

DIMERIC SESQUITERPENE LACTONES AND KOLAVANE DERIVATIVES FROM *GOCHNATIA PANICULATA**

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Key Word Index—*Gochnatia paniculata*, Compositae, sesquiterpene lactones, dimeric lactones, diterpenes, kolavane derivatives, curcumine derivatives

Abstract—*Gochnatia paniculata* afforded two dimeric sesquiterpene lactones, which are derived from dehydrozalu-
 zanin C, two α -curcumene derivatives and eight kolavane derivatives. The structures were elucidated by spectroscopic
 methods, especially by highfield ^1H NMR spectroscopy. The chemotaxonomy of this genus is discussed briefly.

INTRODUCTION

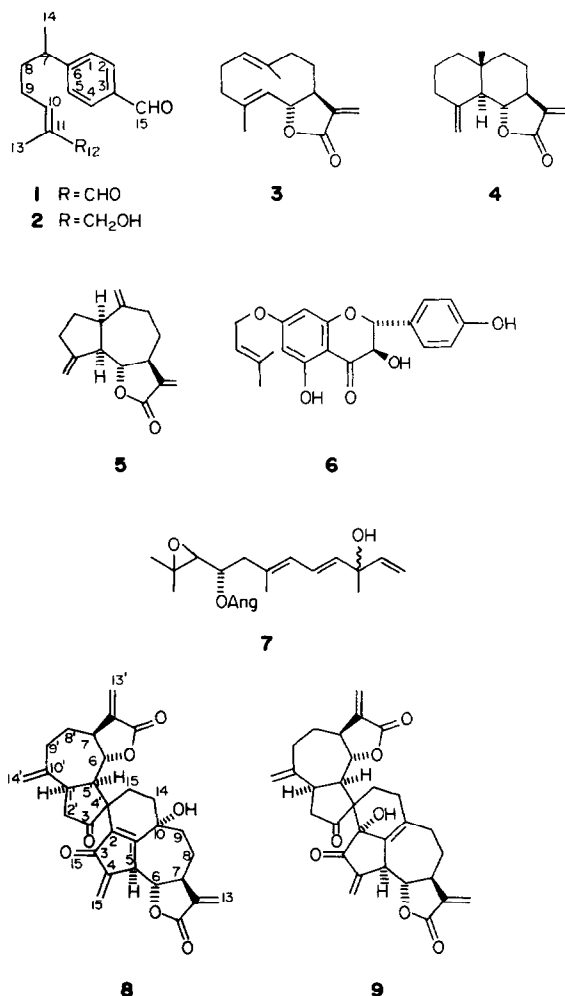
So far only four species of the large South American genus *Gochnatia* (tribe Mutisieae, subtribe Gochnatinae) [1] have been studied chemically. In addition to widespread triterpenes two species afforded sesquiterpene lactones. While *G. discoidea* contains 8,12-germacranolides [2], *G. rusbyana* afforded zaluzanin C [3]. We have now investigated a further species, *G. paniculata* (Less.) Cabrera

RESULTS AND DISCUSSION

The roots of *Gochnatia paniculata* afforded the α -curcumene derivatives 1 and 2, costunolide (3), β -cyclo-costunolide (4), dehydrocostuslactone (5), the flavanol 6 [4], the dehydronerolidol derivative 7 [5] and minute amounts of the dimeric sesquiterpene lactones 8 and 9. The structures of 1 and 2 were deduced from their molecular formulae and their ^1H NMR spectra (Table 1). In the spectrum of 1 two singlets at δ 9.99 and 9.37 were due to aldehyde protons. The latter indicated the presence of a conjugated aliphatic aldehyde with the *E*-configuration. Accordingly, a low field broadened triplet at δ 6.43 was visible, which together with an olefinic methyl singlet indicated the nature of the side chain. Two broadened doublets of aromatic protons (each two protons) showed that a *para*-substituted benzene derivative was present. The chemical shifts required a carbonyl group as an electron withdrawing group, thus indicating the presence of a *para*-substituted benzaldehyde. Spin decoupling allowed the assignment of the remaining signals. The chemical shift of the signal of the methine proton, which was coupled with the methyl group, required a benzylic position. Therefore, the proposed structure was compatible with these data. The mass spectroscopic fragmentation pattern also supported this assignment. The ^1H NMR spectrum of 2 was also close to that of 1, except for the signals of H-10 (5.27 *br t*) and H-12 (4.02 *br s*), which showed that we were dealing with the correspond-

ing alcohol which most likely had the same stereochemistry of the Δ^{10} double bond as 1.

The molecular formula of both 8 and 9 was $\text{C}_{30}\text{H}_{30}\text{O}_7$, which already indicated that these compounds were



*Part 465 in the series "Naturally Occurring Terpene Derivatives" F or Part 464 see Bohlmann, F., Ates (Goren) N. and Jakupovic, J. *Phytochemistry* (in press)

Table 1 ^1H NMR spectral data of compounds **1** and **2** (400 MHz, CDCl_3 , TMS as int standard)

	1	2
H-1, H-6	7.36 <i>br d</i>	7.35 <i>br d</i>
H-2, H-5	7.84 <i>br d</i>	7.82 <i>br d</i>
H-7	2.84 <i>ddq</i>	2.80 <i>ddq</i>
H-8	1.83 <i>dt</i>	1.65 <i>m</i>
H-9	2.25 <i>m</i>	1.95 <i>m</i>
H-10	6.43 <i>br t</i>	5.27 <i>br t</i>
H-12	9.37 <i>s</i>	4.02 <i>br s</i>
H-13	1.64 <i>br s</i>	1.77 <i>dt</i>
H-14	1.33 <i>d</i>	1.27 <i>d</i>
H-15	9.99 <i>s</i>	9.99 <i>s</i>

J (Hz) 1, 2 = 8.5, 7, 8 = 7, 14 = 8, 9 = 9, 10 = 7, compound **2** 9, 13 = 10, 13 = 1

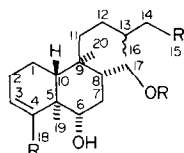
isomers of dimeric sesquiterpenes. Furthermore in the mass spectrum of **9** a fragment at m/z 242 ($\text{C}_{15}\text{H}_{14}\text{O}_3$) was present which most likely was the result of a retro-Diels-Alder fragmentation. The ^1H NMR spectra (Table 2) showed that both compounds were dilactones as could be deduced from the characteristic signals of H-13 as well as from the signals of the protons under the lactone oxygen. In the spectrum of **8** most signals could be assigned by spin decoupling in the usual way starting with the signals of H-7 and H-7'. The unusual downfield shift of H-7 can be explained by the proposed 10α -hydroxy group, while the chemical shift of H-5 was compatible with the proposed arrangement of the double bonds. The signals of the second part showed that here the keto group was not conjugated. The corresponding α -protons (H-2') were at a relatively low field which may be due to a deshielding effect of the keto group at C-3. The stereochemistry at C-5 through C-10, C-1' and C-5' through C-7' could be deduced from the couplings, while that at C-4' could not

Table 2 ^1H NMR spectral data of compounds **8** and **9** (400 MHz, CDCl_3 , TMS as int standard)

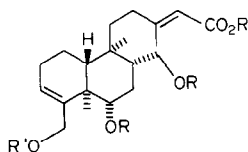
	8	9		8*	9
H-5	3.86 <i>br d</i>	3.86 <i>br d</i>	H-1'	3.23 <i>br dd</i>	3.26 <i>br dd</i>
H-6	3.73 <i>dd</i>	4.31 <i>dd</i>	H-2' ₁	2.61 <i>br d</i>	2.64 <i>br d</i>
H-7	3.82 <i>m</i>	2.83 <i>m</i>	H-2' ₂	3.35 <i>dd</i>	3.36 <i>dd</i>
H-8	2.35 <i>m</i>	—	H-5'	3.31 <i>br dd</i>	3.35 <i>br dd</i>
H-9	2.02 <i>m</i>	—	H-6'	4.20 <i>dd</i>	4.21 <i>dd</i>
H-13 ₁	6.20 <i>d</i>	6.23 <i>d</i>	H-7'	3.05 <i>dddd</i>	3.02 <i>m</i>
H-13 ₂	5.47 <i>d</i>	5.54 <i>d</i>	H-13' ₁	6.28 <i>d</i>	6.27 <i>d</i>
			H-13' ₂	5.61 <i>d</i>	5.57 <i>d</i>
H-15 ₁	6.22 <i>br s</i>	6.24 <i>br s</i>	H-15' ₁	5.06 <i>br s</i>	5.08 <i>br s</i>
H-15 ₂	6.02 <i>br s</i>	6.15 <i>br s</i>	H-15' ₂	4.68 <i>br s</i>	4.72 <i>br s</i>

*H-8'₁ = 2.32 *m*, H-8'₂ = 1.5 *m*, H-9'₁ = 2.61 *br d*, H-9'₂ = 2.22 *ddd*,

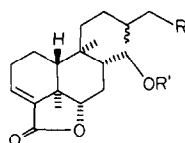
J (Hz) 5, 6 = 6, 7 = 10, 7, 8 = 4, 7, 8' = 10, 7, 13₁ = 3.5, 7, 13₂ = 3, 1', 2' = 1', 5' = 9, 2'₁, 2'₂ = 13, 5', 6' = 6', 7' = 9.5, 7', 8'₁ = 3, 7', 8'₂ = 10, 8'₁, 9'₂ = 5, 8'₁, 9'₂ = 12, 9'₁, 9'₂ = 13



	10	11	12	13
R	CHO	CHO	CH_2OH	CH_2OH
R	CH_2OH	CH_2OH	CH_2OH	CH_2OH
R'	COCH_2Ph	Ac	Ac	COCH_2Ph



	14	15	16	17	18
R	H	Me	H	Me	Me
R	Ac	COCH_2Ph	COCH_2Ph	COCH_2Ph	COCH_2Ph
R'	H	H	H	H	Ac



	19	20	21
R	CH_2OH	CO_2H	CO_2Me
R'	Ac	COCH_2Ph	COCH_2Ph

Table 3 ^1H NMR spectral data of compounds 10–13, 15, 17–19 and 21 (400 MHz, CDCl_3 , TMS as int. standard)

	10	11	12	13	15	17	18	19	21
H-2	2.57 br dt	2.57 br dt	2.14 br dt	2.13 br dt	2.1 m	2.05 m	2.07 m	2.50 m	2.51 ddd
H-2'	2.40 br dddd	2.40 br dddd	1.85 br dddd	1.80 m	1.87 m	1.85 m	1.90 m	2.30 m	2.30 m
H-3	6.90 br t	6.90 br t	5.60 br dd	5.58 br dd	5.61 br dd	5.59 br dd	5.71 br dd	6.49 t	6.49 t
H-6	3.55 dd	3.55 dd	3.63 dd	3.57 dd	3.64 m	3.58 dd	4.69 dd	3.62 dd	3.61 dd
H-7	1.96 dddd	1.98 dddd	2.0 m	2.0 m	2.0 m	2.0 m	2.0 m	1.95 m	2.0 m
H-7'	1.52 br dd	1.51 br dd	} 1.55 m	} 1.55 m	1.5 m	1.5 m	1.55 m	} 1.60 m	} 1.60 m
H-14	1.60 m	1.62 m			5.68 br s	5.67 br s	5.66 br s		
H-15	} 3.65 m	} 3.66 m	} 3.65 m	} 3.64 m	—	—	—	} 3.65 m	—
H-15'									
H-16	0.88 d	0.90 d	0.89 d	0.87 d	2.18 d	2.15 d	2.15 d	0.89 d	0.84 d
H-17	4.30 dd	4.26 dd	4.25 dd	4.30 dd	4.25 dd	4.29 dd	4.24 dd	4.30 dd	4.32 dd
H-17'	3.76 dd	3.74 dd	3.71 dd	3.79 dd	3.76 dd	3.78 dd	3.78 dd	3.94 dd	3.96 dd
H-18	9.20 s	9.21 s	} 4.29 br d	} 4.29 br d	} 4.30 br d	} 4.29 br d	} 4.50 br d	—	—
H-19	1.09 s	1.10 s	1.08 s	1.05 s	1.09 s	1.06 s	1.13 s	1.03 s	0.97 s
H-20	0.73 s	0.77 s	0.76 s	0.71 s	0.79 s	0.74 s	0.74 s	0.88 s	0.84 s
OCOR	7.30 m	—	—	7.30 m	—	7.30 m	7.30 m	—	7.32 m
	3.61 s	—	—	3.61 s	—	3.61 s	3.61 s	—	3.64 s
OAc	—	2.05 s	2.05 s	—	2.06 s	—	2.02 s (6H)	2.08 s	—
OMe	—	—	—	—	—	3.67 s	3.68 s	—	3.69 s

J (Hz) 1, 2 = 2, 3 = 4, 1, 2' = 7, 1', 2' = 10, 2, 2' = 20, 2', 3 = 3, 6, 7 = 4, 6, 7' = 11, 7, 8 = 4, 7', 8 = 11, 7, 7' = 14, 8, 17 = 4, 8, 17' = 9, 5, 13, 16 = 7, 17, 17' = 11, compounds 19 and 21 2, 3 = 2', 3 = 3, 5

be determined. The ^1H NMR spectrum of **9** was in part very similar to that of **8**. However, the chemical shift of H-7 differed drastically, since this proton was not deshielded by the hydroxy group which, therefore, most likely was at C-2, especially as no signal was visible which could be assigned to a proton at C-2. In agreement with this proposal a retro-Diels-Alder fragment occurred (m/z 242) in the mass spectrum of **9**. As the signal of H-5 was shifted downfield a 2α -hydroxy group was most likely. The stereochemistry at all other centres seemed to be the same as that of **8**. We have named the lactones gochnatiolide A and B.

The aerial parts afforded, in addition to squalene, eight diterpenes, the aldehydes **10** and **11**, the diols **12** and **13**, the acids **14** and **16** and the lactones **19** and **20**. Compounds **14**, **16** and **20** were transformed to their methyl esters **15**, **17** and **21**, respectively, while **17** was acetylated yielding the diacetate **18**. The ^1H NMR spectra (Table 3) of all these compounds were in part similar indicating the presence of only one type of diterpene. If the data were compared with those of different types of diterpenes it was obvious that all compounds were kolavane derivatives differing in the nature of the oxygen functions. From the spectrum of **11** the presence of a secondary acetoxymethylene group was proposed (δ 4.26 *dd* and 3.74 *dd*). A singlet at δ 9.21 and a broadened triplet at δ 6.90 indicated a conjugated aldehyde, while a complex signal at δ 3.66 and a methyl doublet at δ 0.90 showed that a hydroxy group was most likely at C-15. A double doublet at δ 3.55 required the presence of a further hydroxy group. Spin decoupling allowed the assignment of most signals, while the proposed stereochemistry agreed nicely with the couplings observed. Compound **10** differed from **11** only by the nature of the ester group at C-17. The mass spectrum and the ^1H NMR spectrum showed that a phenyl acetate was present. The ^1H NMR spectra of **12** and **13** (Table 3) indicated that these diterpenes were the corresponding 18-hydroxy derivatives of **10** and **11**, respectively. Accordingly, the signal of the aldehyde proton was replaced by a pair of doublets and the H-2 and H-3 signals were shifted upfield, while the other signals were nearly identical with those of **10** and **11**, respectively. The configuration at C-13 of **10**–**13** and also of **19** and **20** (see below) could not be determined.

The ^1H NMR spectra of the methyl esters **15**, **17** and **18** indicated that the side chain was different from that of **10**–**13**. The chemical shift of a doublet of an olefinic methyl group indicated a double bond with the *E*-configuration. Compounds **15** and **17** again differed only in the oxygen function at C-17. Accordingly, the ^1H NMR signals of the decalin part were nearly identical with those of **12** and **13**, respectively. The ^1H NMR spectrum of the diacetate of **17** supported the proposed structure. The spectral data of **19** and **21** (Table 3) clearly showed that we were dealing with 6,18-lactones which differed in the nature of the oxygen functions at C-15 and C-17. Spin decoupling allowed the assignment of nearly all signals. The stereochemistry was deduced from the couplings observed. We have given the name gochnatol to 17-desacetyl **19** and the name gochnatic acid to 17-desacetyl **20**.

All the diterpenes were closely related. The optical rotations indicated that they are kolavane derivatives, although this proposal could not be established with certainty. The chemistry of this *Gochnatia* species agreed in part with that of the other species investigated previously. Sesquiterpene lactones were isolated also from the

genera *Actinoseris* [6], *Cnicothamnus* [3], *Dicoma* [7–9] and *Wunderlichia* [6, 10] which are all placed in the same subtribe. However, so far no diterpenes have been isolated from the taxa of this genus. Many more species have to be investigated from other genera of the subtribe Gochnatinae to obtain a clear picture.

EXPERIMENTAL

The air-dried plant material, collected in January 1981 in the province Bahia, Brazil (voucher RMK 8982, deposited in the National U.S. Herbarium, Washington) was extracted with Et₂O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the high field ^1H NMR spectra with those of authentic material.

The roots (40 g) afforded 3 mg **1** (Et₂O–petrol, 1:1), 5 mg **2** (C₆H₆–CH₂Cl₂–Et₂O, 1:1:1), 2 mg **3**, 2 mg **4**, 3 mg **5**, 5 mg **6**, 4 mg **7**, 2 mg **8** and 2 mg **9** (**8** and **9** separated with C₆H₆–CHCl₃–Et₂O, 1:1:1). The aerial parts (280 g) gave 20 mg squalene, 15 mg **10**, 5 mg **11**, 2 mg **12**, 4 mg **13**, 2 mg **14**, 6 mg **16**, 7 mg **19** and 5 mg **20**. Compounds **14**, **16** and **20** were transformed to their methyl esters (excess CH₃N₂ in Et₂O, 5 min). Separation of **10**, **17** and **21** was achieved by C₆H₆–CH₂Cl₂–Et₂O (1:1:1) (several times) and of **11**–**13**, **15** and **19** by C₆H₆–CHCl₃–MeOH (5:5:1) (several times).

α -Curcumene-12,15-dial (1) Colourless oil, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹ 2720, 1705, 1690, 1615 (C=CCHO, PhCHO), MS m/z (rel. int.) 230 [131–M]⁺ (8), (C₁₅H₁₈O₂), 212 [M–H₂O]⁺ (6), 202 [M–CO]⁺ (12), 201 [M–CHO]⁺ (9), 172 [201–CHO]⁺ (52), 134 [C₆H₁₀O]⁺ (80) (McLafferty), 133 [C₉H₉O]⁺ (80) (tropylum ion), 105 [133–CO]⁺ (100).

12-Hydroxy- α -curcumene-15-al (2) Colourless oil, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹ 3600 (OH), 2720, 1710, 1615 (PhCHO), MS m/z (rel. int.) 232 [146–M]⁺ (14), (C₁₅H₂₀O₃), 217 [M–Me]⁺ (18), 214 [M–H₂O]⁺ (6), 204 [M–CO]⁺ (13), 189 [204–Me]⁺ (11), 134 [C₉H₁₀O]⁺ (88), 133 [C₉H₉O]⁺ (100), 105 [133–CO]⁺ (76).

Gochnatolide A (8) Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹ 3600 (OH), 1780 (γ -lactone), 1705 (C=CC=O), MS m/z (rel. int.) 502 [199–M]⁺ (20), (C₃₀H₃₀O₇), 484 [M–H₂O]⁺ (25), 466 [484–H₂O]⁺ (4), 456 [484–CO]⁺ (10), 438 [456–H₂O]⁺ (11), 423 [438–Me]⁺ (5), 91 (68), 55 (100).

Gochnatolide B (9) Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹ 3600 (OH), 1780 (γ -lactone), 1730 (C=C–CO), MS m/z (rel. int.) 502 [199–M]⁺ (4), (C₃₀H₃₀O₇), 484 [M–H₂O]⁺ (100), 466 [484–H₂O]⁺ (9), 456 [484–CO]⁺ (4), 438 [456–H₂O]⁺ (18), 242 [C₁₅H₁₆O₃]⁺ (8) (RDA).

6 α -Hydroxy-17-phenylacetoxyl-18-oxo-kolav-3-en-15-ol (10) Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹ 3620 (OH), 1735 (CO₂R), 2740, 1680 (C=CCHO), MS m/z (rel. int.) 456 [288–M]⁺ (11), (C₂₈H₄₀O₅), 438 [M–H₂O]⁺ (8), 409 [438–CHO]⁺ (3), 320 [M–RCO₂H]⁺ (7), 302 [320–H₂O]⁺ (10), 292 [320–CO]⁺ (10), 274 [302–CO]⁺ (6), 201 [302–C₆H₁₃O]⁺ (51), 173 [201–CO]⁺ (74), 119 [PhCH₂CO]⁺ (28), 91 [119–CO]⁺ (100).

$$[\alpha]_{\text{D}}^{25} = \frac{589}{-33} \frac{578}{-33} \frac{546}{-35} \text{ nm (CHCl}_3, c\ 0.62)$$

6 α -Hydroxy-17-acetoxyl-18-oxo-kolav-3-en-15-ol (11) Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹ 3620 (OH), 1740, 1240 (OAc), 2750, 1680 (C=CCHO), MS m/z (rel. int.) 380 [256–M]⁺ (15), (C₂₂H₃₆O₅), 362 [M–H₂O]⁺ (11), 347 [362–Me]⁺ (6), 320 [M–HOAc]⁺ (6), 302 [320–H₂O]⁺ (7), 292 [320–CO]⁺ (8), 201 [302–C₆H₁₃O]⁺ (62), 173 [201–CO]⁺ (100). $[\alpha]_{\text{D}} = -38^\circ$ (CHCl₃, $c\ 0.2$).

6 α , 18-Dihydroxy-17-acetoxy-kolav-3-en-15-ol (12) Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} 3600 (OH), 1740, 1240 (OAc), MS (CI, *iso*-butane) m/z (rel int) 381 $[M+1]^+$ (1), 365 $[380-\text{Me}]^+$ (28), 347 $[365-\text{H}_2\text{O}]^+$ (52), 287 $[347-\text{HOAc}]^+$ (100) $[\alpha]_{\text{D}} = -28^\circ$ (CHCl_3 , c 0.3)

6 α , 18-Dihydroxy-17-phenylacetoxy-kolav-3-en-15-ol (13) Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} 3600 (OH), 1730 (CO_2R), MS m/z (rel int) 440 293 $[M]^+$ (3) ($\text{C}_{28}\text{H}_{30}\text{O}_4$), 425 $[M-\text{Me}]^+$ (1), 407 $[425-\text{H}_2\text{O}]^+$ (3), 304 $[M-\text{RCO}_2\text{H}]^+$ (8), 203 $[\text{C}_{14}\text{H}_{19}\text{O}]^+$ (60), 185 $[203-\text{H}_2\text{O}]^+$ (48), 91 $[\text{C}_7\text{H}_7]^+$ (100) $[\alpha]_{\text{D}} = -19^\circ$ (CHCl_3 , c 0.13)

Methyl-6 α , 18-dihydroxy-17-acetoxy-kolavenoate (15) Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} 3600 (OH), 1735, 1250 (OAc), 1710 ($\text{C}=\text{CCO}_2\text{R}$), MS m/z (rel int) 358 214 $[M-\text{MeOH}, \text{H}_2\text{O}]^+$ (1) ($\text{C}_{22}\text{H}_{30}\text{O}_4$), 343 $[358-\text{Me}]^+$ (2), 330 $[358-\text{CO}]^+$ (1), 315 $[330-\text{Me}]^+$ (0.5), 57 (100)

Methyl-6 α , 18-dihydroxy-17-phenylacetoxy-kolavenoate (17) Colourless gum IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} 3600 (OH), 1735 (CO_2R), 1720, 1650 ($\text{C}=\text{CCO}_2\text{R}$), MS m/z (rel int) 448 261 $[M-2\text{H}_2\text{O}]^+$ (1), ($\text{C}_{29}\text{H}_{36}\text{O}_4$), 312 $[448-\text{RCO}_2\text{H}]^+$ (15), 297 $[312-\text{Me}]^+$ (18), 91 $[\text{C}_7\text{H}_7]^+$ (100), CI (*iso*-butane) 485 $[M+1]^+$ (1), 467 $[485-\text{H}_2\text{O}]^+$ (1), 449 $[467-\text{H}_2\text{O}]^+$ (1), 417 $[449-\text{MeOH}]^+$ (1), 331 $[467-\text{RCO}_2\text{H}]^+$ (8), 313 $[331-\text{H}_2\text{O}]^+$ (9), 299 $[331-\text{MeOH}]^+$ (8) $[\alpha]_{\text{D}} = -11^\circ$ (CHCl_3 , c 0.2) Compound 17 (3 mg) was heated for 1 hr with 0.1 ml Ac_2O at 70° TLC (Et_2O -petrol, 1:1) afforded 2 mg 18, colourless gum, ^1H NMR see Table 3

Gochnatol-17-O-acetate (19) Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} 3600 (OH), 1775 (γ -lactone), 1740, 1230 (OAc), MS m/z (rel int) 360 230 $[M-\text{H}_2\text{O}]^+$ (19) ($\text{C}_{22}\text{H}_{32}\text{O}_4$), 318 $[M-\text{HOAc}]^+$ (6), 300 $[318-\text{H}_2\text{O}]^+$ (12), 285 $[300-\text{Me}]^+$ (6), 217 $[318-\text{C}_6\text{H}_{13}\text{O}]^+$ (33), 199 $[217-\text{H}_2\text{O}]^+$ (17) 165 (82), 121 (91), 81 (100)

$$[\alpha]_{\text{D}}^{25} = \frac{589}{-45} \quad \frac{578}{-45} \quad \frac{546}{-52} \quad \frac{436 \text{ nm}}{-87} \quad (\text{CHCl}_3, c 0.13)$$

Methylgochnatoate-17-O-phenylacetate (21) Colourless gum IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} 1780 (γ -lactone), 1730 (CO_2R), 1720 ($\text{C}=\text{CCO}_2\text{R}$), MS m/z (rel int) 480 251 $[M]^+$ (1) ($\text{C}_{29}\text{H}_{36}\text{O}_6$), 448 $[M-\text{MeOH}]^+$ (18), 344 $[M-\text{RCO}_2\text{H}]^+$ (2), 312 $[448-\text{RCO}_2\text{H}]^+$ (6), 217 $[344-\text{CH}_2\text{CH}_2\text{C}(\text{Me})=\text{CHCO}_2\text{Me}]^+$ (32), 91 $[\text{C}_7\text{H}_7]^+$ (100) $[\alpha]_{\text{D}} = -10^\circ$ (CHCl_3 , c 0.18)

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