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BENZOFURANS FROM *CLIBADIUM ARMANII*

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Key Word Index—*Clibadium armanii*; *C. microcephalum*; Heliantheae; Compositae; new benzofurans; acetophenone derivatives.

The roots of *C. armanii* Sch. Bip, ex Baker collected in north-eastern Brazil afforded, in addition to squalene, heptadeca-7,9,15-triene-11,13-diyne (**1**) [1],tetradeca-4,6,12-triene-8,10-diyne (**2**) [1], lachnophyllumester (**3**) [1], 6-hydroxytremetone (**4**) [2] and 6-hydroxytoxol (**5**), isolated so far only from *Fitchia speciosa* [3], and two further acetophenone derivatives. In both of the latter compounds the isopropylidene group was replaced by an isopropyl group. The more polar compound **7** was obviously a 10,11-dihydro derivative of **5**, as could be seen by the similar ^{1}H NMR spectral data of both compounds (Table 1). As expected the 2-H signal was shifted upfield. The second compound was the diketone **6**. Again the ^{1}H NMR spectral data (Table 1) clearly showed that the second keto group could only be placed at C-3. Consequently the proton at C-4 was shifted downfield in comparison with the chemical shifts in the spectra of **4**, **5** and **7**. So far no compounds of this type have been previously isolated. The aerial parts of the plant contain **1**, **2**, **4** and squalene as well as germacrene D (**8**) and bicyclogermacrene (**9**).

Table 1. ^{1}H NMR spectral data of compounds **6** and **7** (270 MHz, CDCl$_3$)

	6	7
2-H	4.53 *d*	4.06 *dd*
3-H	—	5.05 *d* (*br*)
4-H	8.18 *s*	7.80 *s*
7-H	6.60 *s*	6.39 *s*
9-H	2.65 *s*	2.60 *s*
10-H	2.38 *dqq*	2.28 *dqq*
11-H	0.96 *d*	1.14 *d*
12-H	1.18 *d*	1.22 *d*
OH	13.19 *s*	12.98 *s*

J(Hz): **6**: 2, 10 = 4; 10, 11 = 10, 12 = 6.5; **7**: 2, 3 = 5; 2, 10 = 10; 10, 11 = 10, 12 = 6.5.

The roots of *C. microcephalum* Blake, however, afforded trideca-1,11-diene-3,5,7,9-tetrayne (**10**) [1] and linolenic alcohol (**11**), while the aerial parts gave phytol and α-copaene (**12**) in addition to **10** and **11**. The chemotaxonomic situation of this genus is still complicated. Some species show chemistry similar to *Ichthyothere* [4, 5], which is placed in the same subtribe [6], while others have constituents of different types, which are not very characteristic [5].

EXPERIMENTAL

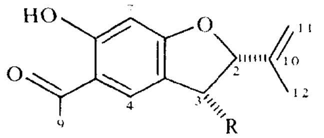
The air-dried plant material, collected in north-eastern Brazil was chopped and extracted with Et$_2$O–petrol (1:2). The resulting extracts were first separated by CC (Si gel) and further by TLC (Si gel, GF 254). Known compounds were identified by comparison of the IR and ^{1}H NMR spectra with those of authentic material.

Clibadium armanii (*voucher RMK* 8000). The roots (150 g) afforded 5 mg **1**, 1 mg **2**, 3 mg **3**, 2 mg squalene, 20 mg **4**, 4 mg **5**, 6 mg **6** (Et$_2$O–petrol, 1:3) and 1 mg **7** (Et$_2$O–petrol, 1:1), while the aerial parts (250 g) gave 25 mg **1**, 4 mg **2**, 4 mg **4**, 25 mg **8**, 13 mg **9** and 13 mg squalene.

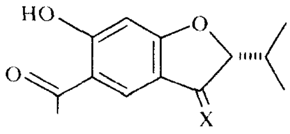
C. microcephalum (*voucher RMK* 7972). The roots (100 g) afforded 6 mg **10** and 150 mg **11**, while the aerial parts (1250g) yielded 70 mg **10**, 200 mg **11**, 30 mg **12** and 50 mg phytol.

10,11-*Dihydro-6-hydroxy-3-oxotremetone* (**6**). Colourless oil, IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3400–2700, 1645 (hydrogen-bonded PhCO); MS *m/e* (rel. int.): 234.089 (M$^+$, 10%) (C$_{13}$H$_{14}$O$_4$); 219 (10, M − $^\cdot$Me); 192 (100, M − C$_3$H$_6$, McLafferty); 177 (25, 192 − $^\cdot$Me).

10,11-*Dihydro-6-hydroxy-toxol* (**7**). Colourless oil, IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3610 (OH), 3500–2800, 1640 (hydrogen-bonded PhCO); MS *m/e* (rel. int.): 236.105 (M$^+$, 42%) (C$_{13}$H$_{16}$O$_4$); 221 (17, M − $^\cdot$Me); 219 (12, M − $^\cdot$OH); 203 (12, 221 − H$_2$O); 173 (100, 203 − CH$_2$O).



4 R = H
5 R = OH



6 X = O
7 X = αOH, H

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A CHALCONE GLYCOSIDE FROM *ABIES PINDROW*

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Key Word Index—*Abies pindrow*; Coniferae; 2′,3′,4′:3,4-pentahydroxy chalcone 4′-(L-arabinofuranosyl-α-1→4-D-glucopyranoside-β); permethylation; structural determination.

Abstract—The EtOH extract of air-dried stems of *Abies pindrow* yielded okanin, okanin 4′-*O*-β-D-glucopyranoside, butein 4′-*O*-β-D-glucopyranoside, 8,3′4′-trihydroxyflavanone-7-*O*-β-D-glucopyranoside and a new chalcone glycoside, 2′,3′,4′:3,4-pentahydroxy-chalcone 4′-(L-arabinofuranosyl-α-1→4-D-glucopyranoside-β).

INTRODUCTION

Abies pindrow is a tall evergreen tree with a dense conical crown of dark green foliage. Several species of *Abies* are regarded as carminative, expectorant, stomachic, toxic and astringent [1]. Since no work seems to have been previously done on the chemical constituents of *A. pindrow*, we have, therefore, examined the stem of this plant and its constituents are reported in the present paper.

RESULTS AND DISCUSSION

From the EtOH extract of the stem six compounds A to F were isolated. Compound A, a chalcone, has been characterized as okanin by spectral studies, derivative formation, mmp and co-PPC with an authentic sample [2, 3]. Chalcone B could not be studied due to lack of material. Compounds C, D and E were characterized as okanin-4′-*O*-β-D-glucopyranoside, butein-4′-*O*-β-D-glucopyranoside and 8,3′,4′-trihydroxy-flavanone-7-*O*-β-D-glucopyranoside, respectively, by comparison of spectral data, mmp and co-PPC with authentic samples [4–7].

Compound F, $C_{26}H_{30}O_{15}$, gave characteristic tests for a chalcone-glycoside [8, 9]. On acid hydrolysis it yielded an aglycone, which was identical to compound A in all respects. The sugar portion on co-chromatographic examination revealed the presence of D-glucose and L-arabinose (BuOH–HOAc–H_2O, 4:1:5, R_f 0.18 and 0.21 respectively). Quantitative hydrolysis of the glycoside indicated the aglycone content was *ca* 49%. Quantitative estimation [10] of the sugars present in the hydrolysate revealed that both sugars were present in equimolecular proportions. On partial hydrolysis [11] with 0.02N H_2SO_4 for 7 days at room temperature, it yielded a glycosidic compound which was purified by column chromatography over Si gel using EtOAc as eluant. It was identical with compound C in all respects. The hydrolysate revealed the presence of L-arabinose only, indicating that it was the terminal sugar of compound F. Permethylation [12] of F, followed by hydrolysis showed the presence of 2:3:6-tri-*O*-methyl-D-glucose and 2:3:5-tri-*O*-methyl-L-arabinose (BuOH–HOAc–H_2O, 4:1:5, R_G 0.83 and 0.95, respectively) [13]. This observation suggested that arabinose was present as the furanoside and that it was attached by C-1 to C-4 of the glucose moiety. The above fact was also confirmed by periodate oxidation [14]. F on