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ENANTIO-EUDESMANE SESQUITERPENES FROM *VERBESINA RUPESTRIS*

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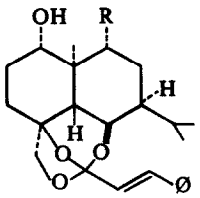
Key Word Index—*Verbesina rupestris*; Compositae; enantio-eudesmane sesquiterpenes.

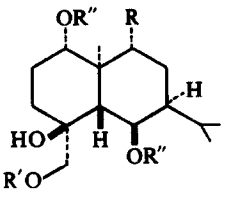
Abstract—The leaves and stems of *Verbesina rupestris* contain enantio-eudesmane sesquiterpenes, isolated as esters of cinnamic acid. This finding supports the reclassification of *Chaenocephalus rupestris* to *V. rupestris*.

INTRODUCTION

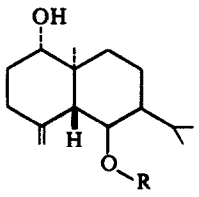
During our investigation of the constitutents of the shrub *Verbesina rupestris*, we isolated a new enantio-eudesmane sesquiterpene, rupestrol, as its cinnamate (**1**) and orthocinnamate (**2**) esters [1]. Further investigation has now yielded two other enantio-eudesmane sesquiterpenes, rupestrinol, as its cinnamate (**3**) and orthocinnamate (**4**) esters, as well as β-chaenocephalol, as its cinnamate ester (**5**).



(**2**) R = OH
(**4**) R = H



(**1**) R = OH, R′ = cinnamoyl, R″ = H
(**3**) R = H, R′ = cinnamoyl, R″ = H
(**7**) R = R′ = R″ = H
(**8**) R = H, R′ = R″ = Ac



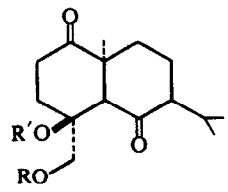
(**5**) R = cinnamoyl
(**17**) R = H

RESULTS AND DISCUSSION

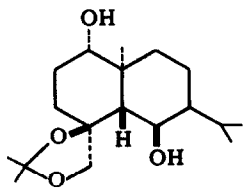
Rupestrinol orthocinnamate, like rupestrol orthocinnamate [1], showed the spectroscopic properties typical of a styrene and was quantitatively converted to the cinnamate (**3**), mp 116–118°, in aqueous acidic solutions.

The NMR spectrum of rupestrinol cinnamate (**3**) (d_6-DMSO) showed the resonances of the isopropyl group (δ 0.93 and 1.11, each 3H, *d*, J = 6.5 Hz), the tertiary, C-15, methyl group (δ 1.0, 3H, *s*), three hydroxyl groups (two secondary and one tertiary), the esterified C-14 hydroxymethyl group (δ 4.52, 2H, *s*) and other signals typical of a cinnamate ester. Oxidation of **3** with the Jones reagent in acetone gave the neutral diketone (**6**), mp 151–153°, ν_{max} 3300 and 1709 cm^{-1}, which showed no base-induced changes in its UV spectrum indicating the absence of an enolizable α- or β- diketone system.

Hydrolysis of the ester (**3**) yielded cinnamic acid and the sesquiterpene rupestrinol (**7**), mp 179–180°, $[\alpha]_D$ + 11°, which on acetylation gave the triacetate (**8**), ν_{max} 3584 and 1730 cm^{-1}; δ 4.69 (1H, *dd*, J = 9.5 and 5.5 Hz, *axial* H-1), 5.47 (1H, *dd*, J = 12.5 and 3.0 Hz,



(**6**) R = cinnamoyl, R′ = H
(**10**) R = R′ = acetonide
(**14**) R = R′ = H



(**9**)

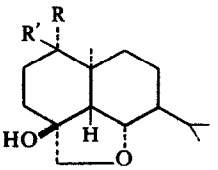
axial H-6), 3.93 (1H, *d*, J = 12.0 Hz, $W_{\frac{1}{2}}$ 1.6 Hz, H-14) and 4.45 (1H, *d*, J = 12.0 Hz, $W_{\frac{1}{2}}$ 2.5 Hz, H′-14). The inertness of **3** to sodium periodate and other reactions to be described, excluded C-3 as the site of one secondary acetoxyl group. A comparison of the NMR spectrum of **3** with that of the corresponding compound of rupestrol (**1**) and the frequency of occurrence of C-1 rather than C-9 hydroxyl groups in eudesmane sesquiterpenes, suggested that these two secondary acetoxyl groups were located at C-1 and C-6.

Acetonation of **7** with acetone and dry cupric sulphate gave **9** whose NMR spectrum (δ 1.93, 1H, *d* J = 9.75 Hz, H-5 and δ 4.20, 1H, *dd*, J = 9.75 and 3.5 Hz, H-6) indicated a *cis* relationship between H-6 and H-7 (J = 3.5 Hz). Thus ring B was either in a flexible or chair conformation, the flexible being favoured because of the conformational instability of an axial isopropyl group necessitated by the chair, and by analogy with rupestrol whose ring B was shown to occupy a flexible conformation.

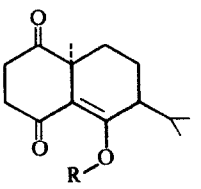
Oxidation of the acetonide (**9**) by the Jones reagent in acetone gave the diketone (**10**), ν_{max} 1712 cm^{-1}, whose NMR spectrum (δ 3.32, 1H, *s*, $W_{\frac{1}{2}}$ 1.25 Hz, H-5; δ 4.0, 1H, *d*, J = 7.5 Hz, $W_{\frac{1}{2}}$ 1.4 Hz, H-14; and δ 5.03, 1H, *dd*, J = 7.5 and 1.75 Hz, H′-14) showed a large long range coupling of the lower-field proton of the C-14 methylene group. This large long range coupling was consistent with an axial C-14 methylene when the classical W arrangement required for such coupling, could be achieved by the bonds connecting H′-14 to H-3β or H-5. H′-14 was coupled to H-3β, however, as shown by the width at half height of the signal due to H-5. Long range coupling of this type was also observed in the NMR spectra of **8** and **6**.

The anhydro-compound (**11**), mp 148–150°, was obtained in 80% yield by the action of dry cupric sulphate and a few drops of concentrated sulphuric acid on a solution of **7** in anhydrous dioxan or THF; without cupric sulphate a complex mixture, which did not contain **11**, was obtained. The NMR spectrum of **11** showed the resonance due to H-6 as a triplet at δ 4.25 (J = 5.5 Hz), suggesting that the configuration at C-6 had been inverted, so resulting in an equatorial H-6 and an axial oxygen (ether) function. Acetylation and oxidation of **11** yielded a mono-acetate (**12**), mp 95–97°, and a mono-ketone (**13**), mp 104–105°, ν_{max} 1709 cm^{-1}, respectively. The ether linkage was therefore from C-14 to C-6, which required an axial C-14 hydroxymethyl group in **7**, consistent with the assignment based on the NMR data already presented.

Hydrolysis of the acetonide linkages of **10** with 70% aqueous acetic acid yielded the diketo-diol (**14**), mp 102–103°, which on oxidation with sodium periodate gave the triketone (**15**), ν_{max} 3413, 1595 cm^{-1}; λ_{max} 291.0 nm (ε 7,500), shifting to 311.5 nm (ε 9.500) on the addition of base (NaOH); δ 16.05 (1H, *s*, enolic proton of the β-diketone system). There was no signal in the NMR spectrum of **15** due to H-5, indicating that **15** was totally, or nearly so, enolised in $CDCl_3$.



(**11**) R = OH, R′ = H
(**12**) R = OAc, R′ = H
(**13**) R = R′ = O



(**15**) R = H
(**16**) R = Ac

Acetylation of **15** with isopropenyl acetate, gave **16** whose NMR spectrum showed a singlet at δ 2.68 (4H, $W_{\frac{1}{2}}$ 3.1 Hz) which was shifted upfield, as a singlet, in a 2:1 deuterochloroform–benzene solution, suggesting that these protons were in similar environments. This was consistent with the structure shown for the acetate (**15**) in which the C-2 and C-3 methylene protons are both α to carbonyl groups.

The CD curve of the ketone (**13**), which showed $\Delta\varepsilon$ + 2.88 at λ_{max} 297 nm, suggested that **13** had the absolute configuration shown and therefore rupestrinol had the absolute configuration shown by **7** [2]. Thus rupestrinol, like its co-metabolite rupesterol, is epimeric at C-4, C-5 and C-10 with dihydroeudesmol.

The NMR spectrum of β-chaenocephalol cinnamate (**5**), showed the resonances typical of a cinnamate ester and other signals at δ 3.47 (1H, *dd*, J = 10.0 and 5.0 Hz, *axial* H-1), 4.32 and 4.80 (each 1H, *s*, exocyclic methylene C-14) and 5.30 (1H, *dd*, J = 11.0 and 4.0 Hz, *axial* H-6). Hydrolysis of **5** with KOH in methanol yielded cinnamic acid and the sesquiterpene (**17**), mp 115–116°, ν_{max} 3325 cm^{-1}; δ 3.49 (1H, *dd*, J = 10.5 and 4.5 Hz, *axial* H-1), 4.27 (1H, *dd*, J = 11.0 and 4.5 Hz, *axial* H-6), 5.05 and 4.80 (each 1H, *s*, exocyclic methylene). The down-field shift of the olefinic proton closer to the generated hydroxyl group suggests that the sesquiterpene was esterified at C-6.

Hydroxylation of **17** by osmium tetroxide occurred, as expected, at the less hindered β face of the double bond and yielded a glycol which was identical with rupestrinol. Thus the structure and absolute stereochemistry of β-chaenocephalol was as shown by **17**.

Verbesina rupestris (Urb.) Blake was initially classified as *Chaenocephalus rupestris* (Urb.). Although there existed some doubt as to the validity of this reclassification [3], we think the chemotaxonomic evidence supports the reclassification as similar eudesmane sesquiterpenes have been isolated from *Verbesina virginica* [4].

EXPERIMENTAL

Mps were taken on a micro hot-stage and are uncorrected. UV spectra were recorded for EtOH solns. IR spectra were obtained for $CHCl_3$ solns unless otherwise stated. Specific rotations were determined for EtOH solns. NMR spectra were obtained for $CDCl_3$ solns, unless otherwise stated, with TMS as internal reference. The petrol used for crystallisation had bp 60–80°.

Isolation of rupestrinol cinnamate (3) *and chaenocephalol cinnamate* (5). The dried, milled leaves and twigs of *Verbesina rupestris* (2.0 kg) were percolated with Me_2CO until the eluate was pale green. The gum (130 g) resulting from evap. of the solvent was partitioned between 80% aq. EtOH (1 l.) and petrol (2 × 500 ml). The petrol soluble portion (65 g) was chromatographed on Al_2O_3. The fraction eluted with C_6H_6 was rechromatographed and further purified by PLC to give chaenocephalol cinnamate (5), 400 mg; IR ν_{max} cm^{-1}: 3400, 3020, 1700, 1670, 1570, 1440, 973, 900, 875, 840; UV λ_{max} nm: 207.0, 213.0, 250.0 (ε 24800, 15100, 22000); NMR: δ 6.30 (1H, *d*, *J* = 16 Hz, φ − CH = C<u>H</u>—CO—), 7.60 (1H, *d*, *J* = 16 Hz, φ-C<u>H</u> = CH − CO—), 7.40 (5H, *m*, $C_6\underline{H}_5$-CH = CH—CO—), 5.35 (1H, *m*, H-6), 4.85 and 4.35 (each 1H, *s*, = C<u>H</u>$_2$), 3.50 (1H, *m*, H-1), 1.70 (1H, —O<u>H</u>), 1.05 and 0.92 (each 3H, *d*, *J* = 6.0 Hz, C-12 and C-13 methyls), 0.85 (3H, *s*, C-15 methyl). A C_6H_6 soln of the aq. EtOH-soluble substances yielded, on standing, a mixture of crystals of rupestrol and rupestrinol cinnamates, (1) and (3). Chromatography of the filtrate on Al_2O_3 afforded more rupestrinol cinnamate (3) which was recrystallized from MeOH–C_6H_6 as cubes (2.98 g) mp 116–118°; IR ν_{max} cm^{-1}: 3460, 3300, 1724, 1640, 1570, 1482, 1440, 977; UV λ_{max} nm: 217.5, 223.0, 277.5 (ε 16200, 14200, 22200), NMR: δ 6.51 (1H, *d*, *J* = 16.0 Hz, φ − CH = C<u>H</u>—CO—), 7.75 (1H, *d*, *J* = 16.0 Hz, φ-C<u>H</u>=CH—CO—), 7.45 (5H, *m*, $C_6\underline{H}_5$—CH=CH—CO—), 5.13 (1H, —O—<u>H</u>), 4.62 (2H, *s*, C-14 —C<u>H</u>$_2$—), 4.42 (1H, *m*, H-6), 3.90 (2H, —O—<u>H</u>), 3.38 (1H, *m*, H-1), 1.11 and 0.93 (each 3H, *d*, *J* = 6.5 Hz, C-12 and C-13 methyls), 1.0 (3H, *s*, C-15 methyl) $[\alpha]_D$ + 8.0, (found: C, 68.61; H, 8.67. $C_{24}H_{34}O_5 . H_2O$ requires C, 68.54; H, 8.63%); and rupestrinol orthocinnamate (4), a gum; IR ν_{max} cm^{-1}: 3400, 1650, 900, 750; NMR: δ 7.45 (5H, *m*, $C_6\underline{H}_5$—CH=CH—), 7.12 (1H, *d*, *J* = 16.5 Hz, φ—C<u>H</u>=CH—), 6.22 (1H, *d*, *J* = 16.5 Hz, φ—CH=C<u>H</u>—), 4.48 (1H, $W_{\frac{1}{2}}$ = 18 Hz, H-6), 4.44 (1H, *d*, *J* = 7.5 Hz, H-14), 3.55 (1H, *dd*, *J* = 7.5 and 1.3 Hz, H'-14), 3.40 (1H, *m*, H-1), 1.12 and 0.95 (each 3H, *d*, *J* = 6.0 Hz, C-12 and C-13 methyls), 1.03 (3H, *s*, C-15 methyl).

The diketone (6). Rupestrinol cinnamate (3), (0.06 g) dissolved in Me_2CO (20.0 ml) was oxidised with the Jones reagent in the usual manner. The ketone (6) was purified by PLC and recrystallized from MeOH–H_2O as needles (0.05 g) mp 151–153°; IR ν_{max} cm^{-1}: 3300, 1709, 1637, 1600, 1581, 1480, 1450, 977; UV λ_{max} nm: 217.5, 223.0, 277.5 (ε 14400, 14200, 22900); NMR: δ 5.30 (1H, *d*, *J* = 12.5 Hz, $W_{\frac{1}{2}}$ 2.9 Hz, H'-14), 4.89 (1H, *d*, *J* = 12.5 Hz, $W_{\frac{1}{2}}$ 1.1 Hz, H-14), 3.08 (1H, *s*, $W_{\frac{1}{2}}$ 1.2 Hz, H-5), 3.08 (1H, —O—<u>H</u>), 1.22 (3H, *s*, C-15 methyl), 0.94 and 0.91 (each 3H, *d*, *J* = 6.0 Hz, C-12 and C-13 methyls) (Found: C, 71.84; H, 7.76. $C_{24}H_{30}O_5$ requires C, 72.33; H, 7.59%).

Rupestrinol (7). Rupestrinol cinnamate (3) (1.21 g) was refluxed with 1% KOH in MeOH (22.0 ml) for 4 h, the reaction mixture diluted with H_2O (150 ml) and extracted with EtOAc (5 × 50 ml). The EtOAc was removed *in vacuo* to yield the alcohol (7), which was recrystallized from EtOAc as needles (0.739 g) mp 179–180°; IR ν_{max}^{nujol} cm^{-1}: 3193; NMR (DMSO): δ 5.6 (1H, *d*, *J* = 3.5 Hz, —O—<u>H</u>), 5.31 (1H, *s*, —O—<u>H</u>), 4.31 (1H, *d*, *J* = 4.5 Hz, —O—<u>H</u>), 4.23 (1H, *m*, H-6), 4.07 (1H, *t*, *J* = 5.5 Hz, —CH$_2$—O—<u>H</u>), 3.52 (2H, *d*, *J* = 5.5 Hz, —C<u>H</u>$_2$—O—H, with D_2O signals changes to *s*), 1.04 and 0.87 (each 3H, *d*, *J* = 6.5 Hz, C-12 and C-13 methyls), 0.80 (3H, *s*, C-15 methyl); $[\alpha]_D$ + 11.0° (Found: C, 66.25; H, 10.27. $C_{15}H_{28}O_4$ requires C, 66.14; H, 10.36%).

Triacetate (8). A soln of rupestrinol (7) (0.1 g) in Py (2.0 ml) and Ac_2O (2.0 ml) was left to stand overnight at room temp. The reaction mixture was diluted with H_2O (150 ml), extracted with EtOAc (3 × 30 ml) and the EtOAc extract washed with 3N H_2SO_4 (2 × 50 ml). Removal of the solvent gave the gummy triacetate (8) quantitatively; IR ν_{max} cm^{-1}: 3584, 1730; NMR: δ 5.47 (1H, *dd*, *J* = 12.5 and 3.0 Hz, H-6), 4.69 (1H, *dd*, *J* = 9.5 and 5.5 Hz, H-1), 4.45 (1H, *d*, *J* = 12.0 Hz, $W_{\frac{1}{2}}$ 2.5 Hz, H'-14), 3.93 (1H, *d*, *J* = 12.0 Hz, $W_{\frac{1}{2}}$ 1.6 Hz, H-14), 3.89 (1H, —O—<u>H</u>), 2.03, 2.07, 2.15 (each 3H, *s*, —O.CO—C<u>H</u>$_3$).

Acetonide (9). A soln of rupestrinol (7) (0.6 g) in Me_2CO (25 ml) was stirred with dry $CuSO_4$ (2.0 g) for 3 days. After filtration and evap. of the solvent, the products were separated by PLC to yield the gummy and unstable acetonide (9) (0.505 g), IR ν_{max} cm^{-1}: 3300; NMR: δ 4.40 (1H, —O—<u>H</u>), 4.20 (1H, *dd*, *J* = 9.75 and 3.5 Hz, H-6), 3.93 (2H, *s*, —C<u>H</u>$_2$—O—) 3.33 (1H, *dd*, *J* = 10.0 and 5.0 Hz, H-1) 2.6 (1H, —O—<u>H</u>), 1.93 (1H, *d*, *J* = 9.75 Hz, H-5), 1.41 and 1.43 (each 3H, *s*, acetonide methyls).

The ether (11). To a stirred solution of rupestrinol (7) (1 g) in anhydrous THF or dioxan (50 ml) was added dry $CuSO_4$ (2.0 g) and conc H_2SO_4 (3 drops). After 3 days, K_2CO_3 (0.50 g) was added and after a further 1 hr the solids were removed by filtration. Evap. of the solvent *in vacuo* yielded the ether (11) which was recrystallized from $CHCl_3$–petrol as needles (0.75 g) mp 148–150°; IR ν_{max} cm^{-1}: 3521, 3344; NMR: δ 4.25 (1H, *t*, *J* = 5.5 Hz, H-6), 3.75 and 3.97 (each 1H, *d*, *J* = 10.0 Hz, C—C<u>H</u>$_2$—O—), 3.48 (1H, *m*, H-1), 2.23 (1H, —O—<u>H</u>), 1.12 (3H, *s*, C-15 methyl) (Found: C, 70.63; H, 10.27. $C_{15}H_{26}O_3$ requires C, 70.70; H, 10.30%).

The ketone 13. The ether (11) (0.147 g) dissolved in Me_2CO (50 ml) was oxidised by the Jones' reagent in the usual manner. The ketone (13) was purified by PLC and was recrystallized from $CHCl_3$–petrol as needles (0.138 g) mp 104–105°, IR ν_{max} cm^{-1}: 3472, 3333, 1709; NMR: δ 4.23 (1H, *t*, *J* = 6.0 Hz, H-6), 4.0 (2H, *s*, C—C<u>H</u>$_2$—O—), 2.92 (1H, —O—<u>H</u>), 1.98 (1H, *d*, *J* = 6.0 Hz, H-5); CD $\Delta\varepsilon_{297.0\,nm}$ + 2.89; (Found: C, 71.55; H, 9.49. $C_{15}H_{24}O_3$ requires C, 71.39; H, 9.59%).

The acetate (12). The ether (11) (0.116 g) was acetylated according to the procedure described for the acetylation of 7 and the product was purified by PLC. 12 was recrystallized from MeOH–H_2O as needles (0.108 g) mp 95–97°; IR ν_{max} cm^{-1}: 3497, 3344, 1727; NMR: δ 4.69 (1H, *m*, H-1), 4.25 (1H, *t*, *J* = 5.5 Hz, H-6), 3.97 and 3.72 (each 1H, d, *J* = 9.5 Hz, —C<u>H</u>$_2$—O—), 2.29 (1H, —O<u>H</u>), 2.03 (3H, *s*, —O . CO . C<u>H</u>$_3$), (Found: C, 68.65; H, 9.53, $C_{17}H_{28}O_4$ requires C, 68.99; H, 9.52%).

The diketone (10). The acetonide (9) (0.097 g) was dissolved in Me_2CO (20 ml) and was oxidised by the Jones' reagent in the usual manner. The product was purified by PLC to give the gummy diketone (10), IR ν_{max} cm^{-1}: 1712; NMR: δ 5.03 (1H, *dd*, *J* = 7.5 and 1.75 Hz, H'-14), 4.00 (1H, *d*, *J* = 7.5 Hz, H-14), 3.32 (1H, *s*, $W_{\frac{1}{2}}$ 1.25 Hz, H-5).

The diketo-diol (14). A soln of the acetonide (10) (0.09 g) in 60% aq. HOAc (10 ml) was set aside for 2 days at room temp. The soln was then diluted with H_2O (100 ml), made alkaline by adding solid K_2CO_3 and extracted with EtOAc (3 × 30 ml). The products (0.079 g), a mixture of 10 and 14, were separated by PLC to give 14 which was recrystallized from $CHCl_3$–petrol as needles (0.063 g) mp 102–103°; IR ν_{max} cm^{-1}:3571, 3390, 1704; NMR: δ 4.35 and 3.65 (each 1H, *d*, *J* = 12.0 Hz, —C<u>H</u>$_2$—O—), 3.65 (2H, *m*, —O—<u>H</u>), 3.32 (1H, *s*, H-5) (Found: C, 67.28; H, 8.95. $C_{15}H_{24}O_4$ requires C, 67.13; H, 9.02%).

The triketone (15). To a soln of the diol (14) (0.15 g) in EtOH (8.0 ml) was added saturated, aq. $NaIO_4$ soln (2 ml) and after 17 min this soln was diluted with H_2O (150 ml) and extracted with EtOAc (4 × 30 ml). Removal of the solvent, *in vacuo*, gave the gummy triketone (15) (0.103 g), IR ν_{max} cm^{-1}: 3413, 1701, 1595; UV λ_{max} nm: 291.0 (ε 7500), with NaOH, 311.5 nm (ε 9500); NMR: δ 16.05 (1H, *s*, enolic —O—<u>H</u>) (Found: C, 71.33; H, 8.70. $C_{14}H_{20}O_3$ requires C, 71.16; H, 8.53%).

The enolacetate (16). A drop of conc H_2SO_4 was added to a soln of the triketone (15) (0.07 g) in isopropenyl acetate (4 ml) and this soln was set aside for 24 h. The reaction mixture was then diluted with EtOAc (50 ml), washed with H_2O (3 × 30 ml) and, after drying the organic layer with $MgSO_4$, the solvent was removed *in vacuo*. The gummy acetate (16) was purified by PLC. IR ν_{max} cm^{-1}: 1748, 1706, 1695, 1618; NMR: δ 2.17 (3H, *s*, —O. CO. C<u>H</u>$_3$).

Chaenocephalol (17). Chaenocephalol cinnamate (5) (1.1 g) was refluxed with $LiAlH_4$ (0.56 g) in dry THF (80 ml) for 1 hr. To the resulting reaction mixture was added EtOAc (25 ml, followed by 5% aq. NaOH soln (10 ml), and the precipitated Al_2O_3 was removed by filtration. The filtrate was conc *in vacuo*, diluted with EtOAc (100 ml), washed with H_2O (3 × 50 ml),

dried with Na_2SO_4 and the solvent removed *in vacuo*. The resulting gum was resolved by PLC to give chaenocephalol (**17**), which was recrystallized from Me_2CO–H_2O as prisms (0.1 g) mp 115–116°; IR ν_{max} cm^{-1}: 3250, 885, 840; NMR: δ 5.08 and 4.80 (each 1H, *s*, $=CH_2$), 4.17 (1H, *dd*, J = 12.0 and 4.0 Hz, H-6), 3.47 (1H, *dd*, J = 10.0 and 5.0 Hz, H-1), 1.77 (1H, —O—H), 1.10 and 0.97 (each 3H, *d*, J = 6.0 Hz, C-12 and C-13 methyls), 0.75 (3H, *s*, C-15 methyl) (Found: C, 75.31; H, 10.79. $C_{15}H_{26}O_2$ requires C, 75.58; H, 11.00%).

Hydroxylation of chaenocephalol (**17**) *with* OsO_4. OsO_4 (0.04 g) was added, with stirring, to a soln of chaenocephalol (**17**) (0.045 g) in dry dioxan (10 ml) and Py (1 ml). The reaction mixture was set aside for 18 h at room temp., then saturated with H_2S and the resulting suspension set aside overnight. The reaction mixture was then filtered through celite, the filtrate evaporated *in vacuo*, and the resulting gum purified by PLC to yield rupestrinol (**7**), crystallised from EtOAc (0.015 g), which was identical with an authentic sample (IR, mp, TLC).

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