Chemical Constituents of *Panax ginseng* Exposed to γ Irradiation†

Joong-Ho Kwon,‡ Jacqueline M. R. Bélanger, Michel Sigouin, Johanne Lanthier, Claude Willemot, and J. R. Jocelyn Paré*,§

Agriculture Canada, Centre de Recherche et de Développement sur les Aliments, 3600 West Casavant Boulevard, Saint-Hyacinthe, Québec, Canada J2S 8E3

Chemical constituents were monitored to assess the biochemical and nutritional safety of *Panax ginseng* powders that were irradiated at doses of 1–10 kGy. Quantitative analysis has shown that the main effective components—saponins—are not altered by ^{60}Co γ irradiation. Ginsenoside-Rg_1 was not affected by the treatment. Negligible changes were observed in the free carbohydrate contents. Doses of more than 5 kGy caused significant decreases in sulfur-containing amino acids and in tyrosine. At doses of 10 kGy, free amino acids, such as proline and lysine, showed an appreciable increase. The composition in minerals was not altered irrespective of the applied doses.

In oriental countries, ginseng (*Panax ginseng* C. A. Meyer) has been used as a mysterious panacea for all kinds of disorders since ancient times. Its name was given after its resemblance with the human body. Its value has been increasingly accepted not only as a natural medicine but also as a health food. Reported activities of ginseng, or ginseng extracts, include effects on the central nervous system, tranquilizing action, histamine-like action, blood pressure elevation, serotonin-like action, analgesic and antipyretic actions, antihistamine action, papaverine-like action, ganglion stimulant action, protection against physical and chemical stress, anticancer activity, and others (Petkov, 1961).

Panax ginseng is reknowned to possess the highest quality among the *Panax* spp. (Araliaceae) cultivated in various countries, i.e., Sanchi-ginseng (Tienchi, roots of *P. notoginseng* (Burk.) F. H. Chen) cultivated in China, American ginseng (*P. quinquefolium* L.) produced in the U.S. and Canada, and Japanese *Panax* (*P. japonicus*).

Saponins are the main effective components of ginseng. They vary widely in their chemical structures; their aglycones are of the dammarane-type triterpenes that derive from the oleanolic acid saponins that are common in nature (Shibata et al., 1963; Shibata et al., 1966). The characteristic dammarane saponins can be divided into two main groups based upon their characteristic aglycone, namely, the ginsenosides-Rb_1, -Rb_2, -Rb_3, -Rc, and -Rd (20(*S*)-protopanaxadiol) and the ginsenosides-Re, -Rf, -Rg_1, -Rg_2, -Rh_1, and glc-Rf (20(*S*)-protopanaxatriol). These structures are the results of various studies by Sanada et al. (1974a,b), by Kasai et al. (1977), and by Tanaka (1985).

Garriques (1854) first isolated the saponin panaquilon ($C_{32}H_{56}O_{14}$) from American ginseng. Since then, there have been a number of studies on the chemical, biochemical, and pharmacological properties of ginseng. Rb_1 reportedly exhibited central nervous system depressant and antipsychotic activities, protection against stress ulcer, increase in gastrointestinal motility, and weak antiinflammatory action, while Rg_1, a major saponin constituent, showed weak central nervous system stimulant action, aggravation of stress ulcer, and antifatigue actions (Takagi et al., 1972a,b; Nabata et al., 1973; Saito et al., 1977). Effects such as these are numerous in the literature and are clearly beyond the scope of this report; readers are referred to Fulder's book (1980) for a more detailed description of the pharmacological properties of ginseng.

Efforts were made to investigate other effective constituents of ginseng roots such as ether-soluble compounds (Takahashi and Yoshikura, 1964), carbohydrates (Lee and Kwon, 1962), and nitrogen-containing components (Hiyama et al., 1978). The recent increase in the demand for ginseng as a health food has spurred an interest in studying functional properties of ginseng along with quality improvement and assurance for processed products.

To that effect, there have been many reports on the degradation of and the decrease in saponins when they are submitted to heat treatment (Choi et al., 1982; Sung and Yang, 1986), to acidic conditions (Han et al., 1982), to storage for variable periods (Choi et al., 1981b; Noh et al., 1983), and to various drying methods (Choi et al., 1984). Furthermore, changes in physicochemical properties of processed ginseng products were investigated. Previous work dealt with sugars, fatty acids, minerals, color, and browning mechanisms (Kim, 1973; Yoon and Kim, 1979; Kim et al., 1983; Sung et al., 1985).

The use of γ irradiation (such as ^{60}Co) in food processing has been extensively studied over the past 4 decades in terms of the wholesomeness of irradiated food and the commercial feasibility aspects of the technology. Food irradiation is increasingly recognized throughout the world as a means to reduce food losses due to microbial degradation and insect contamination (Kwon et al., unpublished results).

The aim of the present study was to evaluate the use of γ irradiation as a means to improve the quality of ginseng products and to increase product hygiene. It concentrated upon gathering data on the effects brought about by the process. These data are used to assess the biochemical and the nutritional safety of the irradiated ginseng.

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‡ Permanent address: Korea Advanced Energy Research Institute, P.O. Box 7, Cheong Ryang, Seoul, South Korea, 130-650.

§ Permanent address: Environment Canada, RRETC, Ottawa, ON, Canada K1A 0H3.

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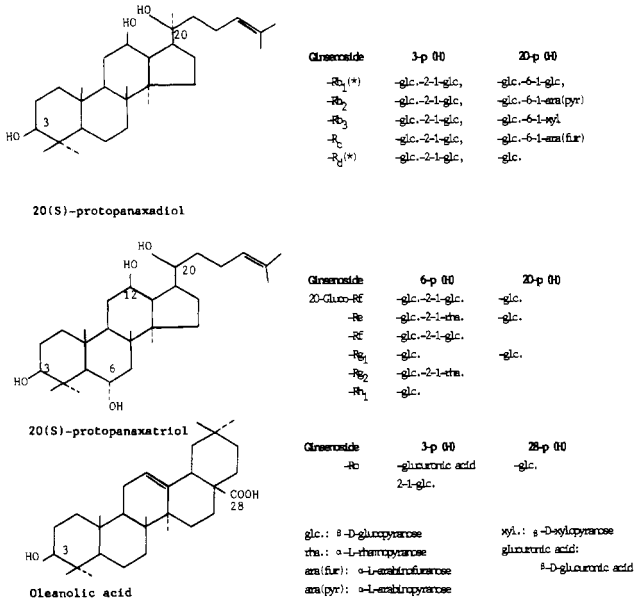

Figure 1. Structures of ginseng saponins.

MATERIALS AND METHODS

Materials. Five-year-old dried ginseng roots (*Panax ginseng* C. A. Meyer) were macerated into a fine powder (120 mesh). The composition of the sample was shown to be ca. 8% moisture, 13% crude protein, 3.7% ash, 1% fat, and >70% carbohydrates.

Irradiation Treatments. Irradiation experiments were carried out in a cobalt-60 irradiator (Gammabeam P-651T) equipped with a 100-kCi activity and operated at a dose rate of 1 kGy·h^{-1}. Samples were placed in cardboard boxes and irradiated at doses ranging from 1 to 10 kGy at ambient temperature and under a normal atmosphere.

Determination of Saponins. Crude saponin fractions were obtained by modifying an earlier method. Ginseng powders were first extracted 3 times with 80% ethanol at 80 °C. The solvent was removed in a rotary evaporator, and the residue was dissolved in water. The aqueous solution was extracted with diethyl ether to remove the residual lipid components and then with a saturated aqueous 1-butanol solution. The butanol layer was concentrated in vacuo, and the residue, containing the saponins, was set aside for high-performance liquid chromatography (HPLC) analysis. The aqueous layer was concentrated and used in sugar analyses (see below). HPLC was performed on a Bio-Rad 402 system equipped with a refractive index detector and a Lichrosorb NH_2 column (5 μm stainless steel, 20 cm); a mobile phase made up of acetonitrile–water–1-butanol (43:7:5 (v:v:v)) was used as eluant. The flow rate and attenuation were set at 1.8 mL·min^{-1} and 16×, respectively. Reference ginsenosides were used to prepare a standard curve of the major saponin components, namely, ginsenosides-Rb_1, -Rb_2, -Rc, -Rd, -Re, -Rf, and -Rg_1. [We thank Professor Osamu Tanaka, Institute of Pharmaceutical Science, Hiroshima University School of Medicine, Japan, and Dr. Jae-Ho Do, Korea Ginseng & Tobacco Research Institute, Korea, for the kind gifts of ginsenoside standards.] The infrared spectra of ginsenoside-Rg_1 (nonirradiated control and irradiated at 25 °C with a dose of 10 kGy in the presence of air) were recorded on a Bruker FT-IR IFS 45 spectrometer as KBr pellets.

Determination of Carbohydrates. Quantitative analyses of free sugar contents in the samples were carried out according to the HPLC method described by Choi et al. (1981a) using the aqueous fraction from above. The chromatograph was used under the same conditions as for the saponins (above) except that the mobile phase consisted of the solvent system acetonitrile–water (43:8).

Determination of Total Amino Acids. Total amino acid analyses were carried out after HCl hydrolysis. One milliliter of 6 N HCl was added to 1 mg of sample protein in a tube that was then sealed in vacuo. It was heated at 110 °C for 24 h to allow for a complete hydrolysis. After cooling, the solution was filtered and evaporated to dryness under reduced pressure. Subsequently, 0.5 mL of 0.01 N NaOH solution was added to the sample and allowed to stand at room temperature for 4 h. Oxidation of cysteine into cystine took place during that period. The volume was adjusted to 2 mL by the addition of 0.02 N HCl. The final solution was then injected into an amino acid analyzer (Hitachi Model 835-50).

Determination of Free Amino Acids. Free amino acids were extracted 3 times with ethanol (75%) for 20 min and then filtered on a Büchner funnel. The solid residue was washed with ethanol. The combined extracts were evaporated by heat to obtain an aqueous solution to which an equal volume of diethyl ether was added and shaken to remove the residual lipids from the sample. After evaporation of the aqueous layer, a 0.01 N NaOH solution was added to allow for the oxidation of cysteine into cystine. A solution of 0.02 N HCl was added to make up the appropriate volume for injection. Tryptophan estimation was not performed in this study.

Determination of Minerals. Fourteen different elements were analyzed in ginseng samples, using an inductively coupled plasma spectrometer (ICP) (ARL Model 3510), following established wet digestion procedures (Osborne and Voogt, 1981).

Statistical Analysis. The results were analyzed statistically by the *t* test and by an analysis of variance.

Table I. Effect of γ Irradiation on the Major Saponin Constituents in Ginseng Powder (mg·g^{-1}, Dry Basis)[a]

ginsenoside	irrad dose, kGy			
	0	1	5	10
Rb_1	8.70 ± 0.54	8.71 ± 0.48	8.71 ± 0.42	8.70 ± 0.36
Rb_2	4.81 ± 0.45	4.79 ± 0.52	4.81 ± 0.38	4.82 ± 0.40
Rc	4.41 ± 0.47	4.42 ± 0.34	4.40 ± 0.57	4.42 ± 0.28
Rd	3.28 ± 0.24	3.30 ± 0.21	3.29 ± 0.18	3.29 ± 0.34
Re	5.21 ± 0.36	5.23 ± 0.26	5.22 ± 0.40	5.22 ± 0.30
Rf	0.57 ± 0.12	0.56 ± 0.06	0.57 ± 0.08	0.56 ± 0.07
Rg_1	2.99 ± 0.13	2.97 ± 0.15	2.98 ± 0.12	2.98 ± 0.10

[a] Mean ± standard deviation of triplicate experiments.

RESULTS AND DISCUSSION

Saponin Fraction. Table I reports the saponin contents (in mg/g) of ginseng that was irradiated at various doses. The pattern of saponin contents in the sample appears to be similar to that published by Kim et al. (1987) and by Sanada et al. (1978). Ginsenoside-Rb_1 was the most abundant, followed by ginsenosides-Re, -Rb_2, -Rc, -Rd, -Rg_1, and -Rf. In this experiment, ginseng saponins were found to be very stable to γ irradiation. No significant variations in the content of ginsenosides were observed with varying irradiation doses. Moreover, it was impossible to point out the most sensitive saponin component to the irradiation treatment. Our analytical method, as described above, has a detection limit of the order of 1 μg. It had been reported previously that ginseng saponins are susceptible to first-order kinetic thermal degradation and that rate constants varied substantially with the types of ginsenosides and the applied treatment temperatures (Choi et al., 1982; Sung and Yang, 1986).

The infrared spectra of nonirradiated and irradiated (10 kGy) ginsenoside-Rg_1 are shown in Figure 2; they show characteristic absorption bands at 1640 (C=C) and 3380 cm^{-1} (OH). There is no detectable difference between the spectra of the nonirradiated and the irradiated samples. Studies on the application of irradiation to ginseng products (Sung et al., 1982; Cho et al., 1985) reported that irradiation doses up to 20 kGy cause negligible changes in the HPLC and TLC patterns of crude saponins extracted from ginseng leaves and roots. This is in good agreement with our results. It can be concluded that γ irradiation is not detrimental to the saponin components of

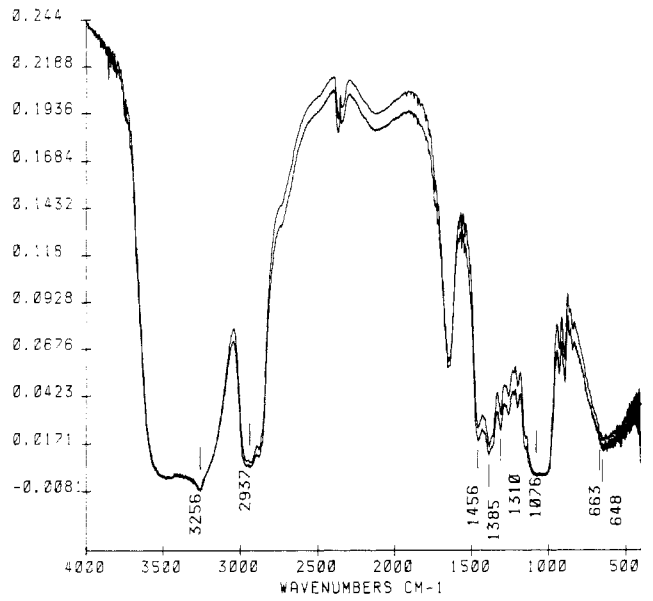

Figure 2. FTIR spectra of nonirradiated control ginsenoside-Rg_1 (bottom curve) and ginsenoside-Rg_1 irradiated with ^{60}Co in the presence of air at 25 °C with a dose of 10 kGy (top curve).

Table II. Effect of γ Irradiation on the Major Free Carbohydrate Constituents in Ginseng Powder (mg·g^{-1}, Dry Basis)[a]

irrad dose, kGy	carbohydrate			
	fructose	glucose	sucrose	maltose
0	1.76 ± 0.06	4.51 ± 0.22	29.88 ± 1.14	6.37 ± 0.52
1	1.78 ± 0.08	4.53 ± 0.26	29.89 ± 1.40	6.38 ± 0.68
5	1.78 ± 0.10	4.58 ± 0.34	29.86 ± 1.48	6.42 ± 0.42
10	1.91 ± 0.16	4.62 ± 0.30	29.79 ± 1.88	6.38 ± 0.30

[a] Mean ± standard deviation of triplicate experiments.

ginseng and that it can be considered as safe within the sterilizing level of ginseng powders.

Free Carbohydrates. Free carbohydrates are the major constituents of ginseng roots, accounting for over 50% (w/w dry basis) of their composition. The main sugar constituents are sucrose, maltose, glucose, and fructose. Under given hydrolytic conditions (acid or heat), the dammarane-based saponins release free sugars along with the aglycone (Han et al., 1982; Choi et al., 1981a). HPLC results on the analysis of free sugars from irradiated ginseng are reported in Table II. Sucrose accounts for ca. 70% of the total sugar content. Although minor changes were observed in the amounts of sugars, they cannot be related significantly to the irradiation process. These results were in agreement with the earlier report dealing with the reducing sugars of irradiated ginseng products by Sung et al. (1982). Negligible changes in sugar contents induced by irradiation at doses below 10 kGy have been reported for various foods (Auda et al., 1978; Park et al., 1970). Higher doses, however, are known to bring about physicochemical changes in pure carbohydrates. Changes are observed in melting point, viscosity, optical rotation, absorption spectra, acidity, production of gases, and radiolytic products (Elias and Cohen, 1977).

Amino Acids. The analysis of 17 different amino acids (aa) revealed decreases in the total aa contents. These results are summarized in Table III. Irradiation doses of more than 5 kGy caused a significant decrease in the content of the sulfur-containing amino acids cysteine ($p < 0.01$) and methionine ($p < 0.05$). In addition, a significant reduction was also observed in the tyrosine content when an irradiation dose of 10 kGy was applied ($p < 0.05$). Chemical changes resulting from irradiation of

Table III. Effect of γ Irradiation on Selected Amino Acids in Ginseng Powder (mg·g^{-1}, Dry Basis)[a]

amino acid	irrad dose, kGy			
	0	1	5	10
aspartic acid	8.12	8.12	8.12	8.10
threonine	3.38	3.37	3.36	3.36
serine	2.35	2.36	2.35	2.34
glutamic acid	8.95	8.90	8.92	8.91
proline	1.98	1.87	1.87	1.86
glycine	2.27	2.28	2.26	2.27
alanine	3.61	3.60	3.58	3.57
cystine	4.32	4.20	4.13[b]	4.11[b]
valine	5.12	5.12	5.12	5.10
methionine	3.06	2.99	2.95[c]	2.96[c]
isoleucine	3.25	3.26	3.25	3.22
leucine	5.15	5.13	5.14	5.12
tyrosine	1.97	1.86	1.85	1.80[c]
phenylalanine	3.66	3.67	3.65	3.64
lysine	4.22	4.23	4.20	4.22
histidine	1.94	1.94	1.94	1.93
arginine	24.52	24.53	24.50	24.26

[a] Each value is the average of triplicate experiments. [b] Significantly different from the nonirradiated control ($p < 0.01$). [c] Significantly different from the nonirradiated control ($p < 0.05$).

Table IV. Effect of γ Irradiation on Selected Free Amino Acids in Ginseng Powder (mg·g^{-1}, Dry Basis)[a]

amino acid	irrad dose, kGy			
	0	1	5	10
aspartic acid	0.38	0.38	0.38	0.40
threonine	1.69	1.69	1.69	1.70
serine	0.27	0.27	0.26	0.28
glutamic acid	0.10	0.10	0.11	0.10
proline	0.16	0.16	0.19	0.21[b]
glycine	0.06	0.06	0.06	0.06
alanine	0.63	0.63	0.63	0.63
cystine	0.28	0.29	0.30	0.32
valine	0.38	0.38	0.37	0.39
methionine	0.21	0.21	0.22	0.25
isoleucine	0.26	0.28	0.29	0.30
leucine	0.36	0.37	0.36	0.38
tyrosine	0.45	0.45	0.48	0.50
phenylalanine	0.41	0.42	0.42	0.46
lysine	0.90	0.92	1.04[b]	1.02[b]
histidine	0.15	0.14	0.15	0.15
arginine	17.10	17.11	17.21	17.38

[a] Each value is the average of triplicate experiments. [b] Significantly different from the nonirradiated control ($p < 0.05$).

food proteins have been extensively studied. The changes were principally associated with the development of undesirable flavors (or odors) when high doses of irradiation were used. In this respect, the effects of irradiation are well documented by Elias and Cohen (1977), indicating that the primary effects involve deamination, decarboxylation, and denaturation of the irradiated proteins and that secondary effects include the decomposition and/or recombination of free radicals that originate from the primary reactions. Thiol or disulfide moieties found in aa are known to be particularly sensitive to ionizing radiation, although no consistent pattern has been presented to account for the resistance of each aa that is subjected to irradiation in relation to the nature of the food and to the physical state of the aa and the proteins.

The free aa content of the samples showed a tendency to increase for most aa with the irradiation dose (Table IV). The increments observed in proline and lysine contents for the irradiated sample (10 kGy) are significant. These results are in partial agreement with the findings of Srinivas et al. (1972), who reported an overall increase in free aa levels in irradiated wheat (10 kGy) but no significant difference in the total composition between the

Table V. Effect of γ Irradiation on Selected Minerals in Ginseng Powder (mg/100 g, Dry Basis)[a]

mineral (wavelength, nm)	irrad dose, kGy 0	5	10
aluminum (309.27)	17.22	17.65	17.35
boron (249.68)	0.96	1.06	0.97
calcium (393.37)	226.70	228.00	227.50
chromium (205.99)	0.43	0.43	0.50
copper (324.75)	0.93	0.93	1.00
iron (259.94)	15.78	15.67	15.35
iodine (178.28)	405.30	404.40	405.20
potassium (766.49)	800.60	801.69	799.80
magnesium (279.55)	295.40	295.00	295.69
manganese (257.61)	5.52	5.59	5.81
nickel (231.60)	0.40	0.36	0.36
phosphorus (214.91)	286.20	285.45	282.60
zinc (206.19)	2.58	2.37	2.37
vanadium (311.07)	trace[b]	trace[b]	trace[b]

[a] Each value is the average of triplicate experiments. [b] Trace < 0.01 mg.

control and the irradiated samples. The variation in response of the amino acids to irradiation can be attributed to the compositional difference and to the physical status of the sample as well as to the irradiation conditions used. It has been indicated that dry amino acids or dry products are very resistant to the effects resulting from exposure to irradiation as compared to the products in a moist state (Elias and Cohen, 1977).

Minerals. Previous work on the elemental composition of ginseng has dealt mainly with nutritional uptake, distribution patterns, and biochemical roles (Kim et al., 1977; Kim and Staba, 1974). Very few reports are available on the effect of processing on element contents of ginseng (Sung et al., 1985). Table V compares the respective contents for 14 different elements between the control and the irradiated samples as determined by ICP. The major elements of the sample were found to be potassium, iodine, magnesium, phosphorus, and calcium. As a whole, no significant changes were observed in the elemental contents of the sample upon irradiation up to doses of 10 kGy. The literature indicates that irradiation for food processing and preservation does not alter the mineral content of food although it possibly changes the nutritional availability of certain minerals (Urbain, 1986; Quaranta, 1986). These facts were confirmed by these experiments.

CONCLUSION

On the basis of the preliminary considerations of irradiation effects on the chemical constituents of ginseng, it was generally observed that dehydrated ginseng products are resistant to chemical changes when exposed to γ irradiation within a dose range of 10 kGy, which is sufficient to improve the microbiological quality of ginseng products. These findings, along with our previously reported ones on the sensory and the physical properties of irradiated ginseng, lead to the conclusion that it is safe to irradiate ginseng at 10 kGy in order to improve shelf life while maintaining wholesomeness and food safety (Kwon et al., unpublished results).

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Lipophilicity–Antifungal Activity Relationships for Some Isoflavonoid Phytoalexins

Anna Arnoldi* and Lucio Merlini

Dipartimento di Scienze Molecolari Agroalimentari, Sezione di Chimica, Università di Milano, Via Celoria 2, I-20133 Milano, Italy

The octanol/water partition coefficients of 18 isoflavonoid phytoalexins have been determined by reversed-phase HPLC and/or calculated by the use of Hansch hydrophobic parameters: The values obtained are in the range 1.5–4.2. From a study of the relationship between these data and the antifungal activity on *Aphanomyces euteiches* and *Fusarium solani* f.sp. *cucurbitae* reported by Van Etten, it appears that within groups of compounds of similar structure an increase in lipophilicity correlates positively with increased antifungal activity, whereas a general correlation for the whole class of isoflavonoid phytoalexins was not found. On the other hand, correlations with some other structural factors, such as the presence of a phenolic OH or benzylic hydrogen atoms, seem possible.

Phytoalexins are chemical compounds involved in the resistance of plants to diseases caused by fungi and bacteria.

Although a large number of studies have been published on this topic, the relationship between the molecular properties of isoflavonoid phytoalexins and their activity has not yet been clarified satisfactorily (Smith, 1982).

Lipophilicity seems, however, very important probably because it is indispensable for effective penetration of fungal membranes (Harborne and Ingham, 1978). Some lipophilic substituents seem particularly favorable for fungicidal activity: for example the dimethylchromene group in phaseollin and glyceollin (Van Etten, 1976) and the dimethylallyl in wighteone (Ingham et al., 1976) and kievitone (Smith, 1978).

Despite these qualitative indications, no systematic study of the possible correlation between partition coefficients of isoflavonoid phytoalexins and antifungal activity as

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