692. *Studies on Sesquiterpenoids. Part VII.*[1] *Isolation and Synthesis of Ujacazulene.*

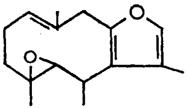
By Ken'ichi Takeda, H. Minato, K. Hamamoto, I. Horibe, T. Nagasaki, and M. Ikuta.

Dehydrogenation of linderane (I), isolated from the root of *Lindera strychnifolia* Vill., afforded a new reddish-purple azulene, ujacazulene. As this azulene was assumed to have structure (II), we have synthesised 3,8-dimethylazuleno[6,5-*b*]furan (II); it is identical with ujacazulene.

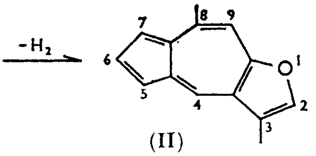
Structure (I) has been suggested[2] for linderane, isolated from the root of *Lindera strychnifolia* Vill. Palladium–charcoal dehydrogenation of linderane afforded a new reddish-purple azulene, $C_{14}H_{12}O$, m. p. 105—106°, which was named " ujacazulene."

Since linderane (I) has a β-methylfurano-function,[2] it was assumed that ujacazulene (II) would probably possess the same function. The n.m.r. spectrum of ujacazulene (II) shows a methyl signal on a furan ring at 7·63τ (doublet, $J = 1{\cdot}1$ c./sec.) and one on an azulene ring at 7·13τ. From these results, ujacazulene may be an azulene having one methyl group and a β-methylfurano-function.

Ujacazulene shows $\lambda_{\text{max.}}$ 534 (ε 511), 545 (494), 575 (432), 600 (283), and 632 mμ (220). According to Plattner's rule,[3] the introduction of a methyl group at the 1(= 3)- or the 4(= 8)-position of the azulene ring causes shifts of +28 or −11 mμ, respectively, in the visible spectra.



(I)



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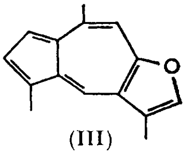
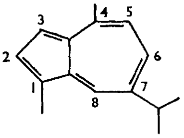


(III)



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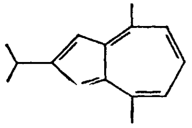

(V)

As linderazulene,[1,4] 3,5,8-trimethylazuleno[6,5-*b*]furan (III), has $\lambda_{\text{max.}}$ 562 mμ, that of 3,8-dimethylazuleno[6,5-*b*]furan (II) is calculated to be 534 mμ on the basis of this rule. This value agrees with that observed for ujacazulene. Moreover, the shapes of the ultraviolet and visible spectra of ujacazulene are similar to those of linderazulene (III).

The methyl signal at the 4(= 8)-position of the azulene ring appears at 7·17 and 7·12τ in the n.m.r. spectrum of guaiazulene (IV) or vetivazulene (V), respectively. It was observed[5] that in the case of guaiazulene the methyl signal at the 1(= 3)-position appeared at a higher field (7·32τ) than that at the 4(= 8)-position. Therefore, the signals at 7·31 and 7·22τ of linderazulene (III) are attributed to the methyl groups at 5- and 8-positions, and the signal at 7·13τ of ujacazulene is also due to the methyl group at the 8-position. From these results, the structure of ujacazulene is assumed to be 3,8-dimethylazuleno-[6,5-*b*]furan (II).[6]

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[1] Part VI, Takeda, Minato, and Ishikawa, *J.*, 1964, 2591.

[2] Takeda, Minato, and Horibe, *Tetrahedron*, 1963, **19**, 2307.

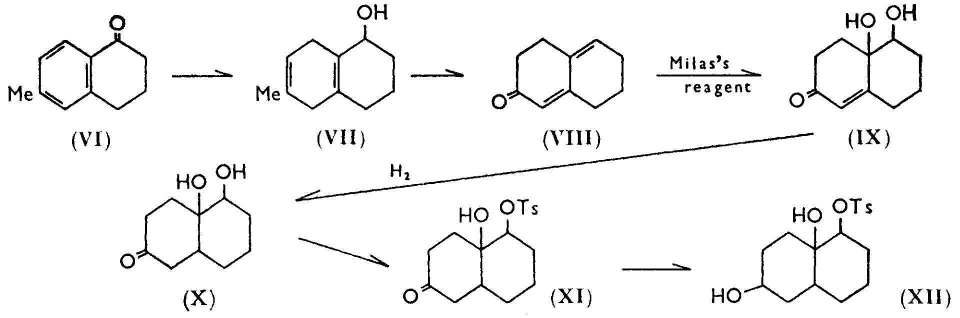
[3] Pommer, *Annalen*, 1953, **579**, 47; Gordon, *Chem. Rev.*, 1952, **50**, 127.

[4] Takeda and Nagata, *Chem. and Pharm. Bull.* (*Japan*), 1953, **1**, 164; Takeda, Minato, and Ishikawa, *Tetrahedron Letters*, 1963, 121.

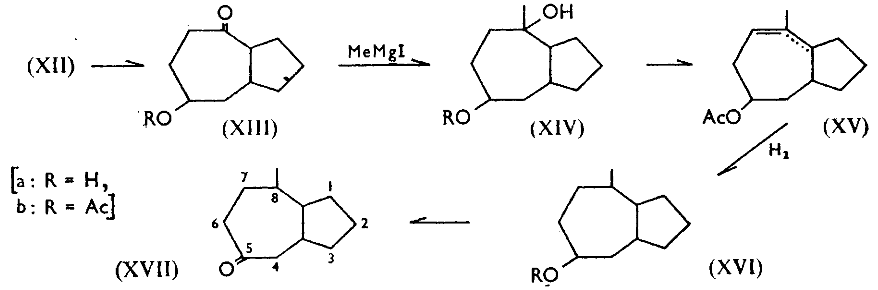
[5] Danyluk and Schneider, *Canad. J. Chem.*, 1962, **40**, 1777; Meuche, Molloy, Reid, and Heilbronner, *Helv. Chim. Acta*, 1963, **46**, 2483.

[6] Romo, Romo de Vivar, and Herz, *Tetrahedron*, 1963, **19**, 2317.

In order to confirm this suggested structure of ujacazulene, and consequently of linderane (I), we have synthesised ujacazulene, starting from 1,2,3,4-tetrahydro-6-methoxynaphthalen-1-one (VI) which was converted[7] into 2,3,4,6,7,8-hexahydronaphthalene-2-one (VIII) by way of the alcohol (VII). The ketone (VIII) was oxidised with Milas's reagent or osmium tetroxide to the dihydroxy-compound (IX) which was easily catalytically hydrogenated with 5% palladium–barium carbonate to give 5,10-dihydroxy-2-decalone (X). Its toluene-*p*-sulphonate (XI) was reduced with lithium aluminium hydride, to give 5-toluene-*p*-sulphonyloxydecalin-2,10-diol (XII). When (XII) was heated in dimethylformamide with calcium carbonate at 160—170° for 6 hours by Mazur's method,[8] a mixture of carbonyl compounds (XIIIa) was obtained. The acetate (XIIIb) shows two peaks, at retention times of 15·0 and 18·0 minutes, in the gas chromatogram (ratio of peak heights 1 : 1·5). From these results, it is reasonable to suppose that this oily acetate (XIIIb) is an equilibrium mixture of the *trans*- and the *cis*-ketone.



Reaction of the mixture of carbonyl compounds (XIIIa) with methylmagnesium iodide afforded an oily alcohol (XIVa), a mixture of the stereoisomers, whose monoacetate (XIVb) afforded an oily compound (XVIb) on dehydration with phosphorus oxychloride in pyridine, followed by hydrogenation. Oxidation of (XVIa) in acetic acid with chromium trioxide afforded the perhydroazulen-5-one (XVII). Since this seven-membered-ring ketone



(XVII) shows three peaks, at retention times of 6·8, 7·8, and 9·0 minutes (the ratio of the peak heights being 2·3 : 7·9 : 1), in the gas chromatogram, (XVII) is a mixture of three ketones. Therefore, (XVII) was converted into its semicarbazone, which was recrystallised and treated with oxalic acid, to afford a colourless mobile oil (XVIIa) which showed only one peak, at a retention time of 7·8 minutes, in the gas chromatogram.

Reformatsky reaction of (XVIIa) with ethyl α-bromopropionate gave a colourless oil (XVIII), which was dehydrated with thionyl chloride–pyridine to give a mixture of the double-bond isomers (XIX). When (XIX) was refluxed with 5% potassium carbonate in methanol for 6 hours, an oily βγ-unsaturated acid (XXa) and the unsaponified

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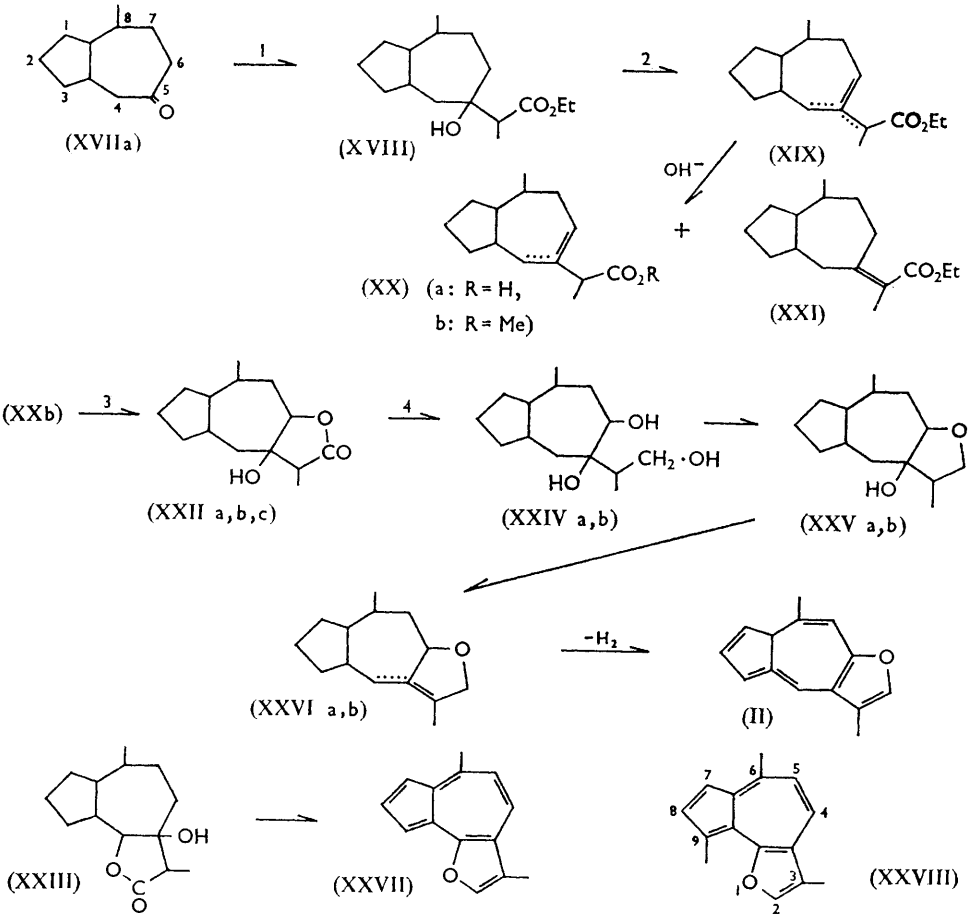
[7] Gaidamovich and Torgov, *Bull. Acad. Sci. U.S.S.R.*, 1961, 1682.

[8] Mazur and Nussim, *J. Amer. Chem. Soc.*, 1961, **83**, 3911.

αβ-unsaturated ester (XXI) were obtained in about 60 and 40% yield, respectively. The ester (XXI) shows an ultraviolet absorption maximum at 231 mμ (ε 8700), whereas the methyl ester of (XXa) shows no maximum above 210 mμ. However, since it is reasonable to suppose that the oily βγ-unsaturated acid (XXa) is a mixture of the 4,5- and 5,6-double-bond isomers, these isomers must be separated in order to synthesise ujacazulene. Oxidation of (XXb) with osmium tetroxide afforded a mixture of hydroxy-actones (XXII), which was separated into crystalline (XXIIa) and (XXIIb) and an oily mixture (XXIIc), by alumina and preparative thin-layer chromatography. The n.m.r. spectrum of (XXIIa) or (XXIIb) shows the signal of a proton attached to a carbon atom bearing an ether oxygen atom of the γ-lactone function as the X part centred at 6·02 or 5·90τ of an ABX system. This indicates the existence of two protons on the adjacent carbon atom of the above-mentioned carbon atom bearing the lactonic oxygen. Thus, (XXIIa) and (XXIIb) should not be represented by formula (XXIII), but by formula (XXII).



Reagents: 1, MeCHBr·CO$_2$Et; 2, SOCl$_2$–pyridine; 3, (i) OsO$_4$, (ii) OH$^-$, (iii) H$^+$; 4, LiAlH$_4$.

Lithium aluminium hydride reduction of (XXIIa) or (XXIIb) afforded a triol, (XXIVa) or (XXIVb). When (XXIVa) or (XXIVb) was treated with toluene-*p*-sulphonyl chloride in pyridine, an oily ring-closed compound, (XXVa) or (XXVb), was obtained. This was dehydrated with thionyl chloride–pyridine to give a colourless mobile oil, (XXVIa) or (XXVIb). When two parts of (XXVIa) or (XXVIb) were mixed with one part of 10% palladium–charcoal and heated at 310—320° for ½~1 minute, a reddish-purple azulene was obtained. The thus obtained 3,8-dimethylazuleno[6,5-*b*]furan, 5-norlinderazulene (II), was purified to give reddish-purple prisms, identical with ujacazulene.

The oily mixture (XXIIc) was converted into an oily compound (XXVI) *via* (XXIV) and (XXV) under the same conditions. Dehydrogenation of (XXVI) afforded an oily azulene which was separated into a reddish-purple azulene and a blue azulene. The former was identical with ujacazulene (II), and the latter was an oily new azulene, $\lambda_{max.}$ 583 mμ. Moreover, as the shapes of the ultraviolet and the visible absorption curves of this blue azulene are very similar to those of artemazulene (XXVIII), it may be 9-norartemazulene (XXVII).

On the assumption that the oily mixture (XXIIc) contains an isomer (XXIII) besides (XXIIa) and (XXIIb), it is reasonable that 9-norartemazulene (XXVII) is obtained on dehydrogenation. However, we could not investigate fully the structure of this blue azulene, because of the very poor yield.

EXPERIMENTAL

Melting points were taken on a Kofler hot-stage apparatus. Unless otherwise specified, ultraviolet spectra were taken in 95% ethanol, visible spectra in n-heptane, and infrared spectra in chloroform. N.m.r. spectra were taken for deuterochloroform solutions with a Varian A-60 n.m.r. spectrometer. For gas chromatography, a column 3 m. in length with a 6 mm. i.d., consisting of Silicone oil KF-54 (Shinetsu Co.) (5% on Chromosorb W, 30—60 mesh) was operated at 160° with a flow rate of 100 ml./min. of hydrogen by means of a Shimadzu Gas Chromatograph-IA.

Isolation of Ujacazulene (II).—When a mixture of linderane (I) (200 mg.) and 10% palladium charcoal (100 mg.) in a test-tube was heated at 300—310° for 30 sec. in a nitrogen atomosphere, a reddish-purple azulene was immediately obtained. A total of 1 g. of linderane was treated. The combined oily azulene was dissolved in light petroleum and chromatographed on neutral alumina (Woelm, activity II) (30 g.), to give reddish-purple prisms (45 mg.). The crude azulene afforded a 2,4,6-*trinitrobenzene adduct*, maroon needles, m. p. 138—139° (from ethanol) (Found: C, 58·7; H, 3·8; N, 10·0. $C_{20}H_{15}N_3O_7$ requires C, 58·5; H, 3·7; N, 10·2%), which was dissolved in light petroleum and chromatographed on neutral alumina, to give *ujacazulene* (II), reddish-purple prisms, m. p. 105—106° (from light petroleum) (Found: C, 85·55; H, 6·2. $C_{14}H_{12}O$ requires C, 85·7; H, 6·2%), $\lambda_{max.}$ (in n-heptane) 225·5 (log ε 4·17), 285 (4·63), 291 (4·61), 296 (4·61), 303·5 (4·31), 317·5 (4·25), 349 (3·75), 358 (3·84), 363 (3·77), 366 (3·79), 376 mμ (3·70), $\lambda_{max.}$ (in n-heptane) 534 (ε 511), 545 (494), 575 (432), 600 (283), 632 mμ (220).

Oxidation of 2,3,4,6,7,8-*Hexahydronaphthalen*-2-*one* [7] (VIII).—(a) *With osmium tetroxide.* A solution of osmium tetroxide (970 mg.) in dioxan (20 ml.) was added to a solution of (VIII), b. p. 111—112°/3·5 mm., $\lambda_{max.}$ 233 (ε 4700) and 289·5 mμ (16,000) (565 mg.) in dioxan (5 ml.) and dry pyridine (0·6 ml.), and left for 4 days at room temperature. Dioxan (20 ml.) was added and the mixture saturated with hydrogen sulphide. The black precipitate was filtered off and well washed with methanol. The filtrate and washings were evaporated *in vacuo*, extracted with chloroform, washed with 2N-sulphuric acid, water, 2N-sodium carbonate, dried (Na_2SO_4), and evaporated, leaving a crystalline substance (344 mg.), which was recrystallised from chloroform, to give 2,3,4,5,6,7,8,10-*octahydro*-5,10-*dihydroxynaphthalen*-2-*one* (IX) (221 mg., 30%), colourless prisms, m. p. 131—132°, $\lambda_{max.}$ 232·5 mμ (ε 12,700) (Found: C, 65·9; H, 7·8. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%).

(b) *With Milas's reagent.* To a solution of 6·1% hydrogen peroxide in t-butyl alcohol (63 m., 1 Equiv.) was added (VIII) (16 g.) with ice-cooling. 10% Osmium tetroxide in t-butyl alcohol (4·2 ml.) was added to this solution with stirring during 10 min. in an ice-bath and stirring continued for 20 min. at the same temperature. This mixture was left for 20 hr. at 0° in an ice-box, diluted with dioxan (100 ml.), saturated with hydrogen sulphide, and extracted with chloroform. The extract was treated as described above and evaporated, leaving a soiled oil (16·2 g.), which crystallised from chloroform–ether to give (IX), m. p. 129—131° (5·1 g.) and the starting material (VIII) (5·4 g.).

Hydrogenation of 2,3,4,5,6,7,8,10-*Octahydro*-5,10-*dihydroxynaphthalen*-2-*one* (IX).—A mixture of 5% palladium–barium carbonate (4·5 g.) in a solution of (IX) (11·2 g.) in 95% ethanol (200 ml.)

was hydrogenated (1·02 equiv. of hydrogen absorbed). The catalyst and solvent were removed, the residue was extracted with chloroform, and the extract washed with water, dried (Na_2SO_4), and evaporated, leaving a crystalline substance (11·2 g., 97%), which was recrystallised from ether, to give *decahydro*-5,10-*dihydroxynaphthalen*-2-*one* (X), prisms, m. p. 90—91° (Found: C, 64·8; H, 8·8. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·75%). Treatment with toluene-*p*-sulphonyl chloride–pyridine at room temperature afforded the *monotoluene*-p-*sulphonate* (XI), prisms, m. p. 134—135° (Found: C, 60·3; H, 6·5; S, 9·8. $C_{17}H_{22}O_5S$ requires C, 60·3; H, 6·5; S, 9·5%).

Reduction of (XI) *with Lithium Aluminium Hydride.*—A solution of (XI) (1·27 g.) in dry tetrahydrofuran (20 ml.) was added, with stirring, dropwise to a suspension of lithium aluminium hydride (140 mg.) in dry tetrahydrofuran (20 ml.) and stirred for 1 hr. in an ice-bath. The mixture was decomposed by addition of ice–water, extracted with chloroform, dried (Na_2SO_4), and evaporated, leaving a crystalline substance (1·3 g.), which was recrystallised from ether–chloroform to give *decahydro*-5-*toluene*-p-*sulphonyloxynaphthlene*-2,10-*diol* (XII) (995 mg., 78%), prisms, m. p. 154·5—155° (Found: C, 59·7; H, 7·2; S, 9·6. $C_{17}H_{24}O_5S$ requires C, 60·0; H, 7·1; S, 9·4%).

Conversion of (XII) *into* 5-*Hydroxyperhydroazulen*-8-*one* (XIIIa).—A mixture of (XII) (14 g.) and calcium carbonate (4·1 g.) in dimethylformamide (140 ml.) was refluxed for 6 hr. at 160—170° in an oil-bath and filtered. The filtrate was evaporated *in vacuo*, extracted with ether, washed with 2N-sodium carbonate, dried (Na_2SO_4), and evaporated, leaving a yellow viscous oil which was distilled at 90—110°/0·3 mm., to give a pale yellow viscous oil (6·5 g.). The product was treated with Girard's reagent T (reflux for 1 hr.), to afford 5-*hydroxyperhydroazulen*-8-*one* (XIIIa) (4·9 g., 70%), a pale yellow viscous oil, b. p. 104—110°/0·3 mm. (Found: C, 71·5; H, 9·5. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%); *acetate* (XIIIb), a colourless mobile oil, b. p. 137—138°/3 mm., $\nu_{max.}$ 1726 and 1698 cm.$^{-1}$ (Found: C, 68·7; H, 8·65. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·6%).

Grignard Reaction of (XIIIa) *with Methylmagnesium Iodide.*—A solution of (XIIIa) (5·7 g.) in dry ether (100 ml.) was added dropwise to Grignard reagent [from magnesium (3·3 g.) and methyl iodide (19·2 g.) in dry ether (200 ml.)], with stirring, during 30 min., and stirred for an additional 2 hr. at room temperature. Ammonium chloride solution was added to the mixture in an ice-bath, and the ether layer was separated, washed with water, dried (Na_2SO_4), and evaporated, leaving a colourless viscous oil (XIVa) (6·08 g., 98%) which was acetylated with acetic anhydride–pyridine at room temperature, to give the monoacetate, which was chromatographed on alumina, to give 5-*acetoxy*-8-*methylperhydroazulen*-8-*ol* (XIVb) (1·4 g.), prisms, m. p. 85—86° (from light petroleum), $\nu_{max.}$ 3625 and 1722 cm.$^{-1}$ (Found: C, 69·1; H, 9·7. $C_{13}H_{22}O_3$ requires C, 69·0; H, 9·8%), and an oily mixture of the stereoisomers of (XIVb) (6·0 g.), which was converted into (XVII) in the same manner as the crystalline acetate (XIVb).

Dehydration of (XIVb).—Phosphorus oxychloride (1·5 g.) was added, with stirring, to a solution of (XIVb) (1·4 g.) in pyridine (15 ml.) in an ice-bath. The mixture was stirred at room temperature for 1 hr. and at 80—90° for 1 hr., poured on to ice–water, extracted with ether, washed with 2N-sulphuric acid and 2N-sodium carbonate, dried (Na_2SO_4), and evaporated, to give a light yellow mobile oil (XV) (1·23 g., 95%), b. p. 95—102°/1·5 mm.

Catalytic Hydrogenation of (XV) *with Adams Catalyst.*—A mixture of Adams catalyst (400 mg.) and (XV) (3 g.) in acetic acid (60 ml.) was hydrogenated at room temperature (1·01 mole of hydrogen absorbed). The catalyst and solvent were removed, the residue was extracted with ether, and the extract washed with 2N-sodium carbonate, dried (Na_2SO_4), and evaporated, leaving a colourless mobile oil (2·9 g., 97%), which was distilled at 95—100°/1·5 mm., to give 5-*acetoxy*-8-*methylperhydroazulene* (XVIb) (Found: C, 74·6; H, 10·6. $C_{13}H_{22}O_2$ requires C, 74·2; H, 10·5%).

Preparation of 8-*Methylperhydroazulen*-5-*one* (XVIIa).—Hydrolysis of (XVIb) with 5% potassium carbonate in methanol afforded an oil (XVIa). A solution of chromium trioxide (3 g.) in water (10 ml.) was added dropwise to a solution of (XVIa) (4·7 g.) in acetic acid (40 ml.), with stirring, for 10 min. in an ice-bath and the mixture stirred for 3 hr. at room temperature. To this solution was added methanol (20 ml.), and then the mixture was stirred for 30 min., evaporated *in vacuo*, extracted with ether, and the extract washed with 2N-sodium carbonate, dried (Na_2SO_4), and evaporated, leaving a mobile oil (4·5 g.) which was distilled at 95—100°/3 mm., to give a colourless mobile oil (XVII) (4·1 g., 85%). The crude ketone (XVII) afforded its semicarbazone (5·5 g.), plates (2·3 g.), m. p. 211—213° (from chloroform–ethanol)

(Found: C, 64·2; H, 9·4; N, 18·85. $C_{12}H_{21}N_3O$ requires C, 64·5; H, 9·5; N, 18·8%). Purified semicarbazone (2·3 g.) was hydrolysed with 10% aqueous oxalic acid (40 ml.) under reflux for 1·5 hr., to give *8-methylperhydroazulen-5-one* (XVIIa), a colourless mobile oil (1·67 g.), b. p. 99—100°/3·5 mm. (Found: C, 79·4; H, 11·0. $C_{11}H_{18}O$ requires C, 79·45; H, 10·9%).

Reformatsky Reaction of (XVIIa).—A solution of ethyl α-bromopropionate (3·84 g.) in dry toluene (35 ml.) was added dropwise to a refluxing solution of (XVIIa) (1·73 g.) in dry toluene (35 ml.) containing zinc dust (1·36 g.) and a crystal of iodine with stirring for 30 min. and refluxed with stirring for another 2 hr. To the mixture were added water (15 ml.) and 2N-sulphuric acid (30 ml.). The toluene layer was washed with 2N-sodium carbonate, dried (Na_2SO_4), and evaporated, leaving a light yellow oil, which was distilled at 140—146°/2 mm., to give the *hydroxy-ester* (XVIII), a colourless oil (2·3 g., 83%) (Found: C, 71·95; H, 10·4. $C_{16}H_{28}O_3$ requires C, 71·6; H, 10·5%).

Dehydration of (XVIII).—Thionyl chloride (2·2 g.) was added dropwise to a solution of (XVIII) (2·3 g.) in pyridine (35 ml.) with stirring in an ice-bath, and left for 1 hr. at the same temperature and for 2 hr. at room temperature. The solution was poured on to ice–water (100 ml.), extracted with ether, and the extract washed with 2N-sulphuric acid and 2N-sodium carbonate, dried (Na_2SO_4), and evaporated, leaving a yellow oil (2·1 g.) which was distilled at 110—120°/1 mm., to give a colourless oil (XIX) (1·86 g., 86%).

Separation of βγ-*Unsaturated Acid* (XXa) *and* αβ-*Unsaturated Ester* (XXI).—A solution of (XIX) (1·82 g.) in 5% potassium carbonate–methanol (50 ml.) was refluxed for 6 hr. on a steam-bath and evaporated. The residue was dissolved in water and extracted with ether. The ether extract gave the αβ-*unsaturated ester* (XXI) as a light yellow oil (810 mg., 42%), b. p. 123—125°/2 mm., $\lambda_{max.}$ 231 mμ (ε 8700).

The alkaline aqueous layer was acidified to Congo Red with 2N-sulphuric acid, extracted with ether, washed with water, dried (Na_2SO_4), and evaporated, leaving the βγ-*unsaturated acid* (XXa), a yellow viscous oil (906 mg., 58%), which was esterified with diazomethane to give the βγ-*unsaturated ester* (XXb), a colourless oil (920 mg.), b. p. 105—110°/1 mm., $\nu_{max.}$ 1728 cm.$^{-1}$.

Osmium Tetroxide Oxidation of βγ-*Unsaturated Ester* (XXb).—A solution of osmium tetroxide (1·13 g., 1·1 Equiv.) in dry benzene (10 ml.) was added to a solution of (XXb) (900 mg.) in dry benzene (10 ml.) and dry pyridine (0·4 ml.) in an ice-bath, and the mixture was left for 3 days at room temperature. Dioxan (70 ml.) and methanol (10 ml.) were added to this mixture which was saturated with hydrogen sulphide. The black precipitate was filtered off and well washed with hot methanol. The filtrate and washings were evaporated *in vacuo*, extracted with chloroform, washed with 2N-sulphuric acid and 2N-sodium carbonate, dried (Na_2SO_4), and evaporated, leaving an oil (950 mg.) which was hydrolysed with 10% potassium carbonate in methanol to give an acid fraction and a neutral fraction * (195 mg.). The acid fraction was converted into a mixture of hydroxy-lactones (605 mg.), which was dissolved in light petroleum (60 ml.) and chromatographed on acid alumina (Merck, activity II) (25 g.). Elution with benzene afforded a crystalline substance (254 mg.) which was purified by recrystallisation (from ether–pentane) and preparative thin-layer chromatography (Merck, Kieselgel G), giving a *hydroxy-lactone* (XXIIa), colourless plates, m. p. 130—132° (155 mg.), $\nu_{max.}$ 3586 and 1776 cm.$^{-1}$, 6·02τ (Found: C, 70·45; H, 9·3. $C_{14}H_{22}O_3$ requires C, 70·55; H, 9·3%). Further elution with benzene–chloroform (95 : 5, 90 : 10, and 80 : 20) afforded a crystalline substance (201 mg.), which was purified by recrystallisation (from ether–pentane) and preparative thin-layer chromatography, giving a *hydroxy-lactone* (XXIIb), colourless needles, m. p. 144—145° (160 mg.), $\nu_{max.}$ 3600 and 1774 cm.$^{-1}$, 5·90τ (Found: C, 70·55; H, 9·35. $C_{14}H_{22}O_3$ requires C, 70·55; H, 9·3%). Further elution with benzene–chloroform (1 : 1), and the mother-liquor from recrystallisations of (XXIIa) or (XXIIb), afforded an oily mixture of hydroxy-lactones (XXIIc) (154 mg.).

Reduction of Hydroxy-lactone (XXIIa) *or* (XXIIb) *with Lithium Aluminium Hydride.*—A solution of (XXIIa) (155 mg.) in dry ether (2 ml.) was added to a suspension of lithium aluminum hydride (80 mg.) in dry ether (2 ml.), with stirring, in an ice-bath, and the mixture stirred for 2·5 hr. at room temperature, decomposed by addition of ice–water, and extracted with ether, to give a *triol* (XXIVa) (160 mg.), colourless plates, m. p. 92—92·5° (from ether) (Found: C, 69·35; H, 10·9. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·8%). Hydroxy-lactone (XXIIb) (155 mg.)

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* It is supposed that this oily fraction is an αβ-unsaturated γ-lactone, which is obtained by dehydration of the tertiary hydroxyl group, $\nu_{max.}$ 1753 (αβ-unsaturated carbonyl) and 1677 cm.$^{-1}$ (double bond).

afforded, under the same conditions, a *triol* (XXIVb) (160 mg.), colourless prisms, m. p. 176—178° (from ether) (Found: C, 69·4; H, 10·7. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·8%).

Ring-closure of Triol (XXIVa) *or* (XXIVb).—A solution of (XXIVa) (150 mg.) and toluene-*p*-sulphonyl chloride (165 mg., 1·3 equiv.) in dry pyridine (2 ml.) was set aside overnight at room temperature and then extracted with ether. The extract (150 mg.) was chromatographed on alumina, giving starting material (XXIVa) (49 mg.) and the *product* (XXVa) (70 mg., 50%), a colourless oil, b. p. 140—143° (bath)/1·5 mm. (Found: C, 74·8; H, 10·85. $C_{14}H_{24}O_2$ requires C, 74·95; H, 10·8%). Triol (XXIVb) (150 mg.) afforded, under the same conditions, the *product* (XXVb) (74 mg., 53%), a colourless viscous oil, and the starting material (XXIVb) (34 mg.).

Dehydration of (XXVa) *or* (XXVb).—Thionyl chloride (50 mg.) was added to a solution of (XXVa) (70 mg.) in pyridine (2 ml.), with stirring, in an ice-bath and the mixture stirred for 1 hr. at room temperature. The ether extract afforded an oil (70 mg.), which was chromatographed on alumina, giving (XXVIa) (57 mg., 88%), a colourless mobile oil. An isomer (XXVb) (74 g.) afforded, under the same conditions, (XXVIb) (54 mg., 83%), a colourless mobile oil.

Dehydrogenation of (XXVIa) *or* (XXVIb). When a mixture of (XXVIa) or (XXVIb) (30 mg.) and 10% palladium–charcoal (15 mg.), in a test-tube, was heated at 310—320° for ½~1 min. in a nitrogen atmosphere, a reddish-purple azulene immediately condensed on the upper part of the test-tube and was extracted with light petroleum. The extract was evaporated, leaving a reddish-purple oil (26 mg.). Under the same conditions, a total of 120 mg. of (XXVIa) and (XXVIb) was dehydrogenated, to give a reddish-purple oil (101 mg.). The combined oil, containing azulene (127 mg.), was dissolved in light petroleum and chromatographed on neutral alumina (Woelm, Activity II) (15 g.), to give a reddish-purple oil (7·8 mg. which was re-chromatographed on neutral alumina, giving reddish-purple prisms. The crude azulene afforded a 2,4,6-trinitrobenzene adduct, maroon needles, m. p. 138—140° (from ethanol), which was identical with that of ujacazulene (mixed m. p.). The adduct was dissolved in light petroleum and chromatographed on neutral alumina, to give 3,8-*dimethylazuleno*[6,5-b]*furan*, 5-*norlinderazulene* (II), reddish-purple prisms, m. p. 105—106° (from light petroleum) (Found: C, 86·0; H, 6·25. $C_{14}H_{12}O$ requires C, 85·7; H, 6·15%), which was identical with ujacazulene (mixed m. p. and ultraviolet, visible and infrared spectra).

Preparation of Azulenes from a Mixture of Hydroxy-lactones (XXII).—The oily mixture (XXIIc) (154 mg.) was converted into an oily mixture (XXVI) (57 mg.), a colourless mobile oil *via* (XXIV) and (XXV), and dehydrogenated, to give a blue-violet oil (44 mg.) under the same conditions as described for (XXIIa). The oil, containing azulene, was chromatographed on alumina, to give an oily blue azulene (1·6 mg.) and an oily reddish-purple azulene (1·2 mg.), which were purified by preparative thin-layer chromatography (Merck, Kieselgel G). The latter was identical with ujacazulene (II) (mixed m. p. and infrared spectra). The former was an oily *blue azulene*, $\lambda_{max.}$ 583 mμ, and afforded a 2,4,6-*trinitrobenzene adduct*, brownish black needles, m. p. 151—153° (from ethanol). This new blue azulene was assumed to be 9-*norartemazulene* (XXVII), but its structure was not fully investigated because of the very poor yield.

SHIONOGI RESEARCH LABORATORY, SHIONOGI & CO., LTD.,
FUKUSHIMA-KU, OSAKA, JAPAN.

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