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Chemical and Chemotaxonomical Studies of Ferns. XXXVII.[1] Chemical Studies on the Constituents of Costa Rican Ferns (2)[2]

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The constituents of five Costa Rican ferns of Preridaceae were investigated. The ferns and isolated compounds are as follows. *Acrostichum aureum*: quercetin 3-O-β-D-glucoside (I), ponasterone A (III). *Neurocallis praestantissima*: 2-deoxy-D-glucose (IV), 3,6-anhydro-2-deoxy-D-glucose (V). *Pteris podophylla*: 6-(2-chloroethyl)-2(*S*)-hydroxymethyl-5,7-dimethylindan-1-one (X), pterosin G (XI), kaempferol 3,7-di-O-α-L-rhamnoside (II), apigenin 7-O-β-D-glucoside (VI), luteolin 7-O-β-D-glucoside (VII). *Pteris livida*: pterosin C (VIII), pterosin S (IX), 9-hydroxy-15-oxo-*ent*-kaur-16-en-19-oyl-β-D-glucoside (XII), 6β,11β-dihydroxy-15-oxo-*ent*-kaur-16-en-19-oyl-β-D-glucoside (XIII), 6β,9-dihydroxy-15-oxo-*ent*-kaur-16-en-19-oyl-β-D-glucoside (XIV), paniculoside III (XV), pterokaurene L_1 (XVI), 11β-hydroxy-15-oxo-*ent*-kaur-16-en-19-oic acid (XIX). *Pteris altissima*: VII, XI, XII, XIII, XV. Among the above products, X, XII, XIII and XIV are new compounds and their structures were elucidated by chemical and physicochemical methods.

Keywords——*Acrostichum aureum*; *Neurocallis praestantissima*; *Pteris podophylla*; *Pteris livida*; *Pteris altissima*; pterosin-type sesquiterpenes; *ent*-kaurane-type diterpenes; flavonoids; 2-deoxy-D-glucose; ^{13}C-NMR

We have been studying the chemical constituents of ferns in Japan and Taiwan to obtain chemical data relevant to the systematics of ferns. As a continuation of this work, the constituents of five Costa Rican ferns of Pteridaceae were investigated. In this paper, the results of this investigation, including the structural elucidation of four new compounds, are described. The ferns investigated were *Acrostichum aureum* L., *Neurocallis praestantissima* (Bory) Fée, *Pteris podophylla* Swartz, *Pteris livida* Mett. and *Pteris altissima* Poir. The isolation procedure and properties of their constituents (except for those of new compounds) are described in the experimental section.

(1) *Acrostichum aureum* L.

From this fern, quercetin-3-O-β-D-glucoside (I) and ponasterone A (III) were isolated. The latter compound is one of the phytoecdysones isolated from several Japanese ferns.[3]

(2) *Neurocallis Praestantissima* (Bory) Fée

2-Deoxy-D-glucose (IV) and 3,6-anhydro-2-deoxy-D-glucose (V) were isolated. These sugars have been isolated from only three species of *Pteris*, *P. inaequalis* Baker var. *aequata* (Miq.) Tagawa, *P. ensiformis* Burm. and *P. formosana* Bak.[4] *Neurocallis* genus is considered to be closely related to *Pteris* genus. Therefore, this finding is very interesting chemotaxonomically.

(3) *Pteris podophylla* Swartz

A new pterosin-type sesquiterpene X was isolated along with pterosin G (XI),[5] kaempferol 3,7-di-O-α-L-rhamnoside (II), apigenin 7-O-β-D-glucoside (VI) and luteolin 7-O-β-D-glucoside

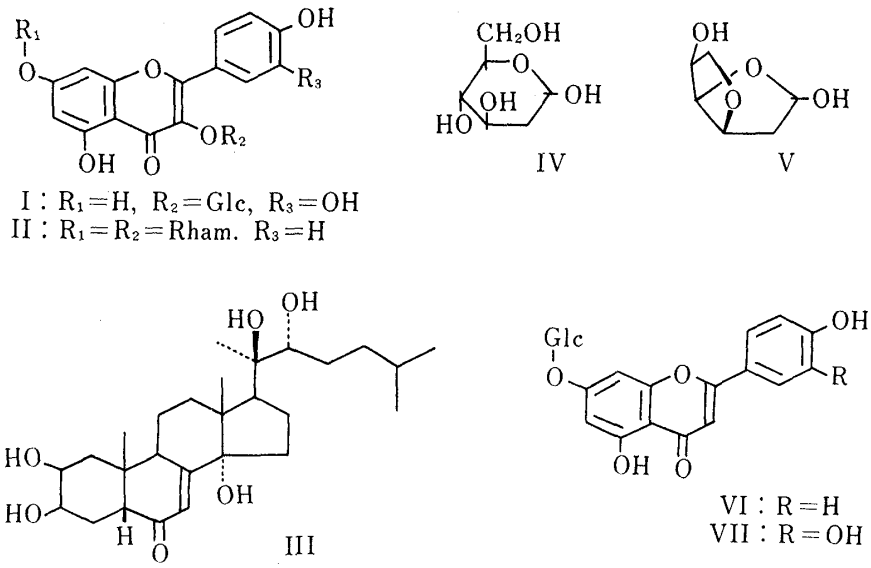
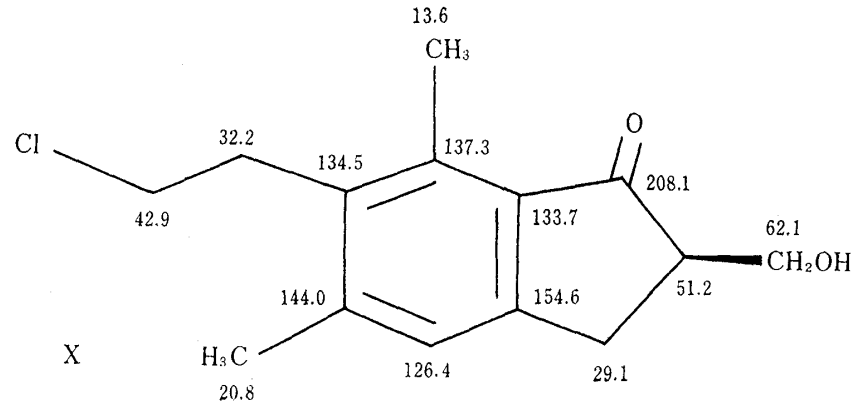


Fig. 1.

(VII). Compound X, $C_{14}H_{17}ClO_2$, colorless needles, mp 130—132°C, $[\alpha]_D^{18}$ −1.2° (c=0.4, MeOH), showed ultraviolet (UV) [λ_{max}^{MeOH} nm (log ε): 219 (4.60), 260 (4.20), 305 (3.45)] and infrared (IR) [ν_{max}^{KBr} cm^{-1}: 3400, 1685, 1600] absorptions characteristic of the pterosin-type compounds.[5] The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum showed signals due to two aromatic methyl groups at δ_{CDCl_3} 2.45 and 2.69, one ethylene group at δ 3.3 (2H, m) and 3.5 (2H, m), one methylene group at δ 3.93 (2H, broadened AB quartet) and one aromatic



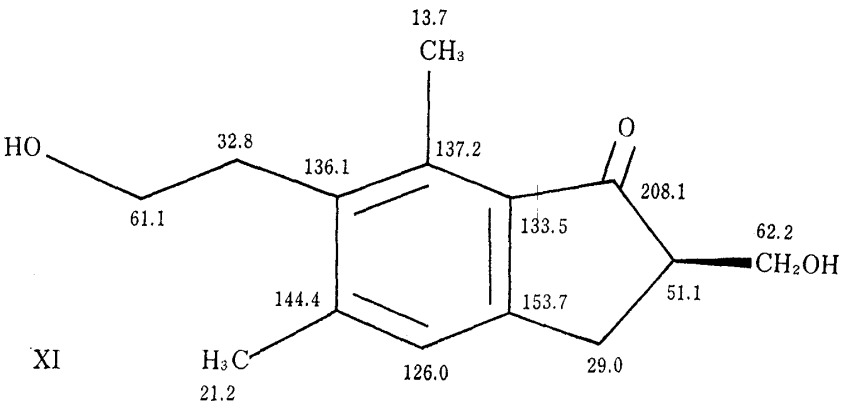


Fig. 2. ^{13}C Chemical Shifts in Pyridine-d_5

proton at δ 7.16 (1H, s) along with three overlapping proton signals in the range of δ 2.6—3.2. These signals are similar to those of pterosin G (XI) except for the ethylene proton signals. The chemical shifts of these ethylene protons coincide more closely with those of the chloroethyl groups in such compounds as pterosins F, J and K.[5] A comparison of the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum of X with that of pterosin G (XI) (Fig. 2) also indicates that the only structural difference between them is in the substituent at C-6, a hydroxyethyl group in pterosin G and a chloroethyl group in X. Thus, the structure of X was determined to be the 6-chloroethyl derivative of pterosin G. The absolute configuration at C-2 in X was established as 2(*S*) by the circular dichroism Cotton effect, $[\theta]_{320}$ +101° in MeOH, as compared with that of pterosin G.

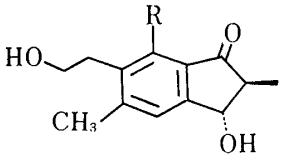
(4) *Pteris livida* Mett.

Three new compounds, XII, XIII and XIV, were isolated along with pterosin C (VIII),[5] pterosin S (IX),[6] 11β-hydroxy-15-oxo-*ent*-kaur-16-en-19-oic acid (XIX),[7] 9-hydroxy-15-oxo-*ent*-kaur-16-en-19-oic acid (=pterokaurene L_1, XVI)[8] and 19-β-D-glucopyranosyl ester of XIX (=paniculoside III, XV).[9] Compound XII, $C_{26}H_{38}O_9$, colorless needles, mp 140—144°C, $[\alpha]_D^{18}$ −77° (c=1.2, MeOH), showed UV [λ_{max}^{MeOH} 234 nm (log ε 3.88)] and IR [ν_{max}^{KBr} cm^{-1}: 3500, 3400, 1715, 1640, 1070, 1025] spectra similar to those of paniculoside III (XV). The ^{1}H-NMR spectrum (in Pyr. -d_5) exhibited two methyl proton signals at δ 1.29 (3H, s) and 1.45 (3H, s), two terminal methylene proton signals at δ 5.14 (1H, s) and 5.97 (1H, s), one anomeric proton signal at δ 6.22 (1H, d, J=7 Hz) and six overlapping proton signals in the range of δ 3.7—4.5. On acid hydrolysis, XII gave D-glucose and several compounds derived from a genuine aglycone. On the other hand, XII gave pterokaurene L_1 (XVI) on enzymatic hydrolysis with crude hesperidinase. These results indicated that XII is a glucoside of pterokaurene L_1. As the anomeric proton signal was found at lower field with a coupling constant of 7Hz, it is concluded that the D-glucosyl moiety of XII is β-linked to a carboxyl group. Comparison of the ^{13}C-NMR data of XII with those of pterokaurene L_1 was also useful for structural elcidation. ^{13}C-NMR signals of the aglycone moiety of XII appeared at almost the same positions as those of pterokaurene L_1, except for C-19 ,indicating that XII is the ester-glucoside of petrokaurene L_1. The ^{13}C-NMR signals of the glucosyl moiety appeared at $\delta_{Pyr.\text{-}d_5}$ 95.7 (G-1), 74.0 (G-2), 79.3 (G-3), 71.0 (G-4), 79.0 (G-5) and 62.1 (G-6). These values are characteristic of a β-D-glucopyranosyl moiety linked with a carboxyl group.[9] Thus, the structure of XII was established as 19-β-D-glucopyranosyl ester of pterokaurene L_1.

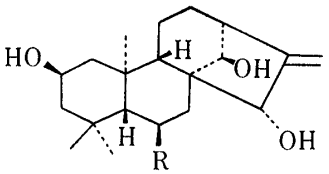
Compound XIII, $C_{26}H_{38}O_{10}$, amorphous powder, $[\alpha]_D^{20}$ −86° (c=1.2, MeOH), showed a UV absorption maximum at 239 nm (in MeOH, log ε 3.98). The ^{1}H-NMR spectrum (in Pyr. -d_5) exhibited two methyl proton signals at δ 1.30 (3H, s) and 1.85 (3H, s), two terminal methylene proton signals at δ 5.16 (1H, s) and 5.92 (1H, s) and one anomeric proton signal at δ 6.24 (1H, d, J=7 Hz) along with eight overlapping proton signals in the range of 3.7—4.6. In the ^{13}C-NMR spectrum of XIII (Table I), twenty-six signals were observed. Among them, signals similar to those of the β-D-glucosyl moiety in XII were found. The remaining signals indicated the presence of one carbonyl ($\delta_{Pyr.\text{-}d_5}$ 177.1, s), one terminal methylene (111.2, t and 151.2, s), one ketone (207.8, s) and two secondary hydroxyl (65.3, d and 67.5, d) groups in the aglycone of XIII. From these spectral data, the structure of XIII was suggested to be an ester glucoside of dihydroxy-15-oxo-*ent*-kaur-16-en-19-oic acid. On enzymatic hydrolysis using crude hesperidinase, XIII gave an aglycone XVII, $C_{20}H_{28}O_5$, colorless needles, mp 204—207°C, $[\alpha]_D^{22}$ −70° (c=0.2, MeOH). The mass spectrum (MS) of XVII showed a molecular ion peak at m/z 348, dehydrated ion peaks at m/z 330 and 312 and an intense ion peak at m/z 109. The last ion peak is characteristic of 18- or 19-kaurenoic acids bearing no substituents in ring A.[10] Therefore, the two hydroxyl groups of XVII are present in rings B and/or C. The ^{1}H-NMR spectrum of XVII exhibited two carbinyl proton signals at δ_{CDCl_3} 4.00 (1H, m) and 4.23 (1H, t of d, J=11 and 4 Hz) along with two methyl proton signals at

δ 1.08 (3H, s) and 1.31 (3H, s), one methine proton signal at δ 3.10 (1H, m, C-13-H) and two terminal methylene proton signals at δ 5.36 (1H, broad s) and 5.97 (1H, broad s). The carbinyl proton signal at δ 4.00 showed the same coupling pattern as that of XV, indicating the location of one of the hydroxyl groups to be at C-11β. The coupling pattern of the other carbinyl proton signal (t of d, J=11 and 4 Hz) indicates that the hydroxyl group is an equatorial one and has two axial protons and one equatorial proton on the neighboring carbons. Accordingly, its location was unequivocally determined to be at C-6β. Thus, the structure of XIII was determined to be the 19-β-D-glucopyranosyl ester of 6β,11β-dihydroxy-15-oxo-*ent*-kaur-16-en-19-oic acid (XIII) (Fig. 3).

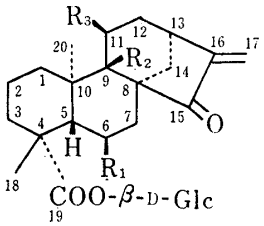
Compound XIV, $C_{26}H_{38}O_{10}$, amorphous powder, $[\alpha]_D^{20}$ $-39°$ (c=1.0, MeOH), showed UV and ^{1}H-NMR spectra similar to those of XIII. The ^{13}C-NMR spectrum of XIV (Table I) also suggested a structure similar to that of XIII except for the location of the hydroxyl groups in the aglycone moiety. The coupling pattern of ^{13}C-NMR signals at $\delta_{Pyr.-d_5}$ 67.6 (d) and 77.0 (s) indicated that one of the hydroxyl groups is secondary and the other is tertiary. On enzymatic hydrolysis using crude hesperidinase, XIV gave an aglycone XVIII, $C_{20}H_{28}O_5$, amorphous powder, $[\alpha]_D^{15}$ $-89°$ (c=0.35, MeOH). The ^{1}H-NMR spectrum of XVIII exhibited two methyl proton signals at δ_{CDCl_3} 1.14 (3H, s) and 1.53 (3H, s), one methine proton signal assignable to C-13-H at δ 3.07 (1H, m), one carbinyl proton signal at δ 4.40 (1H, t of d, J=11 and 4 Hz) and two terminal methylene proton signals at δ 5.33 (1H, s) and 5.99 (1H, s). The MS of XVIII showed the molecular ion peak at m/z 348, two dehydrated ion peaks at m/z 330 and 312 and an intense ion peak at m/z 109. These spectral data also indicate the structure of XVIII to be 15-oxo-*ent*-kaur-16-en-19-oic acid bearing one secondary and one tertiary hydroxyl groups. Though three positions (C-5, C-9 and C-13) are possible for the tertiary hydroxyl group, C-5 and C-13 were excluded in view of the presence of the intense ion peak at m/z 109 in the MS (indicating that ring A bears no hydroxyl groups) and a methine proton signal at δ 3.07 (assignable to C-13-H) in the ^{1}H-NMR spectrum. Therefore, the location of the tertiary hydroxyl group was determined to be at C-9. The location of the remaining secondary hydroxyl group was determined to be at C-6β in view of the coupling pattern of the carbinyl proton signal in the ^{1}H-NMR spectrum of XVIII. Thus, the structure of XIV was determined to be the 19-β-D-glucopyranosyl ester of 6β,9-dihydroxy-15-oxo-*ent*-kaur-16-en-19-oic acid (XIV) (Fig. 3).

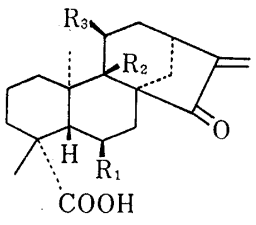


VIII : R=CH_3
IX : R=CH_2OH



XX : R=OH
XXI : R=H





XII : R_1=R_3=H, R_2=OH
XIII : R_1=R_3=OH, R_2=H
XIV : R_1=R_2=OH, R_3=H
XV : R_1=R_2=H, R_3=OH

XVI : R_1=R_3=H, R_2=OH
XVII : R_1=R_3=OH, R_2=H
XVIII : R_1=R_2=OH, R_3=H
XIX : R_1=R_2=H, R_3=OH

Fig. 3.

Table I shows the ^{13}C-NMR data of XIII and XIV compared with those of XV and XII, respectively. The differences of chemical shifts between XIII and XV and between XIV and XII are given in the third and sixth columns, respectively. These differences represent the substituent effects of a 6β-hydroxyl group on the *ent*-kaurane skeleton. The magnitudes of these differences are similar to those observed between compounds XX and XXI[11] as shown in the ninth column. Though the chemical correlations of XIII and XIV to known compounds were not possible because insufficient material was available, the above comparisons are enough to confirm the structures of XIII and XIV.

TABLE I. ^{13}C Chemical Shifts in Pyridine-d_5

	XIII	XV	δXIII$-\delta$XV	XIV	XII	δXIV$-\delta$XII	XX	XXI	δXX$-\delta$XXI
C-1	40.1	39.9		37.6	37.3		50.7	50.5	
C-2	19.3	19.3		19.3	19.3		63.8	64.1	
C-3	40.1	38.2	+1.9	39.9	38.3	+1.6	54.3	52.1	+2.1
C-4	45.2	44.0	+1.2	45.3	44.3	+1.0	36.0	34.9	+1.1
C-5	61.9	56.8	+5.1	55.3	50.0	+5.3	60.8	55.9	+4.9
C-6	67.5	20.5	+47.0	67.6	20.7	+46.9	67.8	19.4	+48.4
C-7	49.6	37.1	+12.5	39.9	34.3	+5.6	39.4	28.6	+10.8
C-8	51.0	50.9	+0.1	57.4	57.5	−0.1	52.8	52.8	0.0
C-9	62.5	63.1	−0.6	77.0	77.1	−0.1	56.2	56.7	−0.5
C-10	41.5	39.2	+2.3	47.2	45.5	+1.7	43.1	41.5	+1.6
C-11	65.3	65.3		30.1	30.2		18.2	18.3	
C-12	41.5	41.4		30.1	30.5		32.7	33.0	
C-13	37.6	37.8		37.6	37.8		50.9	51.3	
C-14	37.6	34.9	+2.7	32.6	31.8	+0.8	77.3	76.5	+0.8
C-15	207.8	208.9		206.9	207.9		83.6	83.5	
C-16	151.2	151.8		149.8	150.0		159.6	160.0	
C-17	111.2	110.7		114.2	113.8		111.1	110.7	
C-18	32.3	28.5	+3.8	32.3	28.8	+3.5	37.6	34.1	+3.5
C-19	177.1	176.7	+0.4	177.5	177.0	+0.5	23.4	22.8	+0.6
C-20	17.2	15.9	+1.3	18.2	17.4	+0.8	20.1	19.2	+0.9
G-1	95.9	95.8		95.8	95.7				
G-2	73.8	74.0		73.8	74.0				
G-3	79.1	79.3		79.1	79.3				
G-4	70.9	71.0		70.9	71.0				
G-5	78.9	79.0		78.8	79.0				
G-6	61.9	62.1		62.0	62.1				

(5) *Pteris altissima* POIR.

Luteolin 7-O-β-D-glucoside (VII), pterosin G (XI) and compounds XII, XIII and XV were isolated.

Derivatives of *ent*-kaurenoic acid, such as XII, XIII, XIV, XV, XVI and XIX, have been isolated from three species of *Pteris* in Japan and Taiwan.[12] Moreover, pterosin-type sesquiterpenes have been isolated from many genera of Pteridaceae. The distribution of these compounds suggests certain groupings of species in the systematics of *Pteris* and Pteridaceae. These interesting results will be discussed in forthcoming papers.

Experimental

Melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were taken with a JASCO DIP-SL automatic polarimeter. Circular dichroism (CD) spectra were recorded on a JASCO J-20 spectropolarimeter. Gas–liquid chromatography (GLC) was run on a Shimadzu GC-4BM-PF gas chromatograph with a flame ionization detector using a capillary column (30 m × 0.25 mm I. D., WCOT, SE-30, Wako Pure Chemical). The ^1H-NMR spectra were measured at 60 MHz

with a Hitachi R24B spectrometer and at 100 MHz with a JEOL FX-100 spectrometer, using tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; q, quartet). MS were taken at 70 eV on a Hitachi RMU-7M mass spectrometer with a direct inlet system. UV spectra were recorded on a Hitachi 323 spectrometer and IR spectra on a Hitachi IR-215 spectrometer. ^{13}C-NMR spectra were measured at 25 MHz with a JEOL FX-100 spectrometer with ^{2}H internal lock, using tetramethylsilane as an internal standard. The droplet countercurrent chromatography (DCC) apparatus consists of 200 column units of glass tubing (2.4 mm I. D., 60 cm long) connected by Teflon tubing (0.5 mm I. D.). The solvent system used was $CHCl_3$–MeOH–H_2O (4: 4: 3), with the upper layer as the mobile and the lower layer as the stationary phase. The flow rate was 20 ml/h and fractions of 5 ml were taken in a fraction collector. Activated charcoal (Wako Pure Chemical), silica gel (above 100 mesh, Kanto Chemical) and aluminium oxide 90 (neutral, activity II, 70-230 mesh ASTM, Merck) for column chromatography were used. Silica gel G (type 60, Merck) and silica gel GF_{254} (type 60, Merck) were used for preparative layer chromatography (PLC).

Isolation Procedure——1) *A. aureum* L.: The ferns were collected around the marsh near the airstrip of Limon, Limon province, Costa Rica, in April. The air-dried fronds (510 g) were extracted 3 times with 1 l of methanol under reflux for 6 hours. The combined extracts (3 l) and then 1 l of methanol were passed over activated charcoal (50 g) packed in a column of 6 cm diameter. The resulting solution (4 l) was concentrated to a syrup under reduced pressure. The syrup was chromatographed twice on silica gel using $CHCl_3$ and methanol as eluents, yielding quercetin-3-O-β-D-glucoside (I, 34 mg) and ponasterone A (III, 16 mg).

2) *N. praestantissima* (Bory) Fée: The ferns were collected in the dense shade of riparian forest at Cerro Zurqui, Heredia province, Costa Rica, in April. The air-dried fronds (400 g) were extracted 3 times with 2 l of methanol under reflux for 6 hours. The combined extracts and then 6 l of methanol were passed over activated charcoal (50 g) packed in a column of 7 cm diameter. The resulting solution (12 l) was concentrated to a syrup under reduced pressure. The syrup was chromatographed on silica gel (150 g) using $CHCl_3$ (600 ml), 10% methanol in $CHCl_3$ (600 ml, Frac. 1), 20% methanol in $CHCl_3$ (600 ml), 30% methanol in $CHCl_3$ (600 ml) and 40% methanol in $CHCl_3$ (600 ml, Frac. 2) as eluents. Frac. 1 was rechromatographed on silica gel using $CHCl_3$ and methanol as eluents to yield 3,6-anhydro-2-deoxy-D-glucose (V, 21 mg). Frac. 2 was concentrated and allowed to stand at 5°C for two weeks, affording 2-deoxy-D-glucose (IV, 130 mg) as a crystalline substance.

3) *P. podophylla* Swartz: The ferns were collected around the marsh near the airstrip of Limon, Limon province, Costa Rica, in April. The air-dried fronds (130 g) were extracted 3 times with 1 l of methanol under reflux for 6 hours. The combined extracts (3 l) and 3 l of methanol were passed over activated charcoal (30 g) packed in a column of 4 cm diameter. The resulting solution was concentrated to a syrup under reduced pressure. The syrup was chromatographed on a silica gel column (60 g) using $CHCl_3$ (300 ml), $CHCl_3$ (450 ml, Frac. 1), 10% methanol in $CHCl_3$ (600 ml, Frac. 2), 20% methanol in $CHCl_3$ (600 ml) and 30% methanol in $CHCl_3$ (900 ml, Frac. 3) as eluents. Frac. 1 was rechromatographed on alumina using 10% methanol in $CHCl_3$ as an eluent followed by PLC (solvent system, $CHCl_3$: ether=3: 1) to yield compound X (12 mg). Frac. 2 was rechromatographed on alumina using 10% methanol in $CHCl_3$ as an eluent to yield pterosin G (XI, 17 mg). Frac. 3 was concentrated to yield a crystalline substance, luteolin-7-O-β-D-glucoside (VII, 36 mg). The mother liquor was rechromatographed on silica gel using 20% methanol in $CHCl_3$ as an eluent followed by DCC to yield kaempferol 3,7-di-O-α-L-rhamnoside (II, 13 mg) and apigenin 7-O-β-D-glucoside (VI, 7 mg).

4) *P. livida* Mett.: The ferns were collected at Limon, Costa Rica, in April. The air-dried fronds (220 g) were extracted 3 times with 1 l of methanol under reflux for 6 hours. The combined extracts (3 l) and then 3 l of methanol were passed over activated charcoal (30 g) packed in a column of 4 cm diameter. The resulting solution (6 l) was concentrated to a syrup under reduced pressure. The syrup was chromatographed on silica gel (60 g) using $CHCl_3$ (500 ml), 10% methanol in $CHCl_3$ (300 ml, Frac. 1), 20% methanol in $CHCl_3$ (200 ml, Frac. 2). 20% methanol in $CHCl_3$ (100 ml, Frac. 3) and 30% methanol in $CHCl_3$ (200 ml, Frac. 4). Frac. 1 was subjected to PLC (solvent system, $CHCl_3$: MeOH=5: 1) to yield pterosin C (VIII, 8 mg) and pterosin S (IX, 11 mg). Frac. 2 was rechromatographed on alumina using 10% methanol in $CHCl_3$ as an eluent to yield 11β-hydroxy-15-oxo-*ent*-kaur-16-en-19-oic acid (XIX, 18 mg) and pterokaurene L_1 (XVI, 16 mg). Frac. 3 was subjected to DCC to yield compound XII (32 mg). Frac. 4 was subjected to PLC (solvent system, $CHCl_3$: MeOH=10: 3) followed by silica gel column chromatography (eluent, 20% methanol in $CHCl_3$) to yield paniculoside III (XV, 23 mg), compound XIII (35 mg) and compound XIV (24 mg).

5) *P. altissima* Poir.: The ferns were collected in the dense shade of riparian forest at Cerro Zurqui, Heredia province, Costa Rica, in April. The air-dried fronds (150 g) were extracted 3 times with 1 l of methanol under reflux for 6 hours. The combined extracts and 2 l of methanol were passed over activated charcoal (20 g) packed in a column of 4 cm diameter. The resulting solution (5 l) was concentrated to a syrup under reduced pressure. The syrup was chromatographed on silica gel (40 g) using $CHCl_3$ (500 ml), 5% methanol in $CHCl_3$ (400 ml, Frac. 1), 10% methanol in $CHCl_3$ (400 ml, Frac. 2), 20% methanol in $CHCl_3$ (400 ml, Frac. 3) and 40% methanol in $CHCl_3$ (800 ml, Frac. 4) as eluents. Frac. 1 was subjected to DCC followed by PLC (solvent system, $CHCl_3$: MeOH=5: 1) to yield pterosin G (XI, 17 mg) and compound XII (25 mg). Frac. 2 was subjected to DCC followed by PLC (solvent system, $CHCl_3$: MeOH=10: 3) to yield

paniculoside III (XV, 21 mg). Frac. 3 was subjected to DCC followed by alumina column chromatography (eluent, 20% methanol in $CHCl_3$) to yield compound XIII (27 mg). Frac. 4 was concentrated to yield a crystalline product, luteolin 7-O-β-D-glucoside (VII, 13 mg).

Quercetin 3-O-β-D-Glucoside (I)——Yellow needles from methanol, mp 180—185°C, $[\alpha]_D^{30}$ −6° (c=1.2, MeOH). UV λ_{max}^{MeOH} nm (log ε): 258 (4.69), 360 (4.67), $\lambda_{max}^{MeOH+MeONa}$ nm: 273, 410, $\lambda_{max}^{MeOH+AlCl_3}$ nm: 276, 306, 438, $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 271, 303, 359, 404, $\lambda_{max}^{MeOH+AcONa}$ nm: 274, 400, $\lambda_{max}^{MeOH+AcONa+H_3BO_3}$ nm: 263, 381. IR ν_{max}^{KBr} cm^{-1}: 3250, 1655, 1605, 1560, 1510, 1445, 1360, 1305, 1205, 1065, 1015, 795. ^{1}H-NMR (100 MHz, in CD_3OD) δ: 3.2—3.9 (6H), 5.20 (1H, d, J=7 Hz), 6.18 (1H, d, J=2 Hz), 6.37 (1H, d, J=2 Hz), 6.86 (1H, d, J=9 Hz), 7.57 (1H, d of d, J=9 and 2 Hz), 7.73 (1H, d, J=2 Hz). MS m/e: 302 (aglycone). It was found to be identical with an authentic sample by direct comparison (TLC, IR and mixed fusion).

Kaempferol 3,7-Di-O-α-L-rhamnoside (II)——Yellow needles from a mixture of methanol and water, mp 198—200°C, $[\alpha]_D^{18}$ −225° (c=0.5, MeOH). UV λ_{max}^{MeOH} nm (log ε): 266 (4.38), 345 (4.25), $\lambda_{max}^{MeOH+MeONa}$ nm: 249, 268, 388, $\lambda_{max}^{MeOH+AlCl_3}$ nm: 275, 302, 350, 400, $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 275, 300, 345, 398, $\lambda_{max}^{MeOH+NaOAc}$ nm: 266, 320, 354, $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm: 266, 320, 348. IR ν_{max}^{KBr} cm^{-1}: 3400, 1655, 1595, 1490, 1350, 1173, 965, 835, 806. ^{1}H-NMR (60 MHz, in Pyr.-d_5) δ: 1.40 (3H, d, J=5 Hz), 1.62 (3H, d, J=5 Hz), 3.8—5.0 (8H), 6.24 (2H, broad s), 6.76 (1H, d, J=2 Hz), 6.95 (1H, d, J=2 Hz), 7.26 (2H, d, J=9 Hz), 8.06 (2H, d, J=9 Hz). On acid hydrolysis (3% HCl), it gave kaempferol and L-rhamnose. They were found to be identical with authentic samples by direct comparison.

Ponasterone A (III)——Colorless needles from methanol, mp 270—272°C, $[\alpha]_D^{25}$ +75° (c=0.8, MeOH). UV λ_{max}^{MeOH} nm (log ε): 244 (4.11), 315 (2.99). IR ν_{max}^{KBr} cm^{-1}: 3380, 2945, 1643, 1052, 875. ^{1}H-NMR (100 MHz, in Pyr.-d_5) δ: 0.84 (6H, d, J=6 Hz), 1.08 (3H, s), 1.23 (3H, s), 1.59 (3H, s), 3.4—3.9 (2H, m), 4.14 (1H, m), 4.21 (1H, broad s), 6.23 (1H, d, J=1.5 Hz). ^{13}C-NMR (in Pyr.-d_5) δ: 203.3 (s), 165.9 (s), 121.6 (d), 84.2 (s), 76.8 (t), 76.8 (s), 68.0 (d), 68.0 (d), 51.3 (d), 50.0 (d), 48.1 (s), 38.7 (s), 38.0 (t), 37.2 (t), 34.5 (d), 32.4 (t), 32.1 (t), 31.8 (t), 30.3 (t), 28.2 (d), 24.4 (q), 23.3 (q), 22.4 (q), 21.5 (t), 21.5 (t), 21.1 (q), 17.9 (q). Its properties and spectral data are in good agreement with those reported.[3]

2-Deoxy-D-glucose (IV)——Colorless prisms from methanol, mp 141—145°C, $[\alpha]_D^{20}$ +43° (c=1.0, H_2O), α-anomer. IR ν_{max}^{KBr} cm^{-1}: 3400, 1465, 1415, 1370, 1155, 1120, 1085, 1065, 1015, 875. MS of its tetraacetate m/z: 332, 273, 272, 213, 170, 153, 128, 86. Its trimethylsilyl ether was identical with an authentic sample in GLC; t_R 10.0 and 13.0 min (column temp. 160°C).

3,6-Anhydro-2-deoxy-D-glucose (V)——Colorless syrup, $[\alpha]_D^{20}$ +46° (c=1.0, H_2O). IR ν_{max}^{neat} cm^{-1}: 3350, 2950, 1430, 1325, 1205, 1120, 1070, 1010, 940, 835. MS m/z: 146, 126, 117, 115, 111, 103, 99, 97, 85, 81. Its trimethylsilyl ether was identical with an authentic sample in GLC; t_R 5.3 and 5.7 min (column temp. 150°C).

Apigenin 7-O-β-D-Glucoside (VI)——Pale yellow needles from a mixture of methanol and water, mp 225—230°C, $[\alpha]_D^{18}$ −98° (c=0.3, MeOH). UV λ_{max}^{MeOH} nm (log ε): 269 (4.37), 335 (4.43), $\lambda_{max}^{MeOH+MeONa}$ nm: 247, 269, 388, $\lambda_{max}^{MeOH+NaOAc}$ nm: 257, 268, 355, 388, $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm: 268, 340, $\lambda_{max}^{MeOH+AlCl_3}$ nm: 276, 301, 349, 384, $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 278, 300, 343, 383. IR ν_{max}^{KBr} cm^{-1}: 3400, 1655, 1605, 1495, 1245, 1173, 1080, 830. ^{1}H-NMR (60 MHz, in Pyr.-d_5) δ: 3.7—4.5 (6H), 5.83 (1H, d, J=6 Hz), 6.81 (1H, d, J=2 Hz), 6.87 (1H, s), 7.09 (1H, d, J=2 Hz), 7.16 (2H, d, J=9 Hz), 7.87 (2H, d, J=9 Hz). On acid hydrolysis (3% HCl), it gave apigenin and D-glucose. They were found to be identical with authentic samples by direct comparison.

Luteolin 7-O-β-D-Glucoside (VII)——Yellow needles from methanol, mp 195—197°C, $[\alpha]_D^{18}$ −53° (c=1.1, Pyr.). UV λ_{max}^{MeOH} nm (log ε): 256 (4.35), 268 (4.32), 350 (4.40), $\lambda_{max}^{MeOH+MeONa}$ nm: 265, 402, $\lambda_{max}^{MeOH+AlCl_3}$ nm: 274, 299, 332, 430, $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 275, 297, 357, 390, $\lambda_{max}^{MeOH+NaOAc}$ nm: 261, 267, 408, $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm: 260, 374. IR ν_{max}^{KBr} cm^{-1}: 3350, 1655, 1600, 1495, 1260, 1175, 1065, 840. ^{1}H-NMR (60 MHz, in Pyr.-d_5) δ: 4.2—4.9 (6H), 5.89 (1H, d, J=7 Hz), 6.90 (1H, d, J=2 Hz), 6.98 (1H, s), 7.06 (1H, d, J=2 Hz), 7.25 (1H, d, J=8 Hz), 7.50 (1H, d of d, J=8 and 2 Hz), 7.83 (1H, d, J=2 Hz). On acid hydrolysis (3% HCl), it gave luteolin and D-glucose. They were shown to be identical with authentic samples by direct comparison.

Pterosin C (VIII)——Colorless needles from a mixture of $CHCl_3$ and CCl_4, mp 134—135°C, $[\alpha]_D^{23}$ +101° (c=0.2, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.53), 260 (4.13), 302 (3.25). IR ν_{max}^{KBr} cm^{-1}: 3350, 1680, 1600. ^{1}H-NMR (60 MHz, in a mixture of $CDCl_3$ and CD_3OD) δ: 1.30 (3H, d, J=7 Hz), 2.44 (3H, s), 2.62 (3H, s), 2.95 (2H, t, J=7 Hz), 3.60 (2H, t, J=7 Hz), 4.61 (1H, d, J=4 Hz), 7.23 (1H, s). MS m/z: 234, 219, 203, 185. It was identical with an authentic sample on direct comparison (TLC, IR and mixed fusion).

Pterosin S (IX)——Colorless needles from $CHCl_3$, mp 121—123°C, $[\alpha]_D^{18}$ +55° (c=0.3, MeOH). UV λ_{max}^{MeOH} nm (log ε): 216 (4.52), 259 (4.13), 302 (3.25). IR ν_{max}^{KBr} cm^{-1}: 3350, 1710, 1600, 1345, 1085, 1065, 995, 920. ^{1}H-NMR (60 MHz, in a mixture of $CDCl_3$ and CD_3OD) δ: 1.35 (3H, d, J=7 Hz), 2.47 (3H, s), 3.04 (2H, t, J=7 Hz), 3.65 (2H, t, J=7 Hz), 4.68 (1H, d, J=4 Hz), 4.93 (2H, s), 7.41 (1H, s). MS m/z: 250, 232, 221, 205, 203, 202. It was identical with an authentic sample on direct comparison (TLC, IR and mixed fusion).

Compound X [=6-(2-Chloroethyl)-2(*S*)-hydroxymethyl-5,7-dimethylindan-1-one]——Colorless needles from methanol, mp 130—132°C, $[\alpha]_D^{18}$ −1.2° (c=0.4, MeOH). UV λ_{max}^{MeOH} nm (log ε): 219 (4.60), 260 (4.20), 305 (3.45). IR ν_{max}^{KBr} cm^{-1}: 3400, 2920, 1685, 1600, 1335, 1230, 1065, 950. ^{1}H-NMR (60 MHz, in $CDCl_3$) δ: 2.45 (3H, s), 2.69 (3H, s), 3.3 (2H, m), 3.5 (2H, m), 3.93 (2H, broadened AB quartet), 7.16 (1H, s), 2.6—3.2 (3H, m). ^{13}C-NMR: Fig. 2. MS m/z: 254, 252, 236, 234, 223, 221, 217, 199, 185. Calcd for $C_{14}H_{17}ClO_2$: 254.089 and 252.092 (M), Found: 254.091 and 252.091 (M^+). $[\theta]_{320}^{20}$ +101° (MeOH).

Pterosin G (XI)——Colorless needles from methanol, mp 151—152°C, $[\alpha]_D^{18}$ −14° (c=0.4, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.51), 261 (4.16), 307 (3.57). IR ν_{max}^{KBr} cm^{-1}: 3400, 1670, 1597, 1035, 947. ^{1}H-NMR (60 MHz, in CD_3OD) δ: 2.43 (3H, s), 2.63 (3H, s), 2.96 (2H, t, J=7 Hz), 3.61 (2H, t, J=7 Hz), 3.85 (2H, AB quartet, J=15 Hz), 7.15 (1H, s), 2.5—3.2 (3H, m). ^{13}C-NMR: Fig. 2. MS m/z: 234, 219, 203, 201, 191, 185, 173. Its properties and spectral data are in good agreement with those reported.[5]

Compound XII (=9-Hydroxy-15-oxo-*ent*-kaur-16-en-19-oyl-β-D-glucoside)——Colorless needles from a mixture of methanol and water, mp 140—144°C, $[\alpha]_D^{18}$ −77° (c=1.2, MeOH). *Anal.* Calcd for $C_{26}H_{38}O_9$: C, 63.14; H, 7.74. Found: C, 63.01; H, 7.68. UV λ_{max}^{MeOH}: 234 nm (log ε 3.88). IR ν_{max}^{KBr} cm^{-1}: 3500, 3400, 1715, 1640, 1070, 1025, 935. ^{1}H-NMR (100 MHz, in Pyr.-d_5) δ: 1.29 (3H, s), 1.45 (3H, s), 3.7—4.5 (6H), 5.14 (1H, s), 5.97 (1H, s), 6.22 (1H, d, J=7 Hz). ^{13}C-NMR: Table I.

Compound XIII (=6β,11β-Dihydroxy-15-oxo-*ent*-kaur-16-en-19-oyl-β-D-glucoside)——Colorless amorphous powder, $[\alpha]_D^{20}$ −86° (c=1.2, MeOH). *Anal.* Calcd for $C_{26}H_{38}O_{10}$: C, 61.16; H, 7.50. Found: C, 62.03; H, 7.61. UV λ_{max}^{MeOH}: 239 nm (log ε 3.98). ^{1}H-NMR (100 MHz, in Pyr.-d_5) δ: 1.30 (3H, s), 1.85 (3H, s), 5.16 (1H, s), 5.92 (1H, s), 6.24 (1H, d, J=7 Hz), 3.7—4.6 (8H). ^{13}C-NMR: Table I.

Compound XIV (=6β,9-Dihydroxy-15-oxo-*ent*-kaur-16-en-19-oyl-β-D-glucoside)——Colorless amorphous powder, $[\alpha]_D^{20}$ −39° (c=1.0, MeOH). *Anal.* Calcd for $C_{26}H_{38}O_{10}$: C, 61.16; H, 7.50. Found: C, 60.91; H, 7.82. UV λ_{max}^{MeOH}: 234 nm (log ε 3.58). ^{1}H-NMR (100 MHz, in Pyr.-d_5) δ: 1.47 (3H, s), 1.85 (3H, s), 5.16 (1H, s), 5.96 (1H, s), 6.14 (1H, d, J=8 Hz), 3.7—4.7 (7H). ^{13}C-NMR: Table I.

11β-Hydroxy-15-oxo-*ent*-kaur-16-en-19-oyl-β-D-glucoside (=Paniculoside III; XV)——Colorless needles from a mixture of methanol and water, mp 160—162°C, $[\alpha]_D^{23}$ −114° (c=1.1, MeOH). UV λ_{max}^{MeOH}: 239 nm (log ε 3.83). IR ν_{max}^{KBr} cm^{-1}: 3400, 1725, 1710, 1640, 1080. ^{1}H-NMR (100 MHz, in Pyr.-d_5) δ: 1.25 (6H, s), 3.8—4.6 (6H), 5.14 (1H, broad s), 5.92 (1H, broad s), 6.17 (1H, d, J=7 Hz). MS m/z: 332, 317, 314, 109. ^{13}C-NMR: Table I. It was shown to be identical with an authentic sample by direct comparison (TLC, IR and mixed fusion).

9-Hydroxy-15-oxo-*ent*-kaur-16-en-19-oic Acid (=Pterokaurene L_1, XVI)——Colorless prisms from benzene, mp 218—219°C, $[\alpha]_D^{23}$ −116° (c=1.1, MeOH). UV λ_{max}^{MeOH}: 235 nm (log ε 3.90). IR ν_{max}^{KBr} cm^{-1}: 3550, 1705, 1690, 1645. ^{1}H-NMR (100 MHz, in Pyr.-d_5) δ: 1.37 (6H, s), 5.17 (1H, broad s), 6.01 (1H, broad s). MS m/z: 332, 314, 286, 269, 268, 246, 176, 165, 164. ^{13}C-NMR (in Pyr.-d_5) δ: 207.8 (C-15), 180.4 (C-19), 150.1 (C-16), 113.9 (C-17), 77.1 (C-9), 57.5 (C-8), 49.4 (C-5), 45.5 (C-10), 44.1 (C-4), 38.6 (C-3), 37.9 (C-13), 37.5 (C-1), 34.4 (C-7), 32.1 (C-14), 30.5 (C-12), 30.2 (C-11), 29.6 (C-18), 21.1 (C-6), 19.7 (C-2), 17.7 (C-20). It was found to be identical with an authentic sample by direct comparison (GLC, IR and mixed fusion).

Acid Hydrolysis of Compound XII——Compound XII (20 mg) was hydrolyzed with 3% HCl (5 ml) at 90°C for 3 hours. The reaction mixture was neutralized with 3% Na_2CO_3 solution and extracted with ethyl acetate. TLC of the ethyl acetate layer indicated the presence of several compounds derived from the genuine aglycone. The water layer was concentrated and the residue was chromatographed on silica gel using 30% methanol in $CHCl_3$ as an eluent to yield 2 mg of D-glucose, $[\alpha]_D^{17}$ +40° (c=0.1, H_2O). Its trimethylsilyl ether was identical with an authentic sample on GLC; t_R 7.5 and 10.6 min (column temp., 190°C).

Enzymatic Hydrolysis of Compound XII——A solution of compound XII (20 mg) and crude hesperidinase (60 mg, Tanabe Pharm. Co.) in 0.05 M citrate buffer (pH 4.0, 20 ml) was stirred at 40°C for 3 hours. The reaction mixture was extracted with ethyl acetate. The ethyl acetate solution was washed with water, dried over anhydrous Na_2SO_4 and concentrated. The residue was subjected to PLC (solvent system, $CHCl_3$: Ether=1:2) to yield pterokaurene L_1 (XVI, 4 mg), which was shown to be identical with an authentic sample by direct comparison (GLC, IR and mixed fusion).

Enzymatic Hydrolysis of Compound XIII——Compound XIII (20 mg) was hydrolyzed in the same way as compound XII to yield 6 mg of aglycone XVII.

6β,11β-Dihydroxy-15-oxo-*ent*-kaur-16-en-19-oic Acid (XVII)——Colorless needles from methanol, mp 204—207°C, $[\alpha]_D^{22}$ −70° (c=0.2, MeOH). UV λ_{max}^{MeOH}: 239 nm (log ε 3.87). IR ν_{max}^{KBr} cm^{-1}: 3480, 1765, 1710, 1640, 1460, 1195, 1100. ^{1}H-NMR (100 MHz, in $CDCl_3$) δ: 1.08 (3H, s), 1.31 (3H, s), 3.10 (1H, m), 4.00 (1H, m), 4.23 (1H, t of d, J=11 and 4 Hz), 5.36 (1H, broad s), 5.97 (1H, broad s). MS m/z: 348, 330, 312, 109. Calcd for $C_{20}H_{28}O_5$: 348.194 (M), Found: 348.193 (M^+).

Enzymatic Hydrolysis of Compound XIV——Compound XIV (20 mg) was hydrolyzed in the same way as compound XII to yield 5 mg of aglycone XVIII.

6β,9-Dihydroxy-15-oxo-*ent*-kaur-16-en-19-oic Acid (XVIII)——Colorless amorphous powder, $[\alpha]_D^{15}$ −89° (c=0.2, MeOH). UV λ_{max}^{MeOH}: 235 nm (log ε 3.50). IR ν_{max}^{KBr} cm^{-1}: 3420, 1710, 1645. ^{1}H-NMR (100 MHz, in $CDCl_3$) δ: 1.14 (3H, s), 1.53 (3H, s), 3.07 (1H, m), 4.40 (1H, t of d, J=11 and 4 Hz), 5.33 (1H, s), 5.99 (1H, s). MS m/z: 348, 330, 312, 109. Calcd for $C_{20}H_{28}O_5$: 348.194 (M), Found: 348.193 (M^+).

11β-Hydroxy-15-oxo-*ent*-kaur-16-en-19-oic Acid (XIX)——Colorless needles from a mixture of $CHCl_3$ and benzene, mp 254—258°C, $[\alpha]_D^{22}$ −152° (c=0.7, MeOH). UV λ_{max}^{MeOH}: 238 nm (log ε 3.74). IR ν_{max}^{KBr} cm^{-1}: 3450, 1728, 1692, 1643. ^{1}H-NMR (100 MHz, in Pyr.-d_5) δ: 1.17 (3H, s), 1.32 (3H, s), 2.98 (1H, m), 4.24 (1H, m), 5.19 (1H, broad s), 5.96 (1H, broad s), 7.4 (1H). MS m/z: 332, 317, 314, 109. ^{13}C-NMR (in Pyr.-d_5) δ: 208.8 (C-15), 179.9 (C-19), 151.8 (C-16), 110.7 (C-17), 65.2 (C-11), 63.2 (C-9), 56.4 (C-5), 50.9 (C-8), 43.9 (C-4), 41.5 (C-12), 40.2 (C-1), 39.3 (C-10), 38.5 (C-3), 37.8 (C-13), 37.3 (C-7), 34.9 (C-14), 29.3 (C-18),20.9(C-6),

19.6 (C-2), 16.0 (C-20). It was shown to be identical with an authentic sample by direct comparison (GLC, IR and mixed fusion).

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