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TETRACYCLIC TRITERPENES FROM *PARTHENIUM FRUTICOSUM**

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Key Word Index—*Parthenium fruticosum*; Compositae; tetracyclic triterpenes; fruticin A; fruticin B.

Abstract—The shrub *Parthenium fruticosum* was shown to contain the three isomeric tetracyclic triterpenes fruticin A, fruticin B and the known incanilin. Fruticins A and B are new substances with lanostane and cycloartane skeletons, respectively. Their structures were determined by chemical and spectroscopic methods. The stereochemistry of fruticin B was established by X-ray diffraction analysis.

INTRODUCTION

The genus *Parthenium* consisting of four sections [1] contains sesquiterpene lactones in the majority of its species [2], the only exceptions being two members of the section *Parthenichaeta*, *P. argentatum* and *P. rollinsianum*. The plants belonging to this section are shrubs or small trees which contain tetracyclic triterpenes as the main secondary metabolites [2–4].

Searching for new tetracyclic triterpenes, we studied the shrubby species *P. fruticosum*, which is a member of the section *Parthenichaeta*.

RESULTS AND DISCUSSION

The aerial parts of *P. fruticosum* contained fruticin A (**2a**) and fruticin B (**3a**) as well as incanilin (**1a**), which was identified by direct comparison with an authentic [3] sample. Fruticin A (**2a**), $C_{30}H_{48}O_4$, is a tetracyclic triterpene isomeric with incanilin, whose mass spectrum shows fragments at *m/z* 143 and 125. These fragments, which in incanilin (**1**) are formed by cleavage of the furan ring [4], must originate in a similar manner in fruticin A thus indicating the presence of a cyclic ether [5]. The ^{1}H NMR spectrum of fruticin A showed at δ4.55 a quartet, which was attributed to H-16 by comparison with similar signals in the spectra of argentatin A [6] (**4**) and incanilin (**1**) [3].

Dehydrofruticin A (**2b**) is the main product of the mild oxidation of **2a** with Jones reagent at 0°. It is a white, crystalline substance, mp 192–194°. It showed an IR band at 1730 cm^{-1}, characteristic of a cyclopentanone, probably due to a keto group at C-16. The only oxidized hydroxyl group is in the main skeleton, since the mass spectral fragments of the side chain at *m/z* 143 and 125 are still present. Oxidation of **2a** with Jones reagent at room temperature gave bisdehydrofruticin A (**2c**), mp 137–139°. This oxidation product contains three keto groups, as indicated by the IR bands at 1700, 1710 and 1730 cm^{-1}. This is in agreement with its mass spectrum, which showed a $[M]^+$ at *m/z* 468 and an important peak at *m/z* 141, the former indicating the loss of four hydrogens in the molecule and the latter, loss of two hydrogens in the side chain. The keto group of fruticin A was easily reduced with sodium borohydride, thus affording dihydrofruticin A (**2d**). The above discussion and biogenetic considerations led us to propose the structure **2a** for fruticin A.

The third constituent of *P. fruticosum*, which we called fruticin B (**3a**), $C_{30}H_{48}O_4$, is, like fruticin A, an isomer of incanilin. Its spectroscopic data are very similar to those of fruticin A, showing IR bands at 1710 and 3450 cm^{-1} (C=O and OH groups) and peaks at *m/z* 143 (100), 43 and 125 in the mass spectrum corresponding to the cleavage of a pyran ring. The ^{1}H NMR spectrum exhibited signals at δ4.55 and 3.375, which are almost superimposable on those corresponding to H-16 and H-24 in fruticin A. Fruticin B possesses a cycloartane skeleton, as indicated by the high-field signal at δ0.57 ascribed to protons on a cyclopropane ring.

From the above discussion, we can deduce that fruticin B differs only from fruticin A in having a cycloartane instead of a lanostane skeleton. The ^{1}H NMR spectrum exhibited seven singlets at δ0.85, 1.05, 1.1, 1.2, 1.3, 1.4 and 1.45 corresponding to the methyl groups in the molecule. Three of these methyl groups should be attached to C-20 and C-25 (both fully substituted), therefore the oxygen bridge of the pyran must lie between C-20 and C-25.

Dehydrofruticin B (**3b**) was obtained from fruticin B by mild oxidation as described for fruticin A. Its IR spectrum still showed the presence of a hydroxyl group and a new carbonyl on a cyclopentane ring (1730 cm^{-1}). The mass spectrum, $[M]^+$ *m/z* 470, indicates the loss of only two hydrogens. Bisdehydrofruticin B (**3c**) was the main oxidation product of **3a** with Jones reagent at room temperature. The reaction was controlled by TLC until the second and less polar spot became predominant. The presence of three keto groups in the molecule was shown by its IR spectrum (bands at 1710, 1720 and 1730 cm^{-1}). The fragment at *m/z* 468 $[M]^+$ indicates the loss of four hydrogens as compared to fruticin B.

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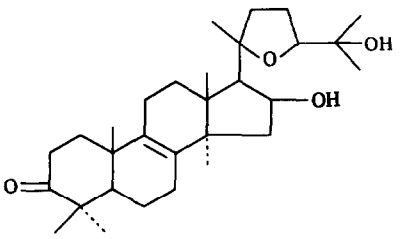

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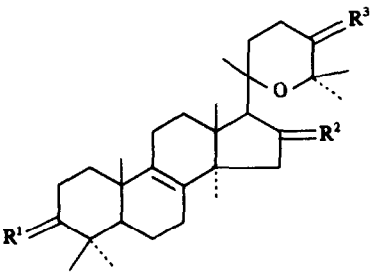
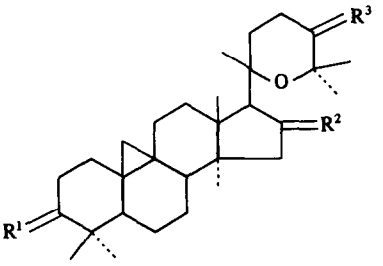
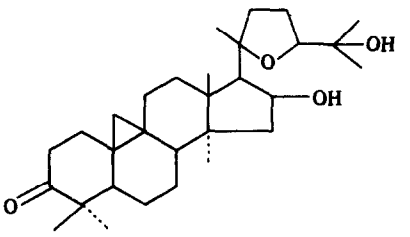


	R^1	R^2	R^3
2a	O	β-OH	α-OH
2b	O	O	α-OH
2c	O	O	O
2d	β-OH	β-OH	α-OH



	R^1	R^2	R^3
3a	O	β-OH	α-OH
3b	O	O	α-OH
3c	O	O	O



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The above discussion and biogenetic considerations led us to postulate the structure **3a** for fruticin B. The structure and stereochemistry were confirmed by an X-ray crystallographic study (Fig. 1).

EXPERIMENTAL

Mps are uncorr. CC was carried out on Merck silica gel 60 (0.063–0.2 mm). ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ solns with TMS as internal standard. MS were recorded at 70 eV.

Isolation of fruticin A (**2a**), *fruticin B* (**3a**) *and incanilin* (**1**). Aerial parts of *P. fruticosum* collected near Jalapa, Ver. (Voucher MEXU-321974) were finely ground and extracted with $CHCl_3$. The solvent was removed *in vacuo* and the remaining syrup (100 g) was chromatographed on silica gel. Fractions eluted with C_6H_6–EtOAc (9:1) afforded 1.55 g fruticin A, mp 217–218°, $[\alpha]_D^{20}$ +7.5° (*c* 20; $CHCl_3$), as white crystals from Me_2CO–diisopropyl ether. IR ν_{max} cm^{-1}: 1710, 3400. MS *m/z* (rel. int.): 472 $[M]^+$, 143 (100), 125 (22), 71 (14), 43 (27). (Found: C, 76.50; H, 10.50; O, 13.58. $C_{30}H_{48}O_4$ requires: C, 76.22; H, 10.24; O, 13.54%.)

Subsequent fractions eluted with the same mixture afforded fruticin B, mp 235–236°, $[\alpha]_D^{20}$ +12.9° (*c* 20; $CHCl_3$), white needles from Me_2CO–diisopropyl ether. (Found: C, 76.00; H, 10.09; O, 14.04. $C_{30}H_{48}O_4$ requires: C, 76.22; H, 10.24; O, 13.54%.) MS *m/z* (rel. int.): 472 $[M]^+$, 143 (100), 43 (71), 125 (23). This structure was confirmed by X-ray crystallographic analysis.

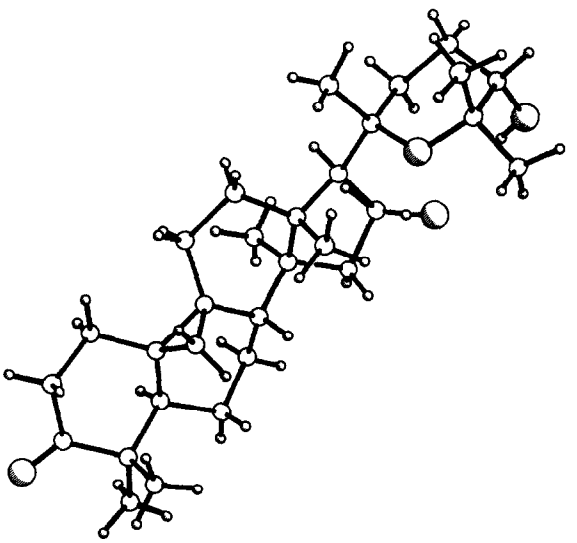

Fig. 1. Stereo-projection of fruticin B (**3a**).

X-ray data were collected on a Nicolet R3m diffractometer. Space group $P2_1$, $a = 12.639$ (6), $b = 7.214$ (2), $c = 15.578$ (7), A = 110.400 (4), $z = 2$, $\mu = (CuK_\alpha) = 5.58\ cm^{-1}$, F (000) = 520. 1931 reflections above 2.5σ (I) were used to refine to $R = 0.039$. (Additional data have been deposited at the Cambridge Crystallographic Data Centre.)

The last crystalline substance eluted with the same solvent mixture was incanilin (**1**), mp 184–185°, identified by comparison with an authentic sample.

Bisdehydrofruticin A (**2c**). A soln of fruticin A (**2a**) in Me_2CO was treated with Jones reagent at room temp. A slight excess was added in order to maintain an orange colour. The reaction was considered complete when a second faster moving spot had developed (TLC). The triketo compound (**2c**) was separated by prep. TLC in C_6H_6–EtOAc (4:1). **2c** showed mp 137–139°; IR ν_{max} cm^{-1}: 1700, 1710, 1730. MS *m/z* (rel. int.): 468 $[M]^+$, 141 (35).

Dehydrofruticin B (**3b**) was obtained by oxidation of 70 mg fruticin B, using the procedure described for the preparation of dehydrofruticin A (**2c**). Yield: 30 mg **3b**, mp 157–159°; IR ν_{max} cm^{-1}: 1710, 1730, 3450.

Bisdehydrofruticin B (**3c**). 60 mg fruticin B was obtained using the same procedure as that described for bisdehydrofruticin A. Yield: 10 mg, mp 137–140°. IR ν_{max} cm^{-1}: 1700, 1710 and 1730. MS *m/z*: 468 $[M]^+$.

Dihydrofruticin A (**2d**). A soln of fruticin A (100 mg) in MeOH (10 ml) was treated with $NaBH_4$ (100 mg in 10 ml MeOH). The reaction mixture was refluxed for 11 hr, H_2O added and the reduced product precipitated. The crystalline product was filtered and recrystallized from MeOH affording 85 mg dihydrofruticin A, mp 297–299°. IR ν_{max} cm^{-1}: 3400. (Found: C, 75.64; H, 10.70; O, 13.58. $C_{30}H_{50}O_4$ requires: C, 75.90; H, 10 62; O, 13.48%.) The same substance was obtained in a similar yield by reduction of fruticin A with $LiAlH_4$.

Dehydrofruticin A (**2b**). A soln of fruticin A (130 mg) in Me_2CO was treated with Jones reagent at 0° until a yellow colour persisted. The reaction was monitored by TLC at room temp. The oxidation product (**2b**) was separated from the starting material and more advanced oxidation products by prep. TLC. Dehydrofruticin A, mp 192–194°, IR ν_{max} cm^{-1}: 1710, 1730, 3450. MS *m/z* (rel. int.): 470 $[M]^+$, 143 (100), 272 (87), 125 (34).

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A FURTHER DITHIENYLACETYLENE FROM *ECLIPTA ERECTA*

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Key Word Index—*Eclipta erecta*; Compositae; acetylenes; dithiophene derivative.

Abstract—The roots and the aerial parts of *Eclipta erecta* afforded, in addition to compounds reported previously, a new dithienyl derivative.

Eclipta erecta L. (= *E. alba* Hassk. = *E. prostrata* L.) has been studied previously [1–3]. The roots especially are rich in thiophene acetylenes. We have re-studied a sample which was grown in the Botanical Garden of Rajasthan University. The roots gave, in addition to the compounds isolated previously [1, 2], the diisovalerate, **1**. The structure followed clearly from the spectroscopic data. A broad UV maximum at 335 nm is typical for dithienylacetylenes while the ^1H NMR spectrum (see Experimental) indicated the presence of two isovalerate residues. A singlet at δ5.21