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STRUCTURE AND STEREOCHEMISTRY OF JATAMANSONE*

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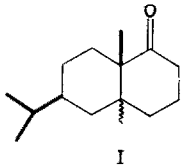
Abstract—On the basis of degradation studies, jatamansone is shown to have the structure and stereochemistry depicted in formula I, representing a new fundamental type.

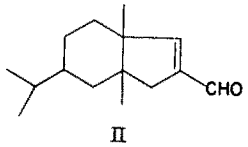
THE isolation of a sesquiterpene ketone, jatamansone from *Nardostachys jatamansi* was reported earlier.[1] On the basis of degradation studies reported in the present communication, jatamansone can unequivocally be assigned the structure and stereochemistry depicted in formula I.

Analytical results on jatamansone, its derivatives and all the degradation products are consistent with the formulation of jatamansone as $C_{15}H_{26}O$. Wolff–Kishner reduction of jatamansone yields the saturated hydrocarbon, jatamansane, $C_{15}H_{28}$ Jatamansone should therefore be a bicyclic saturated ketone.

Jatamansone was reduced by lithium aluminium hydride to jatamansol, which on dehydration with PBr_3–aniline yields jatamansene, $C_{15}H_{26}$. Ozonolysis of jatamansene yields a dialdehyde, $C_{15}H_{26}O_2$, which is converted by refluxing with alcoholic hydrochloric acid to an α,β-unsaturated aldehyde, $C_{15}H_{24}O$, (II) yielding a red 2,4-dinitrophenylhydrazone, obtained also directly from the dialdehyde. With excess benzaldehyde, both under acid as well as base-catalysed conditions, the same monobenzylidene



I



II

derivative is formed, from which it may be concluded that there is no change in the carbon skeleton of jatamansone during this process. Ozonolysis of the benzylidene derivative yields jatamansic acid, also obtained[1] directly by the chromic acid oxidation of jatamansone.

Jatamansone shows infra-red absorption at 1699 cm^{-1}, which may be ascribed to a 2,2-dialkylcyclohexanone system.[2] With one mole of bromine, a monobromojatamansone, $C_{15}H_{25}OBr$ is formed, with carbonyl absorption at 1729 cm^{-1}, indicating an equatorially-oriented α-bromine atom. With excess bromine, only a dibromojatamansone is formed. Since the presence of a —CO—CH_2— group has been established, these results indicate that the other carbon atom adjacent to the carbonyl group is fully substituted.

* The material presented in this paper has been published in the form of two brief communications in *Tetrahedron Letters* No. 15, 5 (1959); *Chem. & Ind.* 1059 (1960).

[1] T. R. Govindachari, S. Rajadurai and B. R. Pai, *Chem. Ber.* **91**, 908 (1958).
[2] E. J. Corey, T. H. Topie and W. A. Wozniak, *J. Amer. Chem. Soc.* **77**, 5415 (1955).

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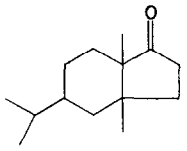
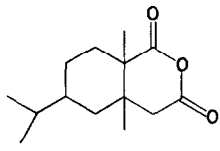
Pyrolysis of jatamansic acid yields norjatamansone, $C_{14}H_{24}O$ (III), showing carbonyl absorption at 1735 cm^{-1} (cyclopentanone). With excess benzaldehyde, norjatamansone gives a monobenzylidene derivative, yielding on ozonolysis, a

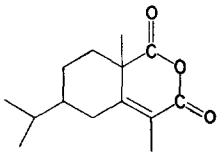


III

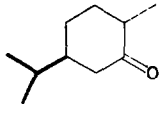


IV

diketone norjatamansadione, $C_{14}H_{22}O_2$ oxidized by sodium meta periodate to norjatamansic acid, $C_{14}H_{24}O_4$. The latter compound on heating with acetic anhydride yields norjatamansic anhydride (IV), having carbonyl bands at 1757 and 1805 cm^{-1} (glutaric anhydride). The anhydride on treatment with excess bromine yields only a monobromo derivative, $C_{14}H_{21}O_3Br$, which is converted by treatment with dimethylaniline to dehydronorjatamansic anhydride, $C_{14}H_{20}O_3$(λ_{max} 225 mμ, log ε, 3·67; infra-red bands at 1786, 1672 and 1595 cm^{-1}) which may be formulated as V. Dehydronorjatamansic anhydride dissolves in alkali, but acidification of the alkaline solution yields the anhydride directly, the isolation of the intermediate acid not being possible. The anhydride is recovered unchanged after prolonged treatment



V



VI

with ozone, from which it may be concluded that there is no terminal methylene group in the compound. This behaviour is consistent with the presence of a highly-hindered double bond as depicted in V.

Oxidation of jatamansic acid (or jatamansone) with manganese dioxide–sulphuric acid (60 per cent) yields trimellitic acid, whose formation should not involve any rearrangement prior to dehydrogenation, since jatamansic acid is recovered unchanged, together with some norjatamansone, under the same conditions in the absence of manganese dioxide.

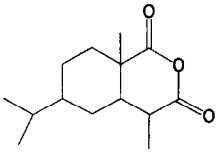
The results so far outlined offer clear proof that jatamansone contains two six-membered rings which are 1:2-fused. The two rings cannot be 1:3-fused, since in that case any structure formulated for dehydronorjatamansic anhydride would violate Bredt's rule, in the absence of an exocyclic double bond.

Oxidation of dehydronorjatamansic anhydride with $KMnO_4$–$NaIO_4$ proceeds quantitatively with formation of 1-*trans*-carvomenthone, (VI), isolated as the semicarbazone. This experiment offers conclusive proof for structure V advanced for dehydronorjatamansic anhydride. From this it would appear that norjatamansic anhydride should itself be formulated as VII. However the formation of dehydronorjatamansic anhydride from norjatamansic anhydride by bromination and dehydrobromination must involve migration of a methyl group from an angular to a ring

[3] R. V. Lemieux, E. Rudolf, *Canad. J. Chem.* **33**, 1701, 1710 (1955).

position and norjatamansic anhydride should itself be represented correctly by IV and not VII for the following reasons:

(a) Dehydrogenation of norjatamansic acid with Pd/c at 300° yields pure 1,2-dimethyl-4-isopropylbenzene[4] and not 2-ethyl-1-methyl-4-isopropylbenzene which could be expected if norjatamansic anhydride has structure VII. Comparison of the dehydrogenation product is most conveniently effected through the crystalline sulphonamide derivatives.



VII

(b) Norjatamansone yields a liquid benzylidene derivative converted by ozonolysis to norjatamansadione, which exhibits a positive Zimmermann reaction, comparable in intensity to that given by jatamansone and norjatamansone. The dione shows a peak at 1418 cm^{-1} characteristic of a —CO—CH_2— group, which disappears in the product (norjatamansatrione) obtained from it by oxidation with selenium dioxide.

(c) The NMR spectrum of norjatamansic anhydride (in chloroform solution at 40 Mc) definitely favours structure IV and not VII. The key feature is the quartet of lines with τ values of 6·4, 6·8, 7·3 and 7·8. The four lines should correspond to the CH_2 group of IV adjacent to the carbonyl function, with a chemical shift between them caused by a rigid six-membered ring, i.e. there are really two hydrogens with τ values of 6·6 and 7·55 with a spin-spin splitting of 16 c/s. The intensity of the lines is also in better accord with this interpretation rather than when this quartet is ascribed to the feature —CH(—CH_3)—CO— present in VII.

The sequence of these degradation results leads unequivocally to structure I for jatamansone, which is the first and only example of a sesquiterpenoid compound with two angular methyl groups in a hydronaphthalene tenplate. Biogenetically it could arise from a normal eudalenoid precursor by migration of the ring methyl group to the adjacent angular position.

The absolute configuration at C(6) follows from that of 1-*trans*-carvomenthone[5] to which it has been degraded. The rotatory dispersion curve[6] of jatamansone exhibits a strong negative Cotton effect and the angular methyl group at C(9) should be therefore β-oriented. Evidence for the nature of the ring fusion is being sought, after which a definite assignment of configuration at C(10) can be made.

We reported earlier[1] that dehydrogenation of jatamansol yielded a bluish violet azulene. This has now been purified by chromatography on paraffin-impregnated paper[7] and freed from blue, reddish violet and violet azulenes present in trace amounts. The purified azulene jatazulene, yields a T.N.B. adduct, m.p. 158°, different from the

[4] A. Klages, *Ber. Dtsch. Chem. Ges.* **39**, 2311 (1906).
[5] A. J. Birch, *Ann. Rep. Chem. Soc.* **47**, 192 (1950).
[6] C. Djerassi, R. Riniker and B. Riniker, *J. Amer. Chem. Soc.* **78**, 6362 (1956).
[7] O. Knessl and A. Vlastiborova, *Coll. Czech. Chem. Comm.* **19**, 782 (1954).

T N.B. adducts of any of the known azulenes obtained from sesquiterpenoid compounds.

The formation of an azulene from a naphthalenic precursor is unusual and should be due to the location of the hydroxyl group in jatamansol adjacent to a fully saturated carbon atom. An analogous case is the formation of chamazulene from dihydrocyclopyrethrosin acetate.[8] The absorption spectrum of jatazulene strongly indicates that it is a trisubstituted azulene, similar to Se-guiazulene. However, there is a depression of 30° in the mixed m.ps. of the respective T.N.B. adducts.

Although no direct comparison has been made, it is likely from the data presented by Křepinský *et al.*[9] that jatamansone and valeranone[10] are identical. Křepinský *et al.* on the basis of further independent and different experimental evidence[11] have also advanced two alternative structures, one of these being I which has been shown by our work to be uniquely assignable to jatamansone.

EXPERIMENTAL

Jatamansene. Jatamansol (15 g) in carbon tetrachloride (60 ml) was treated with phosphorus tribromide (6 g) for 20 min with stirring and the temp maintained between 0° and 10°. Next day the mixture was heated on a water-bath for 15 min then decomposed with ice and the carbon tetrachloride layer thoroughly washed with dil NaOH solution. The residue after removal of solvent was treated with aniline (30 g) and after leaving overnight was heated at 160–180° for 2 hr. Acetic acid (30 ml) was added and the mixture steam distilled. The steam distillate was repeatedly extracted with ether and the ether extract washed with dil HCl, water and finally with saturated $NaHCO_3$ solution. After the removal of solvent the residue was distilled *in vacuo* to give *jatamansene* (7 g), b.p. 106–108°/4 mm n_{30}^{D}: 1·487. $[\alpha]_{30}^{D}$: 81·83° (*c*: 2·20, $CHCl_3$) (Found: C, 87·3; H, 12·6 $C_{15}H_{26}$ requires: C, 87·4; H, 12·7%).

Ozonolysis of jatamansene

(a) Jatamansene (5 g) in ethyl acetate (20 ml) was ozonized to completion (3 hr). The solvent was removed *in vacuo* and the residue was heated with water (50 ml) and pure zinc dust (0·5 g) on a water-bath for 3 hr, extracted with ether and the ether extract washed with $NaHCO_3$ solution to remove acidic materials. The bicarbonate solution on acidification with conc HCl gave jatamansic acid (about 0·2 g), m.p. 233–235°. The ether solution was evaporated and the residue distilled *in vacuo* to give the *dialdehyde* (2·5 g), b.p. 138°/1 mm (Found: C, 76·0; H, 10·5 $C_{15}H_{26}O_2$ requires: C, 75·7; H, 10·9%).

The *dialdehyde* when heated under reflux (3 hr) with water containing a little conc HCl readily lost a molecule of water and gave an *α,β-unsaturated aldehyde*, b.p. 144°/1·2 mm (Found: C, 81·4; H, 10·7 $C_{15}H_{24}O$ requires: C, 81·8; H, 10·9%). It gave a red *2,4-dinitrophenyl hydrazone* (from methanol), m.p. 168° (Found: C, 63·3; H, 7·2 $C_{21}H_{28}N_4O_4$ requires: C, 63·0; H, 7·0%).

The above dialdehyde (0·2 g) was gently heated on a water bath with hydrogen peroxide (15%; 15 ml) for 6 hr, excess hydrogen peroxide decomposed by adding a pinch of platinum oxide and then diluted with water and extracted with ether. After the removal of solvent the acid was crystallized from absolute ether, m.p. 233–235° and found to be identical with jatamansic acid, (m.p. and mixed m.p.).

(b) Jatamansene (2 g) in ethyl acetate (15 ml) was oxidized to completion with ozone (2 hr). The ethy acetate solution was then concentrated *in vacuo* and the residue treated with hydrogen peroxide solution (15%; 30 ml) and heated on a water-bath for 6 hr and a pinch of platinum oxide added to decompose the excess hydrogen peroxide. It was then extracted with ether and the ether solution washed with saturated $NaHCO_3$ solution which on acidification gave jatamansic acid (1·2 g), m.p. 233–235°. $[\alpha]_{30}^{D}$: +40·0° (*c*: 2·43 $CHCl_3$).

[8] D. H. R. Barton and P. de Mayo, *J. Chem. Soc.* 150 (1957).

[9] J. Křepinský, V. Herout and F. Šorm, *Tetrahedron Letters* No. 3, 9 (1960).

[10] A. Stoll, E. Seebeck and D. Stauffacher, *Helv. Chim. Acta* **40**, 135 (1957); J. Křepinský, V. Herout and F. Šorm, *Chem. Listy* **52**, 1784 (1958).

[11] J. Křepinský, M. Romanuk, V. Herout and F. Šorm, *Tetrahedron Letters* No. 7, 9 (1960).

Dimethyljatamansate. To a solution of jatamansic acid (2 g) in methanol (20 ml) an ether solution of diazomethane (prepared from 15 g of nitrosomethyl urea) was added. After leaving overnight and working up as usual the *dimethyl ester* (1·5 g), b.p. 140°/1 mm, n_D^{30}: 1·470 was obtained (Found: C, 68·3; H, 9·8 $C_{17}H_{30}O_4$ requires: C, 68·5; H, 10·1%).

Benzylidene derivative of jatamansone

(a) A solution of jatamansone (5 g) and benzaldehyde (15 g) in absolute ether (50 ml) was saturated with dry HCl gas and left overnight. After removal of ether, the residue was refluxed with fused sodium acetate (20 g) and acetic acid (30 ml) for 4 hr and after excess benzaldehyde was removed by steam distillation was extracted with ether. After the removal of solvent, the *benzylidene derivative* (1·2 g) obtained was crystallized from methanol, m.p. 115°, $[\alpha]_{30}^{D}$: −172·2° (*c*: 2·032 $CHCl_3$) (Found: C, 85·3; H, 9·4 $C_{22}H_{30}O$ requires: C, 85·2; H, 9·7%).

(b) Jatamansone (2 g) in KOH solution (50%; 10 ml) was treated with benzaldehyde (3 g) in absolute alcohol (10 ml) and the mixture heated on a water-bath for 3 hr then diluted with water and the precipitated benzylidene compound (2 g) crystallized from methanol, m.p. 115°.

Ozonolysis of the benzylidene derivative. The above benzylidene derivative (5 g) in chloroform (15 ml) was ozonized to completion (5 hr). The solvent was removed *in vacuo* and the residue treated with hydrogen peroxide solution (30%; 20 ml) heated on a water bath for 12 hr and then filtered hot so as to remove benzoic acid. The acidic product was repeatedly washed with hot water and then crystallized from absolute ether, m.p. 233–235° (3 g) and found to be identical with jatamansic acid, (m.p. and mixed m.p.).

Attempted isomerization of jatamansone

(a) Dry HCl gas was passed through a solution of jatamansone (5 g) in absolute ether (50 ml) to saturation. The mixture was left for 48 hr, the ether removed *in vacuo* and the residue after washing with $NaHCO_3$ solution distilled *in vacuo* to give an oil (4·5 g), b.p. 108°/1 mm which was found to be identical with jatamansone.

(b) A solution of jatamansone (2 g) in H_2O_4 (57%; 30 ml) was heated under reflux for 12 hr and the product, worked up as usual, was identical with the starting material.

Bromination of jatamansone

(a) To jatamansone (2·2 g) in glacial acetic acid (25 ml) a solution of bromine (1·8 g) in acetic acid (10 ml) was added. After ½ hr the mixture was diluted with water and extracted with ether and the ether extract washed with dil $NaHCO_3$ solution. After the removal of solvent the residue was distilled *in vacuo* to give the *monobromo compound* (2 g), b.p. 148°/0·3 mm. It was crystallized from pet ether (b.p. 40–60°), m.p. 105° (Found: C, 59·8; H, 8·6 $C_{15}H_{25}OBr$ requires: C, 59·8; H, 8·3%).

(b) To jatamansone (2 g) in acetic acid (20 ml) a large excess of bromine (10 g) in acetic acid (20 ml) was added. After 5 days, the product was worked up as above and the *dibromo compound* (2 g) obtained distilled *in vacuo*, b.p. 145°/0·6 mm. (Found: C, 47·7; H, 6·4 $C_{15}H_{24}OBr_2$ requires: C, 47·3; H, 6·3%).

Attempted dehydrohalogenation of the above bromo compound

(a) Monobromojatamansone (2 g) in dimethylaniline (20 ml) was heated under reflux for 6 hr, the reaction mixture diluted with water and acidified with conc HCl (30 ml) and extracted with ether. After the removal of ether, the residue was distilled *in vacuo* to give jatamansone and not the unsaturated compound.

(b) The bromo compound after refluxing with 50% NaOH for 3 hr gave only jatamansone.

Jatamansane. To a mixture of jatamansone (5 g) in diethyleneglycol (80 ml) sodium metal (2·5 g) in small bits followed by hydrazine hydrate (85%; 5 ml) was added. After heating under reflux for 1 hr the condenser was removed and the mixture kept at 190–200° (internal temp) for 5 hr and then diluted with water and extracted with ether. After the removal of ether the residue was subjected to the above procedure once again and the product obtained distilled *in vacuo* to give *jatamansane* (3 g), b.p. 90°/0·5 mm n_D^{30}: 1·482 $[\alpha]_{30}^{D}$: +63·02° (*c*: 1·936 $CHCl_3$). (Found: C, 86·3; H, 13·52 $C_{15}H_{28}$ requires: C, 86·5; H, 13·5%).

Norjatamansone. Jatamansic acid (5 g) in acetic anhydride (30 ml) containing barium hydroxide (0·2 g) was taken up in a distillation flask and heated gently first to remove acetic anhydride (i.e. up to

150°), then the temp of the bath was raised to 400° when an oil (3·5 g) distilled over. This oil (3·5 g) in pyridine (25 ml) was treated with semicarbazide hydrochloride (3·5 g) and heated at 70° for 2 hr. After dilution with water, the precipitated *semicarbazone* (3·5 g) was crystallized from alcohol, m.p. 238–240°. (Found: C, 68·0; H, 10·5 $C_{15}H_{27}N_3O$ requires: C, 67·9; H, 10·2%). The semicarbazone (3·5 g) was decomposed by heating under reflux with 4 N H_2SO_4 (150 ml) for 24 hr. The mixture was extracted with ether and after removal of solvent the residue was distilled *in vacuo* to give *norjatamansone* (2 g), b.p. 110°/4 mm n_D^{30}: 1·4815, $[\alpha]_{30}^{D}$: +16·77°, *d*: 0·9729. (Found: C, 80·6; H, 11·3 $C_{14}H_{24}O$ requires: C, 80·7; H, 11·5%).

Bromonorjatamansone. Norjatamansone (2 g) in glacial acetic acid (25 ml) containing hydrobromic acid (2 ml) was added to a solution of bromine (1·8 g) in acetic acid (10 ml). After 3 hr the mixture was worked up as in the case of monobromojatamansone, to give the *bromonorjatamansone* (1·5 g), b.p. 138–140°/3 mm, n_D^{30}: 1·5150. (Found: C, 58·2; H, 8·2 $C_{14}H_{23}OBr$ requires: C, 58·5; H, 8·0%).

When the bromo compound was heated with dimethylaniline under reflux the expected α,β-unsaturated ketone was not formed, but only norjatamansone. The bromo compound was recovered unchanged after heating with 2,4-dinitrophenylhydrazine in acetic acid solution.[12]

Norjatamansol. To a suspension of lithium aluminium hydride (1 g) in absolute ether (50 ml) the above ketone (2 g) in absolute ether (20 ml) was added with stirring and left overnight. The reaction mixture was worked up as usual and the *alcohol* (1·8 g) obtained was crystallized from absolute ether, m.p. 115°. (Found: C, 80·2; H, 12·5 $C_{14}H_{26}O$ requires: C, 80·0; H, 12·4%).

Attempted dehydration of norjatamansol

(a) The method adopted for the preparation of jatamansene from jatamansol was applied but the starting material was recovered unchanged.

(b) A mixture of the above alcohol (1 g) and potassium hydrogen sulphate (5 g) was distilled *in vacuo* but the distillate was found to be starting material.

(c) A mixture of the alcohol (1 g) in 50% H_2SO_4 (20 ml) was heated under reflux for 1 hr. It was extracted with ether, and after the removal of solvent the residue was found to be starting material.

Benzylidene derivative of norjatamansone. A mixture of norjatamansone (2 g), 40% alcoholic KOH solution (10 ml), benzaldehyde (3 g) and water (5 ml) was heated on a water-bath for 3 hr and the mixture diluted with water and extracted with ether. After the removal of solvent the residue was distilled *in vacuo*. The initial fraction was benzaldehyde and the *benzylidene derivative* (1·2 g) distilled at 160°/0·2 mm $[\alpha]_{30}^{D}$: +184·9° (*c*: 2·866 $CHCl_3$). (Found: C, 85·4; H, 9·4 $C_{21}H_{28}O$ requires: C, 85·1; H, 9·4%).

Ozonolysis of the above benzylidene derivative

(a) The benzylidene derivative (2 g) in chloroform (15 ml) was ozonized to completion (2 hr). The chloroform was removed *in vacuo* and the residue was treated with water (20 ml) and zinc dust (0·2 g). The mixture was heated on a water-bath for 6 hr, extracted with ether and washed with $NaHCO_3$ solution to remove acidic materials. After the removal of solvent, the residue was distilled *in vacuo* to give the *norjatamansadione* (0·8 g), b.p. 140°/0·3 mm. (Found: C, 75·3; H, 9·9 $C_{14}H_{22}O_2$ requires: C, 75·7; H, 9·9%).

To the above diketone (0·5 g) in alcohol (100 ml) potassium periodate (0·75 g) in water (250 ml) and 2 N H_2SO_4 (25 ml) was added. After keeping at room temp for 72 hr the mixture was extracted with ether and the ether solution then extracted with saturated $NaHCO_3$ solution (20 ml), which on acidification gave *norjatamansic acid* (0·2 g), m.p. 143°, $[\alpha]_{30}^{D}$: +49·9° (*c*: 1·98 $CHCl_3$). (Found: C, 65·2; H, 9·1 $C_{14}H_{24}O_4$ requires: 65·6, H, 9·4%).

(b) The benzylidene derivative (1 g) in chloroform (10 ml) was ozonized to completion (1 hr). After the removal of solvent, the residue was treated with hydrogen peroxide solution, (30%; 30 ml) heated on a water bath for 12 hr and the hot solution decanted from the viscous oil. The viscous mass was repeatedly washed with hot water to remove benzoic acid and then crystallized from dil methanol to give norjatamansic acid (0·4 g), m.p. 143°.

Selenium dioxide oxidation of norjatamansadione. The dione (1 g) in glacial acetic acid (30 ml) was refluxed with freshly sublimed selenium dioxide (0·6 g) for 4 hr and the mixture left overnight. The

[12] C. Djerassi and D. Marshall, *J. Amer. Chem. Soc.* **80**, 3986 (1958).

precipitated selenium was filtered off, the solvent removed *in vacuo* and the residue taken up in ether and the neutral fraction separated by the usual procedure. After removal of the solvent the residue was passed through a column of silver oxide and alumina using pet ether as eluent. After removal of the solvent the residue was distilled *in vacuo* to give *norjatamansatrione* (0·3 g), b.p. 155–160°/0·3 mm. (Found: C, 70·8; H, 8·6 $C_{14}H_{20}O_3$ requires: C, 71·2; H, 8·5%).

Norjatamansic anhydride. Norjatamansic acid (3 g) was refluxed with acetic anhydride (20 ml) for ½ hr, the acetic anhydride removed by distillation and the residue distilled *in vacuo* to give *norjatamansic anhydride* (2·5 g), b.p. 150°/0·1 mm. The distillate solidified and was crystallized from pet ether, (b.p. 40–60°), m.p. 85–86° $[\alpha]_{30}^{D}$: +38·95° (*c*: 2·22 $CHCl_3$). (Found: C, 70·9; H, 9·0 $C_{14}H_{22}O_3$ requires: C, 70·6, H, 9·3%).

Bromonorjatamansic anhydride. A mixture of the above anhydride (1·2 g) and bromine (0·3 ml) was heated in a sealed tube at 130° for 2 hr, extracted with benzene and the solvent removed *in vacuo*, The residue was crystallized from benzene–pet ether (b.p. 40–60°) to give the *bromo anhydride* (1·3 g). m.p. 143°, $[\alpha]_{30}^{D}$: +38·33° (*c*: 2·09 $CHCl_3$). (Found: C, 52·8; H, 6·8 $C_{14}H_{21}O_3Br$ requires: C, 53·0; H, 6·6%).

Dehydronorjatamansic anhydride. A mixture of the bromo anhydride (0·5 g) and dimethylaniline (5 ml) was heated at 150–160° for 3 hr and then poured on to crushed ice containing HCl and extracted with ether. The ether extract was repeatedly washed with dil HCl, water and dried (Na_2SO_4). After the removal of solvent the product was crystallized from benzene–pet ether to give the *dehydronorjatamansic anhydride* (0·35 g), m.p. 153°, $[\alpha]_{30}^{D}$: +186·7° (*c*: 2·09 $CHCl_3$). (Found: C, 71·6; H, 8·5 $C_{14}H_{20}O_3$ requires: C, 71·2; H, 8·5%).

Oxidation of jatamansone with manganese dioxide and sulphuric acid. To a mixture of jatamansone (5 g) and H_2SO_4 (57%; 20 ml) heated under reflux manganese dioxide (80 g) was added during the course of 5 hr and the heating continued for 18 hr. The mixture was then filtered and the manganese dioxide residue washed with hot water and the filtrate repeatedly extracted with ether. After the removal of ether the acid (0·3 g) was crystallized from acetone–benzene mixture, m.p. 216–218°. The acid was found to be identical with trimellitic acid (m.p. and mixed m.p.). (Found: C, 51·5; H, 3·2 $C_9H_6O_6$ requires: C, 51·4; H, 2·9%).

The imide prepared in the usual way was crystallized from alcohol, m.p. 255–257°. (Found: C, 56·5; H, 2·4 Calc. for $C_9H_5NO_4$; C, 56·5; H, 2·6%).

The anhydride of the acid was obtained by heating the acid above the m.p. and keeping it at that temperature for 5 min, m.p. 172°.

Both jatamansic acid and jatamansene on oxidation with manganese dioxide as in the above procedure gave trimellitic acid.

Dehydrogenation of norjatamansic acid. Norjatamansic acid (1 g) was intimately mixed with 30% palladized charcoal (0·6 g) and heated in a sealed tube at 310–320° for 30 hr. It was then extracted with ether and after the removal of solvent, the residual oil passed through a column of alumina using pet ether (40–60°) as eluent. After the removal of solvent the residue (0·5 g) was distilled, b.p. 190°. The distillate (0·2 g) dissolved in chloroform (3 ml) was treated with chlorosulphonic acid (1 g) with ice cooling. After about 20 min the mixture was poured into ice and extracted with chloroform and dried (Na_2SO_4). After the removal of solvent, the residue was mixed with ammonium carbonate (4 g), heated on a water-bath for ½ hr, water added and the product extracted with ether. The residue, after removal of solvent, was chromatographed (in chloroform) and crystallized from dil methanol, m.p. 158–160° and found to be identical with the *sulphonamide derivative* of 1,2-dimethyl-4-isopropylbenzene (m.p. and mixed m.p. and I.R.). (Found: C, 58·4; H, 7·5 $C_{11}H_{17}O_2NS$ requires: C, 58·2; H, 7·5%).

Oxidation of the dehydrogenation product with manganese dioxide and sulphuric acid. The above oil (1 g) dissolved in 57% sulphuric acid (45 ml) was heated under reflux and manganese dioxide (25 g) was added in small amounts during the course of 4 hr and heating continued for another 6 hr. It was then filtered, the residue washed with hot water, and the filtrate extracted repeatedly with ether. The ether solution was extracted with saturated $NaHCO_3$ solution and the alkaline solution on acidification gave an acid which was extracted with ether. After removal of ether, the acid (0·2 g) was crystallized from acetone–benzene mixture, m.p. 216° and found to be identical with trimellitic acid (m.p. and mixed m.p.).

Synthesis of 1-*methyl-2-ethyl-4-isopropylbenzene.* 2-Methyl-5-isopropylacetophenone[18] (10 g) in

[18] Ad. Claus, *Ber. Dtsch. Chem. Ges.* **19**, 230 (1886).

conc HCl (200 ml) was refluxed with zinc amalgam (45 g), with the addition of HCl (5 ml) every ½ hr for 48 hr. It was then worked up as usual and the hydrocarbon distilled at 210–212°, which gave a crystalline *sulphonamide derivative*, m.p. 136–137°. (Found: C, 59·8; H, 8·0 $C_{12}H_{19}SO_2N$ requires: C, 59·8; H, 7·9%).

1,2-*Dimethyl-4-isopropylbenzene.* 1-Methyl-2-chloromethyl-4-isopropylbenzene (10 g) was added slowly to a suspension of magnesium (1·2 g) in ether (30 ml). The mixture was refluxed for 3 hr and the resulting complex decomposed with water. The product was worked up as usual and the hydrocarbon (7 g) distilled at 190–192°. It gave a crystalline *sulphonamide derivative* (from methanol), m.p. 158°. (Found: C, 58·0; H, 7·3 $C_{11}H_{17}O_2NS$ requires: C, 58·2; H, 7·5%).

Sodium periodate oxidation of dehydronorjatamansic anhydride. A solution of dehydronorjatamansic anhydride (0·48 g) in aqueous pyridine (33%; 150 ml) was treated with a solution of sodium metaperiodate (0·7 g), potassium permanganate (15 mg) in aqueous pyridine (33%; 30 ml) and a solution of potassium carbonate (0·25%; 20 ml). The mixture was shaken for 30 hr, acidified with sulphuric acid and extracted with ether. After the removal of solvent, the residue was characterized as the *semicarbazone*, m.p. 193° (from ethanol) $[\alpha]_{30}^{D}$: −16·04 (*c*: 2·0 $CHCl_3$). (Found: C, 62·4; H, 10·0 $C_{11}H_{21}ON_3$ requires: C, 62·6; H, 10·0%). It was found to be identical with 1-*trans*-carvomenthone semicarbazone (m.p. and mixed m.p. and I.R.).

Jatazulene[1]

Paper chromotagraphy of jatazulene. The jatazulene obtained by the dehydrogenation of jatamansol was found by paper chromotagraphy to be a mixture of azulenes which were separated as follows:

Whatman No. 1 paper was impregnated with liquid paraffin (1·08 mg/cm²) by soaking in 5% solution of paraffin in pet ether (b.p. 40–60°), pressing between the folds of the same type of paper and finally air drying. The mixture of azulenes (30 mg) were placed in a horizontal line about 6 cm from the bottom of the paper and then hung vertically in a glass jar. The chromotagraphy was carried out by the upward irrigation method using 55% phosphoric acid, in a narrow trough below the paper and the acid level adjusted to 3 to 4 cm below the line of azulene. After 48 hr four distinct bands were obtained having the following R_f values:

Blue	R_f: 0·02
Bluish violet	R_f: 0·108
Red	R_f: 0·22
Violet	R_f: 0·30

Each band was cut out and shaken with water and pet ether in a separating funnel till the paper was converted to a pulp. The pet ether extract from each band was extracted with 90% phosphoric acid and the phosphoric acid layer washed with pet ether to remove any non azulenic materials. The azulenes were regenerated from the acid extracts on dilution with water, and extracted with pet ether. After the removal of solvent, the azulenes were passed through a column of alumina using pet ether as eluent. The azulenes obtained from blue, red and violet bands were too small to be characterized. The bluish violet band gave a T.N.B. adduct from methanol (10 mg), m.p. 158°, visible spectrum max 562 and 582 m (cyclohexane). (Found: C, 61·7; H, 5·1. $C_{21}H_{21}N_3O_6$ requires: C, 61·3; H, 5·1%).

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