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# NOVEL C-35 TERPENOIDS FROM THE PANAMANIAN LIVERWORT PLAGIOCHILA MORITZIANA

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**Abstract:** A new class of C-35 terpenoids is described from Hepaticae: plagiospirolide A and plagiospirolide B, two novel heptacyclic spiro-terpenes were isolated from the Panamanian liverwort ***Plagiochila moritziana Lindbg. & Gott.*** Structures were determined by MS, extensive NMR studies and X-ray crystallographic analysis. The compounds may be biosynthesized by condensation of a sesquiterpenoid and a diterpenoid unit in a Diels-Alder like reaction.

## INTRODUCTION

The genus *Plagiochila* is considered to be the largest within the Hepaticae. At the moment, more than 1000 described species exist. However, since there is an extreme polymorphism in the Plagiochilaceae, it is to be expected that this number will be reduced considerably in future.

*Plagiochila* species produce a broad and diverse spectrum of secondary metabolites, mono- sesqui- and diterpenoids as well as bisbenzyls[1-8]. Among the terpene compounds, sesquiterpenoids are the most common.

In the present communication, we report on a further group of terpenoids with a $C_{35}$-skeleton from *Plagiochila moritziana*, collected in Central Panamá. Isolation and characterization of the two novel heptacyclic spiro-terpenoids **plagiospirolide A (1)** and **plagiospirolide B (2)** are described.

## RESULTS AND DISCUSSION

The air-dried and ground material was repeatedly extracted with $CH_2Cl_2$ and the crude extract examined by TLC, GC and GC/MS.

Repeated column chromatography on silica gel, followed by purification with HPLC, afforded **plagiospirolide B (2)**, a colourless, viscous oil, as one of

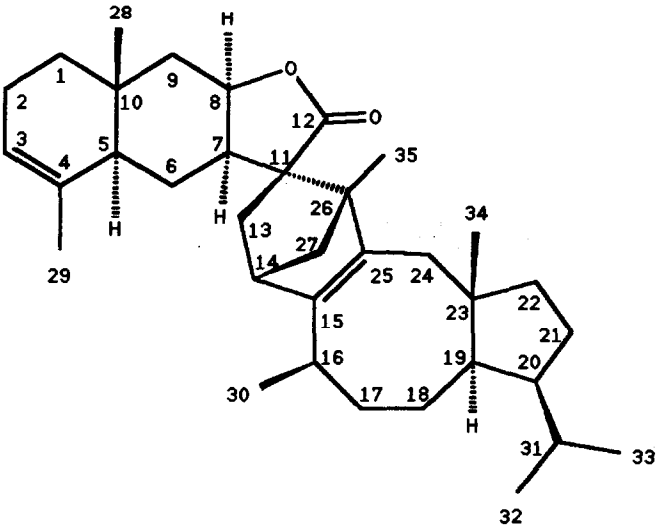



Figure 1. **Plagiospirolide A (1)**

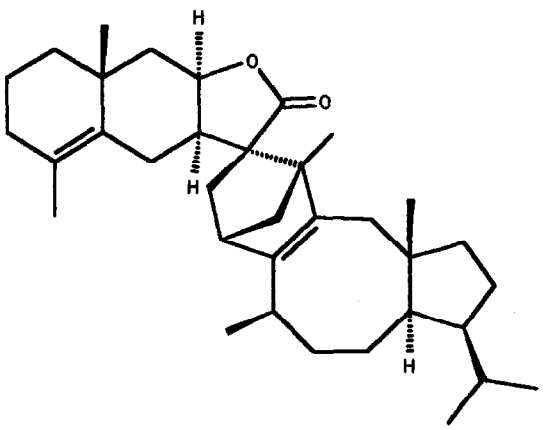



Figure 2. **Plagiospirolide B (2)**

the major constituents, together with **plagiospirolide A (1)**, crystallizing as colourless needles (m.p., 197° C).

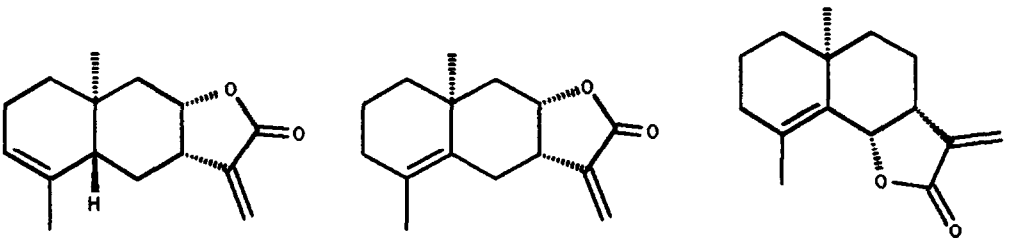
In HPLC, 1 and 2 showed one peak each. However, GC turned to give two peaks for each compound, due to thermal decomposition into two defined, stable fragments 3 and 4 or 5 respectively.

Retention times of the latter eluting fragments were identical in both 1 and 2. The former eluting fragments showed a small difference of 0.18 min in retention times.

GC-EIMS of 2 revealed the first eluting fragment's molecular ion peak at $M^{(+)}$ = 232.1439, corresponding to the molecular composition of $C_{15}H_{20}O_2$.

The second fragment showed its molecular peak at $M^{(+)}$ = 272.2505, indicating

a diterpene hydrocarbon with the molecular formula of $C_{20}H_{32}$.
Mass spectra of 1 corresponded exactly with those of 2. Thus, it could be deduced 1 and 2 to be closely related compounds.
By comparison of the mass spectra with literature data, it was found that the spectrum of the $C_{15}$-moiety was identical with spectra of a series of sesquiterpene lactones of the eudesmane type, such as diplophyllolide (4), diplophyllin (5) and frullanolide (6), all found in Hepaticae[9-11].



Diplophyllolide (4) Diplophyllin (5) (-)-Frullanolide (6)

Figure 3.

The second fragment, $C_{20}H_{32}$, could not be assigned to any structure by MS.
In CIMS of 2, the molecular ion peak $M^{(+1)}$ was detected as a weak signal at the mass of 505 (1%). The more intense signals at masses of 273 (100%) and 233 (97%) resulted from the $M^{(+1)}$-peaks of the fragments 3 and 5.
Thus, 1 and 2 possess the mass of 504 and the molecular formula of $C_{35}H_{52}O_2$, according to 10 double bond equivalents.
IR spectra of both 1 and 2 showed absorptions at 1760 $cm^{-1}$ and 1160 $cm^{-1}$ indicating a $\gamma$-lactone group.
$^{13}C$-NMR indicated the lactone at $\delta_C$ 182 and 4 double bond carbons, which in 1 were all quaternary. In 2, one of the double bond carbons was a methine, the others were also quaternary.
$^1H$-NMR spectra of 1 and 2 were very complex, 48 or 49 protons respectively being found between $\delta_H$ 2.1 and 0.6. Coupling of protons could mainly be assigned by homonuclear $^1H,^1H$ - shift-correlated 2-D spectra (COSY-experiment). In some cases, difference NOE experiments were helpful for the assignment of the signals to their corresponding protons.
Missing of the expected exomethylene group, typical for the eudesmanolides 4, 5 and 6 was obvious in $^1H$-NMR spectra. Therefore, it was assumed the $C_{15}$-moiety to be linked to the diterpene fragment involving C-13, which during decomposition became the exomethylene group of the eudesmanolide.
In 1, the sextet signal at $\delta_H$ 4.65 could be assigned to H-8, from which coupling was observed to H-9$\alpha$ and H-9$\beta$ ($\delta_H$ 1.40 and 2.09) and to H-7 ($\delta_H$ 1.77). H-7 coupled additionally to H-6$\alpha$ and H-6$\beta$ ($\delta_H$ 1.45 and 0.89). The angular C-10 ($\delta_C$ 30.7) was quaternary, bearing a methyl group (C-28). The signal of one olefinic proton was visible at $\delta_H$ 5.34 (H-3). The singlet at

Table 1. $^1$H-NMR Data of 1 and 2.

| | (1) | | (2) | |
|---|---|---|---|---|
| H-2α | 1.70 | m | | |
| H-2β | 1.53 | m | | |
| H-3 | 5.34 | m (br) | | |
| H-6α | 1.45 | m | 1.64 | $J_{6\alpha/\beta}$ = 13.0 |
| H-6β | 0.89 | m | 2.09 | dd, $J_{6\beta/7}$ = 6.5 |
| H-7 | 1.77 | m | 1.94 | m, $J_{7/6\beta}$ = 6.5 |
| H-8 | 4,65 | m | 4.46 | sext, $J_{8/9\alpha}$ = 4.6 |
| | | | | $J_{8/9\beta}$ = $J_{7/8}$ = 7.2 |
| H-9α | 1.40 | | 1.55 | $J_{9\alpha/8}$ = 4.6 |
| H-9β | 2.09 | | 1.75 | dt, $J_{9\alpha/\beta}$ = 14 |
| H-13α | 1.20 | | 1.24 | |
| H-13β | 1.98 | | 2.11 | |
| H-14 | 2.81 | d (br) | 2.84 | d (br) |
| H-16 | 2.70 | sept | 2.66 | sept, J = 6.2 |
| H-17α | 1.45 | m | 1.36 | m |
| H-17β | 1.35 | m | 1.45 | m |
| H-19 | 1.82 | m | | |
| H-24α | 1.97 | d, $J_{24\alpha/\beta}$ = 12.5 | 1.95 | d, $J_{24\alpha/\beta}$ = 12.9 |
| H-24β | 2.01 | d | 2.05 | d |
| H-27α | 2.17 | dd, $J_{27\alpha/\beta}$ = 11.5 | 2.15 | dd, $J_{27\alpha/\beta}$ = 12 |
| H-27β | 1.48 | $J_{27\beta/14}$ = 3.9 | 1.61 | $J_{27\beta/14}$ = 3.6 |
| H-28 | 0.82 | s | 1.03 | s |
| H-29 | 1.55 | s | 1.53 | s |
| H-30 | 1.07 | d | 1.07 | d, $J_{16/30}$ = 6.7 |
| H-31 | 1.66 | m | 1.65 | m, $J_{31/32}$ = 6.6 |
| H-32 | 0.89 | d | 0.84 | d |
| H-33 | 0.72 | d | 0.69 | d, $J_{33/31}$ = 6.6 |
| H-34 | 0.73 | s | 0.71 | s |
| H-35 | 1.30 | s | 1.23 | s |

$\delta_H$ 1.55 indicated a vinylic methyl group at C-4.
Thus, the partial structure 7 could be established, yielding 4 as decomposition product.
Linkage between $C_{15}$- and $C_{20}$-units had to meet the requirements to be split easily under GC and MS conditions, without displacement of protons. Retro-Diels-Alder reaction conformed perfectly to these conditions, suggesting a spiro-linkage between the two fragments (scheme 1).

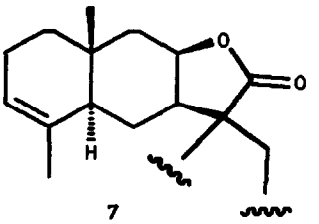


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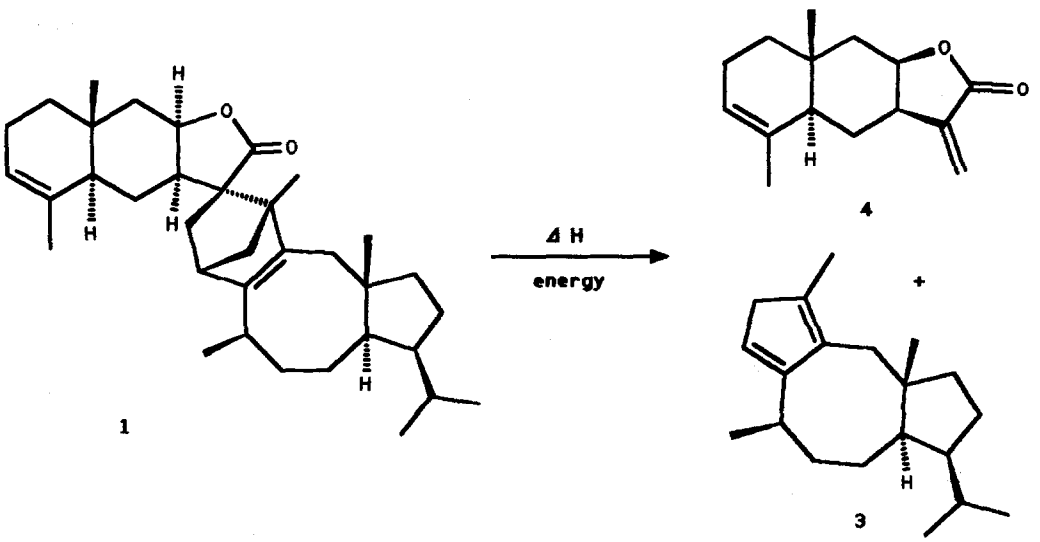
Figure 4.




1 4 3

Scheme 1. Retro-Diels-Alder Reaction of 1.

For the $C_{20}$-moiety, consisting of five $CH_3$, six $CH_2$, five CH groups and four quaternary carbons, four double bond equivalents remained: one fully substituted double bond and three rings.

In order to enable retro-Diels-Alder reaction, the double bond had to be located in β-position to both C-13 and C-11 (the spiro carbon). Further, two tertiary methyl groups ($\delta_H$ 1.30 and 0.73) and one isopropyl group were parts of the $C_{20}$-fragment.

From a third methyl doublet (H-30, $\delta_H$ 1.07), coupling was observed to a proton located in α-position to the double bond (H-16). The sequence could be followed to a methylene group (H-17α and -β), leading to the partial structure shown in figure 5.

The broad signal at $\delta_H$ 2.81 was assigned to another proton in α-position to a double bond (H-14), from which coupling patterns as shown in figure 6 could be observed. Irradiation of H-14 gave a nuclear Overhauser enhancement of the methyl signal H-30 (4.5%), H-13α + β (4.2 and 2.1%) and H-27α + β (6.1 and 1.8%).

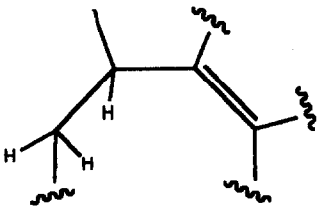



Figure 5.

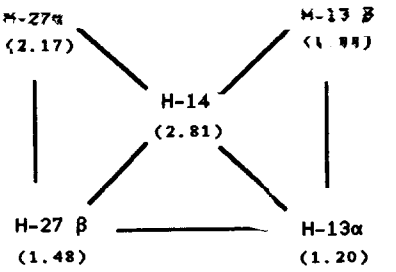



Figure 6.

Structure elucidation could be completed by X-ray crystallographic analysis, showing the relative arrangement of the encountered partial structures, the conformation of the spiro center and the stereochemistry. (Figure 7, tables 2, 3 and 4).

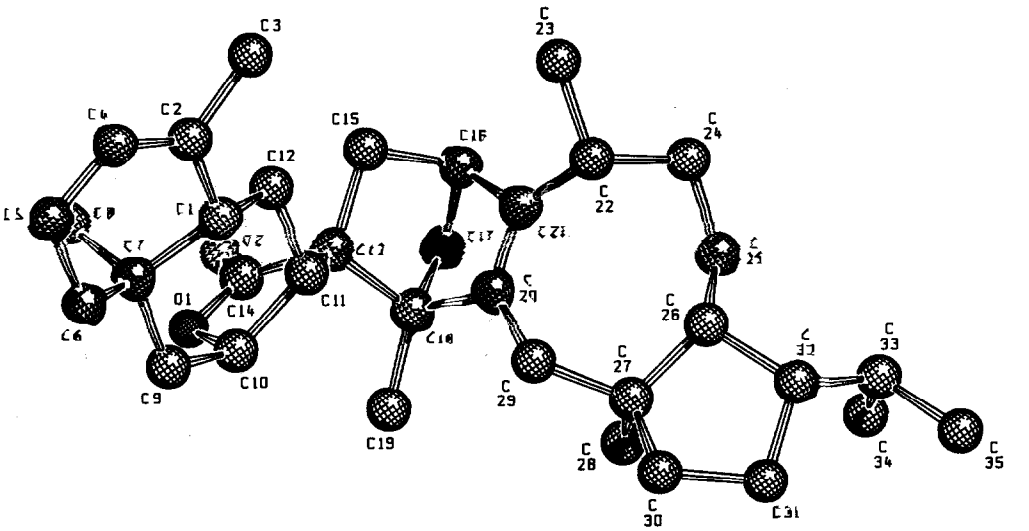



Figure 7.

The NMR spectra of 2 were very similar to those of 1. The most significant difference was the missing of the olefinic proton in 2, indicating the double bond to be fully substituted. For H-6α and β, a significant low-field shift was noticed. Coupling patterns of H-6 to H-9, shown in figure 8 were identical to those in 1.

So structure 2 could be assigned to this compound, being a double bond isomer of 1, with the double bond located in 4,5- position.

$C_{35}$-terpenoids are very uncommon structures in higher plants and have so far not been found in liverworts. The present structures may have been biosynthesized by a Diels-Alder cycloaddition-like reaction. Then, diplophyllolide 4 and diplophyllin 5, both also detected as monomers in the

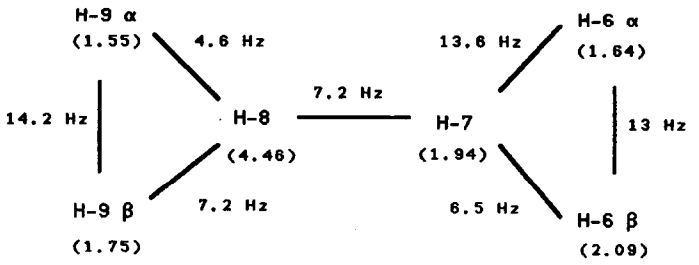



Figure 8.

extract, would act as dienophiles, 3 functioning as diene compound.
It could be readily excluded 1 and 2 to be artifacts originating from reprocessing, since the compounds were detected by TLC in the crude extract immediately after extraction at room temperature. Similar triterpenoid spiro compounds have recently been reported from *Helenium autumnale* (Asteraceae)[12-14]. In those structures, the formal dienophiles were also α-methylene-γ-butyrolactones. It could be shown that synthesis, starting from dienophile- and diene compound, could only be achieved under drastic conditions and with low yields[12,14].
The $C_{20}$-moiety possesses a fusicoccan skeleton, which was recorded for the first time from the fungus *Fusicoccum amygdali*[15-18]. Similar diterpenoid structures have recently also been detected in the liverworts *Anastrepta orcadensis*[19], *Plagiochila acanthophylla ssp. japonica*[20] and *P. spinulosa*[21].
The eudesmanolide structures 4 and 5, forming the $C_{15}$-fragments of 1 and 2, are known from numerous liverworts such as *Diplophyllum albicans*[9,10], *D. taxifolium*[9] and *Chiloscyphus polyanthos*[10], and enantiomers have been isolated from higher plants, e. g. Asteraceae[14,22].
Due to the fact that the described substances are easily decomposed, they may have escaped from the numerous GC-MS orientated phytochemical screenings of liverworts.

## EXPERIMENTAL

GC was carried out on a Carlo Erba GC 6000 Vega series 2, using a 30 m x 0.25 mm DB-1 capillary column (J & W Scientific). Carrier gas He, FID. Temperature program: 155 - 185°C at 5°/min, 185 - 210°C at 3°/min, 210°C: 5 min isotherm. HPLC: Altex 110 A pump, Waters Differencial Refractometer Detector R-401, column: LiChrosorb Si 60, 5 µm, 250 x 8 mm.
GC-EIMS : 70 eV, OV-1 30 m x 0.25mm capillary column; CIMS (direct inlet): 120 eV, reactant gas i-butane, 80°C; both on a Finnigan MAT 90 mass spectrometer.

Table 2. Selected Bond Distances [Å] of 1.

| | | | |
|---|---|---|---|
| C(10)--O(1) | 1.50(2) | C(14)--O(1) | 1.33(2) |
| C(14)--O(2) | 1.19(2) | C(2)---C(1) | 1.52(2) |
| C(7)---C(1) | 1.54(2) | C(12)--C(1) | 1.53(2) |
| C(3)---C(2) | 1.50(2) | C(4)---C(2) | 1.36(2) |
| C(5)---C(4) | 1.48(2) | C(6)---C(5) | 1.50(2) |
| C(7)---C(6) | 1.56(2) | C(8)---C(7) | 1.53(2) |
| C(9)---C(7) | 1.48(2) | C(10)--C(9) | 1.61(2) |
| C(11)--C(10) | 1.49(2) | C(12)--C(11) | 1.52(2) |
| C(13)--C(11) | 1.54(2) | C(14)--C(13) | 1.55(2) |
| C(15)--C(13) | 1.58(2) | C(18)--C(13) | 1.62(2) |
| C(16)--C(15) | 1.54(2) | C(17)--C(16) | 1.54(2) |
| C(21)--C(16) | 1.50(2) | C(18)--C(17) | 1.55(2) |
| C(19)--C(18) | 1.49(2) | C(20)--C(18) | 1.55(2) |
| C(21)--C(20) | 1.32(1) | C(29)--C(20) | 1.49(2) |
| C(22)--C(21) | 1.54(2) | C(23)--C(22) | 1.56(2) |
| C(24)--C(22) | 1.52(2) | C(25)--C(24) | 1.55(2) |
| C(26)--C(25) | 1.53(2) | C(27)--C(26) | 1.54(2) |
| C(32)--C(26) | 1.59(2) | C(28)--C(27) | 1.53(2) |
| C(29)--C(27) | 1.56(2) | C(30)--C(27) | 1.56(2) |
| C(31)--C(30) | 1.53(2) | C(32)--C(31) | 1.54(2) |
| C(33)--C(32) | 1.51(2) | C(34)--C(33) | 1.54(2) |
| C(35)--C(33) | 1.51(2) | | |

Melting points were determined on a hot stage apparatus. IR spectra were recorded on a Perkin Elmer 257 grating infrared spectrometer, for KBr discs or film-method respectively. UV spectra were recorded using a Perkin Elmer Lambda 5 UV/Vis spectrometer for n-hexane solutions. Optical rotation was determined on a Perkin Elmer Polarimeter 241 with $CHCl_3$ as solvent. Concentrations are given in g/100 ml.

NMR spectra were recorded for $CDCl_3$ solutions, using a Bruker AM 400 instrument ($^1H$, 400 MHz, $^{13}C$, 100.5 MHz), relative to $CHCl_3$ at $\delta_H$ = 7.24 or $CDCl_3$ at $\delta_C$ = 77.00. $^{13}C$ multiplicities were determined using the DEPT pulse sequence. COSY and difference NOE experiments were performed using the Bruker COSY.AU and NOEMULT.AU microprograms.

X-ray[25] crystallographic analysis: $C_{35}H_{52}O_2$. Ortho-rhombic. Space group: $P2_12_12_1$. Lattice constants [pm]: a = 7.283(8), b = 12.31(2), c = 33.65(4). Formula units per cell: Z = 4. Four circle diffractometer Siemens AED2. MoKα radiation, ω/Θ - scan. 3080 reflections, 1732 classified as "not observed" ($F_o \leq 1\sigma_{F_o}$). 276 parameters. The hydrogen atoms were refined together with the carbon atoms as a rigid group. Calculations have been performed on a micro-Vax with the following programs: SHELX[23], SCHAKAL[24].

*Plagiochila moritziana* was collected in Cerro Campana region, province of Panamá, Rep. of Panamá in January 1988. Voucher specimens are deposited in the herbaria of the Institut für Pharmakognosie und Analytische Phytochemie, Universität des Saarlandes, and Departamento de Botánica, Escuela de Biologia, Universidad de Panamá.

The cleaned, air-dried and ground material (200 g) was extracted with $CH_2Cl_2$

Table 3. Selected Bond Angles [°] of 1.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(14) | -O(1) | -C(10) | 109(1) | C(7) | -C(1) | -C(2) | 112(1) |
| C(12) | -C(1) | -C(2) | 115(1) | C(12) | -C(1) | -C(7) | 110(1) |
| C(3) | -C(2) | -C(1) | 120(1) | C(4) | -C(2) | -C(1) | 122(1) |
| C(4) | -C(2) | -C(3) | 119(1) | C(5) | -C(4) | -C(2) | 123(2) |
| C(6) | -C(5) | -C(4) | 116(1) | C(7) | -C(6) | -C(5) | 112(1) |
| C(6) | -C(7) | -C(1) | 108(1) | C(8) | -C(7) | -C(1) | 113.0(9) |
| C(8) | -C(7) | -C(6) | 109(1) | C(9) | -C(7) | -C(1) | 108(1) |
| C(9) | -C(7) | -C(6) | 107(1) | C(9) | -C(7) | -C(8) | 112(1) |
| C(10) | -C(9) | -C(7) | 115(1) | C(9) | -C(10) | -O(1) | 109(1) |
| C(11) | -C(10) | -O(1) | 105(1) | C(11) | -C(10) | -C(9) | 115(1) |
| C(12) | -C(11) | -C(10) | 115(1) | C(13) | -C(11) | -C(10) | 102(1) |
| C(13) | -C(11) | -C(12) | 111.4(9) | C(11) | -C(12) | -C(1) | 111.0(8) |
| C(14) | -C(13) | -C(11) | 102(1) | C(15) | -C(13) | -C(11) | 119(1) |
| C(15) | -C(13) | -C(14) | 110(1) | C(18) | -C(13) | -C(11) | 117.9(9) |
| C(18) | -C(13) | -C(14) | 107(1) | C(18) | -C(13) | -C(15) | 101.4(8) |
| O(2) | -C(14) | -O(1) | 121(2) | C(13) | -C(14) | -O(1) | 110(1) |
| C(13) | -C(14) | -O(2) | 129(1) | C(16) | -C(15) | -C(13) | 103.4(9) |
| C(17) | -C(16) | -C(15) | 100.2(9) | C(21) | -C(16) | -C(15) | 107.0(9) |
| C(21) | -C(16) | -C(17) | 100.9(8) | C(18) | -C(17) | -C(16) | 94.6(9) |
| C(17) | -C(18) | -C(13) | 101.1(9) | C(19) | -C(18) | -C(13) | 116(1) |
| C(19) | -C(18) | -C(17) | 118(1) | C(20) | -C(18) | -C(13) | 102(1) |
| C(20) | -C(18) | -C(17) | 99(1) | C(20) | -C(18) | -C(19) | 118(1) |
| C(21) | -C(20) | -C(18) | 107(1) | C(29) | -C(20) | -C(18) | 126(1) |
| C(29) | -C(20) | -C(21) | 127(1) | C(20) | -C(21) | -C(16) | 109(1) |
| C(22) | -C(21) | -C(16) | 125.1(9) | C(22) | -C(21) | -C(20) | 126(1) |
| C(23) | -C(22) | -C(21) | 111.5(9) | C(24) | -C(22) | -C(21) | 112(1) |
| C(24) | -C(22) | -C(23) | 111.9(9) | C(25) | -C(24) | -C(22) | 115.2(9) |
| C(26) | -C(25) | -C(24) | 113.9(9) | C(27) | -C(26) | -C(25) | 117(1) |
| C(32) | -C(26) | -C(25) | 116.3(9) | C(32) | -C(26) | -C(27) | 106.5(8) |
| C(28) | -C(27) | -C(26) | 115.2(9) | C(29) | -C(27) | -C(26) | 114.9(8) |
| C(29) | -C(27) | -C(28) | 108(1) | C(30) | -C(27) | -C(26) | 101.0(9) |
| C(30) | -C(27) | -C(28) | 108.3(8) | C(30) | -C(27) | -C(29) | 108.8(8) |
| C(27) | -C(29) | -C(20) | 115.5(9) | C(31) | -C(30) | -C(27) | 103.8(9) |
| C(32) | -C(31) | -C(30) | 106.0(9) | C(31) | -C(32) | -C(26) | 104.6(9) |
| C(33) | -C(32) | -C(26) | 122(1) | C(33) | -C(32) | -C(31) | 115(1) |
| C(34) | -C(33) | -C(32) | 114(1) | C(35) | -C(33) | -C(32) | 112(1) |
| C(35) | -C(33) | -C(34) | 110(1) | | | | |

using an Ultraturrax homogenizer (3 x 800 ml). The resultant crude extract (8.75 g) was chromatographed over $SiO_2$ (Kieselgel 60, 0.063 - 0.200 mm, Merck), using a n-hexane - EtOAc gradient (0 - 70% EtOAc). 32 Fractions of 250 ml were collected, which, after DC-monitoring were combined to give 9 fractions. Compound 1 and 2, together with some minor products, were found in fraction 4. Fraction 4 was rechromatographed on $SiO_2$ using a n-hexane - EtOAc gradient (1 - 7% EtOAc). 16 Fractions of 150 ml were collected and combined to give 7 fractions (4.1 - 4.7). Both 1 and 2 were found in fraction 4.4, corresponding to 5% EtOAc in n-hexane.

Fraction 4.4 (254 mg) was finally separated by HPLC, eluent 2% EtOAc in n-hexane, to afford 1, named plagiospirolide A, crystallizing as colourless needles, and the major constituent 2, named plagiospirolide B, as a colourless, viscous oil.

Table 4. Position Parameters and B-Values of the Atoms of 1.

| Atom | x | y | z | B[Å²] |
|---|---|---|---|---|
| O(1) | 0.324(1) | 0.0994(8) | 0.2244(3) | 5.7(6) |
| O(2) | 0.161(2) | 0.206(1) | 0.1859(3) | 8.2(8) |
| C(1) | 0.790(2) | 0.180(1) | 0.2658(4) | 4.2(3) |
| C(2) | 0.900(2) | 0.262(1) | 0.2897(4) | 5.1(3) |
| C(3) | 0.992(2) | 0.354(1) | 0.2688(4) | 5.9(3) |
| C(4) | 0.919(2) | 0.253(1) | 0.3296(5) | 6.8(4) |
| C(5) | 0.829(3) | 0.166(1) | 0.3530(5) | 8.1(4) |
| C(6) | 0.740(2) | 0.077(1) | 0.3293(4) | 5.9(4) |
| C(7) | 0.643(2) | 0.1217(9) | 0.2914(3) | 4.4(6) |
| C(8) | 0.487(2) | 0.197(1) | 0.3042(4) | 5.8(3) |
| C(9) | 0.574(3) | 0.027(1) | 0.2689(4) | 5.4(3) |
| C(10) | 0.513(2) | 0.0513(9) | 0.2239(4) | 4.3(3) |
| C(11) | 0.627(2) | 0.1326(9) | 0.2024(3) | 3.5(2) |
| C(12) | 0.702(2) | 0.2240(9) | 0.2279(3) | 3.6(3) |
| C(13) | 0.490(2) | 0.1755(9) | 0.1711(3) | 4.0(7) |
| C(14) | 0.305(3) | 0.167(1) | 0.1938(4) | 6.(1) |
| C(15) | 0.517(2) | 0.2944(9) | 0.1546(4) | 4.6(3) |
| C(16) | 0.534(2) | 0.2774(8) | 0.1094(3) | 3.5(2) |
| C(17) | 0.381(2) | 0.194(1) | 0.1026(4) | 4.2(3) |
| C(18) | 0.467(2) | 0.1067(9) | 0.1303(4) | 4.0(7) |
| C(19) | 0.371(2) | 0.000(1) | 0.1340(4) | 5.7(3) |
| C(20) | 0.666(2) | 0.1081(8) | 0.1135(3) | 3.3(6) |
| C(21) | 0.702(2) | 0.2086(9) | 0.1027(3) | 3.5(6) |
| C(22) | 0.889(2) | 0.2510(8) | 0.0883(3) | 3.2(2) |
| C(23) | 0.932(2) | 0.366(1) | 0.1058(4) | 5.0(3) |
| C(24) | 0.906(2) | 0.2492(9) | 0.0433(3) | 3.7(2) |
| C(25) | 0.856(2) | 0.1392(9) | 0.0233(3) | 3.7(2) |
| C(26) | 0.949(2) | 0.0408(8) | 0.0423(3) | 3.3(2) |
| C(27) | 0.828(2) | -0.0323(8) | 0.0689(3) | 3.1(5) |
| C(28) | 0.644(2) | -0.0655(9) | 0.0509(4) | 3.9(3) |
| C(29) | 0.792(2) | 0.0128(9) | 0.1113(3) | 3.4(2) |
| C(30) | 0.951(2) | -0.1357(9) | 0.0722(3) | 4.1(3) |
| C(31) | 1.024(2) | -0.1524(9) | 0.0300(3) | 4.2(3) |
| C(32) | 1.057(2) | -0.0379(9) | 0.0131(3) | 3.7(2) |
| C(33) | 1.041(2) | -0.028(1) | -0.0315(4) | 5.3(3) |
| C(34) | 0.845(2) | -0.049(1) | -0.0476(5) | 6.4(3) |
| C(35) | 1.177(2) | -0.100(1) | -0.0531(5) | 6.9(4) |

**Plagiospirolide A (1)** (13 mg) was recrystallized from n-hexane (m.p., 197°C ±1°). GC: $C_{15}$-moiety RT 11.87 min, $C_{20}$-moiety RT 14.02 min. UV $\lambda_{max}$ nm, ($\epsilon$): 188.3 (7318.5).

Optical rotation $\frac{[nm]}{[\alpha]^{20}}$ = $\frac{589 \quad 578 \quad 546 \quad 436 \quad 365}{411.9 \quad 44.7 \quad 50.8 \quad 96.1 \quad 173.6}$ (c = 0.36)

IR $\nu_{max}^{KBr}$ [cm$^{-1}$]: 800 (s), 942 (w), 973 (m), 992 (w), 1015 (s), 1035 (s), 1078 (s), 1105 (w), 1130 (w), 1142 (w), 1160 (s), 1173 (w), 1181 (w), 1199 (m), 1224 (m), 1263 (s), 1291 (w), 1346 (w), 1377 (m), 1391 (m), 1425 (w), 1465 (s), 1750 (s), 2940 (s).

GC-EIMS: m/e (rel. int.) $C_{15}$-fragment: 232 ($M^{(+)}$, 42), 217 (100), 199 (5),

178 (7), 171 (33), 161 (10), 145 (21), 131 (19), 121 (23), 105 (24), 91 (24), 79 (21).

$C_{20}$-fragment: 272 ($M^{(+)}$, 25), 229 (12), 177 (13), 147 (6), 135 (100), 122 (64), 107 (22), 95 (31), 91 (17).

$^{13}C$-NMR, $\delta_C$ [ppm]: 182.0 (C-12, s), 150.2 (C-15, s), 140.1 (C-25, s), 133.4 (C-4, s), 122.2 (C-3, d), 76.7 (C-8, d), 61.8 (C-11, d), 52.1 (t), 48.0 (d), 47.3 (d), 46.0 (s), 44.3 (d), 43.8 (d), 41.6 (C-9?, t), 40.0 (t), 39.8 (d), 37.9 (t), 36.8 (t), 36.6 (t), 30.7 (C-10,s) 30.1 (d), 29.7 (t), 28.4 (d), 25.8 (t), 24.0 (t), 23.4 (C-29,q), 22.2 (t), 21.4 (q), 20.9 (q), 20.7 (t), 18.9 (q), 18.7 (q), 17.2 (C-28?, q), 16.4 (q).

For $^1H$-NMR data see table 1.

**Plagiospirolide B (2)**: (86 mg). GC: $C_{15}$-moiety: RT 11.69 min, $C_{20}$-moiety: RT 14.02 min. UV $\lambda_{max}$ nm ($\epsilon$) 192.2 (15647.3).

Optical rotation $\frac{[nm]}{[\alpha]^{20}}$ = $\frac{589 \quad 578 \quad 546 \quad 436 \quad 365}{59.2 \quad 62.1 \quad 71.7 \quad 135.1 \quad 245.3}$ (c = 1.176).

IR: $\nu_{max.}^{liq.}$ [$cm^{-1}$]: 703 (w), 738 (s), 800 (v), 818 (v), 890 (w), 902 (m), 926 (m), 960 (m), 973 (m), 995 (m), 1010 (w), 1040 (m), 1075 (s), 1108 (m), 1130 (w), 1160 (s), 1190 (m), 1220 (s), 1270 (m), 1290 (m), 1350 (m), 1378 (m), 1392 (m), 1465 (s), 1760 (s), 2940 (s).

GC - HR-EIMS: m/e (dev., rel. int., comp): $C_{15}$-moiety: 232.1439 (+2.4, 33, $C_{15}H_{20}O_2$), 217.1208 (+2.0, 100, $C_{14}H_{17}O_2$), 199.1146 (-2.3, 5, $C_{14}H_{15}O$), 181.1026 (-0.9, 3, $C_{14}H_{13}$) 171.1199 (-2.6, 31, $C_{13}H_{15}$), 161.0602 (±0,9, $C_{10}H_9O_2$), 145.1001 (+11.6, 16, $C_{11}H_{13}$), 121.0999 (+1.8, 17, $C_9H_{13}$), 105.0687 (+1.7, 18, $C_8H_9$), 91.0532 (+1.6, 17, $C_7H_7$), 79.0505 (+4.3, 11, $C_6H_7$).

$C_{20}$-moiety: 272.2505 (-0.1, 36, $C_{20}H_{32}$), 229.1948 (+0.9, 13, $C_{17}H_{25}$), 177.1613 (+3.0, 12, $C_{13}H_{21}$), 147.1155 (+1.9, 6, $C_{11}H_{15}$), 135.1158 (+1.5, 100, $C_{10}H_{15}$), 122.1074 (+2.2, 61, $C_9H_{14}$), 119.0859 (+0.2, 12, $C_9H_{11}$), 107.0833 (+2.7, 24, $C_8H_{11}$) 105.0690 (+1.5, 21, $C_8H_9$), 95.0857 (+0.4, 24, $C_7H_{11}$) 91.0530 (+1.8, 17, $C_7H_7$), 79.0513 (+3.5, 7, $C_6H_7$). CIMS: m/e (rel. int.): 505 ($M^{(+1)}$, 1), 465 (12), 329 (4), 273 (100), 233 (97), 217 (2), 135 (3).

$^{13}C$-NMR $\delta_C$ [ppm]: 182.7 (C-12, s), 149.8 (C-15, s), 140.5 (C-25, s), 132.1 (C-4, s), 126.3 (C-5, s), 76,1 (C-8, d), 61.6 (C-11?, s), 58.5 (s), 51.3 (t), 48.0 (d), 47.2 (d), 46.1 (s), 43.1 (C-9, t), 42.8 (d), 41.6 (t), 40.4 (d), 40.1 (t), 37.6 (t), 37.5 (t), 36.8 (C-3, t), 33.4 (C-10, s) 32.1 (C-1, t), 30.2 (d), 28.4 (d), 26.8 (C-29, q), 26.1 (t), 24.0 (t), 23.4 (q), 21.4 (q), 20.6 (t), 19.1 (C-28, q), 18.9, (C-33x, q), 18.7 (C-2), t), 18.5 (C-30x, q) 14.7 (q). The "x"-labelled numbers may be exchanged.Table 4.

For $^1H$-NMR data see table 1.

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