Karounidiol [D:C-*friedo*-Oleana-7,9(11)-diene-3α,29-diol]† and its 3-*o*-Benzoate: Novel Pentacyclic Triterpenes from *Trichosanthes kirilowii*. *X*-Ray Molecular Structure of Karounidiol Diacetate

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Spectroscopic data were used to propose a probable structure for karounidiol [D:C-*friedo*-oleana-7,9(11)-diene-3α,29-diol] and its 3-benzoate, triterpenes isolated from the seeds of *Trichosanthes kirilowii* (Cucurbitaceae). The structure of the skeleton was proved by conversion of the natural product into multiflora-7,9(11)-dien-3β-ol [D:C-*friedo*-oleana-7,9(11)-dien-3β-ol], a known synthetic compound. The configuration at C-20 was determined by *X*-ray analysis of karounidiol diacetate after an attempt to obtain this information by chemical correlation with naturally occurring 3α-hydroxy-D:C-*friedo*-oleana-7,9(11)-dien-29-oic acid had failed. N.m.r. evidence and the results of the *X*-ray analysis indicate that the configuration at C-20 of the latter compound and of two structurally related natural products {bryocoumaric acid [3α-(*p*-hydroxycinnamoyl)-D:C-*friedo*-oleana-7,9(11)-dien-29-oic acid] and bryonolic acid (3β-hydroxy-D:C-*friedo*-olean-8-en-29-oic acid)} was wrongly assigned: all three have a 20β-carboxy configuration (*i.e.* they are the -30-oic acids according to the usual convention).

The seeds of *Trichosanthes kirilowii* Maxim. (Cucurbitaceae) have been used in Chinese medicine as an anti-inflammatory agent, a cough medicine, and an expectorant.[1]

In this paper we report the results of our investigation of the seed extract of *T. kirilowii*, *viz.* the isolation and structure determination of a novel triterpene diol and its monobenzoate. This triterpene diol has been given the trivial name, karounidiol, after karounin, the Japanese word for seeds of *T. kirilowii*.

Results and Discussion

Two oxygenated triterpene alcohols were isolated by silica gel column chromatography from the saponified extract of the seeds of *T. kirilowii*. They were a diol [karounidiol, (**2**), *m/z* 440, $C_{30}H_{48}O_2$] and the monobenzoate (**1**) (*m/z* 544, $C_{37}H_{52}O_3$) of a diol. The benzoate (**1**) was subsequently converted into karounidiol (**2**) by saponification.

Spectral evidence (see Experimental section) indicated that karounidiol (**2**) was derived from multiflora-7,9(11)-dien-3α-ol (**6**) [D:C-*friedo*-oleana-7,9(11)-dien-3α-ol] *via* hydroxylation of one of the C-28, C-29, or C-30 angular methyl groups.

The structure of the skeleton was confirmed by conversion of karounidiol (**2**) into multiflora-7,9(11)-dien-3β-ol (**8**) [D:C-*friedo*-oleana-7,9(11)-dien-3β-ol]. Thus the diacetate (**3**) prepared from diol (**2**) was selectively saponified to give the hydroxy acetate (**4**). Collins oxidation of this primary alcohol (**4**) afforded an aldehyde (**5**) which, upon Huang–Minlon reduction, gave multiflora-7,9(11)-dien-3α-ol (**6**). Multiflora-7,9(11)-dien-3β-ol (**8**), the 3β-epimer of (**6**), was prepared from this 3α-alcohol (**6**) by Collins oxidation and $LiAlH_4$ reduction. The samples of multiflora-7,9(11)-dien-3β-ol (**8**) and its acetate (**9**) were identical by 250 MHz n.m.r. spectroscopy with reference samples prepared from isomultiflorenol acetate (**11**) (D:C-*friedo*-olean-8-en-3β-yl acetate) (see Table 1).

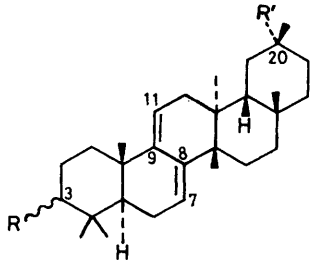
Solution of the remaining problem, *viz.* the location of the hydroxymethylene group, was attempted by conversion of this group into a carboxyl group. Thus Sarett oxidation of karounidiol 3-*o*-acetate (**4**) afforded a carboxylic acid (**12**), which was saponified to give the free hydroxy acid (**13**). Mass spectral data of these compounds (**12**) and (**13**) excluded the possibility of a 28-oic acid or ester because no strong peak due to loss of carboxylic acid or ester group was observed.[2,3] However, there was good agreement with mass spectral data published by Hylands *et al.*[2] for 3α-acetoxy-D:C-*friedo*-oleana-7,9(11)-dien- 29- or -30-oic acid (**12**) or (**15**) [the latter compound was erroneously assigned as having structure (**12**),[2] *vide infra*]. Differences between n.m.r. data published by Hylands *et al.*[2] and our n.m.r. data [compounds (**15**) and (**16**), and (**12**) and (**13**), see Table 1] seemed to indicate that Hylands' compounds and our compounds were epimers at C-20.‡

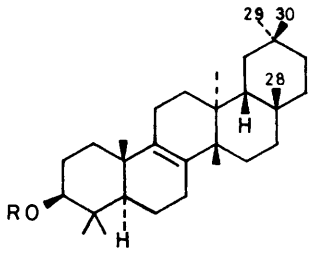
Hylands *et al.* used an n.m.r. argument to assign the configuration at C-20 as 20α-carboxy; they also correlated their natural product with bryonolic acid (assigned as 3β-hydroxy-D:C-*friedo*-olean-8-en-29-oic acid) isolated by Biglino *et al.* from the same plant (*Bryonia dioica*, Cucurbitaceae).[4] We decided to examine this problem by *X*-ray analysis because, in our opinion, these workers had not presented solid evidence to support their assignments.

Single crystals of the quality required for *X*-ray analysis were prepared using karounidiol diacetate (**3**). The overall conformation and the observed 20α-acetoxymethyl configuration are

† The C-20 α-substituent in these compounds has been assigned the locant 29 in accordance with the more common convention.

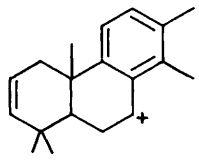
‡ We could not make a direct comparison by 250 or 400 MHz ^{1}H n.m.r. spectroscopy between our and Dr. Hylands' compounds because we were unable to obtain reference samples.



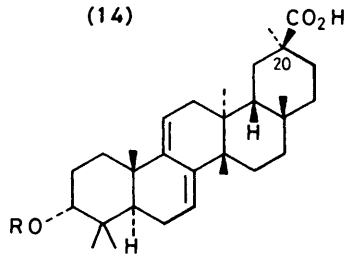


(1) R = α-OCOPh, R' = CH_2OH
(2) R = α-OH, R' = CH_2OH
(3) R = α-OAc, R' = CH_2OAc
(4) R = α-OAc, R' = CH_2OH
(5) R = α-OAc, R' = CHO
(6) R = α-OH, R' = Me
(7) R = =O, R' = Me
(8) R = β-OH, R' = Me
(9) R = β-OAc, R' = Me
(12) R = α-OAc, R' = CO_2H
(13) R = α-OH, R' = CO_2H

(10) R = H
(11) R = Ac



(14)



(15) R = Ac
(16) R = H

Figure 1. Structures of selected triterpenes and of a fragment (**14**) formed in the electron-impact mass spectrum of several of these triterpenes

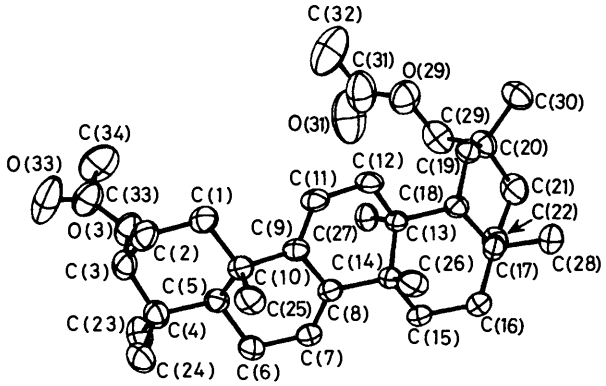


Figure 2. Overall conformation of karounidiol diacetate (**3**) as determined by *X*-ray analysis, showing crystallographic numbering scheme

shown in Figure 2. Karounidiol is thus D:C-*friedo*-oleana-7,9(11)-diene-3α,29-diol* (**2**). This result, in combination with the comparison of our and Hylands' n.m.r. data (*vide supra*), strongly suggests that the compounds which Hylands *et al.* and Biglino *et al.* isolated from *Bryonia dioica*[2,4] have a 20β-carboxy configuration, and not a 20α configuration as had been reported.†

$\Delta^{7,9(11)}$-Unsaturated triterpenoids such as karounidiol (**2**) and its 3-benzoate (**1**) are uncommon. Other examples are five steroidal triterpenes,[5] two multiflorene (D:C-*friedo*-olean-7-ene) derivatives,[2] 7-dehydrofernene[6] [D:C-*friedo*-B':A'-neogammacera-7,9(11)-diene], one steroid,[7] and several holothurinogenins.[8]

Experimental

X-Ray Analysis.‡—Crystals were obtained by vapour diffusion of hexane into a toluene solution (1 ml) of the diacetate (**3**) (*ca.* 50 mg).

Crystal data. $C_{34}H_{52}O_4$, M = 524.79, monoclinic, space group $P2_1$, a = 14.536(11), b = 7.467(3), c = 15.291(5) Å, β = 111.11(2)°, V = 1 546.7(7) Å^3 [by least-squares refinement on diffractometer angles for 25 automatically centred

* We cannot exclude the possibility that karounidiol 3-*o*-benzoate (**1**) is not present in the plant, but has been formed from a 29-ester during work-up of the extract. Pre-treatment of the extract by saponification in order to concentrate the neutral lipids was necessary to facilitate their isolation. Similarly, karounidiol (**2**) might have been present in the extract as a 3,29-diester.

†Sim and Lee (K. Y. Sim and H. T. Lee, *Phytochemistry*, 1972, **11**, 3341) reported the isolation of bryononic acid from *Sandoricum indicum* (Meliaceae). It was identified using reference material supplied by Biglino.[4] Thus it seems likely that this *S. indicum* compound has a 20β-carboxy configuration.

‡ Tables of bond lengths and angles, torsion angles, anisotropic temperature factors for non-hydrogen atoms, and isotropic temperature factors for all atoms have been deposited at the Cambridge Crystallographic Data Centre. See section 5.6.3 of Instructions for Authors, in the January issue.

Table 1. 250 MHz ^{1}H N.m.r. data of compounds described in this paper and 90 MHz ^{1}H n.m.r. data of two reference compounds (**15**) and (**16**) taken from the literature[2] ($CDCl_3$, shifts are δ values)

Compound	29-H (d)[a]		3-H (m)[b]	7-H (m)[c]	11-H (m)[c]	3-OAc (s)	29-OAc (s)	Methyl singlets (unassigned)							
(**1**)	3.235	3.563	4.936	5.528	5.265			0.930	0.939	0.939	0.991	0.991	1.070	1.089	
(**2**)	3.224	3.516	3.456	5.496	5.256			0.862	0.920	0.928	0.938	0.952	0.986	0.079	
(**3**)	3.854	3.920	4.694	5.468	5.220	2.083	2.083	0.830	0.855	0.913	0.933	0.992	0.998	1.080	
(**4**)	3.197	3.557	4.685	5.476	5.237	2.062		0.850	0.906	0.914	0.936	0.986	0.991	1.076	
(**5**)	9.371[e]		4.698	5.447	5.220	2.055		0.645	0.837	0.865	0.928	0.960	0.981	1.046	
(**6**)			3.459	5.474	5.265			0.893	0.893	0.931	0.939	0.953	0.956	0.983	1.035
(**7**)				5.530	5.259			0.875	0.920	0.958	0.977	1.041	1.050	1.126	1.152
(**8**)[f]			3.236[g]	5.487	5.215			0.884	0.888	0.888	0.910	0.959	0.980	0.980	1.036
(**8**)[h]			3.237[g]	5.487	5.213			0.883	0.887	0.887	0.909	0.958	0.978	0.978	1.035
(**9**)[f]			4.507[g]	5.475	5.226	2.057		0.860	0.878	0.887	0.928	0.955	0.955	0.987	1.033
(**9**)[h]			4.507[g]	5.476	5.218	2.054		0.860	0.878	0.888	0.928	0.955	0.955	0.987	1.035
(**12**)			4.687	5.434	5.220	2.055		0.775	0.839	0.861	0.928	0.985	1.026	1.254	
(**13**)[i]			3.454	5.438	5.242			0.763	0.862	0.925	0.932	0.938	1.024	1.257	
(**15**)[j]			4.68	5.43	5.21	2.02		0.75	0.84	0.92	0.98	1.00	1.22	1.25	
(**16**)[j]			3.42	5.42	5.25			0.74	0.85	0.92	0.92	1.02	1.24	1.25	

[a] For compounds (**1**)—(**4**) these values represent the shift of the upfield and the downfield pair of lines of an AB system; the lines of a pair are *ca.* 11 Hz apart. [b] Half-width *ca.* 6 Hz except for compounds (**8**) and (**9**). [c] Half-width *ca.* 10 Hz. [d] Other signals (m) due to 3α-OBz protons at δ 7.44 (2 H), 7.56 (1 H), and 8.02 (2 H). [e] *J* 1.5 Hz. [f] Prepared from karounidiol (**2**). [g] dd (*J* 4, 10 Hz). [h] Prepared from compounds (**10**) and (**11**). [i] Determined at 400 MHz. [j] Taken from Hylands' papers.[2]

Table 2. Fractional non-hydrogen atomic co-ordinates of karounidiol diacetate (**3**) with their estimated standard deviations in parentheses

Atom[a]	*x*	*y*	*z*
O(3)	1.318 5(1)	0.925	0.885 4(1)
O(29)	0.771 6(2)	1.251 5(4)	0.883 4(2)
O(31)	0.870 9(2)	1.137 4(8)	1.018 5(2)
O(33)	1.468 4(2)	1.046 6(6)	0.931 9(2)
C(1)	1.181 5(2)	1.028 3(4)	0.701 3(2)
C(2)	1.291 4(2)	0.991 6(5)	0.724 1(2)
C(3)	1.329 6(2)	0.853 7(5)	0.800 5(2)
C(4)	1.275 0(2)	0.674 6(4)	0.777 9(2)
C(5)	1.161 2(2)	0.709 4(4)	0.745 0(2)
C(6)	1.100 3(2)	0.539 0(4)	0.717 2(2)
C(7)	0.991 6(2)	0.573 4(4)	0.683 7(2)
C(8)	0.950 9(2)	0.733 4(4)	0.661 8(2)
C(9)	1.012 8(2)	0.893 4(4)	0.667 2(2)
C(10)	1.117 7(2)	0.859 3(4)	0.670 8(2)
C(11)	0.974 2(2)	1.057 1(4)	0.665 3(2)
C(12)	0.871 0(2)	1.093 4(4)	0.658 8(2)
C(13)	0.817 9(2)	0.929 6(3)	0.679 7(2)
C(14)	0.839 0(2)	0.766 7(4)	0.625 8(2)
C(15)	0.781 4(2)	0.604 1(4)	0.639 5(2)
C(16)	0.670 1(2)	0.636 9(4)	0.598 5(2)
C(17)	0.633 7(2)	0.808 0(4)	0.632 5(2)
C(18)	0.704 5(2)	0.969 2(4)	0.643 5(2)
C(19)	0.673 4(2)	1.131 0(4)	0.691 4(2)
C(20)	0.630 1(2)	1.102 5(4)	0.769 8(2)
C(21)	0.570 9(2)	0.928 7(5)	0.756 8(2)
C(22)	0.616 4(2)	0.770 6(4)	0.723 8(2)
C(23)	1.308 3(2)	0.580 0(5)	0.704 4(2)
C(24)	1.306 8(2)	0.554 1(6)	0.865 2(2)
C(25)	1.108 0(2)	0.808 1(5)	0.569 9(2)
C(26)	0.864 4(2)	0.894 9(4)	0.785 5(2)
C(27)	0.809 0(2)	0.804 4(5)	0.519 3(2)
C(28)	0.533 4(2)	0.855 8(5)	0.554 9(3)
C(29)	0.707 8(2)	1.096 5(6)	0.868 5(2)
C(30)	0.561 0(2)	1.261 8(5)	0.766 0(2)
C(31)	0.850 6(3)	1.253 8(9)	0.962 1(3)
C(32)	0.911 3(4)	1.414(1)	0.969 1(4)
C(33)	1.392 7(2)	1.022 8(6)	0.942 0(2)
C(34)	1.368 4(3)	1.098 7(7)	1.021 6(2)

[a] Numbering scheme given in Figure 2.

reflections, λ(Mo-K_α) = 0.710 73 Å), Z = 2, D_c = 1.125 g cm^{-3}, clear prisms, approximate dimensions 0.40 × 0.40 × 0.45 mm, μ = 0.667 cm^{-1}, F(000) = 576.

Data collection and processing. CAD-4 Diffractometer, T = 293 K, ω–2θ mode with ω scan width = 0.95 + 0.35tanθ, ω scan speed 2.5—6.8 deg min^{-1}, graphite-monochromated Mo-K_α radiation; 4 175 reflections measured ($1.0 \leq \theta \leq 28°$, $+h$, $+k$, $\pm l$), 4 021 unique (merging R = 0.015), giving 3 083 with $I \geqslant 3\sigma(I)$. Intensity standard varied less than 2% over the course of data collection. Corrections were made for Lorentz and polarization effects but not for absorption.

Structure analysis and refinement. Direct methods gave a fragment (20 atoms) which was elaborated from difference Fourier syntheses. Full-matrix least-squares refinement (on F) with all non-hydrogen atoms anisotropic; methyl hydrogens in calculated positions with a fixed isotropic temperature factor of 6.0 Å^2, all other hydrogens located from difference Fourier maps and refined along with isotropic temperature factors. In final cycles 443 variables including an extinction coefficient of the type defined by Zachariasen[9] which refined to 1.8(5) × 10^6. The weighting scheme was $w = 4F_o^2/\sigma^2(I)$ with $\sigma(I)$ given by the expression $[\sigma(I)^2 + (pF_o)^2]^{\frac{1}{2}}$ and p = 0.05. Final R $(\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.048$, $R_w[\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}} = 0.062$; $(\Delta/\sigma) = 0.05$. Final difference Fourier maps were featureless; maximum positive excursion 0.0261 e Å^{-3}. Values of the maximum neutral atom scattering factors were taken from the International Tables for *X*-ray Crystallography. Fractional atomic co-ordinates for non-hydrogen atoms are given in Table 2.

General Methods.—M.p.s are uncorrected. T.l.c. plates (silica gel) were developed using hexane–EtOAc (6:1). U.v. spectra of compounds (**1**)—(**9**), (**12**), and (**13**) were recorded in absolute EtOH (Shimadzu UV-300 spectrometer). The spectra are indicative of the presence of a conjugated heteroannular diene.[10] The e.i.-m.s. spectra were taken at 70 eV using a direct probe. The m.s. data (*vide infra*) do not include peaks at $m/z \leq 100$. It was confirmed by high-resolution measurements that in the mass spectra of all $\Delta^{7,9(11)}$-unsaturated compounds the peak at m/z 253 was caused by the fragment $C_{19}H_{25}^+$. ^{1}H (250 or 400 MHz) and ^{13}C (62.9 MHz) n.m.r. spectra were recorded

in $CDCl_3$ with $SiMe_4$ as internal standard; shifts are δ values. All other methods used in this study have been described previously.[11] The seeds of *Trichosanthes kirilowii* were purchased from Kinokuniya Kan-yaku Kyoku Co. (Tokyo), and authentic isomultiflorenol (**10**) was isolated from *Cucumis sativus*.[12]

Extraction and Isolation.—Air-dried and ground seeds (5 kg) were extracted with CH_2Cl_2 in a Soxhlet apparatus. Neutral lipids (12 g) were obtained from the extract (1 060 g) by alkaline hydrolysis with 1M-NaOH in MeOH. The neutral lipids were chromatographed over a silica gel column with hexane, hexane–ether, hexane–EtOAc, and MeOH as eluants. Nine fractions (A—I) were obtained. Fraction, weight of residue, and R_F value of main component(s) as determined by silica gel t.l.c.: A (152 mg, 1.00, hexane, 1.4), B [1 285 mg, 0.91, hexane–ether (9:1), 1.0], C [357 mg, 0.74, hexane–ether (9:1), 0.8], D [1 434 mg, 0.64, hexane–ether (4:1), 0.6], E [1 582 mg, 0.50, hexane–ether (4:1), 0.8], F [844 mg, 0.39, hexane–EtOAc (5:1), 0.8], G [1 613 mg, 0.26, hexane–EtOAc (5:1), 0.4], H [768 mg, 0.12, hexane–EtOAc (5:1), 0.8], and I (2 745 mg, 0.07, MeOH, 0.6). Fraction D and G consisted of 10α-curcubita-5,24-dien-3β-ol (9β-methyl-19-nor-8β,10α-lanosta-5,24-dien-3β-ol)[13] and sterols, respectively. Fraction E was separated into two bands by preparative t.l.c. (p.l.c.). The fraction corresponding to the less polar band was a mixture of 3β-monohydroxy triterpenes (524 mg), whereas the more polar band afforded karounidiol 3-benzoate (**1**) (452 mg). Karounidiol (**2**) (88 mg) was obtained from fraction I by rechromatography over a silica gel column.

D:C-friedo-*Oleana*-7,9(11)-*diene*-3α,29-*diol* 3-*Benzoate* (*Karounidiol* 3-O-*Benzoate*) (**1**).—M.p. 119—122 °C, $\lambda_{max.}$ (log ε) 229 (4.18), 235 (4.13), and 245 nm (3.90); $\nu_{max.}$ 3 400 (OH), 1 720 and 1 280 (OBz), 1 605, 1 585, and 710 (C_6H_5), 1 640 (conjugated C=C), and 815 and 800 cm^{-1} (C=CH); *m/z* (assignment, rel. int.) 544.3906 ($C_{37}H_{52}O_3$, M^+, 41%), 422 (3), 407 (19), 253 (8), 239 (3), 227 (8), 213 (9), and 105 (100); δ_C 19.1 (q), 20.6 (q), 22.0 (q), 22.1 (q), 23.1, 23.8 (t), 27.1, 27.5 (t), 27.6, 29.7, 29.9 (t), 30.0, 30.6 (t), 31.0 (q), 31.7 (s), 32.7, 34.2 (t), 36.3 (s), 36.7 (t), 37.2 (s), 37.4 (s), 39.2 (t), 40.1 (s), 43.5 (d), 44.5 (d), 71.1 (t), 79.1 (d), 114.3 (d, C-11), 117.9 (d, C-7), 142.2 (s, C-9), and 144.3 (s, C-8). The aromatic carbons were at δ 128.4 (d, 2 C), 129.5 (d, 2 C), 130.9 (s), and 132.6 (d).

Karounidiol (**2**).—*Determination of the partial structure using spectroscopic data.* The compound has two hydroxy groups [it gives a diacetate (**3**)] and two double bonds (^{13}C n.m.r.). This information in combination with the molecular formula ($C_{30}H_{48}O_2$) shows that compound (**2**) is pentacyclic. The u.v. spectrum[10] and the shift of the olefinic protons are consistent with $\Delta^{7,9(11)}$ double bonds. The shape and shift of a 1 H multiplet at δ 3.456 indicates that the proton is located at a hydroxy-bearing carbon (C-3) of a 4,4-dimethyl-substituted skeleton. The other hydroxy group is part of a hydroxymethyl group at a quaternary carbon: the ^1H n.m.r. spectrum includes an AB quartet at δ 3.37. The presence of the fragment $C_{19}H_{25}^+$ (**14**) in the mass spectrum greatly reduces the number of possible skeletons. This fragment (**14**), which consists of the A, B, and C rings of a triterpene skeleton,[2,3] is diagnostic of several triterpene 3-alcohols having two double bonds, methyl groups at C-13 and C-14, and no methyl groups at C-8 and C-9, such as compounds with bauerenol- (D:C-*friedo*-urs-7-en-3-ol-), multiflorenol-(D:C-*friedo*-olean-7-en-3-ol-), and fernenol- [D:C-*friedo*-B-′:A′-neogammacer-9(11)-en-3-ol-] type skeletons. Fernenol- and bauerenol-type skeletons can be ruled out because only methyl singlets are observed in the ^1H n.m.r. spectrum of compound (**2**). Thus compound (**2**) appears to be an oxygenated D:C-*friedo*-oleana-7,9-(11)-dien-3α-ol. The formation of the above $C_{19}H_{25}^+$ fragment (**14**) also implies that the primary alcohol groups is attached to either C-28, C-29, or C-30.

D:C-friedo-*Oleana*-7,9(11)-*diene*-3α,29-*diol* (*karounidiol*) (**2**) had m.p. 201—203 °C, $\lambda_{max.}$ (log ε) 231 (4.08), 238 (4.10), and 246 nm (3.91); $\lambda_{max.}$ 3 370 (OH), 1 640 (conjugated C=C), and 810 and 800 cm^{-1} (C=CH); *m/z* 440.3641 ($C_{30}H_{48}O_2$, M^+, 100%), 425 (6), 422 (3), 409 (7), 407 (16), 353 (2), 300 (5), 271 (18), 255 (11), 253 (17), 239 (11), 227 (16), and 213 (16); δ_C 19.2 (q), 20.5 (q), 22.0 (q), 22.4 (q), 23.9 (t), 25.5, 27.2, 27.4, 27.7, 29.5, 29.7, 29.8, 29.9, 3.10 (q), 31.6 (s), 32.7 (s), 34.3 (t), 36.2 (s), 36.7 (t), 37.4 (s), 37.5 (s), 39.3 (t), 42.0 (d), 44.5 (d), 71.1 (t), 76.3 (d), 114.1 (d, C-11), 118.1 (d, C-7), 142.1 (s, C-9), and 144.3 (s, C-8).

D:C-friedo-*Oleana*-7,9(11)-*diene*-3,α,29-*diol* *Diacetate* (*Karounidiol Diacetate*) (**3**).—This was prepared from karounidiol (**2**) by acetylation with Ac_2O–pyridine overnight at room temperature, m.p. 197—200 °C; *m/z* 524.3847 ($C_{34}H_{52}O_4$, M^+ 100%), 464 (16), 449 (30), 389 (10), 313 (12), 253 (40), 239 (16), 227 (20), and 213 (18); δ_C 19.6 (q), 20.4 (q), 21.1 (d), 21.4 (d), 21.8 (q), 22.1 (q), 23.1 (t), 23.7 (t), 27.2 (q), 27.3 (t), 28.2 (t), 29.9 (t), 30.2 (q), 30.3 (t), 31.0 (q), 31.2 (s), 31.5 (s), 34.0 (t), 36.2 (s), 36.6 (t), 36.7 (s), 37.3 (t), 39.3 (t), 40.0 (s), 42.9 (d), 44.6 (d), 72.4 (t), 78.3 (d), 113.8 (d, C-11), 118.1 (d, C-7), 141.9 (s, C-9), 144.3 (s, C-8), and 170.8 and 171.4 (s, C=O).

D:C-friedo-*Oleana*-7,9(11)-*diene*-3α,29-*diol* 3-O-*Acetate* (*Karounidiol* 3-O-*Acetate*) (**4**)—Partial hydrolysis of the diacetate (**3**) (180 mg) was achieved on stirring the reactant with KOH (1 g) in MeOH (40 ml) at room temperature for 6 h. Compound (**4**) (118 mg) was obtained after the usual work-up and purification by p.l.c., m.p. 229—232 °C; $\lambda_{max.}$ 230, 237, and 246 nm; $\nu_{max.}$ 3 450 (OH), 1 710, and 1 255 (OAc), and 815 and 800 cm^{-1} (C=CH); *m/z* 482.3743 ($C_{32}H_{50}O_3$, M^+, 100%), 467 (3), 451 (4), 422 (6), 407 (26), 313 (5), 288 (3), 269 (5), 255 (10), 253 (16), 239 (14), 227 (12), and 213 (16).

29-*Oxo*-D:C-friedo-*oleana*-7,9(11)-*dien*-3α-*yl Acetate* (**5**).—CrO_3 (62 mg) was added to a solution of the primary alcohol (**4**) (100 mg) in pyridine (8 ml). After being stirred for 20 h at room temperature the mixture was poured into dil. HCl. After the usual work-up and p.l.c. of the residue, the oxo acetate (**5**) was obtained (32 mg), m.p. 239—241 °C; $\lambda_{max.}$ 230, 237, and 246 nm; $\nu_{max.}$ 1 710 and 1 240 (OAc), 2 720 and 1 730 (CHO), and 815 and 800 cm^{-1} (C=CH); *m/z* 480.3606 ($C_{32}H_{48}O_3$, M^+, 100%), 420 (4), 405 (32), 313 (6), 278 (8), 253 (22), 239 (10), 227 (14), and 213 (10).

D:C-friedo-*Oleana*-7,9(11)-*dien*-3α-*ol* [*Multiflora*-7,9(11)-*dien*-3α-*ol*] (**6**).—The aldehyde (**5**) was reduced under Huang–Minlon conditions. Thus compound (**5**) (28 mg), ethylene glycol (5 ml), hydrazine hydrate (1 g), and KOH (100 mg) were heated under reflux for 3 h. Part of the solvents were removed by distillation until the pot temperature reached 200 °C; this temperature was then maintained for another 3 h. The alcohol (**6**) (8 mg), m.p. 185—186 °C, was obtained after the usual work-up and p.l.c., $\lambda_{max.}$ 230, 237, and 246; *m/z* 424.3690 ($C_{30}H_{48}O$, M^+, 100%), 409 (11), 406 (20), 381 (25), 337 (4), 284 (7), 271 (15), 255 (18), 253 (15), 239 (9), 227 (16), and 213 (11).

D:C-friedo-*Oleana*-7,9(11)-*dien*-3-*one* [*Multiflora*-7,9(11)-*dien*-3-*one*] (**7**).—A solution of the alcohol (**6**) (7 mg) in pyridine (1 ml) was added to a stirred solution of CrO_3 (7 mg) in pyridine (1.4 ml). The mixture was stirred at room temperature for 16 h to afford, after work-up and p.l.c., the ketone (**7**) (3 mg), m.p. 158—161 °C; $\lambda_{max.}$ 230, 237, and 245 nm; $\nu_{max.}$ 1 700 (ketone), 1 640 (conjugated C=C), and 810 (C=CH) cm^{-1}; *m/z* 422.3530 ($C_{30}H_{46}O_1$, M^+, 100%), 407 (18), 297 (2), 283 (8), 271 (19), 269 (25), 255 (13), 243 (14), 229 (10), and 211 (8).

D:C-friedo-*Oleana*-7,9(11)-*dien*-3β-*ol* [*Multiflora*-7,9(11)-*dien*-3β-*ol*] *and* D:C-friedo-*Oleana*-7,9(11)-*dien*-3β-*yl Acetate* (**8**) *and* (**9**).—Solutions of the ketone (**7**) (3 mg) in dry THF (1 ml) and of $LiAlH_4$ (2 mg) in the same solvent (2 ml) were combined and the mixture was left at room temperature for 18 h. The crude product was worked up by p.l.c. The fraction from the less polar band afforded the 3α-alcohol (**6**) (0.6 mg), whereas the fraction from the more polar band consisted of multiflora-7,9(11)-dien-3β-ol (**8**) (1.9 mg), m.p. 192—195 °C. Compound (**8**) was converted into the acetate (**9**), m.p. 219—222 °C (lit.,[14] 216—218 °C); $\nu_{max.}$ of (**8**) 3 400 (OH), 1 640 (conjugated C=C), and 810 (C=CH) cm^{-1}; *m/z* of (**8**) 424.3706 ($C_{30}H_{48}O$, M^+, 100%), 409 (13), 391 (7), 295 (3), 284 (6), 271 (21), 259 (2), 255 (14), 253 (9), 241 (5), 227 (11), and 213 (8); *m/z* of (**9**) 466.3786 ($C_{32}H_{50}O_2$, M^+, 100%), 451 (8), 406 (3), 391 (13), 313 (13), 301 (6), 289 (8), 284 (6), 255 (15), 253 (18), 241 (10), 229 (10), 227 (15), and 213 (11).

Dehydrogenation of D:C-friedo-*Olean*-8-*en*-3β-*yl Acetate* (*Isomultiflorenol Acetate*) (**11**).—A solution of SeO_2 (150 mg) in 96% AcOH (3 ml) was added to a solution of the acetate (**11**) (20 mg) in glacial AcOH (20 ml) and the mixture was gently refluxed for 24 h. After the usual work-up and p.l.c., multiflora-7,9(11)-dien-3β-yl acetate (**9**) (5 mg), m.p. 216—219 °C (lit.,[14] 216—218 °C) was obtained. Saponification of the acetate afforded the free alcohol (**8**), m.p. 197—199 °C. The mass spectra and n.m.r. spectra of compounds (**8**) and (**9**) prepared from isomultiflorenol acetate (**11**) and from karounidiol (**2**) were identical. See Table 1 for n.m.r. data of both compounds (**8**) and (**9**). It was deemed necessary to synthesize compounds (**8**) and (**9**) because n.m.r. data of these compounds had not been reported in the literature.

Sarett Oxidation of D:C-friedo-*Oleana*-7,9(11)-*diene*-3α,29-*diol* 3-o-*Acetate* (*Karounidiol* 3-o-*Acetate*) (**4**).—A solution of karounidiol 3-*o*-acetate (**4**) (27 mg) in pyridine (1.5 ml) was added to a well stirred, ice-cold suspension of CrO_3–pyridine complex prepared from CrO_3 (0.6 g) and pyridine (6 ml). After being stirred overnight the mixture was worked up and the product was purified by p.l.c. to afford 3-acetoxy-D:C-*friedo*-oleana-7,9(11)-dien-29-oic acid (**12**) (5 mg), m.p. 265—269 °C. Alkaline hydrolysis of the acetoxy acid (**12**) afforded the free hydroxy acid (**13**), m.p. 246—249 °C. For (**12**), $\lambda_{max.}$ 230, 237, and 246 nm; $\nu_{max.}$ 3 300 and 1 740 (CO_2H), 1 705 and 1 280 (OAc), and 815 cm^{-1} (C=CH); *m/z* 496.3565 ($C_{32}H_{48}O_4$, M^+, 100%), 436 (12), 422 (15), 421 (47), 314 (5), 313 (5), 285 (7), 253 (20), 227 (24), and 213 (15); for (**13**), *m/z* 454.3467 ($C_{30}H_{46}O_3$, M^+, 100%), 439 (7), 436 (9), 421 (28), 408 (4), 368 (6), 271 (14), 253 (13), 239 (10), 227 (19), and 213 (11).

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