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Reference Data

Applications of Two-Dimensional NMR in Spectral Assignments of Some Friedelanes and Secofriendelanes

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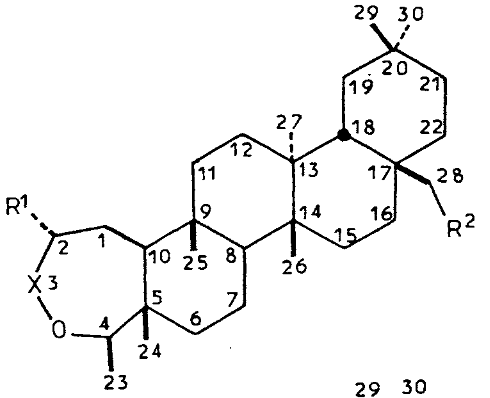
Carbon-13 spectral assignments of three friedelanes and nineteen secofriedelanes have been made from mutual correlations, 2D X–H correlation analyses and comparison with the carbon shifts of friedelin, which were firmly established by an INADEQUATE experiment that required reassignment of some of its resonances. Specific methyl and methine proton resonance assignments for some friedelanes, established from X–H correlation studies, are also reported.

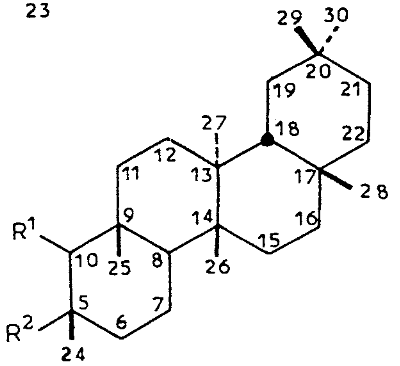
KEY WORDS Friedelanes secofriedelanes ^{13}C NMR and ^{1}H NMR spectral assignments

INTRODUCTION

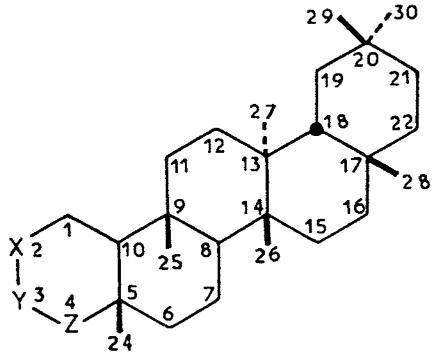
In recent years, ^{13}C NMR spectral assignments on friedelanes have been of interest.[1–12] In this context we have studied the ^{13}C NMR spectra of some secofriedelanes[13] (**1–19**) and friedelanes (**20–22**). Two-dimensional X–H correlation (^{13}C–^{1}H)



1 $R^1 = OH$, $R^2 = H$, $X = CO$
2 $R^1 = H$, $R^2 = OH$, $X = CO$
3 $R^1 = H$, $R^2 = OAc$, $X = CO$
4 $R^1 = R^2 = H$, $X = CH_2$
33 $R^1 = R^2 = H$, $X = CO$
34 $R^1 = OAc$, $R^2 = H$, $X = CO$



5 $R^1 = -\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2OH$, $R^2 = -\overset{4}{C}HOH\overset{23}{C}H_3$
6 $R^1 = -CH_2CH_2CH_2OAc$, $R^2 = -CHOAcCH_3$
7 $R^1 = -CH_2CHOHCH_2OH$, $R^2 = -CHOHCH_3$
8 $R^1 = -CH_2CHOAcCH_2OAc$, $R^2 = -CHOAcCH_3$
9 $R^1 = -\overset{1}{C}H_2\overset{2}{C}H_2OAc$, $R^2 = -\overset{4}{C}HOAc\overset{23}{C}H_3$
10 $R^1 = -CH_2CH_2CH_2OH$, $R^2 = -COCH_3$
11 $R^1 = -CH_2CH_2CH_2OAc$, $R^2 = -COCH_3$
12 $R^1 = -CH_2CH_2COOH$, $R^2 = -COCH_3$
13 $R^1 = -CH_2CH_2COOMe$, $R^2 = -COCH_3$
14 $R^1 = -\overset{1}{C}H_2\overset{2}{C}OOH$, $R^2 = -\overset{4}{C}H(\overset{23}{C}H_3)\text{-}O\text{-}\overset{3}{C}O\text{-}H$
15 $R^1 = -CH_2COOMe$, $R^2 = -CH(CH_3)\text{-}O\text{-}CO\text{-}H$
16 $R^1 = -CH_2CH_2COOMe$, $R^2 = -CHOHCH_3$
17 $R^1 = -CH_2CH_2COOMe$, $R^2 = -CHOAcCH_3$



18 X = CO, Y = O, Z = CH-$\overset{23}{\mathrm{C}}\mathrm{H}_3$(β)

19 X = CH$_2$, Y = CO, Z = O

24 X = CH$_2$, Y = CO, Z = CH-CH$_3$(β)

25 X = CH-OAc (α), Y = CO, Z = CH-CH$_3$(β)

26 X = CH-OH (β), Y = CO, Z = CH-CH$_3$(β)

27 X = CH-OAc(β), Y = CO, Z = CH-CH$_3$(β)

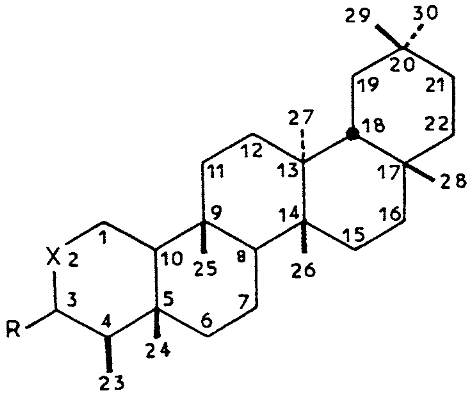
28 X = CH$_2$, Y = CH-OAc(β), Z = CH-CH$_3$(β)

29 X = CH-OH(α), Y = CH-OH(α), Z = CH-CH$_3$(β)

30 X = CH-OAc(β), Y = CH-OAc(β), Z = CH-CH$_3$(β)

31 X = CH-OAc(β), Y = CH-OAc(α), Z = CH-CH$_3$(β)

32 X = CH-OAc(α), Y = CH-OAc(β), Z = CH-CH$_3$(β)



20 R = H, X = CH$_2$, 3,4-epoxy (α)

21 R = H, X = CH$_2$, 3,4-epoxy (β)

22 R = OAc, X = -CH-OAc (α), 3,4-dehydro-

23 R = OAc, X = CO', 3,4-dehydro-

experiments[14] were carried out on friedelin (**24**) and other friedelanes (**25**–**32**) to make specific shift assignments for the methyl and methine protons. An INADEQUATE experiment[15] on **24** further established the connectivity between its various carbon signals.

RESULTS AND DISCUSSION

The carbon–carbon connectivity experiment on **24** indicated that the methyl carbon resonance at δ 20.1 is linked with the quaternary carbon resonance for C-14 at δ 38.1, while that at δ 18.5 is directly linked with the quaternary carbon resonance at δ 39.5 for C-13. The resonance assignments for C-26 and C-27 in **23**–**34** and closely related compounds made earlier[1] should therefore be reversed to around δ 20.1 and 18.5, respectively. The INADEQUATE experiment was otherwise fully commensurate with the carbon shift

Table 1. ^1H NMR signals (ppm) of some friedelanes[a]

Proton	20	21	22	23	24	25	26	27	28	29	30	31	32
23-CH_3	1.18 s	1.18 s	1.47 s	1.76 s	0.87 d (6.4)	0.89 d (6.7)	0.94 d (6.9)	0.91 d (6.7)	0.81 d (7.1)	0.85 d (6.8)	0.83 d (6.9)	0.76 d (6.7)	0.79 d (7.1)
24-CH_3	0.98 s	1.04 s	1.00 s	1.16 s	0.71 s	0.71 s	0.69 s	0.72 s	0.93 s	0.75 s	0.95 s	0.89 s	0.89 s
25-CH_3	0.80 s	0.80 s	0.84 s	0.93 s	0.85 s	0.84 s	0.85 s	0.88 s	0.86 s	0.79 s	0.88 s	0.83 s	0.82 s
26-CH_3	0.97 s	0.98 s	0.98 s	1.01 s	0.99 s	1.00 s	0.99 s	1.01 s	0.99 s	0.97 s	1.00 s	0.99 s	0.97 s
27-CH_3	1.05 s	1.00 s	1.00 s	0.99 s	1.03 s	1.06 s	1.03 s	1.05 s	1.00 s	0.99 s	1.00 s	1.00 s	0.99 s
28-CH_3	1.16 s	1.17 s	1.16 s	1.18 s	1.16 s	1.18 s	1.17 s	1.18 s	1.17 s	1.15 s	1.17 s	1.17 s	1.15 s
29-CH_3	0.98 s	0.98 s	0.98 s	0.99 s	0.99 s	1.00 s	0.99 s	1.00 s	0.99 s	0.97 s	0.98 s	0.99 s	0.97 s
30-CH_3	0.93 s	0.93 s	0.93 s	0.94 s	0.94 s	0.96 s	0.94 s	0.96 s	0.94 s	0.92 s	0.94 s	0.95 s	0.92 s
1-CH_2	1.28 m		1.78 m	2.51 m	1.94 m 1.62 m		2.44 m 1.53 m	2.26 m 1.72 m		1.76 m	1.67 m	1.91 m 1.46 m	1.70 m
H-2	1.92 m (2H)		5.37 bs		2.36 m (2H)	4.95 bt (5.4)	4.09 m	5.15 dd (11.3, 3.8)	1.95 m(1H) 1.55 m(1H)	4.00 m (1H)	5.20 t (3.5)	4.93 m	4.85 bs
H-3	2.84 m	2.90 bs							4.89 m	3.28 dd (11.1, 3.5)	4.85 m	4.87 m	4.77 bs
H-4					2.24 q (6.4)	2.67 q (6.7)	2.27 q (6.9)	2.26 m	1.38 m	1.46 m	1.35 m	1.36 m	1.65 m
H-8	1.30 m	1.30 m	1.35 m	1.41 m	1.38 m	1.41 m	1.42 m	1.40 m	1.30 m	1.30 m	1.25 m	1.28 m	1.30 m
H-10	1.46 m	0.82 m	1.53 m	1.93 m	1.53 m	1.71 m	1.60 m	1.61 m	0.94 m	1.38 m	0.97 m	1.09 m	1.30 m
H-18	1.52 m	1.56 m	1.54 m	1.57 m	1.54 m	1.52 m	1.56 m	1.58 m	1.56 m	1.53 m	1.54 m	1.56 m	1.53 m
$OCOCH_3$			2.04 s 2.09 s	2.24 s		2.12 s		2.14 s	2.03 s		1.96 s 2.08 s	2.00 s 2.02 s	2.04 s 2.06 s

[a] Values in parentheses are coupling constants in hertz.

Reference Data

Table 2. ^{13}C NMR signals (ppm) of some secofriedelanes and friedelanes

Carbon	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	24
C-1	25.2	18.5	18.5	19.3	21.9	21.9	28.5	26.8	24.8	23.5	23.6	22.7	22.8	29.9	29.9	21.2	21.0	28.0	19.0	15.3	14.5	24.7	22.1
C-2	72.5	34.3^a	33.0	21.7	34.9	31.6	79.5	73.2	65.7	34.9	30.7	35.9	35.8	178.2	174.7	34.5	34.6	171.8	28.9	23.2	28.4	68.5	41.4
C-3	170.5	176.0	175.3	69.4	63.2	64.7	67.1	65.5		63.2	64.7		174.0	160.9	160.8	174.2	173.7		171.5	60.8	62.0	138.2	213.0
C-4	83.9	84.8	84.8	85.0	75.7	76.6	75.1	77.1	76.9	215.0	214.4	215.0	214.8	78.1	77.8	75.2	77.4	87.5		65.8	66.3	138.5	58.0
C-5	40.9	40.8	40.7	38.3	41.9	41.3	41.0	40.9	41.0	54.0	53.8	53.8	53.8	40.6	40.6	41.9	41.3	36.1^a	83.8	37.3	37.4	38.8	42.0
C-6	38.6	38.4	38.4	38.1	36.0	33.6	39.4	33.9	34.0	38.0	37.8	38.2	38.2	34.2	33.8^a	36.8	36.6	37.1	41.6	36.6	39.0	38.0	41.1
C-7	17.9	18.0	17.9	17.7	17.7	17.3	18.0	17.4	17.3	17.5	17.4	17.4	17.4	17.4	17.4	17.6	17.4	17.4	15.6	17.9	18.6	17.9	18.0
C-8	52.7	52.1	52.1	53.1	52.8	52.7	52.3	52.1	52.3	52.7	52.6	52.4	52.5	52.4	52.5	52.7	52.7	52.8	52.6	52.3	52.8	52.5	52.9
C-9	37.8	38.2	38.1	36.4	39.2	39.1	39.4	39.4	38.8	38.6	38.4	38.2	38.2	38.6	38.6	39.3	39.4	36.0^a	36.6	36.5	37.4	36.3	37.3
C-10	53.7	64.1	64.0	59.0	58.4	55.7	56.8	52.6	52.7	54.5	54.4	53.4	53.5	51.3	51.2	57.1	56.0	53.8	54.1	48.0	57.9	50.9	59.3
C-11	35.4	34.4^a	34.3	34.9	35.0	35.2	34.8	35.7	35.1	35.5	35.3	35.1	35.2	34.2	34.2^a	35.0	35.1	34.1	34.4	35.4	34.9	34.8	35.5
C-12	30.6	30.1	29.6^a	30.4	30.1	30.0	30.0	29.9	30.0	30.1	30.1	30.0	30.0	30.1	30.3	30.1	30.0	29.9	30.1	30.4	30.4	30.2	30.3
C-13	39.2	39.0	39.0	39.7	39.5	39.4	39.6	39.5	39.4	39.6	39.5	39.4	39.5	39.5	39.5	39.5	39.5	39.7	39.7	39.5	39.5	39.7	39.5
C-14	38.4	38.2	38.1	38.3	38.2	38.1	38.2	38.2	38.2	38.3	38.2	38.4	38.5	38.2	38.2	38.2	38.2	38.0	38.2	38.1	38.2	38.2	38.1
C-15	32.3	31.3^b	31.3	32.2	32.2	32.1	32.2	32.2	32.1	32.3	32.2	32.2	32.3	32.2	32.2	32.2	32.2	32.1	32.2	32.2	32.1	32.1	32.3
C-16	35.9	29.0	29.5^a	36.0	36.0	35.9	36.0	35.9	35.9	36.0	35.9	35.9	35.9	35.9	36.0	36.0	36.0	35.8	35.7	35.9	35.9	35.9	35.9
C-17	29.9	35.1	33.7	30.0	29.9	29.8	29.9	29.9	29.9	29.9	29.8	29.8	29.8	29.9	30.0	29.9	29.9	29.9	29.9	29.8	29.9	29.9	29.8
C-18	42.7	39.3	39.1	42.8	42.8	42.7	42.7	42.8	42.7	42.9	42.7	42.7	42.8	42.8	42.8	42.8	42.8	42.7	42.7	42.6	42.7	42.8	42.6
C-19	35.2	35.2	35.2	35.3	35.2	35.2	35.2	35.2	35.2	35.2	35.2	35.2	35.2	35.2	35.2	35.2	35.2	35.2	35.3	35.2	35.2	35.2	35.2
C-20	28.1	28.0	27.9	28.1	28.1	28.0	28.1	28.0	28.0	28.0	28.0	28.0	28.0	28.1	28.0	28.0	28.0	28.0	28.0	28.0	28.0	28.0	28.0
C-21	32.7	31.4^b	30.2	32.8	32.8	32.7	32.7	32.8	32.7	32.8	32.7	32.7	32.7	32.7	32.7	32.7	32.8	32.7	32.6	32.6	32.6	32.7	32.6
C-22	39.1	33.3	32.1	39.2	39.2	39.1	39.2	39.1	39.1	39.2	39.1	39.1	39.1	39.1	39.1	39.2	39.2	39.1	39.1	39.1	39.1	39.1	39.1
C-23	16.1	16.0	16.1	14.4	16.3	14.7	14.5	14.5	14.7	25.9	25.8	26.0	25.8	14.5	14.5	16.8	14.9	14.3		17.6	19.5	9.9	6.7
C-24	12.5	13.3	13.3	13.6	18.5^a	18.0	18.8	17.9	17.9	17.6	17.6	17.6	17.6	17.9	17.9	18.5^a	17.4	12.3	22.9	18.6	17.7	19.1	14.5
C-25	17.8	17.9	17.9	18.2	17.9	17.8	17.5	17.3	17.5	17.9	17.8	17.7	17.7	17.5	17.8	17.8	17.8	16.5	16.7	17.9	18.5	18.0	17.8
C-26	20.1	19.0	19.0	20.0	20.0	20.0	20.1	20.0	20.1	20.1	20.0	20.0	20.0	20.1	20.0	20.0	20.0	20.1	20.1	20.1	19.9	19.9	20.1
C-27	18.5	18.9	19.0	18.5	18.6^a	18.6	18.5	18.5	18.6	18.6	18.6	18.6	18.6	18.6	18.5	18.6^a	18.6	18.5	18.5	18.4	18.5	18.4	18.5
C-28	32.0	68.0	69.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0
C-29	31.7	32.7	32.5	31.7	31.8	31.7	31.7	31.8	31.7	31.7	31.7	31.7	31.7	31.8	31.8	31.7	31.7	31.7	31.7	31.7	31.7	31.7	31.7
C-30	34.9	34.2	34.2	34.9	34.9	34.8	34.8	34.7	34.8	34.8	34.8	34.8	34.8	34.8	34.8	34.8	34.8	34.8	34.9	34.9	34.9	34.8	34.9
$\mathrm{O}\mathit{C}\mathrm{OCH_3}$			171.3			170.6		170.5	170.6		170.8						170.7					168.7	
						171.0		170.5	170.8													169.2	
								170.8															
$\mathrm{OCO}\mathit{C}\mathrm{H_3}$			20.9			20.8		20.6	20.9		20.7						21.2						
						21.2		21.1	21.2													20.5	
								21.3														21.2	
OCH_3													51.2		51.6	51.3	51.3						

^{a,b} Values with the same superscript in a column are interchangeable.

assignments[1] of **24**. Further, it was observed from the X–H correlation experiment for one-bond couplings on **24** (and also in related compounds) that the methyl carbon resonances at δ 31.7 and 32.0 were associated with proton resonances at δ 0.99 and 1.16, respectively. The protons on C-28 in friedelan-7-one were also observed[2] from an NOE experiment to resonate at δ 1.17 and showed an NOE with the δ 0.99 methyl signal. Hence the revision proposed by Prakash *et al.*[2] for the assignment of C-28 in **24** to the resonance at δ 31.7 and the carbon *syn* to it with the resonance at δ 32.0 is not tenable. The proton resonance assignments for friedelanes **20**–**32**, mostly arrived at from X–H correlation analyses, are given in Table 1.

The carbon resonance assignments of **1** (Table 2) were made by comparison with the spectrum of 2α-acetoxyfriedelolactone[1] (**34**) and further confirmed by an X–H correlation experiment. The signal assignments for apetalactone (**2**) and its acetate (**3**) followed from those of friedelolactone[1] (**33**). The oxygen function at C-28 in **2** and **3** caused a downfield shift of C-17 and upfield shifts for C-16, C-18 and C-22. The resonance assignments of **4**–**7** followed from mutual correlations and consideration of substituent effects. Conversion of 3,4-secofriedelane-3,4-diol (**5**) to 3,4-secofriedelan-3-ol-4-one (**10**) or methyl 3,4-secofriedelan-4-ol-3-oate (**16**) to methyl 3,4-secofriedelan-4-on-3-oate (**13**) differentiated the C-5 resonance from that of C-9, since the C-5 signal underwent a strong downfield shift (about 11.9–12.1 ppm). Comparison of the spectra of **6** and 2,3 : 3,4-diseco-3-norfriedelinyl-2,4-diyl diacetate (**9**) allowed the identification of the C-1 and C-10 resonances in **9**. Again, the spectrum of **9** was similar to that of **14** (or **15**) except for the changes expected. The X–H correlation experiments (for one-bond couplings) on **14**, and also **15**, identified the resonance associated with C-23 at δ 14.5. In 3,4 : 4,5-diseco-4,23-dinorfriedelan-5-ol-3-oic lactone (**19**), C-1, C-2 and C-7 resonated at δ 19.0, 28.9 and 15.6, respectively, and C-6 resonated downfield compared with that in 2,3 : 3,4-diseco-3-norfriedelan-4-ol-2-oic lactone (**18**) owing to the absence of a γ-interaction with C-23. The C-10 signal in 3α,4α-epoxyfriedelane (**20**) experienced a strong upfield shift relative to that in 3β,4β-epoxyfriedelane (**21**), probably owing to the γ-effect of the oxygen and to the shielding influence exerted by the epoxy ring. The Dreiding model of **20** showed C-10 to be over the epoxy ring.

EXPERIMENTAL

The ^{1}H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra were recorded on a Bruker AM 300L NMR spectrometer equipped with an Aspect 3000 computer and an array processor using the DISNMR program version 870101.1. The compounds were submitted to composite pulse decoupling and DEPT sequences to establish the carbon shifts and the degree of protonation. The spectra were recorded in a 5 mm ^{13}C/^{1}H dual probe head using $CDCl_3$ as solvent, as internal lock and the internal standard. The concentration of all solutions was *ca.* 2–5%. The chemical shifts reported are in δ (ppm) downfield from TMS; $\delta_{TMS} = \delta_{CDCl_3} + 76.9$ ppm. The carbon spectra were recorded with a pulse width of 3 μs (approximately 65° flip angle) and approximately 3 s delay between pulses, and the FIDs were acquired over 15 151 Hz (17 241 Hz for **10**–**13**) and 32 K data points. Two-dimensional X–H correlation (^{13}C–^{1}H) spectra were obtained using the INEPT sequence. The FIDs were acquired over 4096 data points and 15 151 Hz for each of 128 values of evolution time. The second-dimension sweep width was ±1250 Hz. The raw data were processed using a sine bell window function in both dimensions in the magnitude mode. The INADEQUATE spectrum was recorded in a 10 mm tube in an approximately 25% solution on a Bruker AM 400 NMR spectrometer. The FIDs were acquired over 2048 data points, a 7812.5 Hz sweep width (in both dimensions) and 768 scans were used for each of 128 values of evolution time. The f_1 dimension was zero filled from 256 to 512 W before Fourier transformation using Gaussian and shifted sine bell window functions in the f_1 and f_2 dimensions, respectively, in the power mode.

The compounds employed in the present studies were either natural products isolated from *Quercus suber*[16] or their transformation products, mostly reported elsewhere,[13] which were characterized by chemical and spectral studies. Friedelan-3-ene (100 mg) in methylene chloride (200 ml) was treated with *m*-chloroperbenzoic acid (150 mg) at 0 °C and the reaction mixture was kept in a refrigerator for 7 days. Washing with aqueous $NaHCO_3$ solution and the usual work-up gave a solid which was chromatographed over silica gel. The residue from benzene–chloroform (1 : 1) eluates was purified by preparative TLC over silica gel to yield 3α,4α-epoxyfriedelane (**20**), $C_{30}H_{50}O$, m.p. 215 °C ($CHCl_3$–light petroleum), ν_{max} (KBr) 870 cm^{-1}, and the more polar 3β,4β-epoxyfriedelane (**21**), $C_{30}H_{50}O$, m.p. 228 °C ($CHCl_3$–light petroleum), ν_{max} (KBr) 890 cm^{-1}. The refluxing of cerin acetate (**25**) (100 mg), acetic anhydride (2 ml) and pyridine (3 ml) for 8 h and the usual work-up furnished a solid which was chromatographed over silica gel. The benzene–chloroform (1 : 1) eluates afforded friedel-3-en-2α,3-diyl diacetate (**22**), crystallizing from $CHCl_3$–MeOH as needles (40 mg), $C_{34}H_{54}O_4$, m.p. 188–190 °C, $[\alpha]_D^{26}$ + 62° ($CHCl_3$), ν_{max} (KBr) 1760, 1735, 1250, 1225 and 1075 cm^{-1}.

Acknowledgement

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References

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