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STRUCTURE OF ALATOL, A HYDROLYSIS PRODUCT OF A SESQUITERPENE POLYESTER, ALATOLIN FROM *EUONYMUS ALATUS* FORMA *STRIATUS* (THUNB.) MAKINO, AND TRANSFORMATION OF EVONINOL TO ALATOL

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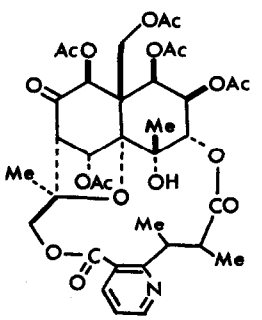
Abstract—Alatol 3, a new hexahydroxy C_{15}-compound was obtained by hydrolysis of alatolin 2, a new nonbasic polyester isolated from *Euonymus alatus* forma *striatus* (Thunb.) Makino. The structure of alatol 3 was determined mainly based on chemical and spectroscopic methods. An evoninol derivative 5, whose structure was previously elucidated was transformed into alatol 3 by ten steps: this conversion provided an unequivocal proof for the structure of alatol 3.

From the plants of the genus *Euonymus* belonging to the family *Celastraceae*, many sesquiterpene alkaloids have been isolated: they are sesquiterpene polyalcohols of dihydroagarofuran type esterified with a pyridine-containing carboxylic acid and with several aliphatic and, in some cases, aromatic carboxylic acids.[1,2] A representative example is evonine 1.[3-7] From these plants, a number of nonbasic sesquiterpene polyesters have also been isolated.[1,2,8-11]



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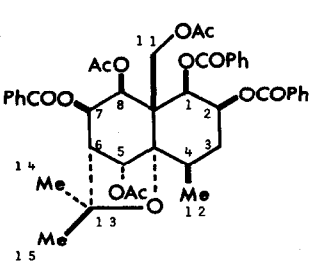
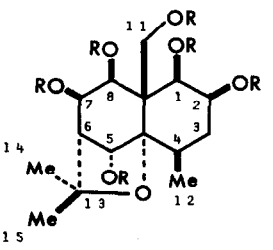
In our continuing studies on the constituents of the plants of *Celastraceae* family, we have isolated, from *Euonymus alatus* forma *striatus* (Thunb.) Makino, a new nonbasic polyester, alatolin 2, hydrolysis of which afforded the parent alcohol, alatol 3.[12] We have determined the structure of alatol 3, which was confirmed by transforming an evoninol derivative 5 to 3, and the results were reported as a preliminary communication.[12] We describe herein the full details of our structural studies on alatol 3 and of transformation of the evoninol derivative 5 to alatol 3.



2 (alatolin)



3 R = H (alatol)
4 R = Ac

In the same year that we elucidated the structure of alatol 3, Budzikiewicz and Römer isolated from *Euonymus europaeus* L. five nonbasic sesquiterpene polyesters, three of which being shown to be the polyesters of alatol 3 (named as "Alkohol A"[8]), and determined the structure of alatol 3.[8] Further, Budzikiewicz *et al.* successfully elucidated the full structure of alatolin (named as "Ester A-1"[8,9]) as depicted in 2 based on the NMR spectral analysis.[9] Isolation of alatolin 2 from *E. europaeus* L. was also reported by Dúbravková *et al.*[11]

Isolation and characterization

The MeOH extracts of the fresh fruits of *Euonymus alatus* forma *striatus* (Thunb.) Makino were concentrated to afford an aqueous mixture, which was extracted with Et_2O repeatedly. The ethereal extracts were evaporated and the residue was again dissolved in Et_2O. The ethereal solution was washed with dil HCl and subsequently with dil NaOH, and concentrated to afford the neutral mixture. Column chromatography of the mixture on silica gel afforded alatolin 2. Physical and spectral properties of 2 are described below.

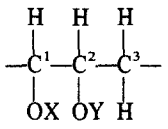
Alatolin 2. $C_{42}H_{44}O_{13}$; amorphous powder, $[\alpha]_D^{27} = 14.0°$ (c 2.3, $CHCl_3$); UV, λ_{max} (EtOH), 230 nm (ϵ 31,000); IR ($CHCl_3$) 1745 (broad), 1595 cm^{-1}; NMR (Table 1); MS 756 (molecular ion peak). The presence of three acetate and three benzoate ester groups in 2 was revealed by the NMR spectrum (footnote of Table 1) and the result of the methanolysis (*vide post*). Further, the following groups (I–III) were shown to be present in alatolin 2 by the analysis of the NMR spin–spin coupling patterns, with the aid of the double resonance (NMDR) experiments: there were observed characteristic signal patterns due to an ABX_2 system [δ 6.38 (1H, d, J = 3.2 Hz, H-1), 6.15 (1H, ddd, J = 2.5, 3.2, 3.8 Hz, H-2), 2.34 (2H, m, H-3)], an ABX system [δ 2.13 (1H, d, J = 3.6 Hz, H-6), 5.92 (1H, dd, J = 3.6, 4.0 Hz, H-7), 5.98 (1H, d, J = 4.0 Hz, H-8)], and an AB system [δ 4.90, 6.17 (2H, ABq, J = 13.0 Hz, H-11)] (*cf* Table 1). Although the

Table 1. NMR spectral data (δ in ppm, 100 MHz, benzene-d_6)

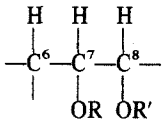
	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-11
2[a]	6.38 d 3.2	6.15 ddd 2.5, 3.2, 3.8	2.34 m	6.77 br.s	2.13 d 3.6	5.92 dd 3.6, 4.0	5.98 d 4.0	4.90, 6.17 AB q 13.0
4[b]	5.68 d 3.5	5.65 m	2.23 m	6.80 br.s	2.15 d 2.0	5.63 m	5.59 d 3.8	4.71, 5.43 AB q 13.5

a) Ac × 3: 1.45 (3H, s), 1.67 (3H, s), 2.03 (3H, s).
PhCO × 3: 6.9 - 8.5 (15H).
Me × 3: 1.19 (3H, d, 8.0, H-12), 1.42 (3H, s, H-14), 1.23 (3H, s, H-15).
b) Me × 3: 1.11 (3H, d, 7.0, H-12), 1.28 (3H, s, H-14), 1.19 (3H, s, H-15).

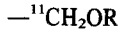
alternative structure (III') was conceivable for the AB-type signal (δ 4.90 and 6.17, ABq, J = 13.0 Hz) due to H-11, the structure (III) was assigned, because the signal arising from the CH_2OR group (C-11) in a variety of polyhydroxy sesquiterpenes of the dihydroagarofuran type was known[1,2,6] to be observed, in most cases, as an AB quartet similarly to the present case.



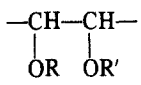
(X, Y = Acyl)
(I)



(R, R' = Acyl)
(II)



(R = Acyl)
(III)



(III')

Methanolysis (NaOMe-MeOH) of alatolin **2** afforded, together with methyl benzoate, a new sesquiterpene hexaol, alatol **3**. Physical and spectral data of **3** are shown below.

Alatol **3**. $C_{15}H_{26}O_7$; amorphous powder, $[\alpha]_D^{24}$ − 29.5° (c 0.92, MeOH); IR (KBr) 3360 cm^{-1} (strong), no C=O bands; NMR (CD_3OD) δ 1.32 (3H, s), 1.43 (3H, d, J = 6.3 Hz), 1.49 (3H, s), 4.02 (1H, m), 4.21 (1H, d, J = 3.2 Hz), 5.03 (1H, br. s); MS 318 (molecular ion peak).

Acetylation (Ac_2O–Py, 50°) of alatol **3** afforded a hexacetate **4**, $C_{27}H_{28}O_{13}$ [m.p. 205–207°, NMR (Table 1)], in which no OH group was present by the IR spectral analysis, indicating that alatol is a tricyclic compound possessing an ethereal ring. The NMR spectrum of the hexaacetate **4** exhibited the presence of three Me groups [δ 1.11 (3H, d, J = 7.0 Hz), 1.19 (3H, s), 1.28 (3H, s)] in addition to six acetate Me groupings. Assuming that alatol was a sesquiterpene of dihydroagarofuran type, the structure of alatol was deduced to be **3** based on these spectral data of alatol and its hexaacetate **4** in conjunction with the partial structures, I–III. It should be noted that although three possibilities, C-11, C-14 and C-15 exist concerning the location of the primary OH group (partial structure III), the primary OH group was deduced to be at C-11 in view of the fact that the signal pattern of the acetoxymethyl group (δ 4.71 and 5.43, ABq, J = 13.5 Hz, $-CH_2OAc$) in the hexaacetate **4** was quite similar to that of the C-11 methylene bearing the acetoxy group in many, known related compounds [e.g. δ 4.50 and 5.13 (ABq, J = 13.5 Hz) in euonymine;[13,14] δ 4.21 and 5.50 (ABq, J = 13.0 Hz) in wilfordine[15,16]].

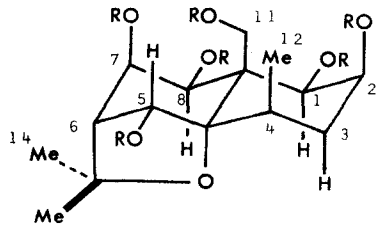
Stereochemistry at C-1, C-4, C-5, C-8, C-9 and C-10 of alatol **3** was inferred from the NOE experiments on alatolin **2** and the hexaacetate **4**, and the results are summarized in Table 2. Based on the coupling constants ($J_{1,2}$ = 3.2 Hz and $J_{7,8}$ = 4.0 Hz) in the NMR spectrum of alatolin **2** the *cis* relationship between H-1 and H-2, and between H-7 and H-8 was established. Thus, the stereostructure of alatol is represented by **3**.

Transformation of evoninol to alatol

Unequivocal proof for the structure of alatol **3** was secured by the transformation of an evoninol derivative **5**[6] to alatol **3**. The primary OH group of evoninol pen-

Table 2. NOE (100 MHz, benzene-d_6)

Compound	Irradiate	Observe	Percentage of enhancement
2	H-3	H-1	14
	H-14	H-8	28
4	H-12	H-11	17
	H-12	H-5	10



tamethyl ether **5** was protected as a trityl ethereal group. After many unsuccessful trials using various methods[17] for conversion of the 1,2-diol function of the trityl ether **6** to the corresponding olefin, the following conditions were found to be satisfactory in the present case: the trityl ether **6** was heated with ethyl orthoformate in the presence of benzoic acid[18] to afford the olefinic trityl ether **7**. The protecting trityl group in **7** was removed at this stage by the action of aqueous acid and the resulting primary OH group was oxidized with chromium trioxide in pyridine, producing the aldehyde **8**. Selective monothioacetalization of the aldehyde group in **8** was effected without difficulty to give the thioacetal **9**, which, on desulfurization with Raney Ni, was smoothly led to the keto olefin **10**. Reduction of the keto group in **10** with LAH followed by methylation of the newly formed OH group with methyl iodide–sodium hydride yielded a mixture of two diastereomeric, olefinic hexamethyl ethers, **11a** and **11b** in the ratio of 1:2, which could easily be separated by PLC on silica gel. Stereochemical assignment for these two diastereomers, **11a** and **11b** as depicted in the Scheme was based on the following evidence: reduction of the C-7 keto group in evonine **1** and many related compounds with LAH invariably produced a mixture of two diastereomeric alcohols at C-7 in the ratio of 2:1, the minor diastereomer being the one possessing a C-7β OH (axial OH).[6,19] This assignment was confirmed by successful transformation of the minor diastereomer, **11a** to alatol **3**, whose stereochemistry at C-7 was clearly proved by the NMR spectral analysis mentioned above. Having secured the desired stereoisomer **11a**, we have proceeded to the next reaction: hydrogenation of **11a** with Pd–C as catalyst afforded a mixture of two diastereomeric hexamethyl ethers, **12a** and **12b** in the ratio of 3:2, which was readily separated by PLC on silica gel. Though inspection of the molecular models suggested the preferential formation of the diastereomer **12a**, stereoselectivity of hydrogenation of **11a** was rather low. The stereostructure **12a** was assigned to the major diastereomer, and the validity of this assignment was established by converting this isomer **12a** to alatol **3**, in which stereochemistry at C-4 was determined by NOE experiments described above. The final step of the transformation of evoninol to alatol was deprotection of the methyl ether groups in **12a**: the hexamethyl ether **12a** was reacted with boron trichloride at room temperature, affording a hexaol, indistinguishable from alatol **3** by spectral and chromatographic comparison.

EXPERIMENTAL

Mp.s were uncorrected. UV spectra were measured on a Perkin-Elmer Model 202 spectrophotometer. IR spectra were recorded with a JASCO Model IRS instrument. NMR spectra were obtained using JNMC-60H, JNM 4H-100 and Varian HA-100D spectrometers. Chemical shifts (δ) are reported in ppm downfield from internal TMS. Mass spectra were determined on a Hitachi RMU-6C mass spectrometer equipped with a direct inlet system and operating with an ionization energy of 70 eV. High resolution mass spectra were recorded on a JEOLCO GMS-01SG mass spectrometer. Optical rotations were measured on JASCO DIP-SL and JASCO DIP-4 spectropolarimeters. For TLC, silica gel GF_{254} and PF_{254} (E. Merck, A. G., Germany) were used. For column chromatography, silica gel (100 mesh, Mallinckrodt, U.S.A.) was used. The organic solns were washed with sat NaCl soln, dried over Na_2SO_4, and evaporated by vacuum rotary evaporator.

Isolation of alatolin **2**. The seeds (28 kg) of *Euonymus alatus* forma *striatus* (Thunb.) Makino were collected at Mt. Ibuki (Shiga Prefecture, Japan) in early November and ground in MeOH (15 l.). The mixture was filtered with suction and the filtrate was concentrated to give an aqueous mixture (*ca* 3 l.), which was extracted with five 3-l. portions of Et_2O. The ethereal extracts were concentrated, and the residue was again dissolved in Et_2O (5 l.). The ethereal soln was washed with 2.5% HCl five times (5 × 1 l.) and subsequently with 5% NaOH (1 l.), and concentrated to give a neutral oily residue (83 g), which was chromatographed on silica gel (1330 g) with benzene–EtOAc to afford **2** (1.1 g, 0.0039%) as amorphous powder. Physical and spectral data of **2** are described in the text. [High resolution mass spectrum. Found: 756.2764 (M^+). $C_{42}H_{44}O_{13}$ requires: 756.2781.]

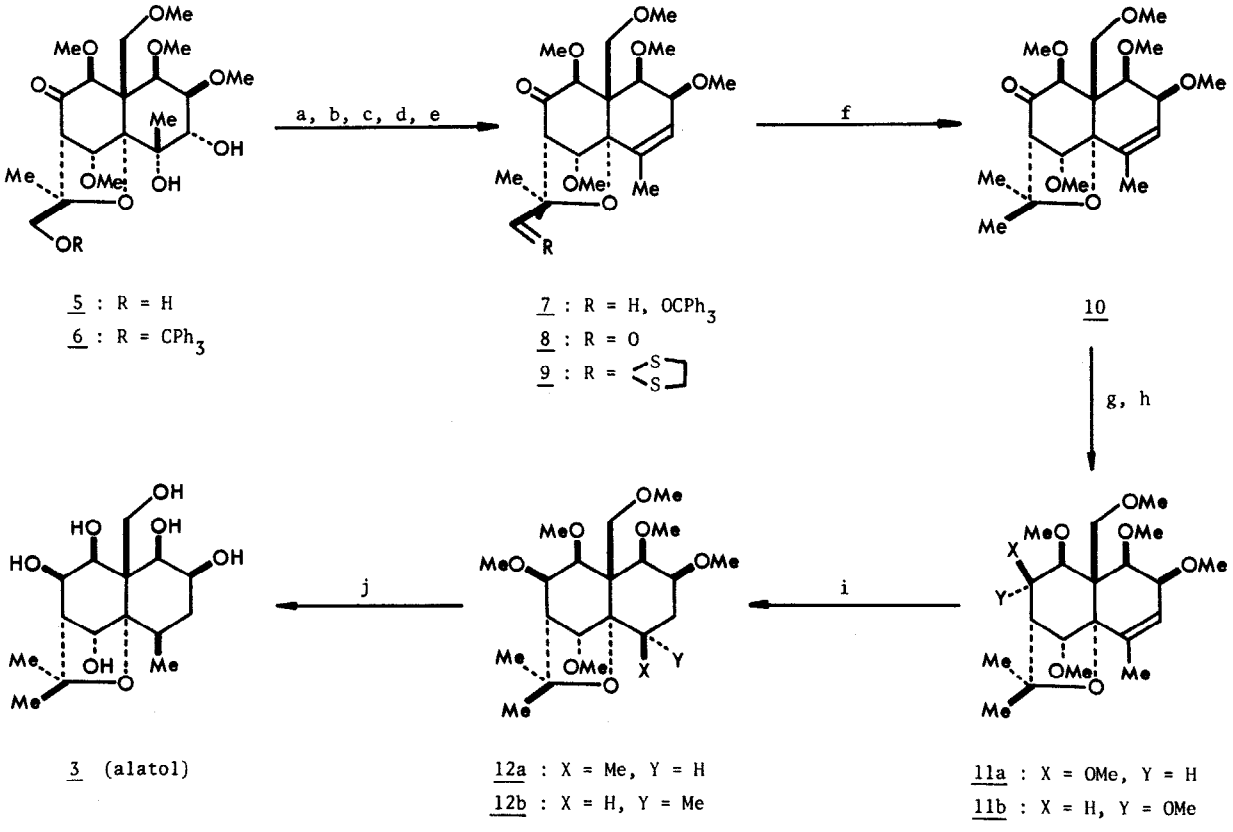
Alatol **3**. Alatolin **2** (31 mg) was dissolved in a soln (0.5 ml) of NaOMe–MeOH (prepared from 163 mg of Na and 20 ml of anhyd MeOH) under N_2. The soln was stirred at room temp for 6 h, and passed through a column of ion-exchange resin Amberlite IRC-50 (H form). The column was eluted with MeOH. The methanolic eluate was concentrated to give an oily residue, which was purified by preparative TLC (silica gel) with MeOH–$CHCl_3$ (12:88) to give methyl benzoate (2.2 mg) as a colorless liquid and **3** (11 mg, 85%) as amorphous powder. Physical and spectral data of **3** are described in the text. [High resolution mass spectrum. Found: 318.1689 (M^+). $C_{15}H_{26}O_7$ requires: 318.1678.]

Alatol hexaacetate **4**. A soln of **3** (12 mg) in Ac_2O (0.5 ml) and pyridine (0.5 ml) was stirred at 60° for 10 h, and concentrated. The residue was separated by preparative TLC (silica gel) with EtOAc to give crystalline **4**, which was recrystallized from ligroin–Et_2O, affording pure **4** (15 mg), m.p. 205–207°; IR ($CHCl_3$) 1740 cm^{-1}, no OH bands; NMR (Table 1); MS 570 (M^+). (Found: C, 56.94; H, 6.65. $C_{27}H_{38}O_{13}$ requires: C, 56.84; H, 6.72%.)

Trityl ether **6**. A soln of **5**[6] (38 mg) and trityl chloride (120 mg) in pyridine (2 ml) was kept under reflux for 13 h, concentrated, and diluted with H_2O (4 ml). The mixture was extracted with three 10 ml portions $CHCl_3$. The combined organic extracts were dried and concentrated. The solid residue was purified by preparative TLC (silica gel) with benzene–EtOAc (6:5) to give crystalline **6**, recrystallization of which from *n*-hexane–Et_2O yielded pure **6** (40 mg, 68%), m.p. 213–214°; IR ($CHCl_3$) 3500, 1730 cm^{-1}; NMR (100 MHz, $CDCl_3$) 1.52 (3H, s), 1.53 (3H, s), 2.93 (3H, s), 3.18 (3H, s), 3.47 (6H, s), 3.59 (3H, s), 5.23 (1H, br.s), 7.1–7.3 (15H, m); MS 433 ($M^+ - CPh_3$). (Found: C, 69.21; H, 7.10. $C_{39}H_{48}O_{10}$ requires: C, 69.21; H, 7.15%.)

Olefinic trityl ether **7**. A soln of **6** (97 mg) and benzoic acid (10.5 mg) in ethyl orthoformate (0.6 ml) was stirred at 100° for 2 h and subsequently at 100° for 10 h. After cooling, the soln was concentrated and the residue was separated by preparative TLC (silica gel) with benzene–EtOAc (6:5) to afford a solid. Recrystallization from n-hexane–Et_2O provided **7** (56 mg, 61%), m.p. 190–193°; IR ($CHCl_3$) 1725 cm^{-1}; NMR (60 MHz, $CDCl_3$) 1.42 (3H, s), 1.73 (3H, br.s), 3.03 (3H, s), 3.21 (3H, s), 3.45 (3H, s), 3.50 (3H, s), 3.60 (3H, s), 5.12 (1H, br.s), 5.80 (1H, m), 7.1–7.4 (15H, m); MS 642 (M^+). (Found: C, 72.66; H, 7.20. $C_{39}H_{46}O_8$ requires: C, 72.87; H, 7.21%.)

Aldehyde **8**. A soln of **7** (142 mg) in AcOH (1.6 ml)–H_2O (0.4 ml) was stirred at 80° for 3 h, and concentrated. The oily residue was separated by preparative TLC (silica gel) with EtOAc to give a resinous solid (55 mg). To a soln of the resinous solid (55 mg) in pyridine (1 ml) was added a suspension of CrO_3 (152 mg) in pyridine (1.5 ml) with stirring under ice-bath cooling. The mixture was stirred at room temp for 12 h, diluted with a mixture of H_2O (4 ml)–$CHCl_3$ (10 ml), and filtered through Super Cel and the ppts were washed thoroughly with $CHCl_3$. The aqueous phase of the filtrate was further extracted with three 10 ml portions $CHCl_3$. The combined $CHCl_3$ extracts were dried and concentrated to give a residue, separation of which by preparative TLC (silica gel) with EtOAc afforded crystalline **8** (42 mg, 48%). Recrystallization from Et_2O–petroleum ether gave pure **8**, m.p. 110–112°; IR ($CHCl_3$) 1735 cm^{-1}; NMR (100 MHz,



a) Ph_3CCl; b) $HC(OEt)_3$ - PhCOOH, Δ; c) AcOH - H_2O, Δ; d) $CrO_3 \cdot Py_2$;
e) $(HSCH_2)_2$ - $BF_3 \cdot OEt_2$; f) Raney Ni; g) $LiAlH_4$; h) MeI - NaH;
i) H_2 / Pd - C; j) BCl_3

Scheme 1.

$CDCl_3$) 1.41 (3H, s), 2.03 (3H, br.s), 3.11 (3H, s), 3.20 (3H, s), 3.48 (3H, s), 3.54 (3H, s), 3.59 (3H, s), 5.00 (1H, br.s), 9.53 (1H, s); MS 398 (M^+). (Found: C, 60.11; H, 7.59. $C_{20}H_{30}O_8$ requires: C, 60.29; H, 7.59%.)

Thioacetal **9**. Ethanedithiol (0.07 ml) and $BF_3 \cdot OEt_2$ (0.05 ml) were added to soln of **8** (48 mg) in CH_2Cl_2 (2 ml) under ice-bath cooling. The mixture was stirred at 0° for 4 h. After addition of sat Na_2CO_3 aq, the mixture was extracted with three 20-ml portions $CHCl_3$. The combined $CHCl_3$ extracts were dried and concentrated giving an oily residue. Separation of the residue by preparative TLC (silica gel) with benzene–EtOAc (6:5) provided **9** (57 mg, 100%) as amorphous solid: IR ($CHCl_3$) 1730 cm^{-1}; NMR (100 MHz, $CDCl_3$) 1.50 (3H, s), 2.07 (3H, s), 3.22 (3H, s), 3.25 (4H, br.s, $-S(CH_2)_2S-$), 3.35 (3H, s), 3.48 (3H, s), 3.52 (3H, s), 3.59 (3H, s), 5.27 (1H, br.s), 5.93 (1H, s); MS 474 (M^+). [High resolution mass spectrum. Found: 474.1767 (M^+). $C_{22}H_{34}O_7S_2$ requires: 474.1745.]

Keto olefin **10**. A mixture of **9** (56 mg) and W-2 Raney Ni (500 mg) in EtOH (4 ml) was stirred at 70° for 2 h, cooled, and filtered. Evaporation of the filtrate gave an oily mixture, which was separated by preparative TLC (silica gel) with benzene–EtOAc (6:5) to afford **10** (32 mg, 70%) as amorphous solid: IR ($CHCl_3$) 1725 cm^{-1}; NMR (100 MHz, $CDCl_3$) 1.40 (3H, s), 1.50 (3H, s), 1.88 (3H, s), 3.22 (3H, s), 3.41 (3H, s), 3.51 (2×3H, s), 3.60 (3H, s), 5.39 (1H, br.s); MS 384 (M^+). [High resolution mass spectrum. Found: 384.2128 (M^+). $C_{20}H_{32}O_7$ requires: 384.2147.]

Olefinic hexamethyl ethers, **11a** *and* **11b**. A soln of **10** (15 mg) in anhyd dimethoxyethane (DME) (0.5 ml) was added with stirring to a soln of LAHs (10 mg) in anhyd DME under ice-bath cooling. The mixture was stirred at room temp for 14 h, diluted with H_2O (2 ml), and extracted with three 10-ml portions $CHCl_3$. The combined $CHCl_3$ extracts were dried and concentrated to give an oily material, which was used without purification for the next step. A mixture of the oily material, MeI (0.4 ml), and NaH (15 mg, 50% dispersion in mineral oil) in anhyd DME was stirred at 50° for 12 h. After addition of H_2O (2 ml), the mixture was extracted with three 15-ml portions $CHCl_3$. The $CHCl_3$ extracts were dried, and concentrated to give an oily residue, which showed two spots on a TLC plate. The residue was separated by preparative TLC (silica gel) with benzene–EtOAc to afford **11a** (4 mg, 26%, resinous solid) and **11b** (8 mg, 51%, resinous solid). **11a**: NMR (100 MHz, $CDCl_3$) 1.42 (3H, s), 1.63 (3H, s), 2.00 (3H, s), 3.23 (3H, s), 3.42 (3H, s), 3.50 (3H, s), 3.54 (3H, s), 3.62 (3H, s), 3.63 (3H, s); MS 400 (M^+). [High resolution mass spectrum. Found: 400.2442 (M^+). $C_{21}H_{36}O_7$ requires: 400.2460.]

Hexamethyl ethers, **12a** *and* **12b**. A mixture of **11a** (11 mg) and 10% Pd–C (10 mg) in EtOH (0.7 ml) was stirred in the atmosphere of H_2 at room temp for 14 h. The catalyst was removed by filtration and the filtrate was concentrated. The residue was separated by preparative TLC (silica gel) with benzene–EtOAc (1:3), giving **12a** (5 mg, 45%, resinous solid) and **12b** (3 mg, 27%, resinous solid).

12a: NMR (100 MHz, $CDCl_3$) 1.23 (3H, d, J = 7.6 Hz), 1.30 (3H, s), 1.37 (3H, s), 3.25 (3H, s), 3.28 (3H, s), 3.36 (3H, s), 3.38 (3H, s), 3.43 (3H, s), 3.44 (3H, s), 3.59 (1H, d, J = 4.0 Hz), 3.75 (1H, d, J = 10.6 Hz), 3.76 (1H, m), 5.03 (1H, br.s), 5.27 (1H, d, J = 10.6 Hz); MS 402 (M^+). [High resolution mass spectrum. Found: 402.2598. $C_{21}H_{38}O_7$ requires: 402.2617.]

Demethylation of hexamethyl ether **12a**: *formation of alatol* **3**. Gaseous BCl_3 was passed into a soln of **12a** (6 mg) in CH_2Cl_2 (0.4 ml) in a sealed tube cooled in a Dry Ice–acetone bath, until the soln was saturated with BCl_3. After the sealed tube was closed, the cooling bath was removed. The mixture was gradually warmed to room temp and kept at room temp for 12 h. After cooled again, the sealed tube was opened, and the mixture was diluted with 2% MeOH–H_2O (0.5 ml) and concentrated. The residue was purified by preparative TLC (silica gel) with $CHCl_3$–MeOH (85:15) to yield **3** (4 mg, 84%) as a resinous solid, identification of which with natural **3** was made by spectral (IR, NMR, MS) and chromatographic (silica gel TLC) comparison.

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REFERENCES

[1]R. M. Smith, *The Alkaloids* (Edited by R. H. F. Manske), Vol. 16, Chap. 4. Academic Press, New York (1977).
[2]R. Brüning and H. Wagner, *Phytochemistry* **17**, 1821 (1978).
[3]H. Wada, Y. Shizuri, K. Yamada and Y. Hirata, *Tetrahedron Letters* 2655 (1971).
[4]Y. Shizuri, H. Wada, K. Sugiura, K. Yamada and Y. Hirata, *Ibid.* 2659 (1971).
[5]H. Wada, Y. Shizuri, K. Sugiura, K. Yamada and Y. Hirata, *Ibid.* 3131 (1971).
[6]Y. Shizuri, H. Wada, K. Sugiura, K. Yamada and Y. Hirata, *Tetrahedron* **29**, 1773 (1973).
[7]M. Pailer, W. Streicher and J. Leitich, *Monatsh. Chem.* **102**, 1873 (1971).
[8]H. Budzikiewicz and A. Römer, *Tetrahedron* **31**, 1761 (1975).
[9]A. Römer, H. Thomas and H. Budzikiewicz, *Z. Naturforsch.* **31b**, 607 (1976).
[10]A. Römer, H. Thomas, B. Kreuels and H. Budzikiewicz, *Ibid.* **36b**, 379 (1981).
[11]L. Dúbravková, L. Dolejš and Z. Votický, *Phytochemistry* **18**, 1740 (1979).
[12]K. Sugiura, Y. Shizuri, K. Yamada and Y. Hirata, *Tetrahedron Letters* 2307 (1975).
[13]K. Sugiura, Y. Shizuri, H. Wada, K. Yamada and Y. Hirata, *Ibid.* 2733 (1971).
[14]K. Yamada, K. Sugiura, Y. Shizuri, H. Wada and Y. Hirata, *Tetrahedron* **33**, 1725 (1977).
[15]Y. Shizuri, K. Yamada and Y. Hirata, *Tetrahedron Letters* 741 (1973).
[16]K. Yamada, Y. Shizuri and Y. Hirata, *Tetrahedron* **34**, 1915 (1978).
[17a]I. T. Harrison and S. Harrison, *Compendium of Organic Synthetic Methods*, pp. 484–488. Wiley-Interscience, New York (1971); [b]I. T. Harrison and S. Harrison, *Compendium of Organic Synthetic Methods*, Vol. 2, pp. 195–197. Wiley-Interscience, New York (1974).
[18]J. S. Josan and F. W. Eastwood, *Aust. J. Chem.* **21**, 2013 (1968).
[19]K. Sugiura, K. Yamada and Y. Hirata, *Tetrahedron Letters* 113 (1973).