A NEW CHROMONE FROM THE STEMS OF *CNEORUM TRICOCCUM**

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

IN A RECENT paper¹ we reported the isolation of 3,3-dimethylallylspatheliachromene (**1**) and spatheliabischromene (**2**)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**, alloptaeroxylin 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 -pyrone (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 δ 5.18 τ , value similar to those reported for the acetates of umtatin and ptaerochromenol.³ Compound **4** is attributed the angular structure because in the UV it behaves like alloptaeroxylin (**6**)⁴ and ptaerochromenol (**7**).³

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 isoheteropeucenin methyl ether (**11**).⁵ Both compounds proved to be identical with those formed when hydrogenating alloptaeroxylin methyl ether (**3**). Compound **11** was also obtained on hydrogenating alloptaeroxylin (**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

* Part IV in the series "Chromenes and Chromones". For Part III see GONZÁLEZ, A. G., CASTAÑEDA, J. P. and FRAGA, B. M. (1974) *Anal. Quím.* **70**, 452.

¹ GONZÁLEZ, A. G., FRAGA, B. M. and TORRES, R. (1974) *Anal. Quím.* **70**, 91.

² TAYLOR, D. R. and WRIGHT, J. A. (1971) *Rev. Latinoam. Quím.* **2**, 84.

³ DEAN, F. M., PARTON, B., PRICE, A. W., SONVICHEN, N. and TAYLOR, D. A. H. (1967) *Tetrahedron Letters* 2737.

⁴ DEAN, F. M. and TAYLOR, D. A. H. (1966) *J. Chem. Soc. (C)* 114.

⁵ DEAN, F. M. and ROBINSON, M. L. (1971) *Phytochemistry* **10**, 3221.

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**.⁶ On the other hand, when hydrogenating **2**, in which the C₅-OH forms part of a chromene ring, the methylchromone is reduced.¹

- (3) R₁ = Me; R₂ = H
 (4) R₁ = Me; R₂ = OH
 (5) R₁ = Me; R₂ = OAc
 (6) R₁ = H; R₂ = H
 (7) R₁ = H; R₂ = OH
 (8) R₁ = Me; R₂ = Cl
 (9) R₁ = Me; R₂ = OMs

EXPERIMENTAL

The m.p.s, 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 tricoccon* (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-dimethylallylspatheliachromene (**1**), spatheliabischromene (**2**), alloptaeroxylin methyl ether (**3**) and ptaerochromenol methyl ether (**4**).

3,3-Dimethylallylspatheliachromene (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): τ -2.90 (1H, s), 3.25 and 4.42 (each 1H, d, J 10 Hz), 3.98 (1H, s), 4.82 (1H, t, W_{1/2} 18 Hz), 6.70 (2H, d, W_{1/2} 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): τ 3.45 and 4.28 (each 1H, d, J 10 Hz), 4.10 (1H, t, W_{1/2} 18 Hz), 4.80 (1H, t, W_{1/2} 18 Hz), 6.60, 6.78 and 8.32 (each 3H, s), 8.55 (6H, s).

Spatheliabischromene (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.⁵ 155-157°). IR and UV spectra identical to those reported.⁵ NMR (CCl₄): τ 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).

Ptaerochromenol methyl ether (4), m.p. 193-194° (Found: C, 67.49; H, 5.85. C₁₆H₁₆O₅ 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: τ 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,

⁶ GONZÁLEZ, A. G., CASTAÑEDA, J. P. and FRAGA, B. M. (1972) *Anal. Quím.* **68**, 447.

227, 243, 244, 257, 259, 271, 273 (100%), 288 (M^+). *Acetate* **5**, m.p. 175–176°. NMR: τ 3.37 and 4.46 (each 1H, *d*, *J* 10 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_2CO (10 ml) was refluxed with MeI (2 ml) and K_2CO_3 (1 g) for 48 hr. The mixture was poured into H_2O , neutralized with 10% aq. HCl, extracted with Et_2O 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°, NMR: τ 4.01 (1H, *s*), 5.45 (1H, *q*, $W_{1/2}$ 24 Hz), 6.18 (3H, *s*), 7.42 (4H, *m*), 8.18 (2H, *m*), 8.55 (3H, *d*, *J* 6 Hz), 8.66 (6H, *s*); and isoheteropeucenin methyl ether (**11**; 20 mg), m.p. 158–159° (lit.³ 157–158°), 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°); NMR: τ 3.80, 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°, 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° for 5 hr. The mixture was poured into $NaHCO_3$ soln, extracted and the residue chromatographed on a dry column, light petrol– $EtAOc$ (1:1) eluting first the chloride **8** (160 mg), m.p. 138–140°, (Found: C, 62.65; H, 4.93; Cl, 11.56. $C_{16}H_{15}O_4Cl$ requires: C, 62.43; H, 4.91; Cl, 12.22%), NMR: τ 3.27 and 4.42 (each 1H, *d*, *J* 10 Hz), 3.68, 3.76 (each 1H, *s*), 5.62 (2H, *s*, $-CH_2Cl$), 6.09 (3H, *s*), 8.52 (6H, *s*); and afterwards the mesylate **9** (100 mg) as an oil, NMR: τ 3.28 and 4.40 (each 1H, *d*, *J* 10 Hz), 3.68, 3.71 (each 1H, *s*), 4.95 (2H, *s*, $-CH_2OMs$), 6.09 (3H, *s*, $-OMs$), 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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