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CONSTITUTION OF VALERANONE

J. Křepinský, M. Romaňuk, V. Herout and F. Šorm
Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Science, Prague

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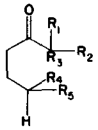
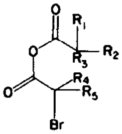
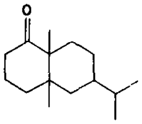
RECENTLY, we determined partial structure (I) for valeranone, the bicyclic, saturated sesquiterpenic ketone $C_{15}H_{26}O$ from *Valeriana officinalis* L.,



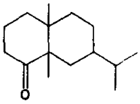
I



II



IIIa



IIIb

and proved its identity with jatamansone, isolated from *Nardostachys jatamansi*.[1] In the course of our further work we succeeded to elucidate the constitution of valeranone (IIIa or IIIb) by means of following reactions.

The natural ketone was submitted to photolysis in U.V.-light[2,3] to

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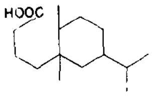
[1] J. Křepinský, V. Herout and F. Šorm, *Tetrahedron Letters* No.3, 9 (1960).

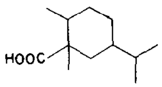
[2] G. Ciamician and P. Silber, *Ber.* **40**, 2415 (1907).

[3] D. Arigoni, D.H.R. Barton, R. Bernasconi, C. Djerassi, J.S. Mills and R. Wolff, *Proc. Chem. Soc.* 306 (1959).

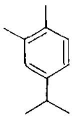
afford a saturated monocyclic acid of molecular formula $C_{15}H_{28}O_2$ (IV) which by three fold Barbier - Wieland degradation was converted into a monocarboxylic acid $C_{12}H_{22}O_2$ (V); this constitutes the proof that R_5 in formula I is hydrogen atom. As the bromoanhydride $C_{14}H_{21}O_3Br$ (II) failed to be dehydrobrominated[4] we take carbon atom R_4 as a quaternary one. We therefore dehydrogenated the acid $C_{12}H_{22}O_2$ (V) in the presence of palladized charcoal (30%) at 290-305° for 3 hr and obtained a uniform monocyclic aromatic hydrocarbon of molecular formula $C_{11}H_{16}$ (VI) which in view of its physical constants (d_4^{20} 0.8647; n_D^{21} 1.4942) and its infra-red spectrum was identical with an authentic sample of 1,2-dimethyl-4-isopropylbenzene (VI). The gaseous products of dehydrogenation were analysed by gas chromatography according to Janak; only hydrogen was estimated.



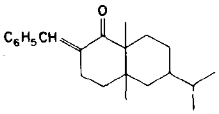
IV



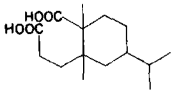
V



VI



VII



VIII

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

Further we dehydrogenated the monocyclic dicarboxylic acid $C_{15}H_{26}O_4$ (VIII), prepared by ozonolysis of monobenzylidene valeranone[1,4] (VII), under the conditions used for the acid $C_{12}H_{22}O_2$ (V) and obtained, besides neutral, hitherto non-identified products and regenerated starting material, a single monocarboxylic volatile acid which, by means of paper chromatography, was identified as propionic acid (butanol - 2N ammonia solution, R_F 0.24). In view of these results we take formula (IIIa or IIIb) for valeranone as proved.

This work will be published in full detail in Collection of Czechoslovak Chemical Communications together with further proof of this unusual structure and its stereochemistry.