Steroidal Adducts. VI.[1] Steroids as Probes of the Relative Reactivities of Enophiles and Dienophiles. Reactions of Dicyanoacetylene with Ergosterol Derivatives

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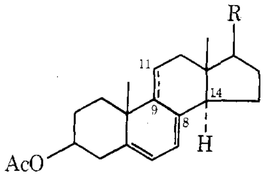
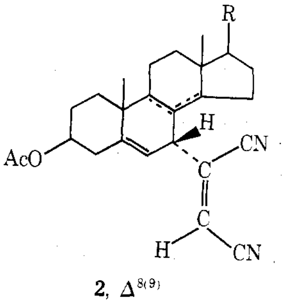
Ergosteryl acetate with dicyanoacetylene gives the two 7α-ene adducts resulting from abstraction of the 9α and 14α hydrogens of the diene; 9(11)-dehydroergosteryl acetate gives both possible ring B Diels–Alder adducts and also the 7α-ene adduct having an 8(14),9(11)-diene system. This ene adduct undergoes allylic rearrangement of the maleonitrile substituent on alumina or silica gel plates. Ergosteryl-B$_3$ benzoate with dicyanoacetylene gives the Diels–Alder adduct only. These three steroids are suggested as convenient substrates for comparative assessment of the reactivities and steric requirements of enophiles and dienophiles.

In previous work,[1,4] steroidal cisoid dienes were found to react with tetracyanoethylene to give products of Diels–Alder addition, ene reaction, dehydrogenation, and/or radical-mediated dimerization, depending on the steroid and the reaction conditions. Steric factors were inferred to be of major importance in determining the outcome of the reactions. To examine this area further, and to make otherwise inaccessible adducts of potential pharmacological significance, we have investigated reactions of three unsaturated steroids with dicyanoacetylene. Our studies also show that steroidal polyenes can serve as sensitive, convenient indicators of the reactivity and steric requirements of enophiles and dienophiles.

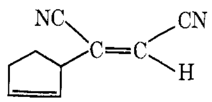
Ergosteryl acetate (1) with dicyanoacetylene gave two 1:1 adducts. The less soluble, minor adduct, mp 247–248°, is assigned the ene-adduct structure 2 from the following data. The uv spectrum [λ_{max} 227 nm (ϵ 13,100)] was in good accord with that of the monosubstituted maleonitrile 3 [λ_{max} 229 nm (ϵ 14,400)],[5] and the nmr spectrum showed the maleonitrile hydrogen as a singlet at τ 4.20 (*cf.* 3, τ 4.06).[5] A 7α orientation of the maleonitrile substituent is indicated by the singlet signal at τ 6.42 arising from the C-7β proton; Dreiding models suggest that this proton has a dihedral angle of almost 90° with respect to the C-6 proton.[4] This assignment is consonant with mechanistic expectation (assuming a concerted ene reaction), and with earlier work.[1,4,6] That the compound has an 8(9) rather than 8(14) double bond is shown by the nmr spectrum, in which the C-18 and C-19 methyl groups are seen at τ 9.34 and 8.76, respectively, in striking agreement with the values (τ 9.32 and 8.76) observed in an analogous case.[6] Steroids having a $\Delta^{5,8(14)}$ diene system generally show coincident C-18 and C-19 methyl peaks at *ca.* τ 9.10.[6]



1, satd.$^{9(11)}$
7, $\Delta^{9(11)}$



2, $\Delta^{8(9)}$
4, $\Delta^{8(14)}$



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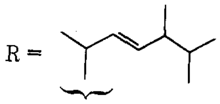
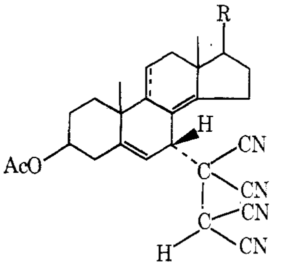
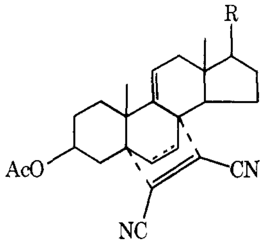


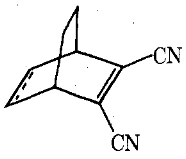
The major, more soluble product, mp 162–164°, from this reaction showed two nearly coincident 3 H singlet signals at τ 9.06, but was otherwise analogous in uv, ir, and nmr spectral characteristics to the minor product. It is therefore assigned the $\Delta^{8(14)}$ structure 4. Adducts 2 and 4 on electron impact showed very similar patterns of fragmentation, in particular the loss of angular methyl groups, acetic acid, and the side chain at C-17. In contrast to the tetracyanoethylene adducts 5 and 6,[1] the C-7 side chain was retained during fragmentation of 2 and 4; in particular, no electron impact induced retro ene reaction was seen (*cf.* ref 1, 4). These reactions are qualitatively analogous to those between 7-dehydrocholesteryl acetate and the dienophiles diethyl diazodicarboxylate[7] and dimethyl acetylenedicarboxylate.[8]



5, satd.$^{9(11)}$
6, $\Delta^{9(11)}$



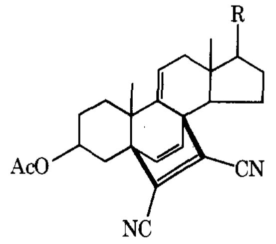
8, $\Delta^{6,7}$
10, satd.^{6,7}



9, $\Delta^{5,6}$
11, satd.^{5,6}

With 9(11)-dehydroergosteryl acetate (7), dicyanoacetylene gave three 1:1 adducts. The major product, mp 237–239°, was assigned structure 8, that a Diels–Alder adduct arising from α approach of the dienophile, from the following data. The uv spectrum [λ_{max} 214, 244 nm (ϵ 9900, 6875)], although somewhat different from that reported[9] for the less strained model compound 9 [λ_{max} 237, 266 s nm (ϵ 8700, 700] suggested charge-transfer interactions such as those found in 9 and related compounds.[9] The nmr spectrum showed an AB system at τ 3.56 and 3.94 (J_{AB} = 7 Hz) from the vinyl protons at C-6 and C-7, strongly reminiscent of signals in the spectra of other ring B Diels–Alder adducts.[10-13] Support for the proposed α

orientation of the dicyanovinyl bridge (expected in view of the observed tendency of tetracyanoethylene and dicyanoacetylene to approach the steroid from the α face) was given by hydrogenation of 8 (Pt, 1 mol of H_2) to compound **10**, in which the nmr resonances of the C-18 and C-19 methyl groups are shifted characteristically downfield. This shift is analogous to others observed previously.[10,13] The uv spectrum of **10** [λ_{max} 242 nm (ϵ 7950)] was in accord with that of the model compound **11**[9] [λ_{max} 238 nm (ϵ 12,000)]. The bathochromic shift of 4 nm in **10** arises from the extra strain in the bicyclo[2.2.2] system, in agreement with the literature.[9,14] In view of the reaction of a steroidal 5,7,9(11)-triene with tetrafluorobenzyne to give both α and β Diels–Alder adducts,[13] we searched for the analogous β adduct from this reaction, and isolated it as a very minor product, compound **12**, mp 196°. The uv spectrum [λ_{max} 215, 248 nm (ϵ 8450, 6170)] was comparable with that of **8**, and the nmr spectrum was consonant with the assigned structure.



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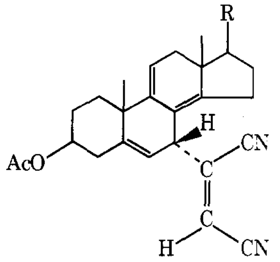

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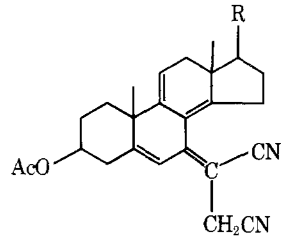

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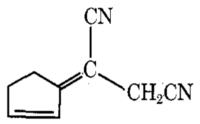
The major by-product from this reaction, after removal of the predominant Diels–Alder adduct **8**, was an adduct, mp 168–169°. The uv spectrum [λ_{max} 227.5, 283 nm (ϵ 8300, 10,950)] indicated maleonitrile and 8(14),9(11)-diene chromophores. The suggested structure **13** was supported by the nmr spectrum, although the angular methyl group signals were not assignable unequivocally.

During preparative layer chromatography of adduct **13**, the presence of a fourth product was observed. This was found to be produced from **13** by contact with silica gel, and on isolation was shown to be an isomeric compound, mp 150–151°, for which structure **14** is proposed. The uv spectrum showed λ_{max} 285 nm (ϵ 12,450). This is not, to our knowledge, diagnostic as such for the unusual chromophore in **14**, yet is reasonable for a ring C diene with cross conjugation in the B ring. The nmr spectrum shows the C-6 proton as a downfield singlet (τ 3.59), with the other three vinyl protons as a multiplet at τ 4.75. A 2 H singlet at τ 6.66 is assigned to the equivalent methylene protons at C-2′. A similar isomerization was noticed by Gassman and Mansfield,[5] alumina rapidly converting **3** into **15** [λ_{max} 265 nm (ϵ 17,100)]. Interestingly, adducts **2** and **4** were stable to alumina, silica gel, or warm acetic acid and were not converted into analogous succinonitrile derivatives.

The mass spectra of the Diels–Alder adducts **8** and **12** were remarkably similar to each other, and showed the bicyclo[2.2.2] system in these compounds to be very stable to electron impact. No peaks were observed for either possible retro Diels–Alder reaction (loss of dicyanoacetylene or acetylene). The most prominent peaks were those representing loss of acetic acid and/or the C-17 side chain. The same was true for the remarkably similar spectra of the adducts **13** and **14**. Clearly the dicyanovinyl moiety in these compounds is much more resistant to cleavage in the mass spectrometer than the tetracyanoethyl group in the compounds previously studied.[1] The dihydro adduct **10**, however, shows peaks in the mass spectrum at M·+ (*m/e* 514) and *m/e* 471 and 428. These, separated by 43 and 43 mass units, probably represent the loss of CH_3CO, and CH_3 plus ethylene. The loss of ethylene here would be analogous to its pyrolytic elimination during the aromatization of **16**.[15]

With ergosteryl-B_3 benzoate (**17**), dicyanoacetylene gave a single 1:1 adduct, which is assigned structure **18** from



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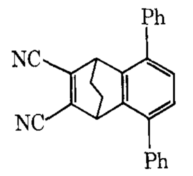

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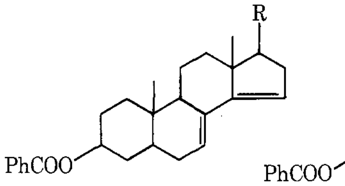

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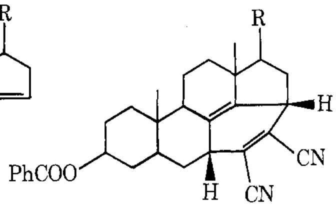
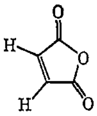
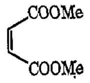
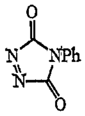
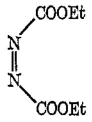
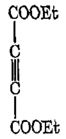
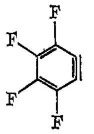
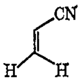
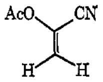
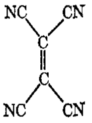


18

the absence of any vinyl proton peaks (other than from the C-17 side chain) in the nmr spectrum. The stereochemistry is suggested in the light of the probable approach of the dienophile from the α face of the steroid. It is interesting that the mass spectrum of this compound indicates neither retro Diels–Alder reaction nor aromatization of the dihydrobenzene ring on electron impact. This may be owing to considerable steric strain in the pentacyclic system, which, from models, may be aggravated on aromatization.

The reactions between dicyanoacetylene and the three steroids described above join our previous work[1,4] and other published reactions between steroidal polyenes and a variety of enophiles and dienophiles. Table I summarizes these results. In general the main influences on the reactions appear to be the steric requirements of the reacting addend and the steric accessibility of the polyene system. For example, the very accessible diene system of ergosteryl-B_3 benzoate reacts with maleic anhydride and, so far as is known, other addends to give Diels–Alder adducts. As the diene is varied with respect to substitution pattern and availability of allylic hydrogens, both ene reactions and Diels–Alder reactions are seen, sometimes together. For the Diels–Alder reactions, only tetrafluorobenzyne and dicyanoacetylene give both stereoisomeric ring B adducts, and then only with the 5,7,9(11)-triene system. Two other factors than these steric influences should be mentioned: first, differences in addend reactivity of electronic origin, such as for benzyne and tetrafluorobenzyne,[13] and second, secondary steric effects such as the length of the C-17 side chain.[27] In our view, these factors will usually be superimposed on the main steric influences. In general, a Diels–Alder reaction with a 5,7-diene

Table I
Reactions of Enophiles and Dienophiles with Steroidal Polyenes

Addend	Steroid		
	$\Delta^{5,7}$-Diene	$\Delta^{5,7,9(11)}$-Triene	$\Delta^{7,14}$-Diene
O_2	α Diels–Alder[16,17]	α Diels–Alder[16]	
SO_2	α Diels–Alder[18,19]		
	α Diels–Alder and ene adducts from 9α- and 14α-H's[11,20]	α Diels–Alder[10,21]	Diels–Alder adducts[22,23]
		α Diels–Alder[24]	
	α Diels–Alder[12]		
	Ene adduct from 9α H[7,25] and 14α-H;[27] small amount of α Diels–Alder adduct also[26]	α Diels–Alder[10,25]	
	Ene adduct from 9α-, 14α-H's[8]	α Diels–Alder[10]	
NC—C≡C—CN (present work)	Ene adducts from 9α-, 14α-H's	α and β Diels–Alder adducts; ene adduct from 14α-H	Diels–Alder adduct
	Ene adducts from 9α-, 14α-H's[13]		
	α Diels–Alder and ene adduct from 9α-H[13]	α and β Diels–Alder adducts[13]	
	Ene adducts from 9α-, 14α-H's[6]		
	Ene adducts from 9α-, 14α-H's[6]		
	Ene adduct from 14α-H (initial product)[1,4,20]	Ene adduct from 14α-H[1,4]	Diels–Alder adduct[1,4]

system, which is tetrasubstituted and flanked by the 9α and 14α hydrogens, will require a reactive addend of small steric requirement, *e.g.*, 4-phenyl-1,2,4-triazoline-3,5-dione, oxygen, or (to a lesser extent) maleic anhydride, but not tetracyanoethylene. Similar comparisons may be made for the other reactions listed in Table I.

Table I shows how the comparative reactivities and steric requirements of addends affect their reactions with three types of steroidal polyene substrates. At this time it has gaps, particularly for the 7,14-diene system, but these do not lessen its usefulness in assessing most addends, which show considerable variation with the 5,7-diene and 5,7,9(11)-triene systems. (Preliminary data suggest that the 7,14-diene system may be applied to comparisons of α and β, and endo and exo, product formations for Diels–Alder reactions of sterically bulky addends.)[23] The three polyene types in Table I are represented in our work by the steroids **1**, **7**, and **17**, which are readily accessible from commercially available ergosterol. Structures may now be assigned to the adducts almost entirely by spectroscopic means, the uv and nmr spectra being particularly revealing. Therefore one may readily use the reactions of a new addend with steroids **1**, **7**, and **17** to assess its comparative reactivity and steric requirements in a more direct, sensitive, and convenient manner than previously possible.

Experimental Section

Microanalyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Dicyanoacetylene. This was prepared by dehydration of acetylene dicarboxamide with phosphorus pentoxide as described by Cookson and coworkers.[9] Small batches (~1 g) of the freshly prepared volatile compound were quickly weighed and dissolved in sodium-dried benzene. Aliquots were then added to solutions of the steroids in the experiments below, so that the mole ratio of dicyanoacetylene to steroid was in all experiments ~1.25:1.

Reaction of Dicyanoacetylene with Ergosteryl Acetate (1). The dicyanoacetylene solution was added to a solution of ergosteryl acetate (1.5 g) in sodium-dried benzene. The yellow coloration initially observed darkened to red during reflux for 24 hr (N_2). Removal of solvent under reduced pressure gave a crude solid, which was dissolved in the minimum amount of chloroform. Addition of methanol caused crystallization of the adduct **2** (610 mg, 35%), 3β-acetoxy-7α-(*cis*-1′,2′-dicyanovinyl)ergosta-5,8(9),22-triene, which was crystallized for analysis from methanol as needles: mp 247–248°; $[\alpha]^{23}_{D}$ −98° (*c* 1.0, $CHCl_3$); uv λ_{max} (EtOH) 226–228 nm (ε 13,100), 266 s; nmr ($CDCl_3$) τ 4.20 (1 H, s, C-2′ H), 4.80–4.92 (3 H, m, C-6, -22, -23 H), 5.40 (1 H, m, C-3α H), 6.42 (1 H, s, C-7 H), 8.05 (3 H, s, CH_3COO–), 8.76 (3 H, s, C-19 H's), 9.34 (3 H, s, C-18 H's); ir (KBr) 2193 cm^{-1} (–CN). *Anal.* Calcd for $C_{34}H_{46}N_2O_2$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.29; H, 8.98; N, 5.37. Mass spectrum *m/e* (rel intensity) M^+ 514 (10), 499 (5), 471 (6), 455 (40), 454 (100), 440 (12), 439 (38), 429 (8), 416 (7), 415 (8), 412 (8), 411 (12), 401 (6), 389 (13), 388 (8), 387 (24), 385 (12), 378 (11), 377 (24), 376 (6), 370 (11), 369 (12), 362 (8), 357 (8), 356 (8), 355 (8), 330 (28), 329 (85), 302 (19), 287 (17), 228 (38), 195 (31), 180 (30), 167 (29), 157 (29), 149 (83), 125 (68).

The mother liquor after removal of adduct **2** was concentrated under reduced pressure, and a little water was added slowly, causing crystallization of the crude major adduct **4** (1.05 g, 60%). Several recrystallizations from heptane gave analytically pure **4**, 3β-acetoxy-7α-(*cis*-1′,2′,-dicyanovinyl)ergosta-5,8(14),22-triene, as needles: mp 162–164°; $[\alpha]^{23}_{D}$ −280° (*c* 1.0, $CHCl_3$); uv λ_{max} (EtOH) 226–228 nm (ε 15,400); nmr ($CDCl_3$) τ 4.27 (1 H, d, *J* = 1.2 Hz, C-2′ H), 4.72–4.88 (3 H, m, C-6, -22, -23 H), 5.4 (1 H, m, C-3α H), 6.42 (1 H, broad s, C-7 H), 8.00 (3 H, s, CH_3COO–), 9.06 (6 H, s, C-18, -19 H). *Anal.* Calcd for $C_{34}H_{46}N_2O_2$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.37; H, 8.94; N, 5.40. Mass spectrum *m/e* (rel intensity) M^+ 514 (3), 499 (9), 484 (4), 470 (4), 455 (12), 454 (100), 439 (6), 415 (4), 411 (4), 384 (6), 377 (5), 376 (5), 330 (11), 329 (18), 302 (10), 149 (21), 125 (33).

Reaction of Dicyanoacetylene with 9(11)-Dehydroergosteryl Acetate (7). The reaction was performed as described for ergosteryl acetate, using 9(11)-dehydroergosteryl acetate[28] (1.0 g). After heating under reflux overnight (N_2), the solution was concentrated under reduced pressure. Addition of methanol caused crystallization of crude adduct **8**, 3β-acetoxy-1′,2′-dicyano-5α,8α-ethenoergosta-6,22,1′-triene (760 mg, 65%), which was recrystallized from methanol to give analytically pure material as fine, long needles: mp 237–239°; $[\alpha]^{23}_{D}$ −80.5° (*c* 1.0, $CHCl_3$); λ_{max} (EtOH) 214, 244 nm (ε 9900, 6875); nmr ($CDCl_3$) τ 3.56, 3.94 (2 H, AB q, J_{AB} = 7 Hz, C-6, -7 H), 4.50 (2 H, m, C-11, 3α H), 4.77 (2 H, m, C-22, -23 H), 7.95 (3 H, s, CH_3COO–), 8.84 (3 H, s, C-19 CH_3), 9.29 (3 H, s, C-18 CH_3). *Anal.* Calcd for $C_{34}H_{44}N_2O_2$: C, 79.64; H, 8.65; N, 5.46. Found: C, 79.69; H, 8.65; N, 5.40. Mass spectrum *m/e* (rel intensity) M^+ 512 (11), 470 (3), 469 (5), 454 (9), 453 (39), 452 (100), 438 (5), 410 (6), 387 (9), 386 (9), 385 (7), 355 (4), 354 (3), 353 (3), 328 (12), 327 (29), 133 (57), 125 (57).

After removal of as much of the above compound as possible, the mother liquor was concentrated to half volume, heated to boiling, and slowly diluted with water till crystallization began. The crude adduct **13**, 3β-acetoxy-7α-(*cis*-1′,2′-dicyanovinyl)ergosta-5,8(14),9(11),22-tetraene (150 mg, 13%), was filtered off and recrystallized either from 50% aqueous methanol or benzene–light petroleum as small, flat needles: mp 168–169°; $[\alpha]^{23}_{D}$ −270° (*c* 1.0, $CHCl_3$); λ_{max} (EtOH) 227.5, 283 nm (ε 8300, 10,950); nmr ($CDCl_3$) τ 4.18 (1 H, d, *J* = 1 Hz, C-2′ H), 4.7 (3 H, m, C-11, -22,-23 H), 5.33 (1 H, m, C-3α H), 6.40 (1 H, m, C-7β H), 7.98 (3 H, s, CH_3COO–), C-18 and C-19 signals not assigned. *Anal.* Calcd for $C_{34}H_{44}N_2O_2$: C, 79.64; H, 8.65; N, 5.46. Found: C, 79.59; H, 8.70; N, 5.24. Mass spectrum *m/e* (rel intensity) M^+ 512 (7), 455 (38), 454 (100), 453 (20), 452 (45), 439 (6), 411 (5), 387 (6), 384 (6), 329 (31), 303 (10), 276 (9), 133 (16), 125 (46).

The residue from removal of adducts **8** and **13** was chromatograhed on a 2.0-mm preparative SiO_2 gel plate in benzene. During development, conversion of the ene adduct **13** to the isomer **14** (see below) was observed. A further, stable band was excised, powered, and extracted (Soxhlet, chloroform) to give, after crystallization from heptane containing a little benzene, 3β-acetoxy-1′,2′-dicyano-5β,8β-ethenoergosta-6,22,1′-triene (**12**, 23 mg, 2%) as needles: mp 196°; $[\alpha]^{23}_{D}$ +6° (*c* 1.0, $CHCl_3$); λ_{max} (EtOH) 215, 248 nm (ε 8450, 6170); nmr ($CDCl_3$) τ 3.40, 3.59 (2 H, AB q, J_{AB} = 7 Hz, C-6, -7 H), 4.26 (1 H, d of d, *J* = 6, 2 Hz, C-11 H), 4.48 (2 H, m, C-22, -23 H), ~4.7 (1 H, m, C-3α H), 7.92 (3 H, s, CH_3COO), 8.77, 9.30 (2 × 3 H, probably C-19, C-18 CH_3's). *Anal.* Calcd for $C_{34}H_{44}N_2O_2$: C, 79.64; H, 8.65; N, 5.46. Found C, 79.25; H, 8.77; N, 5.08. Mass spectrum *m/e* (rel intensity) M^+ 512 (8), 497 (2), 470 (4), 469 (6), 454 (7), 453 (22), 452 (52), 409 (9), 385 (11), 382 (8), 327 (38), 125 (100).

Isomerization of Ene Adduct 13 to 14. This took place when the ene adduct **13** (100 mg) was placed on 2.0-mm neutral alumina or silica gel preparative layer plates, which were then developed with benzene or 5% acetone–light petroleum. After four or five developments, a pair of indistinctly separated bands was discerned. These were excised, powdered, and extracted (Soxhlet, chloroform), and the extract was concentrated. Fractional crystallization of the product from aqueous ethanol or light petroleum gave pure isomer **14** as small, flat needles (25 mg): mp 150–151°; $[\alpha]^{23}_{D}$ −115° (*c* 1.0, $CHCl_3$); λ_{max} (EtOH) 285 nm (ε 12,450); nmr ($CDCl_3$) τ 3.59 (1 H, s, C-6 H), 4.75 (3 H, m, C-11, -22, -23 H), ~5.37 (1 H, m, C-3α H), 6.66 (2 H, s, C-2′ CH_2), 7.94 (3 H, s, CH_3COO–), C-18, -19 CH_3's not assigned. *Anal.* Calcd for $C_{34}H_{44}N_2O_2$: C, 79.64; H, 8.65; N, 5.46. Found: C, 79.82; H, 8.83; N, 5.23. Mass spectrum *m/e* (rel intensity) M^+ 512 (8), 456 (8), 455 (33), 454 (100), 453 (13), 452 (33), 330 (12), 329 (22), 328 (9) 133 (11), 125 (28).

Catalytic Hydrogenation of Diels–Alder Adduct 8. The adduct (373 mg) in ethyl acetate (50 ml) was hydrogenated at atmospheric pressure with Adams catalyst (150 mg) until 1 mol of hydrogen had been absorbed (24 hr). After filtration of the catalyst and removal of solvent under reduced pressure, the dihydro adduct **10** was crystallized in quantitative yield from methanol as fine needles: mp 207–208°; $[\alpha]^{23}_{D}$ −122° (*c* 1.0, $CHCl_3$); λ_{max} (EtOH) 242 nm (ε 7950); nmr ($CDCl_3$) τ 4.5–4.8 (4 H, m, C-11, -3α, -22, -23 H), 7.98 (3 H, s, CH_3COO), 9.20 (3 H, s, C-18 CH_3), 9.13 (3 H, s, C-19 CH_3). *Anal.* Calcd for $C_{34}H_{46}N_2O_2$: C, 79.33; H, 9.01, N, 5.44. Found: C, 79.34; H, 9.00; N, 5.42. Mass spectrum *m/e* (rel intensity) M^+ 514 (22), 472 (12), 471 (32), 429 (15), 428 (26) 416 (60), 387 (100), 329 (43), 302 (11), 301 (18), 287 (14), 285 (10), 273 (9), 259 (13), 245 (14), 205 (10), 165 (21), 125 (33).

Reaction of Ergosteryl-B_3 Benzoate (17) with Dicyanoacetylene. Ergosteryl-B_3 benzoate[29] (525 mg) in sodium-dried benzene (20 ml) was treated with dicyanoacetylene as above, at 20° for 3 hr and under reflux (N_2) for 30 min. The solution was concentrated somewhat and light petroleum was added to precipitate the crude adduct **18**, 3β-benzoyloxy-1′,2′-dicyano-7α,15α-ethenoergosta-8(14),22,1′-triene. The analytical sample crystallized from benzene–light petroleum as needles: mp 201–202°; $[\alpha]^{23}_{D}$ −112° (*c* 1.0, $CHCl_3$); λ_{max} ($CHCl_3$) 239 nm (ε 6800); nmr ($CDCl_3$) τ 2–3 (5 H, m, C_6H_5COO–), 4.75 (2 H, m, C-22, -23 H), 5.0 (1 H, m, C-3α H), 7.0 (2 H, m, C-7, -15 H), 9.10 (3 H, s, C-19 CH_3), 9.17 (3 H, s, C-18 CH_3). *Anal.* Calcd for $C_{39}H_{48}N_2O_2$: C, 81.21; H, 8.39; N, 4.86. Found: C, 81.12; H, 8.46; N, 4.78. Mass spectrum *m/e* (rel intensity) M^+ 576 (33), 454 (10), 327 (10), 125 (30), 105 (100).

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Registry No.—**1**, 2418-45-3; **2**, 51593-31-8; **4**, 51593-32-9; **7**, 1060-56-6; **8**, 51593-33-0; **10**, 51593-34-1; **12**, 51703-86-7; **13**, 51593-35-2; **14**, 51593-36-3; **17**, 51703-87-8; **18**, 51593-37-4; dicyanoacetylene, 1071-98-3.

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Odoriferous C_{11} Hydrocarbons from Hawaiian *Dictyopteris*

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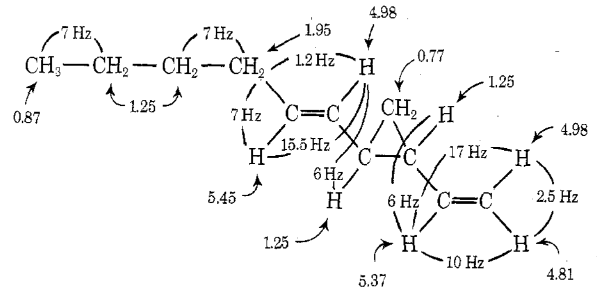
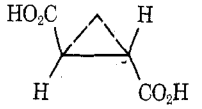
Dictyopterene A [(+)-(*R,R*)-*trans*-1-(*trans*-hex-1′-enyl)-2-vinylcyclopropane], dictyopterene B [(−)-(*R,R*)-*trans*-1-(*trans,cis*-hexa-1′,3′-dienyl)-2-vinylcyclopropane], and dictyopterene C′ [(−)-(R)-6-butycyclohepta-1,4-diene] are the major constituents of the essential oils of the brown Hawaiian seaweeds *Dictyopteris plagiogramma* (Montagne) Vickers and *D. australis* Sonder. Dictyopterene D′ [(+)-(*S*)-6-(*cis*-but-1′-enyl)cyclohepta-1,4-diene], the trans,cis, trans,trans, and cis,trans isomers of 1,3,5-undecatriene, *trans,trans,trans*-2,4,6-undecatriene, *trans,cis,cis*-1,3,5,8-undecatetraene, and *trans,trans,cis*-1,3,5,8-undecatetraene are minor components of the essential oils of Hawaiian *Dictyopteris.*

The odoriferous seaweeds *Dictyopteris plagiogramma* (Montagne) Vickers and *D. australis* Sonder grow abundantly on the shores of the Hawaiian Islands. The essential oils of both species of Hawaiian *Dictyopteris* consist of several identical C_{11} hydrocarbons which can be separated by chromatography.

Dictyopterene A. About 25% of the essential oil is dictyopterene A, an optically active oil which was isolated by gas chromatography of the essential oil or fraction 1 from chromatography of the essential oil on silica impregnated with silver nitrate. A molecular weight of 150 was indicated by mass spectrometry which corresponded to the molecular formula $C_{11}H_{18}$. The 100-MHz proton nmr spectrum, shown in Figure 1a, appeared rather complex but with the aid of double-resonance experiments, could be simplified and completely analyzed and was consistent with a *trans*-1,2-cyclopropane possessing vinyl and *trans*-1-hexenyl substituents.[1,2]



Dictyopterene A had an ultraviolet spectrum similar to that of vinylcyclopropane and its carbon-13 nmr spectrum confirmed the presence of four olefinic (3 CH and 1 CH_2) and seven saturated carbons (2 CH, 4 CH_2, and 1 CH_3). Lemieux oxidation[3] or ozonolysis of dictyterene A afforded formic acid, *n*-valeric acid, and (+)-(*S,S*)-*trans*-cyclopropane-1,2-dicarboxylic acid[4] (1). Isolation of 1 secured the proposed structure and established configuration of dictyopterene A as (+)-(*R,R*)-*trans*-1-(*trans*-hex-1′-enyl)-2-vinylcyclopropane (2).[5]



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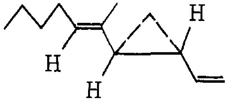

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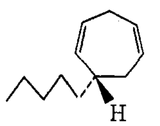

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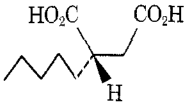
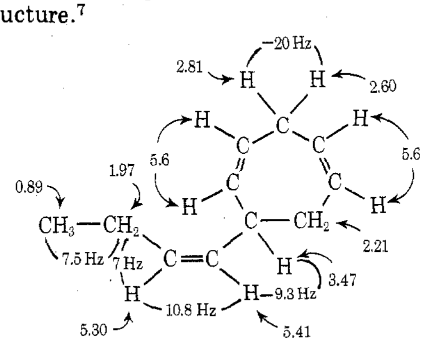


4

Dictyopterene A rearranged above 140° to (+)-(*S*)-6-butylcyclohepta-1,4-diene (3). The absolute configuration of C-6 in 3 was deduced to be *S* as ozonolysis of 3 led to malonic acid and the known (−)-(*S*)-butylsuccinic acid (4).[6]

Dictyopterene B. The major component of the essential oil (50%) was first isolated by preparative gas chromatography as a levorotatory oil showing only end absorption in its ultraviolet spectrum and having a molecular weight of 148 by mass spectrometry ($C_{11}H_{16}$). Analysis of the 100-MHz proton nmr proton was consistent with the following structure.[7]



The carbon-13 nmr spectrum confirmed the presence of six olefinic (6 CH) and five saturated carbons (1 CH, 3 CH_2, 1 CH_3). Ozonolysis of this compound yielded malonic and propionic acids but most importantly partial reduction with diimide gave 3, thus establishing its structure as (−)-(*R*)-6-(*cis*-but-1′-enyl)cyclohepta-1,4-diene (5). The cis geometry of the C=C bond in the butenyl