

THE IDENTITY OF JATAMANSONE AND VALERANONE

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THE preliminary results, published by Govindachari et al.,^{1,2} enabled us to prove the identity of the so called jatamansone from Nardostachys jatamansi (Valerianaceae) with valeranone from Valeriana officinalis L., the isolation of which was carried out by Stoll et al.^{3,4} and by us.⁵ The identity of both compounds in question follows from the comparison of both the physical constants of derivatives (Table 1) and of the physical constants of degradation products which were prepared independently in this Laboratory in a manner which differed from the procedure of the Indian authors in details only (Table 2).

¹ T.R. Govindachari, S. Rajadurai and B.R. Pai, Chem. Ber. 91, 908 (1958).

² T.R. Govindachari, B.R. Pai, K.K. Purushothaman and S. Rajadurai, Tetrahedron Letters No. 15, 5 (1959).

³ A. Stoll, E. Seebeck and D. Stauffacher, Schweiz. Apoth.-Ztg. 95, 115 (1957).

⁴ A. Stoll, E. Seebeck and D. Stauffacher, Helv. Chim. Acta. 40, 1205 (1957).

⁵ J. Křepinský, V. Herout and F. Šorm, Chem. listy 52, 1784 (1958);
Coll. Czech. Chem. Comm. 24, 1884 (1959).

On treatment with lithium aluminium hydride, valeranone afforded the alcohol valeranol $C_{15}H_{28}O$ (d_4^{20} 1.0046, n_D^{20} 1.5005, $[\alpha]_D^{20} + 51.4^\circ$, chloroform) which on dehydration with phthalic anhydride at $270 - 280^\circ$ yielded unsaturated hydrocarbon valerene $C_{15}H_{26}$ (d_4^{22} 0.9045, $[\alpha]_D^{22} + 96.07^\circ$). The latter, on hydrogenation with PtO_2 (Adams) afforded the saturated hydrocarbon valerane of molecular formula $C_{15}H_{28}$ (d_4^{20} 0.8965, n_D^{20} 1.4830). The same hydrocarbon was obtained from valeranone ethylene thioketal on treatment with Raney-nickel in dioxan. Both compounds were proved identical by comparison of infra-red spectra and physical constants; the infra-red spectrum of valerane, however, was unlike the spectra of all hitherto known saturated bicyclic sesquiterpenes.⁶

TABLE 1.

Comparison of physical constants

Valeranone			Jatamansone		
d_4^{20}	0.9712	5	d_4^{30}	0.9623	1
n_D^{20}	1.4944	5	n_D^{30}	1.488	1
α_D^{20}	-43.0°	5	α_D^{30}	-40.1°	1
semicarbazone	m.p. $205-7^\circ$	5	m.p.	$206-8^\circ$	1
oxime	m.p. $113-114^\circ$		m.p.	112°	1
2,4-Dinitrophenyl- hydrazone	m.p. $99-100^\circ$		m.p.	101°	1

Valeranone forms a monobenzylidene derivative (m.p. $101 - 102^\circ$) which

⁶ J.Plíva, M.Horák, V.Herout and F.Šorm, Catalogue of Spectra In press.

on ozonization affords dicarboxylic acid $C_{15}H_{26}O_4$ (m.p. $236 - 237^\circ$). This acid was cyclized, in the presence of barium hydroxide into norvaleranone $C_{14}H_{24}O$ (semicarbazone m.p. $238 - 240^\circ$), the infra-red spectrum of which exhibited a band at 1735 cm^{-1} , due to a keto group in a five-membered ring. The ketone formed a liquid monobenzylinede derivative which on ozonization afforded norvaleranic acid $C_{14}H_{24}O_4$ (m.p. 143°). Both on pyrolysis and on treatment with acetic anhydride, the acid afforded a crystalline anhydride $C_{14}H_{22}O_3$ (m.p. $77 - 78^\circ$) which on subsequent bromination yielded a crystalline bromo anhydride (m.p. $146 - 148^\circ$).

By means of quantitative bromination,⁷ the presence in valeranone of two hydrogen atoms in α -position to the keto group was ascertained, i.e. a methylene group and a quaternary carbon atom are adjacent to the carbonyl group. On dehydrogenation, neither valeranol (sulphur, 180° , 4 hr; selenium, $280 - 300^\circ$, 1 hr) nor valerene (sulphur, 180° , 1.5 hr; $200 - 250^\circ$, 6 hr; iodine 280° , 0.5 hr) afforded any detectable amount of an aromatic derivative (infra-red spectrum) or azulene. Only dehydrogenation of valeranol with

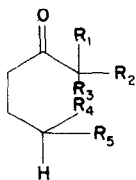
TABLE 2. Comparison of melting points of degradative products

	Valeranone	Jatamansone
Dicarboxylic acid $C_{15}H_{26}O_4$	$236-7^\circ$	$233-234^\circ$ ¹
Dicarboxylic acid $C_{14}H_{24}O_4$	143°	143° ²
Anhydride $C_{14}H_{22}O_3$	$77-78^\circ$	$85-86^\circ$ ²
Bromo anhydride $C_{14}H_{21}O_3Br$	143°	143° ²

⁷ C.S. Barnes, D.H.R. Barton, A.R.H. Cole, J.S. Fawcett and B.R. Thomas, J. Chem. Soc. 571 (1953).

Pd/C (50%) at relatively high temperature (320 - 340^o, 2 hr) led to a mixture of azulenic hydrocarbons.

In view of our present results and in agreement with the statement of Govindachari et al.,² valeranone (the identity of which with jatamansone we regard as proved) may be provisionally formulated with a partial structure as follows.



The full experimental data and some new facts about the structure of valeranone will be published in Collection of Czechoslovak Chemical Communications.