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Triterpenoids of the Bark of *Pieris japonica* D. Don (Japanese Name: Asebi). II.[1] ^{13}C Nuclear Magnetic Resonance of the γ-Lactones of Ursane- and Oleanane-type Triterpenes

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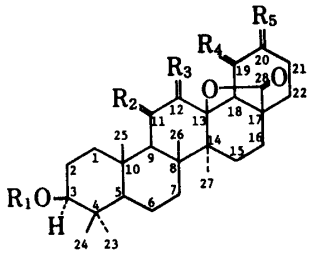
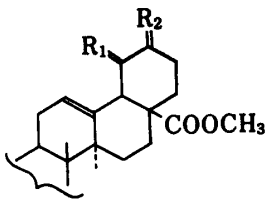
Eight triterpenoids and a sterol were isolated from the bark of *Pieris japonica* D. Don (Japanese name: asebi, Ericaceae) and have been elucidated as 3β-acetoxyurs-11-en-28,13-olide, 3β-acetoxy-12α-hydroxyolean-28,13-olide, 3β-acetoxy-28-hydroxyurs-12-ene, 3β,28-dihydroxyurs-12-ene, 3β-acetoxyurs-12-en-28-al, taraxeryl acetate, taraxerol, taraxerone and β-sitosterone by a combination of chemical and spectroscopic studies. ^{13}C Nuclear magnetic resonance spectral analysis of several γ-lactones of the ursane and oleanane series was undertaken, and all the carbons were assigned by means of single frequency off-resonance and selective decoupling methods and by comparison of the signals with those of methyl esters of acetyl ursolic acid and acetyl oleanolic acid.

Keywords——*Pieris japonica*; bark; triterpenoid; ursane-type γ-lactone; oleanane-type γ-lactone; ^1H-NMR; ^{13}C-NMR

In the preceding paper,[1] we reported the isolation and characterization of six triterpenoids from the bark of *Pieris japonica* D. Don (Japanese name: asebi, Ericaceae). Further detailed examination of the methanolic extract of the bark has led to the isolation of nine compounds (C-I through C-IX). In this paper, we wish to report the structural elucidation and the full assignments of the ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectra of several γ-lactones of the ursane and oleanane series, among the above compounds.

The molecular formula $C_{32}H_{48}O_4$ of C-I was determined by elemental analysis and from the mass spectrum, m/z 496 (M^+). The infrared (IR) and the proton nuclear magnetic resonance (^1H-NMR) spectra indicated that C-I was an ursane-type triterpene acetate having a γ-lactone ring (28,13-olide). The ^1H-NMR spectrum of C-I further showed the presence of a–CHCH=CH– moiety as an AMX type signal at δ 5.53 (1H, dd, J=3.6 and 10.3 Hz)and 5.95 (1H, dd, J=0.9 and 10.3 Hz). The chemical shift and the splitting pattern on these protons were strikingly similar to those reported for urs-11, 14-dien-3β-yl acetate.[2] The above results and a comparison of the ^{13}C-NMR chemical shifts of C-I with those of γ-lactones of the ursane series indicated that C-I possesses an ursane-type skeleton with a disubsti-





1: R_1=Ac, R_2=R_3=H_2, R_4=$\langle^{CH_3}_{H}$, R_5=$\langle^{H}_{CH_3}$

2: R_1=H, R_2=R_3=H_2, R_4=$\langle^{CH_3}_{H}$, R_5=$\langle^{H}_{CH_3}$

3: R_1=Ac, R_2=H_2, R_3=$\langle^{H}_{OH}$, R_4=$\langle^{CH_3}_{H}$, R_5=$\langle^{H}_{CH_3}$

4: R_1=Ac, $H\diagdown R_2 \diagup O \diagdown R_3 \diagup H$, R_4=$\langle^{CH_3}_{H}$, R_5=$\langle^{H}_{CH_3}$

C-I: R_1=Ac, R_2, R_3[$H\rangle\!=\!\langle H$ (11, 12)], R_4=$\langle^{CH_3}_{H}$, R_5=$\langle^{H}_{CH_3}$

5: R_1=Ac, R_2=R_3=R_4=H_2, R_5=$(CH_3)_2$

6: R_1=H, R_2=R_3=R_4=H_2, R_5=$(CH_3)_2$

C-II: R_1=Ac, R_2=H_2, R_3=$\langle^{H}_{OH}$, R_4=H_2, R_5=$(CH_3)_2$

7: R_1=$\langle^{CH_3}_{H}$, R_2=$\langle^{H}_{CH_3}$

8: R_1=H_2, R_2=$(CH_3)_2$

tuted double bond (δ 133.2 and 129.0 due to C-11 and C-12, respectively). Thus, the structure of C-I was established to be 3β-acetoxyurs-11-en-28,13-olide, which has previously been isolated from *Euclea natalensis* (Ebenaceae).[3] Majumder *et al.*[4] have reported the action of hydrogen peroxide on acetyl ursolic acid and described the mechanism of formation of 3β-acetoxy-11α,12α-epoxyurs-28,13-olide through 3β-acetoxyurs-11-en-28,13-olide as an intermediate.

C-II, colorless needles, had the molecular formula $C_{32}H_{50}O_5$ from its elemental analysis and molecular ion (M^+) at m/z 514 in the mass spectrum (MS). The IR, ^{1}H-NMR and mass spectra suggested that C-II is an oleanane-type γ-lactone (28,13-olide) having a secondary axial hydroxyl group (δ 3.88, 1H, br s, $W_{h/2}$=7 Hz). The MS of C-II was similar to that of 3β-acetoxy-olean-28,13-olide. C-II was acetylated with Ac_2O–pyridine on a water bath for 10 h. However, a large amount of the starting material was recovered on silica gel chromatography. It was presumed that the hydroxyl group in C-II might be situated in a hindered position and thus be resistant to acetylation. From these results and the broad signal at δ 3.88 in the ^{1}H-NMR spectrum of C-II, the structure of C-II was deduced to be 3β-acetoxy-12α-hydroxyolean-28,13-olide, which has previously been isolated from *Rhodomyrtus tomentosa* (Myrtaceae).[5] This identification was confirmed by ^{13}C-NMR spectral analysis and direct comparison with an authentic sample derived by Barton's method.[6] The chemical shifts are given in Table I.

TABLE I. ^{13}C Chemical Shifts (δ_C, in $CDCl_3$) of the γ-Lactones

	1	2		3		4		C-I		5	6		C-II	
C-1	38.7	(39.1)	t[a]	38.6	t	37.7	t	38.1	t	38.7	(38.8)	t	38.6	t
C-2	23.7	(27.4)	t	23.7	t	23.0	t	23.4	t	23.9	(27.3)	t	23.7	t
C-3	80.8	(79.0)	d	80.6	d	80.3	d	80.6	d	80.8	(78.8)	d	80.9	d
C-4	37.9	(38.9)	s	37.7	s	37.7	s	37.9	s	37.9	(38.8)	s	37.9	s
C-5	55.4	(55.3)	d	55.3	d	54.5	d	54.9	d	55.2	(55.0)	d	55.4	d
C-6	17.7	(17.8)	t	17.6	t	17.4	t	17.9	t	17.7	(17.7)	t	17.7	t
C-7	34.1	(34.2)	t	33.9	t	31.3	t	31.2	t	34.2	(34.5)	t	34.3	t
C-8	42.5	(42.3)	s	42.4[b]	s	41.2	s	41.7	s	42.3	(42.2)	s	42.4[b]	s
C-9	51.4	(51.4)	d	49.2	d	51.2	d	53.0	d	50.7	(50.6)	d	44.6	d
C-10	37.1	(37.1)	s	36.8	s	36.8	s	36.3	s	36.8	(36.8)	s	36.5	s
C-11	18.9	(18.9)	t	29.1	t	54.5	d	133.2	d	19.7	(19.6)	t	28.0	t
C-12	34.7	(34.7)	t	69.2	d	56.0	d	129.0	d	27.4	(27.3)	t	76.4	d
C-13	93.2	(93.2)	s	94.4	s	88.8	s	89.6	s	91.8	(91.7)	s	90.7	s
C-14	43.3	(43.3)	s	41.9[b]	s	41.3	s	41.9	s	42.3	(42.2)	s	42.2[b]	s
C-15	27.1	(27.0)	t	27.5	t	26.7	t	25.6	t	26.5	(26.6)	t	27.6	t
C-16	22.9	(22.9)	t	22.9	t	22.6	t	22.8	t	20.9	(20.8)	t	21.4	t
C-17	45.8	(45.7)	s	45.4	s	45.0	s	45.1	s	44.1	(44.0)	s	44.8	s
C-18	61.3	(61.2)	d	52.3	d	60.5	d	60.6	d	50.4	(50.4)	d	51.2	d
C-19	38.7	(38.7)	d	38.6	d	37.3	d	38.0	d	37.5	(37.4)	t	39.4	t
C-20	39.9	(39.9)	d	39.6	d	40.1	d	40.3	d	31.5	(31.5)	s	31.6	s
C-21	30.9	(30.8)	t	30.7	t	30.4	t	30.8	t	33.5	(33.5)	t	34.0	t
C-22	31.6	(31.6)	t	31.5	t	31.2	t	31.4	t	31.4	(31.4)	t	28.9	t
C-23	28.0	(28.0)	q	27.9	q	27.6	q	27.9	q	28.0	(28.0)	q	28.0	q
C-24	16.5	(15.3)	q	16.4	q	16.1	q	16.0	q	16.5	(15.2)	q	16.5	q
C-25	16.5	(16.4)	q	16.4	q	16.2	q	16.0	q	16.1	(15.9)	q	16.5	q
C-26	18.5	(18.5)	q	18.4	q	17.1	q	18.9	q	18.3[b]	(18.3)[b]	q	18.7	q
C-27	17.4	(17.4)	q	19.4	q	20.1	q	17.8	q	18.4[b]	(18.1)[b]	q	18.7	q
C-28	180.0	(180.6)	s	179.6	s	178.9	s	179.7	s	180.3	(180.3)	s	180.1	s
C-29	17.7	(17.6)	q	17.1	q	17.1	q	17.6	q	23.7	(23.8)	q	24.0	q
C-30	19.5	(19.5)	q	19.4	q	19.3	q	19.1	q	23.7	(23.8)	q	24.0	q
$^{13}COCH_3$	171.0	—	s	170.8	s	170.6	s	170.9	s	171.0	—	s	171.2	s
$CO^{13}CH_3$	21.3	—	q	21.2	q	21.1	q	21.4	q	21.3	—	q	21.4	q

a) Abbreviations given denote signal patterns observed in the off-resonance experiments and are supported by the PRFT ^{13}C-NMR signals.
b) Values in any column may be reversed, although the assignments given here are preferred.

Several 28,13-olides (γ-lactones) of the ursane and oleanane series have been obtained by biogenetic-type photochemical conversion[7] and chemical reaction with HCl gas in $CHCl_3$[6] as well as by heating with hydrogen peroxide in hot glacial acetic acid.[4] However, no report on a ^{13}C-NMR study of these γ-lactones has appeared in the literature. The availability of a number of the γ-lactones prompted us to undertake a ^{13}C-NMR study. These γ-lactones (**1**—**6**) were prepared from acetyl ursolic acid and acetyl oleanolic acid by the reported methods. The signal assignments were carried out by means of single frequency off-resonance, selective and weak noise decoupling techniques, and a partially relaxed Fourier transformation experiment, as well as by comparison of the spectra with the calculated values derived from the semiempirical equation reported by Beierbeck *et al.*[8] and the reported data for methyl esters of acetyl ursolic acid and acetyl oleanolic acid (**7** and **8**).[9]

Singlet Carbon Signals

In the ^{13}C-NMR spectra of the γ-lactones, the signals due to tertiary carbinyl carbons in the region of δ 88—95 were readily assigned to C-13. Another quaternary carbon was assigned by comparison with the spectrum of **7**,[9] taking into account the lactonization effect[10] and hydroxylation shift.[11]

Doublet Carbon Signals

In the ^{13}C-NMR spectra of **1**, **2** and **4**, the signals at δ 60.5—61.3 were assigned to C-18, because the disappearance of the β-effect of the double bond and the lactonization were expected to cause a large downfield shift. In the spectrum of **3**, the C-18 signal appeared at δ 52.3, since this carbon is located at the γ-position to C12–OH. On irradiation at δ 1.59 in the ^{1}H-NMR spectrum of **4**, the double doublet signal at δ 3.11 was simplified into a clear doublet and the doublet at δ 51.2 in the ^{13}C-NMR spectrum changed into a singlet. Consequently, the signal at δ 51.2 was assigned to C-9. The doublets at δ 54.4 and 56.0 in **4** were assigned to C-11 and C_{-12}, respectively, by means of selective decoupling.

Triplet Carbon Signals

The triplet signals due to carbon on the A-, B-, D- and E-ring of the γ-lactones were characterized by comparison with the corresponding signals of **7** and the calculated values. The triplets at δ 18.9 and 34.7 in **1** were assigned to C-11 and C-12, respectively. These assignments are consistent with the absence of any triplet signal in the range of δ 18—22 and δ 34—37 in the spectra of **3** and **4**.

TABLE II. ^{1}H Chemical Shifts of Methyl Signals and Other Protons (Values at 90 MHz, J in Hz)

	C-23	C-24	C-25	C-26	C-27	C-29	C-30
1	0.85	0.85	0.90	1.18	1.18	1.09	0.93
3	0.86	0.86	0.92	1.18	1.20	1.05	0.91
4	0.87	0.87	0.99	1.06	1.12	1.09	0.93
C-I	0.86	0.86	0.93	1.05	1.16	0.99	0.90

	C_3-H	C_{11}-H	C_{12}-H
3	4.5 (dd, J=6.3, 9.0)		4.00(m) 4.32 (t, J=7.9, in C_5D_5N)
4	4.54 (t, J=7.6)	3.11 (dd, J=2, 4)	2.94 (d, J=4.0)
C-I	4.50 (dd, J=7.2, 9.9)	5.53 (dd, J=3.5 and 10.3)	5.95 (dd, J=0.9, 10.3)

Quartet Carbon Signals

The methyl signals of the γ-lactones were too complicated to be assigned by comparison with that of **7**. The assignments of the signals due to methyls on the ring skeleton were accomplished by means of the selective decoupling technique. The methyl proton signals in the γ-lactones are shown in Table II. The chemical shifts given in Table II were assigned by comparison with those of acetyl ursolic acid and the γ-lactones of oleanane,[5] and confirmed by selective decoupling experiments. Two methyl proton resonances at δ 1.18 in the ^{1}H-NMR spectrum of **1** in $CDCl_3$ were separated into one methyl proton signal at δ 1.18 and another at δ 1.25 in C_5D_5N. The latter should be assigned to C-26 from a consideration of the 1,3-diaxial proximity of the protons to the lactone ring.[12] On irradiation at δ 1.18 and 1.25, the quartet carbon signals at δ 17.1 and 18.5 each changed into singlets. Therfore the former was assigned to C-27 and the latter to C-26. Thus, the ^{13}C-NMR spectra of **1**—**4** were assigned unambigously. The full assignment of the ^{13}C-NMR spectrum of C-I was accomplished by consideration of the reported data for saikogenins,[13] which have the same partial structure, and using the olefin parameter.[8] The assignments of the ^{13}C-NMR spectra of the oleanane series, 3β-acetoxyolean-28,13-olide (**5**), 3β-hydroxyolean-28,13-olide (**6**) and C-II were made by the same techniques as mentioned above for the ursane series.

Inspection of Table I reveals interesting differences in the chemical shifts of **3** and C-II. Tori *et al.*[13] have undertaken a comparative ^{13}C-NMR study of various compounds, including C16α- and C16β-hydroxyoleanane analogs, and reported that structural change of the C-ring from the chair form to a twist chair occurs on α-hydroxylation. From the shift values observed at the α-, β-, γ- and δ-carbons, affected by the 1,3-diaxial relationship between C12–OH and the C-27 methyl group, it can be assumed that the C-ring in C-II adopts a twist chair conformation. The downfield shift (2.0 ppm) at C-27 in **3** is larger than that of C-II (0.3 ppm). This might be attributable to the proximity (δ-effect) of C-19, caused by the interaction between C12–OH and C-29 methyl. The upfield shifts (0.1 and 9.0 ppm) at C-19 in the δ-position and C-18 in the γ-position to C12–OH can be considered as a result of the hydroxyl group being twisted outside the molecule. Furthermore, the chemical shift of C-12 of **3** was appreciably smaller than that of C-II. From the above results and the coupling constant (7.9 Hz, in C_5D_5N) of C12–H in **3**, we consider that the C-ring in **3** might be a boat form rather than a twist chair.

The other constituents, C-III through C-IX were identified as 3β-acetoxy-28-hydroxyurs-12-ene, 3β,28-dihydroxyurs-12-ene, 3β-acetoxyurs-12-en-28-al, taraxeryl acetate, taraxerol, taraxerone and β-sitosterone, respectively, on the basis of spectroscopic evidence and chemical correlations.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. The IR absorption spectra were determined on Shimadzu IR-400 and IR-430 spectrometers. The ^{1}H-NMR and ^{13}C-NMR spectra were taken on a JEOL JNM-FX 90 Q machine (89.55 and 22.5 MHz) in $CDCl_3$ and C_5D_5N, and chemical shifts are given in the δ (ppm) scale with tetramethylsilane as the internal standard (s, singlet; d, doublet; t, triplet; m, multiplet). MS were obtained on a JEOL JMS-01SG mass spectrometer. Thin layer chromatography was done on glass plates coated with Silica gel G (Merck)using benzene: EtOAc (9:1).

Isolation——The MeOH extract of the bark of *Pieris japonica* D. Don was chromatographed on silica gel with hexane–benzene mixtures (stepwise increases benzene from of 0 to 100%), and then subjected to preparative TLC on a silica gel plate (Merck, G, 0.50 mm) with benzene: EtOAc (4: 1) to give eight triterpenoids (C-I—VIII) and a sterol (IX), in addition to the previously reported compounds.

3β-Acetoxyurs-11-en-28,13-olide (C-I)——The fraction of *Rf* 0.79 gave 15 mg of colorless needles (C-I), mp 230—232°C. *Anal.* Calcd for $C_{32}H_{48}O_4$: C, 77.37; H, 9.74. Found: C, 77.18; H, 9.59. High resolution MS Calcd for $C_{32}H_{48}O_4$: 496.3768. Found: 496.3554. MS *m/z*: 496 (M^+), 468 (M^+-28), 452 (M^+-COO, base peak), 436 (M^+-HOAc), 332, 300, 249, 215, 189. IR ν_{max}^{KBr} cm^{-1}: 1756 (γ-lactone), 1726, 1242 (ester),

1630, 903, 868.

3β-Acetoxyurs-28,13-olide (1) and 3β-Hydroxyurs-28,13-olide (2)——Hydrochloric acid gas was passed through a $CHCl_3$ solution of acetyl ursolic acid for 30 min to afford needles (1), and hydrolysis of **1** with methanolic potassium hydroxide gave **2**.

3β-Acetoxy-12α-hydroxyurs-28,13-olide (3) and 3β-Acetoxy-11α,12α-epoxyurs-28,13-olide (4)——Acetyl ursolic acid was treated with hydrogen peroxide in hot glacial acetic acid according to Majumder *et al.*[3] The reaction mixture was chromatographed on silica gel to afford **3** and **4** together with 3β-acetoxy-12-oxours-28-oic acid. The physical data were virtually identical with the reported values, except for the coupling constant of C12–H in **4**. The broad signal at δ 3.95 of **4** (in $CDCl_3$) moved to δ 4.32 (1H, t, J=7.9 Hz in C_5D_5N).

3β-Acetoxyolean-28,13-olide (5) and 3β-Hydroxyolean-28,13-olide (6)——Compounds **5** and **6** were prepared from acetyl oleanolic acid by Barton's method.

3β-Acetoxy-12α-hydroxyolean-28,13-olide (C-II)——The fraction of *Rf* 0.32 gave colorless needles (C-II, yield 20 mg) of mp 301—303°C from MeOH. *Anal.* Calcd for $C_{32}H_{50}O_5$: C, 74.67; H, 9.79. Found: C, 74.87; H, 9.60. IR ν_{max}^{KBr} cm^{-1}: 3500, 3450 (OH), 1770 (γ-lactone), 1750 (shoulder), 1735, 1715, 1250 (ester), 1026. Chromic acid oxidation of C-II in pyridine gave a ketone as needles, mp 286—289°C. IR ν_{max}^{KBr} cm^{-1}: 1778, 1769, 1725, 1240. ^{1}H-NMR: 0.87—1.32 ($CH_3\times7$), 2.02 (3H, s), 4.26 (1H, t-like). C-II was identical (TLC, IR, ^{1}H-NMR and mixed mp) with an authentic sample derived from acetyl oleanolic acid by Barton's method.

3β-Acetoxy-28-hydroxyurs-12-ene (C-III), 3β,28-Dihydroxyurs-12-ene (C-IV) and 3β-Acetoxyurs-12-en-28-al (C-V)——The fraction of *Rf* 0.58 gave colorless needles (C-III), mp 264—267°C. *Anal.* Calcd for $C_{32}H_{52}O_3$: C, 79.28; H, 10.91. Found: C, 79.52; H, 10.78. IR ν_{max}^{KBr} cm^{-1}: 3630 (OH), 1722, 1255 (ester). ^{1}H-NMR: 0.81—1.10 ($CH_3\times7$), 2.03 (3H, s, $COCH_3$), 3.17, 3.53 (2H, ABq, J=11.0 Hz), 4.49 (1H, dd, J=6.2, 9.9 Hz), 5.13 (1H, t, J=3.4 Hz). MS: 484 (M^+), 466 (M^+-H_2O), 453 (M^+-CH_2OH), 424 (M^+-HOAc), 406 ($M^+-H_2O-HOAc$), 393 ($M^+-HOAc-CH_2OH$), 286, 269, 255, 249(a), 234(b), 216 (b$-H_2O$), 203 (100%, b$-CH_2OH$), 189 (a$-$HOAc). Alkaline hydrolysis of C-III gave a diol, which was identical with C-V, colorless needles, mp 235—236°C. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH). ^{1}H-NMR: 0.78—1.15 ($CH_3\times7$), 2.9—3.7 (3H), 5.09 (1H, br s). C-IV was identical with an authentic sample derived from acetyl ursolic acid by $LiAlH_4$ reduction, in TLC, IR and ^{1}H-NMR comparisons and mixed mp determination. The fraction of *Rf* 0.86 gave colorless needles (C-V), mp 209—210°C. *Anal.* Calcd for $C_{32}H_{50}O_3$: C, 79.62; H, 10.44. Found: C, 79.66, 79.58; H, 10.95, 10.78. IR ν_{max}^{KBr} cm^{-1}: 1752, 1712, 1242 (ester and CHO). ^{1}H-NMR: 0.77—1.08 ($CH_3\times7$), 2.04 (3H, s, $COCH_3$), 4.95 (1H, dd, J=7 and 9 Hz, assignable to C3α-H), 5.31 (1H, t, J=3.3 Hz), 9.32 (1H, s, CHO). MS: 482 (M^+), 422 (M^+-HOAc), 249(c), 232(d), 203 (100%, d$-$CHO), 189 (c$-$HOAc). Alkaline hydrolysis of C-V with potassium hydroxide in MeOH afforded an alcohol, mp 235—237°C. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1710, 1705 (CHO). From these results, C-V was presumed to be 3β-acetoxyurs-12-en-28-al. This conclusion was confirmed by the conversion of C-V to acetyl ursolic acid by chromic acid oxidation in C_5D_5N solution at room temperature.

Taraxeryl Acetate (C-VI), Taraxerol (C-VII) and Taraxerone (C-VIII)——The fractions of *Rf* 0.88, 0.52 and 0.85 gave C-VI (mp 293—296°C), C-VII (mp 256—257°C) and C-VIII (mp 236—238°C), respectively, as colorless needles. Alkaline hydrolysis of C-VI with methanolic potassium hydroxide afforded C-VII, and oxidation of C-VII with chromic acid afforded C-VIII. C-VII was identical with an authentic sample of taraxerol obtained from the leaves of "asebi."[14]

β-Sitosterone (C-IX)——The fraction of *Rf* 0.56 gave C-IX as colorless needles, mp 94°C. The IR, UV, MS and ^{1}H-NMR spectral data of C-IX were in good agreement with those of β-sitosterone.[15]

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