Phytochemistry, 1974, Vol. 13, pp. 2305 to 2307. Pergamon Press. Printed in England.

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

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(*Received* 10 *March* 1974)

Key Word Index—*Cneorum tricoccum*; Cneoraceae; olivillo común; 3,3-dimethylallylspatheliachromene; spatheliabischromene; alloptaeroxylin methyl ether; ptaerochromenol methyl ether.

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.

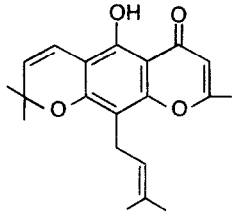
IN A RECENT paper[1] we reported the isolation of 3,3-dimethylallylspatheliachromene (**1**) and spatheliabischromene (**2**)[2] from the leaves of *Cneorum tricocuum* L., a species widely distributed in the Mediterranean area. The present work describes the isolation from the stems of this plant of the chromones **1** and **2**, alloptaeroxylin methyl ether (**3**) and the new natural product ptaerochromenol methyl ether (**4**). The last compound, $C_{16}H_{16}O_5$, m.p. 193–194°, is assigned structure **4** on the basis of the following considerations. It gives no colour with $FeCl_3$, 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 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

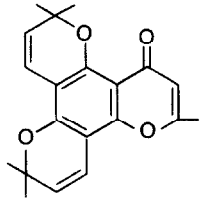
* Part IV in the series "Chromenes and Chromones". For Part III see GONZÁLEZ, A. G., CASTAÑEDA, J. P. and FRAGA, B. M. (1974) *Anal. Quím.* **70,** 452.

[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., SONVICHIEN, 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.

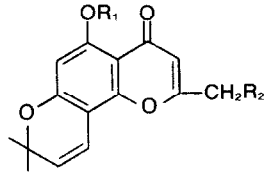
to the C_5–OH in **6** being associated with the carbonyl which prevents hydrogenation of the pyronic double bond. The same behaviour was also observed for compound **1**.[6] On the other hand, when hydrogenating **2**, in which the C_5–OH forms part of a chromene ring, the methylchromone is reduced.[1]



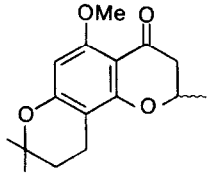
(1)



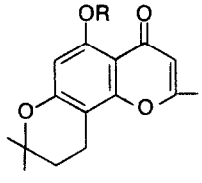
(2)



(3) R_1 = Me; R_2 = H
(4) R_1 = Me; R_2 = OH
(5) R_1 = Me; R_2 = OAc
(6) R_1 = H; R_2 = H
(7) R_1 = H; R_2 = OH
(8) R_1 = Me; R_2 = Cl
(9) R_1 = Me; R_2 = OMs



(10)



(11) R = Me
(12) R = H

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 $CDCl_3$ 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 H_2SO_4–HOAc–H_2O (1:20:4).

Isolation of the chromones. The stems of *Cneorum tricoccum* (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 $CHCl_3$. The $CHCl_3$ soln was chromatographed on a column using $CHCl_3$ and $CHCl_3$–Me_2CO 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 ($CHCl_3$): 3200–2500 (br), 1660, 1620, 1580, 1480, 1420, 1390, 1350, 1180, 1130, 1040, 980, 910, 860 cm^{-1}. NMR (CCl_4): 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 (CCl_4): τ 3·45 and 4·28 (each 1H, *d*, *J* 10 Hz), 4·10 (1H, *s*), 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 (CCl_4): 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. $C_{16}H_{16}O_5$ requires: C, 66·66; H, 5·59%). UV (EtOH): 225 (sh), 238 (sh), 257 (sh), 263, 296 (sh), 333 nm. IR ($CHCl_3$): 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. Quim.* **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**.

Acknowledgements—We thank Prof. E. Primo and J. Sendra (Instituto de Agroquímica, Valencia) for the MS and Dr. D. R. Taylor (University of West Indies, Jamaica) for a sample of spatheliabischromene. This work forms part of the Programme of Chemistry 1971 conceded by the Foundation "Juan March".