{18} column with a mobile phase of H_2O−MeOH (45:55), yielding pure **7** (12.1 mg) and the known kaempferol 3-*O*-(2-*O*-*trans-p*-coumaroyl)glucoside (10.5 mg).

The flowers (1816 g) were air-dried under controlled temperature (22 °C), without exposure to light. Then, they were finely cut and exhaustively extracted with four aliquots of hexane, $CHCl_3$−MeOH (9:1), and MeOH. Each solvent extraction was conducted for 1 day and was repeated four times using 500 mL of solvent, under stirring. The MeOH extract obtained was concentrated in vacuo to afford a crude organic extract (24.7 g). This was chromatographed by MPLC on a RP-18 column using a linear gradient from H_2O to MeOH. Preliminary analysis revealed the presence of the same flavonoid composition as the bulbs contained in fractions eluted from H_2O−MeOH (6:4) to H_2O−MeOH (4:6), while saponins were contained in fractions eluted from H_2O−MeOH (3:7) to H_2O−MeOH (1:9). Fraction 1 (95.7 mg, eluted with H_2O−MeOH, 3:7) was chromatographed by HPLC on a semipreparative C_{18} column with a mobile phase of H_2O−MeOH (1:1), to give pure saponins **1a** (23.7 mg) and **1b** (26.0 mg), and **2a** (4.5 mg) and **2b** (4.0 mg). Fraction 2 [39.9 mg, eluted in H_2O−MeOH (2:8)] was chromatographed by HPLC on a semipreparative C_{18} column in H_2O−MeOH (1:1), to give pure saponins **3** (6.2 mg), **6a** (4.2 mg), and **6b** (3.5 mg). Fraction 3 [28.7 mg, eluted in H_2O−MeOH (1:9)] was chromatographed by HPLC on an analytical C_{18} column with a mobile phase of H_2O−MeOH (4:6), to give pure saponins **4a** (3.8 mg) and **4b** (2.9 mg), and **5a** (3.0 mg) and **5b** (2.5 mg).

Triquetroside A1 (1a). Furost-5(6)-en-1β,22α-diol 3β-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl] 26-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranoside]: $[\alpha]_D^{25}$ −33.3° (*c* 0.1, MeOH); ^{1}H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 1−3; HRFABMS (negative ion) of the equilibrated mixture *m/z* found 1061.5136 [M − H]$^-$ (calcd for $C_{51}H_{81}O_{23}$, 1061.5145).

Triquetroside A2 (1b). Furost-5(6)-en-1β, 22β-diol 3β-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl] 26-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranoside]: $[\alpha]_D^{25}$ −43.3° (*c* 0.1, MeOH); ^{1}H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 1−3; HRFABMS (negative ion) of the equilibrated mixture *m/z* found 1061.5136 [M − H]$^-$ (calcd for $C_{51}H_{81}O_{23}$, 1061.5145).

Triquetroside B (3). Furost-5(6),20(22)-dien-1β-ol 3β-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl] 26-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranoside]: $[\alpha]_D^{25}$ −20.2° (*c* 0.1, MeOH); ^{1}H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 1−3; HRFABMS (negative ion) *m/z* found 1043.5050 [M − H]$^-$ (calcd for $C_{51}H_{79}O_{22}$, 1043.5040).

Triquetroside C1 (4a). Furost-5(6)-en-1β,22α-diol 3β-*O*-β-D-glucopyranosyl 26-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranoside]: $[\alpha]_D^{25}$ −13.7° (*c* 0.1, MeOH); ^{1}H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 1−3; HRFABMS (negative ion) of the equilibrated mixture *m/z* found 915.4560 [M − H]$^-$ (calcd for $C_{45}H_{71}O_{19}$, 915.4569).

Triquetroside C2 (4b). Furost-5(6)-en-1β,22β-diol 3β-*O*-β-D-glucopyranosyl 26-*O*-[α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranoside]: $[\alpha]_D^{25}$ −19.6° (*c* 0.1, MeOH); ^{1}H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 1−3; HRFABMS (negative ion) of the equilibrated mixture *m/z* found 915.4560 [M − H]$^-$ (calcd for $C_{45}H_{71}O_{19}$, 915.4569).

Compound 7. Kaempferol 3-*O*-[2-*O*-(*trans*-*p*-coumaroyl)-3-*O*-β-D-glucopyranosyl]-β-D-glucopyranoside: $[\alpha]_D^{25}$ −12° (*c* 0.1, MeOH); UV λ_{max} in MeOH 355, 295 sh, 264, in NaOMe 400, 320, 272, in $AlCl_3$ 398, 349, 300, 272, in $AlCl_3$/HCl 395, 351, 305, 274, in NaOAc 388, 314, 272, in NaOAc/H_3BO_3 342, 285, 255; ^1H and ^{13}C NMR data, see Table 4; HRFABMS (negative ion) *m*/*z* found 755.1807 $[M - H]^-$ (calcd for $C_{36}H_{35}O_{18}$, 755.1812).

Determination of the Absolute Configuration of Sugars. A solution of each isolated compound (1 mg) in 1 N HCl (0.25 mL) was stirred at 80 °C for 4 h. On cooling, the solution was concentrated in a stream of N_2. The residue was dissolved in 1-(trimethyl silyl)imidazole (Trisil-Z) and pyridine (0.1 mL), and the solution was stirred at 60 °C for 5 min. After drying the solution with a stream of N_2, the residue was separated by water and CH_2Cl_2 (1 mL, 1:1). The CH_2Cl_2 layer was analyzed by GC (Alltech l-Chirasil-Val column, 0.32 mm × 25 m; temperatures for injector and detector, 200 °C; temperature gradient system for the oven, 100 °C for 1 min and then raised to 180 °C; rate 5 °C/min). Peaks of the hydrolysate of **1a**/**1b** were detected at 12.89 and 14.65 min in the ratio of 1:1. Peaks of the hydrolysate of **3** were detected at 12.88 and 14.64 min in the ratio of 1:1. Peaks of the hydrolysate of **4a**/**4b** were detected at 12.90 and 14.66 min in the ratio of 1:2. Retention times for authentic samples after being treated simultaneously with Trisil-Z were 12.78 (D-rhamnose) and 12.89 (L-rhamnose), 14.66 (D-glucose) and 14.73 min (L-glucose). Co-injection of each hydrolysate with standard D-glucose and L-rhamnose gave single peaks.

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