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NOTES

Biogenesis of Steroids A New Aspect and Experimental Analogy

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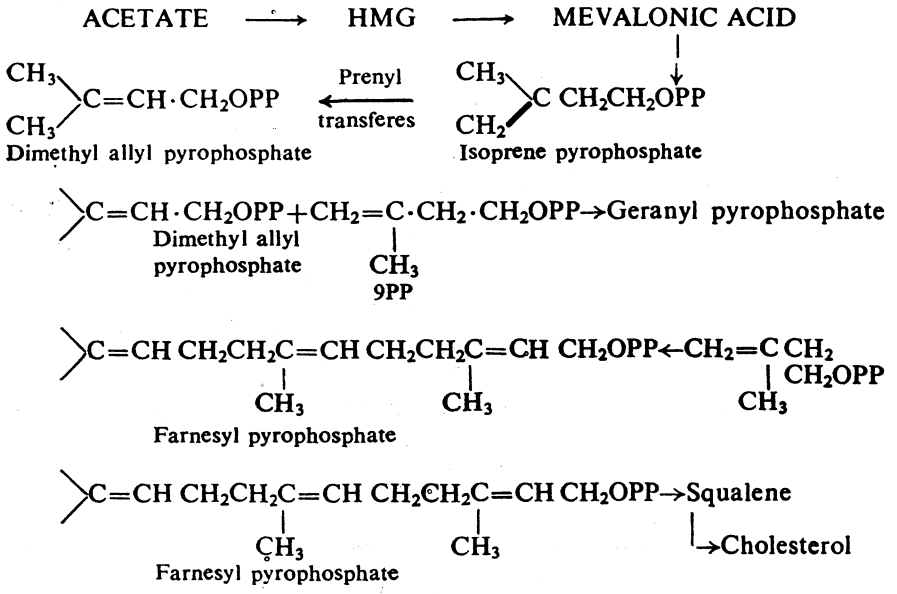
A new aspect on biogenesis of steroids and the *D* ring has been put up in the present communication.

The present pathway that has been put up for the formation of steroidal compounds in animal and plant cells is through mevalonic acid formed from hydroxy methyl glutaric acid (HMG). HMG activating enzyme has been reported to be of not a common occurrence.[1] If forms farnesyl pyrophosphate, giving by tail to tail union squalene.[2] Squalene has been proposed as a precursor.[3] The exact mechanism of the formation of squalene from two molecules of farnesyl pyrophosphate is not fully settled.[4] Looking to carbon atoms Nos. 15 & 16 of steroids in *D* ring, it appears that tail to tail union may be taking place between *C* 20 and geranyl pyrophosphate units. Some other intermediate oxidation compounds may be simultaneously giving rise to Vitamin D, hormonal steroids and nonhormonal excretory steroidal and triterpenoid compounds such as those present in wool degras (lanosterol) and scalp (squalene) etc. being formed by products. The analogy of the formation of ring similar to ring D by irradiation of ienone type of compounds has also been referred below.

CHART 1



Squalene was proposed as a precursor of cholesterol by Heilbron, Kamm and Owens.[5] Robinson proposed the formation of cholesterol from squalene with loss of three methyl groups.[6,7]

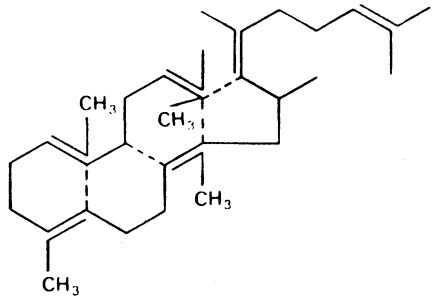


Figure 1

Woodward[8] has taken cyclo geranyl unit as the basis for the formation of ring *A* and the formation of ring *D* has been explained as resulting from 1, 2 shifts of labile methyl group from carbon atom No. 14 to Carbon atom No. 13 and from carbon atom No. 8 to carbon atom No. 14 to give lanosterol from squalene. This later may be yielding cholesterol by the loss of methyl groups at positions 4 and 14.

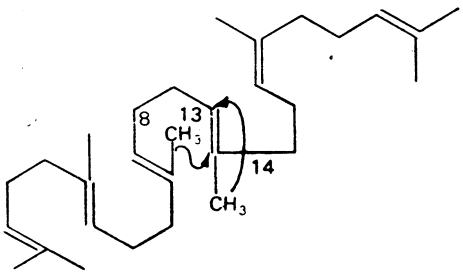


Figure 2

However looking to carbon atom No. 15 and carbon atom No. 16 of cholesterol it would appear that tail to tail union may be taking place between C_{20} and geranyl pyrophosphate units, instead of two farnesyl pyrophosphate (C 15) units. Consequently at carbon No. 20 of squalene a tail to tail union would be taking place instead of head to tail union in the scheme proposed by Woodward and the compound formed by such a tail to tail union would be isomeric with squalene. The formation of a C_{20} unit may be explained by tail to head union of geranyl pyrophosphate unit with IPP and IFP units referred below. The formation of ring *D* proposed here is more in keeping with Markownikoff's rule in contrast to the Woodword's scheme, it presumes 1, 2 shift of methyl group from Carbon No. 8 to Carbon No. 4 only to give lanosterol.

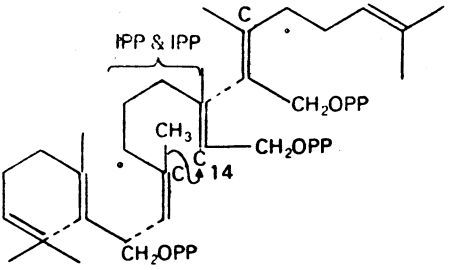
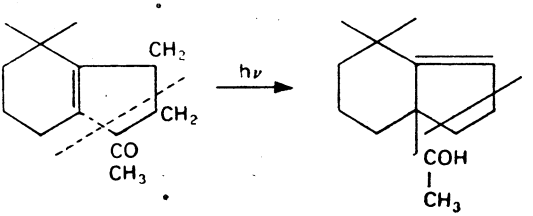


Figure 3

In actual *in vivo* syntheses of cholesterol, dehydrocholesterol Vitamin D_3 in vertebrates it may be taking some other route, lanosterol in wool degras, squalene in scalp being formed as bye-products in biogenesis having actually little role in skeleton formation. Therefore being less required might have been present in wool fat and skull squalene in rat tissues is very little when fed with acetate C_{13}. Dihydro-β-Ionone when irradiated cyclises to give bicyclononenols.[9]



The cyclisation of cyclogeranyl-geranyl is in hand to support the pathway proposed here.

REFERENCES

1. C. O. Chichester, H. Yokoyama, T. O. M. Yakayama, A. Lukton, and G. Mackinney, *J. Biol. Chem.*, 234, 598 (1959).
2. Islar Otto, 'Carotenoids', Birk Hauser Verlag. Bassel and Stuttgart, p. 21 (1971).
3. T. M. Goodwin, 'Carotenoids', Birk Hauser, Verlag, Bassel and Stuttgart, p. 61 (1971).
4. ———, 'Carotenoids', Birk Hauser, Verlag, Bassel and Stuttgart, p. 588 (1971).
5. ——— , 'Carotenoids', Birk Hauser, Verlag, Bassel and Stuttgart, p. 586–587 (1971).
6. Heibron, Kamm & Owens, *J. Chem. Soc.*, 1630 (1926).
7. B. Hobinson, Chemmoo Ind., p. 53, 1062 (1934).
8. R. B. Woodward & K. Bloch, *J. Am. Chem. Soc.*, 75, 2023, 1957.
9. Jagar Oskar, Hans Wolf. & M. Zink, *Swiss J.*, 574, 381, 1976, *Chem. Abstr.*, 85, p. 78236 f.

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