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PHOTOCHEMICAL TRANSFORMATION LEADING TO EUPTELEOGENIN—II

ATTEMPT TO INTRODUCE TERMINAL METHYLENE MOIETY AND TRANSFORMATION OF SPERGULAGENIC ACID TO EUPTELEOGENIN

I. KITAGAWA, K. KITAZAWA, K. AOYAMA, M. ASANUMA and I. YOSIOKA
Faculty of Pharmaceutical Sciences, Osaka University, Toneyama, Toyonaka, Osaka, Japan

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Abstract—As a continuation of the preceding paper, to search for the photochemical means to induce a terminal methylene moiety, which is another unique function of eupteleogenin (**1a**), photolysis of leucotylic acid derivatives (**2a–d**) has been pursued as the model experiment. Although the aimed terminal methylene compound (**3a**) was obtained, the method has been found inapplicable for decarboxylation of **7a, b**. Based on the combined evidence of this and the preceding papers, the transformation of spergulagenic acid derivatives (**5a, b**) into eupteleogenin acetate (**1b**) has been accomplished, in which decarboxylation of **7b** was realized by lead tetraacetate oxidation.

IN the preceding paper,[1] photooxidative single step formation of the 11α, 12α-epoxy-13β,28-lactone system in the oleanane skeleton as seen in eupteleogenin (**1a**)[2] has been detailed and some of the related investigations have been described. In a parallel examination, we have sought after the appropriate means to introduce a terminal methylene function which is another characteristic of eupteleogenin (**1a**) and have chosen a lichen triterpenoid leucotylic acid (**2a**)[2] at hand as a model compound, since the latter possesses a carboxyl function geminal to a tertiary Me and this partial structure has appeared to be a biogenetically precursory system for the terminal methylene moiety. First, photolysis of leucotylic acid derivatives (**2a–d**) has been undertaken to attain the desired decarboxylation. Although photochemical introduction of the terminal methylene moiety has been attained, the method has been found inapplicable to the formation of eupteleogenin (**1a**) and hence the terminal methylene function of the latter has been introduced by $Pb(OAc)_4$ oxidation as described in the later part of this paper.

Irradiation of methyl leucotylate (**2b**) in EtOH for 83 hr with a low pressure mercury lamp furnished a crude product along with recovered starting material. The same mixture was also obtained by irradiation of leucotylic acid (**2a**) or ethyl leucotylate (**2c**), but the yields were fairly poor as compared with **2b**. Acetylation of the total reaction product followed by chromatographic separation effected isolation of a new product and starting material with yields of 12% and 34% respectively. However, since the product at this stage was found to consist of three components by argentized silica gel TLC, it was separated by SiO_2–$AgNO_3$ column chromatography[3,4] to afford three products designated from less polar to increased polar ones as H-1-Ac (crude, 8·3%), H-2-Ac (0·6%), and H-3-Ac (2·5%). The respective yields were calculated on the basis of consumed methyl leucotylate (**2b**).

The most polar product H-3-Ac possesses a hydroxyl (3550 cm^{-1}), an acetoxyl (1740 cm^{-1}), and a terminal methylene (1643, 890 cm^{-1}) function as revealed by the

IR spectrum. The NMR spectrum of H-3-Ac shows the reduced number of the total C-Me functions as six and the presence of one AcO (7·97τ) and one OH (7·02τ, disappeared on D_2O addition) functions. It also demonstrates the presence of a terminal methylene function by two singlets at 5·61 and 5·37τ of one proton each and the presence of C-16α-H geminal to the OAc group by a one-proton multiplet at 4·82τ,[3] but it shows the absence of the methoxycarbonyl function. Furthermore, the isopropanol side chain at C-21 is preserved in H-3-Ac as disclosed by two C-Me singlets at 8·87 and 8·90τ as in **2b**.[3] Alkaline hydrolysis of H-3-Ac gave a nor-triterpenoid (designated as H-3), whose IR spectrum shows the absorption bands due to the OH (3400 cm^{-1}) and the terminal methylene (1643, 890 cm^{-1}) functions but again lacks the absorption band of the methoxycarbonyl group.

These physical properties point out that the chemical environment in rings D and E of the starting compound (**2b**) is preserved while only the methoxycarbonyl function has been lost in the product. Therefore, the structure (**3b**) is assigned to H-3-Ac, which has been brought out by photochemical elimination of the methoxycarbonyl function. The mass spectrum of H-3-Ac corroborates formulation **3b** by the prominent ion peaks at *m/e* 205(**i**), *m/e* 187(**ii**) (base peak), and *m/e* 175(**iii**) as depicted in Chart 2, which are analogously explained as for the fragmentation pattern of the hopane triterpenoids.[3, 5]

It follows therefore that introduction of the terminal methylene function has been achieved *via* photolysis although the yield was not satisfactory. It seems to be noticeable that under the conditions here employed the isopropanol function at C-21 of methyl leucotylate (**2b**) has been kept intact, since the function is quite labile even under mild acidic conditions.[3] In addition, the present observation seems to be a rare example of photochemical elimination of a methoxycarbonyl function as examples of photochemical decarboxylation in a similar chemical environment have been known.[6]

The minor product H-2-Ac was shown to be a demethoxycarbonylation product by examination of the physical properties of H-2-Ac and its deacetylation product (H-2), however, due to insufficient quantity, further examination was abandoned.

The major and least polar product of photolysis was found to contain a minor carbonyl compound from a weak absorption band at 1715 cm^{-1} in its IR spectrum. Therefore, to remove the minority by converting it to the more polar substance, the product was treated with LAH and purified by preparative TLC to afford another nor-triterpenoid designated as H-1. The IR spectrum of H-1 exhibits OH absorption bands at 3580 and 3300 cm^{-1} but no carbonyl band. One of seven C-Me signals is observed as a doublet at 9·15τ (J = 9·6 Hz) in its NMR spectrum, thus suggesting the presence of a secondary Me. The physical properties of H-1-Ac prepared by acetylation of H-1 are in good accord with the above observation. Examination of the mass spectrum of H-1 in comparison with those of methyl leucotylate (**2b**)[3] and H-3-Ac (**3b**) has made structure **4a** for H-1 most probable. Hence, it is assumed that H-1 has been derived *via* photolytic elimination of the methoxycarbonyl function of **2b** followed by hydrogen abstraction from the reaction medium. Although a catalytic hydrogenation product of H-3-Ac (**3b**)* was indistinguishable from H-1 (**4a**); m.m.p., IR, and TLC, the configuration at C-4 of **4a** is still uncertain.

* Acetoxyl function at C-16β of **3b** was unexpectedly hydrolysed during the hydrogenation procedure, which should be a subject of further examination.

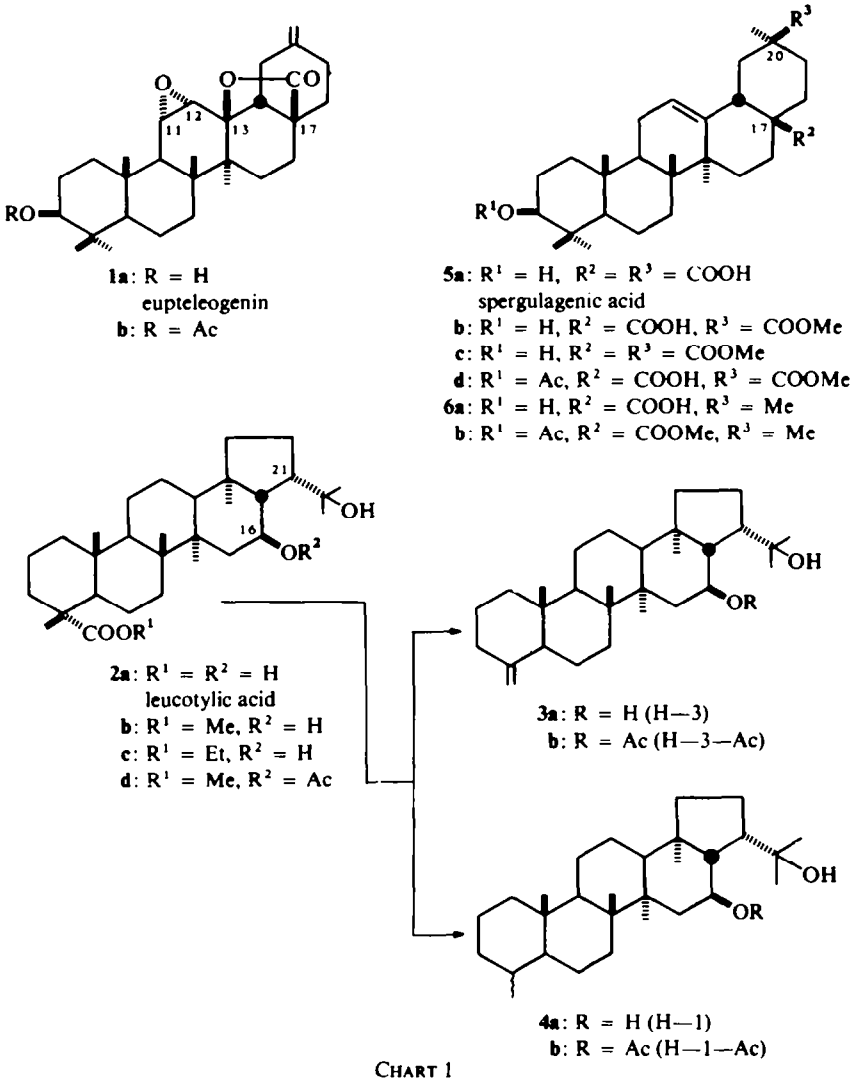

CHART 1

As described above, for convenience of the separation of the reaction products, the total photolysis product was acetylated prior to the separation. To simplify, methyl 16-0-acetyl-leucotylate (**2d**)[3] was subjected to photolysis under the same reaction conditions. However, composition of the total product was found to be unexpectedly almost identical with that from **2b**, which implies that **2d** has suffered deacetylation upon photolysis. Although photochemical deacetylation has often been known to occur among the aromatic compounds (e.g. the photochemical Fries rearrangement),[7] only limited examples have been presented so far in alicyclic chemistry.[8] It is presumed that a radical (for instance, a methoxycarbonyl radical) produced in photolysis of **2d** might have been responsible for the present photodeacetylation.

Now, the combined results presented here and reported in the preceding paper[1] have made the means available for the introduction of an epoxy-lactone system and a

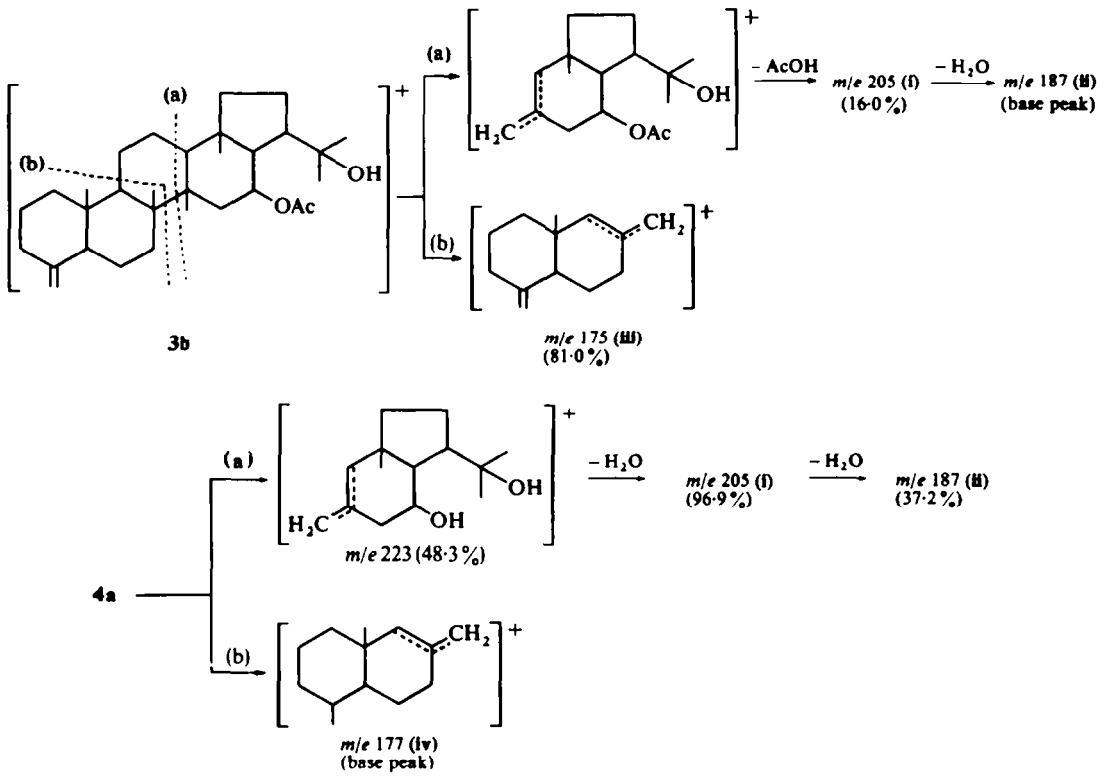

CHART 2

terminal methylene function in eupteleogenin (**1a**) if an appropriate precursory compound is taken as the starting material. Spergulagenic acid (**5a**) appears to be suitable and transformation of **5a** to **1a** by virtue of the above evidences has been attempted as described below.[9]

Spergulagenic acid is one of the root sapogenins of *Mollugo spergula* L. (*Molluginaceae*) and the structure (**5a**) was elucidated by Barua *et al.*[10] We have supposed that spergulagenic acid would be formally a plausible biogenetic precursor for eupteleogenin since it possesses two carboxyl functions at C-17 and C-20, the former being a possible precursor for the epoxy-lactone moiety while the latter for the terminal methylene moiety.

Therefore, spergulagenic acid was tried and isolated from the root sapogenins of of the aforementioned plant material as given in the experimental section. However, free spergulagenic acid was not obtained,* but instead oleanolic acid (**6a**) and methyl spergulagenate in addition to two unknown compounds. The structure (**5b**) was assigned to methyl spergulagenate on the following basis. The IR spectrum shows the presence of the ester and carboxyl functions by the absorption bands at 1718 and 1696 cm^{-1}. CH_2N_2 methylation of the compound afforded dimethyl spergulagenate (**5c**)†,[10] while alkaline hydrolysis gave spergulagenic acid (**5a**). Under the alkaline

* Recently, Hariharan and Rangaswami have also elucidated methyl spergulagenate (**5b**) as one of the sapogenins of the same plant material.[11]

† Kindly provided by Dr. A. K. Barua of Bose Institute, India.

condition employed, the methyl ester function at C-17 is not affected.[10] Comparison of the ester methyl signals in the NMR spectra of methyl 3-O-acetyl-oleanolate (**6b**), methyl 3-O-acetyl-spergulagenate (**5d**) prepared from methyl spergulagenate by acetylation, and dimethyl spergulagenate (**5c**) provides reasonable support of structure (**5b**) for methyl spergulagenate (Table I). In addition, photochemical conversion of **5b** to an epoxy-lactone compound (**7c**, *vide infra*) has further confirmed the structure as described later.

Table I

	6b	**5c**	**5d**
$C_{(17)}$—$COOCH_3$	6·40	6·41	—
$C_{(20)}$—$COOCH_3$	—	6·30	6·31

Irradiation of spergulagenic acid (**5a**) under the same reaction conditions as for oleanolic acid (**6a**)[1] afforded a product designated as MS-E in 13% yield along with recovered **5a** (37%). The desired structure (**7a**) has been assigned to MS-E by the IR absorption bands at 1769 and 872 cm^{-1} due to the epoxy-γ-lactone function. The physical data of an acetate (**7b**) and a methyl ester (**7c**) also corroborate the formulation. Especially, a characteristic two-proton singlet at 7·01τ ($W_{\frac{1}{2}}^{h}$ = 2·5 Hz) assignable to C-11β-H and C-12β-H of the epoxide ring[1] in **7c** is the confirmative evidence for the assignment. It is also noticeable that irradiation of methyl spergulagenate (**5b**) furnished the methyl ester of epoxy-lactone derivative **7c**, since the conversion establishes location of the initial methoxycarbonyl function of **5b** at C-20.

To complete the conversion leading to eupteleogenin (**1a**), photochemical elimination of the carboxyl or the methoxycarbonyl function was attempted using **7a** or **7c** under the same reaction conditions as was effective for the leucotylic acid derivatives. The result was however unsatisfactory presumably due to an axial orientation of the carboxyl function at C-20 in the present material in contrast to the equatorial carboxyl at C-4 of leucotylic acid (**2a**). Therefore, $Pb(OAc)_4$ oxidation[12] was employed and gave the following successful result. Treatment of the acetate (**7b**) with $Pb(OAc)_4$ furnished apparently two products as revealed by ordinary TLC. However, one of the products was disclosed to be a mixture by TLC using argentized silica gel, and consequently separation of the total product was effected by prep. TLC using the latter adsorbent to afford three products designated from most polar to least polar, MS-E-Ac-A (28%), MS-E-Ac-B (36%), and MS-E-Ac-C (12%).

The second major product MS-E-Ac-A shows IR absorption bands at 1648 and 892 cm^{-1} ascribable to the terminal methylene function together with bands at 1763 and 873 cm^{-1} of the epoxy-γ-lactone function. Direct comparison of the product with authentic eupteleogenin acetate (**1b**)[2*] by m.m.p., IR, and TLC confirmed that MS-E-Ac-A is a required compound in the present experiment. Accordingly, it follows that introduction of two unique functional groups of eupteleogenin (**1a**) has now been accomplished in two successive steps.

In addition, direct conversion of **7a** to **1a** was also attempted, however the yield was unsatisfactory. Although it is assumed from the observation that the free OH at C-3

* Kindly provided by Dr. T. Murata of the Res. Lab. of Takeda Chemical Industries, Osaka.

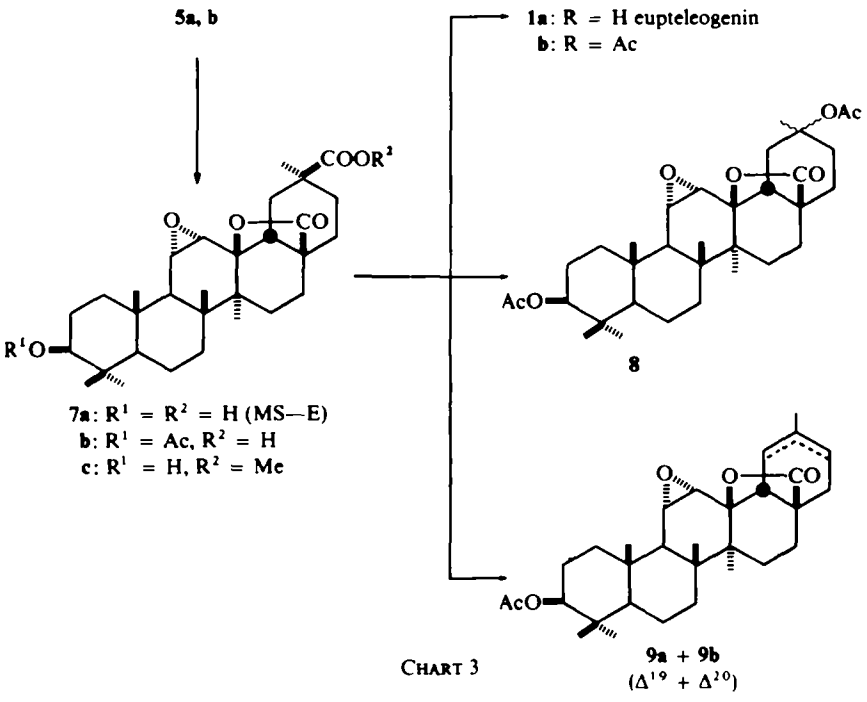

CHART 3

of **7a** might have suffered $Pb(OAc)_4$ oxidation which would induce some side reaction, further examination was not undertaken.

The other products, MS-E-Ac-B and MS-E-Ac-C, are supposedly assigned **9a** + **9b** (not separated) and **8** on the basis of the physical data (Table II) and in comparison with the analogous investigation.[12b]

TABLE II

	9a + **9b**	**8**
Mass	*m/e* 496 (M^+)	*m/e* 556 (M^+)
IR (KBr)	1770 (γ-lactone) 1723 (acetate) 876 (epoxide)	1770 (γ-lactone) 1723 (acetate) 872 (epoxide)
NMR*	Me × 5 AcO × 1 8·33 (1·5H, s) 8·31 (1·5H, s)	Me × 6 AcO × 2 7·01 (2H, s) 5·45 (1H, t-like)

* Measured in a microscale tube due to the shortage of the material and only the data with distinct assignment are given here.

EXPERIMENTAL

Instruments used in the experimental section and the experimental conditions for chromatography were same as for the preceding paper.[1]

Photolysis of methyl leucotylate (**2b**). A solution of **2b** (4 g)[3] in EtOH (400 ml) was irradiated with a 30 W low pressure mercury lamp (Eikosha Co., Model PIL 30) for 83 hr at room temp. A product (*ca.* 4 g) obtained by evaporation of the solvent *in vacuo* was acetylated with Ac_2O (8 ml) and pyridine (20 ml) by keeping overnight at room temp and treated in the usual manner. Column chromatography of the product with silica gel (200 g) eluting with 1% EtOAc–C_6H_6 gave a mixture (540 mg), which contained mainly H-3-Ac (**3b**) was obtained by recrystallization from n-hexane as colorless rods of m.p. 225–226°; $[\alpha]_\omega$ + 164 the acetate (**2d**, 1·68 g).

The mixture containing mainly H-3-Ac and H-1-Ac was then chromatographed on SiO_2–$AgNO_3$ (50 g)[4] column to furnish H-3-Ac (77 mg), H-2-Ac (31 mg), and H-1-Ac (crude, 314 mg). Analytical sample of H-3-Ac (**3b**) was obtained by recrystallization from n-hexane as colorless rods of m.p. 225 226°; $[\alpha]_D$ + 164° ($CHCl_3$); ν_{max} ($CHCl_3$): 3550, 1740, 1643, 890 cm^{-1}; NMR (100 MHz): 9·38 (3H), 9·17 (3H), 9·07 (3H), 8·90 (6H), 8·87 (3H) (all s, totally six Me's), 7·97 (3H, s, AcO), 7·02 (1H, s, disappeared on D_2O addition), 5·61, 5·37 (1H each, both s), 4·82 (1H, m); Mass spectrum *m/e*: 470 (M^+, 6·3%), and the prominent ion peaks as shown in Chart 2 (Found: C, 79·16; H, 10·68. $C_{31}H_{50}O_3$ requires C, 79·10; H, 10·71%).

Treatment of **3b** (30 mg) with 5% NaOH–MeOH (5 ml) by heating for 10 min followed by usual treatment and crystallization from MeOH afforded **3a** as colorless needles m.p. 238–242°; $[\alpha]_D$ + 123° (*c* = 0·4, $CHCl_3$); ν_{max} ($CHCl_3$): 3400, 1643, 890 cm^{-1} (Found: C, 81·25; H, 11·34. $C_{29}H_{48}O_2$ requires C, 81·22; H, 11·29%).

H-2-Ac was purified by recrystallization from n-hexane to give colorless needles m.p. 152–160°; ν_{max} ($CHCl_3$): 3560, 1740, 1220, 1633 cm^{-1}. Alkaline hydrolysis of H-2-Ac followed by crystallization from MeOH gave H-2 as colorless needles m.p. 238–239°; ν_{max} ($CHCl_3$): 3250, 1633 cm^{-1}.

Since the fraction of H-1-Ac obtained above was still accompanied by impurity, a dry ethereal solution (10 ml) of the substance (220 mg) was added to a solution of LAH (400 mg) in dry ether (20 ml) and the total mixture refluxed for 3 hr and treated as usual. Prep. TLC developing with n-hexene-AcOEt (2:1) followed by recrystallization with MeOH afforded a pure sample of H-1 (**4a**, 163 mg) as colorless needles m.p. 246–247°; $[\alpha]_D$ + 60° (*c* = 1·1, $CHCl_3$); ν_{max} ($CHCl_3$): 3580, 3300 cm^{-1}; NMR (60 MHz): 9·23 (3H, s), 9·19 (3H, s), 9·15 (3H, d, *J* = 9·6), 8·98 (6H, s), 8·82 (3H, s), 8·74 (3H, s) (totally seven Me's), 5·95 (1H, m, $>C_{(16)}\underline{H}OH$); Mass spectrum *m/e*: 430 (M^+, 5·7%), and the prominent ion peaks as shown in Chart 2 (Found: C, 80·86; H, 11·70. $C_{29}H_{50}O_2$ requires C, 80·87; H, 11·70%).

Acetylation of **4a** (50 mg) with Ac_2O (0·7 ml) and pyridine (1·5 ml) at room temp in the usual manner followed by crystallization from MeOH afforded **4b** (H-1-Ac, 48 mg) as colorless needles m.p. 191–194°; $[\alpha]_D$ + 100° ($CHCl_3$); ν_{max} ($CHCl_3$): 3550, 1737, 1220 cm^{-1}; NMR (60 MHz): 9·19 (3H, s), 9·16 (3H, d, *J* = 10·2), 9·14 (3H, s), 9·02 (3H, s), 8·89 (3H, s), 8·86 (6H, s) (totally seven Me's), 7·95 (3H, s, AcO), 4·80 (1H, m, $>C_{(16)}\underline{H}OAc$). (Found: C, 79·06; H, 11·10. $C_{31}H_{52}O_3$ requires C, 78·75; H, 11·09%).

Ethyl leucotylate (**2c**). A solution of leucotylic acid (**2a**)[3] (500 mg) in dry acetone (50 ml) was treated with diethyl sulfate (1·5 ml) and dry K_2CO_3 (700 mg) under reflux for 10 hr. After concentration of the mixture in *vacuo* to one third volume, the mixture was diluted with water to give a white precipitate collected by filtration, washed with water and dried (yield 488 mg). Crystallization of the product from EtOH afforded ethyl leucotylate (**2c**) as colorless needles m.p. 262–263°; $[\alpha]_D$ + 38° ($CHCl_3$); ν_{max} ($CHCl_3$): 3400, 1710 cm^{-1} (Found: C, 76·70; H, 10·81. $C_{32}H_{54}O_4$ requires C, 76·44; H, 10·83%).

Catalytic hydrogenation of **3b**. A solution of **3b** (10 mg) in EtOH (4 ml) was hydrogenated over PtO_2 (20 mg) for 9 hr at room temp in the usual manner. Recrystallization of the product from MeOH gave crystals (5 mg), which were identified with H-1 (**4a**) by m.m.p., IR, and TLC.

Isolation of methyl spergulagenate (**5b**). Extraction of the cuts (3 kg) of *Mollugo spergula* L. roots (imported through Tochimoto Tenkaido Co., Osaka) using MeOH three times afforded a resinous product, which was partitioned into n-BuOH–water. The residue obtained by evaporation of the n-BuOH soluble portion was then poured into large quantity of ether and the precipitate collected by filtration to give the crude saponin (48 g, 2·8% from the roots). A solution of which (45 g) in MeOH (500 ml) was added to aq. 10% H_2SO_4 (500 ml), refluxed for 7 hr, and diluted with water to precipitate the hydrolysate which was collected by filtration and dried (yield 20 g). The crude sapogenin mixture (17 g) thus obtained was then chromatographed on silica gel (1 kg) eluting with C_6H_6–EtOAc (5:1) to give methyl spergulagenate (**5b**, 1·95 g). The analytical sample of **5b** was obtained by recrystallization with MeOH as colorless needles m.p. 257–260°; $[\alpha]_D$ + 101° (pyridine); ν_{max} (KBr): 3400, 1718, 1696 (sh) cm^{-1} (Found: C, 74·33; H, 9·62. $C_{31}H_{48}O_5$ requires C, 74·36; H, 9·66%).

Treatment of **5b** (50 mg) with Ac_2O (0·5 ml) and pyridine (1 ml) as usual followed by recrystallization from EtOH–$CHCl_3$ gave the acetate (**5d**, 50 mg) as colorless needles m.p. 220–221°; $[\alpha]_D$ + 96° ($CHCl_3$); ν_{max} (KBr): 1728, 1695 (sh), 1245 cm^{-1}; NMR (60 MHz): 9·26 (3H), 9·12 (6H), 9·03 (3H), 8·84 (6H) (all s, totally six Me's), 7·95 (3H, s, AcO), 6·31 (3H, s, $COOCH_3$), 5·50 (1H, t-like, $>C_{(3)}H$OAc), 4·63 (1H, m, $-C_{(12)}H=$) (Found: C, 72·32; H, 8·98. $C_{33}H_{50}O_6 \cdot \frac{1}{2}H_2O$ requires C, 71·87; H, 9·24%).

Dimethyl spergulagenate (**5c**). Methyl spergulagenate (**5b**, 20 mg) was methylated with ethereal CH_2N_2 in the usual manner. The product (20 mg) was recrystallized from MeOH and identified with authentic dimethyl spergulagenate[1v] by m.m.p., IR, and TLC.

Spergulagenic acid (**5a**). Methyl spergulagenate (**5b**, 1·11 g) was treated with 10% KOH–EtOH (150 ml) under reflux for 8 hr after the procedure described in the literature[10] and spergulagenic acid (**5a**, 830 mg) was obtained.

Photooxidation of spergulagenic acid (**5a**). A 0·5% solution of **5a** (500 mg) in acidified 95% EtOH (pH ≒ 2) was irradiated for 90 hr under the same condition as described in the preceding paper,[1] and the product was purified by prep. TLC developing with $CHCl_3$–MeOH–HCOOH (100:10:0·3) mixture to afford MS-E (**7a**) in 13% yield together with recovered starting material (37%). The analytical sample of **7a** was prepared by recrystallization from MeOH as colorless needles m.p. 320–323°; $[\alpha]_D$ +116° (pyridine); ν_{max} (KBr): 3440, 1769, 1708, 872 cm^{-1} (Found: C, 72·00; H, 8·79. $C_{30}H_{44}O_6$ requires C, 71·97; H, 8·86%).

Acetylation of **7a** (50 mg) with Ac_2O (0·6 ml) and pyridine (1 ml) as usual followed by crystallization from MeOH gave the acetate (**7b**, MS-E-Ac, 50 mg) as colorless needles m.p. 301–303°; $[\alpha]_D$ + 86° (c = 0·5, $CHCl_3$); ν_{max} (KBr): 1768, 1734, 1702 (sh), 1247, 873 cm^{-1} (Found: C, 70·85; H, 8·64. $C_{32}H_{46}O_7$ requires C, 70·82; H, 8·54%).

Treatment of **7a** (30 mg) with ethereal CH_2N_2 followed by recrystallization from MeOH–CH_2Cl_2 afforded the methyl ester (**7c**, colorless needles, 30 mg) m.p. 324–326°; $[\alpha]_D$ + 46° ($CHCl_3$); ν_{max} (KBr): 3502, 1768, 1710, 874 cm^{-1}; NMR (100 MHz): 9·21, 9·02, 8·97, 8·90, 8·78, 8·75 (3H each, all s, totally six Me's), 7·10 (2H, s, $W_{\frac{1}{2}}$ = 2·5 Hz), 6·78 (1H, t-like, $>C_{(3)}H$OH), 6·32 (3H, s, $COOCH_3$) (Found: C, 71·78; H, 8·80. $C_{31}H_{46}O_6$ requires C, 72·38; H, 9·01%).

Photooxidation of methyl spergulagenate (**5b**). Irradiation of a 0·5% solution of **5b** in acidified 95% EtOH (pH ≒ 2) under the same condition as for **5a** followed by prep. TLC developing with $CHCl_3$–MeOH (20:1) furnished **7c** (recrystallized from MeOH–CH_2Cl_2 and identified with the product obtained above by m.m.p., IR, and TLC) in 13% yield together with recovered **5b** (35%).

$Pb(OAc)_4$ *oxidation of* **7b**. To a solution of **7b** (10 mg) in dry pyridine (1·5 ml), was added excess $Pb(OAc)_4$ (30 mg) and the mixture stirred at room temp for 4 hr and then at 40° for 2 hr under N_2. The product was subjected to prep. TLC with SiO_2–$AgNO_3$ developing with $CHCl_3$–MeOH (100:1) to afford MS-E-Ac-A (**1b**, 28%), MS-E-Ac-B, m.p. 319–321° (**9a** + **9b**, 36%), and MS-E-Ac-C, m.p. 281–284° (**8**, 12%). MS-E-Ac-A was identified with authentic eupteleogenin acetate (**1b**)[2] by m.m.p., IR, and TLC.

The physical properties of MS-E-Ac-B and MS-E-Ac-C are tabulated in Table II.

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