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NEW DITERPENES FROM CHILIOTRICHIUM ROSMARINIFOLIUM AND NARDOPHYLLUM LANATUM

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Abstract – From the aerial parts of Chiliotrichium rosmarinifolium in addition to known compounds nine diterpenes were isolated, three isolabdanes, three seco-isolabdanes, a cis-clerodane, a rearranged dilactone and a geranyl geraniol derivative. The aerial parts of Nardophyllum lanatum gave two of the new diterpenes and three further diterpenes which are closely related to those of the Chiliotrichium species. Furthermore two new geranyl geraniol derivatives were present. The structures were elucidated by highfield NMR spectroscopy.

The small genera Chiliotrichium and Nardophyllum (Compositae, tribe Astereae) are native in South America, south of the tropics. So far nothing is known about the chemistry of these genera. We therefore have studied the aerial parts of Chiliotrichium rosmarinifolium Less. and Nardophyllum lanatum (Meyen) Cabrera. In addition to large amounts of oleanolic acid we have isolated from the former δ-cadinene, dammadienyl acetate, pinoresinol and nine new diterpenes (1 - 3 and 7 - 12) while in the latter the diterpenes 3 - 6, 13 and 14 were present. Compounds 3, 4 and 11 were transformed to their methyl esters.

The structure of 1, which we have named 3α,5α-dihydroxychiliolide, followed from the spectral data. In the mass spectrum the highest ion was m/z 330 corresponding to $C_{20}H_{26}O_4$ but by chemical ionization the M + 1-ion indicated that the molecular formula was $C_{20}H_{28}O_5$. The ^{13}C NMR data (Table II) indicated the presence of a furano diterpene with a lactone carbonyl carbon and three further oxygen bearing carbons. This also followed from the ^1H NMR spectrum (Table I) where all signals could be assigned by spin decoupling and by NOE difference spectroscopy which established the stereochemistry. Thus clear effects were observed between the lowfield double doublet at δ = 4.85 (H-12) and H-1β, between H-18, H-19, H-6α and 5-OH, between H-8 and H-11', between H-10, H-11 and H-19, between 3-OH, H-1α, H-19 and 5-OH as well as between 5-OH and H-7α. An interesting fact is the position of the lactone carbonyl band at 1740 cm^{-1}. This is most likely due to a hydrogen bond with 5-OH which further is hydrogenbonded with 3-OH. Accordingly, a large coupling $J_{3,OH}$ is visible. All data indicated that 1 is member of the rare isolabdanes [1], which are rearranged labdanes.

The ^1H NMR spectra of 2 and 3a were similar (Table I), however, 2, showed a signal of an aldehyde proton. Again by spin

decoupling most signals could be assigned. While many signals of 2 and the corresponding acid 3 were similar to those of 1 the presence of seco-compounds followed from the signals of two olefinic methyl groups. Most likely 2 is biogenetically formed by fragmentation as shown in the Scheme. We therefore have named this compound seco-chiliolide aldehyde.

The ^{1}H NMR spectrum of 5 (Table I) was close to that of 3a. However, one of the olefinic methyl signals was replaced by a pair of doublets at $\delta = 4.19$. Accordingly, 5 was a hydroxy derivative of 3a. The position was determined by NOE difference spectroscopy. Clear effects between H-18, H-2, H-10 and H-19 as well as between H-19 and H-6 excluded an other possibility. Furthermore the configuration of all chiral centers was established by NOE's between H-10, H-8, H-11 and H-12. The ^{13}C NMR data nicely agreed with the structure. The data of 4 showed that this diterpene was the corresponding acid. Thus esterification yielded 5.

The ^{1}H NMR spectrum of 6 (Table I) again was in part similar to that of 3a. However, a different situation at C-5 was indicated by the typical signals of a isopropenyl group. The ^{13}C NMR signals at $\delta = 170.9$ and 176.4 required two lactone rings as an acid derivative could be excluded. All data therefore agreed with the presence of the dilactone 6. The stereochemistry was assigned by NOE difference spectroscopy. Clear effects were observed between H-17, H-11 and H-7β, between H-8, H-11, H-10 and H-6β, between H-12 and H-1β as well as between H-18 and H-10. The latter effect indicated a cis-fused δ-lactone. This also followed from the small couplings of H-10. The dilactone 6 we have named seco-chiliolide lactone.

The spectral data of 7 indicated that this diterpene was closely related to 1. From a signal of an olefinic proton in the ^{1}H NMR spectrum (Table I) the presence of a 5,6-double bond could be deduced which was established by spin decoupling. Thus an allylic coupling of H-10 with the olefinic proton was observed which was further coupled with protons which themselves coupled with H-8 and the latter with H-17 as followed by decoupling. The stereochemistry was determined by NOE difference spectroscopy. Clear effects were observed between H-10, H-11', H-12 and H-19, between H-18, H-3, H-6α and H-19, between H-19, H-3, H-10 and H-18 as well as between H-12 and H-1β. The ^{13}C NMR data supported the structure (Table II). Oxidation of 7 gave the corresponding ketone. The observed Cotton effect supported the proposed absolute configuration.

The structure elucidation of 8 was more difficult. Again in the ^{1}H NMR spectrum (Table I) several signals were close to those of 1 indicating the presence of a further isolabdane with a furan ring. However, several couplings and chemical shifts differed typically. Furthermore spin decoupling indicated the absence of H-10 and the molecular formula ($C_{20}H_{26}O_5$) required an additional ring. The presence of an epoxide was established by the ^{13}C NMR data (Table II) which clearly showed in addition to signals for furan and carbonyl carbons four signals for oxygen bearing carbons. Spin decoupling showed that a 5,10-epoxide was present. Comparison of the chemical shift with those of similar compounds indicated that a 5β,10β-epoxide was most likely. Accordingly, the signals of H-3β and H-8β were shifted downfield. The ^{13}C shifts supported this proposal. As in related cases the β-epoxide caused an upfield shift of C-3 and C-8 [2]. NOE difference spectroscopy established the configuration at C-3, C-8, C-9 and C-12. In the mass spectrum a characteristic fragmentation pattern was observed. In addition to the fragments m/z 81 and 94, which are typical for the side chain moiety, m/z 168 most likely is formed by RDA of the isomerized epoxide (10-hydroxy,5,6-double bond). Elimination

of water then leads to the base peak m/z 150.

The ^{1}H NMR spectrum of 9 (Table I) indicated that again a furoditerpene with a lactone ring was present while the molecular formula was identical with that of 7. However, the IR spectrum showed that 9 had no hydroxy group. From a slightly broadened doublet at δ = 3.01 the presence of an epoxide was proposed. All signals could be assigned by spin decoupling. The sequences thus obtained showed that we were dealing with a clerodane with a 3,4-epoxide group. From the couplings observed and from NOE difference spectroscopy the stereochemistry could be deduced. The presence of a cis-decaline followed from the W-coupling between H-6β and H-10. This was supported by the observed NOE between H-10 and H-12. Further NOE's between H-8, H-11 and H-19, between H-18, H-3 and H-6β, between H-19, H-6β, H-7β, H-8 and H-11' as well as between H-17, H-11 and H-14 indicated the configuration at C-5, C-8, C-9 and C-12 and a boat conformation for ring B which also followed from the couplings $J_{7,8}$ (9 and 6.5 Hz). The presence of a 3β,4β-epoxide was further supported by the coupling $J_{2\alpha,3}$. The ^{13}C NMR data (Table II) agreed with the structure of 9 which we have named chiliomarin.

Compound 10, molecular formula $C_{20}H_{24}O_5$, showed a very strong IR band at 1780 cm^{-1} which was an indication that two γ-lactone rings may be present. This was supported by the ^{13}C NMR spectrum (Table II) which showed two singlets for carbonyl carbons at 178.3 and 174.0 ppm. Furthermore in addition to the signals of a β-substituted furan ring a singlet at 91.9 and a doublet at 70.6 were present. While the latter is typical for C-12 in diterpene lactones like 1 - 3 and 7 - 9 the chemical shift of the former indicated a carbon which must have several highly substituted neighbouring carbons. The ^{1}H NMR spectrum (Table I) again was in part similar to those of 8 and 9. Spin decoupling showed that no proton was at C-10. The changed situation of ring A was obvious as only two neighbouring methylene groups were present. As three signals for methyl groups were visible a dilactone needed a rearranged carbon skeleton. Biogenetic considerations led to the structure 10 which was established by NOE difference spectroscopy. Thus clear effects were observed between H-19, H-1β, H-7β and H-11, between H-18 and H-2β, between H-17, H-6α, H-7α and H-8 as well as between H-11, H-1β and H-12. These effects led to the proposed stereochemistry with ring B in a chair conformation which also followed from the small vicinal couplings of H-8. We have named the diterpene 10 isochiliolide lactone.

The spectral data of 11a (Tables I and II) were in part close to those of 3a. The absence of the lactone ring followed from the ^{1}H NMR data. A broadened double doublet for two protons at δ = 2.28 (H-12) was sharpened on irradiation of H-16 and was coupled with a pair of double doublets at δ = 1.58 and 1.42 (H-11). Furthermore an additional methyl singlet at δ = 0.97 was due to H-20. The couplings of H-8 indicated that ring B was in a boat conformation. NOE difference spectroscopy established the configurations. Clear effects were observed between H-1, H-10 and H-17, between H-20 and H-12 as well as between H-8 and H-12. The ^{13}C NMR data and the fragmentation pattern in the mass spectrum fully agreed with the proposed structure. Especially m/z = 237 surely was formed by fission of the 9,11-bond. Thus 11, which we have named seco-chiliotrin, was the only diterpene which had no lactone carbonyl at C-20. Surely it is formed by fragmentation of a diterpene corresponding to 1.

The diterpenes 1 - 10 are all biogenetically closely related. The diol 1 could be transformed by elimination of water to 7 or the $\Delta^{5(10)}$-isomer which was isolated as its epoxide 8. The corresponding triol most

likely is the precursor of 10. Protonation of the 5α-hydroxy group would lead to a cation which by migration of a methyl group from C-4 to C-5 followed by migration of C-2 to C-4 would give a carbonyl group at C-4 which could react with the 10-hydroxy group to give the dilactone 10. Allylic oxydation of 3 would lead to 4 and an addition elimination reaction of 4 could be a reasonable pathway for the biogenesis of 6. If the application of the octant rule is valid for 7 the proposed absolute configuration is very likely for all the furoditerpenes. Especially as most diterpenes in the tribe have this configuration [3].

The ^{1}H NMR data of 12 clearly showed that an acetoxy methylene and two hydroxy methylene groups were present. Three signals for olefinic methyls and for four olefinic protons showed that a geranyl geraniol derivative was present. However, the relative position of the oxygen functions and the stereochemistry could not be deduced directly from the ^{1}H NMR data. Spin decoupling allowed the assignment of most signals. The chemical shift of H-20 and H-17 indicated the presence of a 2E,14Z-configuration. The position of the acetoxy group could be determined by spin decoupling. The signals of the olefinic protons were assigned by their chemical shifts. Starting with the signal of H-14 those of H-13 and H-12 could be assigned. As the latter showed an allylic coupling with the olefinic proton next to the acetoxymethylene group the position of that group was settled. A NOE between H-18 and H-9 further indicated a 10Z-configuration. Thus 12 was 17-hydroxy-18-acetoxygeranyl geraniol.

The ^{1}H NMR spectra of 14 showed that this diterpene was the acetate of 13. The structure of the latter could be deduced by systematic spin decoupling which allowed the assignment of most signals. The presence of an α-substituted butenolide ring followed from the typical ^{1}H NMR signals (δ = 4.78 dt (2H) and 7.12 tt). The chemical shift of the olefinic methyl indicated a Δ^{14} double bond. The configuration followed from a NOE between the methyl and the olefinic proton. The presence of an acetoxy group caused a downfield shift of one of the secondary methylene groups. The position of this group was determined by spin decoupling. Starting with H-14, H-13, H-12 and H-11 could be assigned. In ^{13}C NMR data also supported the structure. The spectrum of 14 mainly differed from that of 13 by the chemical shift of H-19 which now was identical with that of H-18.

The cooccurrence of unusual seco-diterpenes in Chiliotrichium and in Nardophyllum strongly supports a close relationship. So far these genera have been placed in different subtribes (Solidagiinae and Asterinae) [4]. However, the separation of the tribe into subtribes still is one of the main problems in this tribe [5].

EXPERIMENTAL

IR spectra were recorded in $CHCl_3$ on a Beckmann IR 4230 instrument, the NMR spectra on a Bruker WM 400 and EIMS were obtained at 70 eV with a Varian MAT 711. TLC were performed on Si gel, PF 254 and HPLC by using RP 8 columns, flow rate ca. 3 ml/min. and ca. 100 bar. Plant material was collected in February 1985 in Argentina. The air dried material was extracted with methanol/ether/petrol ether, 1 : 1 : 1, and after separation of saturated long chain hydrocarbons by treatment with methanol the obtained extracts were separated first by column chromatography (CC). Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

The extract of Chiliotrichium rosmarinifolium (300 g aerial parts, voucher RMK 9399, US National Herbarium, Washington) gave by CC four crude fractions (1: ether/petrol ether (= E/P), 1 : 9; 2: E/P, 1 : 3;

3: E/P, 1 : 1 and 4: E). TLC of fraction 1 (E/P, 1 : 9) gave 9 mg δ-cadinene and 70 mg dammadienyl acetate. TLC of fraction 2 (E/P, 1 : 3) gave 39 mg 11 (R_f 0.55) which was purified as its methyl ester 11a (CH_2N_2 in ether) (TLC E/P, 1 : 9).
Fraction 3 gave 320 mg crystalline oleanolic acid. TLC of the mother liquor (E/P, 3 : 7) afforded 65 mg oleanolic acid and a mixture which was separated by HPLC (MeOH/H_2O, 4 : 1) yielding 7 mg 2 (R_t 4 min.) and 5 mg 3 (R_t 4.5 min.). TLC of fraction 4 (E/P, 1 : 1) gave two bands. The less polar band gave by HPLC (MeOH/H_2O, 17 : 3) 7 mg 9 (R_t 2.5 min.) and 42 mg 7 (R_t 2.75 min.). The polar band gave by repeated TLC (E/P, 4 : 1) two bands (4/2/1 and 4/2/2). TLC of 4/2/1 (C_6H_6/acetone, 9 : 1) gave two bands (4/2/1/1 and 4/2/1/2). Fraction 4/2/1/1 gave by HPLC (MeOH/H_2O, 17 : 3) 2 mg 8 (R_t 2.5 min.) and 4/2/1/2 gave by HPLC (MeOH/H_2O, 4 : 1) 10 mg 12 (R_t 3.7 min.). HPLC of 4/2/2 (MeOH/H_2O, 17 : 3) gave 7 mg pinoresinol (R_t 1.7 min.), 5 mg 1 (R_t 2 min.) and 15 mg 10 (R_t 3 min.).

The extract of 400 g of aerial parts of Nardophyllum lanatum (voucher RMK 9420) was separated by CC affording three polar fractions (1: E/P, 1 : 1; 2: E and 3: E/MeOH, 9 : 1). TLC (E/P, 1 : 1) gave 10 mg 3 and 2 mg 7. TLC of fraction 2 (E) gave 95 mg 5 (R_f 0.65) and mixtures which were separated by HPLC (MeOH/H_2O, 3 : 2) affording 2.5 mg 14 (R_t 8 min.), 12 mg 6 (R_t 6 min.) and 7 mg 13 (R_t 4 min.). TLC (E) of fraction 3 gave 7 mg 4 (R_f 0.2) which gave after addition of CH_2N_2 5, identical with the natural ester.

3α,5α-Dihydroxychiliolide (1). Colourless crystalls, mp. 207°; IR ν_{max} cm^{-1}: 3410 (OH), 1740 (hydrogen bonded lactone CO), 880 (furan); EIMS m/z: 330 M - H_2O (34), 302 (28), 249 (24), 218 (12), 203 (30), 82 (100); CIMS m/z: 349 M + 1 (100); $\alpha_D^{24°}$ = + 22 ($CHCl_3$, c = 0.48).

Seco-chiliolide aldehyde (2). Colourless oil; IR ν_{max} cm^{-1}: 1770 (γ-lactone), 1725 (CHO); EIMS m/z: 330.183 M^+ (20) ($C_{20}H_{26}O_4$), 236 M - C_6H_6O (36), 193 (50), 179 (52), 149 (80), 95 (100), 81 (80); $\alpha_D^{24°}$ = + 13 ($CHCl_3$, c = 0.12).

Seco-chiliolide acid (3). Colourless oil; IR ν_{max} cm^{-1}: 3500 - 2600, 1720 (CO_2H), 1770 (γ-lactone), 880 (furan); EIMS m/z: 346.178 M^+ (40) ($C_{20}H_{26}O_5$), 328 (40), 300 (31), 234 (44), 95 (100), 81 (83); $\alpha_D^{24°}$ = + 14 ($CHCl_3$, c = 0.35); addition of CH_2N_2 in ether gave 3a, colourless oil; ^1H NMR s. Table I.

19-Hydroxy-seco-chiliolide acid methyl ester (5). Colourless oil; IR ν_{max} cm^{-1}: 3610 (OH), 1765 (γ-lactone), 1740 (CO_2R), 890 (furan); EIMS m/z: 376.189 M^+ (3.5) ($C_{21}H_{28}O_6$), 358 M - H_2O (27), 246 (62), 95 (100).

Seco-chiliolide lactone (6). Colourless oil; IR ν_{max} cm^{-1}: 1770 (γ-lactone), 1740 (γ-lactone), 880 (furan); EIMS m/z: 344.162 M^+ (40) ($C_{20}H_{24}O_5$), 326 M - H_2O (18), 303 M - CH_2=CMe (46), 232 326 - vinylfuran (40), 95 (100); $\alpha_D^{24°}$ = + 23 ($CHCl_3$, c = 0.73).

3α-Hydroxy-5,6-dehydrochiliolide (7). Amorphous solide; IR ν_{max} cm^{-1}: 3600 (OH), 1770 (γ-lactone), 880 (furan); EIMS m/z: 330.183 M^+ (2.5) ($C_{20}H_{26}O_4$), 312 (5), 267 (30), 218 (35), 96 (100), 81 (62); $\alpha_D^{24°}$ = + 58 ($CHCl_3$, c = 0.9).
10 mg 7 in 3 ml Et_2O were stirred for 5 h with 150 mg MnO_2. TLC (E/P, 1 : 1) gave 3 mg of the corresponding 3-oxo-derivative. ^1H NMR ($CDCl_3$: 2.15 and 1.85 m (H-1), 2.60 and 2.50 ddd (H-2), 2.15 m (H-7β), 2.34 br ddd (H-7α), 1.85 m (H-8), 2.68 br d (H-10), 1.28 and 1.27 s (H-18, 19) (remaining signals as those of 7). CD (MeCN): $\Delta\varepsilon_{303}$ + 0.20, $\Delta\varepsilon_{296}$ + 0.22.

3α-Hydroxy-5β,10β-epoxychiliolide (8). Colourless oil; IR ν_{max} cm^{-1}: 3600 (OH),

1770 (γ-lactone); EIMS m/z: 346.178 M^+ (18) ($C_{20}H_{26}O_5$), 328 (18), 302 (20), 234 (50), 219 (26), 179 (30), 168 (70), 161 (74), 150 (100), 135 (38), 94 (65), 81 (52); CIMS: 347 M + 1 (100); $\alpha_D^{24°}$ = + 90 ($CHCl_3$, c = 0.17).

Chiliomarin (9). Colourless oil; IR ν_{max} cm^{-1}: 1765 (γ-lactone), 880 (furan); EIMS m/z: 330.183 M^+ (10) ($C_{20}H_{26}O_4$), 285 (16), 236 (16), 179 (50), 161 (62), 95 (100), 81 (80); $\alpha_D^{24°}$ = - 13 ($CHCl_3$, c = 0.72).

Isochiliolide lactone (10). Colourless, amorphous solid; IR ν_{max} cm^{-1}: 1780 (γ-lactone), 880 (furan EIMS m/z: 344.162 M^+ (10) ($C_{20}H_{24}O_5$), 300 (3), 95 (100); α_D = + 40 ($CHCl_3$, c = 0.26).

Seco-chiliotrin methyl ester (11a). Colourless oil; IR ν_{max} cm^{-1}: 1735 (CO_2R); 880 (furane); EIMS m/z: 332.235 M^+ (20) ($C_{21}H_{32}O_3$), 317 (4), 237 (80), 182 (38), 163 (36), 149 (50), 95 (58), 81 (100) $\alpha_D^{24°}$ = - 28 ($CHCl_3$, c = 4.1).

17-Hydroxy-18-acetoxygeranyl geraniol (12). Colourless oil; IR ν_{max} cm^{-1}: 3600 (OH), 1740 (OAc); CIMS m/z: 365 M + 1 (4), 347 (16), 329 (10), 287 (98), 269 (100); ^1H NMR (C_6D_6): 4.08 br d (H-1), 5.48 tq (H-2), 2.20 br t (H-4), 2.26 br q (H-5), 5.24 br t (H-6), 2.08 br t (H-8), 2.17 br q (H-9), 5.42 br t (H-10), 2.04 br t (H-12), 2.20 br q (H-13), 5.27 br t (H-14), 1.16 br s (H-16), 4.05 br s (H-17), 4.72 br s (H-18), 1.54 br s (H-19), 1.85 dt (H-20); J [Hz]: 1,2 = 4,5 = 5,6 = 8,9 = 9,10 = 12,13 = 13,14 7; 2,20 = 1.

17,19-Dihydroxy-18-acetoxy-6,7,10,11-tetrahydrogeranyl geraniol-20-acid lactone (13). Colourless oil; IR ν_{max} cm^{-1}: 3600 (OH), 1760 (γ-lactone), 1740 (OAc); EIMS m/z: 378.241 M^+ (28) ($C_{22}H_{24}O_5$), 363 (12), 360 (6), 95 (66), 55 (100); ^1H NMR ($CDCl_3$): 4.78 dt (H-1), 7.12 tt (H-2), 2.29 br t (H-4) 1.58 tt (H-5), 1.34 m (H-6, -8, -9), 1.49 m (H-7), 1.40 m (H-10, -12), 1.67 m (H-11), 5.29 br t (H-14), 1.79 dt (H-16), 4.14 and 4.08 br d (H-17), 4.00 and 3.95 dd (H-18), 3.52 d (H-19); J [Hz]: 1,2 = 1,4 = 2; 2,4 = 1.5; 7,19 = 11,18 = 13,14 ~ 7; 16,16' = 18,18' = 11.5; ^{13}C NMR: 20.2 t (C-1), 144.4 d (C-2), 134.2 s (C-3), 128.5 d (C-14), 134.5 s (C-15), 21.4 q (C-16), 174.5 s (C-20), 171.4, 21.0 (OAc), 66.9, 65.4, 61.5 t (C-17 - C-19), 31.4, 31.2, 30.9, 25.4, 24.9, 24.6, 23.8 t (CH_2): 39.7, 37.0 d (C-7, C-11).

Diacetate 14: Colourless oil; IR ν_{max} cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1740 (OAc); EIMS m/z: 438.262 M^+ (0.3) ($C_{24}H_{38}O_7$), 378 M - HOAc (6), 360 (10), 300 (8), 95 (100); ^1H NMR ($CDCl_3$) as 13 except 4.01 (H-18, -19), 3.95 dd (H-18', -19') J = 11,6 Hz.

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Table I. ^{1}H NMR spectral data of 1 - 10 and 11a (400 MHz, $CDCl_3$, TMS as internal standard)

	1(C_6D_6)$^+$	2	3a	5	6(C_6D_6)	7(C_6D_6)	8(C_6D_6)	9	10	11a$^+$
H-1α	1.98 m	2.16 m	2.23 m	2.02 m	1.30 br dd	1.95 m	1.70 ddd	1.84 ddd	1.90 ddd	1.96 dddd
H-1β	1.12 m				1.67 m	1.49 ddd	1.83 ddd	1.36 br d	2.11 ddd	1.79 dddd
H-2α	2.00 m	2.30 m	2.43 m	2.22 m	2.61 ddd	1.77 m	1.43 dddd	2.13 dddd	1.69 ddd	2.21 ddd
H-2β	1.71 m				2.26 br dd		1.30 dddd	1.74 dddd	1.82 ddd	2.09 ddd
H-3	3.62 dt	9.66 t	-	-	-	3.49 t	3.62 dd	3.01 br d	-	-
H-6α	1.84 dt	x	x	2.51 br dt	1.79 ddd	5.64 ddd	1.98 ddd	2.39 dddd	1.55 ddd	1.98 m
H-6β	1.09 ddd	x	x	2.22 m	1.37 ddd		1.60 ddd	1.52 dddd	1.21 m	2.34 m
H-7α	1.94 m	x	x	1.52 m	2.65 dddd	2.54 br dd	2.20 dddd	1.65 dddd	1.52 m	1.66 m
H-7β	1.16 dddd	x	x	1.72 m	1.05 dddd	1.86 ddt	1.10 dddd	1.76 m	1.80 m	1.38 dddd
H-8	0.84 ddq	x	x	1.72 ddq	0.90 ddq	1.44 ddd	1.50 ddq	1.96 ddq	1.97 ddq	1.52 ddq
H-10	1.37 dd	2.86 dd	2.93 dd	2.89 dd	1.50 m	2.14 ddd	-	1.36 dd	-	2.35 dd
H-11	1.74 dd	2.46 dd	2.46 dd	2.44 dd	1.92 dd	2.00 dd	2.49 dd	2.44 dd	2.79 dd	1.58 m
H-11'	1.60 dd	2.01 dd	2.01 dd	2.00 dd	1.58 dd	1.77 dd	1.83 dd	2.41 dd	2.24 dd	1.42 m
H-12	4.85 br t	5.37 br t	5.36 br t	5.34 dd	4.89 dd	5.22 br t	4.96 br t	5.33 br t	5.46 br t	2.28 br dd
H-14	6.04 dd	6.40 dd	6.40 dd	6.36 br s	6.19 br s	6.21 dd	6.14 dd	6.37 dd	6.36 dd	6.21 br s
H-15	7.07 dd	7.47 dd	7.47 dd	7.38 dd	7.10 dd	7.12 dd	7.06 dd	7.42 dd	7.42 dd	7.15 br s
H-16	7.13 dd	7.42 dd	7.42 dd	7.43 br s	7.21 br s	7.21 dd	7.12 dd	7.41 dd	7.44 dd	7.31 dd
H-17	0.75 d	1.36 d	1.36 d	1.30 d	0.80 d	1.00 d	0.83 d	1.00 d	1.25 d	1.03 d
H-18	1.44 s	1.67 d	1.72 d	1.77 d	1.50 br s	1.26 s	1.17 s	1.25 s	1.10 s	1.60 d
				4.17 d	5.34 br s					
H-19	0.80 s	1.72 br s	1.74 br s	4.12 d	4.86 br s	1.00 s	1.05 s	1.22 s	1.00 s	1.68 br s

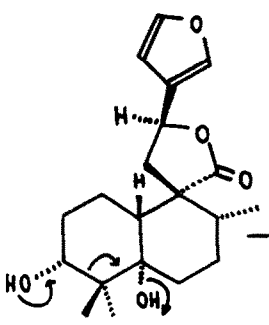
x) overlapping multiplets; +) OH 5.78 d, 5.77 s; +) H-20 0.97 s; OCH_3 3.63 s.

J [Hz]: 1α,10 = 12; 1β,10 = 3; 8,17 = 7; 11,11' = 14; 11,12 = 11',12 = 8.5; 14,15 = 15,16 ~ 1.5; 14,16 ~1; compound 1: 1α,10 = 13; 1β,10 = 3.5; 2,3 = 2',3 = 2.5; 3,OH = 10; 6α,6β = 6β,7α = 12.5; 6α,7α = 6α,7β = 3; 6β,7β = 3.5; 7α,7β = 12; 7α,8 = 13; 7β,8 = 3; compound 2: 2,3 = 1.7; compound 5: 6α,6β = 15; 6α,7α = 6α,7β = 4.5; 19,19' = 10; compound 6: 1α,1β = 15; 1α,2β = 9; 1β,2α = 10; 1α,10 ~ 1; 2α,2β = 19; 6α,6β = 6β,7α = 14; 6α,7α = 6α,7β 3; 6β,7β = 4; compound 7: 1α,1β = 1α,10 = 13; 1β,2α = 1β,2β = 3.5; 2α,3 = 2β,3 = 2.5; 6,7β = 7β,8 = 5; 6,10 = 7β,10 = 1.5; 7α,7β = 18; 7α,8 = 9; compound 8: 1α,1β = 14; 1α,2α = 8; 1α,2β = 2; 1β,2α = 11; 1β,2β = 8.5; 2α,2β = 13; 2α,3 = 12; 2β,3 = 4; 6α,6β = 14; 6α,7α = 6; 6α,7β = 2; 6β,7α = 6β,7β = 6.5; 7α,7β = 7α,8 = 13; 7β,8 = 3; compound 9: 1α,1β = 1α,2β = 1α,10 = 12.5; 1α,2α = 1β,2α = 1β,2β ~ 4; 2α,2β = 13.5; 2α,3 = 3; 6α,6β = 13; 6α,7α = 7; 6α,7β = 6; 6α,19 ~ 1; 6β,7α = 3; 6β,7β = 7.5; 6β,10 = 1; 7α,7β = 13; 7α,8 = 9; 7β,8 = 6.5; compound 10: 1α,1β = 2α,2β = 13; 1α,2α = 9; 1α,2β = 1β,2α = 4; 1β,2β = 10; 6α,6β = 13.5; 7α,8 = 2; 7β,8 = 4; compound 11a: 1,1' = 13; 1,2 = 9.5; 1,2' = 6.5; 1,10 = 3; 1',2 = 5.5; 1',2' = 9; 1',10 = 12.5; 2,2' = 16; 6α,7β = 6β,7β = 4; 7α,7β = 13.5; 7β,8 = 4.

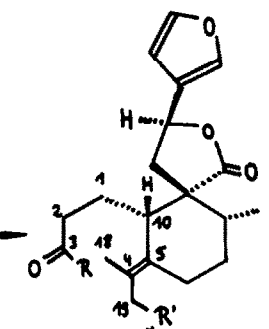
Table II. ^{13}C NMR spectral data of 1 and 5 - 11[+] ($CDCl_3$, 100.6 MHz)

	1	5	6	7	8	9	10	11
C-1	25.1 t	25.6 t	18.9 t	23.0 t	25.8 t	25.6 t	27.9 t	25.2 t
C-2	29.6 t	32.5 t	43.8 t	28.7 t	26.2 t	25.7 t	28.3 t	33.3 t
C-3	77.3 d	173.8 s	170.9 s	75.9 d	71.9 d	60.6 d	50.7 s	180.0 s
C-4	41.0 s	133.4 s	147.5 s	41.4 s	39.4 s	62.7 s	174.0 s	125.8 s
C-5	77.2 s	131.5 s	85.4 s	139.4 s	66.5 s	36.5 s	48.6 s	131.2 s
C-6	31.6 t	20.8 t	25.0 t	121.5 d	25.7 t	25.3 t	24.7 t	20.8 t
C-7	18.6 t	29.9 t	24.9 t	31.5 t	25.5 t	21.4 t	23.7 t	29.5 t
C-8	40.4 d	36.1 d	39.9 d	34.7 d	35.1 d	33.3 d	36.9 d	35.6 d
C-9	53.6 s	51.8 s	50.2 s	51.0 s	54.1 s	52.7 s	54.5 s	39.9 s
C-10	45.9 d	41.8 d	41.8 d	42.6 d	73.9 s	51.0 d	91.9 s	46.1 d
C-11	43.0 t	44.9 t	35.8 t	42.8 t	38.4 t	46.4 t	39.2 t	42.0 t
C-12	74.1 d	70.5 d	71.6 d	71.0 d	71.1 d	70.9 d	70.6 d	19.6 t
C-13	124.1 s	124.0 s	125.3 s	126.3 s	125.9 s	125.3 s	126.1 s	124.8 s
C-14	108.0 d	108.3 d	108.0 d	108.6 d	108.5 d	108.2 d	107.9 d	111.0 d
C-15	144.2 d	143.9 d	144.2 d	144.1 d	144.1 d	143.9 d	144.3 d	142.5 d
C-16	139.5 d	139.9 d	139.4 d	139.6 d	139.5 d	139.4 d	138.9 d	138.3 d
C-17	17.2 q	15.7 q	16.8 q	17.4 q	16.9 q	18.1 q	15.5 q	17.2 q
C-18	24.0 q	16.9 q	19.7 q	27.6 q	20.8 q	29.7 q	16.7 q	20.7 q
C-19	20.9 q	63.1 t	113.9 t	25.7 q	16.6 q	20.5 q	9.2 q	20.3 q
C-20	181.7 s	176.9 s	176.4 s	176.6 s	176.5 s	176.7 s	178.3 s	21.0 q

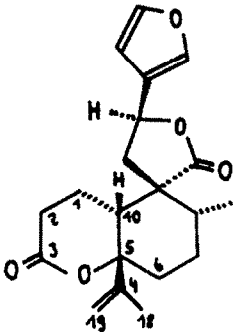
[+] Signals were assigned by comparison with the values of similar compounds and by 2 D techniques but some signals may be interchangeable.



1



2 R=R'= H 3* R = OH, R' = H
4 R = R' = OH 5 R = OMe, R' = OH



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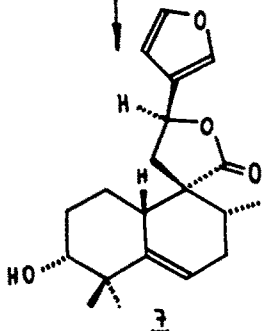
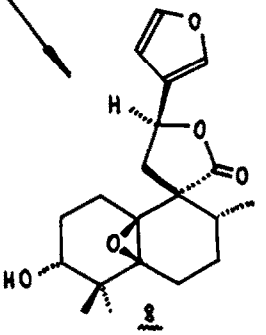
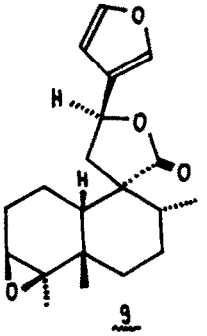


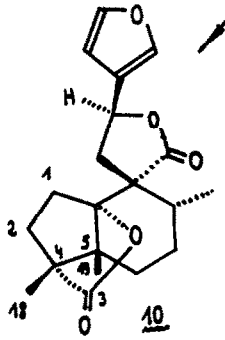
7



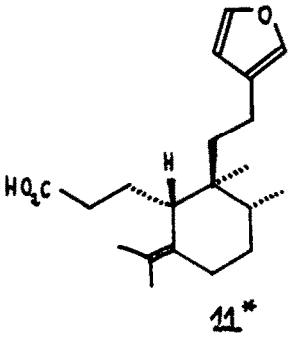
8



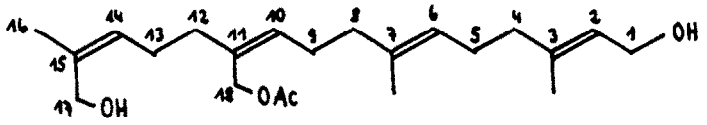
9



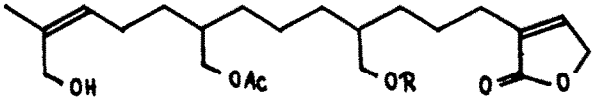
10



11*



12



13 R = H
14 R = Ac

*) 3a and 11a are the methyl esters