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Triterpenoids from the orchids *Agrostophyllum brevipes* and *Agrostophyllum callosum*

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Abstract

Agrostophyllinol and agrostophyllinone, two new triterpenoids, were isolated from the orchid *Agrostophyllum brevipes*. Agrostophyllinone was also isolated from another orchid *Agrostophyllum callosum*. The structures of agrostophyllinol and agrostophyllinone were established as 24-methylene-lanosta-9(11)-en-3β-ol (**5a**) and 24-methylene-lanosta-9(11)-en-3-one (**5c**), respectively, from spectral and chemical evidence. The above triterpenoids are of considerable biogenetic importance.

Keywords: *Agrostophyllum brevipes*; *Agrostophyllum callosum*; Orchidaceae; Agrostophyllinol; Agrostophyllinone; Triterpenoids

1. Introduction

We reported earlier the isolation of a fairly large number of compounds from a series of Indian orchids. These compounds encompass a wide variety of stilbenoids (Majumder et al., 1998, 1999a, b, c, 2001), viz. stilbene, bibenzyls, phenanthrenes and 9,10-dihydrophenanthrenes and their dimers, phenanthropyrans and pyrones and their 9,10-dihydro derivatives, fluorenone and a few other polyphenolics (Majumder et al., 1994, 1995b), several triterpenoids (Majumder and Ghosal, 1991), steroids of biogenetic importance (Majumder and Pal, 1990) and some simple aromatic compounds (Majumder and Lahiri, 1989). As part of this general programme of research, we have chemically investigated yet another orchid *Agrostophyllum brevipes* which has afforded two new triterpenoids, designated agrostophyllinol and agrostophyllinone, besides the known stilbenoids imbricatin (**1a**) (Majumder and Sarkar, 1982), flaccidin (**1b**) (Majumder and Maiti, 1988), callosinin (**1c**) (Majumder et al., 1995a), agrostophyllin (**2a**) (Majumder and Sabzabadi, 1988), flaccidinin (**2b**) (Majumder and Maiti, 1989), 6-methoxycoelonin (**3a**) (Juneja et al., 1987), flavanthrinin (**4a**) (Majumder and Banerjee, 1990) and nudol (**4b**) (Stermiz et al., 1983; Bhandari et al. 1985). Agrostophyllinone has also been isolated from the neutral fraction of the methanolic extract of another taxonomically related orchid *Agrostophyllum callosum*, in addition to the known stilbenoids **1c**, callosumin (**3b**) and callosuminin (**4c**) (Majumder et al., 1996). While the known compounds isolated from *A. brevipes* and *A. callosum* were characterized by direct comparison with their respective authentic samples, the structures of agrostophyllinol and agrostophyllinone were established as 24-methylene-lanosta-9(11)-en-3β-ol (**5a**) and 24-methylene-lanosta-9(11)-en-3-one (**5c**), respectively, from the following spectral and chemical evidence.

2. Results and discussion

Agrostophyllinol (**5a**), mp 175 °C, $[\alpha]_D + 46°$ ($CHCl_3$) and agrostophyllinone (**5c**), mp 125 °C, $[\alpha]_D + 79°$ ($CHCl_3$), analyzed for $C_{31}H_{52}O$ and $C_{31}H_{50}O$, respectively, which were confirmed by their respective mass spectrometrically derived molecular weights 440 and 438.

The IR spectra of both **5a** and **5c** showed bands [**5a**: ν_{max} (cm^{-1}) 1637, 1373, 889 and 850; **5c**: ν_{max} (cm^{-1}) 1650, 1400, 870 and 830] characteristic of a terminal methylene group and a trisubstituted olefinic double bond. While the spectrum of the former showed a band at ν_{max} 3383 cm^{-1} for a hydroxyl function, that of the

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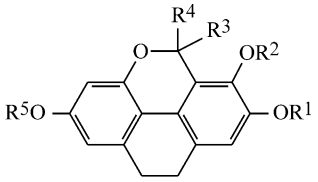
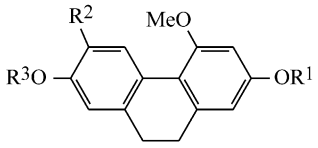
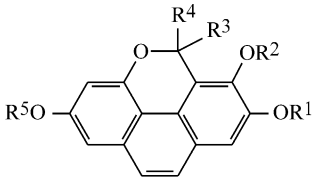


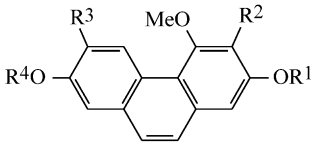
1a : $R^1=R^3=R^4=R^5=H$, $R^2=Me$
1b : $R^1=Me$, $R^2=R^3=R^4=R^5=H$
1c : $R^1=R^2=R^5=Me$, $R^3=R^4=H$



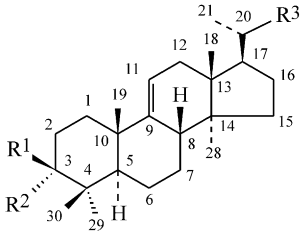
3a : $R^1=R^3=H$, $R^2=OMe$
3b : $R^1=R^3=Me$, $R^2=OMe$

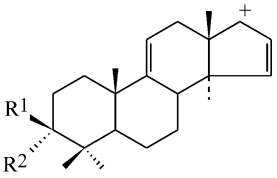


2a : $R^1=R^3=R^4=H$, $R^2=R^5=Me$
2b : $R^1=Me$, $R^2=R^5=H$, $R^3R^4=O$



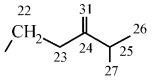
4a : $R^1=R^2=R^3=R^4=H$
4b : $R^1=R^3=R^4=H$, $R^2=OMe$
4c : $R^1=R^4=Me$, $R^2=H$, $R^3=OMe$

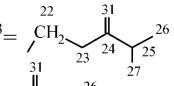


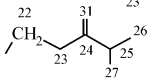


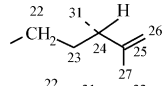
a : $R^1=OH$, $R^2=H$ (m/z 313)

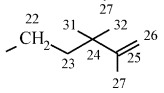
b : $R^1R^2=O$ (m/z 311)

5a : $R^1=OH$, $R^2=H$, $R^3=$ 

5b : $R^1=OAc$, $R^2=H$, $R^3=$ 

5c : $R^1R^2=O$, $R^3=$ 

5d : $R^1R^2=O$, $R^3=$ 

5e : $R^1R^2=O$, $R^3=$ 

latter is devoid of any such absorption, and, instead, exhibited an intense band at ν_{max} 1715 cm^{-1} for a six-membered cyclic keto carbonyl function. This would suggest that while **5c** contains a cyclohexanone moiety, **5a** is the corresponding secondary alcohol. The above contention was confirmed by the fact that **5c** on reduction with $NaBH_4$ in MeOH afforded **5a**. The presence of a hydroxyl function in **5a** was also confirmed by the formation of an acetyl derivative **5b**, $C_{33}H_{54}O_2$ ([M^+] at m/z 482), mp 140 °C, on treatment of **5a** with Ac_2O and pyridine.

The ^1H NMR spectrum of each of **5a**, **5b** and **5c** showed signals for eight methyl groups attached to sp^3 carbon atoms [**5a**: δ 0.64, 0.74, 0.81, 0.98, 1.03 (each 3H, *s*), 0.90 (3H, *d*, $J=6.39$ Hz) and 1.02 (6H, *dd*, $J_1=7.55$ Hz and $J_2=1.38$ Hz); **5b**: δ 0.64, 0.73, 0.85, 0.88, 1.06 (each 3H, *s*), 0.87 (6H, *d*, $J=7.72$ Hz), 1.02 (3H, *d*, with fine splitting, $J=6.95$ Hz); **5c**: δ 0.67, 0.74, 1.22 (each 3H, *s*), 1.06 (6H, *s*), 0.91 (3H, *d*, $J=6.32$ Hz) and 1.02 (6H, *ddd*, $J_1=6.80$ Hz, $J_2=1.31$ Hz and $J_3=0.95$ Hz)], a terminal methylene group [**5a**: δ 4.71 and 4.66 (each 1H, br. signal); **5b**: δ 4.71 and 4.65 (each 1H, br. signal); **5c**: δ 4.71 and 4.66 (each 1H, br. signal)] and a trisubstituted olefinic proton [**5a**: δ 5.22 (1H, *m*); **5b**: δ 5.23 (1H, *m*); **5c**: δ 5.28 (1H, *m*)]. The above ^1H NMR spectral data thus indicate the triterpenoid skeletal structure of **5a**, **5b**

and **5c**, each possessing a terminal methylene group and a trisubstituted olefinic double bond. The presence of a hydroxyl function attached to a cyclohexane ring in **5a** was indicated by the appearance of a signal at δ 3.21 (1H, *dd*, $J_1 = 11.19$ Hz and $J_2 = 4.4$ Hz) for a hydroxymethine proton in the ^{1}H NMR spectrum of the compound. The corresponding signal for the acetoxymethine proton of **5b** appeared at δ 4.47 (1H, *dd*, $J_1 = 10.93$ Hz and $J_2 = 4.34$ Hz). The chemical shifts and the splitting patterns of the above protons of **5a** and **5b** indicate their axial nature coupling with an axial and an equatorial proton attached to one of the neighbouring carbon atoms, the other adjacent carbon atom being fully substituted. The hydroxyl group in **5a** and the acetoxyl function in **5b** must, therefore, be equatorially oriented. The ^{1}H NMR spectrum of **5c**, as expected, is devoid of the above signal, and, instead, showed a two-proton multiplet at δ 2.65–2.78 for a ketomethylene group.

The mass spectra of **5a** and **5c** showed intense peaks at *m*/*z* 313 and 311, respectively. These peaks were attributed to the ion-fragments **a** and **b** and were assumed to be formed by the loss of the C-17 side chain and two hydrogen atoms from the respective molecular ions of **5a** and **5c**. The appearance of these peaks in the mass spectra of **5a** and **5c** not only indicates the tetracyclic lanostane type of skeletal structure of the compounds, but also suggests the placement of the terminal methylene group and the trisubstituted double bond in the C-17 side chain and the carbocyclic part, respectively, of both the compounds. These peaks also indicate the placement of the hydroxyl group in **5a** and the keto group in **5c** in the alicyclic part of their respective molecules.

The structures of **5a** and **5c** were finally confirmed by the ^{13}C NMR spectral data of the compounds and those of **5b** (Table 1). The degree of protonation of each carbon atom of the compounds were determined by DEPT and APT experiments. The presence of a terminal methylene group and a trisubstituted double bond in all the three compounds were indicated by the appearance of four sp^2 carbon signals in each compound (**5a**: δ_C 105.9, 156.7, 148.5 and 114.9; **5b**: δ_C 106.0, 156.6, 148.1 and 115.2; **5c**: δ_C 106.0, 156.7, 147.1 and 116.3). Again, the presence of a hydroxymethine carbon in **5a**, an acetoxymethine carbon in **5b** and a cyclic keto carbonyl function in **5c** were indicated by the characteristic carbon resonances at δ_C 78.9, 80.8 and 217.1, respectively, in the spectra of the compounds. The assignments of the carbon chemical shifts of **5a**, **5b** and **5c** in terms of a lanostane skeletal structure having a terminal methylene group at C-24 and a 9,11-double bond in all the three compounds and their respective oxygen functions at C-3 were made by comparison of their δ_C values with those of the structurally similar compounds. Thus, the placement of the terminal methylene group at C-24 in the C-17 side chain of **5a**, **5b** and **5c** was affirmed by the virtually identical δ_C values of C-20, C-21, C-22, C-23, C-24, C-25, C-26, C-27 and C-31 of the above compounds and those of the corresponding carbon atoms of cycloeucaneol and its acetyl derivative (Wehrli and Nishida, 1979), 24-methylene cycloartanyl-*p*-hydroxy-*trans*-cinnamate (Majumder and Pal, 1985) and pholidotin (24-methylene-cycloartanyl-*p*-hydroxy-*cis*-cinnamate) (Majumder et al., 1987) all having a terminal methylene group at C-24 in their C-17 side chain. Again, the essentially identical δ_C values of C-1— C-21, C-28, C-29 and C-30 of **5c** and those of the corresponding carbon atoms of **5d** (Boonyaratavej et al., 1990) and **5e** (Hui et al., 1971) confirmed the identical structure of the carbocyclic part of all the three compounds having a keto group at C-3 and a 9,11-double bond. The original assignments of the δ_C values of C-6 and C-7 of **5d** and

Table 1
^{13}C NMR spectral data of **5a**, **5b**, **5c**, **5d** and **5e**[a]

C	Chemical shifts (δ ppm)[b]				
	5a	**5b**	**5c**	**5d**	**5e**
1	36.1	35.8	36.7	36.7	36.7
2	27.8a	24.1	35.0	34.9	34.9
3	78.9	80.8	217.1	217.2	217.2
4	39.3b	38.0	47.0	46.9	46.9
5	52.5	52.6	53.5	53.4	53.4
6	21.3	21.0	22.6	22.5[c]	22.5[d]
7	28.1a	27.9	27.7	27.7[c]	27.7[d]
8	41.8	41.6	41.9	41.8	41.8
9	148.5	148.1	147.1	147.0	147.0
10	39.0b	39.2	39.0	39.0	39.0
11	114.9	115.2	116.3	116.7	116.7
12	37.2	37.2	37.2	37.1	37.1
13	44.3	44.3	44.3	44.2	44.2
14	47.0	47.0	47.6	47.7	47.7
15	33.9	33.9	33.9	33.9	33.9
16	27.9a	27.9	27.9	27.9	27.9
17	50.9	50.9	50.9	50.8	50.7
18	14.3	14.4	14.4	14.4	14.4
19	22.2	22.2	22.0	21.8	21.8
20	36.1	36.0	36.1	36.0	36.6
21	18.4c	18.4a	18.4a	18.6	18.5
22	35.1	35.1	34.8	33.9	30.7
23	31.2	31.3	31.3	31.4	37.3
24	156.7	156.6	156.7	41.6	38.7
25	33.8	33.8	33.8	150.1	152.3
26	21.9d	21.9b	21.7b	109.4	109.3
27	21.8d	21.8b	21.8b	20.2	19.4
28	18.3c	18.3a	18.3a	18.4	18.4
29	28.2	28.1	25.7	25.6	25.6
30	15.5	16.7	22.0	22.0	22.0
31	105.9	106.0	106.0	18.0	27.2
32	–	–	–	–	27.5
OAc	–	170.4 21.2b		–	–

[a–d] Values are interchangeable in each column.

[b] Spectra were run in $CDCl_3$ and the chemical shifts were measured with $\delta_{(TMS)} = \delta_{(CDCl3)} + 76.9$ ppm.

[c] Original assignments are interchanged.

[d] Original assignments are interchanged.

5e made by the respective authors (Boonyaratavej et al., 1990; Hui et al., 1971) were interchanged (Table 1) in the light of a comprehensive ^{13}C NMR spectral analysis of the lanostane type of triterpenoids (Wehrli and Nishida, 1979). The placement of the trisubstituted double bond between C-7 and C-8 in **5c** and hence in **5a** was ruled out by the fact that this would have led to a considerable downfield shift of the olefinic methine carbon [ca. δ_C 121.0 (C-7)] as observed in 20(*R*), 24(*E*)-3-oxo-9β-lanosta-7,24-dien-26-oic acid (Das et al., 1990) [δ_C 148.6 (C-8) and 121.4 (C-7)]. The δ_C values of **5a** are again essentially similar to those of **5c** except the resonances of their C-2, C-3 and C-4. Thus, the signals at δ_C 35.0 (C-2), 217.1 (C-3) and 47.0 (C-4) of **5c** were replaced by those at δ_C 27.8, 78.9 and 39.3, respectively, in the spectrum of **5a**. The observed upfield shifts of the above carbon atoms of **5a** compared with those of the corresponding carbon atoms of **5c** are intelligible only in terms of the presence of a hydroxyl group at C-3 in the former in place of a keto group at the same position in the latter—an assumption which has already been confirmed by the conversion of **5c** to **5a** upon reduction with $NaBH_4$. That **5a** is the corresponding 3-hydroxy derivative of **5c** was also corroborated by the characteristic upfield shifts of C-2 and C-4 of **5b** by ca. 3.7 and 1.3 ppm compared with the corresponding carbon atoms of **5a**. The C-3 of **5b**, as expected, showed a downfield shift of 1.9 ppm compared with that of **5a**. The equatorial orientation of the hydroxyl group in **5a** and acetoxy group in **5b** was established by the chemical shifts and the splitting patterns of H-3 of the compounds.

Agrostophyllinol (**5a**) and agrostophyllinone (**5c**) are thus two new additions to the growing list of naturally occurring tetracyclic triterpenoids of the lanostane skeleton having an additional carbon atom at C-24. Biogenetically, they represent preformed precursors for further modification of the C-17 side chain of the above group of triterpenoids.

3. Experimental

Melting points: uncorr. CC: silica gel (100–200 mesh). TLC: silica gel G. IR: KBr discs. ^1H and ^{13}C NMR: 300 and 75 MHz, respectively. NMR spectra were recorded in $CDCl_3$ and chemical shifts were expressed in δ (ppm). MS: direct inlet system, 70 eV. All analytical samples were routinely dried over P_2O_5 for 24 h in vacuo and were tested for purity by TLC and MS. The petrol used had bp 60–80 °C.

3.1. Plant materials

A. brevipes K. and P. and *A. callosum* Reichb.fil were collected from Kalimpong (Darjeeling, India) in October 2000 and September 1999, respectively. Separate Voucher specimens (Majumder s.n.) were deposited in the Herbarium of the Department of Botany, University of Calcutta (CUH).

3.2. Isolation of agrostophyllinol (*5a*) and agrostophyllinone (*5c*)

Air-dried finely powdered whole plants of *A. brevipes* and *A. callosum* (each 5 kg) were separately kept soaked in MeOH (10 l) for 3 weeks. The MeOH extract in each case was concentrated to ca. 100 ml, diluted with H_2O (750 ml) and exhaustively extracted with Et_2O. The Et_2O extracts were separately fractionated into acidic and nonacidic fractions with 2M NaOH. The aqueous alkaline solution in each case was acidified in the cold with conc. HCl and the liberated solids were extracted with Et_2O. The Et_2O extracts of the acidic and neutral compounds (left after NaOH treatment) in each case were separately washed with H_2O, dried and the solvent removed. The residues obtained from the acidic and neutral fractions of *A. brevipes* and that obtained from the neutral fraction of *A. callosum* were separately subjected to CC. The acidic fraction from *A. callosum* had earlier been investigated.

3.2.1. (a) Chromatography of the acidic fraction obtained from A. brevipes

The petrol–EtOAc (20:1) eluate afforded a gummy solid which on rechromatography gave pure **2a** (0.08 g), crystallized from petrol–EtOAc, mp 86 °C. Washing the column with petrol–EtOAc (10:1) gave a solid consisting of a mixture of **3a**, **4a** and **4b**. Rechromatography of this solid using the same eluent afforded in the early fractions pure **4a** (0.06 g) as a glassy solid. The later fractions of the same eluate gave a mixture of **3a** and **4b**. Repeated chromatography of this mixture using the same eluent afforded pure **3a** (0.05 g), as a semisolid mass, in the early fractions, and pure **4b** (0.08 g), in the later fractions, crystallized from petrol–EtOAc, mp 185 °C.

Elution of the main column with petrol–EtOAc (6:1) gave a gummy solid containing a mixture of **1a**, **1b** and **2b**. Rechromatography of this solid using the same eluent gave in the early fractions pure **1a** (0.3 g), crystallized from petrol–EtOAc, mp 145 °C. The later fractions of the same eluate afforded a mixture of **1b** and **2b**, which on repeated chromatography gave pure **1b** (0.07 g), crystallized from petrol–EtOAc, mp 200 °C, and **2b** (0.09 g), also crystallized from the same solvent mixture as golden yellow needles, mp 360 °C (dec.).

3.2.2. (b) Chromatography of the neutral fraction obtained from A. brevipes

The petrol–EtOAc (80:1) eluate afforded agrostophyllinone (**5c**) (0.25 g), crystallized from petrol–

EtOAc, mp 125 °C. (Found: C, 84.82; H, 11.47; $C_{31}H_{50}O$ requires: C, 84.85; H, 11.50%.) IR ν_{max} cm^{-1}: 1715 (six-membered cyclic ketone), 1650 (non-conjugated C=C), 1400, 870 (C–H stretching of trisubstituted double bond), 830 (terminal methylene group), 1470, 1390, 1375, 1280, 1215, 1130, 1000 and 910; MS *m/z* (rel. int.): 438 [M^+] (6.0), 423 (9.0), 395 (8.0), 311 (44.0), 272 (8.5), 271 (20.0), 257 (13.5), 245 (17.5), 218 (5.5), 187 (8.5), 175 (12.5), 173 (20.5), 161 (15.0), 159 (22.5), 149 (17.0), 147 (16.5), 145 (23.0), 134 (18.0), 133 (25.0), 131 (13.5), 125 (54.0), 123 (22.0), 121 (18.5), 119 (32.0), 109 (15.0), 95 (10.0), 81 (25.0), 71 (20.0), 69 (100.0), 67 (27.5), 55 (84) and 43 (27.0).

Elution of the main column with petrol–EtOAc (40:1) afforded **1c** (0.12 g), crystallized from petrol–EtOAc, mp 101 °C.

Further elution of the column with petrol–EtOAc (30:1) gave agrostophyllinol (**5a**) (0.20 g), crystallized from petrol–EtOAc, mp 175 °C. (Found: C, 84.44; H, 11.87; $C_{31}H_{52}O$ requires: C, 84.47; H, 11.90%). IR ν_{max} cm^{-1}: 3383 (OH), 1637, 1373, 889 and 850 (trisubstituted double bond and terminal methylene group), 1462, 1097 and 1045; MS *m/z* (rel. int.): 440 [M^+] (25.0), 425 (68.3), 413 (21.0), 407 (25.0), 397 (26.0), 314, (22.0), 313 (83.3), 273 (20.6), 259 (18.6), 215 (12.4), 189 (22.0), 187 (16.0), 175 (21.8), 173 (30.8), 161 (21.8), 159 (30.1), 147 (21.4), 145 (22.8), 135 (27.9), 133 (29.0), 123 (23.9), 121 (34.1), 119 (40.8), 109 (36.0), 107 (37.5), 105 (37.5), 95 (54.5), 94 (28.3), 93 (31.2), 91 (28.6), 83 (32.6), 81 (39.2), 79 (23.2), 71 (19.2), 69 (88.5), 67 (30.5), 57 (35.4), 55 (100), 43 (89.9) and 41 (91.3). Acetylation of **5a** with Ac_2O and pyridine in the usual manner gave **5b**, crystallized from petrol–EtOAc, mp 140 °C (Found: C, 82.04; H, 11.25; $C_{33}H_{54}O_2$ requires: C, 82.08; H, 11.28%). IR ν_{max} cm^{-1}: 1259 and 1724 (OAc), 1643, 1376, 889, 772 and 668 (trisubstituted double bond and terminal methylene group), 1459, 1040 and 980; ^1H NMR: δ 0.64, 0.73, 0.85, 0.88 and 1.06 (each 3H, *s*; 5 X –C–C$\underline{H}_3$), 0.87 (6H, *d*, $J = 7.7$ Hz; 2 X –CH(C$\underline{H}_3$)$_2$, 1.02 (3H, *d*, with fine splitting; >CH–C$\underline{H}_3$), 2.11 (3H, *s*; OAc), 4.65 and 4.71 (each 1H, br. signal; H_2-31), 4.47 (1H, *dd*, $J_1 = 10.93$ Hz and $J_2 = 4.34$ Hz; H-3).

3.2.3. (c) Chromatography of the neutral fraction obtained from *A. callosum*

Elution of the column with light petroleum ether gave an uncharacterized oily mass. Further elution of the column with petrol–EtOAc (80:1) afforded agrostophyllinone (**5c**) (0.30 g), crystallized from the same solvent mixture, mp 125 °C. Washing the column with petrol–EtOAc (40:1) gave a mixture of **1c**, **3b** and **4c**. Rechromatography of this mixture using the same eluent finally afforded pure **4c** (0.06 g) in the early fractions, **3b** (0.05 g) in the middle fractions, each as a semisolid mass, and **1c** (0.09 g) in the end fractions, crystallized from petrol–EtOAc, mp 101 °C.

3.3. Reduction of agrostophyllinone (5c) to agrostophyllinol (5a) with $NaBH_4$

To a solution of 0.1 g of agrostophyllinone (**5c**) in 30 ml MeOH was added 0.20 g of $NaBH_4$ in small portions with stirring in the cold (0-5 °C). The mixture was then kept at room temperature with stirring for 30 min and thereafter heated under reflux for 1 h. MeOH was removed under reduced pressure. The residue was treated with H_2O (20 ml), acidified with dilute HCl in the cold and extracted with Et_2O, washed with H_2O, dried and the solvent removed. The residue was chromatographed. The petrol–EtOAc (30:1) eluate gave agrostophyllinol (**5a**) (0.098 g).

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