α-Diceroptene: A New Dimeric Structure for Isoceroptene

Christian Vilain, André Hubert
Chimie Générale et Organique, Université de Liège, B-4000 Liège, Belgium
Léon Dupont
Laboratoire de Cristallographie, Université de Liège, B-4000 Liège, Belgium
Kenneth R. Markham
Chemistry Division, DSIR, Petone, New Zealand
Eckhard Wollenweber
Institut für Botanik der Technischen Hochschule, D-6100 Darmstadt,
Bundesrepublik Deutschland

Z. Naturforsch. **42c,** 849–854 (1987); received February 16, 1987
Pityrogramma triangularis, Pteridaceae, Ceroptene, Isoceroptene, Photodimerisation

Prolonged UV irradiation of ceroptene yielded substantial quantities of a compound identical with the previously described isoceroptene, a trace constituent isolated from the farinose exudate of *Pityrogramma triangularis.* The improved MS, ^{1}H NMR and ^{13}C NMR analyses, together with X-ray diffraction, made possible by the availability of synthetic isoceroptene has led to a revision of the originally proposed structure. Isoceroptene is shown to be a novel, centrosymmetrical dimer of ceroptene, and accordingly the more appropriate name, α-diceroptene, is suggested to replace that of isoceroptene. An improved method for the synthesis of ceroptene is also described.

Introduction

Small quantities of a new flavonoid referred to as isoceroptene [1] have been found to accompany the major constituent, ceroptene (**1**), in the farinose frond exudate of the Californian gold-back fern, *Pityrogramma triangularis* (Kaulf.). "Isoceroptene" has been assigned provisionally a monomeric structure (**2**) on the basis of spectroscopic data obtained on the 1–2 mg of available material [1]. The reported chemical conversion of ceroptene to isoceroptene occurred only at exceedingly low levels and defied attempts at improvement.

We report here on a method for the substantial conversion of ceroptene to isoceroptene and on further structural studies made possible by the resultant availability of quantities of isoceroptene. A revised structure for isoceroptene is proposed as a result of these studies, and an improved method for the synthesis of the starting material, ceroptene, has been developed.

Materials and Methods

2,4-Diacetylphloroglucinol [2]

To the commercial complex containing 40% (w, w) boron trifluoride in glacial acetic acid (200 ml), was added anhydrous phloroglucinol (50 g) and the mixture heated on a steam-bath for 2 h. After cooling, the mixture was added dropwise to a well stirred solution of potassium acetate (105 g) in water (2.5 l). The precipitated solid, after one recrystallisation from aqueous methanol gave 2,4-diacetylphloroglucinol (56 g, 67%) as yellow-orange needles, m.p. 169 °C (lit., [3] 168 °C; lit., [2] 168–170 °C). MS *m/z* (rel. int.): 210 (75, M^+), 195 (100), 177 (71).

*2,6-Diacetyl-4,4-dimethylcyclohexane-1,3,5-trione (diacetylfilicinic acid (**3**) [2]*

Anhydrous 2,4-diacetylphloroglucinol (30 g) was dissolved in a solution of sodium (13.2 g) in methanol (300 ml) at 0 °C and methyl iodide (27 ml) was added during 15 min while the temperature was held at 0 °C. The mixture was set aside at room temperature for 2 days and then the solvent was evaporated off. The residue was dissolved in ice-cold water (375 ml), acidified with (6 M HCl (75 ml), and the tarry solid collected and subsequently extracted with light petroleum (40–60 °C) (3 × 200 ml).

Reprint requests to Dr. C. Vilain.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0341–0382/87/0700–0849 $ 01.30/0

This extract was evaporated to dryness to give diacetylfilicinic acid (23 g, 68%) as a pale yellow crystalline solid, m.p. 63 °C (lit., [2], 60–61 °C; lit., [4] 65–66 °C. MS *m/z* (rel. int.): 238 (68, M^+), 224 (66), 196 (20), 195 (36), 155 (100), 154 (64).

*2-Acetyl-4,4-dimethylcyclohexane-1,3,5-trione (3-acetylfilicinic acid) (**4**) [2]*

2,6-Diacetyl-4,4-dimethylcyclohexane-1,3,5-trione (21 g) was heated in 80% sulphuric acid (21 ml) on a steam-bath for 40 min. The mixture was then poured with vigorous stirring onto crushed ice (150 g) and the liberated solid crystallized from ethyl acetate to give the monoacetylfilicinic acid (9.2 g, 53%) as white prisms, m.p. 176 °C (lit., [3], 174–176 °C; lit., [2], 174–175 °C). MS *m/z* (rel. int.): 196 (100, M^+), 182 (7), 155 (18), 154 (9), 114 (19), 113 (12).

*O-Methyl-3-acetylfilicinic acid (**5**) [5]*

A mixture of dichloromethane (100 ml), aqueous 0.3 M NaOH (100 ml), 3-acetylfilicinic acid (4 g), dimethyl sulphate (5 ml) and benzyltributylammonium chloride (0.6 g) was agitated with a vibromixer at room temperature for 4 h. The organic layer was then separated and the aqueous layer extracted twice with 100 ml portions of methylene chloride. The combined organic extracts were washed by water (100 ml), dried over $MgSO_4$, filtered off and evaporated to dryness.

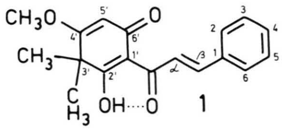
The residue was redissolved in hot light petroleum (40–60 °C) and, on cooling, deposited crystals of O-methyl-3-acetylfilicinic acid (4.06 g, 95%), m.p. 108 °C (lit., [6], 107–109 °C), MS *m/z* (rel. int.): 210 (73, M^+), 195 (52), 182 (14), 167 (10), 127 (100), 112 (36).

^1H NMR (300 MHz) δ ($CDCl_3$): major tautomer (**5**) ~ 80%; 11.32 (s, 2-OH), 5.42 (s, 1H, H-5), 3.82 (s, 3H, OCH_3), 2.58 (s, 3H, $COCH_3$), 1.35 (s, 6H, CH_3); tautomer (**6**) ~ 15%: 11.45 (s, 6-OH), 5.45 (s, 1H, H-5), 3.72 (s, 3H, OCH_3), 2.56 (s, 3H, $COCH_3$), 1.36 (s, 6H, CH_3); tautomer (**7**) ~ 5%: 5.60 (s, 1H, H-5), 3.80 (s, 3H, OCH_3), 3.50 (s, 1H, H-1), 2.70 (s, 3H, $COCH_3$), 1.46 (s, 6H, CH_3).

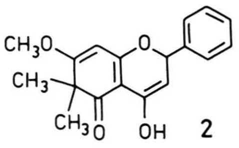
$\tilde{\nu}_{max}$ (KBr): 3400br, 2940, 2900, 1635, 1600, 1515, 1500, 1460, 1420, 1370, 1345, 1220, 1185, 1155, 980, 955, 830.

*Ceroptene (**1**) [6]*

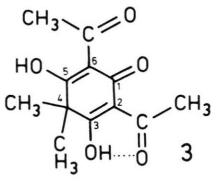
O-methyl-3-acetylfilicinic acid (4 g), benzaldehyde (20 g) and piperidine (2 ml) were heated on a boiling water bath for 0.5 h and then methanol (150 ml) was added; the hot solution was filtered off and, on cooling, deposited ceroptene (2.5 g, 44%) as yellow prisms, m.p. and mixed m.p. 139–140 °C (lit., [6], 138–140 °C). MS *m/z* (rel. int.): 296 (100, M^+), 297 (25), 283 (16), 280 (14), 227 (16), 221 (56), 210 (11), 195 (9), 131 (18), 126 (39), 125 (21), 111 (21), 103 (16), 77 (14).



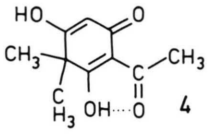
1



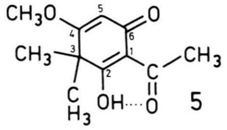
2



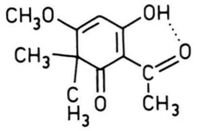
3



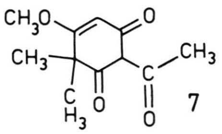
4



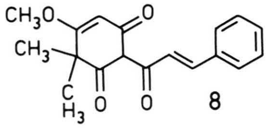
5



6



7



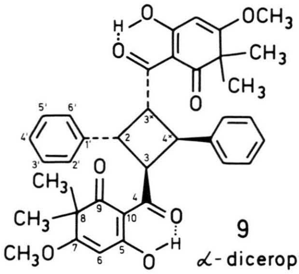
8

^1H NMR (300 MHz) δ ($CDCl_3$): major tautomer (**1**) ~ 87%: 18.98 (s, 1H, 2′-OH), 8.34 (d, $J = 16$, 1H, H-α), 7.93 (d, $J = 16$, 1H, H-β), 7.70–7.65 and 7.44–7.36 (2m, 5H, B-ring), 5.51 (s, 1H, H-5′), 3.84 (s, 3H, OCH_3), 1.42 (s, 6H, CH_3); contributions of the minor tautomer (**8**) ~ 13%: 8.59 (d, $J = 16$, 1H, H-α), 7.97 (d, $J = 16$, 1H, H-β), 5.48 (s, 1H, H-5′), 3.77 (s, 3H, OCH_3), 1.50 (s, 6H, CH_3).

$\tilde{\nu}_{max}$ (KBr): 3400br, 3080, 3040, 2960, 2950, 2900, 1635, 1610, 1560, 1510, 1460, 1425, 1360, 1345, 1285, 1220, 1185, 1170, 1150, 975, 965, 955, 845, 740, 680.

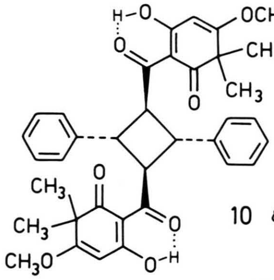
*α- and ε-diceroptenes (**9** and **10**)*

Ceroptene (0.1 g) was dissolved in benzene (1.0 ml) in a small test-tube which was stoppered. Up to 4 tubes were so prepared and attached around

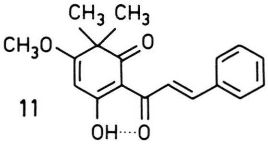


9

α- diceroptene



10 ε-diceroptene



11

the Pyrex apparatus of a high-pressure mercury lamp (Philips HPK 125 W) and were irradiated at room temperature for 48 h. The resulting combined solution (from 0.4 g of ceroptene) was examined by TLC using system I*: 4 major spots were observed in UV (254 nm) light showing unchanged ceroptene (R_f 0.64) and three new products (R_f 0.52, 0.44 and 0.34). Then, the mixture was exhaustively separated by preparative TLC with system I. The lowest R_f band (0.34) appeared to be a mixture of two products when examined by TLC with system II* and it was thus re-chromatographed with this system. However, these compounds were so far obtained in insufficient amounts to allow recrystallisation and were not pure enough for spectral measurements.

On the other hand, the highest and the middle R_f colourless bands yielded pure compounds which gave prismatic crystals from a $CHCl_3$-MeOH mixture. Their structure were elucidated by X-ray diffraction: the compound of R_f 0.52 (90 mg, 22.5%), was assigned structure **9** = α-diceroptene [7], identical in all respects to natural "isoceroptene", and the compound of R_f 0.44 (18 mg, 4.5%), was assigned structure **10** = ε-diceroptene [8].

*α-diceroptene (**9**)*

Colourless crystals, m.p. 205–206 °C; $\tilde{\nu}_{max}$ (KBr): 3010, 2950, 2910, 1640, 1610, 1580, 1520, 1450, 1435, 1370, 1325, 1215, 1155, 1030, 980, 965, 910, 830, 820, 790, 745, 690. MS *m/z* (rel. int.): 596 (3.5, M^+), 581 (1), 578 (2.5), 504 (25), 401 (3), 387 (10), 384 (10), 311 (5), 300 (5), 299 (27), 298 (100), 297 (45), 283 (17), 280 (29), 227 (26), 221 (60), 194 (30), 131 (25), 126 (35), 125 (25), 111 (27), 105 (11), 103 (18), 77 (28).

^{1}H NMR (300 MHz) δ ($CDCl_3$): 11.36 (s, 1H, 5-OH), 7.32–7.28 (m, 2H, H-2', 6'), 7.20–7.09 (m, 3H, H-3', 4', 5'), 5.23 (s, 1H, H-6), 5.095 and 5.085 (A_2B_2 pattern showing 8 lines, 2H, H-2 and H-3, J_{cis}/J_{trans}: 11/6; 3.73 (s, 3H, OCH_3), 1.27 (s, 3H, CH_3), 1.07 (s, 3H, CH_3); contributions from the tautomer with the *gem*-dimethyl at C-6: (~ 10%) 11.38 (s, 1H, 5-OH), 5.25 (s, 1H, H-8), 3.67 (s, 3H, OCH_3), 1.31 (s, 3H, CH_3), 1.10 (s, 3H, CH_3). ^{13}C NMR δ ($CDCl_3$): see Table 1; contribution from the tautomer with the *gem*-dimethyl at C-6 (~ 10%): 99.9 (C-8).

*ε-diceroptene (**10**)*

Colourless crystals, m.p. 239–240 °C; $\tilde{\nu}_{max}$ (KBr): 3000, 2950, 2910, 1645, 1600, 1565, 1500, 1450, 1435, 1370, 1340, 1210, 1185, 1155, 975, 955, 815, 740, 730, 685. MS *m/z* (rel. int.): 596 (1, M^+), 578 (2), 401 (2), 387 (8), 384 (11), 311 (2), 300 (5), 299 (26), 298 (100), 297 (45), 283 (20), 280 (27), 227 (26), 221 (57), 194 (36), 131 (21), 126 (30), 125 (22), 111 (24), 105 (12), 103 (17), 77 (33).

^{1}H NMR (300 MHz) δ ($CDCl_3$): 11.16 (s, 1H, 5-OH), 7.42–7.37 (m, 2H, H-2', 6'), 7.31–7.16 (m, 3H, H-3', 4', 5'), 5.46 (t, $J=9.6$, 1H, H-3), 5.38 (s, 1H, H-6), 4.10 (t, $J=9.6$, 1H, H-2), 3.78 (s, 3H, OCH_3), 1.06 (s, 6H, CH_3); contributions from the tautomer with the *gem*-dimethyl at C-6 (~ 10%): 11.17 (s, 1H, 5-OH), 5.39 (s, 1H, H-8), 3.67 (s, 3H, OCH_3), 1.44 (s, 6H, CH_3).

---

* System I: toluene-acetone (19:1) SiO_2 60 F254 Merck, 0.25 mm layer for analytical purpose and 0.5 mm layer for preparative separation. System II: chloroforme-methanol (99:1), adsorbants as above.

Results and Discussion

Synthesis of ceroptene (1)

Ceroptene was previously synthesized on a small scale by Nilsson [6]. This synthesis started by C-methylation of phloroacetophenone which gave 3-acetylfilicinic acid (**4**) in 5% yield [9]. The latter was methylated using methylorthocarbonate to give O-methyl-3-acetylfilicinic acid (**5**, 70%) which was condensed with benzaldehyde in the presence of piperidine to produce ceroptene (58%). The overall yield was only ~ 2% and ceroptene was prepared only in small amounts (11 mg).

We have now developed a higher yield, large-scale synthesis of ceroptene, using inexpensive reagents.

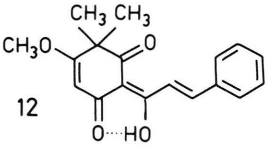
Acetylation of phloroglucinol with commercial boron trifluoride-acetic acid complex [2, 3] gave 2,4-diacetylphloroglucinol (67%), which on methylation with methyl iodide in the presence of NaOMe, afforded 3,5-diacetylfilicinic acid [2, 4] (**3**, 68%).

This compound was partially deacetylated with 80% sulphuric acid to monoacetylfilicinic acid [2] (**4**, 53%). Subsequent O-methylation of **4** was best achieved using the phase-transfer catalytic method developed by McKillop *et al.* [5], with dimethylsulphate as the alkylating agent and benzyltributylammonium chloride as the catalyst. O-Methyl-3-acetylfilicinic acid was obtained with high yield (**5**, 95%). Condensation of **5** with benzaldehyde as above gave ceroptene (**1**, 44%). The overall yield of this synthesis of ceroptene is ~ 10%.

Direct comparison (m.m.p., TLC co-chromatography in system I & II and IR spectroscopy) has proven our synthetic product to be identical with natural ceroptene.

The high resolution ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of O-methyl-3-acetylfilicinic acid (**5**) indicates the presence of two tautomers in addition to the major compound (**5**) which constitutes about 80% of the mixture at room temperature. The minor tautomers are thought to be the isomeric enol tautomer (**6**) and the triketo tautomer (**7**) which integration indicates represent about 15% and 5% respectively.

Ceroptene itself appeared to be a mixture of two tautomers, as indicated by the ^{1}H NMR spectrum (300 MHz, $CDCl_3$). The major tautomer has the conventional structure, **1** (or **11**/**12** which have been shown recently by X-ray crystallography to be equivalent representations of ceroptene in the crystalline state [10]) and constitutes some 87% of the equilibrium mixture. The minor tautomer (13%) is presumed to possess structure **8** (or alternatively that of the 6,8-isomer of the major tautomer, **11**). In both tautomers the *gem*-dimethyl group is represented by a singlet and it would seem therefore that the ^{1}H NMR spectrum might not permit distinction of the 6,8-isomers, **1** and **11**, as had earlier been presumed [1], but could also support structure **12** as being the major tautomer of ceroptene.



12

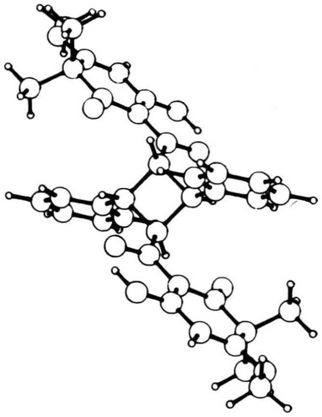
Photodimerization of ceroptene

Natural isoceroptene is present in trace amount in the frond exudate of the Californian goldback fern, *Pityrogramma triangularis* (Kaulf.) Maxon [1].

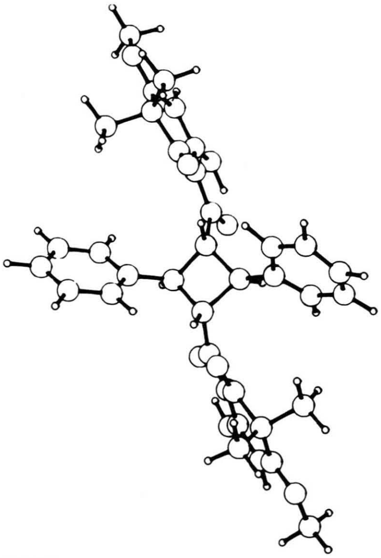
In order to substantiate evidence for the originally proposed structure of isoceroptene (**2**), numerous attempts at the quantitative conversion of ceroptene to isoceroptene were made. However, known methods available for the isomerization of chalcones to flavanones all failed to yield more than trace quantities of isoceroptene. The "flavanone" formulation (**2**) for isoceroptene was thus not confirmed by this approach. A rerun of the MS of isoceroptene under carefully controlled conditions revealed an ion of low intensity (3.5%) at *m/z* 596, exactly double the molecular weight of ceroptene. A dimeric formulation was thus suspected, and finds some support in the known fact that some crystalline α,β-unsaturated carboxylic compounds are known to produce photodimers of the α-truxillic acid type [11].

As ceroptene in the fern frond exudate is directly exposed to sunlight, it is possible that a photodimer could be produced by natural UV irradiation. Accordingly this hypothesis has been checked by irradiating a thin coat of solid ceroptene in a testtube, overnight with a powerful UV lamp. TLC analysis of the irradiated compound revealed a partial conversion (~ 5%) into 3 colourless products, the major of which was identical with natural isoceroptene.

An improved conversion rate of ceroptene was achieved by UV irradiation of concentrated solutions in benzene (0.1 g/ml). By this means an approximately 50% transformation was reached after 48 h. This appeared to be a photostationary state as the yield was not improved when the exposure time was prolonged. The substantial quantities of isoceroptene (and one of the minor products) so produced, enabled the isolation of crystals suitable for structure elucidation by X-ray diffraction. Isoceroptene was thus revealed as the centrosymmetric dimer *α-diceroptene* (**9**) [7] and the minor product as a stereoisomer of this, *ε-diceroptene* (**10**) [8]. The prefixes indicate the stereochemistry of the substituted cyclobutane ring according to Hallas [12] and stereographic views of both compounds are shown (**13**, and **14**).



13 α-Ceroptene



14 ε-Ceroptene

The mass and IR spectra of α- and ε-diceroptene are very similar and do not exhibit any significant difference. Nevertheless, the high resolution ^1H NMR spectra (300 MHz) of both compounds present clearly different chemical shifts as well as coupling patterns for H-2 and H-3, reflecting thus the stereochemical differences of the cyclobutane rings.

In α-diceroptene, H-2 and H-3 present almost identical chemical shifts resulting in a signal (~ δ 5.09) approaching a singlet: an enlarged spectrum indeed shows an eight lines pattern typical for an A_2B_2 spin system. H-2 and H-3 appear as doublets of doublets because, in this centrosymmetric structure, each proton on the cyclobutane ring is *cis*-coupled with one of its neighbours and *trans*-coupled with the other. Both coupling constants are of the magnitudes expected for a bichalcone with configuration as in **9** [13], but are unassigned because there is no clear correlation between the relative values of J_{cis} and J_{trans} in cyclobutanes [13, 14].

In ε-diceroptene, H-2 and H-3 appear as two well separated triplets. As this structure possesses two pseudo-planes of symmetry passing the diagonals of the cyclobutane, each proton of this ring is *trans*-coupled with its two identical neighbours, which gives rise to the expected [13] 9–10 Hz triplets.

It is known that the phenyl ring causes resonances due to the *cis*-vicinal protons to appear upfield of those due to the *trans*-vicinal protons [15]: this effect explains the noticeable chemical shifts difference between H-2 and H-3 in ε-diceroptene relative to α-diceroptene. In ε-diceroptene, H-3 is *cis* relative to both phenyl rings and must therefore be assigned to the upfield triplet (δ 4.10), the low field triplet (δ 5.46) being consequently assigned to H-2. In α-diceroptene, H-3 is *cis* relative to one phenyl ring and *trans* relative to the other; as a result, H-3 is in the shielding zone of only one phenyl ring and resonates downfield (relative to H-3 in ε-diceroptene) at about the same chemical shift than H-2 (~ δ 5.09).

As a substantial amount of synthetic α-diceroptene was available, the ^1H-decoupled ^{13}C NMR of this compound was rerun because some resonances were lost in the background noise of the previously reported weak spectrum of isoceroptene [1]. Also, in order to confirm the assignments and structure **9**, the ^1H-coupled ^{13}C NMR spectrum of α-diceroptene with and without D_2O were measured (Table I). C-2 and C-3 are the singly protonated carbons in the 41–56 ppm range and the low field signal is assigned

Table I: Assignments of the signals observed on the ^{1}H-coupled ^{13}C NMR spectrum of α-diceroptene.

Carbon	Chemical shift	Coupling pattern	$^1J_{CH}$(Hz)	$^2J_{CH}$ and $^3J_{CH}$(Hz)[a]
C-2	41.0	dxm	145	H-2*, H-3*, H-2′,6′
C-3	52.0	dxm	144	H-3*, H-2*
C-4	201.6	d		$^2J_{C\text{-}4/H\text{-}3} = 2.4$
C-5	187.6	dxd		$^2J_{C\text{-}5/H\text{-}6} = 2.6$; $^2J_{C\text{-}5/OH\text{-}5} = 4.6^b$
C-6	93.1	dxd	164	$^3J_{C\text{-}6/OH\text{-}5} = 5.5^b$
C-7	180.3	m		H-6, CH_3C
C-8	48.7	m		CH_3C
C-9	195.6	m		CH_3C
C-10	105.9	dxd		$^3J_{C\text{-}10/H\text{-}6} = 3.3$; $^3J_{C\text{-}10/OH\text{-}5} = 6.5^b$
C-1′	139.9	t		$^3J_{C\text{-}1'/H\text{-}3',5'} = 5.4$
C-2′,6′	128.4	dxdxd	158	$^3J_{C\text{-}2',6'/H\text{-}4'}$ and $^3J_{C\text{-}2',6'/H\text{-}6',2'}$, ~ 7 and ~ 10
C-3′,5′	127.7	dxd	159	$^3J_{C\text{-}3',5'/H\text{-}5',3'} = 7.0$
C-4′	126.3	dxt	160	$^3J_{C\text{-}4'/H\text{-}2',6'} = 6.5$
CH_3O	56.2	q	146	
CH_3C	25.4 23.7	qxm	131	the ^{13}C of each CH_3 is coupled with the ^{1}H of the other

[a] When a multiplet was observed, the ^2J or $^3J_{CH}$ were not measurable and we have only indicated the hydrogen atoms with which the ^{13}C are likely coupled.

* H-2* and H-3* are the symmetric atoms of H-2 and H-3 respectively (see structure IX).

[b] These couplings vanished after D_2O addition.

to C-3 since it is adjacent to the electron withdrawing carbonyl. C-6 shows good coupling with the proton on the 5-OH which is lost when D_2O is added, and C-10 and C-5 also show this effect. The presence of some tautomeric material, in which the *gem*-dimethyl is at C-6, is also revealed by the low intensity (~ 10%) doublet at 99.9 ppm accounted for C-8.

Although the finding of a naturally occurring photodimer such as α-diceroptene is unusual, it is not unique. An equivalent photodimer of cinnamic acid, truxillic acid (referred to as gratissimic acid) together with its dimethyl ether (gratissimin) has previously been reported as occurring in *Ocimum gratissimum* [16]. The present finding however does seem to be the first example of a naturally occurring "chalcone" photodimer although such compounds have previously been prepared photochemically in the laboratory [13, 17, 18].

Acknowledgements

The authors are grateful to Dr. H. Wong of Chemistry Division, DSIR, and Dr. J. Grandjean, Department of Chemistry, University of Liège for running the NMR spectra.

[1] K. R. Markham, C. Vilain, E. Wollenweber, V. H. Dietz, and G. Schilling, Z. Naturforsch. **40c,** 317 (1985).

[2] T. Meikle and R. Stevens, J. C. S. Perkin I **1978,** 1303.

[3] T. W. Campbell and G. M. Coppinger, J. Amer. Chem. Soc. **73,** 2708 (1951).

[4] K. Hoefer and W. Riedl, Annalen **656,** 127 (1962).

[5] A. McKillop, J.-C. Fiaud, and R. P. Hug, Tetrahedron **30,** 1379 (1974).

[6] M. Nilsson, Acta Chem. Scand. **13,** 750 (1959).

[7, 8] M. Sbit, L. Dupont, O. Dideberg, and C. Vilain, Acta Cryst., in press (1987).

[9] W. Riedl and K. H. Risse, Annalen **585,** 209 (1954).

[10] M. Sbit, L. Dupont, O. Dideberg, and C. Vilain, paper submitted to Acta Crystallographica.

[11] J. Dekker and T. G. Dekker, J. Org. Chem. **33,** 2604 (1968).

[12] G. Hallas, in: Organic Stereochemistry, p. 157, McGraw-Hill.

[13] G. Montaudo, S. Caccamese, and V. Librando, Organic Magnetic Resonance **6,** 534 (1974).

[14] L. M. Jackman and S. Sternhell, in: Organic Chemistry (D. H. R. Barton and W. Doering, eds.), p. 287, Pergamon Press, Oxford 1969.

[15] Id.; p. 234.

[16] M. Qudrat-i-Khuda, M. Erfan Ali, and L. A. M. Samsuzzaman, Sci. Res. **2,** 8 (1965); CA **63,** 11416g.

[17] H. Stobbe and K. Bremer, J. prakt. Chem. **123,** 1 (1929); CA **24,** 92.

[18] H. Stobbe and A. Hensel, Berichte **59 B,** 2258 (1926); CA **21,** 396.