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A DIHYDROCINNAMOYL NEOFLAVANOID FROM *PITYROGRAMMA CALOMELANOS*

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Key Word Index—*Pityrogramma calomelanos;* Gymnogrammoideae; 8-dihydrocinnamoyl-5,7-dihydroxy-4-phenyl-2*H*-1-benzopyran-2-one; neoflavanoid.

Abstract—The structure of a neoflavanoid isolated from *Pityrogramma calomelanos* was confirmed by an X-ray diffraction study.

INTRODUCTION

Pityrogramma calomelanos (L.) Link, a widespread tropical fern, produces a farinaceous covering on the underside of its fronds. The farina of material collected in the Himalayas was found to consist predominantly of 2′,6′-dihydroxy-4′-methoxydihydrochalcone, which crystallized from the concentrated acetone solution. The residue yielded two additional products in very limited quantities. One of these compounds, reported as 'compound D-1' in a survey of the farina composition in the genus [1], was assigned a dihydrocinnamoyl-5,7-dihydroxy-4-phenyl-2*H*-1-benzopyran-2-one 1 or 2 from an examination of its spectral data [2]. This neoflavanoid $C_{24}H_{20}O_5$ had a double melting point 65.5° and 164°, and upon methylation with diazomethane afforded a monomethyl ether ($C_{25}H_{22}O_5$) as yellow plates (mp 167.5–168.5°) [2]. The latter gave a positive ferric chloride reaction and registered a chemical shift value of $\delta 6.30$ for the isolated proton in ring A.

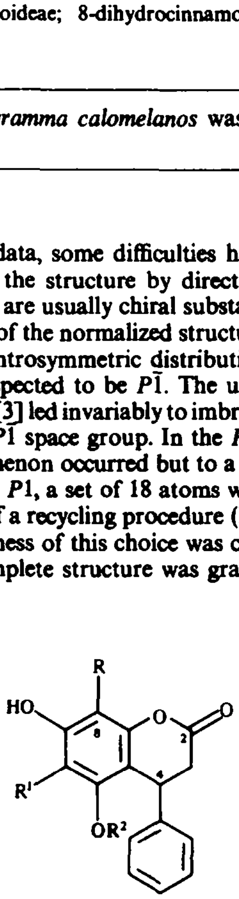
The structure of the natural product was unequivocally established by single crystal X-ray analysis of 8-dihydrocinnamoyl-5,7-dihydroxy-4-phenyl-2*H*-1-3,4-dihydrobenzopyran-2-one (1). The monomethyl ether has therefore structure 3.

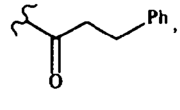
RESULTS AND DISCUSSION

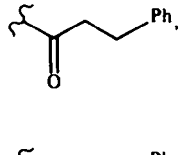
Compound 1 crystallizes as tiny prisms from methanol. Upon standing in air, the crystals are destroyed rapidly because of solvent loss from the packing. A wet crystal of approximate size 0.2 × 0.5 × 0.1 mm was therefore sealed in a Lindemann capillary and mounted on a Phillips PW 1100 automatic diffractomer, equipped with a graphite monochromator and operating with Cu-K_α radiation ($\lambda = 1.5418$ Å).

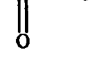
The system is triclinic corresponding to two molecules of 1 in the cell. The parameters are: $a = 13.005$ (4); $b = 10.358$ (5); $c = 9.085$ (3) Å; $\alpha = 111.5$ (6)°; $\beta = 83.9$ (5)°; $\gamma = 105.3$ (6)°; and $V = 1098.2$ Å^3.

Of a total of 2730 scanned intensities only 1309 with $I \geqslant 2\sigma(I)$ were considered as observed. Due to the paucity of the data, some difficulties have been encountered in solving the structure by direct methods. Natural compounds are usually chiral substances, however the distribution of the normalized structural factors was in favour of a centrosymmetric distribution and the space group was suspected to be $P\bar{1}$. The use of multisolution techniques [3] led invariably to imbricated hexagonal patterns in the $P\bar{1}$ space group. In the $P1$ space group, the same phenomenon occurred but to a lesser extent. After many trials in $P1$, a set of 18 atoms was chosen as the starting point of a recycling procedure (Dirdif program [4]). The correctness of this choice was checked at each cycle and the complete structure was gradually developed in four



1 R = , R¹ = R² = H

2 R = , R¹ = R² = H

3 R = , R¹ = H, R² = CH₃ cycles. Two molecules of methanol were also found after an additional Fourier-difference synthesis. At the end of this procedure the two independent molecules were found related by a centre of symmetry. The $P\bar{1}$ space group was then demonstrated as well as the racemic nature of **1**.

The refinement of the structure was undertaken with block-diagonal least-squares procedures using isotopic thermal factors for all the non-hydrogen atoms. After 10 cycles, the *R* value was 13%. At this stage, an absorption correction according to the method described by Walker and Stuart [5] was applied. The refinements were continued with anisotropic thermal factors. The hydrogen atoms were placed at their theoretical positions with a fixed isotropic factor equal to the $\langle U \rangle$ isotropic factor on the bonded carbon. The final *R* value was 9.2%.

The view of the molecule is given in Fig. 1. The

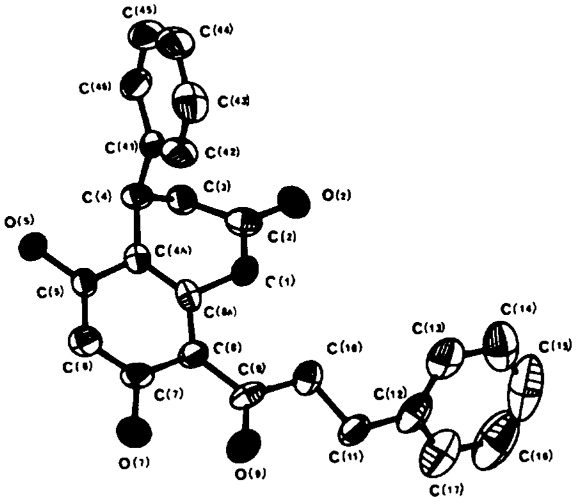


Fig. 1. Perspective view of compound 1 showing crystallographic numbering scheme.

Table 1. Positional parameters and mean recalculated isotropic factor for the non-hydrogen atoms (× 10⁴)

Atom	*X*	*Y*	*Z*	$\langle U \rangle$
C1	570 (6)	− 2540 (8)	1827 (9)	72 (11)
C2	1052 (9)	− 3535 (13)	730 (14)	51 (18)
C2	1013 (6)	− 4582 (8)	1046 (10)	90 (13)
C3	1565 (9)	− 3184 (11)	− 656 (13)	63 (17)
C4	2195 (8)	− 1617 (11)	− 167 (13)	47 (16)
C4A	1447 (9)	− 719 (12)	765 (14)	67 (18)
C6	1527 (8)	651 (12)	721 (13)	48 (16)
C6	2330 (6)	1142 (8)	− 169 (9)	71 (11)
C6	806 (9)	1461 (12)	1576 (15)	56 (17)
C7	− 3 (9)	895 (11)	2412 (14)	59 (18)
C7	− 672 (6)	1744 (8)	3188 (9)	83 (12)
C8	− 128 (8)	− 463 (11)	2549 (14)	51 (16)
C8A	626 (9)	− 1216 (11)	1641 (14)	50 (17)
C8	− 1033 (9)	− 987 (12)	3474 (13)	63 (17)
C9	− 1621 (7)	− 186 (9)	4189 (11)	135 (15)
C10	− 1263 (9)	− 2458 (11)	3601 (13)	49 (16)
C11	− 2266 (9)	− 2711 (12)	4587 (16)	80 (19)
C13	− 3525 (13)	− 5053 (19)	4397 (18)	93 (28)
C14	− 3802 (18)	− 6435 (23)	4488 (28)	125 (41)
C15	− 3044 (25)	− 6854 (22)	4994 (25)	155 (48)
C17	− 2020 (16)	− 6016 (19)	5307 (19)	124 (31)
C16	− 1746 (13)	− 4683 (14)	5171 (16)	87 (23)
C12	− 2521 (11)	− 4215 (14)	4679 (15)	58 (21)
C45	3316 (9)	− 615 (14)	2342 (16)	62 (20)
C42	4265 (11)	− 388 (14)	3035 (16)	65 (22)
C44	5137 (11)	− 830 (19)	2181 (27)	137 (34)
C43	5035 (11)	− 1534 (16)	567 (23)	102 (27)
C46	4094 (10)	− 1749 (12)	− 134 (15)	70 (20)
C41	3200 (8)	− 1330 (11)	719 (15)	60 (17)
Solvent:				
O1	2531 (7)	3824 (9)	65 (12)	97 (15)
Cl	3560 (14)	4710 (19)	601 (21)	103 (5)

*Calculated as: $\langle U \rangle = \frac{1}{3}[U_{11} + U_{22} + U_{33} + 2(U_{23}\cos\alpha + U_{13}\cos\beta + U_{12}\cos\gamma)]$.

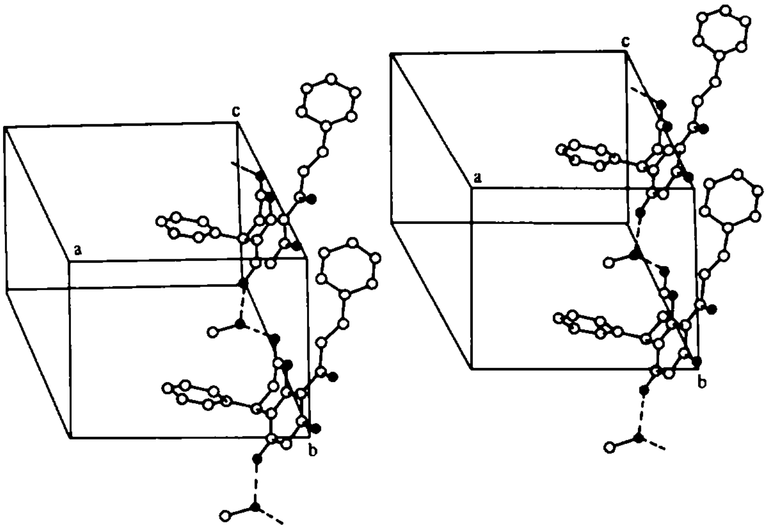


Fig. 2. Steric view of the hydrogen bond network around the molecule of methanol.

positional parameters are given in Table 1. All the crystallographic details are given as a supplementary material and deposited with the Cambridge Crystallographic Data Centre.

The molecule of methanol found in the crystal structure has the important role of stabilizing the packing by hydrogen bonding via O(5) of one molecule (with the 1 000 symmetry operator); $d = 3.52$ Å, and via the O(2) atom of another translated molecule (1 010 symmetry operator); $d = 3.45$ Å. This leads to an infinite hydrogen bond network running along the *b* axis. This essential network in the built-up and the stability of the crystal is displayed on the stereo picture given in Fig. 2.

A survey of closely related complex flavanoids from *Pityrogramma* frond exudates is reported in [6].

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR were taken in $CDCl_3$ at 25° using TMS as internal standard. EIMS were taken on a VG 70-70 spectrometer. A voucher specimen of *Pityrogramma calomelanos* is deposited in the herbarium (E.W). Institut für Botanik, Technische Hochschule, Darmstadt.

Isolation of the constituents was performed as described for *P. trifoliata* [7]. The residue (34 mg) from the Me_2CO extract was purified by dry CC (silica gel, Woelm) using $CHCl_3$ as eluant and monitored by TLC ($CHCl_3$–MeOH–H_2O, 10:1:0.17). The band R_f 0.65 gave prisms (**1**) (20 mg) mp 65.5–66° and 164° [1].

Methylation of **1**. The neoflavanoid (**1**) (10 mg) in tetrahydrofuran (30 ml) was methylated exhaustively with CH_2N_2. The oil, obtained on evaporation of the solvent, was dissolved in EtOH (95%). On cooling, yellow plates (7 mg) of 8-dihydrocinnamoyl-7-hydroxy-5-methoxy-4-phenyl-2*H*-1-3,4-dihydrobenzopyran-2-one (**3**) mp 167.5–168° were obtained (found: C, 74.51; H, 5.27; $C_{25}H_{22}O_5$ requires C, 74.61; H 5.51%). ^{1}H NMR (60 MHz): δ 13.75 [1H, *s* (*br*), OH] 7.55–7.1 (5H, *m*, C_6H_5), 6.30 (1H, *s*, H-6), 4.8–4.5 (1H, *m*, H-4), 3.87 (3H, *s*, 5-OMe), 3.7–2.9 (6H, *m*, H-3) and CH_2–CH_2–); IR ν_{max}^{KBr} cm^{-1}: 3655, 3595 and 3430 (hydroxyl groups), 1770, 1690 and 1630 (>CO groups); UV λ_{max}^{MeOH} nm (ε), 325 sh (10, 649), 283 (25, 958), 230 sh (39, 936), 208 (73, 881); EIMS (direct inlet) 75 eV, *m/z* (rel. int.): 402 $[M]^+$ (82), 297 (100), 270 (99), 265 (93), 227 (21), 91 (99), 77 (25), 69 (15).

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