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TERT-BUTANOLYSIS OF LICHEN DEPSIDES*

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Key Word Index—Depsides *tert*-butanolysis

Abstract—The scope and limit of the *tert*-butanolysis of 12 lichen depsides is described Neither 2-*O*-methylated nor 2-*O*-acetylated compounds are cleaved by heating with *tert*-butanol

INTRODUCTION

The structural elucidation of a depside includes the cleavage of the ester bond as a main step In 1979 and 1981 Bachelor *et al* [1] and Meyyappan *et al* [2] described the *tert*-butanolysis of atranorin and lecanoric acid, respectively, and Huneck [3] applied this method successfully to the structural elucidation of the new depsides pseudocyphellarin A and B

To analyse the scope and limit of the *tert*-butanolysis of lichen depsides the reaction of the following compounds with *tert*-butanol was investigated barbatic acid (**1**), chloroatranorin (**2**), confluentic acid (**3**), methyl evernate (**4**), 4-*O*-demethylbarbatic acid (**5**), perlatolic acid (**6**), sphaerophorin (**7**), methyl tri-*O*-methyllecanorate (**8**), tri-*O*-methylpseudocyphellarin A (**9**), tri-*O*-acetyllecanoric acid (**10**), nephroarctin (**11**) and barbatolic acid (**12**)

RESULTS AND DISCUSSION

The depsides **1**–**7** yielded the corresponding *tert*-butyl esters and phenolics, namely **1** *tert*-butyl rhizonate (**13**) and β-orcinolcarboxylic acid (**14**), **2** *tert*-butyl 5-chlorohaematommate (**15**) and methyl β-orcinolcarboxylate (**16**), **3** *tert*-butyl 4-*O*-methylolivetonate (**17**) and 2-*O*-methyl olivetolcarboxylic acid (**18**), **4** *tert*-butyl everninate (**19**) and methyl orsellinate (**20**), **5** *tert*-butyl β-orcinolcarboxylate (**21**) and **14**, **6** *tert*-butyl 4-*O*-methylolivetolcarboxylate (**22**) and olivetolcarboxylic acid (**23**), **7** **19** and sphaerophorolcarboxylic acid (**24**) All new compounds were identified by their ^{1}H NMR spectra Neither the 2-*O*-methylated compounds **8** and **9** nor tri-*O*-acetyllecanoric acid (**10**) were cleaved by prolonged heating with *tert*-butanol Although nephroarctin (**11**) has a free hydroxyl group at C-2 only traces of cleavage products could be detected by TLC after heating with *tert*-butanol for 30 hr Alectorialic and barbatolic acids are the only known depsides where the S-part is connected to the A-part via a benzylic group Only 3% of **12** was cleaved after heating with *tert*-butanol for 20 hr

The following conclusions can be drawn from these results (1) A free 2-hydroxyl group seems to be essential for the *tert*-butanolysis of depsides, (2) an aldehyde group at position 5 prevents the cleavage, and (3) the rate of the cleavage of benzylic depsides like barbatolic acid is much slower than that of normal depsides

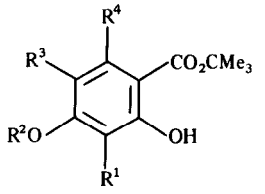
EXPERIMENTAL

Tert-*butanolysis* The depside (100–200 mg) was refluxed with *tert*-BuOH (50–100 ml) for 20–40 hr, after removal of solvent the residue was chromatographed on silica gel (with 5% H_2O) using C_6H_6 and C_6H_6–Et_2O gradients

Tert-*butyl rhizonate* (**13**) Prismatic plates of mp 68–70° (from *n*-hexane) $C_{14}H_{20}O_4$ (252 3) IR ν_{max}^{KBr} cm^{-1} 830, 854, 968, 1000, 1030, 1060, 1130, 1156, 1180, 1228, 1248, 1300, 1370, 1402, 1446, 1460, 1498, 1572, 1616, 1638, 2950, 3300 ^{1}H NMR (100 MHz, $CDCl_3$) δ1 59 (*s*, 9H, CMe_3), 2 04 (*s*, 3H, Me), 2 48 (*s*, 3H, Me), 3 80 (*s*, 3H, OMe), 6 19 (*s*, 1H, arom H), 11 90 (*s*, 1H, OH) MS *m/z* (rel int) 252 $[M]^+$ (34), 197 $[M-C(Me)_2=CH]^+$ (83), 178 (100), 150 (91), 135 (18), 122 (21), 107 (27)

Tert-*butyl* 5-*chlorohaematommate* (**15**) Needles of mp 108–109° (from *n*-hexane) $C_{12}H_{15}ClO_5$ (274 7) IR ν_{max}^{KBr} cm^{-1} 716, 850, 1048, 1164, 1208, 1262, 1340, 1390, 1410, 1440, 1590, 1648, 2800, 3030, 3500 ^{1}H NMR (100 MHz, $CDCl_3$) δ1 60 (*s*, 9H, CMe_3), 2 63 (*s*, 3H, Me), 10 25 (*s*, 1H, CHO), 12 5–13 1 (*br s*, 2H, 2 × OH)

Tert-*butyl* 4-O-*methylolivetonate* (**17**) Oil $C_{19}H_{28}O_5$ (336 4) IR ν_{max}^{film} cm^{-1} 754, 820, 850, 960, 1046, 1114, 1154, 1198, 1266,



	R^1	R^2	R^3	R^4
13	Me	Me	H	Me
15	CHO	H	Cl	Me
17	H	Me	H	$CH_2-CO-n-C_5H_{11}$
19	H	Me	H	Me
21	Me	H	H	Me
22	H	Me	H	$n-C_5H_{11}$

*Part 142 in the series "Lichen Substances" For part 141 see Connolly, J D, Freer, A A, Kalb, K and Huneck, S (1984) *Phytochemistry* **23**, 857

1304, 1334, 1374, 1428, 1464, 1572, 1610, 1640, 1708, 2990, 3400 ^{1}H NMR (100 MHz, $CDCl_3$) δ0 80 (*t*, 3H, CH_2–Me), 1 20 (*m*, 6H, $(CH_2)_3$–Me), 1 50 (*s*, 9H, CMe_3), 2 34 (*t*, 2H, CO–CH_2–CH_2) 3 72 (*s*, 3H, OMe), 3 93 (*s*, 2H, benzyl CH_2), 6 13, 6 32 (2 × *d*, 2H, 3-H, 5-H), 11 64 (*s*, 1H, OH)

Tert-*butyl everninate* (**19**) Crystals, mp 28° (from *n*-pentane) $C_{13}H_{18}O_4$ (238 3) IR ν_{max}^{KBr} cm^{-1} 700, 758, 818, 850, 952, 992, 1040, 1062, 1118, 1160, 1200, 1262, 1300, 1330, 1370, 1420, 1450, 1576, 1610, 1640, 3000, 3450 ^{1}H NMR (200 MHz, $CDCl_3$) δ2 80 (*s*, 9H, CMe_3), 3 45 (*s*, 3H, Me), 4 45 (*s*, 3H, OMe), 6 39, 6 45 (2 × *d*, 2H, 3-H, 5-H), 10 80 (*s*, 1H, OH)

Tert-*butyl β-orcinolcarboxylate* (**21**) Prisms, mp 128–130° (from Et_2O–*n*-hexane) $C_{14}H_{18}O_4$ (250 3) IR ν_{max}^{KBr} cm^{-1} 730, 842, 966, 1024, 1058, 1100, 1140, 1158, 1248, 1300, 1368, 1394, 1430, 1450, 1590, 1620, 1640, 3000, 3480 ^{1}H NMR (100 MHz, $CDCl_3$) 1 55 (*s*, 9H, CMe_3), 2 04 (*s*, 3H, 3-Me), 2 36 (*s*, 3H, 6-Me), 5 50 (*br s*, 1H, 4-OH), 12 18 (*s*, 1H, 2-OH)

Tert-*butyl* 4-O-*methyloliveto1carboxylate* (**22**) Oil $C_{17}H_{26}O_4$ (294 4) IR ν_{max}^{film} cm^{-1} 710, 754, 780, 820, 832, 850, 960, 1042, 1110, 1154, 1194, 1260, 1300, 1330, 1370, 1422, 1462, 1570, 1606, 1636, 2970, 3400 ^{1}H NMR (100 MHz, $CDCl_3$) δ0 83 (*t*, 3H, CH_2–Me), 1 28 (*m*, $(CH_2)_3$–Me), 1 56 (*s*, 9H, CMe_3), 2 80 (*t*, 2H, benzyl CH_2), 6 17, 6 23 (2 × *d*, 2H, 3-H, 5-H), 11 84 (*s*, 1H, OH)

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FLAVONOIDS FROM *ACHYROCLINE FLACCIDA*

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Key Word Index—*Achyrocline flaccida*, Compositae, Inuleae, aerial parts, prenylated flavonoids, flavonoids, caffeic acid derivatives

Abstract—Three new flavonoids 5-hydroxy-7-(3-methyl-2,3-epoxybutoxy)flavanone, 5-hydroxy-3,8-dimethoxy 7-(3-methyl-2,3-epoxybutoxy)flavone and 4′-hydroxy-5-methoxy-7-(3-methyl-2,3-epoxybutoxy)flavone were isolated and identified from the aerial parts of *Achyrocline flaccida* Tamarixetin, gnaphalin, isognaphalin, 5,7,8-trihydroxy-3-methoxyflavone, chrysoeriol, galangin 3-methyl ether, naringenin 5-methyl ether, caffeic acid, chlorogenic acid and isochlorogenic acid were also isolated

INTRODUCTION

In continuation of our chemosystematic search of the tribe Inuleae (Compositae), we have now investigated *Achyrocline flaccida* (Weinm) DC, a shrub, widely distributed in the North of Argentina and the South of Brazil In a previous paper we reported the identification of galangin, galangin 3-methyl ether, quercetin 3-methyl ether and two esters of calleryanin (3,4-dihydroxybenzyl alcohol 4-glucoside) with caffeic acid and protocatechuic acid from *Achryrocline satureioides* [4] Investigation of the acetone extract of *A flaccida* resulted in the isolation and determination of the structure of 7,4′-dihydroxy-5-methoxyflavanone and the corresponding 4,2′4′-trihydroxy-6-methoxychalcone [5]

The most characteristic features distinguishing members of the Inuleae from those of other Compositae tribes is the presence of flavonols lacking B ring hydroxylation, 6 and/or 8 hydroxyflavonols and their methyl ethers [6] In the present report we describe the occurrence of such typical flavonoids, together with the identification of three new prenylated flavonoids

RESULTS AND DISCUSSION

The hexane extract of the aerial parts of *A flaccida* was subjected to silica gel CC affording three new flavonoids The first of these, compound 1 showed a brown colour in UV (365 nm) and a yellow–green colour with methanolic ferric chloride Its UV spectrum exhibited maxima at 272 and 280 (sh) nm characteristic of a flavanone The shifts induced in the UV spectra by aluminium chloride, sodium acetate and sodium methoxide led us to conclude that there is only one free hydroxyl attached to C-5 The ^{1}H NMR spectrum (in $CDCl_3$) showed a multiplet at δ7 6 characteristic of an unsubstituted aromatic ring (B ring), δ6 2 and 5 8 signals from protons H-6 and H-8 δ5 3 corresponding to H-2 and δ2 6 (multiplet) to H-3 *trans* and H-3 *cis* The aliphatic chain showed the gem-dimethyl