what more deshielded than its counterpart in **33** and, therefore, at lower field. This is indeed the case. The steroids assigned to the anti configuration by uv maxima have C_4-proton peaks at 6.65–6.85 ppm, while the other isomer has peaks at 6.00–6.28 ppm. Further, the assigned anti isomers have *N*-methyl peaks at 3.67–3.70 ppm while the other isomer has peaks at 3.71–3.84 ppm. These data, summarized in Table II, confirm the stereochemical sssignments made for the isomers and corroborate the use of uv maxima for distinguishing between conjugated syn and anti nitrone pairs.

Table I lists the androstene, the pregnene nitrones, and the saturated 3-ketonitrones prepared. The latter compounds were homogeneous by tlc analysis and had no outstanding spectral characteristics. Thus, although these nitrones, too, must exist as stereoisomeric pairs, they were not detected. Biological testing of the nitrones found them less active than the parent ketones.

Experimental Section[17]

***N*-(2-Hydroxyethyl)-α-(17β-hydroxy-3-methoxyandrosta-3,5-dien-6-yl)nitrone (14). General Procedure for 6- and 20-Aldonitrones.** A mixture of 17-acetoxy-3-methoxyandrosta-3,5-diene-6-carboxaldehyde (30.1 g, 81 mmol), $NaHCO_3$ (40 g), and *N*-(2-hydroxyethyl)hydroxylamine oxalate (25 g, 0.116 mol) in MeOH (1 l.)–H_2O (50 ml)–pyridine (15 ml) was stirred under reflux in the dark for 22 hr. The hot reaction mixture was filtered and the filtrate was concentrated to a yellow paste. The resulting solid (43 g) was crystallized from aqueous MeOH to give **14** (23.5 g).

17α-Methyl-3-methyliminoandrost-4-en-17β-ol *anti*- and *syn*-*N*-Oxide (40 and 41). General Method for 3-Ketonitrones. A mixture of methyltestosterone (30.6 g, 0.1 mol), $NaHCO_3$ (35 g), and *N*-methylhydroxylamine oxalate (18.9 g, 0.1 mol) in absolute EtOH (75 ml) was stirred overnight in the dark under reflux. The reaction mixture was filtered and the filtrate was concentrated. The residue was chromatographed on silica gel (350 g), collecting 250-ml fractions and eluting with Me_2CO (1 l.), Me_2CO–5% MeOH (1 l.), and Me_2CO–10% MeOH (7 l.). Fractions 11–16 were combined and concentrated and the residue was crystallized from acetone–ether–hexane to give **40** (8.0 g). Fractions 28–33 were combined and concentrated and the residue was triturated with ether to give **41** (2.0 g).

Acknowledgment. The authors wish to thank Dr. Vladimir Petrow for suggesting this problem and to his helpful discussions throughout the course of this work.

Registry No.—**12** (R_2 = OH), 50276-51-2; **12** (R_2 = OAc), 5490-78-8; **14**, 50324-69-1; **15**, 50324-70-4; **16**, 50324-71-5; **17**, 50324-72-6; **18**, 50324-73-7; **19**, 50324-74-8; **19** 6-carboxaldehyde derivative, 50323-68-7; **20** (R_2 = CH_3), 24254-01-1; **22**, 50324-77-1; **23**, 50324-78-2; **24**, 50324-79-3; **25**, 50324-80-6; **25** 20-carboxaldehyde derivative, 50323-70-1; **27**, 50324-81-7; **28**, 50324-82-8; **29**, 50324-83-9; **29** 20-oxo derivative, 50324-76-0; **30**, 50324-84-0; **37**, 50324-85-1; **37** 3-oxo derivative, 58-22-0; **38**, 50324-87-3; *syn*-**39**, 50324-88-4; *anti*-**39**, 50324-89-5; **40**, 50324-90-8; **40** 3-oxo derivative, 58-18-4; **41**, 50324-92-0; **42**, 50324-93-1; **42** 3-oxo derivative, 434-03-7; *syn*-**43**, 50324-95-3; *anti*-**43**, 50324-96-4; **43** 3-oxo derivative, 2352-19-4; **44**, 50324-98-6; **44** 3-oxo derivative, 434-22-0; **45**, 50325-00-3; **45** 3-oxo derivative, 63-05-8; *syn*-**46**, 50325-01-4; **46** 3-oxo derivative, 57-83-0; **47**, 50325-02-5; **48** (R_2 = α-OAc), 50325-03-6; **48** (R_2 = α-OAc) 3-oxo derivative, 2268-98-6; **48** (R_2 = α-OH), 50325-05-8; **48** (R_2 = α-OH) 3-oxo derivative, 80-75-1; *syn*-**49**, 50276-50-1; *anti*-**49**, 50325-07-0; **49** 3-oxo derivative, 68-96-2; *syn*-**50**, 50276-49-8; *anti*-**50**, 50324-68-0; **50** 3-oxo derivative, 302-23-8; **51**, 50325-08-1; **51** 3-oxo derivative, 56-47-3; *syn*-**52**, 50325-10-5; *anti*-**52**, 50325-12-7; **52** 3-oxo derivative, 50-23-7; **53**, 50325-14-9; **54**, 50323-53-0; **54** 3-oxo derivative, 1816-78-0; **55**, 50323-55-2; **55** 3-oxo derivative, 71-58-9; **56**, 50323-57-4; *syn*-**57**, 50323-58-5; *anti*-**57**, 50278-60-9; **57** 3-oxo derivative, 595-33-5; **58**, 50323-60-9; **58** 3-oxo derivative, 846-46-8; **59**, 50323-62-1; **59** 3-oxo derivative, 521-18-6; **60**, 50323-64-3; **61**, 50323-65-4; **61** 3-oxo derivative, 521-11-9; **62**, 50323-67-6; *N*-(2-hydroxyethyl)hydroxylamine oxalate, 50323-86-9; *N*-methylhydroxylamine oxalate, 7665-00-1; *N*-methylhydroxylamine hydrochloride, 593-56-6; *N*-(2-hydroxyethyl)hydroxylamine hydrochloride, 24395-54-8.

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(17) All melting points were determined in open capillary tubes on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 521 grating spectrophotometer using KBr pellets. Ultraviolet spectra were recorded on a Perkin-Elmer 350 spectrophotometer in ethanol. Nmr spectra were run on a Varian A-60A with Me_4Si as an internal standard. The standard drying agent used was $MgSO_4$ and the solvents were removed under vacuum on a rotary evaporator.

Steroidal Alkaloids. CLXI.[1] Stereospecific Synthesis of (22*R*)- and (22*S*)-22-Aminocholesterol

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The stereospecific syntheses of the two epimeric 22-aminocholesterols from the two known epimeric 22-hydroxycholesterols *via* tosylate → azide → amine are described. These amines are also obtained by the reduction of 22-ketocholesterol oxime.

Recent reviews,[2,3] describing the biogenesis of pregnenolone from cholesterol, feature the importance of a C-22 hydroxylated species. Therefore it seemed interesting to synthesize 22-substituted derivatives of cholesterol in

Table I

Concn of 3, M	Change, % Nonsaponifiable lipids Acetate	Nonsaponifiable lipids Mevalonate	Cholesterol Acetate	Cholesterol Mevalonate
1×10^{-4}	−3	+19	−99	−95
1×10^{-5}	+4	+10	−77	−66
1×10^{-6}	+7	+2	−20	−10

order to study their activity on the biogenesis of cholesterol.

As starting material we used the known 22-ketocholesterol (1) prepared according to a published procedure[4] from methyl 3β-acetoxy-23,24-bisnorchol-5-enate. The benzoate of 1 was reduced with sodium borohydride and the mixture of the two isomeric alcohols 5 (22*R*) and 7 (22*S*) was separated[5] by fractional crystallizations and transformed into their tosylates. The 22*S*-tosylate 8 was displaced with sodium azide in hexamethylphosphoric triamide at room temperature, giving a quantitative yield of the azide 12 (22*R*) with inversion of configuration. Under these conditions, no elimination products could be observed. However, when the 22*R*-tosylate 6 was treated in identical fashion, the 22*S*-azide **9a** (85%), together with a small amount of elimination product **9b**[6,7] (15%), was obtained. The reduction of these azides **9a** and **12** with lithium aluminum hydride in ether under reflux yielded the desired 22*S*-(**10**) and 22*R*-amines (**13**).

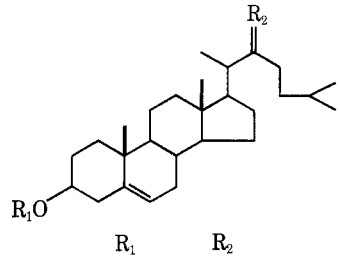
It has already been pointed out by Barton, *et al.*,[8] that the C-22 oxygenated sterols of the 22*S* configurations are more levorotatory than their analogs of the 22*R* configuration. We have observed similar properties for 22*R*- and 22*S*-sterols bearing a nitrogen substitution at C-22. Having established the absolute configuration of the 22-aminocholesterols, we were interested in the determination of the stereoselectivity of the reduction of 22-ketocholesterol (1) and of 22-ketocholesterol oxime (3) by lithium in ethylamine. At this point it should be reiterated that a number of authors[9-11] have claimed that the 22-oxo group of 22-oxocholesterol is particularly hindered and unable to react with the common carbonyl reagents. We have now obtained the crystalline oxime 3 and the hydrazone 4 of 22-oxocholesterol (1). The reduction of the oxime 3 with lithium–ethylamine led to a mixture of the epimeric amines 22*R* (**13**) and 22*S* (**10**) in a ratio of 3:2, respectively. The stereospecific synthesis described above allows the unambiguous assignment of configuration to the reduction products of the oxime. The alcohol amines **10** and **13** were selectively benzoylated at the amino function to give the amides **15** and **16**, respectively. The nmr spectra of the (22*R*)- and (22*S*)-*N*-benzoates reveal a difference in their 21-methyl resonance. The doublet assigned to the 21-methyl, which is only partially visible, is shifted downfield for the (22*S*)-benzamide to 63 Hz, while the 22*R* product gives a value of 59 Hz. The reduction of 22-ketocholesterol (1) with lithium in ethylamine gives a mixture of epimeric alcohols 22*R* and 22*S* in a ratio of 3:2[12] (separable on silver nitrate treated silica thin layer plates).

The mass spectra of C-22 nitrogen-substituted compounds were studied. It is known[13] that the basic nitrogen of amines readily retains the positive charge and induces fragmentation of the C–C bond at the α position to the nitrogen. Thus a base peak of *m/e* 100 is obtained from the spectra of the 22-aminocholesterols. However, the hydrazone 4 does not fragment in this fashion, but undergoes two McLafferty rearrangements. The first rearrangement leads to the ion *m/e* 358, which undergoes a second rearrangement to give the base peak of *m/e* 86. The same holds for the oxime 3, exhibiting the analog peaks of *m/e* 359 and 87, respectively.

Assays[14] for inhibition of cholesterogenesis reveal the oxime 3[15] to be an active inhibitor at 1×10^{-5} but not at 1×10^{-6} *M*. The data (Table I) show that the site of inhibition was at a late stage in the biosynthetic pathway, *i.e.*, after the formation of squalene.

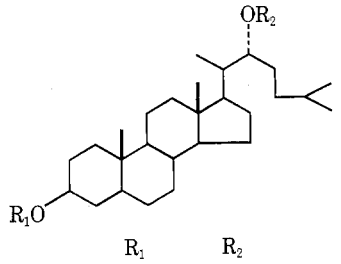
Experimental Section

Melting points are uncorrected. The rotations were measured in chloroform solution (*c* ~1). The nmr spectra were obtained in



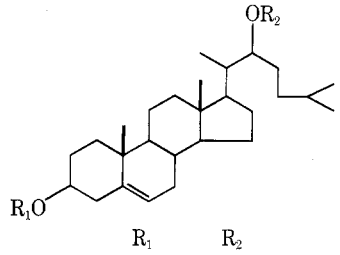
	R_1	R_2
1	H	O
2	COC_6H_5	O
3	H	NOH
4	H	NNH_2

(22*R*)



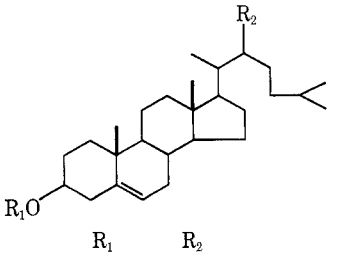
	R_1	R_2
5	COC_6H_5	H
6	COC_6H_5	OTs

(22*S*)

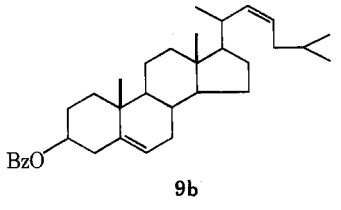


	R_1	R_2
7	COC_6H_5	OH
8	COC_6H_5	OTs

(22*S*)

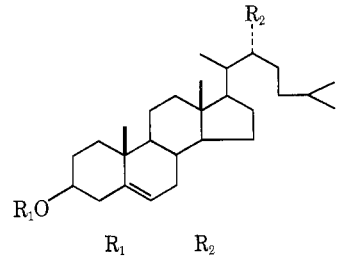


	R_1	R_2
9a	COC_6H_5	N_3
10	H	NH_2
11	H	NHAc
15	H	$NHCOC_6H_5$



9b

(22*R*)



	R_1	R_2
12	COC_6H_5	N_3
13	H	NH_2
14	H	NHAc
15	H	$NHCOC_6H_5$

deuteriochloroform solution with tetramethylsilane as the internal standard on a 60-MHz Varian A-60 spectrometer. The chemical shifts are expressed in parts per million. The mass spectra were obtained on an Associated Electronics Industry AEI MS 9 spectrometer. The microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

22-Oxocholesterol Oxime (3). To a solution of 1.411 g of 22-ketocholesterol (1) in 10 ml of pyridine was added 2 g of hydroxylamine hydrochloride, and the solution was heated to 90° for 36 hr. After cooling, the oxime was extracted with methylene chloride, which gave 1.420 g of crude product. After tlc and crystallization from ethanol there was obtained 609 mg of oxime: mp 178°; $[\alpha]^{22}D$ −73°; nmr δ 0.72 (18-CH_3), 1.01 (19-CH_3), 1.11 (doublet, J = 7 Hz, 21-CH_3); mass spectrum m/e (rel intensity) M 415 (48), M − 17 (53), M − C_3H_7 372 (56), M − C_4H_8 359 (22), M − C_4H_8 − 15 334 (33), C_4H_9ON 87 (100).

Anal. Calcd for $C_{27}H_{45}NO_2$: C, 78.02; H, 10.91; N, 3.37. Found: C, 78.30; H, 10.88; N, 3.45.

(22R)-22-Azidocholesterol Benzoate (12). To the solution of 200 mg of (22S)-22-hydroxycholesterol 3-benzoate (7) in 3 ml of pyridine was added 100 mg of toluenesulfonyl chloride and the solution was kept at 23° for 4 days. After addition of water the tosylate 8 was extracted with methylene chloride and worked up as usual.[16] The 250 mg of crude product was dried in a desiccator over phosphorus pentoxide and then added to the solution of 1 g of sodium azide in 30 ml of freshly distilled hexamethylphosphoric triamide. After the mixture was stirred for 3 hr at room temperature, water was added and the azide was extracted with benzene. The benzene layer was dried and evaporated *in vacuo*. The crude residue of 195 mg gave mp 174°. An analytical sample was obtained after two recrystallizations from acetone which gave 95 mg: mp 179°; $[\alpha]^{23}D$ +6°; ir 2084 cm^{-1} (N_3); mass spectrum m/e (rel intensity) M − C_6H_5 COOH 409 (100), M − C_5H_{11} 460 (4), M − C_5H_{11} − N_2 432 (14), M − C_6H_5COOH − $C_6H_{12}N_3$ 283 (11), $C_6H_{12}N$ 98 (81).

Anal. Calcd for $C_{34}H_{49}O_2N_3$: N, 7.90. Found: N, 7.64.

(22R)-22-Aminocholesterol (13). To the solution of 86 mg of azide 12 in 6 ml of ether was added 60 mg of lithium aluminum hydride and the mixture was heated under reflux for 2 hr. After usual[16] work-up there was obtained 71 mg of crude amine, which was recrystallized from ether–hexane. A sample gave a single spot on a silica tlc developed with ethanol. The pure material had mp 140°, $[\alpha]^{22}D$ −37°, mass spectrum M 401 (trace), m/e 100.

Anal. Calcd for $C_{27}H_{47}ON$: C, 80.73; H, 11.80; N, 3.49. Found: C, 80.43; H, 11.80; N, 3.27.

(22S)-22-Azidocholesterol Benzoate (9a). This compound was prepared under similar conditions as described for the preparation of its epimer 12. From 144 mg of alcohol 5 there was obtained 107 mg of crude azide, which upon purification gave 62 mg of pure 22S-azide 9a and 11 mg of olefin 9b, originating from the elimination of the 22R-tosylate 6. The azide 9d, recrystallized from acetone–methanol, gave material which appeared uniform on tlc, and had mp 166°; $[\alpha]D$ −19°; ir 2084 cm^{-1} (N_3); mass spectrum similar to that of its 22R epimer 12.

Anal. Calcd for $C_{34}H_{49}O_2N_3$: N, 7.90. Found: N, 7.64.

The olefin 9b, which was not further characterized, showed in its nmr spectrum three olefinic protons between 5.20 and 5.65 ppm (H-6, H-22, and H-23); mass spectrum m/e (rel intensity) M − C_6H_5COOH 366 (100), M − C_6H_5COOH − C_8H_{15} 255 (21).

(22S)-22-Aminocholesterol (10). This compound was produced as described for 13. The 22S-amine 10 was recrystallized from petroleum ether (bp 30–60°), mp 144°, $[\alpha]D$ −45°. On silica thin layer plates (methanol) the 22S-amine 10 is less polar than the 22R-amine 13. The mass spectrum of 10 is very similar to that of 13 while their nmr spectra are identical.

Anal. Calcd for $C_{27}H_{47}ON$: N, 3.49. Found: N, 3.31.

(22S)-22-Benzoylaminocholesterol (15). To the solution of 50 mg of the amine 10 in 2 ml of benzene and 2 ml of methylene chloride was added 15 ml of a 5% aqueous Na_2CO_3 solution. While stirring, 0.3 ml of benzoyl chloride was added, and the mixture was stirred magnetically for 1 hr. The methylene chloride extract gave 60 mg of amide 15, which when recrystallized from benzene gave a single spot on tlc: mp 202°; $[\alpha]D$ −45°; nmr δ 0.72 (18-CH_3), 1.0 (19-CH_3), 1.05 (doublet, partially visible, 21-CH_3); mass spectrum m/e (rel intensity) M 505 (2), M − C_6H_{11} 434 (2), $C_6H_5CONHC_6H_{12}$ 204 (100), C_6H_5CO 105 (7).

(22R)-22-Benzoylaminocholesterol (16). This was prepared in the same fashion as 15. The amine 13 (50 mg) gave the amide 16 (55 mg), which was recrystallized from benzene–ethyl acetate and appeared pure on tlc: mp 215°; $[\alpha]D$ −25°; nmr δ 0.70 (18-CH_3), 1.0 (19-CH_3), 0.97 (partially visible doublet, 21-CH_3); the mass spectrum very closely resembles the spectrum of cholesterol 15.

(22S)-22-Acetylaminocholesterol (11). To the saturated methanolic solution of 70 mg of the amino alcohol 10 a few drops of acetic anhydride (slight excess) was added. The product was crystallized from methanol to give 52 mg of amide, single spot on tlc: mp 256°; $[\alpha]D$ −48°; nmr δ 0.70 (18-CH_3), 1.02 (19-CH_3), 0.95 (partially visible doublet, 21-CH_3); mass spectrum m/e (rel intensity) M 443 (0.5), M − C_5H_{11} 372 (0.5), $CH_3CONHC_6H_{12}$ 142 (100), 142 − 42 = 100 (36).

(22R)-22-Acetylaminocholesterol (14). This compound was prepared as described for 11. The amide crystallized from methanol: mp 215°; $[\alpha]D$ −31°; nmr δ 0.68 (18-CH_3), 1.02 (19-CH_3), 0.92 (partially visible doublet, 21-CH_3); mass spectrum very similar to that of its epimer 11.

(22R)- and (22S)-22-aminocholesterol (10 and 13). To the solution of 315 mg of 22-ketocholesterol oxime (3) in 20 ml of ethylamine, 200 mg of lithium was added in small portions at a rate which maintained the blue color. The excess lithium was destroyed with a few drops of methanol after 2 hr. The thus formed amines were extracted with methylene chloride and the organic phase was washed with water and saline and finally evaporated to dryness *in vacuo*. The residue gave 306 mg of crude amines which could be separated by tlc into 108 mg of 22R-amine 13 and 75 mg of 22S-amine 10, both identical with the amines obtained by stereospecific synthesis described above: 10, mp 144°, $[\alpha]D$ −45°; 13, mp 142°+ $[\alpha]D$ −37°.

22-Ketocholesterol Hydrazone (4). The solution of 360 mg of ketone 2 and 1 ml of hydrazine hydrate in 3 ml of absolute ethanol was heated under reflux for 48 hr. The extraction with methylene chloride gave 370 mg of crude hydrazone, which contained a trace of starting material. The mixture was purified by thin layer chromatography, which gave 209 mg of hydrazone as a uniform band. Recrystallization from hexane gave 135 mg of 4: mp 146°; $[\alpha]D$ −68°; nmr δ 0.72 (18-CH_3), 1.01 (19-CH_3), 1.14 (doublet, partially visible, 21-CH_3); mass spectrum m/e (rel intensity) M 414 (6), M − 15 399 (6), M − C_3H_7 371 (10), M − C_4H_8 358 (15), M − C_4H_8 − 15 343 (11), $C_4H_{10}N_2$ 86 (100).

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Registry No.—1, 19243-30-2; 2, 17976-38-4; 3, 50921-59-0; 4, 50921-60-3; 5, 17954-94-8; 7, 17954-95-9; 9a, 50921-61-4; 10, 50921-62-5; 11, 50921-63-6; 12, 50921-64-7; 13, 50921-65-8; 14, 50921-66-9; 15, 50921-67-0; 16, 50921-68-1; hydroxylamine hydrochloride, 5470-11-1.

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(13) W. Vetter, P. Longevialle, F. Khuong-Huu-Lainé, Q. Khuong-Huu, and R. Goutarel, *Bull. Soc. Chim. Fr.*, 1325 (1963).

(14) The cholesterol synthesis was tested *in vitro* by a rat liver homogenate preparation. A pooled liver homogenate was incubated simultaneously with acetate-^{14}C and mevalonate-^{3}H in the presence of different concentrations of 22-oxocholesterol oxime and the incorporation into nonsaponifiable lipids and cholesterol was measured.
(15) Other compounds in this series have not been assayed as yet.
(16) For procedure compare R. C. Nickolson and M. Gut, *J. Org. Chem.*, **37**, 2119 (1972).

New Monoterpenes from *Artemisia filifolia* (Torrey). Structure, Synthesis, Rearrangements, and Biosynthesis[1a]

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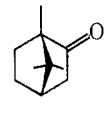
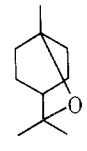
The steam distillate of the leaves and stems of sand sage [*Artemisia filifolia* (Torrey)] contains two new monoterpene lactones, filifolide A and filifolide B. These have been characterized as 1(*R*),5(*S*)-(−)-5-hydroxy-2,2,4-trimethylcyclohex-3-ene-1-carboxylic acid γ-lactone (**8**) and 1(*R*),3(*S*)-(+)-3-hydroxy-2,2,4-trimethylcyclohex-4-ene-1-carboxylic acid γ-lactone (**9**). Other major constituents of the distillate are the cyclobutanone (−)-filifolone, (−)-camphor, 1,8-cineole, and isophorone. Minor constituents are piperitenone, borneol, (−)-verbenone, and 3,3,5-trimethylcyclohex-2-ene-1,4-dione (**13**). The chloroform extract of the plant contains the monoterpene 1(*R*)-(+)-5-keto-2,2,4-trimethylcyclohex-3-ene-1-carboxylic acid (**14**), the flavone acacetin, and the sesquiterpene lactone colartin. In addition to the synthesis of lactones **8** and **9**, another new monoterpene lactone was prepared, 2-hydroxy-α,α,3-trimethylcyclopent-3-ene-1-acetic acid γ-lactone (**2**).

Sand sage [*Artemisia filifolia* (Torrey)] has been used by Hopi Indians and early white settlers as a medicinal plant.[1b] It grows at elevations ranging from 4000 to 6000 ft in the state of Arizona. The strong "cough medicine" fragrance of the plant, particularly after a rainfall, prompted us to investigate the steam distillate of the plant.

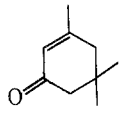
Preliminary studies[2] showed a relatively high (1% wet weight) percentage of steam volatile oil. The major constituents were separated by gas–liquid chromatography and identified as (−)-camphor, 1,8-cineole, and isophorone. The structure of the fourth constituent was subsequently shown[3] to be the cyclobutanone (−)-filifolone.



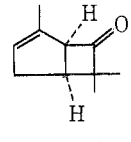
(−)-camphor



1,8-cineole

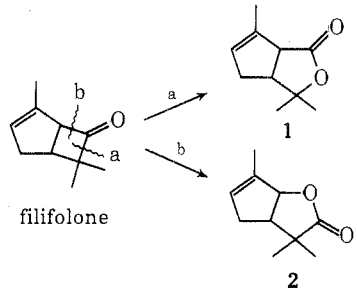


isophorone



(−)-filifolone

A fifth fraction appeared to be a 1:1 mixture of two monoterpene lactones (filifolide A and filifolide B), both having the molecular formula $C_{10}H_{14}O_2$. Catalytic hydrogenation of the lactone mixture gives a neutral and an acid fraction, indicating an allylic lactone system.[4] Structures **1** and **2** were originally proposed for the two lactones on the assumption that these could have arisen by a simple Baeyer–Villiger oxidation of filifolone. The present report is chiefly concerned with the structures of filifolides A and B.

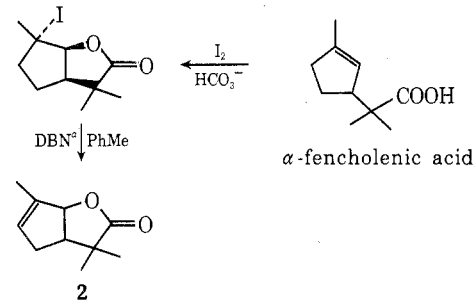


filifolone

1

2

Scheme I
The Synthesis of Lactone 2

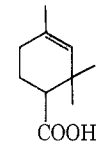


[a] DBN = 1,5-diazabicyclo[4.3.0]non-5-ene.

Results

Lactones. Compound **1** (carvenolide) has been reported by Wallach more than 70 years ago.[5] Its structure was recently confirmed[6] and its nmr spectrum[6] was shown to be different from those of filifolides A and B. Compound **2** had not been previously reported; so its synthesis was carried out, as shown in Scheme I. The spectral data for lactone **2** did not coincide with either filifolide A or B from *A. filifolia;* hence neither structure **1** or **2** was tenable.

A careful reexamination of the hydrogenation reaction gave us the first clue to the structures of filifolides A and B. Surprisingly, both lactones underwent hydrogenolysis to yield two unsaturated carboxylic acids, both $C_{10}H_{16}O_2$, which on further hydrogenation gave the single acid, $C_{10}H_{18}O_2$. Their respective structures were deduced from nmr spectra reported[7] for **3** and **4** and from the hydrogenation product **5**.



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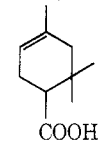
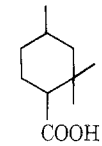


4



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