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TRITERPENOIDS OF *SCOPARIA DULCIS*

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Key Word Index—*Scoparia dulcis*; Scrophulariaceae; friedelin; glutinol; α-amyrin; ifflaionic acid; dulcioic acid.

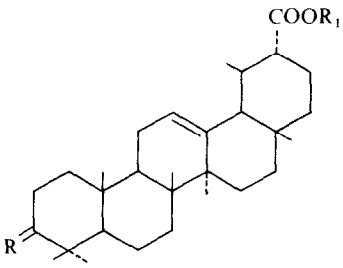
Abstract—The triterpenoids of *Scoparia dulcis* were identified as friedelin, glutinol, α-amyrin, betulinic acid, ifflaionic acid and dulcioic acid.

Scoparia dulcis L. (Scrophulariaceae) is reputed for its medicinal property. 'Amellin', which has been used in India as an antidiabetic principle, was obtained from the fresh plant [1, 2]. The plant is reported to be used as a cure for hypertension in Taiwan [3]. Several groups of investigators carried out phytochemical work on this plant and reported the isolation of hexacosanol, tritriacontane, sitosterol, D-mannitol, three unidentified compounds, dulciol, dulciolone and scoparol [4–6], betulinic acid, ifflaionic acid and benzoxazolinone [7]. The present communication reports the isolation and characterization of the three unidentified compounds in addition to a new triterpenic acid designated as dulcioic acid (**1**).

Repeated Si gel column chromatography of a petrol extract of the dried and powdered whole plant led to the isolation of pure crystalline compounds SD-I, SD-II, SD-III, SD-IV and a mixture of SD-V and SD-VI. SD-V and SD-VI could be separated by esterification with CH_2N_2 followed by chromatography. Compound SD-1, mp 264–266° was identical with friedelin (mmp, IR, ^{1}H NMR, MS). By comparison of the physical data, dulciolone, previously isolated from the plant [5, 6], seemed to be identical with friedelin. SD-II, mp 209–210° was characterized as glutinol by comparison of its mass and ^{1}H NMR spectra with those of an authentic sample. The ^{13}C NMR spectrum of this compound was recorded and carbon chemical shifts were assigned by multiplicity information obtained from single frequency off-resonance spectra, known chemical shift rules [8] and by comparison of shift data of other triterpenes [9–11]. The reported physical data of dulciol [5–6] indicated its identity with glutinol. SD-III, mp 184–186°, whose physical data compared well with those of scoparol was identical with α-amyrin. SD-IV was characterized as betulinic acid. SD-V', 180–182°, showed positive Liebermann–Burchard and tetranitromethane tests. The IR spectrum showed absorbance at 1730 and 1695 cm^{-1} indicating the presence of an ester carbonyl and a ketonic function. The ^{1}H NMR spectrum displayed signals attributable to seven methyls, a carbomethoxy group, a trisubstituted double bond and two α-protons to a carbonyl group. The mass spectrum showed peaks at *m/e* 468 (M^+), 262 (retro Diels–Alder fragment *a*, base peak) and 247 (*a* − Me) characteristic of methyl ifflaionate (**2**) [7]. On saponification, SD-V' readily yielded an acid, mp 265–266°, which was found to be identical with an authentic sample of ifflaionic acid (**5**) (mp, mmp, TLC, IR, MS).

SD-VI' (**3**), mp 192–194°, formed an acetate (**4**), mp 258–259°, which showed in its ^{1}H NMR spectrum signals assignable to seven methyls, a carbomethoxy group, an acetoxy methyl, a trisubstituted double bond and a carbonyl proton. The MS of **3** showed a fragmentation

pattern characteristic of a Δ^{12}-oleanene or ursene skeleton [12]. The appearance of the base peak at *m/e* 262 (retro Diels–Alder fragment *a*), a peak at 247 (*a* − Me) and a peak of relatively low intensity at 203 (*a* − COOMe) indicated the presence of the carbomethoxy group at C-19 or C-20 which was supported by the facile formation of dulcioic acid (**1**) on saponification of **3**. Moreover, the ^{1}H NMR spectrum of **3** showed a doublet at δ 2.22 assignable to 18-H which is characteristic of an ursane skeleton [13]. Finally, the structure of dulcioic acid (**1**) was confirmed as follows: Jones oxidation of **1** yielded ifflaionic acid (**5**). On the other hand, $NaBH_4$ reduction of ifflaionic acid methyl ester yielded two products. The major product (β-isomer) was identical in all respects to methyl dulcioate (**3**). It may be mentioned that the structure of bryonolic acid [14], previously proposed as **1**, has now been revised [15, 16].



1 R = H, OH(β), R_1 = H
2 R = O, R_1 = Me
3 R = H, OH(β), R_1 = Me
4 R = H, OAc(β), R_1 = Me
5 R = O, R_1 = H

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR spectra were measured at 60 or 100 MHz in $CDCl_3$ with TMS as internal standard; MS were recorded with a direct inlet system at 70 eV.

Extraction and isolation of triterpenoids. Air-dried and powdered plant material (1 kg), collected in August from southern areas of Calcutta, was exhaustively extracted with petrol (60–80°). The residue (24 g) obtained after removal of solvent was subjected to chromatography on Si gel (300 g). Elution with petrol–C_6H_6 (3:2) yielded successively friedelin, mp 264–266°, ^{1}H NMR and MS identical with those of an authentic sample; glutinol, mp 209–210°, $[\alpha]_D$ + 61° (*c* 1.1 in $CHCl_3$); ^{1}H NMR: δ 0.85, 0.95, 0.98, 1.00, 1.05, 1.09, 1.15 and 1.17 (each 3H, *s*), 3.45 (1H, *br. s*) and 5.60 (1H, *m*); MS *m/e* (rel. int.): 426 (M^+, 12), 411 (M^+ − Me, 6), 408 (M^+ − H_2O, 4), 393 (M^+ − H_2O − Me, 5), 274 (retro Diels–Alder fragment *a*, 100), 259 (*a* − Me, 84), 205 (25), ^{13}C NMR: δ (assignment) 39.1 (C-1), 28.0 (C-2), 76.4 (C-3), 39.4 (C-4), 141.7 (C-5), 122.1 (C-6), 33.3 (C-7), 49.9[a] (C-8), 38.0 (C-9), 47.6[a] (C-10), 35.2 (C-11), 23.8 (C-12), 31.8 (C-13), 34.9 (C-14), 32.4[b] (C-15), 30.5 (C-16), 30.2 (C-17), 43.2 (C-18), 36.1 (C-19), 29.8 (C-20), 29.0 (C-21), 34.5[b] (C-22), 34.7 (C-23), 18.3 (C-24), 19.7 (C-25), 16.3 (C-26), 18.3 (C-27), 28.3 (C-28), 32.2 (C-29), 25.5 (C-30) [superscript *a*, *b* = may be reversed], acetate, mp 190–191°, $[\alpha]_D$ + 80° (*c*, 0.8 in $CHCl_3$). α-Amyrin, mp 184–186°, $[\alpha]_D$ + 81° (*c*, 1.3 in $CHCl_3$), ^{1}H NMR and MS identical with those of authentic sample. Elution of the column with $CHCl_3$ afforded betulinic acid (identified by comparison with an authentic sample). The gummy solid obtained by elution of the column with $CHCl_3$–MeOH (19:1) was esterified with an ethereal soln of CH_2N_2 and then chromatographed on a Si gel column using petrol–C_6H_6 (3:7) as eluent. The earlier fractions yielded methyl ifflaionate; the later fractions on further purification by chromatography afforded methyl dulcioate.

Methyl ifflaionate (**2**) crystallized from MeOH–$CHCl_3$ as colourless needles, mp 180–182°; $[\alpha]_D$ + 74° (*c* 1.6 in $CHCl_3$); IR ν_{max} cm^{-1}: 1730, 1695; ^{1}H NMR: δ 0.83 (6H, *s*), 1.07, 1.11 (15H, *s* each), 2.45 (2H, *m*), 3.65 (3H, *s*), 5.03 (1H, *t*-like); MS *m/e* (rel. int.): 468 (M^+, 15.5), 453 (M^+ − Me, 6.5), 409 (M^+ − COOMe, 2.2), 408 (M^+ − HOAc, 1.8), 262 (retro Diels–Alder fragment *a*, 100), 249 (8), 247 (*a* − Me, 5.5), 215 (13), 203 (8), 201 (9), 187 (20), 161 (18). (Found: C, 79.40; H, 10.29. Calc. for $C_{31}H_{48}O_3$: C, 79.43; H, 10.32%).

Ifflaionic acid (**5**). Methyl ifflaionate (20 mg) on saponification with 5% KOH–EtOH (12 ml) for 2 hr at steam-bath temp. yielded **5** which crystallized from MeOH as colourless needles, mp 265–266°, $[\alpha]_D$ + 88° (*c* 1.2 in $CHCl_3$): IR ν_{max} cm^{-1}: 3230, 1735, 1705, 1690, ^{1}H NMR: δ 0.84 (6H, *s*), 1.07, 1.10 (15H, each *s*), 2.45 (2H, *m*), 5.03 (1H, *t*-like). (Found: C, 79.26; H, 10.24. Calc. for $C_{30}H_{46}O_3$: C, 79.24; H, 10.20%).

Methyl dulcioate (**3**) crystallized from *n*-hexane–Me_2CO as needles, mp 192–194°; $[\alpha]_D$ + 72° (*c* 0.6 in $CHCl_3$); IR ν_{max} cm^{-1}: 3400, 1725, 1165, 1020; ^{1}H NMR: δ 0.85 (6H, *s*), 1.06, 1.07, 1.12 (15H, *s* each), 3.45 (1H, *br. s*), 3.65 (3H, COOMe, *s*), 5.04 (12-H, *t*-like); MS *m/e* (rel. int.): 470 (M^+, 6), 455 (M^+ − Me, 1.2), 452 (M^+ − H_2O, 6.5), 439 (M^+ − OMe, 1.2), 437 (1.6), 411 (M^+ − COOMe, 1), 316 (1.8), 263 (20), 262 (retro Diels–Alder fragment *a*, 100), 249 (2.5), 247 (*a* − Me, 4), 233 (3.8), 215 (11.5), 207 (15.4), 203 (7.5), 202 (6), 201 (8), 189 (8.8), 187 (17), 173 (11), 161 (15.4). (Found: C, 79.22; H, 10.65. $C_{31}H_{50}O_3$ requires: C, 79.10; H, 10.71%).

Acetate of methyl dulcioate (**4**). Methyl dulcioate (20 mg) furnished the acetate (**4**) wih Ac_2O (2 ml) and pyridine (1 ml) when heated on a steam bath for 1 hr. It crystallized as plates from MeOH–$CHCl_3$, mp 258–259°, $[\alpha]_D$ + 75° (*c* 1.5 in $CHCl_3$); IR ν_{max} cm^{-1}: 1730 (br), 1235, 1165; ^{1}H NMR: δ 0.84 (6H, *s*), 1.07, 1.08, 1.12 (15H, *s* each), 2.01 (acetoxy methyl), 3.65 (COOMe), 4.46 (3-H, *t*, *J* = 7 Hz) and 5.03 (12-H, *t*-like); MS *m/e* (rel. int.): 512 (M^+, 6.3), 497 (M^+ − Me, 1), 481 (M^+ − OMe, 1.2), 453 (M^+ − COOMe, 5.6), 452 (M^+ − HOAc, 12), 437 (4.5), 409 (3.5), 314 (4.5), 263 (30), 262 (retro Diels–Alder fragment *a*, 100), 249 (fragment *b*, 11), 247 (*a* − Me, 5.6), 205 (17), 203 (*a* − COOMe, 16), 201 (15), 189 (*b* − HOAc, 30), 187 (29), 161 (30.5). (Found: C, 77.21; H, 10.18. $C_{33}H_{52}O_4$ requires: C, 77.29; H, 10.22%).

Dulcioic acid (**1**). Treatment of **3** (15 mg) with 5% KOH–EtOH (10 ml) for 2 hr at steam-bath temp. furnished **1** (10 mg) which crystallized from MeOH, mp 275–277°, $[\alpha]_D$ + 69° (*c*, 1.2 in $CHCl_3$); M^+ 456. (Found: C, 78.76; H, 10.54. $C_{30}H_{48}O_3$ requires: C, 78.89; H, 10.59%).

Oxidation of dulcioic acid (**1**) *to ifflaionic acid* (**5**). A soln of dulcioic acid (15 mg) in Me_2CO (12 ml) was cooled to 0° and excess Jones reagent [17] was added. The reaction mixture was stirred at 0° for 20 min and worked-up in the usual way. The product was purified by chromatography and crystallized from MeOH as needles, mp 265–266°.

Conversion of methyl ifflaionate (**2**) *to methyl dulcioate* (**3**). To a soln of methyl ifflaionate (10 mg) in MeOH (5 ml), $NaBH_4$ (3 mg) was added and the reaction mixture was kept at room temp. for 1 hr. After work-up in the usual way, the major product (β-isomer) was purified by prep. TLC and crystallized from *n*-hexane–Me_2CO as needles, mp 192–194°.

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PROCERANONE, A NEW TETRANORTRITERPENOID FROM *CARAPA PROCERA*

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Key Word Index—*Carapa procera*; Meliaceae; tetranortriterpenoid; proceranone.

Abstract—A new tetranortriterpenoid, named proceranone, has been isolated from the seeds of *Carapa procera* and its structure elucidated by IR, NMR and mass spectral studies.

We have recently reported [1] the isolation and structure elucidation of evodulone (**1**) from the seeds of *Carapa procera*. In continuation of our investigation on the same seeds, we have isolated α-obacunyl acetate [2], methyl angolensate [3] and a previously undescribed limonoid of novel structure which we name proceranone and formulate as structure **2**.

Compound **2** had absorption bands in the IR (KBr) spectrum attributable to an acetate (1725 cm^{-1}), an α,β-unsaturated carbonyl group (1685 cm^{-1}) and an α,β-substituted furan (875 cm^{-1}). Its ^1H NMR spectrum was particularly informative and was similar to that of evodulone. Thus, evodulone and compound **2** both showed resonances of the same intensity and multiplicity for the protons at C-1, C-2, C-21, C-22 and C-23. The differences between the chemical shifts for corresponding hydrogens were not greater than 0.06 ppm. This similarity extended to the C-methyl region, except for the C-13