

Reactions and rearrangements of triterpenoids — 3-Epitaraxerol and its transformation products

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An interesting rearrangement has been observed with 2,14-taraxeradiene **1** using *m*-chloroperbenzoic acid. With this reagent compound **1**, in methylene chloride, affords olean-2 α -epoxy-12-ene-15 α -ol **3** (confirmed by X-ray crystallographic analysis) through the intermediate 2 α ,14 α -diepoxytaraxerane **4**. The latter **4** has also been isolated from the same reaction mixture. This backbone rearrangement from the Δ^{14} -taraxarene skeleton **4** to Δ^{12} -oleanane structure **3**, with C15- α -ol, confirms α -orientation of the epoxy ring formed at Δ^{14} in **4**. Subsequent opening of the intermediate oxirane at Δ^{14} therefore must occur via the generation of an incipient carbonium ion at C(14) to allow the migration of C(13)CH₃ to C(14) from the same α -phase. Compound **4** also undergoes rearrangement to olean-12-ene-2 α ,3 β ,15 α -triol **5** with boron trifluoride etherate in methylene chloride.

Epoxide ring opening induced transformations with pentacyclic triterpenoids have been reported¹⁻⁸ in the literature. The present paper describes a series of interesting reactions and rearrangements starting with 2,14-taraxeradiene **1** which was obtained by the dehydration of epitaraxerol **2**, a major constituent⁹ of *Euphorbia antiquorum* L. (Euphorbiaceae). This is the first report on the isolation of compound **2** from this plant.

2, 14-Taraxeradiene **1** on treatment with *m*-chloroperbenzoic acid in methylene chloride at 27°C for 5 hr yielded 2 α ,14 α -diepoxytaraxerane **4** and olean-2 α -epoxy-12-ene-15 α -ol **3**.

Compound **4**, C₃₀H₄₈O₂ (M⁺ 440), mp 185-87°C (benzene), [α]_D²⁷ + 4.2° (EtOH) could be isolated in 25% yield. It showed characteristic bands for epoxy groups (C-O-C, symmetric stretching) at 1275 and 1270 cm⁻¹ in the infrared spectrum. The important structural features were evident in the 300 MHz ¹H NMR spectrum. This indicated the presence of three epoxy protons. One epoxy proton appeared at δ 3.16 (1H, dd, *J*=6.0 and 3.8 Hz). The remaining two epoxy protons resonated at δ 3.02 (1H, d, *J*=6.6 Hz) and 2.76 (1H, d, *J*=3.8 Hz). The coupling constants proved that the epoxy protons appearing at δ 3.16 and 2.76 were *vicinal* in character. The signal at δ 2.76

was assigned to the C₃-proton which coupled only with the proton at C₂. Hence the signal at δ 3.16 should originate from the C₂-proton which experienced coupling with the proton at C₃ (*J*=3.8 Hz) and also with one of the adjacent methylene protons at C₁ (*J*=6.6 Hz). The other proton at C₁ showed ~ 90° dihedral angle relationship with the C₂-proton. From steric consideration, as evident from the molecular model, the reagent can approach the C₂-C₃ double bond only from the α -phase as otherwise it would experience steric hindrance from the β -axial methyl groups at C₁₀ and C₄ positions. The epoxy proton at C₁₅ which coupled only with one of the *vicinal* methylene protons at C₁₆ appeared at δ 3.02. The oxirane ring formation at C₁₄-C₁₅ position must be α -oriented due to facile approach of the reagent from the more exposed α -phase owing to the boat conformation assumed by the unsaturated ring D.

The 75.5 MHz ¹³C NMR spectrum (including APT experiment) (Table I) of compound **4** revealed the presence of nine sp³-secondary carbons, six sp³-tertiary carbons, seven sp³-quaternary carbons and eight sp³-primary carbons. The four epoxy carbons appeared at 68.6 (C₁₄), 61.6 (C₃), 57.1 (C₂) and 52.3 (C₁₅) ppm.

The fragments arising from the molecule on

Table I—¹³C NMR spectral data of epitaraxerol, epitaraxeryl acetate, compounds 1, 3, 4, 5 and β-amyrin
(Chemical shifts in ppm)

Carbon number	Epi-Taraxerol	Epi taraxeryl acetate	Taraxeryl acetate	Compound 1	Compound 4	Compound 3	Compound 5	β-Amyrin
C(1)	37.8	37.8	37.8	39.9	39.2	40.2	47.4	38.7
C(2)	22.6	23.6	23.4	121.4	52.3	52.5	69.1	27.3
C(3)	79.1	81.1	81.1	138.3	61.6	61.6	78.2	78.9
C(4)	38.8	38.0	37.9	37.6	36.9	36.1	37.6	38.8
C(5)	55.7	55.8	55.7	52.5	46.2	46.1	50.7	55.3
C(6)	18.9	18.8	18.8	20.0	18.1	19.1	20.2	18.5
C(7)	33.2	33.3	33.2	33.2	33.1	34.7	34.7	32.8
C(8)	39.1	39.1	39.1	39.1	39.4	33.1	33.1	38.8
C(9)	49.4	49.3	49.3	48.0	47.1	46.6	48.2	47.7
C(10)	38.0	37.7	37.6	34.5	32.8	32.5	37.4	37.0
C(11)	17.5	17.6	17.6	17.2	17.0	23.5	23.7	23.6
C(12)	36.8	36.8	36.7	36.8	33.0	123.3	123.5	121.8
C(13)	37.8	37.8	37.8	37.2	36.5	146.0	146.0	145.1
C(14)	158.2	158.2	158.0	158.1	68.6	41.1	41.4	41.8
C(15)	116.9	117.0	116.9	116.9	57.1	68.3	68.3	26.2
C(16)	33.8	33.8	33.7	33.9	30.0	30.6	36.8	27.0
C(17)	35.8	35.7	35.8	35.8	32.4	31.1	31.1	32.5
C(18)	49.0	49.1	48.9	48.9	48.1	48.0	47.9	47.4
C(19)	41.5	41.4	41.3	40.6	39.6	46.4	46.3	46.9
C(20)	28.8	28.9	28.8	28.9	30.9	31.1	35.1	31.1
C(21)	35.2	35.3	35.2	35.2	34.5	35.4	35.6	34.8
C(22)	37.6	37.5	37.5	37.8	37.6	37.6	37.8	37.2
C(23)	28.0	28.0	28.0	31.8	28.0	28.1	24.0	28.2
C(24)	15.4	16.6	16.5	22.9	22.1	22.3	23.3	15.5
C(25)	15.4	15.5	15.5	15.4	18.3	17.9	21.1	15.6
C(26)	25.9	25.9	26.0	25.8	23.0	16.7	17.1	16.9
C(27)	29.9	29.9	29.9	29.9	31.1	19.6	19.9	26.0
C(28)	29.9	29.9	29.9	29.9	24.4	28.9	23.9	28.4
C(29)	33.4	33.4	33.4	33.4	33.5	33.3	33.3	33.3
C(30)	21.3	21.3	21.3	21.4	23.4	23.6	23.6	23.7
-CH ₃ -C-O	—	21.2	21.3	—	—	—	—	—
-CH ₃ -C-O	—	171.0	171.0	—	—	—	—	—

electron impact were observed at m/z 440 (100%, M^+), 234, 219 and 206. The mass spectrum confirmed the structure of compound **4** as 2,14-diepoxytaraxerane.

Compound **3**, $C_{30}H_{48}O_2$, M^+ 440, $[\alpha]_D^{27} + 32.7$ (EtOH), mp 190-93°C (benzene-ethyl acetate, 1:1), was isolated in 10% yield after repeated thin layer chromatography. It showed significant peaks at 3540 (hydroxyl) and 1270 cm^{-1} (epoxy) in the IR spectrum. The 300 MHz 1H -NMR spectrum of compound **4** revealed the presence of two epoxy protons at δ 3.19

(1H, dd, $J=6.6$ and 3.8 Hz) and 2.80 (1H, d, $J=3.8$ Hz). These were assigned to the C_2 and C_3 -protons respectively. A doublet of doublet appeared at δ 4.19 (1H, $J=11.5$ Hz and 5.3 Hz). The downfield shift together with the coupling constant values confirmed this signal to be due to C_{15} -H which was attached to the carbon bearing hydroxyl function and coupled with both the adjacent non-equivalent methylene protons at C_{16} . A triplet at δ 5.29 (1H, $J=3.7$ Hz) showed the presence of an olefinic proton. On the basis of the 1H NMR spectrum the structure of this

rearrangement product could be established as olean-2 α -epoxy-12-ene-15 α -ol **4**.

This structure was further corroborated from the 75.5 MHz ^{13}C NMR data (including APT experiment) of compound **3**. During the formation of **3** from **1** an interesting backbone rearrangement of the taraxerane skeleton to oleanane framework was observed (**Chart 1**). A significant change in the chemical shift values occurred involving rings C and D. The assignments of the carbon chemical shifts of compounds **1**, **4**, **3** and **5** were made by comparison with epitaraxerol, epitaraxeryl acetate, taraxeryl acetate and β -amyrin⁹ (**Table I**). The APT experiment demonstrated the presence of eight sp^3 -secondary carbons, six sp^3 -

tertiary carbons, six sp^3 -quaternary carbons, eight sp^3 -primary carbons, one sp^2 -quaternary carbon and one sp^2 -tertiary carbon. The epoxy carbons C_2 and C_3 resonated at δ 52.5 and 61.5 ppm respectively. The C_{15} -carbon, bonded to a hydroxyl group, appeared at 68.3 ppm while the olefinic carbons C_{12} and C_{13} were observed at 123.3 and 146.0 ppm respectively.

The molecular ion peak appeared at m/z 440. The base peak at m/z 234 (due to Retro-Diels Alder collapse in ring C) together with significant ion fragments at m/z 219 and 206 were in conformity with structure **3**.

Structure **3** was unequivocally confirmed from its X-ray crystallographic analysis (**Figure 1**). The three rings B, D and E were in chair conformation (*trans*) while the two other rings were somewhat distorted (**Table II**). All the ring junctures were *trans* except ring E which was *cis* with respect to ring D. The angular methyl groups at C_8 , C_{10} and C_{17} were β while the epoxy bridge at C_2 - C_3 , the angular methyl at C_{14} and the hydroxyl group at C_{15} were α . The epoxide group had the same effect as a double bond in flattening ring A compared to ring C. This backbone rearrangement to the Δ^{12} -oleanane skeleton **3** from 2,14-taraxeradiene **1** could only be explained *via* the formation of **4** where both C_2 - C_3 and C_4 - C_5 -epoxides are α -oriented. Under the reaction conditions only the C_{14} - C_{15} -epoxide ring opened up leading to the α -oriented C_{15} -hydroxyl function with the generation of an incipient carbonium ion at C_{10} . Methyl migration occurred from C_{13} to C_{14} , from the same α -phase, with subsequent loss of proton from C_{12} .

2 α ,14 α -Diepoxytaraxerane **4** on treatment with boron trifluoride etherate in methylene chloride at 0°C for three hr underwent rearrangement to olean-12-en-2 α ,3 β ,15 α -triol **5**.

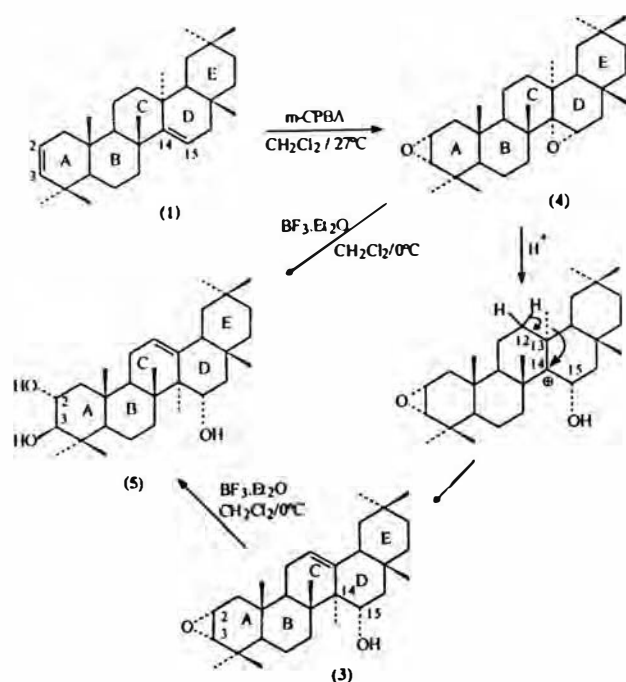


Chart 1

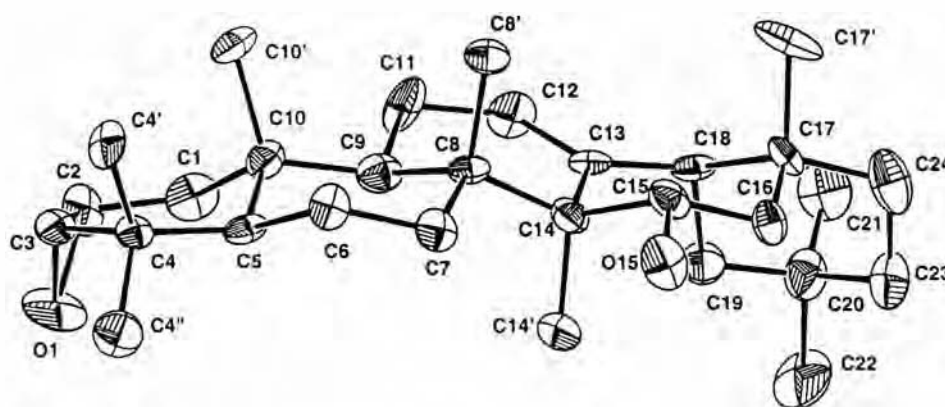


Figure 1—Ortep diagram of compound **3**

Table II—Conformational parameters¹¹ of rings in compound 3

Ring	q ²	ph ²	q ³	q	th	Conformation*
A	0.37670	-71.34036	0.29871	0.48076	51.58685	Env ¹⁰
B	0.12071	-87.98132	-0.53387	0.54734	161.25984	Chair
C	0.40111	18.21580	0.34727	0.53056	49.11476	Env ⁸
D	0.12415	-5.63761	-0.48872	0.50425	165.74712	Chair
E	0.12343	21.19201	-0.50923	0.52398	166.37500	Chair

*Env = Envelope, superscript denotes the atom out of the plane defined by the others.

Product **5**, C₃₀H₅₀O₃, (M⁺ 458), [α]_D²⁷ + 56.7° (EtOH), mp 134-35°C (benzene), was isolated in 10% yield by preparative thin layer chromatography. In the 300 MHz ¹H NMR spectrum of **5** a broad 3-proton signal (D₂O exchangeable) appeared at δ 2.4 indicating the presence of three hydroxyl groups in the molecule. A doublet at δ 3.62 (1H, *J*=10.5 Hz) was assigned to C₃-H while the multiplet at δ 3.74 was due to C₂-methine proton. The coupling constant of the C₃-proton (10.5 Hz) confirmed that the C₂ and C₃-protons were *trans*-diaxially oriented. Thus, the C₂-OH was oriented as α -equatorial and C₃-OH as β -equatorial. The C₁₅-proton resonated as a doublet of doublet at δ 4.21 (*J*=11.3 and 5.1 Hz) while the olefinic proton at C₁₂ appeared as an ill-resolved signal at δ 5.30. All these data established the structure of **5** as olean-12-en-2 α ,3 β ,15 α -triol.

Further confirmation of the structure was provided by the 75.5 MHz ¹³C NMR data (including APT experiment) (Table I). The carbons comprising rings C, D and E of compound **5** showed chemical shifts similar to those observed for compound **3** while significant changes were discernible for the chemical shifts for rings A and B carbons due to the opening of epoxide ring at C₂ and C₃.

Compound **5** was also obtained from olean-2 α -epoxy-12-ene-15 α -ol **3** in 30% yield when treated with boron trifluoride etherate under similar condition. Hence, in the case of 2 α ,14 α -diepoxytaraxerane **4** the triol **5** must have been formed *via* the product **3**.

Experimental Section

General. Melting points were determined in an electrically heated melting point bath and are uncorrected. The infrared spectra were recorded using KBr pellets on a Perkin-Elmer 782 spectrometer, ¹H NMR spectra on a Bruker AM 300L Spectrometer

and mass spectra on a Jeol D-300 spectrometer. Rotations were measured on a Perkin Elmer 241 electronic polarimeter. Column and thin layer chromatographic analyses were carried out using silica gel BDH (60-120 mesh). Preparative thin layer chromatographic experiments were carried out on plates coated with silica gel G (Merck) as adsorbent. Spots were detected in an iodine chamber. Analytical samples were routinely dried *in vacuo* over P₂O₅ for 24 hr at room temperature. Anhydrous sodium sulphate was used for drying the organic extracts. Petrol refers to pet. ether having bp 60-80°C.

Isolation of epitaraxerol from *Euphorbia antiquorum* L.

Dried whole plant of *Euphorbia antiquorum* L. was extracted with petrol in a Soxhlet apparatus for 48 hr. The solid which separated was filtered and dissolved in benzene. Column chromatography was carried out using silica gel as adsorbent and from the petrol : benzene (3:1) eluate epitaraxerol was isolated, mp 257-58°C [benzene [α]_D²⁷ + 2.0° (CHCl₃)] Anal. Calcd for C₃₀H₅₀O: C 84.51; H, 11.74% Found: C, 84.49; H, 11.67%; ¹H NMR (300 MHz, CDCl₃) : δ 0.80, 0.82, 0.90, 0.92, 0.95, 0.97, 1.09 (each s, 3H, C₂₃/C₂₄/C₂₅/C₂₆/C₂₈/C₂₉/C₃₀-CH₃), 3.18 (brs, 1H, C₃-OH), 3.63 (t, 1H, C₃-H), 5.52 (q, 1H, C₁₅-H); ¹³C-NMR (75.5 MHz, CDCl₃) : δ 37.8, 22.6, 79.1, 38.8, 55.7, 18.9, 33.2, 39.1, 49.4, 38.0, 17.5, 36.8, 37.8, 158.2, 116.9, 33.8, 35.8, 49.0, 41.5, 28.8, 35.2, 37.6, 28.0, 15.4, 15.4, 25.9, 29.9, 29.9, 33.4, 21.3 ppm.

Acetylation of epitaraxerol. Epitaraxerol (200 mg) was dissolved in pyridine (5 mL) and acetic anhydride (1 mL) added to the solution. The reaction mixture was heated on a water-bath for 3 hr. The reaction was quenched by pouring the reaction mixture over crushed ice-chips. The solid was filtered and washed with dilute hydrochloric acid and then with water until neutral. The crude product was crystallised from chloroform-methanol (3:1) as white

crystals, mp 278°C (CHCl₃); [α]_D²⁷ -14° (CHCl₃) in 80% yield. Anal. Calcd for C₃₂H₅₂O₂: C, 82.05; H, 11.11%. Found: C, 82.00; H, 11.07%. ¹H NMR (300 MHz, CDCl₃): δ 0.81, 0.85, 0.87, 1.08, 2.03 (each s, 3H, 5-CH₃), 0.90, 0.95 (each s, 6H, 4-CH₃), 4.45 (t, 1H, *J*=5.7 Hz, C₃-H), 5.52 (br.s, 1H, C₁₅-H); ¹³C NMR (75.5 MHz, CDCl₃): δ 37.8, 23.6, 81.1, 38.0, 55.8, 18.8, 39.3, 39.1, 49.3, 37.7, 17.6, 36.8, 37.8, 158.2, 117.0, 33.8, 35.7, 49.1, 41.4, 28.9, 35.3, 37.5, 28.0, 16.6, 15.5, 25.9, 29.9, 29.9, 33.4, 21.3, 21.2, 171.0; MS: *m/z* 468 (M⁺), 408, 344, 329, 204, 284 and 269.

Dehydration of epitaraxerol **1** to 2,14-taraxeradiene **2**. Compound **1** (1g) was dissolved in dry pyridine (20 mL) and distilled phosphorus oxychloride (6 mL) added to it. The reaction mixture was refluxed for 4 hr and kept for 18 hr. It was poured over crushed ice-chips, extracted with methylene chloride (4×50 mL), washed with 2*N* hydrochloric acid (3×50 mL), then with water until the reaction mixture became neutral and dried. The concentrate afforded a white solid. It showed a single spot on a TLC plate (benzene as solvent). The solid was purified by column chromatography using silica gel as adsorbent and eluting with solvents of increasing polarity. The petrol eluate afforded compound **2**, mp 194-95°C (C₆H₆) in 80% yield. Anal. Calcd for C₃₀H₄₈: C, 88.24; H, 11.76%. Found: C, 88.18; H, 11.70%. MS: *m/z* 408, 284, 269 and 204.

Epoxidation of 2,14-taraxeradiene 2. Compound **2** (600 mg) was dissolved in dry methylene chloride (20 mL) and *m*CPBA (750 mg) in dry methylene chloride (30 mL) was added to it dropwise with stirring at 25°C. The reaction mixture was further stirred for five hr at 25°C and kept for a further period of 18 hr. This was treated with 10% sodium sulphite solution until it gave a negative test with starch iodide paper, then washed with 5% sodium bicarbonate solution (3×20 mL) and finally with water (3×20 mL) and dried. The concentrate was subjected to preparative thin layer chromatography using benzene as solvent system. Compound **4**, mp 185-87°C (benzene) was isolated in 25% yield. Anal. Calcd for C₃₀H₄₈O₂: C, 81.82; H, 10.91%. Found: C, 81.75; H, 10.83%; MS: *m/z* 440, 234, 219 and 206.

Compound **3**, mp 190-93°C (benzene-ethyl acetate, 1:1), was isolated in 10% yield. Anal. Calcd for C₃₀H₄₈O₂: C, 81.82; H, 10.91%. Found: C, 81.77; H, 10.82%. MS: *m/z* 440, 234, 219 and 206.

Boron trifluoride catalysed rearrangement of

2 α ,14 α -diepoxytaraxerane 4. Compound **4** (100 mg) was dissolved in dry methylene chloride (10 mL) and boron trifluoride etherate (0.4 mL) in dry methylene chloride (7 mL) added to it dropwise at 0°C under nitrogen atmosphere with stirring for 3 hr. The reaction mixture was poured over ice-chips, extracted with methylene chloride (4×10 mL), washed with 2% sodium bicarbonate solution (3×10 mL), water (3×10 mL) and dried. The concentrate was subjected to preparative thin layer chromatography using benzene:ethyl acetate (9:1) as the solvent system. Compound **5**, mp 134-35°C (benzene), was isolated in 15% yield. Anal. Calcd for C₃₀H₅₀O₃: C, 78.60; H, 10.92%. Found: C 78.55, H: 10.83%; MS: *m/z* 458, 440, 234, 219 and 206.

Boron trifluoride catalysed rearrangement of olean-12-en-2 α -epoxy-15 α -ol 3. Compound **3** (50 mg) was dissolved in dry methylene chloride (5 mL) and boron trifluoride etherate (0.2 mL) in dry methylene chloride (1 mL) added to it dropwise with continuous stirring at 0°C under nitrogen atmosphere for 3 hr. The reaction was quenched over ice-chips, extracted with methylene chloride (4×5 mL), washed with 2% sodium bicarbonate solution (3×5 mL), water (3×5 mL) and dried. The concentrate was subjected to preparative thin layer chromatography using the solvent system benzene-ethyl acetate (9:1) Compound **5** was isolated in 30% yield.

X-Ray crystallographic analysis. Compound **3** was recrystallised by slow evaporation of a methanol solution at 4°C. A colourless prismatic crystal 0.2 × 0.2×0.6 mm in size was used for X-ray diffraction analysis.

Crystal data—C₃₀H₄₈O₂, *M* 440, monoclinic space group *P*2₁, *a* = 15.002 (9) Å, *b* = 11.783 (7) Å, *c* = 7.423 (3) Å, *b* = 98.94 (6) Å, *Z* = 2, *V* = 1296.2 (9) Å³, *F*(000) = 488, λ = 1.5418 Å (CuK α), *R* = 7.3% for 1892 Fobs with *I* > 2 σ (*I*), *R* = 8.7% for all Fobs (2031).

Data collection, processing and refinement—X-ray crystallographic analysis was carried out on a Philips PW 1100 four circle diffractometer, operating the CuK α radiation (λ = 1.5418 Å). The orientation matrix and cell parameters were deduced from the angular settings of 25 reflections randomly distributed between 20 and 30 degrees in θ and refined by least squares procedure. Diffraction data were recorded within the 3-65°: θ range. The structure was solved by direct methods (SHELXS). Most of the atoms were identified on the E-map corresponding to the highest

Table III—Positional parameters ($\times 10^4$) and mean recalculated isotropic factors ($\times 10^3$) for non-hydrogen atoms (*).

ATOM	X	Y	Z	$\langle U \rangle$
O1	2731(4)	5055(5)	2923(8)	49(6)
C1	1481(6)	5876(7)	4386(10)	32(7)
C2	2470(5)	5763(7)	4373(10)	34(7)
C3	2898(5)	6260(6)	2899(10)	26(6)
C4	2366(4)	6918(6)	1328(8)	21(5)
C4'	2776(4)	8127(6)	1426(10)	30(6)
C4''	2569(5)	6374(8)	-483(10)	40(7)
C5	1343(4)	6880(6)	1386(8)	17(5)
C6	787(4)	7772(6)	144(9)	24(6)
C7	-204(5)	7521(7)	-139(9)	28(6)
C8	-625(4)	7493(5)	1616(8)	16(5)
C8'	-668(5)	8735(6)	2304(12)	37(8)
C9	-8(4)	6756(5)	3089(7)	17(5)
C10	1037(4)	6904(5)	3285(7)	12(4)
C10'	1408(5)	8000(6)	4388(10)	25(6)
C11	-355(5)	6804(10)	4919(9)	38(7)
C12	-1341(5)	6703(7)	4729(8)	34(7)
C13	-1935(4)	6768(6)	3173(8)	21(5)
C14	-1598(4)	6939(5)	1340(7)	14(5)
C14'	-1599(4)	5766(6)	535(8)	20(5)
C15	-2319(5)	7702(6)	153(9)	27(6)
O15	-2140(4)	7719(5)	-1686(6)	39(5)
C16	-3283(5)	7331(7)	140(10)	29(6)
C17	-3565(4)	7320(6)	2049(9)	28(6)
C17'	-3472(7)	8553(7)	2831(13)	58(10)
C18	-2911(5)	6560(5)	3339(9)	22(6)
C19	-3160(5)	5282(6)	3176(12)	35(7)
C20	-4143(5)	5017(7)	3273(12)	37(7)
C21	-4410(6)	5308(9)	5112(12)	53(9)
C22	-4283(7)	3717(8)	2934(16)	62(11)
C23	-4719(5)	5664(8)	1731(11)	46(8)
C24	-4565(5)	6957(9)	1948(12)	50(9)

(*) in \AA^2 and recalculated as : $\langle U \rangle = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* \cdot a_j^* \cdot a_i \cdot a_j$

Table IV—Positional parameters ($\times 10^3$) and mean recalculated isotropic factors ($\times 10^3$) for hydrogens atoms.

ATOM	X	Y	Z	U
H11	130	583	565	36
H22	133	510	382	36
H2	302	568	536	36
H3	358	639	322	36
H41'	251	853	25	54
H42'	347	812	152	54
H43'	260	854	252	54
H41''	228	688	-152	54

contd

figure of merit. Two missing positions were obtained by difference – Fourier Synthesis. The overall structure was refined with isotropic, then anisotropic thermal factors, for the non-hydrogen atoms, by full matrix least squares procedures. All hydrogens were introduced with a fixed U isotropic thermal factor of 0.06 subsequently refined as grouped factors, according to their position, one overall value for hydrogens linked to tertiary carbons, and a second value for other hydrogens. The final agreement factor

Table IV—Positional parameters ($\times 10^3$) and mean recalculated isotropic factors ($\times 10^3$) for hydrogens atoms. -contd

ATOM	X	Y	Z	U
H42''	230	558	-62	54
H43''	325	636	-44	54
H5	110	613	86	36
H61	86	856	74	36
H62	107	780	-103	36
H71	-21	678	-83	36
H72	-51	815	-95	36
H81'	-102	869	341	54
H82'	-100	932	141	54
H83'	-2	900	276	54
H9	-3	595	260	36
H101	119	876	377	54
H102	210	803	465	54
H103	118	800	565	54
H111	-6	615	572	36
H112	-12	755	554	36
H12	-162	660	589	36
H141	-135	575	-84	54
H142	-226	549	15	54
H143	-123	524	128	54
H15C	-223	849	72	36
H15O	-161	815	-203	36
H161	-368	793	-58	36
H162	-341	655	-47	36
H171	-369	856	408	54
H172	-387	911	199	54
H173	-281	881	298	54
H18	-290	681	468	36
H191	-298	503	193	36
H192	-268	493	417	36
H211	-404	482	611	54
H212	-509	510	507	54
H213	-434	615	553	54
H221	-410	339	175	54
H222	-497	357	289	54
H223	-395	326	402	54
H231	-540	549	165	36
H232	-451	544	52	36
H241	-487	712	309	36
H242	-496	731	84	36

Table V—Distances (Å) for non-hydrogen atoms with *esd.*'s given in parentheses

O1 – C2	1.462 (9)	C11 – C12	1.468 (10)
O1 – C3	1.443 (9)	C12 – C13	1.347 (9)
C1 – C2	1.491 (11)	C13 – C14	1.537 (8)
C1 – C10	1.553 (10)	C13 – C18	1.509 (9)
C2 – C3	1.473 (10)	C14 – C14'	1.564 (9)

contd

Table V—Distances (Å) for non-hydrogen atoms with *esd.*'s given in parentheses -contd

C3 – C4	1.520 (9)	C14 – C15	1.568 (9)
C4 – C4'	1.549 (10)	C15 – O15	1.432 (8)
C4 – C4''	1.562 (10)	C15 – C16	1.509 (10)
C4 – C5	1.542 (9)	C16 – C17	1.540 (10)
C5 – C6	1.553 (9)	C17 – C17'	1.562 (11)
C5 – C10	1.549 (8)	C17 – C18	1.546 (9)
C6 – C7	1.499 (10)	C17 – C24	1.550 (11)
C7 – C8	1.534 (9)	C18 – C19	1.552 (10)
C8 – C8'	1.554 (10)	C19 – C20	1.521 (11)
C8 – C9	1.580 (8)	C20 – C21	1.520 (12)
C8 – C14	1.582 (9)	C20 – C22	1.561 (13)
C9 – C10	1.561 (9)	C20 – C23	1.526 (12)
C9 – C11	1.529 (9)	C23 – C24	1.545 (14)

Table VI—Bond angles (°C) for non-hydrogen atoms with *esd.*'s given in parentheses

C2–O1–C3	60.9(5)	C1–C10–C5	107.5(5)
C2–C1–C10	114.3(6)	C1–C10–C9	107.7(5)
O1–C2–C1	115.9(6)	C1–C10–C10'	106.1(5)
O1–C2–C3	58.9(5)	C5–C10–C9	110.4(5)
C1–C2–C3	121.2(6)	C5–C10–C10'	110.9(5)
O1–C3–C2	60.2(5)	C9–C10–C10'	114.0(5)
O1–C3–C4	116.1(6)	C9–C11–C12	112.9(7)
C2–C3–C4	122.3(6)	C11–C12–C13	126.9(7)
C3–C4–C4'	106.0(5)	C12–C13–C14	120.1(6)
C3–C4–C4''	107.6(6)	C12–C13–C18	116.2(6)
C3–C4–C5	111.7(5)	C14–C13–C18	123.4(5)
C4'–C4–C4''	106.7(5)	C8–C14–C13	111.3(5)
C4'–C4–C5	114.6(5)	C8–C14–C14'	111.1(5)
C4''–C4–C5	109.9(5)	C8–C14–C15	112.2(5)
C4–C5–C6	114.1(5)	C13–C14–C14'	108.8(5)
C4–C5–C10	117.4(5)	C13–C14–C15	106.2(5)
C6–C5–C10	108.7(5)	C14'–C14–C15	107.0(5)
C5–C6–C7	112.3(5)	C14–C15–O15	109.1(5)
C6–C7–C8	114.5(6)	C14–C15–C16	114.5(6)
C7–C8–C8'	107.6(5)	O15–C15–C16	108.7(6)
C7–C8–C9	109.0(5)	C15–C16–C17	113.3(6)
C7–C8–C14	113.1(5)	C16–C17–C17'	108.2(6)
C8'–C8–C9	109.9(5)	C16–C17–C18	109.6(6)
C8'–C8–C14	110.3(5)	C16–C17–C24	111.1(6)
C9–C8–C14	107.0(5)	C17'–C17–C18	107.3(6)
C8–C9–C10	118.4(5)	C17'–C17–C24	107.8(6)
C8–C9–C11	110.5(5)	C18–C17–C24	112.7(6)
C10–C9–C11	112.9(5)	C13–C18–C17	112.7(5)
C13–C18–C19	112.1(6)	C19–C20–C23	107.6(7)
C17–C18–C19	113.1(6)	C21–C20–C22	108.6(7)
C18–C19–C20	114.7(6)	C21–C20–C23	111.3(7)
C19–C20–C21	112.9(7)	C22–C20–C23	108.8(7)
C19–C20–C22	107.5(7)	C20–C23–C24	110.9(7)
C17–C24–C23	113.9(7)		

Table VII—Anisotropic thermal parameters($\times 10^4$) for non-hydrogen atoms

ATOM	U11	U22	U33	U23	U13	U12
O1	804(43)	131(27)	521(34)	88(26)	88(31)	178(28)
C1	527(48)	208(40)	232(37)	186(33)	-30(35)	1(38)
C2	333(40)	286(40)	407(41)	204(35)	-62(32)	119(35)
C3	373(40)	92(36)	323(38)	-18(31)	-57(31)	47(31)
C4	266(34)	151(32)	208(32)	53(30)	5(26)	7(30)
C4'	208(34)	183(37)	506(45)	43(36)	52(30)	-120(32)
C4''	436(44)	488(48)	269(38)	-22(36)	107(34)	-15(39)
C5	336(35)	39(28)	145(28)	-11(27)	-62(25)	-43(29)
C6	310(35)	217(39)	183(32)	149(30)	15(27)	8(30)
C7	333(42)	271(39)	232(34)	100(31)	-1(30)	86(34)
C8	317(35)	59(30)	111(28)	4(25)	28(24)	7(27)
C8'	386(44)	71(38)	643(58)	-121(38)	-23(40)	-19(33)
C9	403(36)	29(29)	69(27)	16(26)	7(25)	-16(29)
C10	238(30)	69(29)	69(25)	-18(26)	-18(22)	-47(27)
C10'	256(35)	195(37)	286(37)	-175(32)	-54(29)	-116(31)
C11	266(35)	747(60)	128(31)	15(41)	-22(27)	-86(43)
C12	459(41)	451(49)	115(30)	20(34)	97(29)	19(38)
C13	308(34)	154(34)	164(30)	-57(28)	58(26)	-40(30)
C14	257(32)	142(29)	137(27)	-40(27)	29(24)	99(27)
C14'	339(36)	126(33)	147(30)	-90(26)	40(26)	79(29)
C15	318(38)	258(39)	223(33)	25(30)	25(28)	98(32)
O15	415(31)	537(38)	216(24)	140(26)	68(22)	125(29)
C16	262(36)	307(39)	301(37)	53(32)	-48(29)	142(31)
C17	239(34)	219(38)	386(38)	-36(31)	93(29)	103(30)
C17'	885(72)	295(47)	557(58)	-117(43)	290(54)	146(48)
C18	367(37)	106(33)	202(32)	-46(26)	16(28)	-33(28)
C19	336(39)	181(38)	527(48)	-1(35)	12(35)	-17(31)
C20	313(40)	278(43)	514(49)	80(38)	-56(37)	4(36)
C21	532(51)	569(60)	482(51)	80(47)	123(41)	1(46)
C22	476(57)	388(54)	972(82)	-11(54)	6(53)	-249(47)
C23	311(39)	568(56)	481(49)	60(45)	-58(35)	52(41)
C24	414(46)	500(57)	573(53)	155(51)	20(39)	234(47)

$$R = \frac{\sum ||fo| - |fc||}{\sum ||fo|} = 7.3\% \text{ for 1892 reflections}$$

observed above the 2σ background.

The positional parameters are given in **Tables III** and **IV**, the distance (Å) for non-hydrogen atoms and bond angles with estimated deviations are given in **Tables V** and **VI** and the anisotropic thermal parameters in **Table VII**.

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References

- 1 Talapatra S K, Bhar D S & Talapatra B, *Indian J Chem*, 15B, 1977, 806.
- 2 Sil A K, Ganguly J K, Dhara K P, Dutta C P & Roy D N, *Indian J Chem*, 20B, 1981, 201.
- 3 Ganguly J K, Som U K, Haque K E, Dhara K P & Dutta, C P, *Indian J Chem*, 21B, 1982, 1065.

- 4 Corbett R E, Cong A N T, Wilkins A L & Thomson R A, *J Chem Soc Perkin Trans-I*, **1985**, 2051.
- 5 Patra A & Choudhuri S K, *Indian J Chem*, 27B, **1988**, 170.
- 6 Som U K, Sil A K, Haque K E, Dutta C P & Dhara K P, *J Indian Chem Soc*, 65, **1988**, 604.
- 7 Pradhan B P, Roy A & Patra A, *Indian J Chem*, 31B, **1992**, 633.
- 8 Banerji A & Sur R K, *Indian J Chem*, 34B, **1995**, 338.
- 9 *Fortschritte der Chemie Organischer Naturstoffe*, Vol. 36, 1-229, edited by W Herz, H Griesebach and G W Kirby, (Published by Springer – Verlag / Wien) 1979.
- 10 Chatterjee A, Mukhopadhyay S & Chattopadhyay K, *Tetrahedron*, 32, **1976**, 3051.
- 11 Cremer D & People J A, *J Am Chem Soc*, 97, **1975**, 354.