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# NUCLEAR PRENYLATION OF POLYHYDROXY KETONES - PART V:

## Novel Condensation of two Prenyl units to form 3-Prenylchromans

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In a previous communication[1], the reaction of gallacetophenone with 2-methyl-but-3-en-2-ol under anhydrous conditions was reported. One of the products was identified as 5-C-prenylgallacetophenone. The structural elucidation of the second product (A) obtained in minor yield is reported in this paper along with a similar compound obtained from p-hydroxyacetophenone.

Compound A came first as an oil but it crystallised from benzene yielding a colourless solid, m.p. 82-3°; $\lambda_{max}^{MeOH}$ 296 nm (log$\epsilon$ 3.72) and $\nu_{max}^{Nujol}$ 1640 $cm^{-1}$. These spectral properties are very similar to those of gallacetophenone. The dark green ferric colour and positive DNP test along with UV and IR data indicated the presence of an orthodihydroxy system and a chelated carbonyl group. Its $M^+$ at 304 showed that it contained two $C_5$ units attached to the galloacetophenone molecule. In the NMR spectrum the presence of an aromatic proton in the downfield region at $\delta$ 7.01 ppm and absence of O-prenyl signals signified that 6-position was free and the compound had no O-prenyl group. Isolation of 5-C-prenyl gallacetophenone as one of the products of the reaction and the reactivity of the gallacetophenone molecule would suggest the following possible structure (I) for compound A. But, the NMR spectrum of the compound A was not in agreement. It does not contain signals that could be attributed to two allylic $-CH_2-$ groups of two prenyl units as is observed in the case of gem-di-C-prenyl phloracetophenone[2]. Further, though there is a multiplet around $\delta$ 5.2 ppm, which could be attributed to two vinylic protons, one of these protons disappears when shaken with $D_2O$ indicating there is only one such proton and the other is due to a phenolic hydroxyl. Therefore, compound A should have an alternative structure. Formula (II) is in agreement with all its properties including NMR spectrum, the assignments being given in the chart.

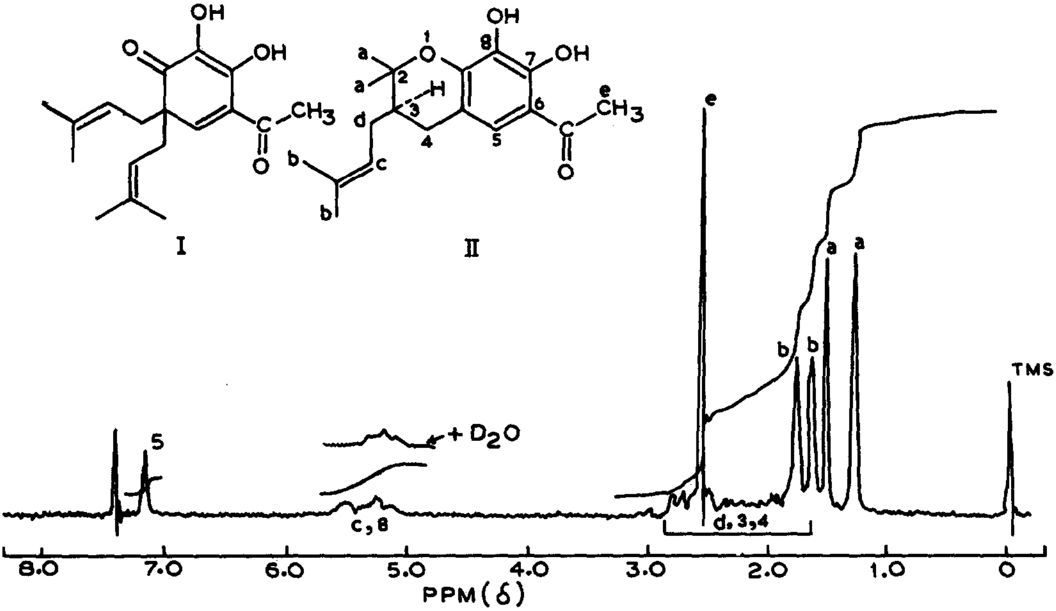
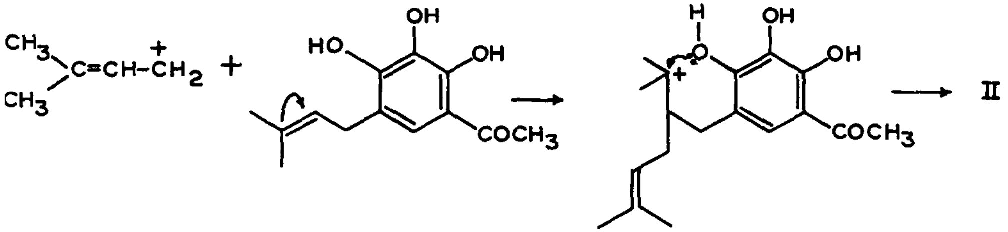
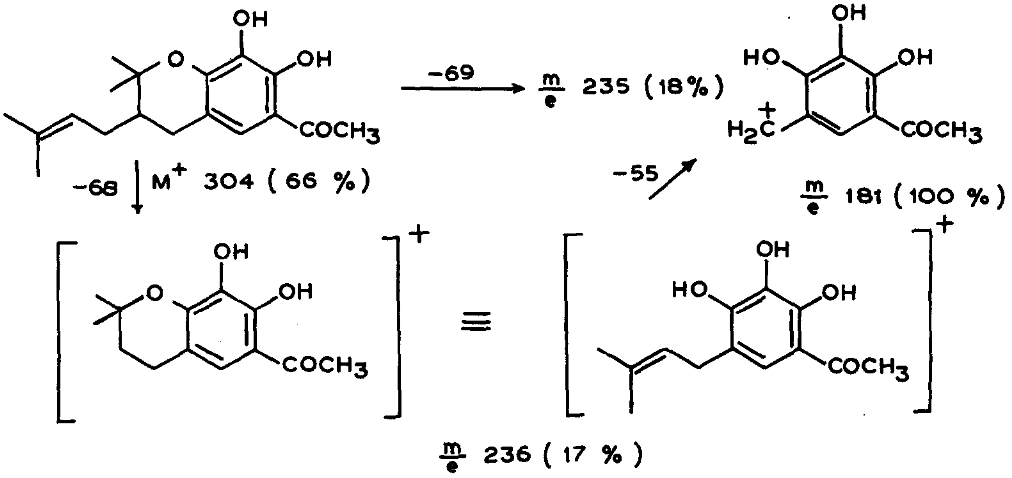


Chart: 60 MHz NMR spectrum of A in $CDCl_3$ with TMS as internal standard

Methylation of the compound A with excess of dimethyl sulphate by the acetone - potassium carbonate method gave a dimethyl ether as an oil, devoid of ferric reaction. NMR spectrum of the methyl ether in $CCl_4$ indicates the absence of hydroxyl group signals. Instead there are signals for two methoxyl groups at $\delta$ 3.75 and $\delta$ 3.88 in addition to all the signals observed in the spectrum of the parent hydroxy compound A. Formation of dimethyl ether indicates the presence of only two free hydroxyl groups and therefore the third should be involved in some modification. This rules out the possibility of any other structure. This chroman structure (II) is confirmed by the preparation of the substance A in 50% yield from 5-C-prenylgallacetophenone by condensation with 2-methyl-but-3-en-2-ol (1 mole) at 50-60°C in anhydrous dioxan in the presence of $BF_3$-etherate. This throws light on the mechanism of the formation of the chroman. It seems to involve the attack of isopentenyl carbonium ion, generated from 2-methyl-but-3-en-2ol, on the prenyl unit of the gallacetophenone derivative as indicated below.

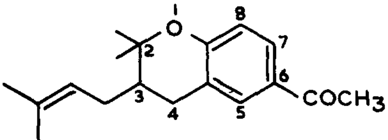


The above chroman structure is in full agreement with the mass spectral fragmentation. In addition to the usual fragmentation common with aromatic hydroxyketones, the following special features were observed.



A similar reaction of p-hydroxyacetophenone with 2-methyl-but-3-en-2ol was earlier reported[1] yielding a mixture of three products viz. 3-prenyl-4-hydroxyacetophenone, 4-prenyloxyacetophenone and an unidentified product B. Compound B gives a positive DNP test and it is insoluble in alkali; $\nu_{max}^{film}$

1685 $cm^{-1}$ indicating the presence of carbonyl group; $\lambda_{max}^{MeOH}$ 226 and 280 nm not changed by the addition of alkali. The NMR spectrum of this compound has a doublet at $\delta$6.67 for one proton at 8-position and multiplet at $\delta$7.60 of two deshielded protons at 5- and 7-positions. The rest of the spectrum is exactly similar to that observed in the case of compound A, thereby suggesting a close similarity between the two compounds. Boiling B with excess of dimethyl sulphate did not effect methylation. Treatment of 3-prenyl-4-hydroxy acetophenone with one mole of 2-methyl-but-3-en-2ol results in the formation of B. All these data suggest the following chroman structure (III) for the compound B. The mass spectrum ($M^+$ 272) is quite similar to the one given by compound A and provides full support.



III

Among natural products or synthetic compounds, this type of diprenyl derivatives has not been recorded before. Their formation does not conform to the usual isoprene rule. Here the linking is between the $C_1$ of one unit and $C_2$ of another unit.

## References

1. B.S. Bajwa, Pyare Lal Khanna & T.R. Seshadri, Ind. J. Chem., **9**, 1322 (1971).

2. B,S. Bajwa, Pyare Lal Khanna & T.R. Seshadri, Ind. J. Chem., in press.