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NEW MACROCYCLIC SESTERTERPENOIDS FROM A SCALE INSECT (*CEROPLASTES CERIFERUS*)

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Abstract—Six new macrocyclic sesterterpenoids **1–6** were isolated from the secretion of a scale insect, *Ceroplastes ceriferus* Anderson, and their structures determined. Chemical correlation has also been accomplished. Stereochemistry was elucidated by comparison of the CD spectra of the ozonolysis product of **1**-acetate and a corresponding synthetic substance of known absolute configuration.

Keywords: Macrocyclic sesterterpenoid; Scale insect; Secreted wax; *Ceroplastes ceriferus*

The interesting discovery of sesquiterpenes secreted by *Ceroplastes ceriferus* belonging to the optically antipodal series compared with those of *C. rubens* on the same host tree has recently been reported.[1] We present here the results of structural elucidation of six new macrocyclic sesterterpenoids, cericerol-I **1**, cericerol-II **2**, 13-methoxy-cericerene **3**, 13-ethoxy cericerene **4**, α-cericerol-I **5**, and cericeroic acid **6**, which were isolated from the secretion of *C. ceriferus* Anderson (fam. Coccidae).

At the time the present investigations were undertaken, it had been reported[2] that the secreted wax consisted of true wax and "cyclic wax" in which the fatty acids were esterified with an unsaturated cyclic alcohol found to be identical to **1**. Though the occurrence of three sesterterpenoids had been reported[3] on the basis of GC-MS, practically nothing was known about their structures. As a result of this work, contrary to biogenetic considerations for albocerol,[4] it has become clear that in 14-membered macrocyclic sesterterpenoids **1–6**, $\Delta^{6,7}$ has the Z-configuration.

C. ceriferus fed on the host *Diospyros kaki* Thunb. was collected in Osaka Prefecture, Japan, in January 1978. The material was soaked in chloroform, which ensured complete removal of insect debris (30%) with coloring matter, and also removed water (20%). The resulting slurry (50%) was precipitated with acetone for separation into acetone-soluble and -insoluble fractions. Usual working up of the acetone-soluble fraction (13%) gave neutral substances (5.8%) which consisted of sesquiterpenoids,[1] diterpenoids,[5] triglycerides,[5] sesterterpenoids **1–4**, and uncharacterized compounds. From an acidic fraction (5.6%), a sesterterpene **6** and diterpenoids[5] were obtained. The acetone-insoluble fraction (36%) consisted of esters (25%) and uncharacterized lipids (10%). The esters,[5] which on mild hydrolysis with base gave a mixture of aliphatic acids,[5] aliphatic alcohols,[5] and sesterterpene alcohols (**1**, **2** and **5**), were considered to consist of polyesters of two types, i.e. aliphatic and cyclic. The separation procedures are shown schematically in Fig. 1.

Structural relationships of sesterterpenoids 1–6

Cericerol-I **1**, $[\alpha]_D^{27}$ −30.6°, has the molecular formula $C_{25}H_{40}O$. The PMR spectrum of **1** shows four vinylic methyls at δ 1.53, 1.61 (each 3H) and 1.67 (6H), and vinylic protons at δ 4.9–5.4 (4H). The presence of an exo methylene group is suggested by signals at δ 4.72 (2H) in the PMR spectrum and the band at ν_{max} 886 cm^{-1} in the IR spectrum. Two protons at δ 3.89 (1H, d, J = 12) and 4.12 (1H, d, J = 12) were assigned to $—CH_2—O—$ adjacent to a double bond exhibiting a downfield

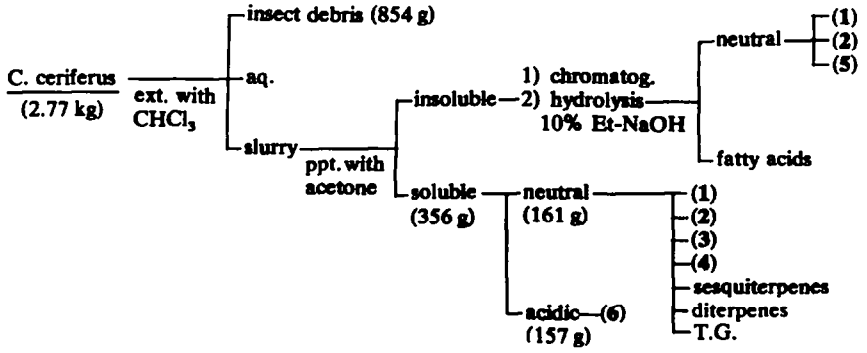

Fig. 1.

Table 1. ^{13}C chemical shifts of cericerol-I **1**, cembrene-A, cericerene **15**, 13-methoxy cericerene **3**, 13-ethoxy cericerene **4**, cericerol-I acetate **7**, α-cericerol-I acetate **13**, cericerol-II **2**, and methyl cericeroate **6'**.

C-atom	**1** (T_1)	cembrene-A	**15**	**3**	**4**	**7**	**13**	**2**	**6'**
C-1	30.7 (0.40)[a]	32.5[a]	30.5[a]	31.0[a]	30.9[a]	30.7[a]	29.4[a]	28.3[a]	30.7[a]
C-2	128.6 (0.72)	125.9	125.1[b]	129.3	128.5	131.5	131.7[b]	129.2	141.6
C-3	136.5 (6.42)	134.7	134.1	134.9	134.7	133.4	133.2	136.5	130.2
C-4	30.3 (0.40)[a]	34.0[a]	31.1[a]	30.8[a]	30.8[a]	30.3[a]	30.3[a]	29.1[a]	30.8[a]
C-5	31.0 (0.41)[a]	24.9[b]	31.4[a]	31.4[a]	31.3[a]	31.0[a]	30.9[a]	30.3	30.4[a]
C-6	125.3 (0.74)	121.9[c]	125.1[b]	125.5	125.4	125.5	125.8	126.4	125.7
C-7	133.3 (6.84)	133.4[d]	132.9[c]	132.7[b]	133.3	131.5[b]	131.7[b]	134.2	133.9
C-8	35.6 (0.39)[b]	39.0[e]	36.2	36.3	36.3	36.1	35.9[c]	35.1	35.5[b]
C-9	24.1 (0.42)[c]	23.8[b]	24.6	24.0	23.9	24.4[c]	24.4[d]	24.4[b]	25.6[c]
C-10	124.8 (0.85)	124.1[c]	125.0[b]	121.4	121.5	124.4[d]	124.6	126.0	124.4
C-11	133.1 (7.03)	133.9[d]	133.0[c]	133.3[b]	133.3	133.4[b]	133.7[b]	134.2	133.2
C-12	36.0 (0.42)[b]	39.4[e]	40.3	31.4[a]	31.6[a]	36.1	36.1[c]	39.0	36.2[b]
C-13	24.6 (0.42)[c]	28.3	24.6	88.3	86.4	24.7[c]	24.8[d]	24.7[b]	26.0[c]
C-14	44.5 (0.66)	46.0	44.6	44.1	44.1	44.7	46.9	47.2	44.7
C-15	152.4 (6.65)	149.2	153.0	153.2	153.2	125.6	137.1	75.7	152.5
C-16	33.4 (0.83)	18.0	33.7	34.1	34.1	33.5	123.6	39.9	33.5
C-17	26.4 (1.02)		26.6	26.7	26.7	26.5	26.9	22.2	26.5
C-18	124.2 (2.85)		124.6[b]	124.6	124.5	124.7[d]	124.6	124.7	124.4
C-19	131.1 (14.30)		131.3	131.4	131.5	131.2[b]	131.7[b]	131.5	131.2
C-20	25.6 (2.72)		25.7	25.7	25.6	25.6	25.7	25.7	25.6
C-21	17.7 (7.40)		17.8	17.8	17.7	17.6	17.8	17.7	17.6
C-22	108.7 (0.37)	110.1	108.9	108.9	108.8	109.0	10.9	23.6	109.0
C-23	59.7 (0.71)	15.5[f]	15.6[f]	15.4	15.4	61.5	61.7	59.8	168.5
C-24	22.4 (2.10)	19.3	22.5	22.5	22.5	22.3	22.4	22.2	22.4
C-25	15.5 (3.19)	15.3[f]	15.5[f]	9.8	10.0	15.5	15.7	15.5	15.3
—OR	(R: Me, Et, Ac)			55.4	62.7	170.9	170.9		
					15.4	20.9	21.0		
—$COOCH_3$									51.0

Values labelled with a given letter (a–f) in each column may be in a different order and do not necessarily apply to the particular carbon atom indicated.

shift to δ 4.54 (2H, br.s) in the acetate **7**, $C_{27}H_{42}O_2$, $[\alpha]_D^{27}$ −88.2°. On catalytic hydrogenation, a saturated hydrogenolysis product **8**, $C_{25}H_{50}$, was obtained, which was inferred to be a 14-membered monocyclic structure with a C-8 unit side chain on the basis of its MS spectrum. Thus, the presence of an allylic primary hydroxyl group was established. Measurement of the spin-lattice relaxation time (T_1) and the observation of NOE at vinyl methyl carbons in the CMR spectrum confirmed the presence of two vinylic methyl groups in *cis* geometry to the vinyl protons. One was inferred to be on the ring and the other on the side chain based on the differences in the relaxation times (Table 1) and by comparison of the chemical shifts in the CMR spectrum of **1** with those of cembrene-A[6], which is a 14-membered diterpene having all-*trans* trisubstituted double bonds. Ozonolysis of cericerol-I acetate **7**, followed by catalytic hydrogenation gave a mixture of aldehydes **9**–**11**, which were separated by column chromatography. The first compound eluted was identified as 4-oxopentanoic aldehyde **9** on the basis of its spectral data. The second compound, $C_7H_{10}O_4$ **10**, gave PMR signals indicative of $CH_3CO—O—CH_2—$ at δ 2.14 (3H, s) and 4.72 (2H, br.s), —CHO at δ 9.75 (1H, s) and methylenes at δ 2.76 (4H). The third compound, $C_{11}H_{16}O_4$, gave two —CHO signals at δ 9.67, 9.78 (each 1H, s) and $—COCH_3$ at 2.14 (3H, s), indicating the formula **11**. The formation of **10** and **11** requires that the allylic alcohol and the side chain are at the positions C-3 (or C-7) and C-14, respectively. The stereochemistry at C-14 was deduced to be R-configuration by comparison of the CD spectra of the ozonolysis product **11** and a corresponding synthetic substance which was prepared from (+)-(R)-limonene. The geometry of the ring-olefinic bonds and the position of the allylic alcohol are not implied and remain to be clarified.

Cericerol-II **2**, $C_{25}H_{42}O_2$, $[\alpha]_D^{27}$ −28.1°, gave a PMR spectrum very similar to that of **1** except for a signal due to a methyl group attached to the carbon with the hydroxyl group at δ 1.03 (3H, s) in place of the exo-methylene group in **1**. Observation of two protons at δ 3.80 and 4.25 (each 1H, d, J = 12) with large differences in chemical shift compared to those of **1** suggests that the position of its primary allylic alcohol group is not at C-7, but at C-3. Dehydration of the tertiary alcohol in cericerol-II acetate **12**, $C_{27}H_{44}O_3$, with thionyl chloride-pyridine gave a mixture of three geometric isomers in a ratio of 7:3:1. They were separated by passage through a silver nitrate-impregnated silica gel column. The major product was identical with cericerol-I acetate **7**. The second product was identical with the acetate **13** of α-cericerol-I, which should be formulated as **5**, in good accord with its spectral data. The minor product can be drawn as structure **14**, having a tetrasubstituted double bond.

This correlation also establishes R-chirality for C-14 in **2** and **5**. The geometry of the ring-olefinic bonds remains to be elucidated.

The minor compounds **3**, $C_{26}H_{42}O$, $[\alpha]_D^{27}$ −69.4°, and **4**, $C_{27}H_{44}O$, $[\alpha]_D^{27}$ −69.5°, showed similar PMR spectra and their spectral characteristics were as follows: —CH—OCH_3: δ, 3.16 (3H, s), 3.28 (1H, d.d, J = 5, 12); —CH—O—CH_2CH_3: δ, 1.17 (3H, t, J = 7), 3.25 (2H, q, J = 7), 3.40 (1H, d.d, J = 4, 12). Except for the substituents, the spectral data indicate a marked structural resemblance to cericerene **15**, $C_{25}H_{40}$, $[\alpha]_D^{27}$ −48.3°, which was derived from (**1**)-tosylate by lithium aluminum hydride reduction, suggesting that the methoxyl group of **3** [ethoxyl group of **4**] should be at C-13, which is the only non-allylic position in the structure, so as to account for the chemical shifts of —CH—OR. Thus, the minor products **3** and **4** can be identified as 13-methoxy cericerene and 13-ethoxy cericerene, respectively. A comparison (Table 1) of the CMR spectrum of a 14-membered diterpene, cembrene-A[6], with those of **3** and **4** suggests that **3** and **4** have three trisubstituted double bonds, one in Z- and two in E-configurations. Clearly, $\Delta^{2,3}$ has an E-configuration, by comparison of **1** with **3** and **4**. Observation in **3** and **4** of a −5 ppm effect on a *trans* vinyl methyl group at around δ 15 ppm in 15 indicates E-$\Delta^{10,11}$ and thus Z-$\Delta^{6,7}$ configurations.

The structure of cericeroic acid **6**, $C_{25}H_{38}O_2$, $[\alpha]_D^{27}$ −116.2°, was readily deducible from additional information in the PMR and CMR spectra concerning the carbon skeleton. After treatment with diazomethane, the product was reduced with lithium aluminum hydride. On the basis of all spectral data, the resulting alcohol was identical with cericerol-I **1**, including the stereochemistry. Though the substituent configurations at C-13 in **3** and **4** and at C-15 in **2** still remain to be clarified, the structures **1**–**6** can be illustrated as shown in Fig. 2.

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 (PMR, CMR; δ (ppm), TMS as an internal standard); 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 Jasco ORD/UV-5 unit (CD, ORD; in EtOH); a Varian Aerograph model 920 (prep. GLC; 3ft × ⅜ in Al column packed with 10% Silicone OV-17 on Diasolid L, with He as a carrier gas); a chromatography column (Malinckrodt, *Silica gel, 100* mesh; 15% $AgNO_3$-silica gel; prepacked Lobar column, silica gel 60).

Isolation. C. ceriferus (2.77 kg) was extracted with $CHCl_3$. After insect debris (854 g) had been filtered off, the filtrate was divided into the $CHCl_3$ and acqueous layers. Chloroform was concentrated to $\frac{1}{10}$ of its original volume and the residue was precipitated with acetone to obtain soluble and insoluble fractions. After concentration of the acetone fraction, the concentrate was dissolved in Et_2O and extracted with 2% NaOH aqueous solution. The ethereal solution was washed with water, dried over anhydrous Na_2SO_4 and evaporated down to give a neutral fraction (161 g). The alkaline solution was acidified with HCl aq. and extracted with Et_2O. The ethereal solution was worked up as usual to give acidic compounds (157 g). The neutral fraction, which contained sesquiterpenoids, diterpenoids, sesterterpenoids, triglycerides and so on, was chromatographed. Four neutral sesterterpenoids, cericerol-I **1**, cericerol-II **2**, 13-methoxy cericerene **3** and 13-ethoxy cericerene **4**, were obtained. The acidic fraction, which contained fatty acids, diterpenoids and a sesterterpenoid, namely cericeroic acid **6**, was esterified with ethereal CH_2N_2. On chromatography methyl cericeroate **6'** was obtained. The acetone-insoluble fraction was chromatographed to yield ca. 30% unsaturated esters, which consisted of fatty acids and sesterterpene alcohols: cericerol-I **1**, cericerol-II **2**, and α-cericerol-I **5**. The fatty acids consisted of saturated C_{28}, C_{30}(major component) and C_{32}.

Cericerol-I **1**, $C_{25}H_{40}O$ (M^+, obsd. 356.3088, calcd. for 356.3089), $[\alpha]_D^{27}$ −84.1° (c, 1.88); ν_{max} (cm^{-1}): 3300, 1636, 1008, 886; PMR (CCl_4): 1.05 (1H, br.s), 3.89, 4.12 (each 1H, d, J = 12), 4.72 (2H, m), 4.9–5.4 (4H, m); *m/e* (%): 356 (M^+, 20), 338 (10), 287 (M-C_5H_9, 15), 269 (13), 229 (10), 93 (94), 69 (100).

Acetylation of 1 (Ac_2O-pyridine, overnight) gave an acetate **7**, $[\alpha]_D^{27}$ −88.2° (c, 1.3); ν_{max} (cm^{-1}): 1738, 1638, 1235, 1012, 886; PMR (CCl_4): 1.53, 1.61 (each 3H, br.s), 1.68 (6H, br.s) 1.98 (3H, s), 4.54 (2H, br.s), 4.72 (2H, m), 4.9–5.4 (4H, m); *m/e* (%): 398 (M, $C_{27}H_{42}O_2$, <1), 338 (44), 269 (34), 93 (100), 69 (66).

Hydrogenation of cericerol-I acetate **7** *to the perhydro derivatives* **8** *and* **8'**

A solution of **7** in MeOH was hydrogenated over 10% Pd-C for 0.5 hr. The catalyst was filtered off and the filtrate was evaporated down to give a mixture of hydrogenolysis product **8** and perhydro derivative **8'** in the ratio of 9:1. These products were isolated by preparative GLC at 150°C. Hydrogenolysis product **8**, *m/e* (%): 350 (M^+, $C_{25}H_{50}$, 14), 236 (M—C_8H_{18}, 100), 97 (52); PMR (CCl_4): 0.89 (18H, d, J = 6), 1.24 (32H, br.s). Perhydro derivative **8'**, *m/e* (%): 408 (M^+, $C_{27}H_{52}O_2$, <1), 348 (M—AcOH, 84), 234 (M—AcOH—C_8H_{18}, 64), 97 (100); ν_{max} (cm^{-1}): 1740, 1240, 1040.

Ozonolysis of cericerol-I acetate **7**. A stream of ozonized oxygen was passed through a solution of **7** (520 mg) in AcOEt (8 ml) at −70°C until it turned faint blue (2 h). The ozonide in the solvent was left overnight at 5°C and hydrogenated over 10% Pd-C. On usual work-up a mixture of aldehydes **9**, **10**, and **11** was obtained. The mixture was separated on a Lobar column eluted with $CHCl_3$—AcOEt (9:1) to give **9** (24 mg), (10) (92 mg) and an optically active product **11** (10 mg). Product **9**, *m/e* (%): 100 (M^+, $C_5H_8O_2$, <1), 101 (M+1, 4), 85 (50), 57 (15), 43 (100); PMR ($CDCl_3$): 2.20 (3H, s), 2.74 (4H, br.s), 9.78 (1H, br.s). Product **10**, *m/e* (%): 159 (M^++1, $C_7H_{10}O_4$+1, <1), 98 (11), 85 (100), 57 (14), 43 (76); PMR ($CDCl_3$): 2.14 (3H, s), 2.76 (4H, br.s), 4.72 (2H, br.s), 9.75 (1H, br.s). Product **11**, *m/e* (%): 212 (M^+, $C_{11}H_{16}O_4$<1), 127 (9), 108 (7), 85 (100), 71 (10), 58 (10), 57 (14), 43 (85); PMR ($CDCl_3$): 1.16 (2H, m), 2.14 (7H, br.s), 2.35–2.9 (5H, m), 9.67, 9.78 (each 1H, br.s); $[\alpha]_D^{27}$ +51.2° (c, 0.5, EtOH); CD: $[\theta]_{316}$ 0, $[\theta]_{278}$ +313, $[\theta]_{246}$ 0; ORD: $[\phi]_{600}$ +127, $[\phi]_{298}$ +848, $[\phi]_{270}$ +466.

Ozonolysis of (+)-β-*bisabolene*. (+)-β-Bisabolene, which was identical with an authentic sample, was synthesized from (+)-R-limonene by the method of Crawford *et al.*[7] and subjected to ozonolysis. Decomposition of the resulting ozonide was accomplished by hydrogenation under the same conditions as for 7. On usual work-up, the optically active product obtained was identical with 11, having R chirality as expected from the CD spectrum.

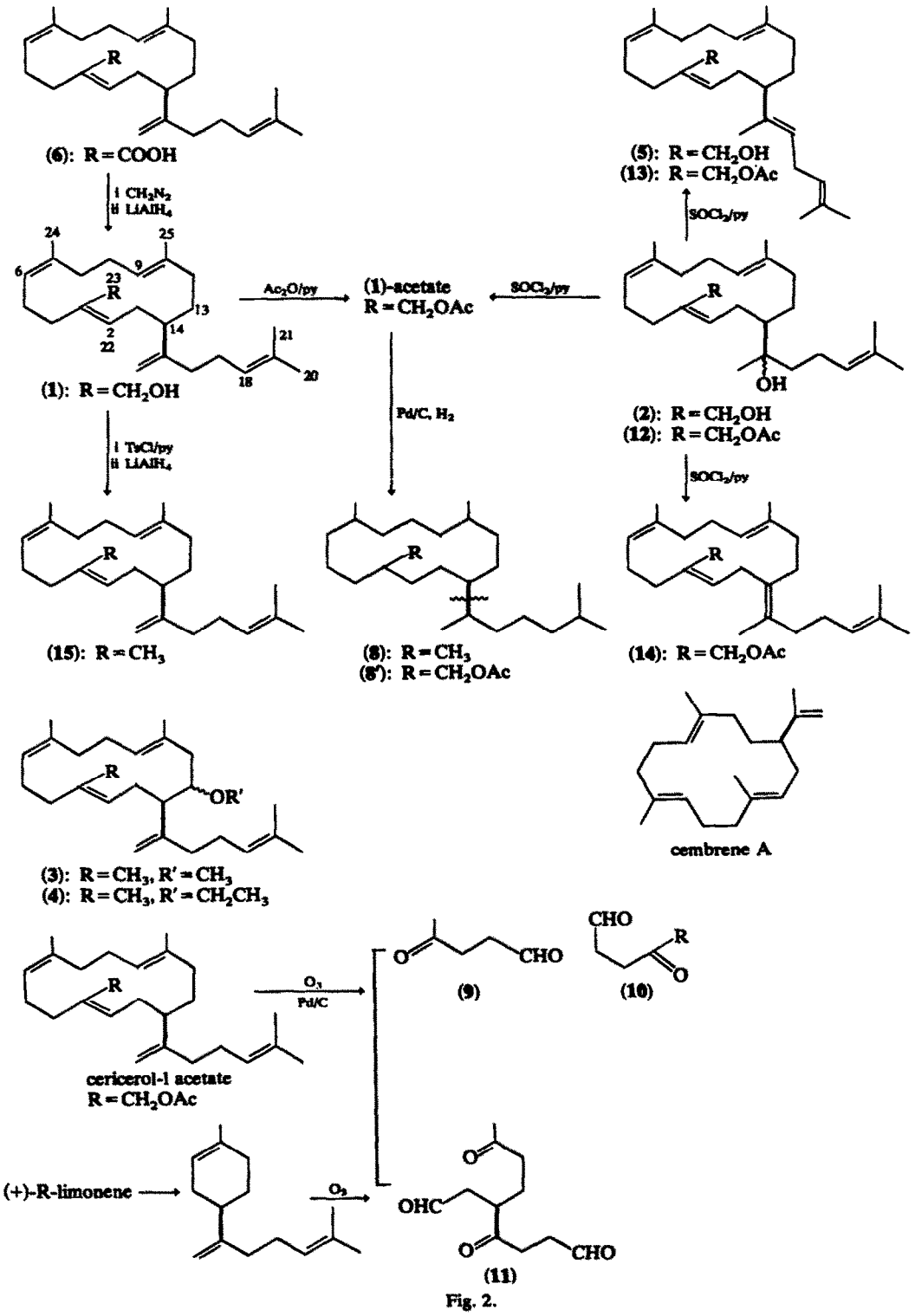

Fig. 2.

*Reduction of cericerol-*I **1** *to cericerene* **15**. A solution of **1** (100 mg) in pyridine (1 ml) was treated with TsCl (130 mg) at 0°C and left overnight at 5°C. The reaction mixture was poured into ice-water with stirring and extracted to give a colorless oil. The oil was refluxed in THF (7 ml) for 1 h with $LiAlH_4$ (16 mg). Excess $LiAlH_4$ was decomposed by the addition of 1% HCl aqueous solution. This mixture was extracted with Et_2O, washed, dried, evaporated down and purified on a Lobar column using hexane to give a hydrocarbon which was named cericerene **15** (36 mg). Cericerene **15**, $[\alpha]_D^{27}$ −48.3° (c, 0.48); *m/e* (%): 340 (M^+; $C_{25}H_{40}$, 30), 271 (M—C_5H_9, 18),. 229 (13), 93 (100), 69 (100) 41 (100); ν_{max} (cm^{-1}): 1620, 1640, 892; PMR ($CDCl_3$): 1.56, 1.59, 1.64 (each 3H, br.s), 1.69 (6H, br.s), 4.75 (2H, m), 4.9–5.3 (4H, m).

α-*Cericerol-*I **5**, $C_{25}H_{40}O$, $[\alpha]_D^{27}$ −71.6° (c, 0.24); *m/e*

(%): 356 (M^+, 8), 338 (52), 269 (M—H_2O—C_5H_9, 42), 93 (100), 69 (78); ν_{max} (cm^{-1}) 3400, 1630, 1008; PMR ($CDCl_3$): 1.53 (6H, br.s), 1.77 (9H, br.s), 2.69 (2H, t, J = 7), 4.00, 4.27 (each 1H, d, J = 12), 4.9–5.4 (5H, m).

Acetylation of **5** (Ac_2O-pyridine, overnight) gave an acetate **13**. α-Cericerol-I acetate **13**, $[\alpha]_D^{27}$ −84.3° (c, 1.08); *m/e* (%) 398 (M^+, $C_{27}H_{42}O_2$, 4), 338 (32), 269 (30), 93 (100), 69 (68); ν_{max} (cm^{-1}): 1740, 1660, 1235; PMR ($CDCl_3$): 1.53 (6H, br.s), 1.64 (6H, br.s), 1.69 (3H, br.s), 2.07 (3H, s), 2.70 (2H, t, J = 7), 4.64 (2H, br.s), 4.9–5.5 (5H, m).

Cericerol-II **2**. $C_{25}H_{42}O_2$ (M^+, obsd. 374.3128, calcd. for 374.3123); $[\alpha]_D^{27}$ −28.1° (c, 1.3); ν_{max} (cm^{-1}): 3400, 1660, 1020; PMR (CCl_4): 1.04 (3H, s), 1.53, 1.65 (each 3H, br.s), 1.67 (6H, br.s), 3.80, 4.25 (each 1H, d, J = 12), 4.9–5.4 (4H, m); in CD_3OD δ, 3.80, 4.25 shifted to δ, 4.12 (2H, br.s); *m/e* (%): 374 (M^+, <1), 356 (28), 338 (9), 287 (M—H_2O—C_5H_9, 15), 269 (19), 109 (C_8H_{13}, 98), 69 (100).

Acetylation of **2** (Ac_2O-pyridine, overnight) gave the monoacetate **12**. Cericerol-II monoacetate **12**, *m/e* (%): 416 (M^+, $C_{27}H_{44}O_3$, <1), 398 (10), 338 (40), 269 (50), 109 (56), 69 (86), 43 (100); ν_{max} (cm^{-1}): 3500, 1730, 1650, 1240; PMR (CCl_4): 1.09 (3H, s), 1.53 (3H, br.s), 1.64 (9H, br.s), 1.99 (3H, s), 4.54 (2H, br.s), 4.9–5.4 (4H, m).

Dehydration of cericerol-II *monoacetate* **12** *to* **7**, **13** *and* **14**. Thionyl chloride (0.4 ml) was added dropwise to **12** (90 mg) in pyridine (1 ml) at 0°C and left to stand for 15 min. The reaction mixture was poured into ice-water slowly with stirring and extracted with Et_2O. The ethereal solution was washed, dried, evaporated down, and chromatographed on a 15% $AgNO_3$-silicic acid column, eluting with increasing amounts of AcOEt in $CHCl_3$, to give **14** (5 mg), **13** (17 mg) and **7** (35 mg) in this order. The compounds **13** and **7** were identical in all respects with α-cericerol-I acetate and cericerol-I acetate, respectively. Compound **14**, *m/e* (%): 398 (M^+, $C_{27}H_{42}O_2$, 9), 338 (7), 109 (72), 93 (50), 69 (42), 43 (100); PMR ($CDCl_3$): 1.58 (6H, br.s), 1.68 (6H, br.s), 1.70 (3H, br.s), 2.61 (2H, m), 4.63 (2H, br.s), 4.9–5.5 (4H, m).

13-*Methoxy cericerene* **3**, $C_{26}H_{42}O$ (M^+, obsd. 370.3209, calcd. for 370.3207); $[\alpha]_D^{27}$ −69.4° (c, 0.36); ν_{max} (cm^{-1}): 1634, 1094, 886; PMR ($CDCl_3$): 1.58 (6H, br.s), 1.63 (3H, br.s), 1.68 (6H, br.s), 3.16 (3H, s), 3.28 (1H, d.d, J = 5, 12), 4.73, 4.81 (each 1H, br.s), 4.9–5.4 (4H, m); *m/e* (%): 370 (M^+, 6), 338 (M—CH_3OH, 4), 301 (M—C_5H_9, 2), 269 (7), 229 (3), 164 ($C_{11}H_{16}O$, 39), 98 ($C_6H_{10}O$, 100), 69 (36).

13-*Ethoxy cericerene* **4**, $C_{27}H_{44}O$ (M^+, obsd. 384.3395, calcd for 384.3395); $[\alpha]_D^{27}$ −69.5° (c, 0.6); ν_{max} (cm^{-1}): 1638, 1086, 888; PMR ($CDCl_3$): 1.17 (3H, t, J = 7), 1.58 (6H, br.s), 1.62 (3H, br.s), 1.68 (6H, br.s), 3.25 (2H, q, J = 7), 3.40 (1H, d.d, J = 4, 12), 4.73, 4.80 (each 1H, br.s), 4.9–5.4 (4H, m); *m/e* (%): 384 (M^+, 7), 338 (3), 315 (2), 269 (5), 229 (3), 178 (42), 112 (100), 69 (40).

Cericeroic acid **6**, *m/e* (%): 370 (M^+, $C_{25}H_{38}O_2$, 40), 301 (M—C_5H_9, 30), 109 (73), 93 (74), 69 (100); PMR (CCl_4): 1.56, 1.65 (each 3H, br.s), 1.69 (6H, br.s), 4.8 (2H, m), 4.9–5.4 (3H, m), 5.92 (1H, m).

Esterification of **6** *(ethereal* CH_2N_2*) to yield methyl cericeroate* **6'**. Methyl cericeroate **6'**, $C_{26}H_{40}O_2$, *m/e* (%): 384 (M^+, 32), 315 (30), 93 (88), 69 (94), 41 (100); $[\alpha]_D^{27}$ −116.2° (c, 7.93); ν_{max} (cm^{-1}): 1720, 1638, 886; PMR ($CDCl_3$): 1.53, 1.62 (each 3H, br.s), 1.70 (6H, br.s), 3.75 (3H, s), 4.74, 4.80 (each 1H, br.s), 5.0–5.4 (3H, m), 5.71 (1H, d.d, J = 4, 10).

Reduction of methyl cericeroate **6'** *to cericerol*-I **1**. Methyl cericeroate **6'** (45 mg) was refluxed in Et_2O (7 ml) for 1 h with $LiAlH_4$ (10 mg). Excess $LiAlH_4$ was decomposed by the addition of 1% HCl aqueous soln. The mixture was extracted with Et_2O, washed, dried and evaporated down to give an alcoholic compound (36 mg) which was identical with cericerol-I **1**.

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