Fig. 2. Numbering of atoms and bond orders in the conjugated system.

single- and double-bond lengths of 1·47 and 1·27 Å, respectively (Pauling, 1960).

The main difference between the two molecules of (I) is in deviations of atoms from the least-squares ring plane. The deviations are up to 30σ [$\Delta C(2) = 0{\cdot}032$, $\Delta O(2) = 0{\cdot}103$, $\sigma_{mean} = 0{\cdot}003$ Å] in molecule A and 3σ in molecule B. The interplanar angle between rings A and B is 18·1 (1)°.

The bond lengths and angles in both independent molecules agree within 4σ limits.

This work is part of research project RPII.10.

Discussion. A view of the two independent molecules forming a dimer, together with bond lengths and angles for the non-hydrogen atoms, is shown in Fig. 1. Almost the whole molecule forms a conjugated system. The p atomic orbitals at the O(methoxy) and N(1) atoms overlap with π systems of the double C=O and C=N bonds, as evidenced by (i) shortening of O(1)—C(4), O(3)—C(6), N(1)—C(6) and N(1)—C(2) bonds to 1·33, 1·32, 1·35 and 1·38 Å, respectively, and (ii) co-planarity of methoxy groups with the triazine ring. All four independent methoxy groups are in a *syn* orientation towards the neighbouring 'most double' bond of the ring with the torsional angles N=C—O—Me less than 3·5°. There are significant differences among the C—N bond orders in the ring (Fig. 2) varying from 1·4 for N(1)—C(2) to 1·9 for N(5)—C(6), assuming

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(±)-2-(4-Methoxyflavan-3-yl)-7-methoxyisoflav-3-ene*†

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Abstract. $C_{32}H_{28}O_4$, $M_r = 476{\cdot}6$, monoclinic, $P2_1/n$, $a = 12{\cdot}044$ (3), $b = 9{\cdot}517$ (5), $c = 21{\cdot}630$ (5) Å, $\beta = 91{\cdot}26$ (2)°, $U = 2479$ Å^3, $Z = 4$, $D_x = 1{\cdot}28$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}70926$ Å, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 1008$, $T = 293$ K, $R = 0{\cdot}045$ for 1399 observed reflections. The product from the condensation of 7-methoxyisoflavylium perchlorate with 3-(o-hydroxyphenyl)-1-(p-methoxyphenyl)propene is determined to be (±)-2-(4-methoxyflavan-3-yl)-7-methoxyisoflav-3-

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ene. The overall conformation of the molecule is defined by the fully staggered H—C—C—H torsion angle about the C—C bond which links the two component halves. There are no unusual bond lengths or angles.

Introduction. During an *in vitro* investigation of our hypothesis (Badran & Whalley, 1976) concerning the mode of biosynthesis of the pigments Santalin and Santarubin (Mathieson, Millard, Powell & Whalley, 1973; Arnone, Camarda, Merlini & Nasini, 1975) from the 'insoluble red woods', we condensed isoflavylium salts of type (1) with 3-(*o*-hydroxyphenyl)-1-phenyl-propenes of type (2) to give products which were formulated as 2-(flavan-3-yl)isoflav-3-enes of type (3), on the basis of the usual spectral and analytical data (Oluwadiya & Whalley, 1978). Each product had a sharp melting point, and was homogeneous on TLC in a variety of solvents. These data, together with the NMR spectra, indicated that the products probably contained only one of the four theoretically possible racemates of type (3).
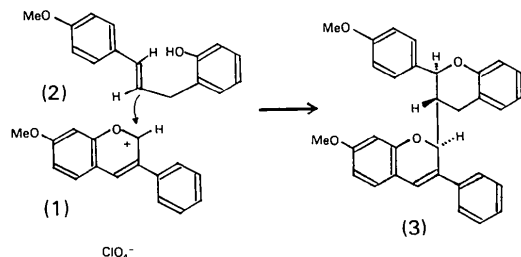
These conclusions have been confirmed by X-ray crystallographic definition of the product from the condensation of 7-methoxyisoflavylium perchlorate (1) with 3-(*o*-hydroxyphenyl)-1-(*p*-methoxyphenyl)pro-pene (2) as the (±)-2-(4-methoxyflavan-3-yl)-7-methoxyisoflav-3-ene (3) with stereochemistry defined as in Figs. 1 and (3).

Experimental. Colourless crystals, $0.13 \times 0.18 \times 0.55$ mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, 25 reflections with $10 < \theta < 15°$ used to determine cell constants, $2 < \theta < 20°$ for intensity data, ω–2θ scans, ω scan width $(0.60 + 0.35\tan\theta)°$, three standard reflections monitored every 160 minutes of exposure time showed no significant variation, Lp corrections, 2310 independent reflections, 1399 (60·6%) with $I > 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0.04(S-B)]^2$, $S =$ scan count and $B =$ time-averaged background count. h 0 to 11, k −9 to 0, l −20 to 20.

The structure was solved using *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982); refinement on F (Frenz & Associates, 1984) by full-matrix least-squares calculations initially with isotropic and then with anisotropic vibration parameters.

A difference map computed at an intermediate stage in the refinement revealed maxima in positions expected for all hydrogen atoms. These were allowed for in geometrically idealized positions and assigned an overall isotropic thermal parameter $B = 5.0$ Å^2. Scattering factors used in the structure-factor calculations were taken from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) and allowance was made for anomalous dispersion (Cromer & Liberman, 1970). No corrections for absorption or secondary extinction.

Refinement converged with $R = 0.045$ and $wR = 0.058$ for the 1399 reflections with $I > 3\sigma(I)$. $w = 1/\sigma^2(F)$. A final difference map was devoid of any significant features. The maximum shift/e.s.d. ratio in the last cycle for a non-hydrogen coordinate was 0·03 for z of C(12) and for a thermal parameter was 0·02 for b_{13} of C(12). Final fractional coordinates are in Table 1 and details of molecular dimensions are in Table 2.* Other computer programs used: *ORTEP*II (Johnson, 1976).

Discussion. The high degree of stereospecificity associated with the formation of (3) is compatible with initiation of the condensation by normal *trans*-addition of the propene (2) to the isoflavylium carbocation of (1) as in the scheme.

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* Lists of structure factors, anisotropic thermal parameters and the calculated hydrogen coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43319 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
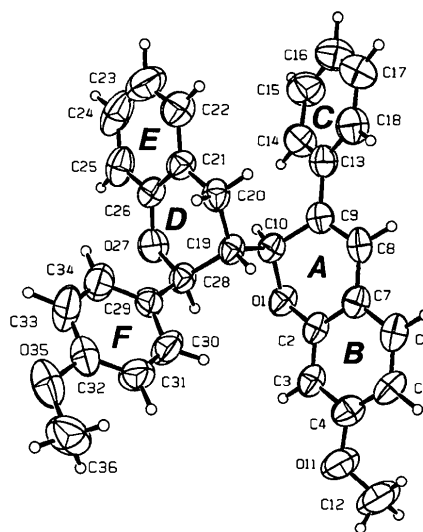

Fig. 1. A view of the title compound showing the crystallographic numbering scheme.

The crystal structure contains discrete well resolved molecules (Fig. 1) of (3) with only van der Waals distances between them. There are three asymmetric centres in (3) but of the eight possible isomers only two (that shown in Fig. 1 and its mirror image) are found in the crystal structure.

The bond lengths (Table 2) [with mean values: aromatic C_{sp^2}—C_{sp^2} 1·378 (5), C_{sp^2}—C_{sp^3} 1·502 (5), C_{sp^3}—C_{sp^3} 1·527 (5), C_{sp^3}—O 1·425 (5), aromatic C_{sp^2}—O 1·369 (5) Å] are unexceptional and serve to define the structure. Ring A (Fig. 1) is in a distorted boat conformation, with C(9) 0·305 (4) Å and C(10) 0·692 (4) Å from the O(1), C(2), C(7), C(8) plane (plane A); ring D adopts an envelope conformation with C(19) −0·628 (4) Å from the C(20), C(21), C(26), O(27), C(28) plane (plane D). The orientation of the two halves of the molecule about the C(10)—C(19) bond which links them is such that the H—C(10)—C(19)—H torsion angle (−178°) is essentially fully staggered. Phenyl ring C is rotated out of the ring A plane [torsion angle C(8)—C(9)—C(13)—C(18) −33·8 (5)°], and phenyl ring F is oriented to form a torsion angle O(27)—C(28)—C(29)—C(34) of

Table 1. *Final fractional coordinates with estimated standard deviations in parentheses and equivalent isotropic thermal parameters*

	x	y	z	$B_{eq}(\text{Å}^2)$
O1	0·2611 (2)	0·2004 (3)	0·7017 (1)	4·30 (7)
O11	0·5421 (3)	0·0875 (4)	0·5650 (2)	7·2 (1)
O27	−0·0406 (2)	0·1508 (3)	0·6770 (1)	5·13 (8)
O35	−0·0386 (3)	−0·3283 (4)	0·4743 (2)	7·11 (9)
C2	0·3557 (3)	0·1240 (4)	0·6902 (2)	3·9 (1)
C3	0·4021 (4)	0·1365 (5)	0·6334 (2)	4·5 (1)
C4	0·5029 (4)	0·0720 (5)	0·6229 (2)	4·9 (1)
C5	0·5559 (3)	−0·0059 (5)	0·6686 (2)	5·3 (1)
C6	0·5073 (3)	−0·0153 (5)	0·7259 (2)	5·0 (1)
C7	0·4056 (3)	0·0470 (5)	0·7377 (2)	4·2 (1)
C8	0·3542 (3)	0·0477 (5)	0·7971 (2)	4·5 (1)
C9	0·2509 (3)	0·0937 (5)	0·8041 (2)	4·0 (1)
C10	0·1879 (3)	0·1398 (5)	0·7468 (2)	3·9 (1)
C12	0·6466 (4)	0·0289 (8)	0·5520 (3)	9·0 (2)
C13	0·1981 (3)	0·0980 (5)	0·8650 (2)	4·4 (1)
C14	0·1249 (4)	0·2054 (5)	0·8804 (2)	5·5 (1)
C15	0·0811 (4)	0·2104 (6)	0·9386 (2)	7·0 (1)
C16	0·1068 (4)	0·1108 (6)	0·9820 (2)	7·1 (2)
C17	0·1767 (4)	0·0046 (6)	0·9675 (2)	6·6 (1)
C18	0·2216 (4)	−0·0023 (5)	0·9093 (2)	5·4 (1)
C19	0·1241 (3)	0·0193 (5)	0·7150 (2)	3·7 (1)
C20	0·0484 (3)	−0·0648 (5)	0·7559 (2)	4·3 (1)
C21	−0·0549 (3)	0·0141 (5)	0·7698 (2)	4·3 (1)
C22	−0·1146 (4)	−0·0101 (6)	0·8225 (2)	6·5 (1)
C23	−0·2108 (4)	0·0611 (7)	0·8338 (3)	8·1 (2)
C24	−0·2494 (4)	0·1590 (7)	0·7932 (3)	8·2 (2)
C25	−0·1914 (4)	0·1864 (5)	0·7410 (2)	5·8 (1)
C26	−0·0947 (3)	0·1133 (5)	0·7295 (2)	4·4 (1)
C28	0·0570 (3)	0·0745 (5)	0·6590 (2)	4·1 (1)
C29	0·0297 (3)	−0·0381 (5)	0·6118 (2)	4·0 (1)
C30	0·1127 (4)	−0·0901 (6)	0·5764 (2)	6·2 (1)
C31	0·0947 (4)	−0·1877 (6)	0·5308 (2)	6·2 (1)
C32	−0·0095 (4)	−0·2336 (5)	0·5196 (2)	5·2 (1)
C33	−0·0942 (4)	−0·1876 (6)	0·5553 (2)	6·8 (1)
C34	−0·0749 (4)	−0·0906 (6)	0·6009 (2)	5·9 (1)
C36	0·0469 (5)	−0·3865 (6)	0·4397 (2)	7·9 (2)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23})$.

Table 2. *Interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses*

O1—C2	1·379 (4)	C14—C15	1·375 (5)
O1—C10	1·449 (4)	C15—C16	1·366 (6)
O11—C4	1·356 (5)	C16—C17	1·357 (6)
O11—C12	1·410 (5)	C17—C18	1·383 (6)
O27—C26	1·369 (4)	C19—C20	1·513 (5)
O27—C28	1·442 (4)	C19—C28	1·533 (5)
O35—C32	1·372 (5)	C20—C21	1·491 (5)
O35—C36	1·400 (5)	C21—C22	1·380 (5)
C2—C3	1·366 (5)	C21—C26	1·365 (5)
C2—C7	1·389 (5)	C22—C23	1·369 (7)
C3—C4	1·384 (5)	C23—C24	1·356 (7)
C4—C5	1·381 (5)	C24—C25	1·366 (7)
C5—C6	1·385 (5)	C25—C26	1·384 (5)
C6—C7	1·390 (5)	C28—C29	1·511 (5)
C7—C8	1·439 (5)	C29—C30	1·366 (5)
C8—C9	1·331 (5)	C29—C34	1·371 (5)
C9—C10	1·505 (5)	C30—C31	1·369 (6)
C9—C13	1·474 (5)	C31—C32	1·346 (5)
C10—C19	1·536 (5)	C32—C33	1·365 (5)
C13—C14	1·396 (5)	C33—C34	1·367 (6)
C13—C18	1·378 (5)		

C2—O1—C10	115·4 (3)	C16—C17—C18	120·2 (5)
C4—O11—C12	118·1 (4)	C13—C18—C17	121·5 (4)
C26—O27—C28	119·9 (3)	C10—C19—C20	115·8 (3)
C32—O35—C36	117·5 (4)	C10—C19—C28	110·3 (3)
O1—C2—C3	118·2 (4)	C20—C19—C28	109·2 (3)
O1—C2—C7	119·4 (4)	C19—C20—C21	111·6 (3)
C3—C2—C7	122·2 (4)	C20—C21—C22	122·3 (5)
C2—C3—C4	119·1 (4)	C20—C21—C26	120·1 (4)
O11—C4—C3	115·3 (5)	C22—C21—C26	117·5 (4)
O11—C4—C5	123·7 (4)	C21—C22—C23	121·5 (5)
C3—C4—C5	120·9 (4)	C22—C23—C24	120·3 (5)
C4—C5—C6	118·5 (4)	C23—C24—C25	119·5 (5)
C5—C6—C7	121·9 (4)	C24—C25—C26	120·0 (5)
C2—C7—C6	117·3 (4)	O27—C26—C21	122·9 (4)
C2—C7—C8	118·1 (4)	O27—C26—C25	115·8 (5)
C6—C7—C8	124·4 (4)	C21—C26—C25	121·2 (4)
C7—C8—C9	121·7 (4)	O27—C28—C19	112·2 (3)
C8—C9—C10	117·3 (4)	O27—C28—C29	111·9 (3)
C8—C9—C13	122·2 (4)	C19—C28—C29	113·2 (3)
C10—C9—C13	120·6 (4)	C28—C29—C30	119·0 (4)
O1—C10—C9	111·5 (3)	C28—C29—C34	124·1 (4)
O1—C10—C19	107·6 (3)	C30—C29—C34	116·9 (4)
C9—C10—C19	112·9 (3)	C29—C30—C31	123·0 (4)
C9—C13—C14	121·4 (4)	C30—C31—C32	118·8 (4)
C9—C13—C18	121·1 (4)	O35—C32—C31	124·4 (5)
C14—C13—C18	117·5 (4)	O35—C32—C33	115·6 (5)
C13—C14—C15	120·1 (4)	C31—C32—C33	120·0 (4)
C14—C15—C16	121·3 (4)	C32—C33—C34	120·5 (4)
C15—C16—C17	119·3 (4)	C29—C34—C33	120·8 (4)

−18·3 (4)°. These orientations presumably serve to minimize intra- and intermolecular contacts. The methoxy groups are effectively coplanar with the aromatic rings to which they are bonded [torsion angles C(5)—C(4)—O(11)—C(12) −4·6 (4); C(31)—C(32)—O(35)—C(36) 3·5 (4)°].

It may be concluded that the other 2-(flavan-3-yl)isoflav-3-enes of type (3) (Oluwadiya & Whalley, 1978) have analogous structures in the same stereochemical series.

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Structures of Dimorphs of Hexamethyleneiminium* p-Hydroxybenzoate and Pyrrolidinium p-Hydroxybenzoate

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Abstract. Cu $K\alpha$, $\lambda = 1.5418$ Å, $T = 295$ K. Hexamethyleneiminium p-hydroxybenzoate, $C_6H_{14}N^+.C_7H_5O_3^-$, $M_r = 237.30$; orthorhombic form: $P2_12_12_1$, $a = 11.984$ (2), $b = 14.326$ (1), $c = 7.612$ (1) Å, $V = 1306.9$ (3) Å^3, $Z = 4$, $D_m = 1.20$, $D_x = 1.206$ Mg m^{-3}, $\mu = 0.70$ mm^{-1}, $F(000) = 512$, $R = 0.047$ for 1127 non-zero reflections; monoclinic form: $P2_1/n$, $a = 14.816$ (2), $b = 14.719$ (2), $c = 6.0611$ (7) Å, $\beta = 93.768$ (9)°, $V = 1318.9$ (3) Å^3, $Z = 4$, $D_m = 1.20$, $D_x = 1.195$ Mg m^{-3}, $\mu = 0.70$ mm^{-1}, $F(000) = 512$, $R = 0.061$ for 2006 non-zero reflections. Pyrrolidinium p-hydroxybenzoate, $C_4H_{10}N^+.C_7H_5O_3^-$, $M_r = 209.25$, monoclinic, Cc, $a = 5.93$ (2), $b = 17.97$ (2), $c = 10.26$ (2) Å, $\beta = 96.0$ (2)°, $V = 1088$ (4) Å^3, $Z = 4$, $D_m = 1.27$, $D_x = 1.278$ Mg m^{-3}, $\mu = 0.78$ mm^{-1}, $F(000) = 448$, $R = 0.066$ for 734 non-zero reflections. In dimorphs of hexamethyleneiminium p-hydroxybenzoate, the benzoate ions related by a twofold screw axis are held together by an O—H···O hydrogen bond between the p-hydroxyl group and the carboxylate group to form a ribbon of benzoate ions, while in pyrrolidinium p-hydroxybenzoate a similar ribbon is formed by the benzoate ions related by an n-glide plane. This difference can be attributed to the size of the cations. In all these crystals, the ribbons are held together by the cations through two kinds of N—H···O hydrogen bonds between the iminium N and the carboxylate O atoms. The hexamethyleneimine rings take twist-chair conformations disordered between two

conformers. The pyrrolidine ring takes an approximate C_s conformation.

Introduction. Many salts of p-substituted benzoic acids with cyclic secondary amines crystallize in *Pbca* or its maximal subgroup $P2_1/c$ (Kashino, Sumida & Haisa, 1972; Kashino, 1973; Kashino, Kataoka & Haisa, 1978; Kashino, Sasahara, Kataoka & Haisa, 1981), while piperidinium p-hydroxybenzoate (PIH) crystallizes in *Cc* (Fukuyama, Kashino & Haisa, 1973). In the present work, the study has been extended to the crystal structures of dimorphs of hexamethyleneiminium p-hydroxybenzoate (HMI) and pyrrolidinium p-hydroxybenzoate (PYH), and it has been ascertained that the intermolecular O—H···O hydrogen bonding involving the p-hydroxyl and carboxyl groups plays an important role in the crystal structures.

Experimental. Experimental details are listed in Table 1. All the crystals obtained from ethanol solutions by slow evaporation at room temperature. Monoclinic crystals of HMI grown at first, then orthorhombic crystals from the same batch. D_m by flotation in benzene–CCl$_4$.

For HMI weak diffuse scattering evident in Weissenberg photographs (211 and 121 for orthorhombic form; $\bar{1}01$, $\bar{1}11$, 401 and 411 for monoclinic form), but no attempt made to analyze it. Intensity data, Rigaku AFC-5 four-circle diffractometer equipped with rotating anode, ω–2θ scan method [scan speed 4° min^{-1} in ω, scan range (2θ): $1.2° + 0.15°\tan\theta$], Ni-filtered Cu $K\alpha$ at 40 kV, 200 mA, background measured for 4 s on either side of the peak; three standard reflections

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* IUPAC name: perhydroazepinium.

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