TRITERPENE GLYCOSIDES OF ALFALFA.

VI. MEDICOSIDE L

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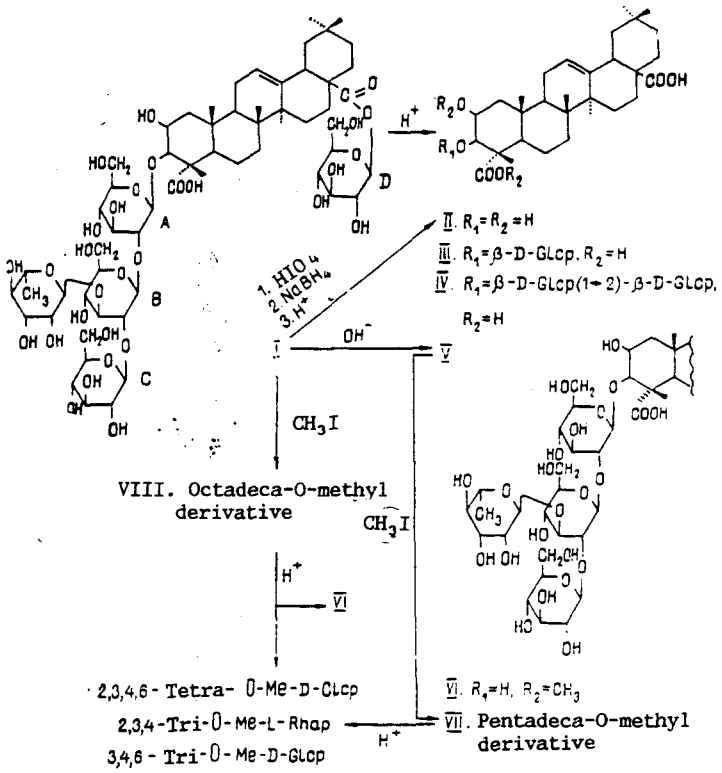
A new triterpene pentaglycoside — medicoside L — has been isolated from the roots of Medicago sativa L. (Leguminosae). It has the structure of medicagenic acid 28-O-β-D-glucopyranoside 3-O-{[O-β-D-glucopyranosyl-(1 → 2)][O-α-L-rhamnopyranosyl-(1 → 3)]-O-β-D-glucopyranosyl-(1 → 2)}-β-D-glucopyranoside.

Continuing investigations of the triterpene glycosides of alfalfa [1-3] we have studied the structure of medicoside L (I) — one of the polar components of the saponin fraction of a methanolic extract from alfalfa roots. Its isolation was described in [2].

With the aid of the GLC method [4] it was established that medicoside L (I) contains D-glucose and L-rhamnose residues in a ratio of 4:1. Partial acid hydrolysis of glycoside (I) gave medicagenic acid (II), medicagenic acid 3-O-β-D-glucopyranoside (III) [5], and medicagenic acid 3-O-[O-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside] (IV). The first two compounds were identified from their physicochemical constants, and we established the structure of the last from its FAB mass spectrum and its ^{13}C NMR spectrum.



In the FAB mass spectrum of compound (IV), quasi-molecular ions cationized to various degrees (m/z 941, 903,...) and fragments corresponding to them formed as the result of the splitting out of two hexose residues were observed. In the ^{13}C NMR spectrum of this compound (Table 1), as compared with the spectrum of medicagenic acid 3-O-β-D-glucopyranoside (III) [3], we observed a 2.4 ppm upfield displacement of the signal of the anomeric carbon atom

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TABLE 1. Chemical Shifts of the Carbon Atoms of Medicoside L (I) and its Progenins (V) and (IV) (C_5D_5N, δ, ppm, O–TMS)

C-atom	Compound			C-atom	Compound		
	I	V	IV		I	V	IV
Aglycon							
1	44,1	43,9	44,0	3-O-Glcp A 1	103,0	102,6	102,9
2	70,2	70 3	70,1	2	84,3	84,6	83,6
3	85,6	85,6	85,6	3	77,6	77,4	78,1[d]
4	52,5[a]	52,6[a]	52,6	4	71,2[c]	71,0[e]	71,1[e]
5	52,5[a]	52,6[a]	52,4	5	78,0	78,0	78,1[d]
6	20,9	20,8	20,9	6	62,5[d]	62,5[f]	62,6[f]
7	33,1[b]	33 1[b]	33,2[a]	Glcp B 1	104,6	104,4	106,1
8	40,3	40,1	40,1	2	84,8	84,8	76,9
9	48,7	48,7	48,7	3	85,3	85,4	78,3
10	36,8	36,8	36,8	4	69,7	69,8	71,1[e]
11	23,9	23,7[c]	23,7	5	79,7	79,5	78,1[d]
12	123,5	123,5	123,5	6	62,5[d]	62,5[f]	62,6[f]
13	144,1	144,8	144,8	Glcp C 1	106,4	106,4	
14	42,2	42,2	42,2	2	76,8	76,8	
15	28,1	28,1	28,2	3	78,6	78,7	
16	23,6	23,7[c]	23,7[b]	4	71,2[c]	71,0[e]	
17	46,9	46,6[d]	46,6[c]	5	78,2	78,4	
18	41,7	41,9	42,0	6	62,5[d]	62,5[f]	
19	46,2	46,6[d]	46,6[c]	Rhap 1	101,9	101,9	
20	30,7	30,9	30,9	2	72,5	72,7[g]	
21	33,9	34,2	34,2	3	72,1	72,7[g]	
22	33,1[b]	33,1[b]	33,2[a]	4	74,1[e]	74,7	
23	180,6	181,0	180,6	5	70,0	70,3	
24	14,2	14,2	14,2	6	18,5	18,4	
25	16,8	16,8	16,8	28-O-Glcp D 1	95,7		
26	17,3	17,3	17,3	2	74,1[e]		
27	26,0	26,2	26,2	3	78,8		
28	176,4	180,2	180,1	4	70,8		
29	33,1[b]	33,1[b]	33,2[a]	5	79,2		
30	23,4	23,7[c]	23,7[b]	6	62,3		

The signals marked with the letters a-g are superposed upon one another.

of the D-glucose residue directly linked to the polycyclic nucleus (Glcp A). In addition, the C-2 signal of the same D-glucose molecule was shifted from its position at 75.1 ppm to 83.6 ppm. All this showed the 1 → 2-linkage of the two D-glucose residues (Glcp A and Glcp B).

The alkaline hydrolysis of medicoside L (I) led to the progenin (V). It was shown with the aid of GLC that D-glucose and L-rhamnose residues were present in glycoside (V) in a ratio of 3:1. In the FAB mass spectrum of this compound taken with the addition of KCl there was the peak of the quasi-molecular ion $[M + 2K - H]^+$ at m/z 1211, which corresponds to a molecule containing three D-glucose and one L-rhamnose residues. Its fragmentation took place by two routes in parallel: $[M + 2K - H]^+ - Rha$ and $[M + 2K - H]^+ - Glc$, corresponding to mass numbers of 1065 and 1049. Such fragmentation showed the presence of two terminal sugars and branching in the carbohydrate chain.

Glycoside (I) was methylated by Hakomori's method [6], which gave an octadecyl-O-methyl derivative (VIII). In the PMR spectrum (C_5D_5N) of the polyester-ether (VIII) the signals of the anomeric protons of four D-glucose residues were observed – at (ppm) 4.44 (1 H, d, ^3J = 7 Hz), 4.88 (2 H, d, ^3J = 7 Hz), and 5.70 (1 H, d, ^3J = 7 Hz) and of a L-rhamnose residue at 5.45 (1H, s). The composition of the methylated sugars was determined by Aspinall's method [7] and it was found that compound (VIII) contained 2,3,4,6-tetra-O-methyl-D-glucopyranose, 2,3,4-tri-O-methyl-L-rhamnopyranose, and 3,4,6-tri-O-methyl-D-glucopyranose

residues. It was impossible to identify a di-O-methyl-D-glucopyranose corresponding to the branching center. As a result of the hydrolysis of the polyester-ether (VIII) 23-methyl 2-O-methylmedicagenate (VI) was obtained. Consequently, the carbohydrate chains were attached at C-3 and C-28 of the aglycon.

Hakomori methylation [6] of the alkali-derived progenin (V) led to a pentadeca-O-methyl derivative (VII). The PMR spectrum (C_5D_5N) of the derivative (VII) obtained the signals of the anomeric protons of three D-glucose residues at (ppm) 4.44, 4.88, and 4.90 (each 1 H, d, ^3J = 7 Hz) and of a L-rhamnose residue at 5.46 ppm (1 H, d, $^3J \approx 2$ Hz). As was to be expected, a comparison of the PMR spectra of the derivatives (VIII) and (VII) showed the absence in the latter of the weak-field signal of the anomeric proton of the glucose residue attached to one of the acid groups (Glcp D).

Analysis of the methylated sugar residues in the permethylate (VII) by the GLC method [7] showed the presence of 2,3,4,6-tetra-O-methyl-D-glucopyranose, 2,3,4-tri-O-methyl-L-rhamnopyranose, and 3,4,6-tri-O-methyl-D-glucopyranose. As in the case of the polyester-ether (VIII) it was impossible to identify the corresponding D-glucose di-O-methyl ether. The mass spectrum of the pentadeca-O-methyl derivative (VII) revealed fragmentation characteristic for permethylates of triterpene glycosides of the oleanene type [8]. The spectrum contained peaks with m/z 187 and 219 due to the splitting out of terminal L-rhamnose and D-glucose residues. This also confirmed the conclusion that the tetrasaccharide chain was branched.

Medicoside L (I) was subjected to Smith degradation [9], which led to medicagenic acid (II). This result excluded branching at a D-glucose molecule directly attached to C-3 of medicagenic acid (Glcp A) and showed that branching was possible only at the second D-glucose molecule (Glcp B).

The ^{13}C NMR spectrum of medicoside L (I) had the signals of anomeric carbon atoms at 95.7, 101.9, 103.0, 104.6, and 106.4 ppm. From the size of its chemical shift, the first signal must be assigned to the glucose attached to the acyl group (Glcp D), the second belongs to L-rhamnose, while the signal at 103.0 ppm is characteristic for the anomeric carbon atom of D-glucose substituted in the second position (Glcp A). Of the other two signals the last had a value characteristic for a terminal D-glucose residue (Glcp C). The signal at 104.6 ppm must therefore belong to the D-glucose residue forming the center of branching (Glcp B). Since the signal at 104.6 ppm was shifted upfield by 1.5 ppm in comparison with the corresponding signal in compound (IV), it must be assumed that the C-2 hydroxy group of this molecule is substituted.

Then, in the spectrum of medicoside L (I) signals of glycosylated carbon atoms were observed at 84.3, 84.8, and 85.3 ppm. L-rhamnose attached in the second or fourth position of D-glucose shifts the signal of the glycosylated carbon atom to 78.1-79.5 ppm [11] and in the third position to 84.5 ppm [12]. Consequently L-rhamnose was most probably substituted in the third position. This was also confirmed by the presence of signals at 69.7 and 79.7 ppm assigned to the C-4 and C-5 atoms of the center of branching (Glcp B), since characteristic shifts of the fourth carbon atom upfield and of the fifth carbon atom downfield are observed on the substitution of the third position of D-glucose [12]. This means that we are justified in assuming that the second hydroxyl of this D-glucose residue is glycosylated by another D-glucose residue. The chemical shifts of the latter are in good agreement with the chemical shifts of the terminal D-glucose residue in compound (IV) which has an analogous 1 → 2-bond. On the basis of what has been said, the terminal D-glucose and terminal L-rhamnose are attached to the second and third positions of a D-glucose residue, respectively.

A conclusion concerning the configurations of the glycosidic bonds was made on the basis of the chemical shifts of the anomeric carbon atoms in the ^{13}C NMR spectrum of medicoside L (I) and the spin-spin coupling constants of the anomeric protons in the PMR spectra of the permethylates (VII) and (VIII). Thus, medicoside L (I) has the structure of medicagenic acid 28-O-β-D-glucopyranoside 3-O-{[O-β-D-glucopyranosyl-(1 → 2)][O-α-L-rhamnopyranosyl-(1 → 3)]-O-β-D-glucopyranosyl-(1 → 2)}-β-D-glucopyranoside.

EXPERIMENTAL

General Observations. The following solvent systems were used: 1) chloroform—methanol—water (400:100:13); 2) benzene—acetone (a – (5:1); b – (10:1)); and 3) chloroform—methanol (a – (100:1); b – (10:1)).

^{13}C NMR spectra were taken on a Jeol FX-90Q instrument in deuteropyridine with TMS as internal standard under conditions of complete decoupling from protons, using the INEPT procedure. FAB mass spectra were taken on LKB-2091/PDP-11/34 instrument with an Iontech Ltd, Teddington (U.K.), ion source. Ionization was effected with a beam of accelerated xenon atoms having an energy of 6 kV at a discharge current of 1.2 mA. Glycerol with the addition of KCl was used as the matrix.

For other observations, see [5].

Medicoside L (substance L [2], I) $C_{60}H_{96}O_{30}$, $[\alpha]_D^{21}$ + 12.7 ± 2° (c 3.35; methanol), ν_{max}^{KBr}, cm^{-1}: 3570–3200, 1730–1710, 1265. The results of a determination of the sugar residues present in compound (I) by the GLC method [4] showed L-rhamnose and D-glucose in a ratio of 0.24:1.00. PMR (C_5D_5N, δ, ppm): 0.74 × 2, 0.96, 1.04, 1.36, 1.82 (each 3 H, s, 6 × CH_3); 1.58 (3 H, d, ^3J = 5 Hz, CH_3 of L-rhamnose); 5.04 (3 H, m, anomeric protons of three D-glucose residues); 5.29 (1 H, broadened singlet, H-12); 5.90 (1 H, s, anomeric proton of L-rhamnose); 6.06 (1 H, d, ^3J = 7 Hz, anomeric proton of D-glucose). FAB mass spectrum m/z (%): 1227 ($[M + 2K - H - Rha]^+$, 32), 1211(100), 1173(27), 1065(23), 1049(23), 1003(23), 903(41), 885(14), 857(18), 741(32), 723(23), 695(18).

Medicagenic Acid (II), Medicagenic Acid 3-O-β-D-Glucopyranoside (III) and Medicagenic Acid 3-O-[O-β-D-Glucopyranosyl-(1 → 2)-β-D-glucopyranoside] (IV) from (I). A solution of 200 mg of medicoside L (I) in 30 ml of 0.5% methanolic sulfuric acid was boiled for 2 h. The solution was diluted with water, the methanol was evaporated off, and the precipitate that had deposited was separated off and washed with water. The residue (100 mg) was chromatographed on a column with elution by system 1. This gave: 11 mg of medicagenic acid (II), $C_{30}H_{46}O_6$, mp 352-354°C (from methanol), $[\alpha]_D^{21}$ + 111.6 ± 2° (c 0.10; ethanol); 15 mg of medicagenic acid 3-O-β-D-glucopyranoside (III), $C_{36}H_{56}O_{11}$, mp 288-291°C (from methanol), $[\alpha]_D^{21}$ + 64.3 ± 2° (c 0.50; ethanol); and 60 mg of amorphous medicagenic acid 3-O-[O-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside] (IV), $C_{42}H_{66}O_6$, $[\alpha]_D^{22}$ + 57.9 ± 2° (c 1.00; methanol); FAB mass spectrum, m/z (%): 941 ($[M + 3K - 2H]^+$, 67), 903 (100), 857 (33), 779 (33), 761 (33), 741 (33), 723 (17), 617 (67), 599 (33).

Alkaline Hydrolysis of Medicoside L (I). A solution of 500 mg of medicoside L (I) in 10 ml of 3% KOH solution was left at room temperature for two days. The reaction product was extracted with butanol and, after evaporation of the butanol extracts, the residue was chromatographed on a column in system 1. This gave 160 mg of the amorphous compound (V) $C_{54}H_{86}O_{25}$, $[\alpha]_D^{23}$ + 43.4 ± 2° (c 0.87; methanol).

Result of the determination of the sugar residues present in compound (V) by the GLC method [4]: D-glucose and L-rhamnose in a ratio of 1.00:0.27. PMR (C_5D_5N, δ, ppm): 0.82, 0.91 × 2, 1.14, 1.39, 1.88 (each 3 H, s, 6 × CH_3); 1.64 (3 H, d, ^3J = 5 Hz, CH_3 of L-rhamnose); 4.89, 5.04, 5.12 (each 1 H, d, ^3J = 7 Hz; anomeric protons of D-glucose residues); 5.34 (1 H, broadened singlet, H-12); and 5.95 (1 H, s, anomeric proton of L-rhamnose).

FAB mass spectrum, m/z (%): 1287 ($[M + 4K - 3H]^+$, 13), 1249 (13), 1211 (13), 1173 (20), 1141 (20), 1125 (13), 1103 (47), 1087 (40), 1065 (100), 1049 (87), 1027 (27), 1019 (33), 1011 (33), 1003 (13), 979 (13), 941 (13), 903 (33), 885 (13), 817 (20), 779 (33), 761 (27), 741 (60), 723 (27), 617 (47), 579 (60), 561 (53).

The Octadeca-O-methyl Derivative (VIII) from (I). Medicoside L (I) (500 mg) was methylated by Hakomori's method [6]. The product obtained (770 mg) was transferred to a column and was chromatographed in system 2a. This led to the isolation of 146 mg of the amorphous octadeca-O-methyl derivative (VIII) $C_{85}H_{144}O_{54}$, $[\alpha]_D^{23}$ + 25.7 ± 2° (c 1.10; methanol). The IR spectrum showed no absorption in the region of hydroxy groups. PMR (C_5D_5N, δ, ppm): 0.77 × 2, 0.88, 1.14, 1.28, 1.70 (each 3 H, s, 6 × CH_3); 3.20-3.87 (s, 18 × OCH_3); 4.44 (1, H, d, ^3J = 7 Hz, anomeric proton of D-glucose); 4.88 (2 H, d, ^3J = 7 Hz, anomeric protons of two D-glucose residues); 5.30 (1 H, broadened singlet, H-12); 5.45 (1 H, s, anomeric proton of L-rhamnose); 5.70 (1 H, d, ^3J = 7 Hz, anomeric proton of D-glucose). PMR ($CDCl_3$, δ, ppm): 0.70, 0.86 × 2, 1.04, 1.13, 1.36 (each 3 H, s, 6 × CH_3); 3.28-3.70 (s, 18 × OCH_3); 4.14 (1 H, d, ^3J = 5 Hz, anomeric proton of D-glucose); 4.57 (2 H, d, ^3J = 6 Hz, anomeric protons of two D-glucose residues); 5.12 (1 H, s, anomeric proton of L-rhamnose); 5.25 (1 H, broadened singlet, H-12); and 5.29 (1 H, d, ^3J = 7 Hz, anomeric proton of D-glucose).

Mass spectrum, m/z (%): 528 (11), 527 (33), 469 (15), 468 (11), 467 (28), 453 (12), 409 (11), 391 (33), 361 (18), 359 (11), 347 (11), 262 (22), 233 (11), 219 (16), 205 (15), 204 (25), 203 (63), 202 (24), 201 (37), 190 (15) 189 (79), 188 (17), 187 (100), 175 (36), 173 (57), 171 (12), 161 (15), 159 (19), 157 (40), 155 (33), 149 (11), 147 (17), 145 (27), 144 (11), 143 (29), 141 (21), 135 (12), 133 (19), 131 (18), 129 (15), 127 (21), 125 (12), 121 (13), 119 (31), 115 (26), 113 (23), 111 (39), 109 (11), 107 (21), 105 (15), 102 (13), 101 (79).

The composition of the methylated monosaccharide residues in the octadeca-O-methyl derivative (VIII) was determined by Aspinall's method [7] in two phases: 20% poly(butane-1,4-diyl succinate) on Celite, 30-60 mesh (phase 1) and 10% of poly(phenyl ether) 5F4E on Chromaton N-AW-HMDS (0.100-0.125 mm) (phase 2). Phase 1, T_{rel}: 0.42 (2,3,4-tri-O-methyl-L-rhamnopyranose); 1.00, 1.42 (2,3,4,6-tetra-O-methyl-D-glucopyranose); 3.10, 3.69 (3,4,6-tri-O-methyl-D-glucopyranose). Phase 2, T_{rel}: 0.46 (2,3,4-tri-O-methyl-L-rhamnopyranose); 1.00, 1.33 (2,3,4,6-tetra-O-methyl-D-glucopyranose); 1.69 (3,4,6-tri-O-methyl-D-glucopyranose).

23-Methyl-2-O-Methylmedicagenate (VI) from (VIII). A solution of 100 mg of compound (VIII) in 20 ml of 4% methanolic sulfuric acid was heated at the boiling point of the solvent for 5 h and was then diluted with water, the methanol was distilled off, and the reaction product was extracted with chloroform. The chloroform extracts were washed and evaporated. The dry residue was chromatographed on a column with elution by system 3a. This gave 13 mg of 23-methyl-2-O-methylmedicagenate (VI), $C_{32}H_{50}O_6$, identified in TLC with an authentic sample in system 2a and by its mass spectrum.

The Pentadeca-O-methyl Derivative (VII) from (V). Compound (V) (120 mg) was methylated by Hakomori's method [6]. The reaction product (148 mg) was chromatographed on a column, and elution by system 2b gave 92 mg of the amorphous pentadeca-O-methyl derivative (VII) $C_{66}H_{116}O_{25}$, $[\alpha]_D^{25}$+ 83.6 ± 2° (c 0.28; methanol). In the IR spectrum there was no absorption in the region of hydroxy groups. PMR (C_5D_5N, δ, ppm): 0.73; 0.79; 0.81, 1.10, 1.26, 1.26 (each 3 H, s, 6 × CH_3); 3.27; 3.29; 3.36; 3.37; 3.39; 3.41; 3.44; 2.55; 2.57; 3.65; 3.68; 3.76, 3.85, 3.87 (each 3 H, s, 15 × OCH_3); 4.44, 4.88, 4.90) (each 1 H, d, ^3J = 7 Hz, anomeric protons of D-glucose residues); 5.28 (1 H, broadened singlet, H-12); 5.46 (1 H, d, $^3J \approx 2$ Hz, anomeric proton of L-rhamnose).

Mass spectrum, m/z (%): 528 (40), 527 (97), 495 (20), 468 (23), 467 (57), 393 (20), 391 (60), 361 (26), 359 (20), 263 (29), 262 (86), 249 (20), 233 (20), 219 (20), 205 (29), 204 (43), 203 (97), 202 (34), 201 (51), 190 (20), 189 (97), 188 (20), 187 (100), 175 (26), 173 (57), 159 (23), 157 (63), 155 (26), 149 (23), 147 (23), 145 (37), 143 (49), 141 (26), 133 (31), 131 (26), 129 (23), 127 (23), 125 (20), 121 (20), 119 (31), 115 (31), 113 (20), 111 (51), 109 (20), 107 (23), 105 (26), 102 (26), 101 (86).

The methylated monosaccharide derivatives in compound (VII) were analyzed in a similar way to that described for compound (VIII) by Aspinall's method [7]. Phase 1, T_{rel}: 0.42 (2,3,4-tri-O-methyl-L-rhamnopyranose); 1.00, 1.40 (2,3,4,6-tetra-O-methyl-D-glucopyranose); 3.06, 3.63 (3,4,6-tri-O-methyl-D-glucopyranose). Phase 2, T_{rel}: 0.45 (2,3,4-tri-O-methyl-L-rhamnopyranose); 1.00, 1.31 (2,3,4,6-tetra-O-methyl-D-glucopyranose); 1.65 (3,4,6-tri-O-methyl-D-glucopyranose).

Smith Degradation of Medicoside L (I). A solution of 120 mg of medicoside L in 5 ml of methanol was treated with 0.5 g of periodic acid in 5 ml of water and the mixture was stirred at room temperature for 1 h. To decompose the excess of oxidant, 0.6 ml of ethylene glycol was added and the solution was diluted with 20 ml of water. The reaction products were extracted exhaustively with chloroform. The chloroform extracts were combined, the solvent was distilled off, and the residue was dissolved in 10 ml of methanol. The solution was treated with 0.17 g of sodium tetrahydroborate in small portions and was then left at room temperature for 2 h. After this, the reaction mixture was acidified with dilute sulfuric acid to pH 2, and after 4 h, it was extracted with butanol and the butanol extract was washed and evaporated. The reaction product was identified by the GLC method in the presence of an authentic sample in systems 1 and 3b as medicagenic acid; no medicagenic acid 3-O-β-D-glucopyranoside was detected.

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