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Constituents of the Lichen in the Genus *Hypogymnia*. I. Oxyphysodic Acid a New Depsidone from *Hypogymnia enteromorpha* (Ach.) Nyl.

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A new depsidone named oxyphysodic acid (2), which has been known to occur often concomitantly with physodic acid (1) in the lichen belonging to the genus *Hypogymnia* (Parmeliaceae) and also in the lichen of several other species, has been isolated from the lichen *Hypogymnia enteromorpha* (Ach.) Nyl. The structure (2) possessing the pyrogallol-type oxygenation pattern has been established for oxyphysodic acid on the basis of chemical and physicochemical evidence.

In the phytochemical survey by thin-layer chromatography (TLC) on the constituents of sixteen species of the lichen in the genus *Hypogymnia* (Parmeliaceae), Nuno reported that physodic acid (1) contained in fourteen of them was quite often (also depending upon the collected place) accompanied by an unidentified phenolic substance which was colored bluish violet by the ferric chloride reagent.[2] The presence of the same phenolic substance along with physodic acid was also noted in the other kinds of lichen: *Cetraria rugosa* (Asah.) Sato, *C. rhytidocarpa* f. *nipponensis* Asah., and *Pseudevernia furfuracea* (L.) Zopf (syn. *Parmelia furfuracea* (L.) Ach.).[2]

We have examined by TLC the acetone extractives of eight species of the genus *Hypogymnia* from our collection (Fig. 1) and noticed the presence of the unknown phenolic substance (spot b) in seven species as pointed out by Nuno and also that of another minor substance (spot f) in *H. vittata*.[3] As a continuative study on the lichen metabolites in our laboratories, we have been investigating the constituents of one of the above eight species *Hypogymnia enteromorpha* (Ach.) Nyl. (syn. *Parmelia enteromorpha* Ach.) which was collected at Mt. Ōdaigahara in Nara prefecture and have isolated the unknown phenolic substance (a new depsidone). The present paper provides the full account on the structure elucidation of the new depsidone named oxyphysodic acid (2).[4]

Successive extraction with ether and acetone of the lichen materials followed by chromatographic separation furnished physodic acid (1),[5a] oxyphysodic acid (2), physodalic acid (3),[5b] and atranorin (4).[5c] The molecular formula $C_{26}H_{30}O_9$ of oxyphysodic acid revealed by elemental analysis and mass spectrometry comprises one more oxygen than that of physodic acid. The infrared (IR) spectrum of oxyphysodic acid shows the absorption bands at 3550, 3150 (br) cm^{-1} (hydroxyl), 1690, 1660 cm^{-1} (depsidone, carbonyl, and carboxyl), and 1620, 1605 cm^{-1} (aromatic ring). Isolated oxyphysodic acid was also colored bluish violet by the ferric chloride reagent but was negative for the sodium hypochlorite and *p*-phenylenediamine

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1) Location: *a) Yamashina-misasagi, Higashiyama-ku, Kyoto, 607, Japan; b) 133-1, Yamada-kami, Suita, Osaka, 565, Japan.*

2) M. Nuno, *Journ. Jap. Bot.*, 39, 97 (1964).

3) Named vittatolic acid. Structure: T. Hirayama, F. Fujikawa, I. Yosioka, and I. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), 23, 693 (1975) (preliminary report); also see the following paper.

4) T. Hirayama, F. Fujikawa, I. Yosioka, and I. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), 22, 1678 (1974) (preliminary report).

5) Y. Asahina and S. Shibata, "Chemistry of Lichen Substances," Japan Society for the Promotion of Science, Tokyo, 1954, *a)* p. 115; *b)* p. 140; *c)* p. 94; *d)* p. 10; *e)* p. 68; *f)* p. 75.

reagent,[5d)] and the blue coloration is reminiscent of that of the known depside diploschistesic acid (**5**)[5e)] which possesses a pyrogallol-type oxygenation pattern in its molecule.

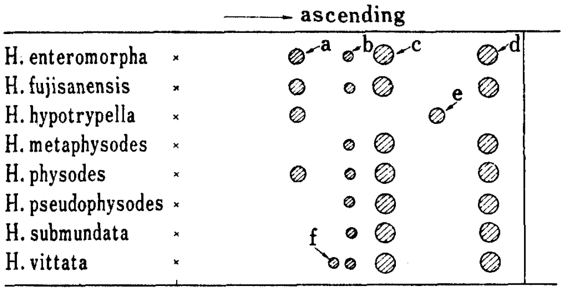


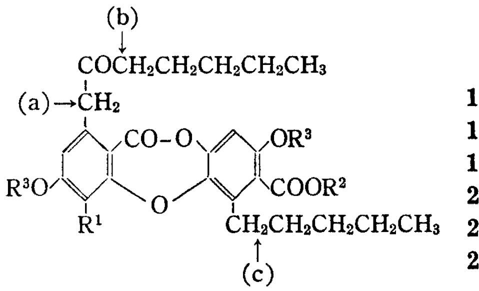
Fig. 1. TLC Diagram of the Acetone Extractives of the Lichen in the Genus *Hypogymnia*

developing solvent: benzene–dioxane–AcOH=90: 25: 4
coloration: 1% $FeCl_3$ soln.
a) physodalic acid (**3**, violet)
b) oxyphysodic acid (**2**, bluish violet)
c) physodic acid (**1**, violet)
d) atranorin (**4**, purple)
e) usnic acid (violet)
f) vittatolic acid (violet)[8)]

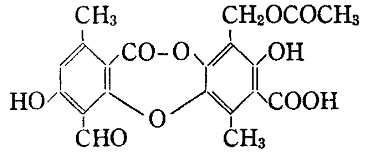
Brief treatment with ethereal diazomethane of oxyphysodic acid (**2**) gave methyl oxyphysodate (**2a**) and acetylation with acetic anhydride and conc. sulfuric acid yielded oxyphysodic acid triacetate (**2b**).

The examinations of proton magnetic resonance (PMR) spectra (Table I) of **2**, **2a**, and **2b** in comparison with those of physodic acid (**1**),[6)] methyl physodate (**1a**),[6,7)] and physodic acid diacetate (**1b**),[7)] have shown the close resemblance of the structures of **1** and **2** except i) the presence of three aromatic proton signals in the spectra of **1**, **1a**, and **1b** while two in those of **2**, **2a**, and **2b**, and ii) two phenolic hydroxyls in **1** but three in **2**.

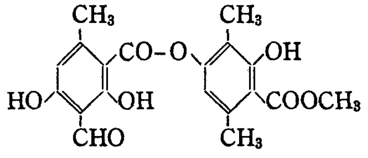
In the PMR spectra of methyl physodate (**1a**) and methyl oxyphysodate (**2a**), two aromatic protons are observed at δ 6.57 and δ 6.79 as *meta*-coupled doublets (J=2 Hz) along with a one-proton singlet at δ 6.70 in **1a** while two one-proton singlets are observed at δ 6.40 and δ 6.71 in **2a** which lacks one of the *meta*-coupled protons in **1a** and the rest of the signals appear at the resembled positions. In the PMR spectra of the acetates (**1b** and **2b**), same similarities and differences as between **1a** and **2a** are observed in addition to a finding that two phenolic acetoxyl signals present in **1b** but three of those in **2b**.



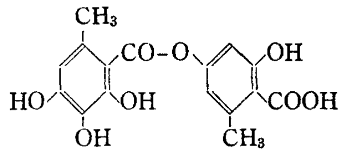
	R^1	R^2	R^3	
1	H	H	H	physodic acid
1a	H	CH_3	H	
1b	H	H	Ac	
2	OH	H	H	oxyphysodic acid
2a	OH	CH_3	H	
2b	OAc	H	Ac	



3 physodalic acid



4 atranorin



5 diploschistesic acid

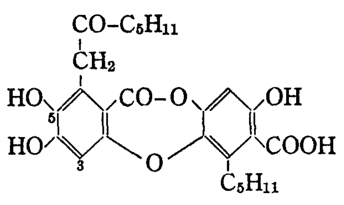


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Chart 1

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6) S. Huneck and P. Linscheid, *Z. Naturforsch.*, **23b**, 717 (1968).
7) Prepared from physodic acid (**1**).[5a)]

Based on the above evidence, the structure of oxyphysodic acid has been expressed as **2** or isomeric **6** (possessing an additional phenolic hydroxyl at C-3 or C-5 in the left aromatic ring of physodic acid (**1**)), of which **2** is preferable from the point of ferric chloride coloration (*cf.* diploschistesic acid (**5**)) and has been rationalized by the following nuclear Overhauser effect (NOE) measurements. Thus, irradiation of the signal due to benzyl methylene (a) (δ 4.03 in **1b** or δ 4.05 in **2b**) caused the increase of aromatic proton signal intensity (12% at δ 6.87 in **1b** or 8% at δ 6.96 in **2b**). Consequently, the presence of an aromatic proton at C-5 in the left benzene ring of the depsidone skeleton of oxyphysodic acid has been revealed and the structure **2** has taken precedence of **6** for oxyphysodic acid.

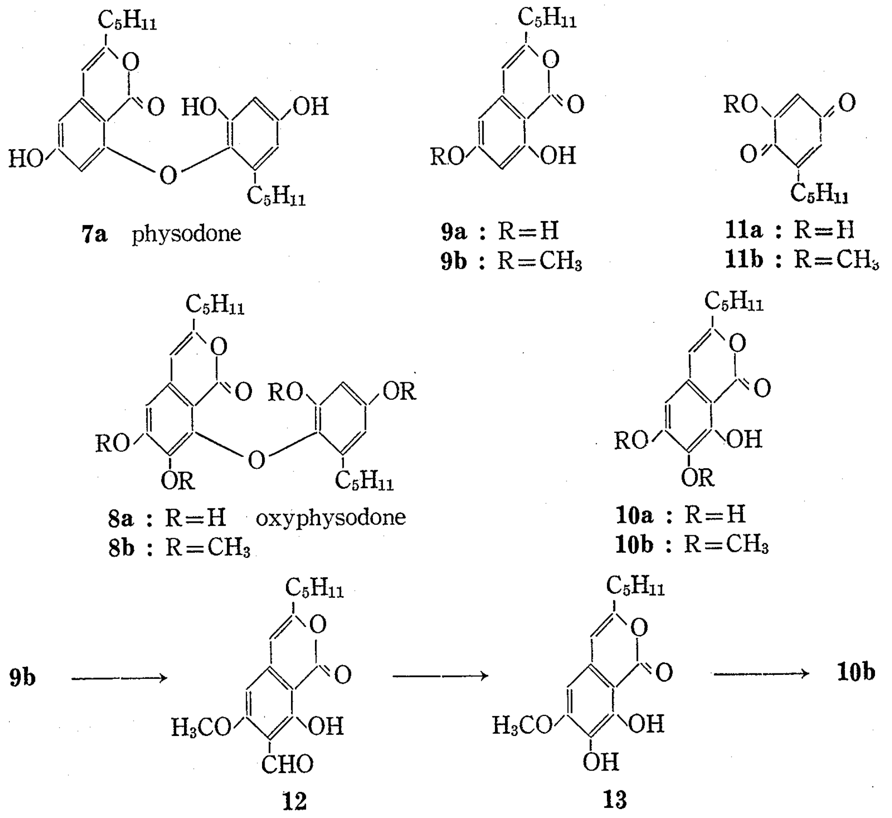

Chart 2

In order to achieve the chemical support of the structure **2** for oxyphysodic acid, the following degradations of physodic acid (**1**) and oxyphysodic acid were undertaken. Among several degradation methods for the depsidones (*e.g.* potassium fusion,8,9) potassium permanganate oxidation,8) sodium dichromate oxidation,8) and nitric acid oxidation10)), the nitric acid oxidation was adopted. Thus, formic acid treatment of oxyphysodic acid (**2**) gave oxyphysodone (**8a**) through concomitant cleavage of the ester linkage in the depsidone, lactone formation, and decarboxylation. Subsequent oxidation of **8a** with nitric acid in acetic acid furnished a yellow crystalline product which was found identical in all respects with 2-hydroxy-6-pentyl-1,4-benzoquinone (**11a**) obtained also from physodone (**7a**) through the same degradation procedure. Although olivetonide (**9a**) was also obtained by the nitric acid oxidation of physodone (**7a**), hydroxy-olivetonide (**10a**) could not be isolated from the degradation product of oxyphysodone (**8a**) probably due to its instability for the oxidation. Next, oxyphysodone

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8) Y. Asahina and H. Nogami, *Chem. Ber.*, **67**, 805 (1934); *idem*, *ibid.*, **68**, 77, 1500 (1935).
9) Y. Asahina and M. Yanagita, *Chem. Ber.*, **67**, 1936 (1934).
10) *a*) F.M. Dean, J.C. Roberts, and A. Robertson, *J. Chem. Soc.*, **1954**, 1432; *b*) F.M. Dean, D.S. Deorha, A.D.T. Erni, D.W. Hughes, and J.C. Roberts, *ibid.*, **1960**, 4829; *c*) S. Neelakantan, T.R. Seshadri, and S.S. Subramanian, *Tetrahedron*, **18**, 597 (1962).

Table I. PMR Data of Physodic Acid (**1**), Oxyphysodic Acid (**2**), and Their Derivatives[a]

	CH_3	CH_2	Ar-H	Others
1[b]	0.86(t, J=6) 0.91(t, J=6)	(a)3.97(s) (b)2.46(t, J=7) (c)2.81(br)	6.60(1H, s) 6.62(2H, s)	1.11—2.14 (12H, br, -C$\underline{H}_2$-×6)
2[b]	0.88(t, J=6) 0.92(t, J=6)	(a)3.82(s) (b)2.42(t, J=7) (c)3.04(br)	6.52(1H, s) 6.56(1H, s)	1.11—2.11 (12H, br, -C$\underline{H}_2$-×6)
1a[c]	0.90(t, J=6) 0.94(t, J=6)	(a)3.80(s) (b)2.38(t, J=7) (c)3.20(br)	6.57(1H, d, J=2) 6.70(1H, s) 6.79(1H, d, J=2)	1.11—1.95 (12H, br, -C$\underline{H}_2$-×6) 3.96(3H, s, COOC$\underline{H}_3$)
2a[c]	0.90(t, J=6) 0.92(t, J=6)	(a)3.80(s) (b)2.61(t, J=7) (c)3.26(br)	6.40(1H, s) 6.71(1H, s)	1.11—1.84 (12H, br, -C$\underline{H}_2$-×6) 3.94(3H, s, COOC$\underline{H}_3$)
1b[c]	0.88(t, J=6) 0.91(t, J=6)	(a)4.03(s) (b)2.51(t, J=7) (c)3.00(br)	6.87(1H, d, J=2) 7.00(1H, s) 7.03(1H, d, J=2)	1.15—2.05 (12H, br, -C$\underline{H}_2$-×6) 2.24, 2.30 (3H each, s, OAc×2)
2b[c]	0.88(t, J=6) 0.89(t, J=6)	(a)4.05(s) (b)2.51(t, J=7) (c)3.09(br)	6.96(1H, s) 7.05(1H, s)	1.04—1.85 (12H, br, -C$\underline{H}_2$-×6) 2.23, 2.27, 2.41 (3H each, s, OAc×3)

a) abbreviations: br=broad signal, d=doublet, s=singlet, t=triplet
b) measured in d_6-dimethyl sulfoxide
c) measured in $CDCl_3$

tetramethyl ether (**8b**), which was prepared by prolonged treatment of oxyphysodone (**8a**) with ethereal diazomethane, was subjected to the nitric acid degradation as for **8a** and two products were isolated. The one obtained as orange needles was shown to be identical with 2-methoxy-6-pentyl-1,4-benzoquinone (**11b**) which was prepared from **11a** by diazomethane methylation. The other colorless crystalline product was proved to be desired hydroxy-olivetonide dimethyl ether (**10b**) by synthesizing it from olivetonide monomethyl ether (**9b**) *via* the successive reactions: formylation (giving **12**),[11] alkaline hydrogen peroxide oxidation (giving **13**),[12] and partial methylation with diazomethane.

The structure **2** has now been established for oxyphysodic acid which often accompanies physodic acid (**1**) as the lichen metabolite. Oxyphysodic acid (**2**) seems to be the first example possessing the pyrogallol-type oxygenation pattern among the depsidones. Very recently, Elix reported the isolation of oxyphysodic acid (named hydroxyphysodic acid)[13] from the lichen *Hypogymnia billardieri* (Mont.) R. Filson and reached the same conclusion as ours on the structure.

Experimental[14]

Isolation of Depside and Depsidones——Air-dried lichen materials (150 g), collected at Mt. Ōdaigahara in Nara prefecture, were extracted with ether twice (500 ml and 48 hr each) at room temperature and then extracted with acetone (200 ml) for 6 hr using a Soxhlet extractor. The ether extractive (7 g) was treated with $CHCl_3$ and the insoluble portion (4.1 g) separated by filtration contained most of the depsidones and was

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11) R. Adams and I. Levine, *J. Am. Chem. Soc.*, **45**, 2373 (1923).
12) W.M. McLamore, *J. Am. Chem. Soc.*, **73**, 2225 (1951).
13) J.A. Elix, *Aust. J. Chem.*, **28**, 849 (1975).
14) The following instruments were used for obtaining the physical data. Melting points: Yanagimoto Micro-meltingpoint Apparatus (a hot-stage type) and recorded uncorrected; IR spectra: Shimadzu IR Spectrometer IR-27G; PMR spectra: Hitachi R-22 (90 MHz) nuclear magnetic resonance (NMR) Spectrometer (tetramethylsilane as the internal standard, the chemical shifts are given in δ values, and the coupling constants in Hz); Mass spectra: Hitachi RMU-6E or JEOL JMS-01SG Mass Spectrometer. The NOE experiments were undertaken in the frequency-swept and external CF_3COOH–locked mode for the degassed solution in $CDCl_3$.
Preparative TLC was carried out on the thick-layer plates of silica gel (Merck PF_{254}) and the detection was made by irradiation with an ultraviolet lamp (254 nm).

subjected to repeated preparative TLC developing with benzene–dioxane–AcOH (90: 25: 4). The fraction of *Rf* 0.6 was collected, extracted with ether, and crystallized from aq. MeOH to give physodic acid (**1**, 2.7 g, 1.8%) as colorless needles of mp 205°. Identification was made by direct comparison with the authentic specimen by mixed mp, TLC, and IR (KBr). The fraction of *Rf* 0.5 was crystallized from aq. MeOH to give oxyphysodic acid (**2**, 0.75 g, 0.5%) as colorless needles of mp 187° (decomp.). *Anal.* Calcd. for $C_{26}H_{30}O_9$: C, 64.18; H, 6.22. Found: C, 64.18; H, 6.21. IR ν_{max}^{KBr} cm^{-1}: 3550, 3510 (br) (OH), 1690, 1660 (depsidone, CO, COOH), 1620, 1605 (aryl C=C). Mass Spectrum *m/e* (%): 486 (M^+, 2), 442 (M^+-CO_2, 100). PMR (d_6-DMSO) δ: as given in Table I.

Silica gel (Merck, 70—230 mesh) column chromatography of the $CHCl_3$ soluble portion eluting with benzene–AcOEt (9: 1) gave a depside which was crystallized from acetone to give atranorin (**4**, 2.2 g, 1.5%) being identical with the authentic sample (mixed mp, TLC, and IR ($CHCl_3$)). The acetone extractive was crystallized from acetone to give physodalic acid (**3**, 2.3 g, 1.5%), which was identified with the authentic sample by mixed mp, TLC, and IR (KBr).

Methyl Oxyphysodate (2a)——An ice-cooled solution of **2** (100 mg) in ether (5 ml) was treated with ethereal diazomethane for one min and added with acetic acid (one drop). Concentration of the ether solution gave colorless needles which were recrystallized from aq. MeOH to furnish methyl oxyphysodate (**2a**, 73 mg) of mp 104—106°. *Anal.* Calcd. for $C_{27}H_{32}O_9$: C, 64.79; H, 6.44. Found: C, 64.64; H, 6.45. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3250 (OH), 1725, 1670 (depsidone, CO, $COOCH_3$), 1615 (aryl C=C). Mass Spectrum (%): 500 (M^+, 100). PMR ($CDCl_3$) δ: as given in Table I.

Oxyphysodic Acid Triacetate (2b)——Acetylation of **2** (100 mg) with acetic anhydride (8 ml) and conc. H_2SO_4 (one drop) followed by usual work-up and crystallization from aq. MeOH afforded colorless needles (**2b**, 90 mg) of mp 104° (decomp.). *Anal.* Calcd. for $C_{32}H_{36}O_{12}$: C, 62.74; H, 5.92. Found: C, 62.77; H, 5.86. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780 (OAc), 1745 (br), 1725 (sh) (depsidone, CO, COOH), 1610 (aryl C=C). Mass Spectrum *m/e* (%): 612 (M^+, 7), 568 (M^+-CO_2, 100). PMR ($CDCl_3$) δ: as given in Table I.

Oxyphysodone (8a)——A solution of **2** (500 mg) in formic acid (20 ml) was refluxed for 2 hr in an oil bath and the reaction mixture was poured into ice-cooled water (100 ml). The precipitate was collected by filtration and crystallized from aq. MeOH to give colorless plates of **8a**, mp 202—203°. *Anal.* Calcd. for $C_{25}H_{30}O_7$: C, 67.85; H, 6.83. Found: C, 67.81; H, 6.93. IR ν_{max}^{KBr} cm^{-1}: 3200 (OH), 1695 (br), 1660 (w) (lactone CO, C=C), 1605 (aryl C=C). Mass Spectrum *m/e* (%): 442 (M^+, 100). PMR (d_6-acetone) δ: 0.86, 0.91 (3H each, both t, $J=6$ Hz, terminal $CH_3\times 2$), 1.16—1.95 (12H, br, $-CH_2-\times 6$), 2.25, 2.72 (2H each, both t, $J=7$ Hz, pyrone–$\underline{CH_2}$–CH_2–, Ar–$\underline{CH_2}$–CH_2–), 6.13, 6.52 (1H each, both s, Ar–H, pyrone-H), 6.26, 6.35 (1H each, both d, $J=3$ Hz, Ar–H$\times$2).

Oxidative Degradation of 8a giving 11a——To a solution of **8a** (150 mg) in glacial AcOH (20 ml) was added conc. HNO_3 ($d=1.42$, 0.2 ml) and the total mixture was kept stirring for 20 min under ice-cooling, poured into water (100 ml) and extracted with ether three times (100 ml each). The combined ether extract was washed with aq. $NaHCO_3$ until the aqueous layer became neutral, washed with water, dried over $MgSO_4$, and evaporated to dryness to give an orange product. The product was crystallized from benzene–*n*-hexane to furnish **11a** as orange needles (19 mg) of mp 172—173°, which was identified by mixed mp, TLC, and IR ($CHCl_3$) with 2-hydroxy-6-pentyl-1,4-benzoquinone (**11a**) obtained from physodic acid (**1**) below.

Oxidative Degradation of Physodone (7a) giving 9a and 11a——To a solution of **7a** (200 mg) in glacial AcOH (20 ml) was added conc. HNO_3 ($d=1.42$, 0.2 ml) and the total mixture was kept stirring for 20 min under ice-cooling and treated similarly as for the oxidative degradation of **8a** described above. The ether extractive, which comprised two products, was separated by column chromatography (Merck silica gel PF_{254}) eluting with benzene–AcOEt (9: 1). The first eluting product was crystallized from benzene to furnish the colorless plates of **9a** (70 mg), which was identified with authentic olivetonide (**9a**)[15] by mixed mp, TLC, and IR ($CHCl_3$). The second eluting product was crystallized from benzene–*n*-hexane to furnish the orange needles of **11a** (25 mg), mp 172—173°. *Anal.* Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.11; H, 7.23. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300 (OH), 1705, 1660, 1619 (quinone CO, C=C). Mass Spectrum *m/e* (%): 194 (M^+, 100). PMR ($CDCl_3$) δ: 0.88 (3H, t, $J=6$ Hz, terminal CH_3), 1.05—1.90 (6H, br, $-CH_2-\times 3$), 2.45 (2H, t-like, $J=ca.$ 6 Hz, –C=C–$\underline{CH_2}$–), 6.10, 6.46 (1H each, both s, ring H$\times$2).

Complete Methylation of Oxyphysodone (8a) giving Oxyphysodone Tetramethyl Ether (8b)——To a solution of oxyphysodone (**8a**, 150 mg) in ether (4 ml) was added excess ethereal diazomethane and the mixture was left standing for 3 days. Evaporation of ether gave a pale yellow residue which was purified by column chromatography (Merck silica gel PF_{254}) eluting with benzene–AcOEt (9: 1) to give **8b** as a glassy substance (140 mg). Crystallization of **8b** was unsuccessful. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1727 (br), 1657 (w) (lactone CO, C=C), 1600 (aryl C=C). High resolution mass spectrum: Found: 498.261. Calcd. for $C_{29}H_{38}O_7$: 498.262. Mass Spectrum *m/e* (%): 498 (M^+, 100). PMR ($CDCl_3$) δ: 0.83, 0.89 (3H each, both t-like, terminal $CH_3\times 2$), *ca.* 1.0—2.0 (12H, br, $-CH_2-\times 6$), 2.43 (2H, t, $J=7$ Hz, pyrone–$\underline{CH_2}$–CH_2–), 2.67 (2H, t-like, Ar–$\underline{CH_2}$–CH_2–), 3.22, 3.56, 3.73, 3.86 (3H each, all s, $OCH_3\times 4$), 6.00, 6.39 (1H each, both s, Ar–H, pyrone–H), 6.22, 6.29 (1H each, both d, $J=2$ Hz, Ar–H$\times$2).

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15) Prepared from microphyllic acid.[5f]

Oxidative Degradation of 8b giving 10b and 11b——To a solution of oxyphysodone tetramethyl ether (**8b**, 140 mg) in glacial AcOH (20 ml) was added conc. HNO_3 (d=1.42, 0.2 ml) and the total mixture was kept stirring at 70° for 30 min in a water bath and treated similarly as for the oxidative degradation of **8a** described above. The ether extract was evaporated to give two products, which were purified by column chromatography (Merck silica gel PF_{254}) eluting with benzene–AcOEt (9 : 1). The first eluting product was crystallized from MeOH to furnish the colorless needles of **10b** (35 mg), which was identified by mixed mp, TLC, and IR ($CHCl_3$) with hydroxy-olivetonide dimethyl ether (**10b**) prepared from olivetonide monomethyl ether (**9b**) (*vide infra*). The second eluting product was crystallized from ligroin to furnish **11b** (orange needles, 30 mg) of mp 63°, which was identified (mixed mp, TLC, and IR ($CHCl_3$)) with 2-methoxy-6-pentyl-1,4-benzoquinone prepared by diazomethane methylation of 2-hydroxy-6-pentyl-1,4-benzoquinone (**11a**) (*vide infra*).

Formylation of Olivetonide Monomethyl Ether (9b) giving 12——To a solution of **9b** (500 mg) in dry ether (30 ml) was added $Zn(CN)_2$ (1 g) and the stirred solution was bubbled with dry hydrogen chloride for 2 hr and the reaction mixture was left standing at room temperature overnight. An oily product obtained by evaporation of the solvent was washed three times with ether (50 ml each), added with water (30 ml), and refluxed for 20 min. After cooling, the aqueous mixture was extracted with ether (50 ml), and the combined ether extract was washed with aq. $NaHCO_3$ until the aqueous layer became alkaline, washed with water, dried over $MgSO_4$, and evaporated to dryness to give the colorless needles. Recrystallization from MeOH furnished a pure sample of **12** (colorless needles, 100 mg) of mp 62°. *Anal.* Calcd. for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.23; H, 6.22. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1683, 1667, 1633 (CHO, lactone CO, C=C), 1603, 1572 (aryl C=C).[16] Mass Spectrum *m/e* (%): 290 (M^+, 100). PMR ($CDCl_3$) δ: 0.89 (3H, t, J=6 Hz, terminal CH_3), 1.06—2.00 (6H, br, $-CH_2-\times 3$), 2.51 (2H, t, J=7 Hz, pyrone–$\underline{CH_2}$–CH_2–), 3.95 (3H, s, OCH_3), 6.39, 7.87 (1H, each, both s, pyrone–H, Ar–H), 10.39 (1H, s, CHO).

Hydrogen Peroxide Oxidation of 12 giving Hydroxy-olivetonide Monomethyl Ether (13)——To a solution of **12** (50 mg) in aq. 1N KOH (1 ml) was added dropwise 3% H_2O_2 (1 ml). The colorless needles separated out within a few min were collected by filtration and recrystallized from aq. MeOH to furnish **13** as colorless needles (20 mg) of mp 112—113°. *Anal.* Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.69; H, 6.53. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3566 (OH), 1683, 1650 (lactone CO, C=C), 1631 (aryl C=C). Mass Spectrum *m/e* (%): 278 (M^+, 100). PMR ($CDCl_3$) δ: 0.89 (3H, t-like, terminal CH_3), *ca.* 1.1—2.0 (6H, br, $-CH_2-\times 3$), 2.48 (2H, t, J=7 Hz, pyrone–$\underline{CH_2}$–CH_2–), 3.93 (3H, s, OCH_3), 6.44, 6.48 (1H each, both s, Ar–H, pyrone–H).

Monomethylation of 13 giving 10b——To a solution of **13** (15 mg) in ether (0.5 ml) was added ethereal diazomethane and the mixture was left standing at room temperature for 1.5 hr. Evaporation of the solvent gave a pale yellow residue which was crystallized from MeOH to afford **10b** as colorless needles (8 mg) of mp 76—77°. *Anal.* Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.68; H, 6.95. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680, 1644 (lactone CO, C=C), 1612 (aryl C=C). Mass Spectrum *m/e* (%): 292 (M^+, 100). PMR ($CDCl_3$) δ: 0.91 (3H, t-like, terminal CH_3), *ca.* 1.1—2.0 (6H, br, $-CH_2-\times 3$), 2.50 (2H, br,[17] pyrone–$\underline{CH_2}$–CH_2–), 3.78, 3.92 (3H each, both s, $OCH_3\times 2$), 6.43 (2H, s, Ar–H, pyrone–H).

Methylation of 11a giving 2-Methoxy-6-pentyl-1,4-benzoquinone (11b)——To a solution of **11a** (10 mg) in ether (1 ml) was added excess ethereal diazomethane and the mixture was allowed to stand for 1 hr. Evaporation of ether gave an orange yellow residue which was crystallized from ligroin to afford **11b** as orange needles (8 mg) of mp 63°. *Anal.* Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.23; H, 7.69. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680, 1654, 1635, 1606 (quinone CO, C=C). Mass Spectrum *m/e* (%): 208 (M^+, 100). PMR ($CDCl_3$) δ: 0.80 (3H, t, J=6 Hz, terminal CH_3), *ca.* 1.0—1.8 (6H, br, $-CH_2-\times 3$), 2.35 (2H, t, J=7 Hz, –C=C–$\underline{CH_2}$–CH_2–), 3.76 (3H, s, OCH_3), 6.20, 6.29 (1H each, d, J=2 Hz, ring H×2).

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[16] The absorption band of hydrogen bonded OH is obscure due to overlapping by the C–H absorption bands.

[17] The coupling pattern is obscure due to shortage of the material.