

- FRENZ, B. A. (1978). *Enraf-Nonius CAD-4 SDP, Real Time System for Concurrent X-ray Data Collection and Crystal Structure Determination in Crystallography*.
International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- TOUPET, L. & MESSENGER, J. C. (1983). *Acta Cryst. C* **39**, 750–753.
- VEBREL, J. & CARRIÉ, R. (1982a). *J. Org. Chem.* To be published.
- VEBREL, J. & CARRIÉ, R. (1982b). *Can. J. Chem.* To be published.
- VEBREL, J., CERUTTI, E. & CARRIÉ, R. (1979a). *C.R. Acad. Sci. Paris Sér. C*, **228**, 265–267.
- VEBREL, J., CERUTTI, E. & CARRIÉ, R. (1979b). *C. R. Acad. Sci. Paris, Sér. C*, **288**, 265–267.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

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1,5-Bis(α -isopropyl-2,4-dimethoxybenzyl)-2,4-dimethoxybenzene, C₃₂H₄₂O₆

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Abstract. $M_r = 522.7$, triclinic, $P\bar{1}$, $a = 15.818$ (4), $b = 11.180$ (3), $c = 8.570$ (2) Å, $\alpha = 96.6$ (1), $\beta = 94.8$ (1), $\gamma = 98.7$ (1)°, $U = 1480.3$ (9) Å³, $Z = 2$, $D_m = 1.18$, $D_x = 1.173$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.067$ mm⁻¹, $F(000) = 564$, room temperature. Final $R = 0.083$ for 2452 observed reflections. This isomer has been defined as *cis*, having the terminal phenyl rings (*A* and *C*) on the same side of the mean plane through the central phenyl ring (*B*) and it is characterized by the angles between the best mean planes through the phenyl rings: $A \wedge B$ 67.8 (2), $A \wedge C$ 60.2 (2) and $B \wedge C$ 68.3 (2)°.

Introduction. Dimethoxy aromatic moieties are frequently present in several synthetic and natural drugs; this fact, together with the large use of *o*-, *m*- and *p*-dimethoxybenzenes as starting products in industrial syntheses, makes the study of these compounds of interest (Natoli, Agozzino, Ceraulo & Lamartina, 1982). The solid-state structure of a number of substituted dimethoxybenzenes is being studied in our laboratory to see if some correlation can be drawn between their molecular structure, spectroscopic features and chemical properties. In this paper we report on the crystal and molecular structure of an isomer of 1,5-bis(α -isopropyl-2,4-dimethoxybenzyl)-2,4-dimethoxybenzene (hereinafter IDD), derived from a single-crystal X-ray analysis.

Experimental. D_m measured by flotation; white prism, 0.2 × 0.3 × 0.2 mm; Siemens Stoe diffractometer, scan range $2\theta = 3$ –50°, graphite-monochromatized Mo $K\alpha$ radiation, ω - θ scan technique; 5224 reflections collected, 2452 independent with $I > 3\sigma(I)$; structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971), refined by a full-matrix least-squares procedure; function minimized $\sum w||F_o| - |F_c||^2$ with $w = 5.138|\sigma^2(F_o) + 7.7 \times 10^{-4}(F_o)^2|^{-1}$; scattering factors from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965); O and *sp*³-C atoms anisotropic, benzene-ring C atoms isotropic, H contributions in calculated positions [$d(\text{C-H}) = 0.95$ Å]; final $R = 0.083$, $R_w = 0.092$; IBM 4331 computer of the University of Messina with *SHELX* 76 (Sheldrick, 1976).

Discussion. Atomic parameters are given in Table 1.* bond lengths and angles in Table 2.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes data and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38346 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A view of the molecule down *c* showing its solid-state conformation and the atomic-numbering scheme used in the analysis is presented in Fig. 1. There are several conformers of IDD, due to the allowed rotation about the $C(sp^3)-C(sp^2)$ single bonds and their conformation can be conveniently described by the mutual position of the external phenyl rings (*A* and *C*) with respect to the mean plane through the central phenyl ring *B*. In the examined isomer, *A* and *C* lie on the same side of the mean plane through *B* and we propose to label this the *cis* isomer, as distinct from the, as yet missing, *anti* isomer. Bond lengths and valence angles of the phenyl rings, which are planar within experimental error, are in the range of values found in these systems. The dihedral angles between the mean planes through *A*, *B* and *C* are approximately the same being $A \wedge B$ 67.8 (2), $A \wedge C$ 60.2 (2) and $B \wedge C$ 68.3 (2)°. Relevant torsion angles about $C(sp^2)-C(sp^3)$ bonds are $C(3)-C(4)-C(47)-C(7)$ -91.0 (7), $C(4)-C(47)-C(7)-C(8)$ 116.9 (6), $C(10)-C(11)-C(113)-C(13)$ -120.2 (6) and $C(11)-C(113)-C(13)-C(14)$ 90.0 (7)°. The dimensions of the remaining parts of the molecule are not unusual.

The crystal packing is mainly determined by van der Waals forces and all intermolecular contacts agree with those predicted from radii-sum rules.

Table 1. Atomic fractional coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) for non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U_{iso}(\text{\AA}^2)$
C(25)	5296 (6)	-5490 (9)	7486 (15)	144 (9)
O(1)	5087 (4)	-4541 (8)	7395 (12)	182 (8)
C(1)	4272 (5)	-4228 (7)	7500 (8)	827 (21)*
C(2)	3599 (4)	-4777 (7)	6417 (8)	774 (20)*
C(3)	2792 (4)	-4396 (6)	6535 (7)	586 (16)*
C(4)	2665 (3)	-3522 (5)	7726 (6)	478 (14)*
C(5)	3382 (4)	-2988 (6)	8768 (8)	744 (19)*
C(6)	4196 (5)	-3348 (7)	8608 (9)	891 (23)*
O(3)	2084 (3)	-4874 (4)	5511 (6)	91 (4)
C(26)	2152 (6)	-5712 (8)	4181 (10)	106 (7)
C(47)	1786 (3)	-3162 (5)	7876 (6)	47 (3)
C(19)	1584 (5)	-2865 (7)	9594 (9)	79 (5)
C(20)	672 (5)	-2566 (8)	9632 (10)	99 (6)
C(21)	1633 (6)	-4037 (7)	10503 (9)	104 (7)
C(7)	1668 (3)	-2095 (5)	6966 (6)	424 (13)*
C(8)	1035 (3)	-2225 (5)	5690 (6)	498 (15)*
O(8)	524 (3)	-3336 (3)	5332 (5)	72 (3)
C(80)	-101 (3)	-3529 (7)	4042 (9)	83 (5)
C(9)	925 (3)	-1242 (5)	4873 (6)	493 (15)*
C(10)	1439 (3)	-108 (5)	5359 (6)	455 (14)*
O(10)	1325 (3)	906 (3)	4635 (5)	63 (3)
C(100)	953 (3)	736 (7)	3074 (8)	83 (5)
C(11)	2057 (3)	61 (5)	6640 (6)	398 (13)*
C(12)	2160 (3)	-952 (5)	7384 (6)	428 (13)*
C(113)	2595 (3)	1309 (5)	7244 (6)	46 (3)
C(22)	2374 (4)	1805 (5)	8893 (6)	49 (4)
C(23)	1408 (4)	1786 (7)	8894 (8)	77 (5)
C(13)	3548 (3)	1264 (4)	7171 (6)	391 (13)*
C(14)	3938 (3)	1521 (5)	5810 (6)	477 (14)*
O(14)	3390 (3)	1774 (4)	4601 (5)	74 (3)
C(24)	2868 (5)	3086 (5)	9439 (7)	71 (4)
C(27)	3681 (6)	1837 (8)	3109 (8)	93 (6)
C(15)	4800 (4)	1520 (5)	5690 (7)	538 (15)*
C(16)	5309 (4)	1246 (5)	6941 (7)	563 (16)*
O(16)	6183 (2)	1272 (4)	6989 (5)	78 (3)
C(28)	6605 (4)	1697 (7)	5707 (9)	86 (5)
C(17)	4952 (4)	955 (5)	8306 (7)	573 (16)*
C(18)	4077 (3)	967 (5)	8392 (6)	505 (15)*

* Isotropic.

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

C(100)-O(10)	1.396 (7)	C(47)-C(4)	1.515 (7)
C(10)-O(10)	1.380 (6)	C(47)-C(7)	1.523 (7)
C(28)-O(16)	1.423 (8)	C(1)-C(2)	1.371 (9)
C(16)-O(16)	1.376 (7)	C(1)-C(6)	1.313 (11)
C(27)-O(14)	1.401 (7)	C(2)-C(3)	1.413 (9)
C(14)-O(14)	1.377 (6)	C(3)-C(4)	1.378 (7)
C(80)-O(8)	1.395 (7)	C(4)-C(5)	1.395 (8)
C(8)-O(8)	1.363 (6)	C(5)-C(6)	1.418 (11)
C(26)-O(3)	1.411 (10)	C(7)-C(8)	1.399 (7)
C(3)-O(3)	1.363 (7)	C(7)-C(12)	1.383 (7)
C(25)-O(1)	1.166 (14)*	C(8)-C(9)	1.393 (7)
C(1)-O(1)	1.393 (11)	C(9)-C(10)	1.397 (7)
C(24)-C(22)	1.526 (8)	C(10)-C(11)	1.384 (7)
C(23)-C(22)	1.527 (8)	C(11)-C(12)	1.385 (7)
C(113)-C(22)	1.545 (7)	C(13)-C(14)	1.403 (7)
C(113)-C(11)	1.529 (7)	C(14)-C(15)	1.376 (7)
C(113)-C(13)	1.523 (7)	C(15)-C(16)	1.377 (8)
C(20)-C(19)	1.531 (12)	C(16)-C(17)	1.391 (8)
C(21)-C(19)	1.607 (9)	C(17)-C(18)	1.393 (8)
C(19)-C(47)	1.542 (9)	C(18)-C(13)	1.386 (7)
C(10)-O(10)-C(100)	118.7 (5)	C(6)-C(5)-C(4)	121.0 (5)
C(16)-O(16)-C(28)	117.8 (5)	C(5)-C(6)-C(1)	119.7 (7)
C(14)-O(14)-C(27)	118.9 (5)	C(8)-C(7)-C(47)	121.0 (5)
C(8)-O(8)-C(80)	119.3 (5)	C(12)-C(7)-C(47)	121.9 (5)
C(3)-O(3)-C(26)	120.1 (6)	C(12)-C(7)-C(8)	117.1 (5)
C(1)-O(1)-C(25)	128.0 (10)	C(7)-C(8)-O(8)	116.8 (5)
C(23)-C(22)-C(24)	110.9 (5)	C(9)-C(8)-O(8)	122.5 (5)
C(113)-C(22)-C(24)	111.1 (5)	C(10)-C(9)-C(8)	119.5 (5)
C(113)-C(22)-C(23)	110.8 (5)	C(9)-C(10)-O(10)	121.6 (5)
C(22)-C(113)-C(13)	113.6 (5)	C(7)-C(8)-C(9)	120.7 (6)
C(11)-C(113)-C(22)	114.4 (4)	C(10)-C(11)-C(12)	117.0 (6)
C(13)-C(113)-C(11)	110.7 (4)	C(11)-C(10)-O(10)	117.1 (5)
C(21)-C(19)-C(20)	107.5 (6)	C(11)-C(10)-C(9)	121.3 (5)
C(47)-C(19)-C(20)	110.5 (6)	C(10)-C(11)-C(113)	122.1 (5)
C(47)-C(19)-C(21)	109.5 (6)	C(12)-C(11)-C(113)	120.9 (5)
C(4)-C(47)-C(19)	114.2 (6)	C(11)-C(12)-C(7)	124.4 (5)
C(7)-C(47)-C(19)	109.8 (5)	C(14)-C(13)-C(113)	120.2 (5)
C(6)-C(1)-O(1)	117.2 (8)	C(18)-C(13)-C(14)	116.2 (5)
C(6)-C(1)-C(2)	122.3 (8)	C(13)-C(14)-O(14)	114.7 (5)
O(1)-C(1)-C(2)	120.3 (8)	C(15)-C(14)-O(14)	122.6 (5)
C(4)-C(47)-C(7)	111.1 (5)	C(15)-C(14)-O(13)	122.7 (5)
C(3)-C(2)-C(1)	118.3 (7)	C(16)-C(15)-O(14)	119.4 (6)
C(2)-C(3)-O(3)	123.0 (6)	C(15)-C(16)-O(16)	124.8 (5)
C(4)-C(3)-O(3)	115.3 (7)	C(17)-C(16)-C(16)	114.9 (5)
C(4)-C(3)-C(2)	121.7 (6)	C(17)-C(16)-C(15)	120.3 (6)
C(3)-C(4)-C(47)	121.0 (7)	C(18)-C(17)-C(16)	118.8 (6)
C(5)-C(4)-C(47)	122.1 (5)	C(17)-C(18)-C(13)	122.5 (5)
C(5)-C(4)-C(3)	116.8 (6)		

* The unrealistic short distance is due to a not well identified disorder in the C(25) and O(1) atom positions.

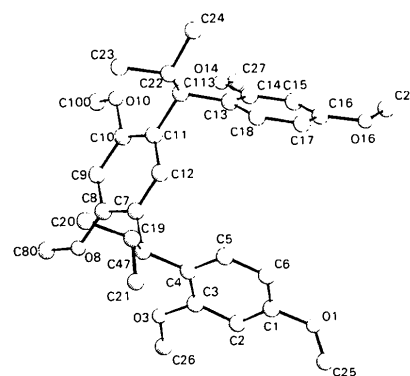


Fig. 1. View of the molecule down *c*.

References

- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- International Tables for X-ray Crystallography* (1974). Vol. IV, p. 99. Birmingham: Kynoch Press.
- NATOLI, M. C., AGOZZINO, P., CERAULO, L. & LAMARTINA, L. (1982). *Gazz. Chim. Ital.* In the press.
- SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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The Structures of Tanacetols A, C₁₇H₂₆O₄, and B, C₁₉H₃₀O₅, Two New Sesquiterpene Alcohols from *Tanacetum vulgare* L.*

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Abstract. Tanacetol A, m.p. 371 K, $[\alpha]_D^{25^\circ} = -99^\circ$ (CHCl₃, 1.0 g dm⁻³), is a ketol sesquiterpene isolated from a rare chemotype of *Tanacetum vulgare* L.: $M_r = 294.4$, orthorhombic, $P2_12_12_1$, $a = 11.132$ (4), $b = 11.255$ (3), $c = 13.782$ (4) Å, $U = 1726.8$ (8) Å³, $Z = 4$, $D_x = 1.13$ Mg m⁻³, $F(000) = 640$, $\mu(\text{Mo } K\alpha) = 0.09$ mm⁻¹, room temperature. Tanacetol B is the main constituent of the above chemotype and its monoacetyl derivative, m.p. 413 K, $[\alpha]_D^{25^\circ} = -205^\circ$ (CHCl₃, 0.4 g dm⁻³), was investigated: $M_r = 338.4$, orthorhombic, $P2_12_12_1$, $a = 7.589$ (3), $b = 10.997$ (5), $c = 23.416$ (9) Å, $U = 1954$ (1) Å³, $Z = 4$, $D_x = 1.14$ Mg m⁻³, $F(000) = 736$, $\mu(\text{Mo } K\alpha) = 0.09$ mm⁻¹, room temperature. The structures were solved by direct methods and refined to $R = 0.041$ for tanacetol A and to $R = 0.046$ for tanacetol B acetate using, respectively, 1088 and 1594 unique reflexions. Both ten-membered rings show a C(1)–C(10) *trans* double bond and present the energetically less favoured boat–chair conformation. The C(14) methyl and the C(15) methene are *syn* and on the α face of the rings; the oxygen of the keto group in tanacetol A is on the β face whereas the C(5) acetyl group in tanacetol B acetate is on the α face.

Introduction. In spite of the frequent occurrence of germacranes bearing the C(7) side chain oxidized at the

lactone level (Fischer, Olivier & Fischer, 1979), only a few compounds are known with this side chain unoxidized or oxidized at levels lower than the lactone (Geissman, 1973). A recent finding and investigation of a rare chemotype of *Tanacetum vulgare* L., from the South of Piedmont (Italy), revealed that this tansy produces C(12) unoxidized analogues of germacranolides (Appendino, Gariboldi & Nano, 1983). These constituents have been called tanacetols and they have in common a 1'-hydroxyisopropyl side chain. The structural elucidation of the two most abundant and less polar of them by spectroscopic methods was made difficult by the absence of substituents on the carbons C(6) or C(8) next to that bearing the side chain with the consequent impossibility of relating the orientation of the ring substituents to that of the hydroxyisopropyl function (Appendino *et al.*, 1983). It was then impossible to distinguish between the configurationally pseudo-enantiomeric alternatives (*A*) or (*A'*) and (*B*) or (*B'*), which are equally likely because of the conformational flexibility of the ten-membered ring. The present diffraction study showed that the correct stereostructures are (*A*) and (*B*) for tanacetol A and tanacetol B acetate, respectively. With these configurations, in order to have the 1'-hydroxyisopropyl side chain in the less hindered equatorial position, the ten-membered rings must adopt the boat–chair instead of the thermodynamically more stable chair–chair conformation (Guy, Sim & White, 1976) that would be compatible with the pseudo-enantiomers (*A'*) and (*B'*).

* Tanacetol is 5-(2-hydroxyisopropyl)-2-methyl-8-methylene-7-oxo-1-cyclodecen-10-yl acetate.