A NEW CHROMONE FROM THE STEMS OF CNEORUM TRICOCCUM*

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Abstract—From the stems of Cneorum tricoccum L. 3,3-dimethylallylspatheliachromene, spatheliachromene and alloptaeoxylin methyl ether have been isolated as well as the new natural product ptaerochromenol methyl ether, which was chemically interconverted to isoheteropeucin methyl ether.

In a recent paper we reported the isolation of 3,3-dimethylallylspatheliachromene (1) and spatheliachromene (2) from the leaves of Cneorum tricoccum L., a species widely distributed in the Mediterranean area. The present work describes the isolation from the stems of this plant of the chromones 1 and 2, alloptaeoxylin methyl ether (3) and the new natural product ptaerochromenol methyl ether (4). The last compound, C₁₆H₁₆O₅, m.p. 193-194°, is assigned structure 4 on the basis of the following considerations. It gives no colour with FeCl₃, reduces Fehling reagent and in the IR displays the characteristic absorptions of hydroxyl and γ-pyrene (3350 and 1660, 1600 cm⁻¹). From the NMR spectrum we deduce the presence of a dimethylchromene ring, a methoxy and hydroxymethylene group and an aromatic and pyrone hydrogen. Acetylation of 4 gave the monoacetate 5, in whose NMR spectrum the methylene group appears at 5·18 τ, value similar to those reported for the acetates of umatin and ptaerochromenol.³ Compound 4 is attributed the angular structure because in the UV it behaves like alloptaeoxylin (6) and ptaerochromenol (7).

When 4 was treated with MsCl the chloride 8 and mesylate 9 were obtained. Hydrogenation of 8 over Pd/C in EtOAc gave a mixture of two compounds; one of them was assigned structure 10 on the basis of its NMR data and the other one was identified as isoheteropeucin methyl ether (11).⁵ Both compounds proved to be identical with those formed when hydrogenating alloptaeoxylin methyl ether (3). Compound 11 was also obtained on hydrogenating alloptaeoxylin (6) under the same conditions as for 8 and subsequent treatment of the resulting product 12 with MeI. In this case 10 was not formed, probably due


to the C₅–OH in 6 being associated with the carbonyl which prevents hydrogenation of the pyronic double bond. The same behaviour was also observed for compound 1. On the other hand, when hydrogenating 2, in which the C₅–OH forms part of a chromene ring, the methylchromone is reduced.¹

![Chemical structures](image)

**EXPERIMENTAL**

The m.ps, determined on a Kofler block, are uncorrected. The recrystallization solvent was light petrol–EtOAc unless otherwise stated. NMR spectra were measured at 60 MHz in CDCl₃ if not otherwise indicated, with TMS as internal reference. Column and dry column chromatography was performed on silica gel 0·2–0·5 and 0·063–0·20 mm respectively. The spray reagent for TLC was H₂SO₄–HOAc–H₂O (1:20:4).

**Isolation of the chromones.** The stems of Cneorum trioccum (13 kg), collected in La Herradura (Granada, Spain) in Feb, were chopped and extracted several times with EtOH in a Soxhlet. The combined extracts were filtered in cold, concentrated in vacuo and extracted with CHCl₃. The CHCl₃ soln was chromatographed on a column using CHCl₃ and CHCl₃–Me₂CO as eluents. Rechromatography on a dry column gave the following compounds, in order of elution: 3,3-dimethylallylspatheliachromone (1), spatheliabischromone (2), alloptaeroxylin methyl ether (3) and ptaerochenomol methyl ether (4).

![Chemical structures](image)

**3,3-Dimethylallylspatheliachromone (1), m.p. 90–96° (lit.¹ 95–97°). IR (CHCl₃): 3200–2500 (br), 1660, 1620, 1580, 1480, 1420, 1390, 1350, 1180, 1130, 1040, 980, 910, 860 cm⁻¹. NMR (CCl₄): δ ~ 2-90 (1H, s), 3-25 and 4-42 (each 1H, d, J 10 Hz), 3-98 (1H, s), 4-82 (1H, t, W₁/₂ 18 Hz), 6-70 (2H, d, W₁/₂ 12 Hz), 7-68, 8-20 and 8-32 (each 3H, s), 8-48 (6H, s). MS: m/e 128, 134, 148, 189, 214, 215, 217, 229, 244, 254, 256, 271, 283, 311 (100%), 326 (M⁺). It was identical with the product isolated previously.¹ The acetate would not crystallize. NMR (CCl₄): δ 3-45 and 4-28 (each 1H, d, J 10 Hz), 4-10 (1H, s), 4-80 (1H, t, W₁/₂ 18 Hz), 6-60, 6-78 and 8-32 (each 3H, s), 8-55 (6H, s).

**Spatheliabischromone (2), m.p. 146–149° (lit.² 146–148.5°). IR and NMR spectra superimposable with those of an authentic sample.**

**Alloptaeroxylin methyl ether (3), m.p. 154–156° (lit.³ 155–157°). IR and UV spectra identical to those reported.⁵ NMR (CCl₄): δ 3-38 and 4-48 (each 1H, d, J 10 Hz), 3-86 (1H, s), 4-30 (1H, s), 6-16, 7-76 (each 3H, s), 8-60 (6H, s).

**Ptaerochenomol methyl ether (4), m.p. 193–194°.** (Found: C, 67-49; H, 5-85. C₂₁H₁₆O₃ requires: C, 66-66; H, 5-59%). UV (EtOH): 225 (sh), 238 (sh), 257 (sh), 263, 296 (sh), 333 nm. IR (CHCl₃): 3350, 3000, 2940, 2840, 1660, 1600, 1570, 1480, 1460, 1395, 1350, 1320, 1160, 1120, 1090, 1000, 900, 860 cm⁻¹. NMR: δ 3-38 and 4-52 (each 1H, d, J 10 Hz), 3-74, 3-80 (each 1H, s), 5-52 (2H, s), 6-16 (3H, s), 8-60 (6H, s). MS: m/e 128, 146, 174, 187, 202, 213, 217, 244.⁶

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A new chromone from *Cneorum tricoccum*

227, 243, 244, 257, 259, 271, 273 (100%), 288 (M\(^+\)). *Acetate 5*, m.p. 175–176\(^\circ\). NMR: \(\tau 3\cdot37\) and 4·46 (each 1H, \(d, J 10 \text{ Hz}\)), 3·72, 3·84 (each 1H, s), 5·18 (2H, s), 6·22, 7·87 (each 3H, s), 8·58 (6H, s).

*Methylation of alloptaeroxylin (6).* 6 (48 mg) in Me\(_2\)CO (10 ml) was refluxed with MeI (2 ml) and K\(_2\)CO\(_3\) (1 g) for 48 hr. The mixture was poured into H\(_2\)O, neutralized with 10% aq. HCl, extracted with Et\(_2\)O and the solvent evaporated. Dry column chromatography (light petrol–EtOAc 1:1) of the residue gave starting material and alloptaeroxylin methyl ether (3; 20 mg), identical with the natural product (m.m.p., IR, NMR).

*Hydrogenation of 3.* 3 (50 mg) in EtOAc (25 ml) was hydrogenated over Pd/C(10\%) at room temp. and atm. pres. for 30 min. Dry column chromatography (light petrol–EtOAc 1:1) of the residue gave dihydroisoheteropeucenin methyl ether (10; 25 mg), m.p. 119–124\(^\circ\), NMR: \(\tau 4\cdot01\) (1H, s), 5·45 (1H, q, \(W_{1/2} 24 \text{ Hz}\)), 6·18 (3H, s), 7·42 (4H, \(m\)), 8·18 (2H, \(m\)), 8·55 (3H, \(d, J 6 \text{ Hz}\)), 8·66 (6H, s); and isoheteropeucenin methyl ether (11; 20 mg), m.p. 158–159\(^\circ\) (lit.\(^3\) 157–158\(^\circ\)), UV, IR and NMR spectra identical to those reported.\(^3\)

*Hydrogenation of 6.* 6 (300 mg) was hydrogenated for 2 hr as mentioned for 3. This gave isoheteropeucenin (12; 260 mg), m.p. 241–242 (lit.\(^4\) 243–244\(^\circ\)); NMR: \(\tau 3\cdot80\), 4·00 (each 1H, s), 7·22, 8·10 (each 2H, q), 7·60 (3H, s), 8·61 (6H, s); MS: \(m/e 165, 176, 192, 205 (100\%), 245, 260 (M^+\)).

*Methylation of isoheteropeucenin (12).* 12 (60 mg) was methylated as described for 6. This gave isoheteropeucenin methyl ether (11; 22 mg), m.p. 156–159\(^\circ\), identical with that obtained by hydrogenating 3 (m.m.p., IR, NMR). 10 and 11 from 4. 4 (390 mg) in pyridine (8 ml) was treated with MsCl (0·3 ml) at 0\(^\circ\) for 5 hr. The mixture was poured into NaHCO\(_3\) soln, extracted and the residue chromatographed on a dry column, light petrol–EtOAc (1:1) eluting first the chloride 8 (160 mg), m.p. 138–140\(^\circ\), (Found: C, 62·65; H, 4·93; Cl, 11·56. C\(_{16}\)H\(_{15}\)O\(_4\)Cl requires: C, 62·43; H, 4·91; Cl, 12·22\%), NMR: \(\tau 3\cdot27\) and 4·42 (each 1H, \(d, J 10 \text{ Hz}\)), 3·68, 3·76 (each 1H, s), 5·62 (2H, s, \(-\text{CH}_2\text{Cl}\)), 6·09 (3H, s), 8·52 (6H, s); and afterwards the mesylate 9 (100 mg) as an oil, NMR: \(\tau 3\cdot28\) and 4·40 (each 1H, \(d, J 10 \text{ Hz}\)), 3·68, 3·71 (each 1H, s), 4·95 (2H, s, \(-\text{CH}_2\text{OMs}\)), 6·09 (3H, s, \(-\text{OMs}\)), 6·87 (3H, s), 8·52 (6H, s).

8 was hydrogenated as described for 6. Dry column chromatography of the residue gave compounds 10 and 11, which proved to be identical with those obtained from 3.

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