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STRUCTURE OF LINIFOLIOSIDE, AN ISOPIMARANE RHAMNOGLUCOSIDE FROM *LEUCAS LINIFOLIA*

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Key Word Index—*Leucas linifolia*; Labiatae; linifoliol; linifolioside; diterpene; diterpene glycoside.

Abstract—The structure of a new isopimarane rhamnoglucoside isolated from *Leucas linifolia*, linifolioside, has been defined as isopimara-8(14),15-diene-7-keto-3-*O*-α-L-rhamnopyranosyl (1 → 2)-β-D-glucopyranoside based on its spectral properties and some chemical transformations.

INTRODUCTION

Leucas linifolia Spreng (syn. *L. lavandulaefolia* Rees) is a herbaceous annual weed which grows abundantly in fields, pastures and waste lands throughout India. It has a strong flavour and is reputed for its use as sedative, vermifuge, stomachic and dermatosis [1]. However, no chemical work appears to have been done on this plant. This paper is concerned with the isolation and structure elucidation of a new diterpene rhamnoglucoside.

RESULTS AND DISCUSSION

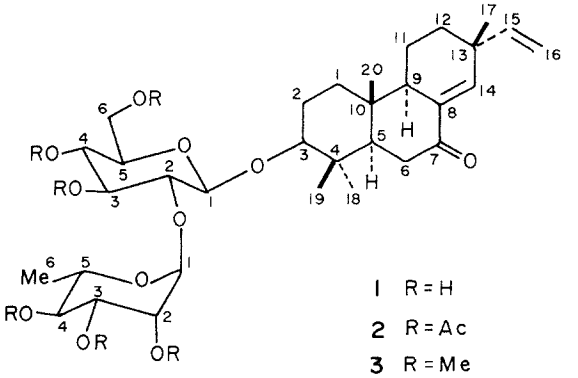
The ethanolic extract of the whole plant on repeated chromatographic purification yielded a glycoside designated as linifolioside (**1**). That the glycoside (**1**) contained D-glucose and L-rhamnose was established by acid hydrolysis of **1** and identification of the monosaccharides by paper chromatography and GLC. The molecular weight of **1** was successfully determined by fast atom bombardment mass spectrometry (FABMS) [2–4]. Other ions of interest are shown in Table 1. The copper adduct of both the molecular ion and the dimer of the molecular ion was presumably derived from the MS probe tip. The assignment of the copper adduct to the higher masses measured was confirmed by the absence of these ions in the negative FAB spectrum, where metal ion adducts would not be expected to occur. The negative FAB spectrum showed only three ions at *m/z* 609, 463 and 301 assigned to $[M-H]^-$, $[609-\text{rhamnosyl}+H]^-$ and $[463-\text{glucosyl}+H]^-$ respectively. The sequential loss of rhamnose and then glucose together with the absence of an initial loss of a glucose indicated the presence of a disaccharide chain attached to the aglycone with rhamnose being the terminal sugar. Treatment of **1** with acetic anhydride and pyridine afforded an acetate (**2**) whose ^{1}H NMR spectrum showed five singlets corresponding to six acetoxy methyl protons. The linifolioside permethylate (**3**) prepared by treatment of **1** with sodium hydride–methyl iodide in hexamethylphosphoramide on hydrolysis liberated 2,3,4-tri-*O*-methyl-L-rhamnose and 3,4,6-tri-*O*-methyl-D-glucose. These results demonstrated that the terminal rhamnose was linked to the glucose unit by a (1 → 2) linkage. The ^{1}H NMR spectrum of **3** exhibited signals at δ4.34 (1H, *d*, $J = 7$ Hz) and 5.28 (1H, *br s*) assignable to two anomeric protons, indicating a β-orientation ($^4C_1$ conformation for the glucose) and one α-linkage ($^1C_4$ conformation for the rhamnose). The ^{13}C NMR spectrum of **1** (Table 2) also supported the linkages of the sugar units shown.

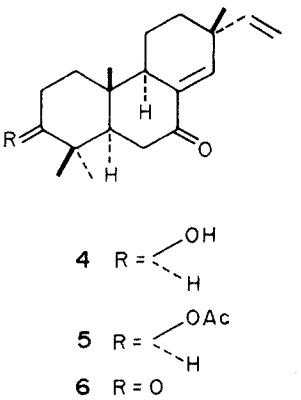
The aglycone, designated linifoliol (**4**), $C_{20}H_{30}O_2$ (M^+ 302), was obtained as a colourless crystalline compound, mp 150–152°, $[\alpha]_D$ −40° ($CHCl_3$). Its IR spectrum was characterized by a carbonyl absorption at 1670 cm^{-1} suggesting that one of the oxygens in **4** was present as an α,β-unsaturated ketone moiety which was cisoid because of the strong intensity of the 1615 cm^{-1} band [5]. This was confirmed by the UV spectrum which exhibited absorption at 247 nm (log ε 3.4). That the other oxygen atom was present as a secondary hydroxyl group was demonstrated by preparation of the acetate **5** and the ketone **6**. Its ^{1}H NMR spectrum displayed four quaternary methyl singlets at δ0.84, 0.88, 0.97 and 1.10, a doublet at δ6.74 ($J = 2$ Hz) assignable to a β-proton of an α,β-unsaturated ketone, a multiplet at δ2.36–2.56 ascribable to a ketomethylene group and a very characteristic splitting pattern at δ5.02 (2H, *m*) and a four line system at 5.82 (1H) typical of vinyl protons of C-13 of a vinylidene grouping in a pimarane type skeleton [6, 7]. The other discernible signal in the spectrum was that of an axial carbinyl proton (δ3.32, $W_{1/2} = 12$ Hz) geminal to an equatorial hydroxyl group. The ^{13}C NMR data disclosed the presence of four quaternary methyls, five methylenes, two methines, one >CHOH, three quaternary carbons, a carbonyl, a trisubstituted double bond (>C=CH–) and a monosubstituted double bond (–CH=CH_2). Comparison of the olefinic carbon shifts of **4** with those of pimaradiene, sandaracopimaradiene and isopimaradiene [8], taking into consideration the chemical shift changes expected on introduction of a keto group into cyclic hydrocarbon skeletons [9, 10], revealed the compound to be of the sandaracopimaradiene type. The δ values of the rings B and C carbons of **4** could thus be assigned by the placement of the ketonic function at C-7 which also limited the secondary hydroxyl group to ring A. The doublet at δ6.74 ($J = 2$ Hz) was assigned to H-14 and the small coupling constant was due, probably, to an allylic coupling with H-9. Moreover, comparison of the A-ring

Table 1. Characteristic mass spectral ions in the positive FAB spectrum of linifolioside (**1**) and EIMS ions (experimental high resolution values) of linifoliol (**4**)

FABMS of **1**			EIMS of **4**			
m/z	Rel. int.	Assignment	Accurate mass	Empirical formula	Rel. int.	Assignment
1285	3		302.2244	$C_{20}H_{30}O_2$	100.0	$[M]^+$
1284	3		287.2009	$C_{19}H_{27}O_2$	16.9	$[M-Me]^+$
1283	3	$[M+M+Cu]^+$	284.2117	$C_{20}H_{28}O$	12.4	$[M-H_2O]^+$
1223	2		269.1910	$C_{19}H_{25}O$	15.0	$[M-H_2O-Me]^+$
1222	3		181.1210	$C_{11}H_{17}O_2$	10.6	a
1221	3	$[M+M]^+$	163.1119	$C_{11}H_{15}O$	41.7	b
675	63		162.1043	$C_{11}H_{14}O$	70.0	c
674	63		149.0962	$C_{10}H_{13}O$	65.3	d
673	94	$[M+Cu]^+$	148.0885	$C_{10}H_{12}O$	66.6	e
655	49		147.0804	$C_{10}H_{11}O$	26.9	f
625	38		139.1113	$C_9H_{15}O$	14.6	g
613	16		136.1242	$C_{10}H_{16}$	11.3	h
612	21		133.0651	C_9H_9O	80.3	i
611	67	$[M+H]^+$	122.1073	C_9H_{14}	34.0	—
610	13		121.1016	C_9H_{13}	97.0	j
609	12		120.0937	C_9H_{12}	63.9	—
479	15		106.0770	C_8H_{10}	28.1	—
465	42	$[(M+H)+H-rh]^+$	105.0710	C_8H_9	73.5	—
303	78	$[(M+H)+H-rh-g]^+$	93.0702	C_7H_9	46.4	—
285	100	$[303-H_2O]^+$	91.0547	C_7H_7	54.8	—

*See Scheme 1; rh, rhamnosyl; rh-g, rhamnoglucosyl.





carbon shifts of **4** with those of the 3β (equatorial) hydroxylabdane-type diterpenes [11] indicated the location of the hydroxyl group of **4** at C-3 possessing β (equatorial) configuration. The expected shift perturbations [12] at C-4, C-18 and C-19 due to the 3β-hydroxyl were noticeable when compared with those of analogous carbon shifts of sandaracopimaradiene [8]. Thus all the carbon shifts of **4** (Table 2) were found to be compatible with the structure shown. Compelling evidence for the carbon skeleton in **4** was obtained by conversion of the diketone **6** to a dienic hydrocarbon by the Huang–Minlon modification [13] of the Wolff–Kishner reduction. The product was found to be identical [14] (mp, $[\alpha]_D$) with sandaracopimaradiene. The electron impact mass spectrum of **4** showed a fragment ion characteristic of such a skeleton [15] and the significant mass fragment ions could be rationalized (Scheme 1) on the basis of their high resolution values (Table 1).

The ^{13}C NMR spectrum of linifolioside (**1**) was recorded in pyridine-d_5. The ^{13}C chemical shifts of methyl α-D-glucopyranoside and methyl-α-L-rhamnopyranoside are available [16] and the ^{13}C signals of linifoliol (**4**) were assigned as already described. Assignments of the signals of **1** (Table 2) were made by comparison with those of **4** and sugar moieties using glycosylation shifts [16, 17].

The CD spectrum of **4** showed a negative Cotton effect at 246 nm of $\Delta\varepsilon$ 5.1 which was in agreement with the corresponding transition for a known 5α,8(14)-ene-7-one

Table 2. ^{13}C chemical shifts $\delta_C(\pm 0.1)$ of linifoliol (**4**) ($CDCl_3$) and linifolioside (**1**) (pyridine-d_5)

C	4	1	C	4	1
1	36.8	37.0	17	25.8	25.8
2	27.3	25.8	18	27.4	27.2
3	78.4	88.3	19	14.6	15.8
4	38.8[a]	39.2[a]	20	13.8	13.6
5	50.6	50.6	g-1		105.1
6	34.0	34.1	g-2		79.5
7	200.2	199.4	g-3		77.8[a]
8	134.7	135.6	g-4		71.9[b]
9	49.5	50.1	g-5		77.6[a]
10	38.6[a]	38.7[a]	g-6		61.2
11	19.1	18.5	r-1		101.4
12	35.8	35.4	r-2		72.2[b]
13	38.6[a]	38.7[a]	r-3		72.2[b]
14	144.5	143.3	r-4		73.8
15	146.2	146.8	r-5		69.4
16	111.8	111.7	r-6		18.5

g, Glucose; r, rhamnose; [a,b]may be interchanged in each vertical column.

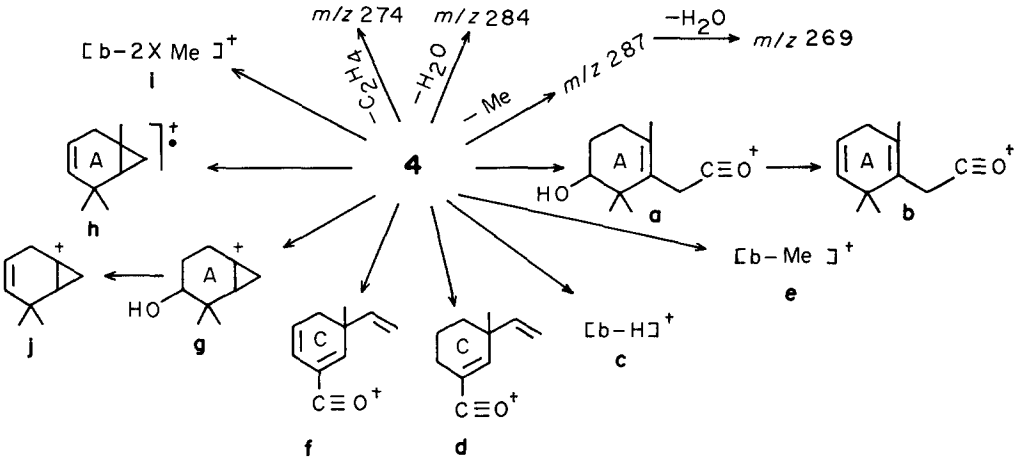
steroid [18]. This indicated that the absolute stereochemistry at C-5, C-9 and C-10 was as shown. Determination of the absolute configuration of a secondary hydroxyl group in a chiral secondary alcohol using glycosylation shifts in ^{13}C NMR had been reported [16, 17]. Comparison of the ^{13}C values of **1** and **4** (Table 2) showed that a signal due to C-3 of **1** was deshielded by +9.9 ppm and signals attributable to C-2 and C-4 were displaced by −1.5 and +0.5 respectively. Moreover, C-1′ (anomeric carbon) of glucose was remarkably deshielded and in spite of the shielding effect of α-L-rhamnose linked at the 2-position it resonated at δ105.1. These displacements were indicative of the β-D-glucose being linked to C-3 equatorial hydroxyl group of **4** and that the chirality of this hydroxyl group was *S* [17]. Thus the absolute configuration of linifoliol was determined to be as shown in **4** and the structure of linifolioside was established as isopimara-8(14),15-dien-7-keto-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside (**1**).

It is noteworthy that although steroid and triterpenoid glycosides are of common occurrence in nature [19, 20] the diterpenoid glycosides are comparatively rare. It appears that linifolioside (**1**) is the first reported rhamnoglucoside of a genin containing either a pimarane or an isopimarane skeleton. Moreover, its activity profile is of interest in view of its structural similarity with some diterpenoid phytoalexins [21].

EXPERIMENTAL

The plant material was collected from waste lands of Garia near Calcutta and was identified by Mr. U. Bhattacharya, Indian Botanic Garden, Howrah. A voucher specimen has been deposited at the herbarium of IICB. Mps: uncorr.; ^1H NMR: 99.6 MHz, $CDCl_3$ or C_5D_5N; ^{13}C NMR: 25.05 MHz, $CDCl_3$ or C_5D_5N with TMS as internal standard. Low and high resolution MS: 70 eV; FABMS (Kratos MS 80 RFA mass spectrometer): potential 5–8 kV applied to the xenon gun with glycerol as matrix; GLC: (i) ECNSS-M, 3% on Gas Chrom Q at 190° for alditol acetates and (ii) OV-225 on Gas Chrome Q at 195° for partially methylated alditol acetates; TLC: silica gel G (B.D.H.) using the solvent systems: (A) C_6H_6–$CHCl_3$–EtOAc (1:2:2); (B) $CHCl_3$–MeOH (4:1). TLC plates were developed by spraying with Liebermann–Burchard reagent; PC: Whatman paper No. 1 using the solvent system (C) *n*-BuOH–C_5H_5N–H_2O (6:4:3). A satd soln of aniline oxalate in H_2O was used as staining agent.

Isolation of linifolioside (**1**). The air-dried and powdered whole plant (1.5 kg) was successively extracted with petrol, $CHCl_3$ and 90% EtOH. The ethanolic extract, on removal of the solvent under red. pres., yielded a viscous dark brown mass (20 g). This extract was chromatographed on silica gel (300 g) with petrol, petrol–$CHCl_3$ (1:1), $CHCl_3$–MeOH (19:1, 9:1, and 4:1) as successive eluents. The $CHCl_3$–MeOH (4:1) eluate (0.5 g) which showed one spot on TLC was subjected to rechromatography to yield a colourless solid (0.28 g). This was crystallized (MeOH) to give colourless needles of **1**, mp 242–244° (dec), $[\alpha]_D$ −70.5° (*c* 1.2; MeOH); IR ν_{max}^{nujol} cm^{-1}: 3300, 1675, 1610, 1265, 925, 815; ^1H NMR (C_5D_5N): δ0.80 (3H, *s*, 20-Me), 0.84 (3H, *s*, 18-Me), 0.92 (3H, *s*, 19-Me), 1.04 (3H, *s*, 17-Me), 1.06 (3H, *d*, *J* = 7 Hz, rhamnose-Me), 4.36 (1H, *d*, *J* = 7 Hz, H-1 of glucose unit), 4.96 (2H, *m*, 16-H_2), 5.24 (1H, *br s*, H-1 of rhamnose unit), 5.80 (1H, *dd*,



Scheme 1.

J = 10 and 17 Hz, H-15) and 6.44 (1H, *br s*, H-15); (Found: C, 62.89; H, 8.28. $C_{32}H_{50}O_{11}$ requires: C, 62.91; H, 8.25%).

Acetate (**2**) of **1**. Acetylation of **1** (10 mg) with C_5H_5N (0.6 ml) Ac_2O (1 ml) on a water bath for 3 hr and usual work up afforded colourless leaflets of **2** (6 mg), mp 190–192° (dec); IR ν_{max}^{nujol} cm^{-1}: 1730, 1670, 1610, 1240; ^1H NMR ($CDCl_3$): δ0.84 (3H, *s*, 20-Me), 0.92 (3H, *s*, 18-Me), 1.03 (3H, *s*, 19-Me), 1.09 (3H, *s*, 17-Me), 1.16 (3H, *d*, J = 7 Hz, rhamnose-Me), 1.94 (3H, *s*, OAc), 1.96 (6H, *s*, 2 × OAc), 1.98 (3H, *s*, OAc), 2.02 (3H, *s*, OAc), 2.04 (3H, *s*, OAc), 4.20 (2H, *m*, CH_2OAc), 4.52 (1H, *d*, J = 7 Hz, H-1 of glucose unit), 4.80–5.36 (8H, 16-H_2, H-1 of rhamnose unit and 5 × CHOAc), 5.76 (1H, *dd*, J = 10 and 17 Hz, H-15) and 6.72 (1H, *d*, J = 2 Hz, H-14); (Found: C, 61.20; H, 7.26. $C_{44}H_{62}O_{17}$ requires: C, 61.23; H, 7.24%).

Hydrolysis of linifolioside (**1**) *to yield linifoliol* (**4**). Linifolioside (**1**) (100 mg) was boiled with 2 M HCl–MeOH for 4 hr and worked up in the usual way; the sapogenol, linifoliol (**4**) was crystallized from MeOH to give colourless needles (30 mg), mp 150–152°, $[\alpha]_D$ −40° (*c* 0.61; $CHCl_3$); IR ν_{max}^{nujol} cm^{-1}: 3400, 1670, 1615; UV (MeOH) 247 nm (log ε 3.4); ^1H NMR ($CDCl_3$): δ0.84 (3H, *s*, 20-Me), 0.88 (3H, *s*, 19-Me), 0.97 (3H, *s*, 18-Me), 1.10 (3H, *s*, 17-Me), 2.36–2.52 (2H, *m*, 6-H_2), 3.32 (1H, *m*, $W_{1/2}$ = 12 Hz, H-3), 5.02 (2H, *m*, 16-H_2), 5.82 (1H, *dd*, J = 10 and 17 Hz, H-15) and 6.74 (1H, *d*, J = 2 Hz, H-14); CD(MeOH) $[\theta]_{246}$ −16912 ($\Delta\varepsilon$ 5.1); (Found: C, 79.40; H, 9.93. $C_{20}H_{30}O_2$ requires: C, 79.42; H, 10.00%).

The filtrate from the hydrolysate was neutralized with Ag_2CO_3 and filtered. The filtrate was concd under red. pres. and the residue was tested for the presence of D-glucose and L-rhamnose by PC using solvent system (C), by comparison with authentic samples. The presence of these monosaccharides was also confirmed by GLC of the carbohydrate mixture after preparation of their alditol acetates using column (i).

Permethylation of **1** *and hydrolysis*. Linifolioside (**1**, 25 mg) in hexamethylphosphoramide (5 ml) was treated with NaH (200 mg) and MeI (5 ml) at room temp. for 3 hr. The reaction mixture was extracted with Et_2O, the extract evaporated and the residue chromatographed on silica gel eluting with petrol–EtOAc (2 : 1) to give permethylate **3** as a white powder, mp 138–140° (no hydroxyl absorption in the IR spectrum); ^1H NMR ($CDCl_3$): δ0.84 (3H, *s*, Me), 0.92 (3H, *s*, Me), 1.10 (3H, *s*, Me), 1.17 (3H, *d*, J = 6 Hz, Me) 1.22 (3H, *s*, Me), 3.40 (3H, *s*, OMe), 3.44 (3H, *s*, OMe), 3.46 (3H, *s*, OMe), 3.48 (6H, *s*, 2 × OMe), 3.56 (3H, *s*, OMe), 4.34 (1H, *d*, J = 7 Hz, H-1 of glucose unit), 4.96 (2H, *m*, 16-H_2), 5.28 (1H, *s* (*br*), H-1 of rhamnose unit), 5.80 (1H, *dd*, J = 10 and 17 Hz, H-15) and 6.64 (1H, *s* (*br*), H-14).

The permethylate **3** (15 mg) was hydrolysed by refluxing with 2 M HCl in MeOH (6 ml) for 3 hr. The reaction mixture was cooled, evaporated to dryness *in vacuo*, diluted with H_2O and filtered. The filtrate was neutralized with Ag_2CO_3 and filtered. The filtrate was reduced with $NaBH_4$ and worked up in the usual manner. The residue was acetylated with Ac_2O–C_5H_5N (1 : 1) at water bath temp. for 1 hr, purified by chromatography over silica gel and subjected to GLC analysis using column (ii). The peaks corresponding to alditol acetates of 2,3,4-tri-*O*-methyl-α-L-rhamnose and 3,4,6-tri-*O*-methyl-β-D-glucose, were identified by comparison of their R_t values with those reported in lit. [22].

Jones oxidation of **4** *to yield* **6**. To a soln of **4** (15 mg) in Me_2CO (10 ml) was added Jones reagent (2 drops) and the suspension was stirred at room temp. for 30 min. Evaporation of the filtered soln gave crude **6** which was purified by chromatography on silica gel eluting with petrol–$CHCl_3$ (7 : 3) to yield pure **6** (10 mg), mp 130–132°, $[\alpha]_D$ −60° (*c* 0.56; $CHCl_3$); IR ν_{max}^{nujol} cm^{-1}: 1705, 1670; UV λ_{max}^{MeOH} nm: 247 (log ε 3.1); ^1H NMR ($CDCl_3$): δ1.08 (3H, *s*, 20-Me), 1.12 (3H, *s*, 17-Me), 1.14 (6H, *s*, 18-Me, 19-Me), 2.30–2.92 (4H, *m*, 2-H_2, 6-H_2), 5.06 (2H, *m*, 16-H); 5.86 (1H, *dd*, J = 10 and 17 Hz, 15-H) and 6.86 (1H, *s* (*br*), 14-H); MS *m/z* 300 $[M]^+$, 285 $[M-Me]^+$, 179, 147 and 137 (Found: C, 79.92; H, 9.41. $C_{20}H_{28}O_2$ requires: C, 79.95; H, 9.39%).

Acetylation of **4** *to produce* **5**. Compound **4** (10 mg) furnished the acetate **5** with Ac_2O (0.5 ml) and C_5H_5N (0.5 ml) at 100° for 3 hr. It was crystallized from MeOH to yield **5** (9 mg), mp 159–161°; IR ν_{max}^{nujol} cm^{-1}: 1730, 1670 and 1240; MS *m/z* 344 $[M]^+$, 329 $[M-Me]^+$, 284 $[M-AcOH]^+$, 269 $[M-AcOH-Me]^+$, 223, 181, 163, 149, 147 and 121 (Found: C, 76.68; H, 9.35. $C_{22}H_{32}O_3$ requires: C, 76.70; H, 9.36%).

Huang–Minlon reduction of **6** *to yield* **8**. The diketo compound **6** (30 mg), KOH (50 mg), diethylene glycol (3 ml) and 85% hydrazine hydrate (1 ml) were refluxed for 1.5 hr. The H_2O was then drained from the condenser and the temp. was allowed to rise to 195°. Refluxing was continued for 5 hr more. The product was purified by chromatography followed by crystallization to yield sandaracopimaradiene (14 mg), mp 39–40°, $[\alpha]_D$ −13° (*c* 2.4; $CHCl_3$) (lit. [14] mp 39–39.5°, $[\alpha]_D$ −12.4°, $CHCl_3$).

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