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NOVEL MELIACINS (LIMONOIDS) FROM THE WOOD OF PSEUDOCEDRELA KOTSCHYII

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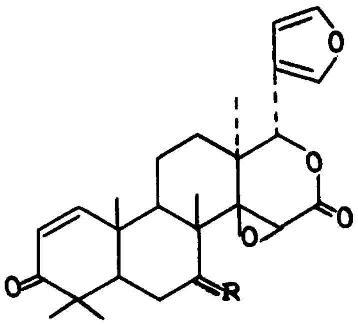
From the wood of Pseudocedrela kotschyii have been isolated a number and a variety of oxidised triterpenoids related to gedunin. Two of these have been shown to be 7-deacetyl gedunin(I) and 7-deacetoxy-7-oxogedunin(II)(1).



I: R = α-OH, β-H

II: R = O

We wish now to report on the chemistry of two other limonoids which we call Pseudrelone-A_1 and -A_2 and which represent novel types of this class of compounds. Pseudrelone-A_1, m.p. 265 - 268° has the constitution $C_{38}H_{50}O_{14}$ (elemental analysis and mass spectrum). Its ultra violet (u.v.) spectrum indicates that it is an enolised β-diketone [λ_{max} 270 mμ (ε 9000) in methanol shifting to 290 mμ (ε 18000) in alkaline methanol]. This is supported by its infra red (i.r.) spectrum [ν_{max} (nujol) 1630 and 1600 cm^{-1}] and nuclear magnetic resonance (n.m.r.) spectrum which shows an enol hydroxyl hydrogen at τ -4.15 exchangeable with D_2O. Furthermore it reacts with diazomethane to afford a methyl ether $C_{39}H_{52}O_{14}$, m.p. 220 - 222°

(n. m. r. band at τ 6. 11). There is a β-substituted furan [ν_{max} 1500 and 874 cm^{-1}; λ_{max} 212 mμ (ε 5, 500); and n. m. r. bands at τ 2. 54, 2. 62 and 3. 57]. In addition the n. m. r. spectrum shows three low field singlets at τ 4. 12, 4. 61 and 5. 1 corresponding to one hydrogen each. It also indicates a carbomethoxy (τ 6. 27), two COMe (τ 7. 70 and 8. 02), a tertiary hydroxyl (τ 7. 23, disappearing on addition of D_2O) and seven CMe groups.

Alkaline hydrolysis and titration show the presence of two non-volatile and three volatile acids. The non-volatile acids are accounted for by the carbomethoxy group and probably a lactone. The volatile acids were identified from the n. m. r. spectrum of their potassium salts(2) as acetic acid (two moles) and iso-butyric acid (one mole).

The position of the u. v. maximum at 270 mμ is not that of an enolised 1, 3 cyclohexanedione(3), but agrees with the value calculated for an enolised α-acylcyclohexanone. One of the volatile acids therefore could have arisen from hydrolytic cleavage of the β-diketone: the other two moles originating from acyloxy groups. This deduction is supported by the results of ozonisation followed by decomposition of the ozonide with boiling 30% hydrogen peroxide. This gives acetic and a non volatile acid. The latter could not be crystallised but the n. m. r. spectrum of its methyl ester showed four carbomethoxy groups and one COMe group. There is thus an acetylcyclohexanone, an acetoxyl and an isobutyroxyl group in pseudrelone-A_1.

We assign two of the low field singlets at τ 4. 62 and 5. 10 to hydrogens at the base of acyloxy groups. They both show downfield shifts of 0. 10 and 0. 22 p. p. m. respectively in the methyl ether while the third low field signal remains quite unchanged. In one experiment to prepare the methyl ether, a small amount of a second product was obtained in which the acetoxyl group had been apparently accidentally hydrolysed off. In the n. m. r. spectrum of this product the COMe signal at τ 7. 70 had disappeared while the band at τ 5. 10 had moved 1. 2 p. p. m. upfield. That the pseudrelones are gedunin derivatives is very probable in view of their co-occurrence with other gedunin derivatives. The third low field singlet at τ 4. 12 has therefore been assigned to the H-17 of a gedunin nucleus with a ring D lactone. Assuming therefore a gedunin C_{26} nucleus and adding the structural elements described, there remain three carbon and two oxygen atoms as well as one double bond equivalent unaccounted for. The nature of these is still under investigation.

Pseudrelone-A_2, $C_{40}H_{54}O_{13}$, M (mass spectrum) 742, is very similar to A_1(i. r. and u. v.) except that it gives two moles of isobutyric and one mole of acetic acid, and it has no tertiary hydroxyl group. Their n. m. r. spectra are otherwise identical. Comparison of their mass spectra shows that A_2 is an isobutyryl cyclohexanone rather than an acetylcyclohexanone as is A_1. The extinction coefficient of the β-diketone u. v. absorption is higher in A_2 than in A_1 (14, 000 and 9, 000) suggesting a transoid and a cisoid configuration respectively. The difference may be due to steric factors.

Pseudrelone-A_1 and A_2 are thus new types of limonoids involving not only O-acylation as has now been observed in a number of cases but also C-acylation of the gedunin nucleus. Another meliacin which has also been shown to belong to this class is bussein which was recently isolated by our colleague Professor D. A. H. Taylor from an East African timber *Entandrophragma bussei*(4). We are grateful to Professor Taylor for exchange of information.

REFERENCES

1. E.O. Olagbemi, M. Sc. Thesis, University of Ibadan, 1966.
2. D. A. Calam and D. A. H. Taylor, *J. Chem. Soc.* (C), 949 (1966).
3. W. Chan and C. H. Hassall, *J. Chem. Soc.*, 2860 (1955)
4. D. A. H. Taylor, *Chem. and Ind.*, 582 (1967).