of acetylenes including some types which are not otherwise accessible.¹ A number of other applications of this valuable reagent are presently being investigated in these laboratories, especially in connection with total synthesis of natural products. Because of the potentially broad range of utility of 1 a convenient, large-scale preparation was desirable. Although 1 is prepared by simply heating a neat mixture of 1 equiv of tri-n-butyltin hydride with 1 equiv of tri-n-butylethynylstannane (2),¹⁻³ the preparation of 2 in quantity by current procedures is complicated and cumbersome.



Reaction of tri-n-butyltin halides with ethynylmagnesium halides⁴ or with sodium acetylide in ether⁵ results in only a very low yield of 2, the major side product being bis-(tri-n-butylstannyl)acetylene (3).⁶ A modification of the latter process has been described⁷ in which 1 equiv of trin-butyltin chloride in ether is added to a solution of sodium acetylide prepared in liquid ammonia. Although this procedure results in a higher yield of 2, the reaction in our hands was found to be very capricious and usually resulted in large amounts of the side product 3.

A new method has been developed for the synthesis of 1 which possesses the advantages of (1) high yield, (2) applicability on a large scale, (3) avoidance of low temperatures or the use of liquid ammonia, and (4) elimination of further reaction of 2 and specifically the by-product 3. Tri-n-butyltin chloride was added to the readily prepared anion, lithium chloroacetylide,⁸ and the product, tri-n-butylchloroethynylstannane (4), was isolated in 83% yield by distillation. Treatment of 4 with 2 equiv of tri-n-butyltin hydride afforded tri-n-butyltin chloride (99%) and trans-1,2-bis-(tri-n-butylstannyl)ethylene (1, 86%) by direct distillation of the reaction mixture. The readily separated tri-n-butyltin chloride was very pure and could be recycled for the preparation of more 1.

Experimental Section

trans-1,2-Bis(tri-n-butylstannyl)ethylene (1). To a cooled (0°) solution of 50.0 ml (82.4 mmol) of 1.65 M methyllithium in ether under an argon atmosphere was added dropwise a solution of 3.2 ml (42 mmol) of trans-1,2-dichloroethylene in 15 ml of ether during 1 hr (gas evolution). The mixture was warmed to room temperature, stirred for 90 min, then recooled (0°), and 11.1 ml (41.2 mmol) of tri-n-butyltin chloride was added. After stirring for 1 hr at room temperature, 1 ml of methyl iodide was added and stirring was continued for 30 min. The mixture was filtered (quickly in the air) through a pad of Celite and concentrated in vacuo. Distillation at bp 100-105° (0.01 mm) afforded 12.0 g (83%) of pure chloroacetylene 4, ir (neat) 4.72 μ . This material could be used in the next step; redistillation did not change the spectra.

A neat mixture of 17.8 g (50.9 mmol) of tri-n-butylchloroethynylstannane, 29.7 g (102 mmol) of tri-n-butyltin hydride, and 0.18 g of azobisisobutyronitrile were heated at 90° for 4 hr. Distillation afforded 16.4 g (99%) of tri-n-butyltin chloride, bp 102-105° (0.1 mm), and 26.4 g (86%) of *trans*-bis(tri-*n*-butylstannyl)ethylene (1)¹: bp 175–195° (0.07 mm); ir (neat, partial) 6.83 and 10.4 μ ; NMR (CCl₄) δ 0.50–1.90 (br m, 54 H) and 6.85 (s, 2 H, $J_{117Sn-H} =$ 106, $J_{119Sn-H} = 110$ Hz). The NMR, ir, and near ir spectra of 1 were identical with those of material prepared as previously de-scribed.^{1,9}

Registry No.-1, 14275-61-7; trans-1,2-dichloroethylene, 156-60-5; tri-n-butyltin chloride, 1461-22-9.

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The Structure of Hallol¹

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A study of the heartwood constituents of the New Zealand podocarp Podocarpus hallii Kirk has revealed the presence of the terpenic substances sugiol, podocarpic acid, totarol, its 19-hydroxy and 19-oxo derivatives,² sellowin A,³ and a compound (B, mp 204°) of unknown constitution.² The following discussion shows the latter, herewith named hallol, to be 8(14)-sandaracopimaren- 2α , 15ξ , 16, 18-tetrol (1).



Both elemental and mass spectral analyses indicate the compound to possess a C₂₀H₃₄O₄ molecular framework, while the mass spectrum of a sample exposed to deuterium oxide reveals the incorporation of four deuteriums and hence the presence of a hydrogen on each of the oxygens. The ¹H NMR spectrum of a deuteriomethanol solution contains three methyl singlets at 0.82, 0.87, and 0.97 ppm, a six-hydrogen multiplet at 2.9-4.0 ppm corresponding to two oxymethylenes and two oxymethines, and an olefinic hydrogen multiplet at 5.32 ppm. These facts are accommodated most readily, albeit not exclusively, by tricarbocyclic, monoolefinic, diterpenic structures reminiscent of pimarenic and related triols and tetrols containing 15,16-dihydroxy units.⁴ As a consequence, hallol was oxidized with periodic acid, yielding a noraldehyde (2a), whose reaction with methylenetriphenylphosphorane led to a dienediol (2b). If the relationship of hallol to the earlier pimarenic 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 2α configuration. Alternative hydroxyl locations at 1α , 1β , 2β , 3α , and 3β 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 hallol 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 2α -hydroxy

Table I Carbon Chemical Shiftsg

Carbon Chemical Shirts				
	1a	$2b^a$	$2\mathbf{b}^{b}$	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 <i>f</i>
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 <i>f</i>
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_s solution; $\delta(\text{Me}_4\text{Si}) = \delta(\text{pyridine-}d_s \text{ C-4}) + 134.6 \text{ ppm.}$ ^b In CDCl₃ solution; $\delta(\text{Me}_4\text{Si}) = \delta(\text{CDCl}_3) + 76.9 \text{ ppm.}$ ^{c,e,f} Signals in any vertical column may be reversed. ^d Signal under solvent signal. ^g The δ valves 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 quarternary γ carbons in rigid ring systems, as shown also by the $\Delta\delta$ value of ca. 1 ppm for C(9) of the decalol 8¹ and C(14) of the lupane derivative 9.¹²



Experimental Section¹³

Hallol (1):² mp 204°; $[\alpha]^{20}$ D +18.7° (c 0.14, EtOH); ir (KBr) OH 3300–3620 cm⁻¹ (m); ¹H NMR (methanol-d₄) 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 hallol (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 15 min a solution of 57 mg of crude aldehyde 2a in 5.5 ml of dry tetrahydrofuran was added quickly. Upon further stirring at room temperature for 30 min the mixture was refluxed for 4 hr, then diluted with 75 ml of ether and filtered through Celite. The filtrate was evaporated under vacuum and the residue rinsed thoroughly with water and extracted with ether. The extract was dried over magnesium sulfate and evaporated. The solid residue was purified by two successive preparative TLC operations on silica gel (one by elution with chloroform and the second with ether). Crystallization of the colorless solid, 45 mg, from ether yielded colorless needles of diene 2b: mp 192–193.5° $[\alpha]^{24}$ D +10.3° (c 1.6, EtOH); ir (CHCl₃) OH 3670 (w), 3615 (m), 3450 (m), C=C 1631 cm⁻¹ (w); ¹H NMR (CDCl₃) & 0.84, 0.88, 1.04 (s, 3 each, methyls), 3.12, 3.39 (AB pair of d, 1 each, J = 11.0 Hz, OCH₂), 4.65, 4.69, 4.71, 4.74, 4.87, 4.90, 4.95, 4.98, 5.49, 5.64, 5.78, 5.93 (ABX lines, 3, vinyl H's), 5.18 (broad s, 1, nuclear olefinic H); MS m/e (rel intensity) 304 (M⁺, 9), 286 (40), 256 (33), 187 (100). Anal. m/e 304.2399 (calcd for C₂₀H₃₂O₂, 304.2401).

Anal. Calcd for C20H32O2: C, 78.90; H, 10.59. Found: C, 78.75; H, 10.46

Registry No.---1, 56816-57-0; 2a, 56783-50-7; 2b, 56783-51-8.

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Preparation of Mono- and Diiodocyclopropene

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A variety of methods used for the preparation of monoand diiodoperfluorocycloalkenes possessing the general structure shown below have been previously reported.¹⁻³

$$(CF_2)n X = Cl \text{ or } I$$

$$Y = I$$

$$Y = I = 2, 3, 4,$$

These perfluorovinyl iodides have shown unique synthetic utility in copper coupling reactions^{4,5} and in the preparation of various organometallic derivatives.^{6,7}

Previous attempts to prepare the iodo derivatives of the highly strained cyclopropene system (where n = 1) have been unsuccessful.⁸ Although many perhalocyclopropenes have been prepared, including tetrabromocyclopropene,⁹ a recent report indicated that iodocyclopropenes are expected to be very unstable.¹⁰

We wish now to report on a facile synthesis of 1-chloro-2-iodo-3,3-difluorocyclopropene (5) and 1,2-diiodo-3,3-difluorocyclopropene (4). These compounds are readily distilled under vacuum and darken slowly on standing and exposure to sunlight. Studies on the reactions of 4 and 5 with copper powder and various nucleophiles are being investigated and will be reported in another paper.

The method of Tobey and West⁹ was used to prepare 1,2-dichloro-3,3-difluorocyclopropene (3). We have introduced several changes in this procedure which have increased the overall yield of 3 eightfold. The principal changes occur in the first and third step below.



The yield of pentachlorocyclopropane (1) was doubled by employing approximately half the quantity of glyme previously suggested. This change causes the decomposition of sodium trichloroacetate to proceed more slowly; however, there are fewer by-products arising from the reaction of glyme with the generated dichlorocarbene.

A significant improvement in the reaction of tetrachlorocyclopropene (2) with SbF_3 has been obtained by using freshly sublimed SbF_3 . The reaction initiates at a much lower temperature and the distillate contains nearly pure 3 in 76% yield. Sublimed ${\rm SbF}_3$ permits only trace amounts of the monofluoro product (3-fluoro-1,2,3-trichlorocyclopropene) to be formed even when 2 is used in excess. This would tend to give further support to a proposed intermediate involving both allylic chlorine atoms of 2 and three fluorine atoms in a tight coordination sphere around a pentacoordinated antimony.9

Previous studies on the reaction of anhydrous KI with 1,2-dichloroperfluorocycloalkenes in DMF indicated that the degree of substitution, yields, and reaction rates were largely determined by ring size or strain energies of the perfluorocycloalkene.¹ It was not surprising to observe that 3 reacted with KI in DMF at room temperature.