Isokarounidiol [D:C-Friedooleana-6,8-diene-3α,29-diol]:[1] The First Naturally Occurring Triterpene with a $\Delta^{6,8}$-Conjugated Diene System. Iodine-Mediated Dehydrogenation and Isomerization of Its Diacetate

Toshihiro Akihisa,*[,2] W. C. M. C. Kokke,[3] Yumiko Kimura,[4] and Toshitake Tamura[2]

College of Science and Technology, Nihon University, 1-8, Kanda Surugadai, Chiyoda-ku, Tokyo, 101 Japan, College of Business and Administration, Graduate MBA, St. Joseph's University, Philadelphia, Pennsylvania 19131, and College of Pharmacy, Nihon University, 7-7-1, Narashinodai, Funabashi, Chiba, 274 Japan

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In previous papers[5-7] we reported the isolation and structure determination of karounidiol[5] (3), its 3-*O*-benzoate,[5] 7-oxo-*D*:*C*-friedoolean-8-ene-3α,29-diol[6] (7-oxodihydrokarounidiol), and 5-dehydrokarounidiol[7] (5) from the seeds of *Trichosanthes kirilowii* (Cucurbitaceae). These seeds ("karounin" in Japanese) have been used in Chinese medicine as an antiflammatory agent, a cough medicine, and an expectorant.[8] We want to report here the isolation of a structurally related triterpene, *D*:*C*-friedooleana-6,8-diene-3α,29-diol (isokarounidiol) (1), from the same seed extract and the occurrence of an unexpectedly facile dehydrogenation reaction when we attempted to isomerize the double bonds in isokarounidiol diacetate (2) using iodine in benzene. The products included two triterpenoids with an aromatic B-ring.

Results and Discussion

Isokarounidiol (1) ($C_{30}H_{48}O_2$, M^+ 440; diacetate (2), $C_{34}H_{52}O_4$, M^+ 524) was isolated from the saponified seed extract of *T. kirilowii* by silica gel column chromatography followed by reversed-phase HPLC. Analysis of the spectral data (^1H and ^{13}C NMR, MS, UV) in the manner described previously[5] and comparison with those of compounds previously isolated from the same extract[5-7] indicated that 1 and karounidiol (3) were probably double-bond isomers. The structure of the skeleton of 1 was proved by chemical correlation. Partial catalytic hydrogenation (prereduced PtO_2/EtOH) of its diacetate 2 afforded a mixture of 7 and its Δ^8 isomer 8,[9] which are known semisynthetic compounds.[6] Also, refluxing 2 with iodine in benzene produced karounidiol diacetate[5] (4) in addition to three dehydrogenation products (vide infra).

The only remaining problem was the determination of the position of the conjugated double bonds[11] (λ_{max} 263 nm, log ε 3.65). The mass spectra of 1 and 2 included the fragment $C_{19}H_{25}^+$ (*m/z* 253) which consists of the A, B, and C ring of a skeleton having two double bonds somewhere in these rings.[5,12] The possibilities were a $\Delta^{5,7}$, $\Delta^{6,8}$, or $\Delta^{8,11}$ diene system. Decoupling experiments of the double doublets at δ 5.70 and 6.06 (both 1 H, olefinic protons, J = 2.8, 9.8 Hz) and at δ 2.36 (1 H, allylic proton, J = 2.8, 2.8 Hz) ruled out the $\Delta^{5,7}$ and the $\Delta^{8,11}$ system. Irradiation of each of the olefinic protons collapsed the other olefinic signals into a doublet (J = 2.4 Hz) and the allylic signal into a broad singlet. Irradiation of the allylic proton caused the other double doublets to collapse into doublets (J = 9.8 Hz each). This suggested that the olefinic protons were coupled with each other with a large geminal cis coupling constant (J = 9.8 Hz) and with the allylic proton to form an ABX system (J = 2.8 Hz). Thus, the structure of the novel triterpene had to include the substructure >CHCH=CH– which is present in isokarounidiol diacetate (2) but not in its $\Delta^{5,7}$ and $\Delta^{8,11}$ double-bond isomers.

The heliticity rule[13] for skewed cisoid dienes states that a strong negative Cotton effect is associated with the $\pi \rightarrow \pi^*$ transition at about 270 nm if the diene is twisted in the conformation of a left-handed helix as is the case in steroidal $\Delta^{5,7}$ dienes. Molecular model calculations and examination of Dreiding models of isokarounidiol (1) and its acetate 2 and of (22*E*,24*S*)-ergosta-6,8,22-trien-3β-ol acetate (14), which was synthesized for spectral comparison[14] (see Experimental Section), showed that the $\Delta^{6,8}$-diene chromophore in these compounds is twisted in the conformation of a right-handed helix, and circular dichroism (CD) measurements confirmed the expected positive Cotton effect. The Cotton effects in CD (Δε) of (22*E*,24*S*)-ergosta-5,7,22-trien-3β-ol, 2, and 14 are –15.7 (270 nm),[13c] +3.94 (262 nm) and +2.34 (268 nm), respectively. Thus, isokarounidiol is *D*:*C*-friedooleana-6,8-diene-3α,29-diol (1). It is the first example of a triterpene with a $\Delta^{6,8}$ diene chromophore. The only known naturally occurring steroidal $\Delta^{6,8}$ dienes are (22*E*,24*S*)-ergosta-6,8,22-trien-3β-ol and (22*E*,24*S*)-stigmasta-6,8,22-trien-3β-ol, isolated from the soil amoeba *Acanthamoeba polyphyga*.[10]

Iodine-Mediated Isomerization/Dehydrogenation Reaction of Isokarounidiol Diacetate (2). As mentioned above, refluxing 2 with iodine in benzene afforded a desired isomerization product[15] 4 in addition to three

(1) The C20 α-substituent in this compound has been assigned the locant 29 in accordance with the more common convention. The Experimental Section includes Chemical Abstracts nomenclature for all triterpenes/triterpenoids in this paper.

(2) College of Science and Technology, Nihon University.

(3) St. Joseph's University.

(4) College of Pharmacy, Nihon University.

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(15) Iodine has been reported to induce double-bond migration in butene,[16] α-podocarprene,[17] the sterol side chain,[18-20] and the sterol skeleton.[19] Double-bond migration presumably takes place via an intermediate possessing a diradical structure.[19]

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dehydrogenation products.[21] The dehydrogenation products were identified as 5-dehydrokarounidiol diacetate[7] (6) and two C25-demethylated and ring B aromatized products, viz. 25-nor-*D*:*C*-friedooleana-5,7,9-triene-3α,29-diol (10) and 25-nor-*D*:*C*-friedooleana-5(10),6,8,11-tetraene-3α,29-diol (11). The isolated yields of 4, 6, 10, and 11 were 27, 16, 20, and 11%, respectively. Under the same reaction conditions 10 was also obtained from karounidiol diacetate (4). It was the only product; the reaction mixture contained mainly unreacted starting material 4. See Experimental Section for the identification of 10 and 11.

The facile B-ring aromatization reaction of 2 was unexpected because the aromatization of α-phellandrene[22] with iodine was carried out at 170 °C.[23] There is no previous report of the dehydrogenation of a conjugated diene (e.g., 2 → 6) with iodine.

An obvious question to ask is: does this dehydrogenation reaction have any synthetic significance? More specifically, would it be possible to prepare 19-nor steroids in acceptable yield using precursors with double bonds in the B/C ring? We will address this question in one of our next papers.

The structures of all triterpenes are given in Figure 1, the partial structures of 14 and of its reaction products with iodine are shown in Figure 2, and assigned ^{1}H and ^{13}C NMR data of the novel compounds (1, 2, 10, 11) are listed in Table I and in the Experimental Section, respectively. The supplementary material includes the structures of all steroildal compounds (12–16).

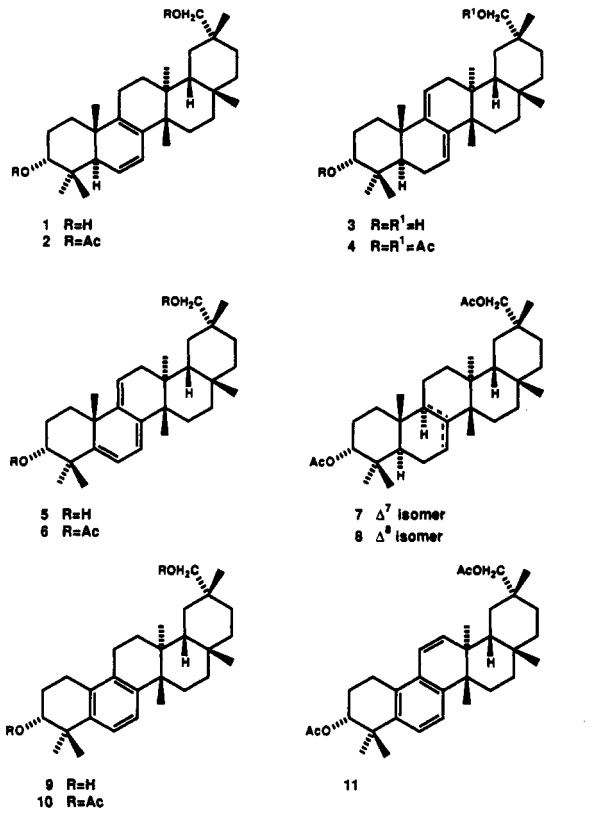

Figure 1. Structures of triterpenes/triterpenoids described in this paper.

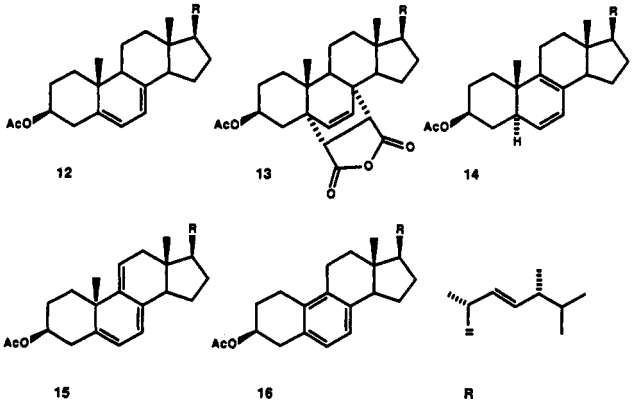

Figure 2. Structures of steroidal compounds described in this paper.

Experimental Section

General methods were essentially the same as in our previous papers.[5-7] See supplementary material for complete information and plotted ^{1}H NMR spectra. All compounds were pure by reversed-phase HPLC and ^{1}H NMR; the ^{13}C NMR spectra of the new compounds included only the required number of peaks. Circular dichroism was measured with a JASCO J-500A spectrometer in EtOH at 30 °C.

Isolation of *D*:*C*-Friedooleana-6,8-diene-3α,29-diol (1) (Isokarounidiol). See earlier papers[5-7] for details of the isolation procedure. Isokaroundiol (1) is the only triterpene which remained unidentified when the previous paper[7] was written. 1: isolated yield 100 mg from 10 kg of ground seeds of *T. kirilowii*.

***D*:*C*-Friedooleana-6,8-diene-3α,29-diol (isokarounidiol) (1):** mp 246–248 °C; RRT (HPLC) 0.34; λ_{max} (log ϵ) 263 nm (3.65); MS *m*/*z* (assignment, relative intensity) 440.3622 ($C_{30}H_{48}O_2$, M$^+$, 52, calcd 440.3651), 422.3499 ($C_{30}H_{46}O_1$, 19), 407.3290 ($C_{29}H_{43}O_1$, 100), 391.3322 ($C_{29}H_{43}$, 3), 389.3241 ($C_{29}H_{41}$, 4), 353.2841 ($C_{25}H_{37}O_1$, 13), 307.2373 ($C_{23}H_{31}$, 5), 279.2162 ($C_{21}H_{27}$, 3), 271.2089 ($C_{19}H_{27}O_1$, 5), 257.1968 ($C_{18}H_{25}O_1$, 5), 253.2001 ($C_{19}H_{25}$, 12), 245.1947 ($C_{17}H_{25}O_1$, 11), 239.1823 ($C_{18}H_{23}$, 24), 227.1819 ($C_{17}H_{23}$, 42), 221.1951 ($C_{15}H_{25}O_1$, 5), 213.1651 ($C_{16}H_{21}$, 11), 211.1496 ($C_{16}H_{19}$, 11); ^{13}C NMR (carbon no., δ) 1, 27.58; 2, 25.68; 3, 75.20; 4, 37.25; 5, 45.34; 6, 125.46; 7, 125.71; 8, 136.61; 9, 136.92; 10, 38.17; 11, 19.93; 12, 30.65; 13, 37.56; 14, 38.37; 15, 29.30; 16, 35.79; 17, 31.36; 18, 42.10; 19, 29.68; 20, 33.36; 21, 28.24; 22, 38.55; 23, 23.28; 24, 26.96; 25, 13.42; 26, 27.89; 27, 18.27; 28, 31.00; 29, 74.03; 30, 26.19.

***D*:*C*-Friedooleana-6,8-diene-3α,29-diol Diacetate (2) (Isokarounidiol Diacetate).** 2 was prepared from 1 by acetylation; mp 202–204 °C; RRT (HPLC) 0.80; λ_{max} (log ϵ) 264 nm (3.66); $\Delta\epsilon$ (262 nm) +3.94; MS *m*/*z* (assignment, relative intensity) 524.3848 ($C_{34}H_{52}O_4$, M$^+$, 5, calcd 524.3862), 464.3625 ($C_{32}H_{48}O_2$, 1), 462.3551 ($C_{32}H_{46}O_2$, 1), 449.3399 ($C_{31}H_{45}O_2$, 100), 395.2990 ($C_{27}H_{39}O_2$, 4), 375.3037 ($C_{28}H_{39}$, 1), 307.2386 ($C_{23}H_{31}$, 1), 285.1864 ($C_{19}H_{25}O_2$, 1), 279.2144 ($C_{21}H_{27}$, 1), 265.1973 ($C_{20}H_{25}$, 1), 253.1942 ($C_{19}H_{25}$, 2), 239.1789 ($C_{18}H_{23}$, 9), 227.1848 ($C_{17}H_{23}$, 6), 225.1665 ($C_{17}H_{21}$, 6), 211.1487 ($C_{16}H_{19}$, 6), 201.1628 ($C_{15}H_{21}$, 6). ^{13}C NMR (carbon no., δ) 1, 28.26; 2, 23.22; 3, 77.00; 4, 36.36; 5, 45.31; 6, 125.02; 7, 125.45; 8, 136.31; 9, 136.75; 10, 38.10, 11, 19.89; 12, 30.55; 13, 37.33; 14, 38.45; 15, 28.88; 16, 35.74; 17, 31.15; 18, 42.09;

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Table I. ^{1}H NMR Data (400 MHz, $CDCl_3$) of Four Novel Compounds (1, 2, 10, 11)[a]

	1	2	10	11
C1-H_2	1.45 (2 H, m)	1.49 (2 H, m)	2.61 (2 H, m)	2.790 (dt) (16.9, 5.9), 2.906 (dt) (17.6, 9.5)
C2-H_2	1.667 (ddt) (4.9, 5.2, 15.9), 1.933 (ddt) (2.3, 4.4, 15.5)	1.704 (dq) (11.8, 3.3), 1.90 (m)	2.04 (2 H, m)	2.03 (2 H, m)
C3-H	3.458 (dd) (2.6, 2.8)	4.698 (dd) (2.5, 3.0)	4.958 (dd), (3.3, 8.8)	4.957 (dd) (2.9, 8.8)
C5-H	2.361 (dd) (2.7, 2.7)	2.349 (dd) (2.8, 2.8)		
C6-H	5.701 (dd) (2.8, 9.7)	5.699 (dd) (2.5, 9.6)	7.136 (d) (8.5)	7.161 (d) (8.1)
C7-H	6.055 (dd) (2.8, 9.7)	6.054 (dd) (3.0, 9.6)	7.108 (d) (8.5)	7.038 (d) (8.1)
C11-H/H_2	1.844 (br dd) (7.3, 19.3)	1.856 (br dd), (6.8, 19.5)	2.55 (2 H, m)	6.478 (d) (9.5)
C12-H/H_2	1.35 (m)	1.353 (dt) (8.9, 13.5)	1.65 (m)	5.963 (d) (9.5)
	1.57 (m)	1.554 (ddt) (3.3, 8.0, 12.9)	1.798 (ddd) (1.4, 7.4, 13.2)	
C15-H_2	1.68 (2 H, m)	1.67 (2 H, m)	2.05 (2 H, m)	1.94 (m)
				2.10 (m)
C16-H_2	1.37 (m)	1.41 (m)	1.59 (m)	1.62 (m)
	1.64 (m)	1.60 (m)	1.71 (m)	1.75 (m)
C18-H	1.58 (m)	1.57 (m)	1.69 (m)	1.93 (m)
C19-H_2	1.19 (m)	1.249 (dd) (4.1, 12.4)	1.368 (dd) (4.1, 12.1)	
	1.50 (m)	1.51 (m)	1.63 (m)	1.73 (m)
C21-H_2	1.38 (2 H, m)	1.40 (2 H, m)	1.403 (ddd) (3.0, 3.0, 12.9)	1.40 (m)
			1.476 (br dd) (3.9, 14.3)	1.52 (m)
C22-H_2	0.97 (m)	0.969 (dt) (13.2, 3.3)	0.995 (dt) (13.2, 3.2)	1.015 (dt) (16.1, 3.8)
	1.49 (m)	1.515 (dt) (12.7, 8.9)	1.61 (m)	1.66 (m)
C23-H_3	0.977 (s)	1.028 (s)	1.269 (s)	1.277 (s)
C24-H_3	1.013 (s)	0.920 (s)	1.286 (s)	1.288 (s)
C25-H_3	9.752 (s)	0.762 (s)		
C26-H_3	1.184 (s)	1.171 (s)	1.229 (s)	1.185 (s)
C27-H_3	1.013 (s)	1.023 (s)	0.884 (s)	0.894 (s)
C28-H_3	1.175 (s)	1.171 (s)	1.200 (s)	1.207 (s)
C29-H_2	3.264 (d) (10.4)	3.793 (2 H, s)	3.802 (d) (10.7)	3.826 (d) (10.3)
	3.334 (d) (10.4)		3.843 (d) (10.7)	3.862 (d) (11.0)
C30-H_3	1.013 (s)	1.033 (s)	1.042 (s)	1.057 (s)
COMe(C3)		2.077 (s)	2.076 (s)	2.081 (s)
COMe(C29)		2.087 (s)	2.080 (s)	2.070 (s)

[a] Splitting constants (Hz) are bracketed.

19, 29.76; 20, 31.77, 21, 28.50; 22, 37.94; 23, 22.94; 24, 26.54; 25, 13.36; 26, 27.40; 27, 18.31; 28, 30.99; 29, 74.29; 30, 26.91; CO*Me*(C3), 21.33; CO*Me*(C29), 21.02; *C*OMe(C3), 170.73; *C*OMe(C29), 171.57.

Hydrogenation of *D*:*C*-Friedooleana-6,8-diene-3α,29-diol Diacetate (2). Hydrogenation of **2** (10 mg) in EtOH (5 mL) over prereduced PtO_2 (10 mg) followed by HPLC fractionation of the reaction mixture yielded two major products: *D*:*C*-friedooleana-7-ene-3α,29-diol diacetate[6] (**7**) (2.0 mg) and *D*:*C*-friedooleana-8-ene-3α,29-diol diacetate[6] (3-epibryonolol diacetate) (**8**) (3.4 mg), in addition to unreacted **2** (1.7 mg).

***D*:*C*-Friedooleana-8-ene-3α,29-diol Diacetate (3-Epibryonolol Diacetate) (8).** See supplementary material for assigned ^{13}C NMR data. ^{1}H NMR and MS data have already been reported.[6]

Reaction of Isokarounidiol Diacetate (2) with Iodine. A solution of **2** (70 mg) and I_2 (8 mg) in C_6H_6 (30 mL) was refluxed for 19 h. After removal of I_2 (aqueous $Na_2S_2O_3$) and evaporation of the solvent the crude product (69 mg) was fractionated by HPLC. The following compounds were obtained: *D*:*C*-friedooleana-7,9(11)-diene-3α,29-diol diacetate[5] (**4**) (19 mg), *D*:*C*-friedooleana-5,7,9(11)-triene-3α,29-diol diacetate[6] (**6**) (11 mg), 25-nor-*D*:*C*-friedooleana-5,7,9-triene-3α,29-diol diacetate (**10**) (14 mg), and 25-nor-*D*:*C*-friedooleana-5,7,9,11-tetraene-3α,29-diol diacetate (**11**) (8 mg).

***D*:*C*-Friedooleana-7,9(11)-diene-3α,29-diol diacetate (karounidiol diacetate) (4):** λ_{max} (log ε) 233 nm (4.06), 237 (4.10), 246 (3.91). ^{1}H and ^{13}C NMR and MS data have already been reported.[5]

***D*:*C*-Friedooleana-5,7,9(11)-triene-3α,29-diol diacetate (5-dehydrokarounidiol diacetate) (6):** mp 167–169 °C; λ_{max} in nm (log ε) 303 (4.05), 314 (4.07), 330 (3.86). The ^{1}H and ^{13}C NMR and MS data were reported recently.[7]

25-Nor-*D*:*C*-friedooleana-5,7,9-triene-3α-29-diol diacetate (10): mp 172–174 °C; RRT (HPLC) 0.52; λ_{max} (log ε) 267 nm (2.70); MS *m*/*z* (assignment, relatively intensity) 508.3553 ($C_{33}H_{48}O_4$, M$^+$, 12, calcd 508.3550), 493.3335 ($C_{32}H_{45}O_4$, 1), 448.3308 ($C_{31}H_{44}O_2$, 71), 433.3057 ($C_{30}H_{41}O_2$, 27), 373.2909 ($C_{28}H_{37}$, 16), 297.1842 ($C_{20}H_{25}O_2$, 7), 283.1715 ($C_{19}H_{23}O_2$, 35), 271.1637 ($C_{18}H_{23}O_2$, 100), 251.1770 ($C_{19}H_{23}$, 5), 237.1662 ($C_{18}H_{21}$, 19), 223.1516 ($C_{17}H_{19}$, 34), 211.1477 ($C_{16}H_{19}$, 86); ^{13}C NMR (carbon no., δ) 1, 24.04; 2, 23.76; 3, 77.70; 4, 37.68; 5, 140,23; 6, 123.54; 7, 122.62; 8, 146.72; 9, 131.66; 10, 131.97; 11, 23.53; 12, 31.09; 13, 37.02; 14, 40.25; 15, 29.89; 16, 36.12; 17, 31.24; 18, 42.95; 19, 29.54; 20, 31.77; 21, 28.90; 22, 36.99; 23, 25.98; 24, 29.16; 26, 30.27, 18.57; 28, 31.06; 29, 73.70; 30, 27.79; CO*Me*(C3), 21.31; CO*Me*(C29), 21.02; *C*OMe(C3), 171.03; *C*OMe(C29), 171.50.

The M$^+$ at *m*/*z* 508 observed in the MS of **10** suggested that this was a demethylation product of **2**. The ^{1}H NMR (two aromatic protons with cis vicinal couplings; six tertiary methyls in addition to two acetyl methyls; see Table I) and the ^{13}C NMR (six olefinic carbons; six methyl carbons besides two acetyl methyl carbons) spectral data suggested that **10** possessed an aromatic B ring resulting from C25 demethylation. The position and intensity of the UV absorption of **10** were almost identical with those of neoergosterol acetate (**16**) (see supplementary material) which has an aromatic B ring.[11] Presence of the fragments $C_{20}H_{25}O_2^+$ (*m*/*z* 297; formed by cleavage at C13–C18 and C14–C15 with 1H loss), $C_{19}H_{23}O_2^+$ (*m*/*z* 283; formed by cleavage at C12–C13 and C15–C16 with 2H loss), and $C_{18}H_{23}O_2^+$ (*m*/*z* 271; formed by cleavage at C11–C12 and C15–C16), accompanied with the ions $C_{18}H_{21}^+$ (*m*/*z* 237), $C_{17}H_{19}^+$ (*m*/*z* 223), and $C_{16}H_{19}^+$ (*m*/*z* 211), formed by the loss of HOAc from the above fragments, respectively, in the mass spectrum[12] was consistent with structure **12**.

25-Nor-*D*:*C*-friedooleana-5,7,9-triene-3α,29-diol (9). **9** was prepared from **10** by saponification: mp 254–256 °C; RRT (HPLC) 0.20; λ_{max} in nm (log ε) 267 (2.70); MS *m*/*z* (assignment, relative intensity) 424.3369 ($C_{29}H_{44}O_2$, M$^+$, 14, calcd 424.3339), 409.3101 ($C_{28}H_{41}O_2$, 4), 406.3164 ($C_{29}H_{42}O_1$, 1), 391.2984 ($C_{28}H_{39}O_1$, 23), 373.2876 ($C_{28}H_{37}$, 3), 283.2110 ($C_{20}H_{27}O_1$, 3), 255.1779 ($C_{18}H_{23}O_1$, 8), 241.1598 ($C_{17}H_{21}O_1$, 35), 229.1613 ($C_{16}H_{21}O_1$, 100), 211.1491 ($C_{16}H_{19}$, 12).

25-Nor-*D*:*C*-friedooleana-5,7,9,11-tetraene-3α,29-diol diacetate (11): mp 158–160 °C; RRT (HPLC) 0.44; λ_{max} in nm (log ε) 273 (4.08); MS *m*/*z* (assignment, relative intensity) 506.3358 ($C_{33}H_{46}O_4$, M$^+$, 58, calcd 506.3393), 491.3110 ($C_{32}H_{43}O_4$, 6), 446.3169 ($C_{31}H_{42}O_2$, 48), 431.2906 ($C_{30}H_{39}O_2$, 77), 386.2944 ($C_{29}H_{38}$, 6), 371.2736 ($C_{28}H_{35}$, 39), 323.2011 ($C_{22}H_{27}O_2$, 5), 311.2009

($C_{21}H_{27}O_2$, 13), 295.1711 ($C_{20}H_{23}O_2$, 94), 284.1778 ($C_{19}H_{24}O_2$, 13), 275.1789 ($C_{21}H_{23}$, 19), 263.1778 ($C_{20}H_{23}$, 25), 249.1636 ($C_{19}H_{21}$, 25), 235.1484 ($C_{18}H_{19}$, 100), 221.1352 ($C_{17}H_{17}$, 45), 209.1324 ($C_{16}H_{17}$, 25), 207.1185 ($C_{16}H_{15}$, 25). ^{13}C NMR (carbon no., δ) 1, 24.22; 2, 23.73; 3, 77.32; 4, 37.75; 5, 141.20; 6, 125.40; 7, 121.16; 8, 145.06; 9, 129.69; 10, 129.54; 11, 121.04; 12, 138.67; 13, 39.99; 14, 41.62; 15, 27.10; 16, 36.20; 17, 31.67; 18, 39.71; 19, 28.87; 20, 31.58; 21, 29.43; 22, 36.52; 23, 25.99; 24, 29.07; 26, 24.73; 17.74; 28, 31.41; 29, 72.90; 30, 28.76, CO*Me*(C3), 21.33; CO*Me*(C29), 21.03; *C*OMe-(C3), 170.99; *C*OMe(C29), 171.44.

The M^+ (*m/z* 506) of **11** corresponded to the diacetate formed from **2** by demethylation and dehydrogenation. The ^1H NMR showed the presence of two aromatic and two olefinic protons and six tertiary methyls in addition to two acetyl methyls (Table I), and the ^{13}C NMR exhibited the occurrence of eight olefinic carbons and six methyl carbons in addition to two acetyl methyl carbons (Table II). This suggested that **11** was a C11-dehydro analog of **10** as supported by the UV absorption (λ_{max} 273; log ϵ 4.08) which was almost identical with that of a sterol with a 19-nor-$\Delta^{5(10),6,8,11}$ skeletal structure, viz. (22*E*,24*S*)-ergosta-5,7,9,11,22-pentaen-3β-ol acetate (λ_{max} 270 nm; log ϵ 4.06).[11] The MS showed the prominent fragments $C_{20}H_{23}O_2^+$ (*m/z* 295; formed by cleavage at C13–C18 and C14–C15 with 1 H loss), $C_{18}H_{19}^+$ (*m/z* 295–HOAc), and $C_{17}H_{17}^+$ (*m/z* 221; formed by cleavage at C12–C13 and C15–C16 with loss of 2 H and HOAc) which supported further the structure of **11**.[12]

Hydrogenation of 25-Nor-*D*:*C*-friedooleana-5,7,9,11-tetraene-3α,29-diol Diacetate (11). Hydrogenation of **11** (4 mg) in EtOH (5 mL) over prereduced PtO_2 (10 mg) followed by HPLC yielded only 25-nor-*D*:*C*-friedooleana-5,7,9-triene-3α,29-diol diacetate (**10**) (3.1 mg).

Reaction of Karounidiol Diacetate (4) with Iodine. A solution of **4** (50 mg) and I_2 (6 mg) in C_6H_6 (20 mL) was refluxed for 19 h. Workup of the reaction mixture, by the same way as above for **2**, followed by HPLC of the crude product (46 mg) yielded only one reaction product, 25-nor-*D*:*C*-friedooleana-5,7,9-triene-3α,29-diol diacetate (**10**) (1.4 mg); unreacted **4** (24.6 mg) was recovered.

(22*E*,24*S*)-Ergosta-6,8,22-trien-3β-ol Acetate (14). **14** was synthesized by modification of Kircher and Rosensteins's procedure[25] for the large-scale preparation of (24*R*)-ergosta-5,7-dien-3β-ol. See supplementary Material for experimental details. **14**: mp 168–170 °C; RRT (HPLC) 0.75; RRT (GC) 1.23; λ_{max} (log ϵ) 272 nm (3.65) [lit.[10] 272 nm (log ϵ 3.66); lit.[25] 273 nm (log ϵ 3.67) (ergosta-6,8-dien-3β-ol)]; $\Delta\epsilon$(268nm) +2.34. See supplementary material for NMR and MS data.

Supplementary Material Available: General experimental methods, ^{13}C NMR data for **8**, procedure for the preparation of **14**, HRMS, ^1H NMR, and ^{13}C NMR data for **14**, HRMS and ^1H NMR data for (22*E*,24*S*)-19-norergosta-5,7,9,22-tetraen-3β-ol acetate (neoergosterol acetate, **16**), and ^1H NMR spectra for compounds **1**, **2**, **5**, **8**, **10**–**13**, **16** and **18** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(25) Kircher, H. W.; Rosenstein, F. U. *Lipids* **1975**, *10*, 517.