Tetrahedron, 1964, Vol. 20, pp. 2605 to 2615. Pergamon Press Ltd. Printed in Northern Ireland

TERPENOIDS—LII*

JATAMANSIN, A NEW TERPENIC COUMARIN FROM *NARDOSTACHYS JATAMANSI*

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(*Received* 23 *June* 1964)

Abstract—Two terpenic coumarins, oroselol and jatamansin, have been isolated from the oil obtained from the roots of *Nardostachys jatamansi*. The compound oroselol is known. The structure of jatamansin which is new, has been established mainly by NMR spectral studies and further confirmed by chemical degradation to known compounds.

Nardostachys jatamansi D.C. (Valerianaceae), a herb growing at great elevations up to 17000 ft. on the Himalayas has been known for its medicinal properties.[1] Two compounds, jatamansone[2] (valeranone) and jatamanshic acid[3], have been reported to occur in the Indian jatamansi oil and β-maaliene and calarene have been isolated by Büchi *et al.*[4] from another variety.

From the solvent-extracted oil from the roots of *Nardostachys jatamansi* (obtained from Jummu and Kashmir), we have isolated, along with several other products, two terpenic coumarins by refrigeration and elaborate column chromatography, one of which is identical with oroselol(Ia) and the other is a new optically active coumarin, which we propose to name as 'jatamansin'.

The isolation of oroselol, $C_{14}H_{12}O_4$, m.p. 148–151°, has been reported previously.[5,6] Comparison of the spectral data along with the physical constants of the natural product, its acetate(Ib) and the product of dehydration, oroselone (II), revealed the identity of one of our coumarins with oroselol(Ia).

The NMR spectrum† of oroselol (Fig. 1) is in agreement with its structure (Ia): a pair of doublets (τ = 2·25 and 3·68; J = 9 c/s) can be assigned for protons (4) and (3) respectively; a doublet (τ = 2·68) which is merging with the absorption of solvent is due to proton at (5); a doublet (τ = 3·18; J = 9 c/s, 2 H) is due to one proton at (6) and one proton at (3′), the absorption due to proton at (3′) is merging with one of the signals of this doublet (τ = 3·1), and a sharp singlet (τ = 8·3, 6 H) is due to two tertiary methyl groups at (6′). The identity of our product with oroselol was further confirmed by comparing the IR spectrum with that of an authentic sample‡ and mixed m.p.

* Contribution No. 685 from the National Chemical Laboratory, Poona-8, India.

† NMR spectra were measured by Dr. P. M. Nair and Mr. Iqbal Mulla on a A-60 (Varian instrument set at 60 MC). Tetramethyl silane was used as an internal standard; carbon tetrachloride and deuterochloroform solutions were used.

‡ We are indebted to Prof. H. Mitsuhashi for these determinations.

[1] A. K. Nadkarni, *Indian Materia Medica* Vol. I (3rd Edition) p. 840. (1954).

[2] C. Djerassi, T. R. Govindachari, B. R. Pai and K. K. Purushothamann, *Tetrahedron Letters*, 226 (1961).

[3] G. R. Chaudhari, M. M. Dhar, N. Anand and M. L. Dhar, *J. Sci. Ind. Research (India)* **17B**, 159 (1958).

[4] G. Büchi, F. Greuter and Takashi Tokoroyama, *Tetrahedron Letters*, No. 18, 827 (1962).

[5] O. Halpern, P. Weser and H. Schmid, *Helv. Chim. Acta* **40**, 758 (1957).

[6] H. Mitsuhashi and T. Itoh, *Chem. Pharm. Bulletin (Japan)* **10**, 514 (1962).

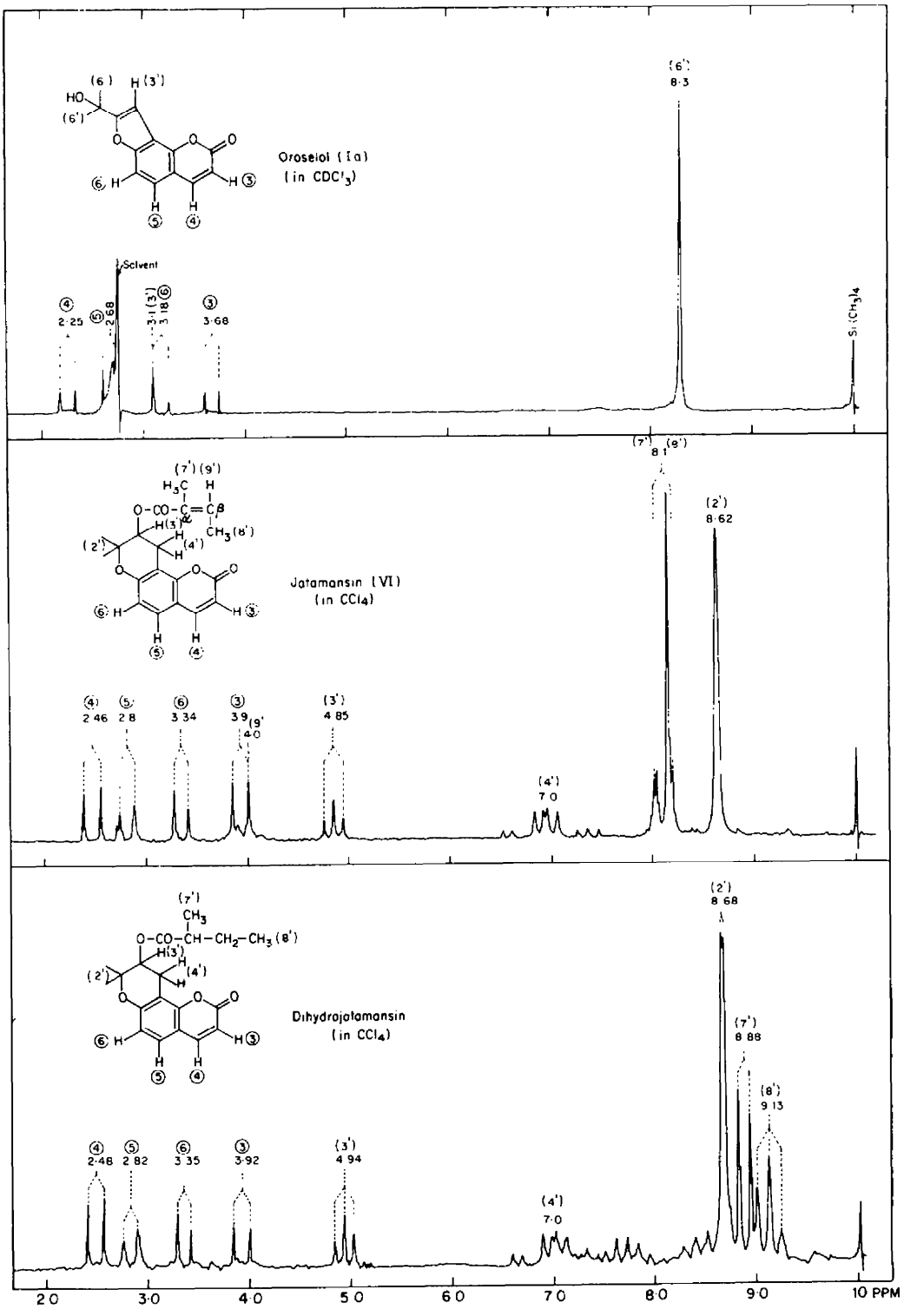

Oroselol (Ia)
(in CDCl3)
Solvent
Jatamansin (VI)
(in CCl4)
Dihydrojatamansin
(in CCl4)
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10 PPM

FIG. 1

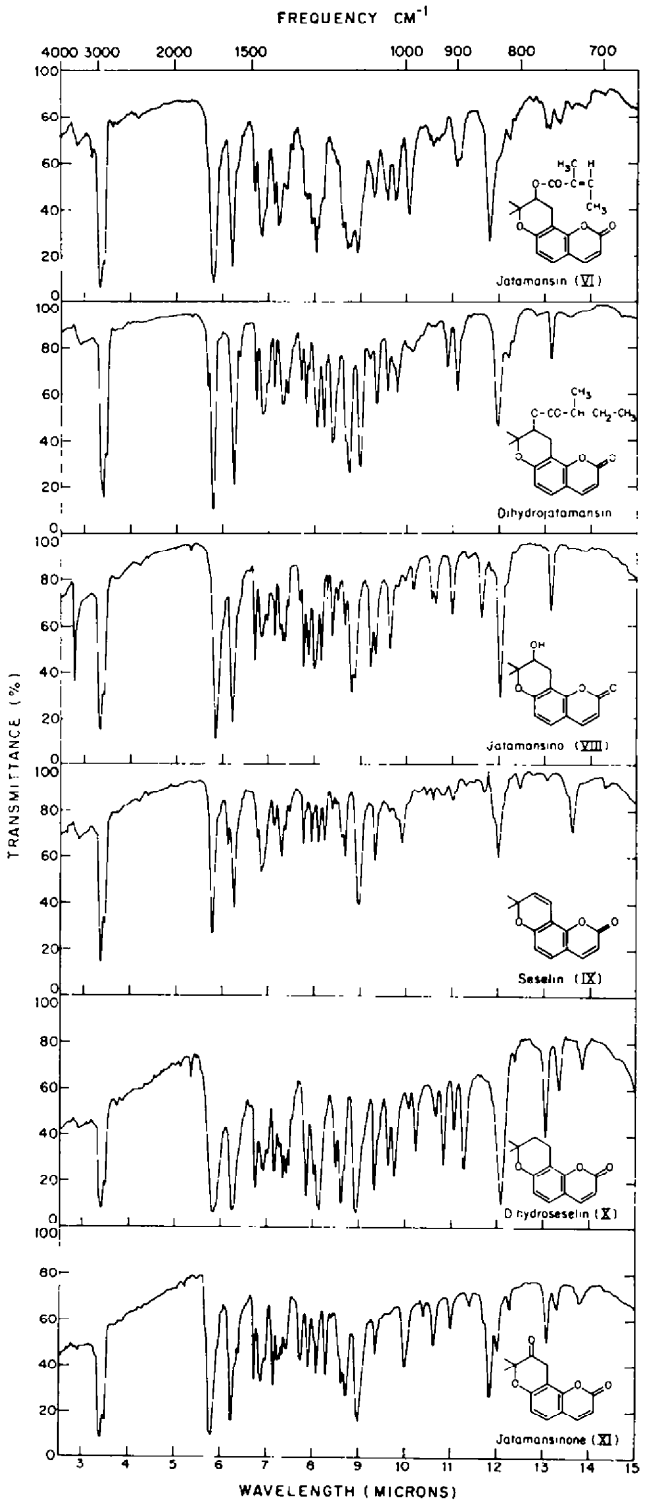

FREQUENCY CM⁻¹
4000 3000 2000 1500 1000 900 800 700
TRANSMITTANCE (%)
Jatamansin (VI)
Dihydrojatamansin
Jatamansino (VIII)
Seselin (IX)
Dihydroseselin (X)
Jatamansinone (XI)
WAVELENGTH (MICRONS)
3 4 5 6 7 8 9 10 11 12 13 14 15

FIG. 2

From the results described subsequently, it will be seen that the other terpenic coumarin, jatamansin, is represented by the structure VI. It is a highly crystalline material, m.p. 97–98°, and its homogeneity was proved by TLC and column chromatography. It analysed for the molecular formula, $C_{19}H_{20}O_5$, and the estimated molecular weight values 321 and 326 (calculated 328·37) corresponded to the same. It does not contain any hydroxyl, phenolic, active carbonyl, methoxy or acetoxy group. On hydrogenation (PtO_2/glacial acetic acid), it absorbs only one mole of hydrogen to

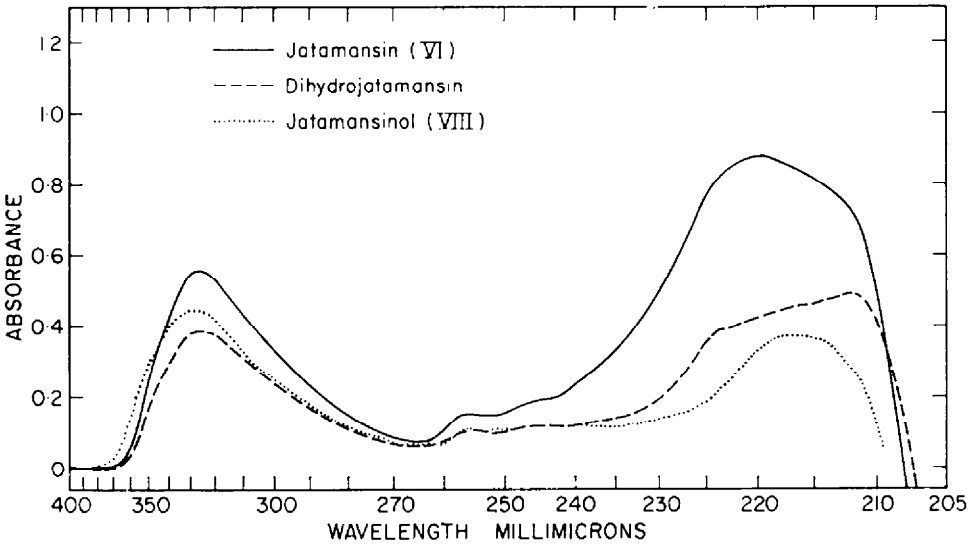
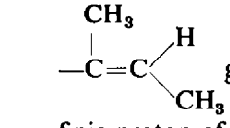


FIG. 3

give crystalline dihydrojatamansin, $C_{19}H_{22}O_5$, m.p. 100–101°. Jatamansin showed IR absorption bands (Fig. 2) at: 1724 and 1610 (conjugated δ-lacone), 1490 and 847 cm^{-1} (aromatic), and UV absorption (Fig. 3) at: λ_{max} 326, 256, 246 and 220 mμ (log ε_{max} 4·13, 3·38, 3·47 and 4·30 respectively). Dihydrojatamansin showed IR absorption bands (Fig. 2) at: 1724 and 1600 (conjugated δ-lactone), 1484 and 833 cm^{-1} (aromatic) and UV absorptions (Fig. 3) at: λ_{max} 326, 256, 246, 223·5 and 211·8 mμ (log ε_{max} 4·13, 3·47, 3·49, 4·16 and 4·24 respectively. The spectral data suggested that the reducible double bond in jatamansin is isolated from the main chromophore, which is not substantially affected during hydrogenation.

The NMR spectrum of jatamansin (Fig. 1) shows two tertiary methyl groups (singlet at $\tau = 8{\cdot}62$, 6 H) and two methyl groups on olefinic linkage (multiplet at $\tau = 8{\cdot}1$, 6 H) and that of dihydrojatamansin (Fig. 1) shows two tertiary methyl groups (doublet at $\tau = 8{\cdot}68$, 6 H); one CH_3—CH (doublet at $\tau = 8{\cdot}88$, 3 H, J = 7 c/s) and one —CH_2—CH_3 group: (triplet at $\tau = 9{\cdot}13$, 3 H). This indicates the presence of



grouping. The disappearance of the signal ($\tau = 4{\cdot}0$, 1 H) due to olefinic proton of jatamansin during hydrogenation indicates that the reducible double

bond of jatamansin is in conjugation with some group. This was proved by hydrolysis of jatamansin and dihydrojatamansin with 5% methanolic KOH at room temperature to give conjugated and non-conjugated acids respectively which were identified to be angelic acid (III) and its hydrogenation product methylethylacetic acid (IV).

The presence of angelic acid moiety was further identified by mild ozonolysis of jatamansin; acetaldehyde was identified as its 2:4 DNP derivative and acetic and pyruvic acids were identified by paper chromatography in the volatile products of ozonolysis.

The neutral products of hydrolysis of jatamansin, dihydrojatamansin and the neutral ozonization product of jatamansin were found to be the same crystalline optically active alcohol, $C_{14}H_{14}O_4$, m.p. 182–183°, which we propose to name as jatamansinol and which showed IR absorption bands (Fig. 2) at: 3623 (—OH group), 1721 and 1618 (conjugated δ-lactone), 1499 and 833 (aromatic), 1387 and 1368 cm^{-1} (gem dimethyl group), and UV absorption bands (Fig. 3) at: λ_{max} 329, 256, 246 and 216 mμ (log ε_{max} 4·06, 3·36, 3·41 and 4·01 respectively).

Jatamansinol does not give any test for phenol. It forms a crystalline tosylate (m.p. 158–159°), which shows IR absorption bands at: 1727 and 1610 (conjugated δ-lactone), 1488, 840, 820, 789 and 759 (aromatic), 1190, 1176 and 1112 cm^{-1} (tosyl group). It also forms an acetate, m.p. 137–138°, with IR bands at: 1733 and 1600 (conjugated δ-lactone and acetate), 1481 and 840 (aromatic), and 1232 cm^{-1} (acetate); UV absorption at: λ_{max} 327, 256, 246 and 216 mμ (log ε_{max} 4·17, 3·51, 3·56 and 4·15 respectively).

Jatamansin, therefore, is the ester of the alcohol jatamansinol with angelic acid and can be represented by the partial structure V.

The spectral data of jatamansin, dihydrojatamansin and jatamansinol indicate the presence of highly conjugated δ-lactone group, possibly coumarin group, which is also indicated by their colour tests. All the above compounds give yellow coloration on warming with alcoholic alkali[7] and give violet fluorescence on adding conc. sulphuric acid,[8] which turns deep red on warming. The lithium aluminium hydride reduction product of jatamansin gives positive test for phenolic group (ferric chloride test, solubility in sodium hydroxide and reprecipitation with hydrochloric acid). The presence of δ-lactone grouping is confirmed by hydrolysing the lactonic alcohol, jatamansinol, with hot alcoholic potash and getting back the jatamansinol after treatment with methanolic hydrochloric acid.[7]

The UV spectra of all the above three products are comparable with those of known compounds having coumarin unit.[9] The presence of coumarin ring accounts for two more oxygen atoms in jatamansin. The remaining one oxygen atom, which could not be accounted on the basis of chemical evidence, is presumably in the form of an ethereal oxygen.

The NMR data of jatamansin and its derivatives give valuable information and suggest that it may be represented by two alternative structures VI and VII. In the NMR spectrum of jatamansin (Fig. 1) a pair of doublets forming an AB system (τ = 2·46 and 3·9; J = 9 c/s) can be assigned respectively to the (4) and (3) protons in the

[7] C. R. Ghoshal, S. Sen Gupta and A. Chatterjee, *Chem. & Ind.*, 1430 (1963).
[8] J. C. Bell and A. Robertson, *J. Chem. Soc.* 1829 (1936).
[9] E. Smith, N. Hosansky, W. G. Bywater and E. Van Tamelen, *J. Amer. Chem. Soc.* **79**, 3534 (1957).

lactone ring by comparison with the coumarin compound discophoridin,[10] where the doublets occur at $\tau = 2{\cdot}4$ and $3{\cdot}8$, J = 9 c/s. The position of the other pair of doublets (5 and 6) in the aromatic region ($\tau = 2{\cdot}8$ and $3{\cdot}34$, J = 9 c/s) is typical of the signals from ortho protons in a 1,2,3,4-substituted benzene ring. It is known[11] that aromatic protons which are not adjacent to an oxygen substituent give signals at $\tau = 2{\cdot}6$–$2{\cdot}7$, whereas, if there is an adjacent oxygen atom, the signal is shifted upfield to $\tau = 3{\cdot}2$–$3{\cdot}3$. From the positions of signals of two aromatic protons (5 and 6) in jatamansin, it is evident that one (6,$\tau = 3{\cdot}34$) has an oxygen adjacent to it, while the other (5,$\tau = 2{\cdot}8$) has not. The triplet at $\tau = 4{\cdot}85$ (1 H) is due to one proton at 3′ and the multiplet centered at $\tau = 7$ (2 H) is due to two benzylic protons at 4′. The multiplet centered at τ 8·1 (6 H) has been assigned to α- and β-methyl groups (7′ and 8′) of angelic ester side chain. The absorption due to β-proton (9′) of angelic ester side chain ($\tau = 4{\cdot}0$) is merged with one of the absorptions of doublet due to proton at (3), but the integration curve clearly shows the presence of two protons at $\tau = 3{\cdot}9$. The absorption at $\tau = 4{\cdot}0$ is characteristic of β-proton of methyl angelate and not of methyl tiglate[12] ($\tau = 4{\cdot}02$ methyl angelate and $\tau = 3{\cdot}27$ methyl tiglate). A strong absorption at $\tau = 8{\cdot}62$ (6 H) has been assigned to two tertiary methyl groups (2′).

The NMR spectrum of dihydrojatamansin (Fig. 1) is almost like that of the parent compound except that the signal due to the β-proton of angelate side chain ($\tau = 4{\cdot}0$) and the two methyl groups on olefinic linkage disappear and give rise to new absorptions in the region $\tau = 9$ (doublet at $\tau = 8{\cdot}88$, 3 H; J = 7 c/s, due to CH_3—CH and a triplet centered at $\tau = 9{\cdot}13$, 3H, due to CH_3—CH_2 group).

The NMR spectral evidence can explain both the structures VI and VII. But of these two possible structures, VI is favoured on biogenetic grounds, because from the same source oroselol (Ia) has also been obtained, in which the linkage of oxygen is at position 7. On the basis of this assumption dihydrojatamansin will be represented by the structure VI (R′ = CO—$CH(CH_3)$—CH_2—CH_3) and jatamansinol by VIII. This was established by the following experiments.

The tosylate of jatamansinol, on heating in 2:4:6-collidine, furnished an optically inactive chromene, $C_{14}H_{12}O_3$, identified as seselin[13] (IX) from the m.p. (119–120°) and UV spectrum.[14] The NMR spectrum of this chromene (Fig. 4) is in agreement with the structure of IX. A pair of doublets ($\tau = 2{\cdot}46$ and $3{\cdot}9$; J = 9 c/s) has been assigned to (4) and (3) protons respectively, and another pair of doublets ($\tau = 2{\cdot}83$ and $3{\cdot}38$; J = 9 c/s) has been assigned to ortho protons (5 and 6) respectively. The remaining pair of doublets ($\tau = 3{\cdot}12$ and $4{\cdot}32$, J = 10 c/s) is very much characteristic of two *cis*-hydrogens (4′ and 3′ respectively) on a double bond conjugated with an aromatic ring[15] (chromene system). The last pair of doublets is absent in the NMR spectrum of jatamansinol (VIII) (Fig. 4), but instead of that a triplet ($\tau = 6{\cdot}05$, 1 H) due to one proton at 3′) and a multiplet ($\tau = 6{\cdot}95$, 2 H, due to two benzylic protons at 4′) are present, which disappear in seselin (IX) due to formation of a double bond between

[10] W. Bottomley, *Aust. J. Chem.* **16**, 143 (1963).
[11] J. B. Bredenberg and J. N. Schoolery, *Tetrahedron Letters* [9] 285 (1961).
[12] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.* 2886 (1960).
[13] E. Späth, P. K. Bose, J. Matzke and N. C. Guha, *Ber. Dtsch. Chem. Ges.* **72**, 821 (1939).
[14] D. P. Chakraborty and Sachindra K. Chakraborti, *Trans. Bose Res. Inst. (India)* **24** [1], 15 (1961).
[15] (a) B. F. Burrows, W. D. Ollis and L. M. Jackman, *Proc. Chem. Soc.* 177 (1960); (b) L. Chrombie and J. W. Lown *J. Chem. Soc.* 775 (1962).

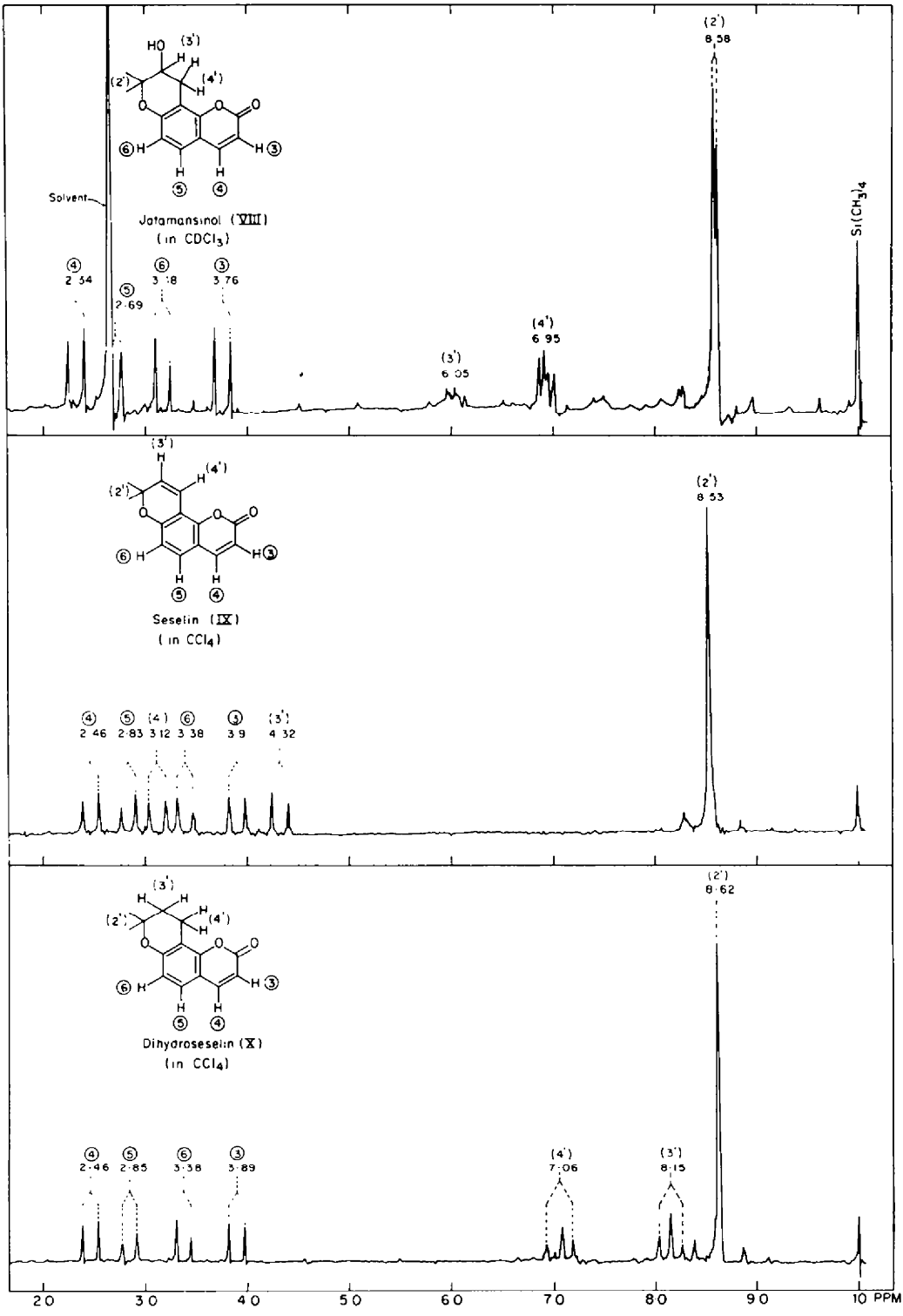
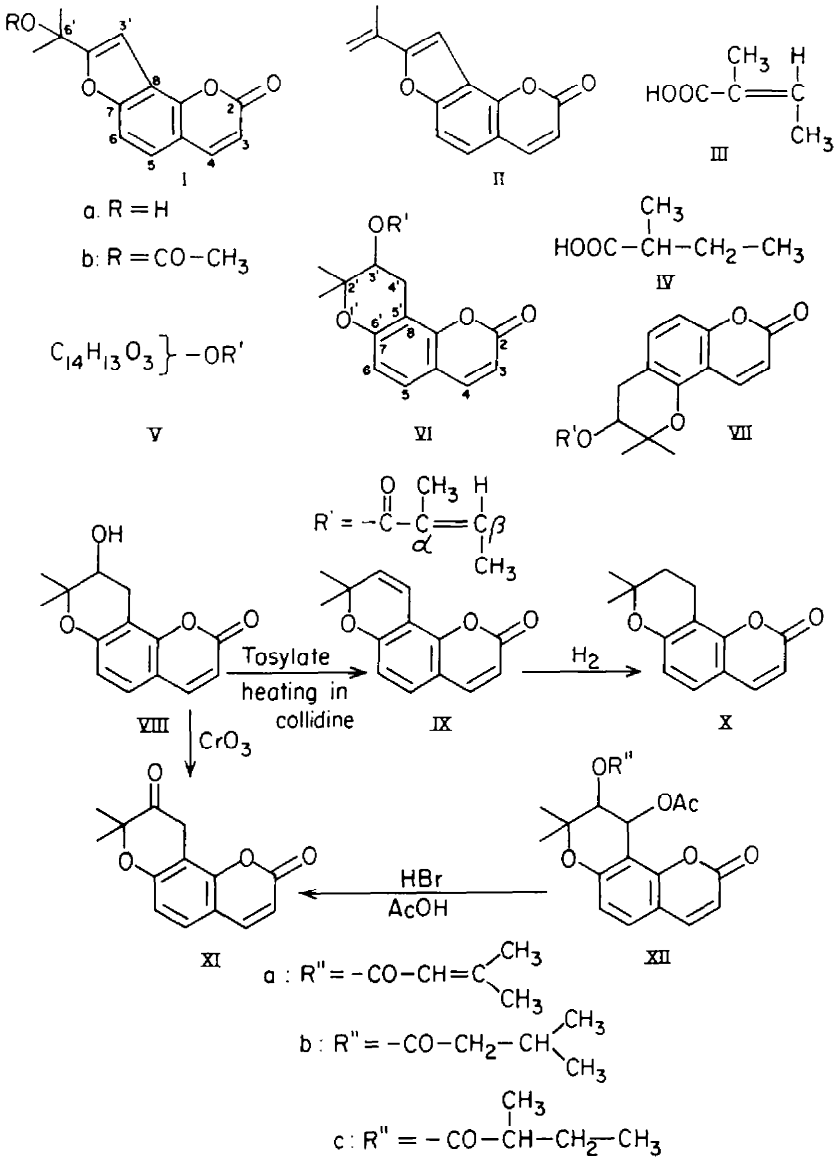

Solvent
Jatamansinol (VIII)
(in $CDCl_3$)
④ 2·54
⑤ 2·69
⑥ 3·18
③ 3·76
(3') 6·05
(4') 6·95
(2') 8·58
$Si(CH_3)_4$
Seselin (IX)
(in CCl_4)
④ 2·46
⑤ 2·83
(4') 3·12
⑥ 3·38
③ 3·9
(3') 4·32
(2') 8·53
Dihydroseselin (X)
(in CCl_4)
④ 2·46
⑤ 2·85
⑥ 3·38
③ 3·89
(4') 7·06
(3') 8·15
(2') 8·62
20 30 40 50 60 70 80 90 10 PPM

FIG. 4



C_3', and C_4'. Lastly the NMR spectrum of IX also shows a strong sharp signal at $\tau = 8{\cdot}53$ (6 H) due to two tertiary methyl groups at 2'.

On hydrogenation (PtO_2/glacial acetic acid), IX absorbs only one mole of hydrogen to furnish the known product, dihydroseselin (X), m.p. 104–105°, the UV spectrum of which is identical with that reported earlier.[16]

The alcohol jatamansinol (VIII), on oxidation with Jone's reagent,[17] affords the

[16] W. Bottomley and D. E. White, *Aust. J. Sci. Res. Series, A*, **4**, 112 (1951).
[17] K. Bowden, J. M. Heilborn, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* 39 (1946).

crystalline keto compound (XI), $C_{14}H_{12}O_4$, which we propose to name as jatamansinone and which is identical with 2′,2′-dimethyl-3′-oxo-tetrahydropyrano(6′,5′:7,8)-coumarin[18] as shown by its m.p. 157–158° and UV spectrum. This ketone has been recently obtained by acid hydrolysis of the potent vasodilatory agents, samidin (XIIa), dihydrosamidin (XIIb) and visnadin (XIIc) isolated from 'visnagan' fraction of *Ammi visnaga* L. (Bishop's weed).[9,18] The formation of the ketone (XI) further confirms that ester side chain is attached at C_3' in jatamansin. This conclusively proves that jatamansin is represented by structure VI.

EXPERIMENTAL

All m.ps are uncorrected. The b.ps unless otherwise stated correspond to bath temps. Rotations were taken in $CHCl_3$ solution. Neutral alumina, graded according to Brockman scale[19,20] of activity was used in chromatography. The pet. ether refers to the fraction boiling between 60–80°. The IR spectra were recorded as liquid film or in nujol suspension on a Perkin–Elmer Model No. 137B infracord spectrophotometer by Mr. Gopinath and Mr. Deshpande. The UV spectra were measured in ethanol solution on a Beckman ratio recording spectrophotometer, Model DK-2 and Perkin–Elmer Model No. 350 by Mr. Bhalerao. Microanalyses were carried out by Mr. Pansare and colleagues.

Isolation. Powdered jatamansi roots (greyish brown variety from Jammu and Kashmir; 74·9 kg) were extracted with pet. ether (40–60°, 450 l.) at room temp following essentially countercurrent principle, and the extract concentrated *in vacuo* at a bath temp of 40 ± 2° to give 7·3 kg of the extractive, light brown in colour with the following properties: n_D^{27} 1·5254; $[\alpha]_D^{30}$ −10·36° (*c*, 1·15); acid number, 6·5; ester number, 104·8; alcohol number, 78·52; IR bands at: 3425, 1700 (broad), 1616, 1590, 1393, 1359, 1242, 1140, 1105, 1075, 1034, 905, 885, 847, 830 and 766 cm^{-1}; UV spectrum: λ_{max} 326, 256, 246 and 220 mμ ($E_{1cm}^{1\%}$ 204·1, 142·9, 163·3 and 678·6 respectively).

Jatamansin separates out partly on freezing the oil at 0° for several days. Complete isolation of jatamansin and oroselol was achieved by chromatography of the residual oil on grade III alumina (30 times). Benzene and ether fractions afforded jatamansin (ca, 25% of the total extractive) and oroselol (0·4%) respectively.[21]

Oroselol (Ia). Oroselol coming in the ether fraction was crystallized several times from benzene. m.p. 148–151°, $[\alpha]_D^{28}$ ±0° (*c*, 2·5); IR bands at: 3597, 1718, 1634, 1597, 1383, 1374, 1319, 1279, 1242, 1198, 1174, 1160, 1135, 1100, 1075, 1033, 976, 942, 876, 840, 819, 806 and 770 cm^{-1}; UV spectrum: λ_{max} 301 and 252 mμ, (log ε_{max} 4·02 and 4·40 respectively). (Found: C, 68·93; H, 4·90. Calc. for $C_{14}H_{12}O_4$: C, 68·84; H, 4·95%).

Oroselol acetate (Ib). Oroselol (370 mg) was dissolved in a mixture of pyridine (1 ml) and acetic anhydride (3 ml) and kept overnight at room temp. The reaction mixture was poured on crushed ice, the resulting white precipitate was extracted with ether (3 times). The ethereal layer was washed with dil. HCl (0·1N), then with $NaHCO_3$ aq. (10%) and finally with water. The ethereal portion was dried (Na_2SO_4) and the solvent removed to give crude acetate (365 mg), which on crystallization from methanol gave white crystalline Ib, m.p. 138–44°; IR bands at: 1736, 1631, 1408, 1377, 1320, 1285, 1250, 1205, 1149, 1126, 1109, 1029, 970, 945, 900, 850, 832, 816, 806 and 772 cm^{-1}; UV spectrum: λ_{max} 301 and 252·5 mμ (log ε_{max} 3·9 and 4·37 respectively). (Found: C, 67·57; H, 5·26. Calc. for $C_{16}H_{14}O_5$: C, 67·12; H, 4·93%).

Oroselone (II). Oroselol (138 mg) was heated on a water bath for ½ hour with methanol (3 ml) and conc. HCl (2 ml). The mixture was diluted with water, and the white precipitate formed was washed well with water, dried and crystallized from ethanol to give white needles of II (128 mg), m.p. 179–80°; IR bands at: 1754, 1626, 1565, 1471, 1380, 1302, 1279, 1245, 1160, 1117, 1030, 962, 935, 893, 839, 798 and 775 cm^{-1}; UV spectrum λ_{max} 299 and 286 mμ (log ε_{max} 4·26 and 4·33 respectively). (Found: C, 74·47; H, 4·81. Calc. for $C_{14}H_{10}O_3$: C, 74·33; H, 4·46%).

Jatamansin (VI). It was crystallized from excess of hot pet. ether, m.p. 97–98°, $[\alpha]_D^{25}$ −24·060. (*c*, 5·1); IR bands at: 1724, 1610, 1490, 1458, 1404, 1385, 1348, 1245, 1147, 1119, 1075, 1042, 1022,

[18] Menefa Pharmaceutical Co. Inc., C.A., **60**, No. 3, 2932 (1964).
[19] H. Brockman and F. J. McQuillin, *J. Chem. Soc.* 2423 (1955).
[20] E. Lederer and M. Lederer, *Chromatography*, p. 26. Elsevier, N.Y. (1957).
[21] Details of isolation will be published elsewhere.

994, 900, 847, 769, and 751 cm $^{-1}$; UV spectrum: (described in the theoretical part). (Found: C, 69·55; H, 6·22. $C_{19}H_{20}O_5$ requires: C, 69·50; H, 6·14%).

Dihydrojatamansin. Jatamansin (1 g) dissolved in glacial acetic acid (50 ml) was stirred in H_2 with prereduced Adams' PtO_2 catalyst (100 mg). The equivalent of 1 mole H_2 was absorbed in 4 hr, after which there was no further absorption. The catalyst was filtered and the solvent was removed *in vacuo* to furnish a residue, which on crystallization from pet. ether afforded dihydrojatamansin in the form of colourless needles (880 mg), m.p. 100–101°, $[\alpha]_D^{27}$ +5·06° (*c*, 6·11); IR bands at: 1724, 1600, 1484, 1403, 1364, 1346, 1292, 1279, 1241, 1218, 1190, 1146, 1111, 1070, 1042, 1020, 917, 900, 833 and 760 cm^{-1}; UV spectrum: (described earlier). NMR spectrum (Fig. 1, in CCl_4): doublets at τ = 2·48 (1 H, J = 9 c/s, due to one proton at 4), τ = 2·82 (1 H, J = 8 c/s; due to one proton at 5), τ = 3·35 (1 H, J = 8 c/s due to one proton at 6); τ = 3·92 (1 H, J = 9 c/s, due to one proton at 3); a triplet at τ = 4·94 (1 H, due to one proton at 3′); a multiplet centered at τ = 7·0 (2 H, due to two benzylic protons at 4′); a strong doublet at τ = 8·68 (6H, due to *gem*-dimethyl group at 2′); a doublet at τ = 8·88 (3 H, J = 7 c/s due to CH_3—CH grouping) and a triplet at τ = 9·13 (3 H, due to CH_3—CH_2 grouping). (Found: C, 69·4; H, 7·0. $C_{19}H_{22}O_5$ requires: C, 69·07; H, 6·71%).

Hydrolysis of jatamansin. Jatamansin (5·0 g) in methanol (10 ml) was treated with 1N methanolic KOH (50 ml) and the solution was allowed to stand at room temp for 15 hr. The reaction mixture was diluted with water, concentrated *in vacuo* to remove the solvent, acidified with dil. H_2SO_4 and extracted with ether (4 times). The combined ether extract was washed well with $NaHCO_3$aq to separate the acidic portion.

Acidic portion. The $NaHCO_3$ extract of the ethereal solution was acidified with dil. H_2SO_4aq and extracted thoroughly, with ether. The ether extract was dried and the solvent removed to give an oily residue, which was distilled at 135–140°/58 mm (1·12 g). The distillate on cooling in freeze gave crystals, m.p. 43–45°, identical with angelic acid (III); IR bands at: 2985 (v. broad), 1695, 1645, 1418, 1379, 1346, 1282, 1185, 1163, 1085, 1044, 1018, 938, 854, 792 and 739 cm^{-1}; UV spectrum λ_{max} 216 mμ (log ε_{max} 3·69). (Found: C, 60·23; H, 8·17. Calc. for $C_5H_8O_2$: C, 59·94; H, 8·05%).

Preparation of methylethylacetic acid (IV). On hydrogenation (PtO_2/glacial acetic acid), (III consumed 1 mole equiv. H_2 to yield methylethylacetic acid which on esterification with *p*-bromophenacyl bromide (in the usual manner) furnished *p*-bromo-phenacyl ester of methylethylacetic acid, crystallized from aqueous methanol to give colourless plates, m.p. and mixed m.p. with authentic sample, 52–53°.

Isolation of jatamansinol (VIII). The ethereal extract containing the neutral product of hydrolysis of jatamansin was washed with water, dried (Na_2SO_4) and the ether removed to furnish a solid residue, which was crystallized from benzene to yield colourless needles (2·5g) of jatamansinol, m.p. 182–183°; $[\alpha]_D^{28}$ +7·6° (*c*, 5·8); IR bands at: 3623, 1721, 1618, 1499, 1471, 1408, 1387, 1368, 1297, 1279, 1256, 1235, 1198, 1160, 1140, 1130, 1088, 1075, 1041, 989, 943, 911, 862, 833 and 762 cm^{-1}; UV spectrum: (described earlier); NMR spectrum (Fig. 4, in $CDCl_3$): a pair of doublets at τ = 2·34 (1 H) and 3·76 (1 H), J = 9 c/s (due to protons at 4 and 3 respectively); another pair of doublets at τ = 2·69 (1 H, one of the absorptions of doublet merging with the absorption of solvent) and 3·18 (1 H), J = 9 c/s due to protons at 5 and 6 respectively); a broad signal at τ = 6·05 (1 H, due to one proton at 3′); a multiplet at τ = 6·95 (2 H, due to two benzylic protons at 4′) and a strong doublet at τ = 8·58 (6 H, due to *gem*-dimethyl group at 2′). (Found: C, 68·26; H, 5·63. $C_{14}H_{14}O_4$ requires: C, 68·28; H, 5·73%).

Acetate of jatamansinol. Jatamansinol (791 mg) was mixed with a mixture of acetic anhydride (5 ml) and pyridine (10 ml) and kept at room temp overnight. The product was worked up in the customary manner to furnish a crystalline acetate (829 mg), which on recrystallization from pet. ether–benzene mixture gave colourless needles, m.p. 137–138°, $[\alpha]_D^{30}$ −6·79° (*c*, 5·33); IR bands at: 1733 (slightly broad and strong), 1600, 1567, 1481, 1453, 1308, 1383, 1366, 1337, 1266, 1232 (vs), 1161, 1136, 1111, 1099, 1064, 1053, 1001, 992, 930, 909, 893, 840, 821, 806, 772, 760 and 685 cm^{-1}; UV spectrum: (described earlier); NMR spectrum (in CCl_4); a pair of doublets at τ = 2·41 (1 H) and 3·87 (1 H), J = 9 c/s (due to protons at 4 and 3 respectively); another pair of doublets at τ = 2·76 (1 H) and 3·3 (1 H), J = 8·5 c/s (due to protons at 5 and 6 respectively); a triplet at τ = 4·87 (1 H, due to one proton at 3′); a multiplet at τ = 6·95 (2 H, due to two benzylic protons at 4′); a strong signal at τ = 7·95 (3 H, due to —CO—CH_3 group) and a strong signal at τ = 8·65 (6 H, due to *gem*-dimethyl group at 2′). (Found: C, 66·97; H, 5·97; CO—CH_3 15·25. $C_{16}H_{16}O_6$ requires: C, 66·66; H, 5·59; CO—CH_3, 14·93%).

Hydrolysis of dihydrojatamansin. The hydrolysis of dihydrojatamansin (3·1 g) was carried out

under the same conditions as used for that of jatamansin. The acidic portion furnished the methylethylacetic acid (IV, 605 mg), the *p*-bromophenacyl ester of which did not depress the m.p. 52–53° of an authentic specimen. The neutral portion on working up was found to be VIII (1·8 g).

Ozonolysis of jatamansin. Jatamansin (3·6 g) was dissolved in CCl_4 (50 ml) and ozonized oxygen was passed for 4 hr at 0°. The solvent was removed *in vacuo*, the reaction mixture was mixed with water (30 ml) and steam distilled.

Non-volatile Product. The non-volatile product left after steam distillation was extracted in ether and worked up in the usual manner to give a residue which on chromatography on grade III alumina (40 g, elution with 450 ml benzene), furnished a crystalline compound (1·4 g), m.p. 182–183°, identical with VIII.

Volatile product. The volatile product of ozonolysis was neutralised with $NaHCO_3$ and steam distilled. The distillate was converted into its crystalline 2,4-dinitrophenylhydrazone (500 mg) by the usual procedure and identified as that of acetaldehyde by mixed m.p. 147–48°, with an authentic specimen. (Found: C, 42·9; H, 3·66. Calc. for $C_8H_8O_4N_4$: C, 42·86; H, 3·60%).

The non-volatile portion containing the Na salts was concentrated and subjected to paper chromatography[22] (n-butanol–aq ammonia–developing solvent and bromophenol blue and citric acid–indicator) to show the presence of acetic acid and pyruvic acid, confirmed by comparison with authentic samples.

Preparation of seselin (IX). *p*-Toluenesulphonyl chloride (2·0 g) was added to the solution of jatamansinol (1·93 g) dissolved in pyridine (20 ml) and kept at room temp for 12 hr. After working up the product in the customary manner and crystallization from methanol, the crystalline tosylate (1·9 g) was obtained, m.p. 158–59°; IR bands at: 1727, 1610, 1488, 1406, 1353, 1323, 1282, 1250, 1215, 1190, 1176, 1151, 1136, 1112, 1074, 1035, 1017, 982, 947, 917, 883, 840, 820, 781, 759, 738 and 697 cm^{-1}. (Found: C, 62·67; H, 5·02. $C_{21}H_{20}O_6S$ requires: C, 62·99; H, 5·04%).

The tosylate (1·35 g) was heated under reflux in 2,4,6-collidine (8 ml) for 6 hr. in an oil bath at 180–190°. The product was worked up, chromatographed over grade III alumina (25 g, elution with 250 ml pet. ether) and crystallized from aq. ethanol to give seselin (608 mg) in the form of colourless needles, m.p. 119–120°, $[\alpha]_D^{30}$ ±0° (*c*, 7·67); IR bands at: 1724, 1631, 1595, 1480, 1401, 1370, 1287, 1258, 1235, 1217, 1193, 1153, 1114, 1074, 1009, 909, 833, 803 and 734 cm^{-1}; UV spectrum: λ_{max} 330, 294, 284 and 218 mμ, (log ε_{max} 4·07, 4·05; 4·04 and 4·42 respectively). (Found: C, 74·12; H, 5·55. Calc. for $C_{14}H_{12}O_3$: C, 73·67; H, 5·30%).

Preparation of dihydroseselin (X). Seselin (500 mg) dissolved in glacial acetic acid (25 ml) was stirred in H_2 atm in the presence of pre-reduced Adams' catalyst, PtO_2 (50 mg). Absorption of H_2 equivalent to one mole was over in 3 hr, after which there was no further absorption. The product was worked up in the usual manner to give a residue (450 mg), which on crystallization from aq methanol afforded dihydroseselin, m.p. 104–105°; IR bands at: 1709, 1600, 1477, 1418, 1393, 1361, 1267, 1232, 1176, 1161, 1117, 1071, 1036, 1021, 978, 936, 923, 903, 885, 826, 766, 749 and 722 cm^{-1}; UV spectrum: λ_{max} 329, 255 and 213 mμ (log ε_{max} 4·09, 3·37 and 4·17 respectively); NMR spectrum (Fig. 4, in CCl_4): a pair of doublets at τ = 2·46 (1 H) and 3·89 (1 H), J ≃ 9 c/s (due to protons at 4 and 3 respectively); another pair of doublets at τ ≃ 2·85 (1 H) and 3·38 (1 H), J = 8·5 c/s (due to protons at 5 and 6 respectively); a multiplet at τ = 7·06 (2 H, due to two benzylic protons at 4′); another multiplet at τ = 8·15 (2 H, due to two protons at 3′) and a strong signal at τ = 8·62 (6 H, due to *gem*-dimethyl group at 2′). (Found: C, 73·21; H, 5·99. Calc. for $C_{14}H_{14}O_3$: C, 73·02; H, 6·13%).

Preparation of jatamansinone (XI). The solution of jatamansinol (1·2 g) in acetone (50 ml) was treated with Jones' reagent[17] (5 ml) at 0° for 2½ hr. The excess of the reagent was destroyed with methanol. The solution was concentrated *in vacuo*, diluted with water and extracted with ether. After drying (Na_2SO_4), the solvent was removed to give a residue (1 g). This was chromatographed on grade II alumina (25 g). Elution with benzene (400 ml) gave jatamansinone (700 mg), which was crystallized from ethyl acetate, m.p. 157–158°, $[\alpha]_D^{30}$ ±0° (*c*, 2·7); IR bands at: 1721, 1600, 1570, 1484, 1430, 1395, 1379, 1366, 1357, 1342, 1289, 1263, 1235, 1205, 1159, 1144, 1111, 1066, 999, 939, 909, 843, 832 and 763 cm^{-1}; UV spectrum: λ_{max} 321, 256 and 218 mμ (log ε_{max} 4·12; 3·5 and 4·15 respectively). (Found: C, 68·89; H, 4·83. Calc. for $C_{14}H_{12}O_4$: C, 68·84; H, 4·95%).

[22] F. Brown and L. P. Hall, *Nature, Lond.* **66**, 166 (1950).