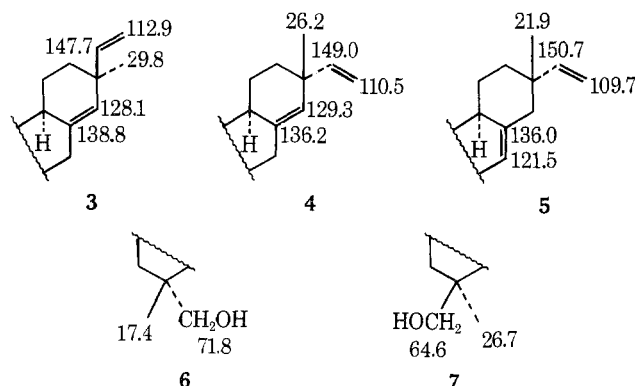


dated most readily, albeit not exclusively, by tricyclic, monoolefinic, diterpenic structures reminiscent of pimaric and related triols and tetrols containing 15,16-dihydroxy units.⁴ As a consequence, hallow was oxidized with periodic acid, yielding a noraldehyde (**2a**), whose reaction with methylenetriphenylphosphorane led to a dienediol (**2b**). If the relationship of hallow to the earlier pimaric natural products were well founded, the two-step procedure would have furnished a pimaradiene derivative, a substance ideally suited for ¹³C NMR analysis in view of the previous accumulation of ¹³C NMR data in this field.⁵

Comparison of the olefinic carbon shifts of the dienic degradation product **2b** with those of pimaradienic (**3**), sandaracopimaradienic (**4**), and isopimaradienic (**5**) systems⁵ shows the compound to be of the sandaracopimaradiene type and comparison of the oxymethylene shift of 18-hydroxy (**6**) and 19-hydroxy (**7**) diterpenic substances⁶ with that of **2b** classifies the degradation product, and hence the natural product, as an 18-hydroxy diterpene.



These facts are confirmed by the three methyl shifts of **2b**.⁵ The virtual identity of the δ values of the ring B and C methylenes and methines of **2b** with those of analogous carbon centers of ring B of pimarol and ring C of sandaracopimaric acid⁵ limits the secondary hydroxy group of **2b** to ring A and a 2 α configuration. Alternative hydroxyl locations at 1 α , 1 β , 2 β , 3 α , and 3 β sites are precluded by the absence of shift perturbations at C(9) and C(10), at C(10), C(11), and C(20), at C(19) and C(20), at C(4), C(5), and C(18), and at C(4), C(18), and C(19), respectively.^{6,7}

The ¹³C NMR data for diene **2b** readily permits shift assignment for aldehyde **2a**. Since the natural tetrol (**1**) is not soluble in deuteriochloroform, the common ¹³C NMR spectral solvent, its spectrum, and, for sake of comparison, that of diene **2b** were obtained in deuteriopyridine solution. Shift differences only in the vicinity of C(13) and the replacement of the resonances of the vinyl group of **2b** by those of an oxymethylene and oxymethine show hallow to be a 15,16-dihydroxy compound and to possess the relative configuration depicted in formula 1. The carbon shifts of compounds **1** and **2** are listed in Table I.

The ¹H NMR signals of the hydrogens of the vinyl group and nuclear double bond of the pimaradienes **3**, **4**, and **5** are distinct,^{8,9} making the olefinic hydrogens of diene **2b** readily recognizable as those of the sandaracopimaradiene system (**4**). Similarly, the ¹H NMR signals of both the methyl and hydroxymethyl groups occupy different field positions in structures **6** and **7**,^{9,10} permitting the identification of the C(4) stereochemistry of **2b** as that illustrated in partial structure **6**.

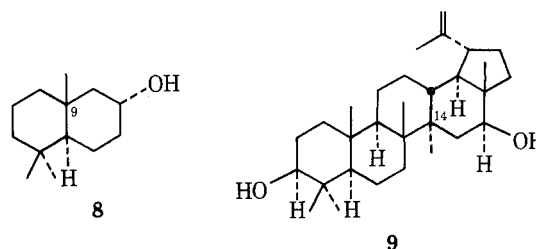
Table I of ¹³C NMR data reveals an unusually strong attenuation of the γ -anti-periplanar heteroatom effect.¹¹ While equatorial hydroxy groups shield the γ carbons in cyclohexane compounds by ca. 3 ppm, the 2 α -hydroxy

Table I
Carbon Chemical Shifts^a

	1 ^a	2b ^a	2b ^b	2a ^b
C(1)	48.7	48.7	48.1	48.0
C(2)	63.6	63.7	65.1	65.0
C(3)	45.2	45.3	44.7	44.6
C(4)	39.1 ^c	39.1	39.4 ^e	39.4 ^f
C(5)	46.6	46.7	47.0	46.7
C(6)	21.8	21.8	22.1	21.9
C(7)	35.5	35.4	35.5	35.4
C(8)	136.5	^d	136.2	141.0
C(9)	50.6	50.3	50.4	50.4
C(10)	38.9 ^c	39.1	39.6 ^e	39.7 ^f
C(11)	18.4	18.9	18.9	18.1
C(12)	30.2	34.2	34.4	28.3
C(13)	37.8	37.1	36.9	47.3
C(14)	128.1	128.6	129.3	121.7
C(15)	79.1	^d	148.7	192.6
C(16)	62.7	109.8	110.0	
C(17)	22.5	25.4	25.9	20.5
C(18)	70.6	70.8	71.5	71.4
C(19)	18.7	18.9	18.9	18.8
C(20)	16.0	16.1	16.5	16.8

^a In pyridine-*d*₅ solution; $\delta(\text{Me}_4\text{Si}) = \delta(\text{pyridine-}d_5, \text{C-4}) + 134.6$ ppm. ^b In CDCl₃ solution; $\delta(\text{Me}_4\text{Si}) = \delta(\text{CDCl}_3) + 76.9$ ppm. ^{c, e, f} Signals in any vertical column may be reversed. ^d Signal under solvent signal. ^e The δ values are in parts per million downfield from Me₄Si.

function of **2a** and **2b** deshields C(4) and C(10) by ca. 1 ppm. This deshielding seems to affect especially quaternary γ carbons in rigid ring systems, as shown also by the $\Delta\delta$ value of ca. 1 ppm for C(9) of the decalol **8**¹ and C(14) of the lupane derivative **9**.¹²



Experimental Section¹³

Hallow (1):² mp 204°; $[\alpha]^{20}_D +18.7^\circ$ (c 0.14, EtOH); ir (KBr) OH 3300–3620 cm⁻¹ (m); ¹H NMR (methanol-*d*₄) δ 0.82, 0.87, 0.97 (s, 3 each, methyls), 3.02, 3.33 (AB pair of d, 1 each, $J = 9.0$ Hz, OCH₂), 3.67 (t, 1, $J = 7.0$ Hz, OCH), 5.32 (broad s, 1, olefinic H); MS *m/e* 338 (rel intensity) (M⁺, 4), 277 (base), 276 (28), 259 (80), 241 (30), 229 (38), 121 (80).

Anal. Calcd for C₂₀H₃₄O₄: C, 70.97; H, 10.13. Found: C, 70.87; H, 10.08.

Aldehyde 2a. A mixture of 50 mg of hallow (**1**) and 35 mg of finely powdered periodic acid (H₅IO₆) in 5 ml of 95% ethanol was stirred at room temperature for 4 hr. Saturated sodium bicarbonate solution (1 ml) was added, the mixture was filtered, and the residue was washed with ethanol. The combined washings and original solution were evaporated to dryness and the solid residue washed exhaustively with water and extracted with chloroform. The extract was dried over magnesium sulfate and evaporated, leaving 41 mg of aldehyde **2a** as a colorless powder: mp 130.5–132.5°; ir (CHCl₃) OH 3690 (m), 3620 (m), 3460 (m), C=O 1720 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 0.85, 0.87, 1.10 (s, 3 each, methyls), 3.06, 3.39 (AB pair of d, 1 each, $J = 11.0$ Hz, OCH₂), 3.74 (t, 1, $J = 8.0$ Hz, OCH), 5.28 (s, 1, olefinic H), 9.20 (s, 1, aldehydic H); MS *m/e* (rel intensity) 306 (M⁺, 2), 288 (2), 276 (12), 258 (10), 21 (base). Anal. *m/e* 306.2207 (calcd for C₁₉H₃₀O₃, 306.2194).

Diene 2b. A 2.0 M solution of *n*-butyllithium (0.60 ml) in hexane was added over a 10-min period with stirring to a mixture of 429 mg of methyltriphenylphosphonium bromide [dried at 70° (0.1 Torr) for 2 hr and then over phosphorous pentoxide at 25° (0.2 Torr) for 2 hr] in 6.5 ml of tetrahydrofuran (distilled from lithium aluminum hydride onto 4A molecular sieves) under nitrogen at room temperature. After the mixture had been stirred for an extra

