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CAULOPHYLLOGENIN: A NOVEL TRITERPENOID FROM ROOTS OF *CAULOPHYLLUM ROBUSTUM*

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Key Word Index—*Caulophyllum robustum*; Berberidacea; triterpenoid acid; caulophyllogenin; structure.

Abstract—A new triterpenoid acid was isolated from *Caulophyllum robustum* roots. Its structure was proved to be 3β, 16α, 23-tri-hydroxy-olean-12-ene-28-oic acid.

INTRODUCTION

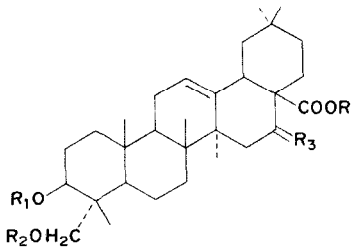
EARLIER, we reported the isolation from *Caulophyllum robustum* of cauloside B, an arabinoside of a new triterpenoid called caulophyllogenin.[1] In this paper, a more detailed characterization of the caulophyllogenin is presented.

RESULTS AND DISCUSSION

Caulophyllogenin (**1a**), $C_{30}H_{48}O_5$, m.p. 277–280°, $[\alpha]_D$ +14·3° (Py), obtained as a result of acid hydrolysis of cauloside B, yielded with diazomethane a methyl ester (**1b**), $C_{31}H_{50}O_5$, m.p. 234–235°, $[\alpha]_D$ +33·32° ($CHCl_3$). The **1a** (M^+ 488) MS displayed intense ion peaks (*m/e* 264, 246 and 201), characteristic of the retro-Diels–Alder fragmentation of 12-oleanen-type triterpenoids possessing a carboxyl and one of the hydroxyl groups in the D/E[2] rings. Treatment of **1a** with acetone and *p*-toluenesulphonic acid resulted in a monoacetonide **1f**, m.p. 136–138°, $[\alpha]_D$ +19·5° ($CHCl_3$), the MS of which (M^+ 528, *m/e* 451, 264, 246, 201, 200) indicated the presence of an acetonide group in the A/B rings. Acetylation of the methyl ester **1a** (**1b**) at 100° afforded an amorphous triacetate **1d**. The NMR spectrum of **1d** showed the presence of six tertiary methyls (3H, δ 0·65*s*, 3H, δ 0·77*s*, 3H, δ 0·89*s*, 6H, δ 0·93*s*, 3H, δ 1·15*s*), one carbomethoxyl (3H, δ 3·54*s*) one proton at a double bond (1H, δ 5·32*bs*) and three acetyl groups (3H, δ 1·89*s*, 6H, δ 1·96*s*). In the low field, **1d** gave signals indicating to the presence of an acetoxymethylene (2H, δ 3·66*bs*) group and two acetoxymethine (1H, δ 4·61*t*, $J_{AX} + J_{BX}$ = 14·5 Hz; 1H, δ 5·47*bs*-similar) groups. Acetylation of **1b** at 0° resulted in an amorphous diacetate **1c**, NMR-spectrum: 3H, δ 1·91*s*, 3H, δ 1·96*bs* (two MeCO groups), 2H, δ 3·69*bs* (CH_2OAc). 1H, δ 4·65*t*, $J_{AX} + J_{BX}$ = 14·5 Hz (CHOAc), 1H δ 4·45*bs*-similar (CHOH). Oxidation of the diacetate **1c** with chromic anhydride in pyridine resulted in the keto-derivative **1e**, $C_{35}H_{53}O_7$, m.p. 174–176°, $[\alpha]_D$ −5·94 ($CHCl_3$). The CD-curve for **1e** displays a strong negative Cotton effect ($\Delta\epsilon_{305}$ −3·7, $\Delta\epsilon_{296}$ −3·68), comparable to that of the methyl ester of a 16-keto-24-nor-olean-12-ene-28-oic acid.[3] The

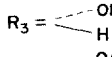
[1] STRIGINA L. I., CHETYRINA N. S. and ELYAKOV G. B. (1970) *Khimija Prirodnikh Sojedinenij* 552.
[2] KUBOTA, T. and KITATANI, H. (1968) *Chem. Commun.* 1005.
[3] RONDEST, J. and POLONSKY, J. (1963) *Bull. Soc. Chim. Fr.* 1253.

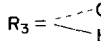
reduction of **1**e in accord with Barton[4] led to hederagenin. The 16α-position of the hydroxyl group in caulophyllogenin was shown by direct correlation of **1**a and **1**b with the quillaic acid*[5] $NaBH_4$-reduction product (m.p. 234–235°, $[\alpha]_D$ +33·35° ($CHCl_3$). The results obtained suggest that caulophyllogenin is: 3β, 16α-23-tri-hydroxyolean-12-en-28-oic acid.



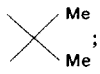
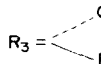
(1a) $R_1 = R_2 = R = H$; $R_3 =$ 

(1b) $R_1 = R_2 = H$; $R_3 =$  ; R = Me

(1c) $R_1 = R_2 = Ac$; $R_3 =$  ; R = Me

(1d) $R_1 = R_2 = Ac$; $R_3 =$  ; R = Me

(1e) $R_1 = R_2 = Ac$; $R_3 = O$; R = Me

(1f) $R_1 - R_2 -$ =  ; $R_3 =$  ; R = H

EXPERIMENTAL

From 0·5 g of cauloside B after hydrolysis with 2N H_2SO_4 0·35 g of crude caulophyllogenin was obtained. Caulophyllogenin was crystallized from 96% EtOH (×2). 0·25 g of this material was methylated with CH_2N_2. Elemental analysis of a methyl ether (Found: C, 74·06; H, 10·24. Required: C, 74·03; H, 10·02%). From 0·2 g of this material, after acetylation amorphous diacetate and triacetate were obtained. Elemental analysis of keto-derivative of methyl ether diacetate (Found: C, 71·53; H, 8·96. Required: C, 71·58; H, 8·96%).

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[4] BARTON, D. H. R. and IVES, D. (1955) *J. Chem. Soc.* 2056.

[5] KUBOTA, T., KITATANI, H. and HONOH, H. (1969) *Tetrahedron Letters* (10), 771.