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STUDY OF THE SECRETION FROM A SCALE INSECT (*CEROPLASTES CERIFERUS*) DITERPENOIDS AND SESTERTERPENOIDS

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Abstract Structures of four new minor sesterterpenoids **1**–**3**, **18** and three new diterpenoids **12**–**14** isolated from the secretion of *Ceroplastes ceriferus* are described. All four sesterterpenoids are 14-membered monocyclic compounds; one of them has been chemically correlated with cericeroic acid[1] of proven absolute stereochemistry. The "cyclic wax" was a complex mixture of esters consisting of fatty acids (C_{10}–C_{32}) and unusual cyclic alcohols (diterpenoids and sesterterpenoids).

We have recently reported[1] the structural elucidation and chemical correlation of six macrocyclic sesterterpenoids which were isolated from the secretion of *C. ceriferus* Anderson (fam. Coccidae). This paper characterizes additional constituents contained in the chloroform extract[1] of the same insect, collected in Osaka Prefecture, Japan, in January 1978.

The acidic fraction of the acetone-soluble portion (Fig. 1) has yielded new minor sesterterpenoid acids **1**–**3** and tricyclicditerpenoid acids **4**–**11**. The diterpenoid acids are all tricyclic and have been characterized as sandaracopimaric **4**,[2] isopimaric **5**,[2] palustric **6**,[2] abietic **7**,[2] neoabietic **8**,[2] dehydroabietic **9**,[2] 7-hydroxydehydroabietic **10**, and 7-oxodehydroabietic acid **11**; the configurations of these diterpenoid acids were the same with those from common terrestrial plants.

The acetone-insoluble fraction,[1] i.e. "wax esters",[3] were also studied and found to be a mixture of aliphatic and cyclic esters. The aliphatic compounds were esters formed between n-C_{16}-, C_{18}-, C_{20}-, C_{22}-, C_{28}-, C_{30}-, C_{32}- and C_{34}-saturated fatty acids and n-C_{26} alcohol; in addition, two acetates of n-C_{26}- and C_{28}- alcohols were present. The "cyclic wax"[3] was found to consist of mono- and di-esters of bicyclic diterpenoid alcohols, i.e. labda-8(20),13-diene-15,16-diol **12**, labda-7,13-diene-15,20-diol **13**, labda-7,13-diene-3,15-diol **14**,[4] and labda 8(20),13-diene-15-ol **15**;[5] as far as we are aware the diterpenoid alcohols **12** and **13** have not been described in the literature. The fatty acid moieties of the diterpenoid esters consisted of n-C_{10}-, C_{12}-, C_{14}-, C_{16}-, C_{18}- and C_{20}- saturated acids. The cyclic wax also contained sesterterpenoid esters which consisted of n-C_{28}-, C_{30}- and C_{32}- acids linked to cericerol-I **16**,[1] and n-C_{10}-, C_{12}- and C_{14}-, acids linked to cericerol-II **17**[1] and a new alcohol **18**.

Spectral data indicated that the four new minor sesterterpenoids **1**–**3** and **18** possessed a 14-membered monocyclic structure with an 8-carbon side-chain. Dehydration of the methyl ester of compound **1** gave cericeroic acid **19** methyl ester of proven absolute configuration. The presence of these unique sesterterpenoids and the enantiomeric series of sesquiterpenoids[6] in the insect secretion should be noted. Recently a similar sesterterpenoid, ceriferic acid **20** which has different arrangements of double bonds has also been found in the same Japanese scale insect.[7] A truly remarkable feature of these sesterterpenoids is the fact that albocerol **21** which has different arrangements of double bonds has also been isolated from a Mexican scale insect species *Ceroplastes albolineatus*.[8] Namely, the 14-membered rings of cericerol[1] and albocerol,[7,8] as represented by **22** and **23**, respectively, owe their geneses to opposing modes of cyclization of the geranylfarnesyl pyrophosphate precursor.

Structures of sesterterpenoids **1**–**3**, **18** *and diterpenoids* **12**–**14**

18-Dihydro-19-hydroxy-cericeroic acid **1**, $C_{26}H_{42}O_3$ (high resolution MS), $[\alpha]_D^{27}$ − 77.5°, was isolated in a pure state, as its methyl ester. The ^{1}H NMR spectrum exhibits four methyls at δ 1.22 (6 H, s), 1.52 (3 H, br. s) and 1.68 (3 H, br. s), two vinyl protons at δ 4.96–5.44 (2 H, m), a methoxyl at 3.75 (3 H, s), an exomethylene at 4.75, 4.80 (both 1 H, br. s) and a strongly deshielded olefin proton at 5.70 (1 H, d.d, J = 4, 10). A comparison of the ^{1}H NMR spectral characteristics of **1**-methyl ester with those of methyl cericeroate **19**[1] indicated that the two were closely related except for the dimethyl carbinol group at 1.22 (6 H, s) in place of an isopropylidene group at 1.62 and 1.70 in **19**, and the presence of five vinyl protons in **1** instead of six in **19**. The ^{1}H NMR data together with the ^{13}C NMR data (Table 1) led to structure **1**. Confirmation of **1** was readily achieved by a direct correlation with methyl cericeroate **19** of established absolute configuration.[1] Namely, methyl ester of **1** was dehydrated with $SOCl_2$/Pyridine to give methyl cericeroate having indistinguishable spectral data from authentic material.

Compound **2**, $C_{26}H_{40}O_2$, colorless oil, $[\alpha]_D^{27}$ − 32.5°, was obtained in a pure state, as its methyl ester, after column chromatography on $AgNO_3$-impregnated silica gel. The IR spectrum (ν_{max} 1712, 1639 cm^{-1}) showed that the carboxylic function must be α,β-unsaturated. The MS fragmentation pattern indicated a marked resemblance to that of methyl

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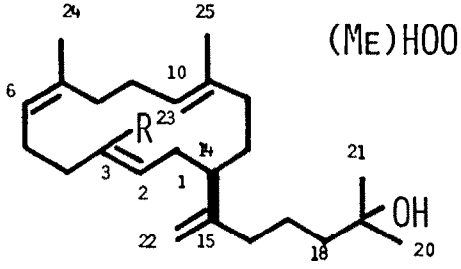
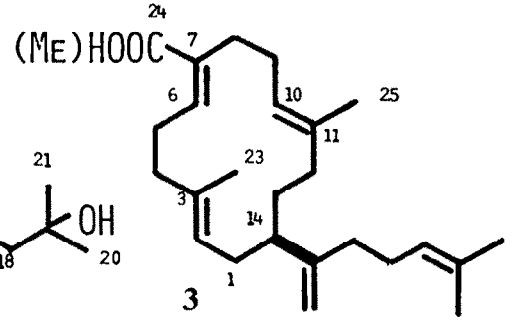


1: R=COOH (ME)



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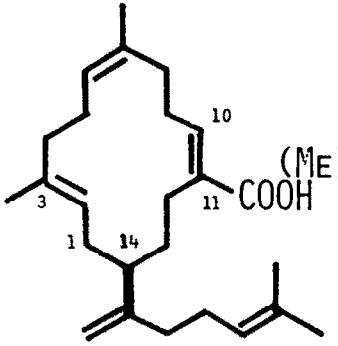

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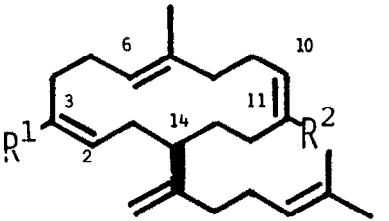
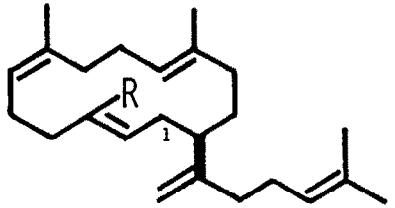


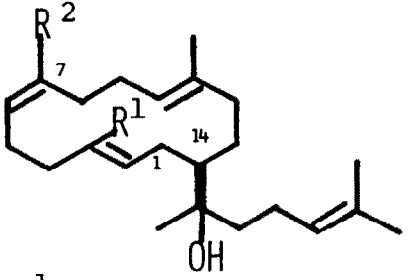
2A: R^1=COOH (ME), R^2=CH_3

2B: R^1=CH_3, R^2=COOH (ME)



16: R=CH_2OH

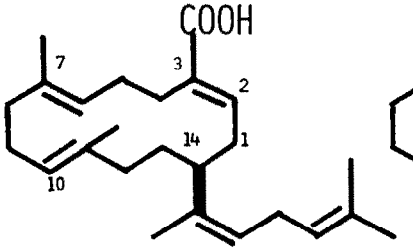
19: R=COOH (ME)



17: R^1=CH_2OH(59.8), R^2=CH_3(22.2)

18: R^1=CH_3(15.3), R^2=CH_2OH (65.9)

(numerals in parentheses denote ^{13}C signals, in ppm)



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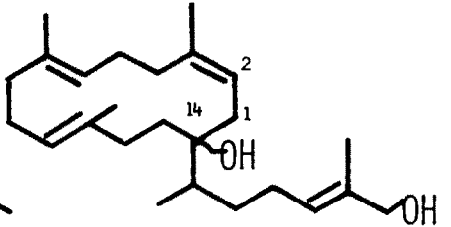

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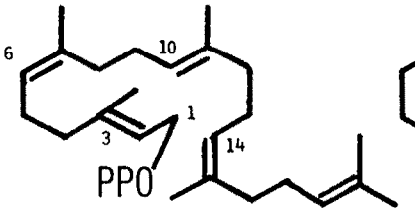

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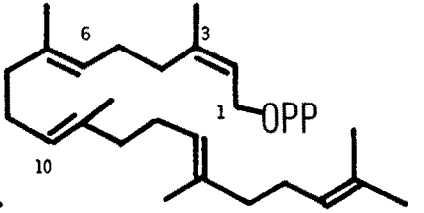

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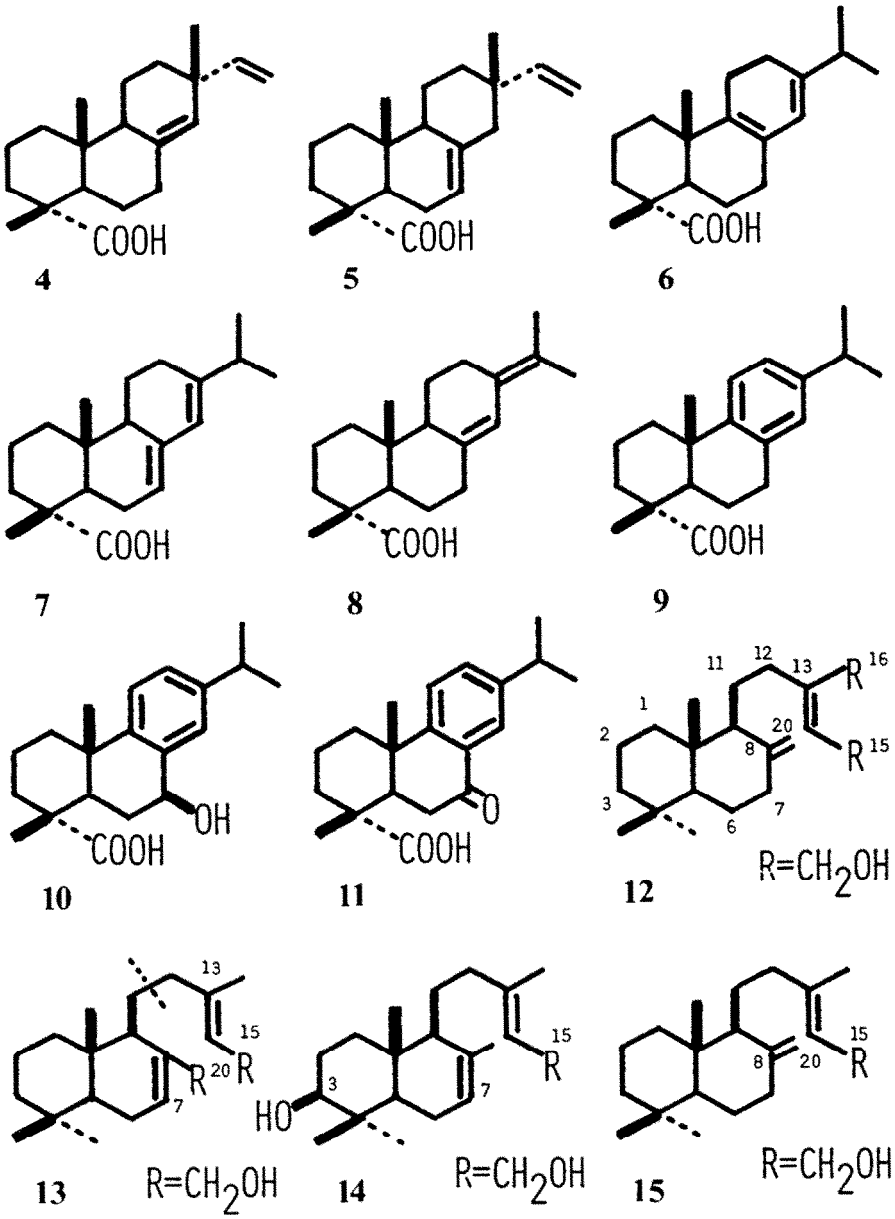

Fig. 1. Additional constituents of *Ceroplastes ceriferus*.[1]

C. ceriferus —ext. with $CHCl_3$→ slurry —ppt. with acetone→ insoluble esters*; soluble → neutral[1]; acidic[1] → diterpenoids (4 11); sesterterpenoids (1-3)

*aliphatic esters
alcohol:n-C_{26}sat. alc./acids:n-C_{16}-, C_{18}-, C_{20}-, C_{22}-, C_{28}-, C_{30}-, C_{32}-, C_{34}-sat. acids n-C_{26}-, C_{32}-, C_{34}-sat. acids n-C_{26}-, and n-C_{28}-acetates
*diterpenoid esters
alcohols: **12**–**15**/acids:n-C_{10}-, C_{12}-, C_{14}-, C_{16}-, C_{18}-, C_{20}-sat. acids
*sesterterpenoid esters
cericerol-I **16**/n-C_{28}-, C_{30}-, C_{32}-acids; cericerol-II **17**/n-C_{10}-, C_{12}-, C_{14}-acids; alcohol **18**/n-C_{10}-, C_{12}-, C_{14}-acids

cericeroate **19**.[1] The ^{1}H NMR spectrum of the methyl ester of compound **2** exhibits four vinylic methyls at 1.54, 1.63 (each 3 H, s) and 1.69 (6 H, br. s) and vinylic protons at 4.95–5.34 (3 H, m); the spectrum also shows an exomethylene group at 4.74 (2 H, br. s). Protons at 3.73 (3 H, s) and 6.74 (1 H, m) are readily assignable to $-\underset{|}{C}=\underset{|}{C}$ with *cis* geometry (E). The ^{13}C NMR

H $COOCH_3$

spectrum indicated the presence of two vinylic methyl groups in *cis* geometry to the vinyl protons, one in the ring (δ 22.9) and the other in the side-chain (δ 25.7).§[1] Since the unsaturated ester has a *cis* geometry (see above), it follows that the remaining annular double bond which carries the methyl group absorbing at 15 ppm has a *trans* geometry.

The fact that compound **2** exhibited a negative CD Cotton effect ($\Delta\varepsilon_{225} - 9.08$) at the wavelength corresponding to the λ_{max} of the unsaturated ester indicated that this chromophore should be close to the single chiral center at C-14. These considerations lead to three possible structures, **2** or **2A** or **2B**. The eight monocyclic sesterterpenoids isolated to date (including the new diol **18**) all have a 2-t/6-c/10-t skeletal structure. On the other hand, the ring moiety of structures **2A** and **2B** consists of 2-c/6-t/10-c double bonds, *i.e.* the geometries of *all three* double bonds are opposite to those of the major congeners. In contrast, the double bonds in structure **2** have 2-t/6-c/10-c arrangements and only the 10-ene geometry differs from those of others. We thus favor structure **2**, i.e. a 2(E), 6(Z), 10(E)-25 acid, for this minor congener. Furthermore, in analogy with other constituents[1] we assign an R-configuration (or "β" as depicted) to C-14 on biogenetic grounds.

Compound **3**, $C_{26}H_{40}O_2$, $[\alpha]_D^{27} - 48.6°$, was also purified as its methyl ester. MS fragments indicated that the side chain is the same with compound **2**. Spectral data showed the presence of an α,β-unsaturated carboxyl group (ν_{max} 1712, 1639 cm^{-1}) in *trans* geometry (δ 5.74, t, J = 7) to the β-vinyl proton. In addition to the transoid ester, the ring contains two additional transoid double bonds as judged from the chemical shifts of the two annular olefinic methyls at 1.61 ppm (6 H);[1] the ring thus consists of 2-t/6-t/10-t double bonds, where the geometry of the 6-ene differs from the eight other major components. The absence of a CD Cotton effect at the wavelength of the unsaturated ester chromophore indicated that this chromophore must be remote from the single chiral

Table 1. Correlation of ^{13}C-chemical shifts of sesterterpenoids **1** and **18** with methyl cericeroate **19** and cericerol-II **17** (in $CDCl_3$, $\delta C^{TMS} = 0$ ppm)

C-atom	**1**	**19**	**18**	**17**
C-1	30.1[a]	30.7[a]	26.4[a]	28.3[a]
C-2	141.4	141.6	125.6	129.2
C-3	129.9	130.2	133.7	136.5
C-4	30.4[a]	30.8[a]	26.6[a]	30.3[a]
C-5	30.6[a]	30.4[a]	28.9[a]	29.1[a]
C-6	125.4	125.7	127.5	126.4
C-7	133.6	133.9	137.8	134.2
C-8	35.2	35.5[b]	39.8[b]	35.1
C-9	25.7[b]	25.6[c]	24.0[c]	24.4[b]
C-10	124.2	124.4	125.6	126.0
C-11	132.9	133.2	132.7	134.2
C-12	35.9	36.2[b]	39.0[b]	39.0
C-13	25.3[b]	26.0[c]	24.8[c]	24.7[b]
C-14	44.2	44.7	46.8	47.2
C-15	152.2	152.5	75.3	75.7
C-16	33.8	33.5	39.9	39.9
C-17	22.3	26.5	22.0	22.2
C-18	43.6	124.4	124.6	124.7
C-19	70.3	131.2	131.2	131.5
C-20	28.9	25.6	25.5	25.7
C-21	28.9	17.6	17.5	17.7
C-22	108.7	109.0	23.7	23.6
C-23	168.3	168.5	15.3[d]	59.8
C-24	22.1	22.4	65.9	22.2
C-25	15.1	15.3	15.2[d]	15.5
$-COOCH_3$	50.8	51.0		

Assignments indicated by alphabets a-d in each column are mutually exchangeable.

§These structure assignments are based on comparison with the methyl peaks of **19** which in turn were deduced from T_1-relaxation measurements.[1]

Table 2. ^{13}C-Chemical shifts of diterpenoids **12–14** and monoacetates of **13** and **14** (in $CDCl_3$, $\delta C^{TMS} = 0$ ppm)

C-atom	**12**	**13**	**13**-acetate	**14**	**14**-acetate
C-1	38.4	39.0	38.9	37.2	36.5
C-2	19.4	18.7	18.7	27.2	23.0
C-3	42.2	42.2	42.1	78.9	80.8
C-4	33.6	32.8	33.0	38.6	37.2
C-5	55.6	51.6	51.8	54.3	53.8
C-6	24.5	25.0	25.0	25.5	25.3
C-7	34.8[a]	124.8	129.0	122.1	121.6
C-8	148.6	138.9	133.9	134.9	134.8
C-9	56.5	49.8	49.6	49.5	49.4
C-10	39.7	36.6	36.6	36.5	36.2
C-11	22.3	23.6	23.8	23.4	23.6
C-12	39.2[a]	41.1	41.1	41.9	41.7
C-13	144.4	139.4	139.4	139.4	138.6
C-14	126.1	123.5	123.7	123.6	123.8
C-15	58.6	59.0	59.2	59.1	58.7
C-16	60.9	16.2	16.2	16.3	16.1
C-17	14.6	13.5	13.5	13.5	13.4
C-18	33.6	33.0	33.0	27.8	27.5
C-19	21.8	21.7	21.8	15.0	15.9
C-20	106.3	65.3	67.7	21.9	21.7
$-OCO\underline{C}H_3$			21.1		21.0
$-\underline{O}COCH_3$			170.8		170.6

Assignment indicated by a letter (a) in a column is mutually exchangeable.

center at C-14, i.e. the COOMe is at C-7 and not at C-3 nor C-11. ^{13}C NMR spectrum was not taken due to insufficient amount.

Cericerene-15,24-diol **18**, $[\alpha]_D^{27} - 35.7°$, has the molecular formula of $C_{25}H_{42}O_2$; *m/e* 374 (M^+). The MS fragmentation indicated a marked structural resemblance to cericerol-II **17**.[1] The ^{1}H NMR spectrum shows a methyl attached to a carbon carrying a hydroxyl group at 1.14, four vinylic methyls at 1.54, 1.69 (each 3 H, s) and 1.62 (6 H, s), and vinylic protons at 4.8–5.2 (3 H).

The hydroxymethyl signal of **18** appears as a singlet (δ 4.02, 2 H, br. s). In contrast, the CH_2OH group of cericerol-II **17**, which is located close to the chiral center at C-14 and the *tert*-hydroxyl shows its ^{1}H NMR signal as a doublet (δ 3.98 and 4.23, both 1 H, d, J = 12). This difference suggested that the hydroxymethyl group is remote from C-14. The positioning of this group on C-7 is based on the following data. The vinyl proton in β position of the primary allylic hydroxyl group was observed at a lower field than that in cericerol-II **17** (δ 5.68 *versus* 5.39). This shows that the hydroxymethyl group and the vinyl proton are attached cisoid to the double bond, i.e. CH_2OH is at C-7. The ^{13}C NMR spectrum of **18** was also compared to that of cericerol-II (Table 1). Conspicuous differences were the appearance of a high-field methyl signal at 15.3 ppm (*versus* 22.2 ppm in **17**) and a lowfield hydroxymethyl signal at 65.9 ppm (*versus* 59.8 ppm in **17**). The chemical shift differences can be accounted for by operation of the ^{13}C NMR γ-effect; these data lead to expression **18** for this minor congener. Again a 14-R configuration is assumed from biogenetic considerations.

Labda-8(20),13-diene-15,16-diol **12**, $[\alpha]_D^{27} + 31.8°$ has the molecular formula $C_{20}H_{34}O_2$. The ^{1}H NMR spectrum shows three singlet methyls (δ 0.67, 0.80, 0.87), an exomethylene (δ 4.49, 4.81, each 1 H, br. s), a vinyl proton (δ 5.57, br. t, J = 8) adjacent to a hydroxymethyl (δ 4.17, 2 H, br. d, J = 8), and an additional hydroxymethyl (δ 4.14, 2 H, br. s). Spectral data lead to the labdane structure **12** for this compound. Full assignment of ^{13}C NMR spectrum is shown in Table 2. Two hydroxymethyl groups were confirmed to be in *cis* geometry by formation of an acetonide.

Labda-7,13-diene-15,20-diol **13**, $[\alpha]_D^{27} - 2°$, has a molecular formula of $C_{20}H_{34}O_2$. The ^{1}H NMR spectrum shows three methyl groups at δ 0.77 (3 H, s), 0.90 (6 H, br. s), vinyl methyl at 1.69 (3 H, br.s) a hydroxymethyl (4.09, 2 H, br. d, J = 7) adjacent to a vinyl proton (5.43, 1 H, br. t, J = 7), another hydroxymethyl bearing nonequivalent methylene protons at 3.90, 4.15 (each 1 H, d, J = 13), and a vinyl proton (7-H) at 5.77 (1 H, m). Spectral data readily led to structure **13** which was supported by the ^{13}C NMR data (Table 2). Mild hydrolysis of **13**-diacetate with MeOH-K_2CO_3 afforded a monoacetate, $C_{22}H_{36}O_3$, $[\alpha]_D^{27} + 5.8°$. The low chemical shifts of the nonequivalent methylene protons (4.40 and 4.58 ppm, d, J = 13) indicated that the monoacetate was attached to C-20; this is supported from the ^{13}C NMR spectrum (Table 2) and the MS fragment at *m/e* 262 ($M-C_5H_{10}O$, 25%, see **13**).

Labda-7,13-diene-3,15-diol **14**,[4] $[\alpha]_D^{27} - 2.1°$ has the molecular formula $C_{20}H_{34}O_2$. All spectral data were identical to those of the reported structure,[4] except for the optical rotation which was taken as a

very dilute solution.[4] To confirm the stereochemistry, **14** was hydrogenated to the tetrahydro derivative which was identical with labdane-3,15-diol of known stereochemistry.[9] The β-configuration of 3-hydroxy group was confirmed by Jones oxidation and subsequent $NaBH_4$ reduction, which gave back the original configuration at C-3. The 3-H ^{1}H NMR peak at δ 3.17, d.d, J = 5, 9 Hz, also leads to a 3β-OH structure. The 3-monoacetate, $C_{22}H_{36}O_3$, $[\alpha]_D^{27}$ − 34.6° was prepared in a manner similar to that described above for **13**; 3-H, 4.47 ppm (d.d, J = 5, 9), 7-, 14-H, 5.40 ppm (2 H, m), 15-H, 4.11 ppm (2 H, br. d, J = 7).

EXPERIMENTAL

The following instruments were used to obtain spectral/analytical data: a Hitachi EPI-G2 infrared spectrometer (compounds were measured as films); Hitachi R-20B and JEOL FX-100 spectrometers (^{1}H, ^{13}C NMR; δ (ppm), TMS as an internal standard in $CDCl_3$); a Hitachi RMU-6 mass spectrometer (70 eV, direct inlet system); a JEOL JMS-01SG (high resolution MS) unit for determination of the molecular formulae of new compounds; a Perkin-Elmer 141 polarimeter ([α], at 589, 578, 546, 436, and 365 nm in $CHCl_3$); a Varian Aerograph model 920 (prep. glc; 5 ft × 1/8 in Al column packed with 10% Carbowax 20M on Diasolid L, with He as a carrier gas); a chromatography column (Mallinckrodt, Silica gel 100 mesh; 15% $AgNO_3$-silica gel; prepacked Lobar column, silica gel 60).

Isolation. The minor sesterterpenoids **1**–**3** and tricyclic diterpenoids **4**–**11** were isolated from the acidic fraction of the acetone-soluble portion after esterification and repeated chromatography. Diterpenoids **4**–**11** were further purified by preparative glc at 200°. The acetone-insoluble fraction was chromatographed on silica gel, $AgNO_3$-impregnated silica gel, prepacked Lobar column of silica gel 60, and prep. tlc. Each single spot on HPTLC was examined by ^{1}H NMR spectrum, then refluxed 1 h with 10% NaOH-EtOH soln. for hydrolysis. After usual working up, the neutral fraction was analyzed by spectroscopic methods; compounds **12**–**18** and aliphatic alcohols (C_{26}-, C_{28}-) were isolated by this procedure. The acidic fraction was esterified with ethereal CH_2N_2 and the methyl esters were analyzed directly by GC-MS or first isolated by prep. glc and then submitted to MS.

18-Dihydro-19-hydroxy-cericeroic acid **1** *methyl ester.* $C_{26}H_{42}O_3$ (M^+, obsd, 402.3119, calcd. 402.3131), $[\alpha]_D^{27}$ − 77.5° (c, 0.94); ν_{max} (cm^{-1}): 3420, 1710, 1636, 1158, 890; ^{1}H NMR: 1.22 (6 H, s), 1.52 (3 H, br. s), 1.68 (3 H, br. s), 3.75 (3 H, s), 4.75, 4.80 (each 1 H, br. s) 4.96–5.44 (2 H, m), 5.70 (1 H, d.d, J = 4, 10); *m/e* (%): 402 (M^+, 8), 384 (M−H_2O, 48), 396 (M−H_2O−CH_3, 14), 315 (M−H_2O−C_5H_9, 24), 93 (82), 81 (100), 69 (70).

Dehydration of **1** *methyl ester to methyl cericeroate* **19**. Thionyl chloride (2 drops) was added dropwise to 1 methyl ester (2 mg) in pyridine (0.5 ml) at 0° and left to stand for 15 min. The reaction mixture was diluted with ice-water and extracted with ether. The ethereal soln. was injected into prep. glc at 220° for isolation. Dehydration product was identical with methyl cericeroate **19**. *m/e* (%): 384 (M^+, 32), 315 (30), 93 (88), 69 (94), 41 (100); negative optical rotation; ^{1}H NMR: 1.53, 1.62 (each 3 H, br. s), 1.70 (6 H, br. s), 3.75 (3 H, s), 4.74, 4.80 (each 1 H, br. s), 5.0–5.4 (3 H, m), 5.71 (1 H, d.d, J = 4, 10).

Compound **2** *methyl ester*, $C_{26}H_{40}O_2$ (M^+, obsd. 384.3008, calcd. 384.3026); *m/e* (%): 384 (M^+, 8), 315 (M−C_5H_9, 8), 93 (70), 69 (C_5H_9, 100); $[\alpha]_D^{27}$ − 32.5 (c, 1.82); ν_{max} (cm^{-1}) 1712, 1639, 885; ^{1}H NMR: 1.54, 1.63 (each 3 H, s), 1.69 (6 H, br. s), 3.73 (3 H, s), 4.74 (2 H, br. s), 4.95–5.34 (3 H, m), 6.74 (1 H, m). ^{13}C NMR: 15.5 (q), 17.7 (q), 22.9 (q), 25.7 (q) triplets at 25.7, 26.4, 26.8, 28.1, 29.6, 30.9, 31.6, 34.6 and 36.7, 44.0 (d), 51.4 (q, OMe), 108. 1 (t), doublets at 124.2, 124.4 and 124.6 singlets at 130.5, 131.3, 134.0 and 134.4, 143.0 (d), 153.0 (s), 168.1 (s).

Compound **3** *methyl ester*, $C_{26}H_{40}O_2$, *m/e* (%): 384 (M^+, 35), 315 (M−C_5H_9, 30), 93 (100), 81 (77), 69 (C_5H_9, 100); $[\alpha]_D^{27}$ − 48.6° (c, 0.07); ν_{max}: (cm^{-1}): 1712, 1634, 885; ^{1}H NMR: 1.53 (3 H, br. s), 1.61 (6 H, br. s), 1.67 (3 H, br. s), 2.66 (1 H, t, J = 6), 3.73 (3 H, s), 4.74 (2 H, br. s), 4.9–5.4 (3 H, m), 5.74 (1 H, t, J = 7).

Cericerene-15,24-diol **18**. Wax ester of R_f = 0.43 (Benzene-ethyl acetate 50:1) was isolated as a single spot on HPTLC. IR and ^{1}H NMR spectra exhibited –OH group (3500 cm^{-1}), C=C (1635 cm^{-1}, δ 4.9–5.3), $COOCH_2$– (1740 cm^{-1}, δ 4.56 br. s). After general procedure, fatty acids were found to be a mixture of capric- (37%), lauric- (44%), myristic- (19%), montanic- (trace) and lacceric-(trace) acids by MS spectra and glc. From the neutral fraction, compound **18** was isolated together with cericerol-II **17**.[1] Compound **18**, $C_{25}H_{42}O_2$, *m/e* (%): 374 (M^+, 1), 356 (M−H_2O, 24), 109 (C_8H_{13}, 61), 69 (C_5H_9, 100); ν_{max} (cm^{-1}): 3370, 1665, 1100, 1015; $[\alpha]_D^{27}$ − 35.7 (c, 0.3); ^{1}H NMR: 1.14 (3 H, s), 1.54, 1.69 (each 3 H, br. s), 1.62 (6 H, br. s), 1.9–2.4 (14 H, m), 4.02 (2 H, br. s), 4.8–5.2 (3 H, m), 5.68 (1 H, t, J = 8).

Labda-8(20),13-diene-15,16-diol **12**. Wax ester of R_f = 0.45 (Benzene-ethyl acetate 50:1) was isolated as a single spot on HPTLC. IR and ^{1}H NMR spectra indicated the functional groups of –$COOCH_2$– (1740, 1180 cm^{-1}, δ 4.12 br. s) and C=C (1635 cm^{-1}, δ 5.0–5.4). After general procedure, fatty acids were identified as a mixture of capric- (13.7%), lauric- (37.1%), myristic- (23.6%), palmitic- (5.9%), stearic (19.3%), arachidic- (0.3%) by MS spectra and glc. Compound **12**, $C_{20}H_{34}O_2$, $[\alpha]_D^{27}$ − 31.8° (c, 0.8); *m/e* (%): 306 (M^+, 1), 288 (M−H_2O, 16), 273 (M−H_2O−CH_3, 45), 205 (M−$C_5H_9O_2$, 14), 137 (95), 81 (100); ν_{max} (cm^{-1}): 3310, 1660, 1379, 1364, 881; ^{1}H NMR: 0.67, 0.80, 0.87 (each 3 H, s), 4.14 (2 H, br. s), 4.17 (2 H, br. d, J = 8), 4.49, 4.81 (each 1 H, br. s), 5.57 (1 H, br. t, J = 8).

Compound **12** (4 mg) was refluxed for 1 h with dry acetone (1 ml) and a small amount of $CuSO_4$. The acetonide was purified by elution with $CHCl_3$ from the Lobar column. ^{1}H NMR: 0.68, 0.80, 0.87 (each 3 H, s), 1.25 (6 H, s), 4.17 (2 H, s), 4.20 (2 H, br. d, J = 7), 4.51, 4.83 (each 1 H, br. s), 5.59 (1 H, br. t, J = 7).

Labda-7,13-diene-15,20-diol **13** was isolated together with compound **12**. $C_{20}H_{34}O_2$, $[\alpha]_D^{27}$ − 2° (c, 0.02); *m/e* (%): 288 (M-H_2O, 8), 270 (M−2H_2O, 19), 220 (M−$C_5H_{10}O$, 35), 189 (21), 109 (100); ν_{max} (cm^{-1}): 3350, 1666, 1386, 1370, 840, 762; ^{1}H NMR: 0.77 (3 H, s), 0.90 (6 H, br. s), 1.69 (3 H, br. s), 3.90, 4.15 (each 1 H, d, J = 13), 4.09 (2 H, br. d, J = 7), 5.43 (1 H, br. t, J = 7), 5.77 (1 H, br. s).

Acetylation of **13** (Ac_2O/Py, over night) gave the diacetate which was left for 30 min with MeOH-K_2CO_3 (2 mol eq.) at room temp. Usual work up gave the monoacetate (C-20). $C_{22}H_{36}O_3$, $[\alpha]_D^{27}$ + 5.8° (c, 0.77); *m/e* (%): 288 (M−AcOH, 4), 270 (M−AcOH−H_2O, 16), 262 (M−$C_5H_{10}O$, 28), 220 (M−$C_5H_{10}O$−CH_2CO, 10), 202 (M−$C_5H_{10}O$−AcOH, 70), 189 (23), 187 (30), 109 (100); ^{1}H NMR: 0.75, 0.86, 0.89 (each 3 H, s), 1.66 (3 H, br. s), 2.07 (3 H, s), 4.13 (2 H, br. d, J = 7), 4.40, 4.58 (each 1 H, d, J = 13), 5.38 (1 H, br. t, J = 7), 5.79 (1 H, br. s).

Labda-7,13-diene-3,15-diol **14**.[4] Compound **14** was obtained together with **15**[5] from the neutral fraction of the hydrolystate of residual wax. Compound **14**, $C_{20}H_{34}O_2$, $[\alpha]_D^{27}$ − 2.1° (c, 0.55); *m/e* (%): 306 (M^+, 1), 288 (M−H_2O, 1), 220 (M−$C_5H_{10}O$, 100), 187 (16), 135 (33), 119 (23), 108 (43), 81 (61); ν_{max} (cm^{-1}): 3360, 1660, 1384, 1366; ^{1}H NMR: 0.76, 0.85, 0.97 (each 3 H, s), 1.69 (6 H, br. s), 3.21 (1 H, d.d, J = 5, 9), 4.12 (2 H, d, J = 7), 5.39 (2 H, m).

Compound **14** was hydrogenated in MeOH over PtO_2 to give a tetrahydro derivative which was identical with labdane-3,15-diol of known stereochemistry.[8] ^{1}H NMR: 0.77, 0.82 (each 3 H, s), 0.88, 0.89 (each 3 H, d, J = 6), 0.97 (3 H, s), 3.17 (1 H, d.d, J = 5, 9), 3.64 (2 H, br. t, J = 7).

Acetylation of **14** (Ac_2O/Py, over night) gave the diacetate which was treated with MeOH-K_2CO_3 as well as **13** to give the monoacetate, $C_{22}H_{36}O_3$, $[\alpha]_D^{27}$ − 34.6° (c, 0.72); *m/e* (%): 330 (M−H_2O, 5), 270 (M−H_2O−AcOH, 8), 262

($M-C_5H_{10}O$, 56), 202 ($M-C_5H_{10}O$ AcOH, 50), 189 (78), 187 (52), 119 (100); ν_{max} (cm^{-1}): 3400, 1730, 1379, 1368, 1248, 760; ^1H NMR: 0.80, 0.86, 0.94 (3 H, each s), 1.68 (6 H, br. s), 2.03 (3 H, s), 4.11 (2 H, br. d, J = 7), 4.47 (1 H, d.d, J = 5, 9), 5.40 (2 H, m).

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