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13-EPI-HOMOVERRUCOSANE DERIVATIVES AND OTHER DITERPENES FROM *PLAGIOCHILA* (HEPATICAE)*

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Key Word Index—*Plagiochila cristata*; *Plagiochila adianthoides*; Jungermanniales; Hepaticae; crystal structure; 13-epi-homoverrucosane-type diterpenes; fusicogigantone-type diterpenes.

Abstract Four new 13-epi-homoverrucosane-type diterpenes: 13-epi-homoverrucosan-5β,6β-diol **2**; 13-epi-homoverrucosan-5β,6β-diol-8-one **3**; 13-epi-homoverrucosan-6β-ol-5-one **4**; 13-epi-homoverrucosan-5β,6β,8β-triol **5**, along with the known 13-epi-homoverrucosan-5β-ol **1** and two known fusicoccane-type diterpenes, fusicogigantone A **6** and B **7**, were isolated from *Plagiochila cristata* collected from the wild. Only the two fusicoccane-type diterpenes were isolated from *Plagiochila adianthoides* grown in axenic culture. All structures were elucidated by spectral data.

INTRODUCTION

Verrucosane-type diterpenes (verrucosane-, neoverrucosane-, homoverrucosane-, 13-epi-neoverrucosane- and 13-epi-homoverrucosane-type diterpenes) are distributed in *Schistochila* [1, 2], *Mylia* [3–9], *Gyrothyra* [10], *Scapania* [11] and *Plagiochila* [12], morphologically different genera of the Hepaticae. To our knowledge, this type of diterpene has not been reported in higher plants. Only one 13-epi-neoverrucosane-type diterpene alcohol was previously isolated from *Plagiochila* [12], a genus of the Jungermanniales (Hepaticae). More than 1,000 *Plagiochila* species are known in the world and are mainly distributed in the tropics. *Plagiochila cristata* (Sw.) Lindenb. was collected in Cundinamarca, Colombia, and *Plagiochila adianthoides* (Sw.) Dum. was originally collected in Panamá. Due to the difficulties in obtaining sufficient plant material from its natural habitat, an axenic culture of *P. adianthoides* was used for this investigation. In this paper we report the isolation and characterization of diterpenes of *P. cristata* collected in the wild and *P. adianthoides* grown in axenic culture.

RESULTS AND DISCUSSION

Air-dried plant material from the Colombian liverwort *P. cristata* was exhaustively extracted with diethyl ether. The evaporated extract was chromatographed by vacuum liquid chromatography (VLC) [13] and separated into six fractions. The 13-epi-homoverrucosane-containing fractions were further purified by a combination of VLC, Sephadex LH-20 chromatography and HPLC, which resulted in the isolation of 13-epi-homoverrucosan-5β-ol (**1**), 13-epi-homoverrucosan-5β,6β-diol (**2**), 13-epi-homoverrucosan-5β,6β-diol-8-one (**3**), 13-epi-homoverrucosan-6β-ol-5-one (**4**), and 13-epi-homoverrucosan-5β,6β,8β-triol (**5**).

The spectral and physical data of **1**, which was obtained as crystalline needles, were in agreement with those of 13-epi-homoverrucosan-5β-ol, previously isolated from the New Zealand liverwort *Schistochila nobilis* [1].

Compound **2** was obtained as a colourless, oily substance. The Cl^+ mass spectrometry $[M + H]^+$ at *m/z* 307 corresponded to the molecular formula $C_{20}H_{34}O_2$. The IR spectrum, ^1H and ^{13}C NMR spectral data were similar to those of 13-epi-homoverrucosan-5β-ol (**1**). The IR absorbance at 3426 cm^{-1}, the ^{13}C NMR signals of two tertiary carbons at $\delta_c = 67.5$ (C-5) and $\delta_c = 82.2$ (C-6), along with the ^1H resonances at $\delta_H = 3.78$ (*dt*, $J = 2.3$, 11.8 Hz, H-5) and $\delta_H = 3.45$ (*s(br)*, H-6) indicated the presence of two secondary hydroxyl groups. Besides two tertiary methyl groups ($\delta_H = 0.84$, $\delta_H = 0.86$, both *s*, H-19/20), the presence of an isopropyl group (1337, 1365 cm^{-1}, $\delta_H = 0.78$, 0.79, both *d*, $J = 6.6$ Hz, H-16/17), a vinylic methyl group ($\delta_H = 1.75$, *s*, H-18) and a vinylic proton ($\delta_H = 5.16$, *d(br)*, $J = 4.8$ Hz, H-2) were confirmed by the IR and ^1H NMR spectroscopic data. The locations of the two hydroxyl groups were estab-

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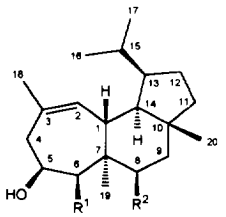
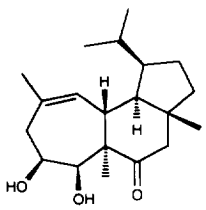


1 R^1 = H; R^2 = H

2 R^1 = OH; R^2 = H

5 R^1 = OH; R^2 = OH



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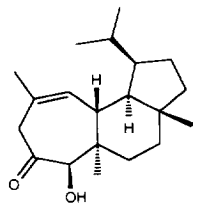

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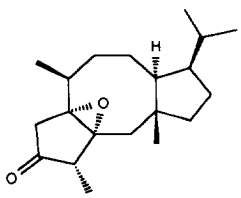

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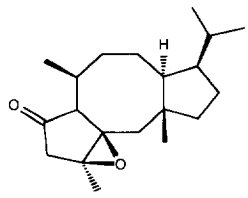

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lished by 2D ^{1}H–^{1}H COSY and double resonance examinations. The vinylic methyl group H-18 (δ_H = 1.75, *s*) showed a long-range coupling to H-4β (δ_H = 2.98, *t*, J = 11.8 Hz). H-4β also showed a coupling to H-4α (δ_H = 1.64, *dd*, J = 11.8 Hz) and a coupling to H-5 (δ_H = 3.78, *dt*, J = 2.3, 11.8 Hz). The coupling constant of H-4β indicated a location geminal to H-4α and vicinal to H-5. H-5 further showed coupling to H-4α. The coupling constant for H-4α could not be determined. The ^{1}H–^{1}H COSY also exhibited a very small coupling between H-5 and H-6 (δ_H = 3.45, *s*(*br*)). The shift values for H-5 and H-6 prove that the hydroxyl groups are located at C-5 and C-6. The α-configuration of both H-5 and H-6 was indicated by NOE effects between H-5 and α-standing methyl group H-19 and between H-5 and H-6 (Fig. 1). Irradiation of H-5 gave a clear enhancement of H-6 (4%) and of the methyl signal H-19 (6%). The coupling constant J = 13.3 Hz of the coupling between H-14 and β-configured H-1 indicated a diaxial coupling between these protons; hence, H-14 is α-configured. NOE effects between H-13 and H-14 (3%), as well as between H-13 and H-2 (7%) were due to the α-configuration of H-13 (Fig. 1). Thus, the structure of **2** was elucidated as (+)-13-epi-homoverrucosan-5β,6β-diol.

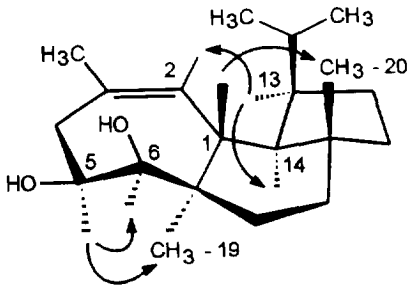
The molecular formula of **3**, a colourless substance with oily consistency, was confirmed as $C_{20}H_{32}O_3$ by HRMS ([M^+] *m/z* 320.2341). The ^{1}H and ^{13}C NMR data indicated another homoverrucosane-type diterpene. In addition to the absorption of hydroxyl and isopropyl groups (3447, 1385, 1375 cm^{-1}), the IR spectrum showed the absorption of a carbonyl group (1699 cm^{-1}), which was confirmed by the ^{13}C signal at δ_c = 216.6, *s*. The ^{13}C NMR signals of two tertiary carbons (δ_c = 66.6, δ_c = 76.5) are in agreement with two secondary hydroxyl groups in the molecule. Their locations at C-5 and C-6

Table 1. ^{1}H NMR spectral data of compounds **2**–**5**

H	2	3	4	5
1	2.86 *dd* (4.8, 13.3)	3.29 *dd* (6.0, 13.0)	2.42 *dd* (7.4, 12.4)	3.71 *m*
2	5.16 *d* (*br*) (4.8)	5.22 *d* (*br*) (6.0)	5.53 *d* (*br*) (7.4)	5.35 *s* (*br*)
4α	1.64 *dd* (11.8,*)	1.77 *dd* (2.7, 13.5)	2.62 *d* (*br*) (19.0)	3.71 *m*
4β	2.98 *t* (11.8,)	2.92 *dd* (11.8, 13.5)	3.47 *d* (19.0)	2.09 *dd* (5.0, 11.3)
5	3.78 *dt* (2.3, 11.8)	3.56 *dt* (2.5, 11.8)	–	4.16 *d* (*br*) (11.3)
6	3.45 *s* (*br*)	4.28 *s* (*br*)	4.07 *s*	4.46 *s*
8α	1.42 *m*	–	1.21–1.72 *m*	4.06 *s* (*br*)
8β	2.26 *dt* (4.1, 13.8)	–	1.21–1.72 *m*	–
9α	1.29 *dt* (3.6, 13.8)	2.48 *d* (12.9)	1.21–1.72 *m*	1.92 *dd* (2.3, 13.7)
9β	0.91 *dt* (3.3, 13.8)	2.24 *d* (12.9)	1.21–1.72 *m*	1.67 *m*
11α	1.10[a] *m*	1.36 *m*	1.21–1.72 *m*	1.10–2.10 *m*
11β	1.45[a] *m*	1.52 *m*	1.21–1.72 *m*	1.10–2.10 *m*
12α	1.48[b] *m*	1.58 *m*	1.21–1.72 *m*	1.10–2.10 *m*
12β	1.66[b] *m*	1.76 *m*	1.21–1.72 *m*	1.10–2.10 *m*
13	1.98 *m*	2.18 *m*	1.99 *m*	2.02 *m*
14	1.49 *m*	2.14 *dd* (2.7, 13.0)	1.69 *m*	1.62 *m*
15	1.79 *m*	1.91 *m*	1.72 *m*	1.98 *m*
16	0.78[c] *d* (6.6)	0.80[a] *d* (6.8)	0.72[a] *d* (6.8)	0.89[a] *d* (6.4)
17	0.79[c] *d* (6.6)	0.82[a] *d* (6.8)	0.76[a] *d* (6.8)	0.98[a] *d* (6.4)
18	1.75 *s*	1.80 *s*	1.80 *s*	1.83 *s*
19	0.84 *s*	0.98 *s*	1.02 *s*	0.95[b] *s*
20	0.86 *s*	0.78 *s*	0.78 *s*	1.33[b] *s*

[a,b,c] The assignment may be interchanged.

*Coupling constant could not be determined.



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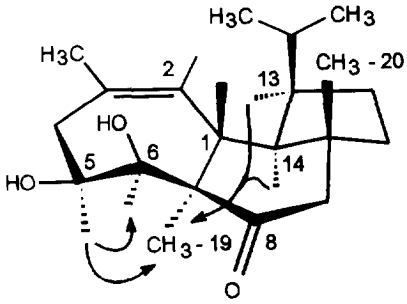

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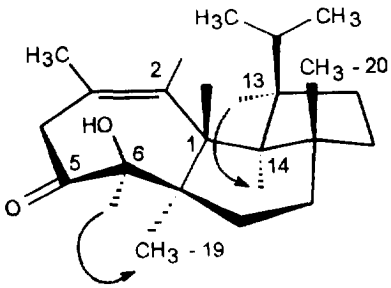

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Fig. 1. NOE interactions of compounds **2**–**4**.

were established by comparing the NMR data of **3** with those of **2**. The location of the carbonyl group in position 8 was determined by close examination of the 2D ^1H–^1H COSY spectrum. The protons H-9α + β (δ_H = 2.48, 2.24, both *d*, *J* = 12.9 Hz, H-9α + β) in vicinal position to the carbonyl group showed a long-range coupling to the methyl group H-20 (δ_H = 0.78, s). The methyl protons H-20 also showed a long-range coupling to H-11α + β (δ_H = 1.36, 1.52, both *m*, H-11α + β). The ^2J and ^3J connectivities of the protons located on the six-membered and the five-membered ring were as expected for the location of the carbonyl group in position 8. The fact that the proton H-14 of **3** experienced a downfield shift compared with H-14 in **2**, which is due to the anisotropic deshielding effect of the carbonyl group, confirmed this location. NOE effects between H-5 and H-6 (5%) and between H-5 and H-19 (4%) were due to the β-configuration of both hydroxyl groups on the seven-membered ring (Fig. 1). For the investigation of configuration at C-13 it was not possible to irradiate only H-13, due to the overlapping signals of H-13 and H-14. Irradiation of both H-13 and H-14 showed an effect on the α-standing methyl group H-19 (3%) and no effect on both the β-standing H-1 and the methyl group H-20. Therefore, the isopropyl group has to be β-positioned on C-13. On the basis of these examinations, the structure of **3** was established as (−)-13-epi-homoverrucosan-5β,6β-diol-8-one.

Compound **4**, also obtained as an oil, showed an IR spectrum indicating a hydroxyl, an isopropyl and a carbonyl group. The EI mass spectrum showed $[M]^+$ at *m/z* 304, corresponding to the molecular composition $C_{20}H_{32}O_2$. Thus, compound **4** possessed only one hydroxyl group and one carbonyl group. The ^2J and ^3J connectivities of H-9α + β and H-8α + β as well as their ^4J couplings to H-20 or H-19 indicated that the carbonyl function was not located on the six-membered ring as in **3**. The geminal protons H-4α (δ_H = 2.62, *d* (*br*), *J* = 19 Hz) and H-4β (δ_H = 3.47, *d*, *J* = 19 Hz) of **4**, when compared to those in **3**, showed a reduction of their multiplicity from a double doublet to a doublet. H-4β showed a long-range coupling to the vinylic methyl group H-18, as in **3**. The singlet corresponding to H-6 was narrower than that in **3**. Based on this evidence, we assigned the carbonyl to the position 5 and the hydroxyl group to the position 6. The α-configuration of H-6 was concluded from the NOE effect between H-6 and α-standing methyl group H-19 (5%) (Fig. 1). The α-configuration of H-14 resulted from the coupling constant (*J* = 12.4 Hz), which indicated a diaxial coupling between H-14 and β-configured H-1. The α-configuration of H-13 was concluded from the NOE effect between H-13 and α-standing H-14 (6%) (Fig. 1). Thus, the structure of **4** was elucidated as (−)-13-epi-homoverrucosan-6β-ol-5-one.

Compound **5** precipitated from the most polar fraction of the diethyl ether extract. The CI mass spectrum

showed the $[M+H]^+$ ion peak at m/z 323, which was in agreement with the molecular formula $C_{20}H_{34}O_3$. The ^1H and ^{13}C NMR spectroscopic data indicated another homoverrucosane-type diterpene. The signals of three tertiary carbons at $\delta_c = 67.7$, 83.5 and 80.3 were in agreement with three secondary hydroxyl groups in the molecule. The locations of two hydroxyl groups in positions 5 and 6 were determined by comparison of the NMR data of **5** with those of **2** and by ^1H–^1H COSY examination, which revealed the same couplings for the protons of the seven-membered ring in **5** as for **2**. This experiment, however, was consistent with the location of the third hydroxyl group in either position 8 or position 9. In order to establish the position of the third hydroxyl group and the stereochemistry of **5** including its relative configuration, X-ray measurements were carried out (Fig. 2). On the basis of these spectral and physical data the relative structure of **5** was established as (−)-13-epi-homoverrucosan-5β,6β,8β-triol.

Both known fusicoccane diterpenes, fusicogigantone A (**6**) and fusicogigantone B (**7**), previously described in *Pleurozia gigantea* [14], were isolated from fraction 2 by a combination of Sephadex LH-20 chromatography and HPLC and identified by comparison of their ^1H,^{13}C NMR and mass-spectrometry data with those in [14]. These compounds were also isolated in this study from the methylene chloride extract of *Plagiochila adianthoides*, which was grown in axenic culture.

EXPERIMENTAL

General. Mps: uncorr.; solvents used for spectral measurements: CD_3Cl, pyridine-d_5. Measurements of all NMR spectra were carried out on a Bruker AM 400 NMR spectrometer [^1H NMR (400 MHz), ^{13}C NMR (100 MHz)]. Assignments of ^1H NMR were confirmed by ^1H–^1H COSY, double resonance and NOE examinations. Assignments of ^{13}C NMR were confirmed by DEPT-spectra and comparison with ^{13}C NMR data of **1**. IR: KBr, Perkin Elmer 2000. CI-MS: 120 eV isobutane, Finnigan MAT TSQ 70. EI-MS: 70 eV, Finnigan MAT 90. X-Ray measurements were carried out on a Siemens Stoe AED2 diffractometer.

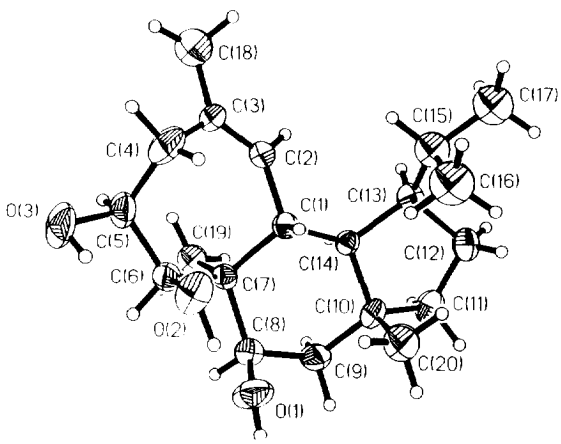

Fig. 2. Schakal plot [18] of compound **5**.

Plant material. Plagiochila cristata was collected in May 1991 in Colombia (Parque Montañes de Chicaque, department Cundinamarca). *Plagiochila adianthoides* was collected in January 1988 in Panamá (summit area of 'Cerro Jefe', Parque Nacional Chargres, Provincia Panamá).

Axenic culture. The culture was grown as a surface culture in 200 ml flasks on modified Gamborg B5 medium [15] under constant illumination (2000 lux) at 20 ($\pm$ 1.5)°. The flasks were closed with cellulose stoppers covered with aluminum foil. Each flask contained 80 ml medium.

Extraction and isolation. Air-dried and powdered plant material (120 g) of *P. cristata* was exhaustively extracted with Et_2O. The evapd extract was applied to VLC on silica gel (Si 60, 15 μm) with an *n*-hexane–EtOAc gradient to yield 6 frs. 13-Epi-homoverrucosan-5β-ol (**1**) (70 mg) and 13-epi-homoverrucosan-6β-ol-5-one (**4**) (12 mg) were obtained from fr. 4 by VLC (silica gel Si 60, 15 μm, *n*-hexane–EtOAc gradient) and HPLC (LiChrospher Si 60, 5 μm *n*-hexane–EtOAc, 89:11). VLC of fr. 5 (RP-18, 20–45 μm, MeOH–H_2O, 8:2) afforded 13-epi-homoverrucosan-5β,6β-diol (**2**) (190 mg). Further separation of fr. 5 with HPLC (LiChrospher RP-18, 5 μm, MeOH–H_2O, 85:15) yielded more **2** (270 mg) and HPLC (LiChrospher RP-18, 5 μm, MeOH–H_2O, 75:25) afforded 13-epi-homoverrucosan-5β,6β-diol-8-one (**3**) (8 mg). Fr. 6 was chromatographed on Sephadex LH-20 using CH_2Cl_2–MeOH (1:1) as eluent. The ppt was washed with *n*-hexane to yield 30 mg 13-epi-homoverrucosan-5β,6β,8β-triol (**5**). Fusicogigantone A (**6**) (20 mg) and fusicogigantone B (**7**) (45 mg) were obtained from fr. 2 by CC on Sephadex LH-20 (CH_2Cl_2–MeOH, 1:1) and HPLC (LiChrospher Si 60, 5 μm, *n*-hexane–EtOAc, 98:2).

Air-dried and powdered plant material (70 g) of axenic culture from *P. adianthoides* was exhaustively extracted with CH_2Cl_2. The evapd extract was applied to VLC on silica gel (Si 60, 15 μm) with an *n*-hexane–EtOAc gradient to yield 7 frs. Frs 2 and 3 were chromatographed on Sephadex LH-20 (CH_2Cl_2–MeOH, 1:1) Fr. 2 was further separated with HPLC (LiChrospher Si 60, 5 μm, *n*-hexane–EtOAc, 97:3) to obtain fusicogigantone B (**7**) (1 mg). Fusicogigantone A (**6**) (0.5 mg) was obtained from fr. 3 by further HPLC (LiChrospher Si 60, 5 μm, *n*-hexane–EtOAc, 92.5:7.5).

Compound **2**. $[\alpha]_D$ +20.3° (*c* 0.2; $CHCl_3$); CI$^+$MS *m/z*: 307 $[M+H]^+$ ($C_{20}H_{34}O_2$); IR ν_{max} cm^{-1}: 3426, 2939, 1450, 1377, 1365, 1034, 995, 938; ^{13}C NMR ($CDCl_3$) δ: 32.5 (*d*, C-1), 132.9 (*d*, C-2), 130.6 (*s*, C-3), 40.5 (*t*, C-4), 67.5 (*d*, C-5), 82.2 (*d*, C-6), 41.8 (*s*, C-7), 32.5 (*t*, C-8), 34.4 (*t*, C-9[a]), 40.5 (*s*, C-10), 36.8 (*t*, C-11[a]), 24.9 (*t*, C-12), 44.7 (*d*, C-13), 51.7 (*d*, C-14), 29.4 (*d*, C-15), 21.3 (*q*, C-16[b]), 23.8 (*q*, C-17[b]), 25.4 (*q*, C-18), 18.6 (*q*, C-19[c]), 19.6 (*q*, C-20[c]). ([a,b,c]Assignments interchangeable.)

Compound **3**. $[\alpha]_D$ −28.0° (*c* 0.3; $CHCl_3$); HRMS *m/z*: 320.2341 $[M]^+$; $C_{20}H_{32}O_3$ requires 320.2351; IR ν_{max} cm^{-1}: 3447, 2953, 2874, 1699, 1457, 1385, 1375, 1039, 1011, 961; ^{13}C NMR ($CDCl_3$): δ 34.3 (*d*, C-1), 129.0

(*d*, C-2), 134.1 (*s*, C-3), 39.7 (*t*, C-4), 66.6 (*d*, C-5), 76.5 (*d*, C-6), 55.1 (*s*, C-7), 216.6 (*s*, C-8), 53.7 (*t*, C-9), 43.6 (*s*, C-10), 35.4 (*t*, C-11), 24.6 (*t*, C-12), 44.2 (*d*, C-13), 50.7 (*d*, C-14), 28.6 (*d*, C-15), 20.6 (*q*, C-16[a]), 23.8 (*q*, C-17[a]), 25.0 (*q*, C-18), 17.1 (*q*, C-19[b]), 19.8 (*q*, C-20[b]). ([a,b,c]Assignments interchangeable.)

Compound **4**. $[\alpha]_D$ − 37.7° (*c* 0.3; $CHCl_3$); EI^+MS *m/z* (rel. int.): 304 $[M]^+$ (15), 261 (4), 243 (8), 232 (8), 191 (20), 161 (13), 149 (21), 109 (28), 95 (38), 81 (34), 69 (33), 55 (50), 43 (100), 41 (71); IR ν_{max} cm^{-1}: 3520, 2928, 1702, 1457, 1435, 1385, 1375, 1062; ^{13}C NMR ($CDCl_3$) δ: 40.3 (*d*, C-1), 130.5 (*d*, C-2), 128.3 (*s*, C-3), 46.1 (*t*, C-4), 211.0 (*s*, C-5), 84.2 (*d*, C-6), 48.6 (*s*, C-7), 27.8 (*t*, C-8[a]), 36.5 (*t*, C-9[a]), 41.4 (*s*, C-10), 40.5 (*t*, C-11[a]), 27.7 (*t*, C-12[a]), 44.8 (*d*, C-13), 49.4 (*d*, C-14), 30.1 (*d*, C-15), 21.3 (*q*, C-16[b]), 23.4 (*q*, C-17[b]), 23.9 (*q*, C-18), 18.2 (*q*, C-19[c]), 19.8 (*q*, C-20[c]). ([a,b,c]Assignments interchangeable.)

Compound **5**. Mp 251–254°C; $[\alpha]_D$ − 19.5° (*c* 0.13; C_5H_5N); CI^+MS *m/z*: 323 $[M+H]^+$ ($C_{20}H_{34}O_3$); ^{13}C NMR (pyridine-d_5) δ: 32.1 (*d*, C-1), 132.6 (*d*, C-2), 132.1 (*s*, C-3), 42.0 (*t*, C-4[a]), 67.7 (*d*, C-5), 83.5 (*d*, C-6), 45.4 (*s*, C-7), 80.3 (*d*, C-8), 45.3 (*t*, C-9[a]), 40.3 (*s*, C-10), 36.1 (*t*, C-11), 25.7 (*t*, C-12), 45.6 (*d*, C-13), 52.7 (*d*, C-14), 30.8 (*d*, C-15), 22.2 (*q*, C-16[b]), 23.1 (*q*, C-17[b]), 26.4 (*q*, C-18[c]), 19.7 (*q*, C-19[c]), 24.3 (*q*, C-20[c]). ([a,b,c]Assignments interchangeable.)

X-Ray analysis of **5**. Experimental details of the X-ray diffraction analysis of **5** are listed in Table 2. The structure was solved using direct methods (SHELXS-86) [16] and refined by full-matrix least-squares analysis on F^2 (SHELXL) [17] for all independent reflections with anisotropic temperature factors for all oxygens and C-1 to C-14 to a final *R* of 0.055. The hydrogen atoms are treated as rigid groups with a fixed C–H distance of 0.098 nm. Goodness of fit $S = 0.979$ of F^2 values for 195 parameters. The absolute structure could not be determined. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory.

Table 2. Crystallographic data and data collection characteristics for the X-ray analysis of compound **5**

Crystal data		
Molecular formula	$C_{20}H_{34}O_3$	
M_r	322.47	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Cell dimensions (nm) a	0.6612(3)	$\alpha = 90°$
b	1.449(8)	$\beta = 90°$
c	1.8839(10)	$\gamma = 90°$
Volume (nm^3)	1.805(2)	
Z	4	
Density (Mgm^{-3})	1.186	
Absorption coefficient (mm^{-1})	0.077	
F(000)	712	
Crystal size (mm)	0.3 × 0.2 × 0.1	
Data collection: Siemens Stoe AED2 Graphite monochromated MoKα;		
ω/Θ scans;	($3° < 2\Theta < 48°$)	
Reflections collected	1634	
Independent reflections	1632 ($R_{int} = 0.0631$)	
Observed reflections	1196 ($I > 2\sigma_I$)	
Parameters refined	195	
Final *R* ($I > 2\sigma_I$)	0.055	

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