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SHORT COMMUNICATION

CHEMICAL INVESTIGATION OF *CEDRELA TOONA*

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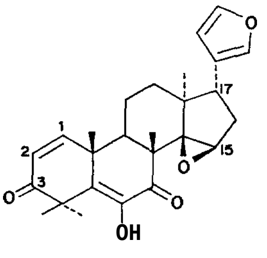
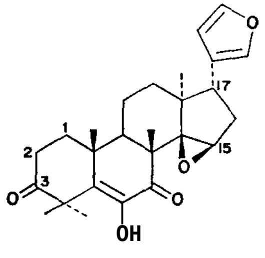
Abstract-Two varieties of ***Cedrela toona*** Roxb. are available in West Bengal and the seeds of one variety produces **cedrelone, 1,2-dihydrocedrelone,** bergapten and **β-sitosterol.** Occurrence of **1,2-dihydrocedrelone,** a new **tetranortriterpenoid,** provides further interesting evidence of the chemotaxonomic feature of ***Meliaceae.***

INTRODUCTION

Earlier investigations on the timber of ***Cedrela*** *toona* Roxb. (Meliaceae) have resulted in the isolation and structure elucidation of cedrelone[1-3] (I) and a number of **sesquiterpenoids.**[4] ***Cedrela toona*** Roxb. grows abundantly in West Bengal and exists in two varieties having different morphological character. Their cytological and other botanical characteristics have not yet been worked out and the occurrence of these two varieties have not been recorded previously by taxonomists[5a,5b]. The larger size of the seeds in one variety of the species may be due to higher level of polyploidy. The petrol extract of the seeds of tht larger sized variety yield two tetranortriterpenoids and a coumarin which are found to be absent in the seeds of the other variety. Four compounds, namelycedrelone(I), 1 ,**2-dihydrocedrelone** (II), bergapten and **β-sitosterol** have been isolated and are reported in the present communication. Of these, **1,2-dihydrocedrelone** is a hitherto unknown natural product.



(I)



(II)

RESULTS AND DISCUSSION

The major component of the seeds, $C_{26}H_{30}O_5$, ($M^+ = 422$), m.p. 208°, λ_{max}^{EtOH} 220 nm (E, 9300) (end absorption), was obtained in 0.001 per cent yield. Direct comparison of this

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[1] K. W. **Gopinath,** T. R. **Govindachari, P. C.** Parthasarathy, *N.* **Viswanathan,** D. **Arigoni** and W. C. Wildmann, ***Proc.*** *Chem.* ***Soc.*** *446* (1961).

[2] I. J. Grant, J. A. Hamilton, T. A. **Hamor,** R. **Hodges,** *S. C.* **McGeachin, R. A. Raphael, I. M. Robertson** and G. A. Sim, ***Proc.*** *Chem.* ***Soc.*** *444* (1961).

[3] R. Hodges, S. C. **McGeachin** and R. A. Raphael, *J. Chem.* ***Soc.*** *2522 (1963).*

[4] **B. A. Nagasampagi,** L. Yankov and Sukh Dev, *Tetrahedron Letters* 1913 (1968).

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[5b] T. D. Hooker, ***The Flora of British India,*** Vol. I, *568 (1875).*

compound (m.p., mixed m.ps, TLC, UV and superimposable IR spectra) with authentic cedrelone (kindly supplied by Prof. R. A. Raphael, Glasgow University, U.K.) confirmed its identity.

The other tetranortriterpenoid, $C_{26}H_{32}O_5$, (M^+ 424), m.p. 216°, $[\alpha]_D$ -55” ($CHCl_3$), λ_{max}^{EtOH} 220 nm (ϵ, 7700) (end absorption) is a new compound and was obtained in the yield of 0.002 per cent. It gave the usual Liebermann-Burchardt colour reaction. The positive Ehrlich’s test and the appearance of bands at 1514 and 875 cm^{-1} in the IR spectrum of the compound suggesting the presence of a furan ring which appears to be mono-/?-substituted as confirmed by the NMR spectrum (two a-furano protons at δ 7·45, 7.42 and one β-furano proton at δ 6·35). The spectrum also discloses the presence of five tertiary C-methyl groups (δ 0·85–1·30, 15H). The compound contains two carbonyl functions, one of which is associated with a diosphenol chromophore (λ_{max}^{EtOH} 276 nm, ϵ, 9400, shifting in alkali to λ_{max} 328 nm, ϵ, 5880; ν_{max}^{Nujol} 1684 and 1610 cm^{-1}) and the other as a six membered cyclic ketone (ν_{max}^{Nujol} 1720 cm^{-1}). The C-17 (furfurylic) and the C-15 protons appear as a two proton multiplet around δ 3·63. Since an AB quartet centered at δ 6·9 and 6·1 is missing in the NMR spectrum, an enone chromophoric system $—CH{=}CH—\underset{|}{C}{=}O$ occurring in cedrelone is absent in this compound.

The above functionalities along with the presence of a C_{26}-carbon skeleton in the molecule and its similar spectral behaviour with cedrelone led us to believe that it is a close relation of cedrelone (M^+ 422) from which it differs only by two mass units. This obviously indicates that the new compound might in all probability be 1,2-dihydrocedrelone. This was finally confirmed by the controlled reduction of cedrelone with sodium borohydride at room temperature.[3] The reaction product, 1,2-dihydrocedrelone, was indeed found identical in all respects with the natural product (m.p., mixed m.ps., superimposable IR and mass spectra). The mass spectral fragmentation pattern is also consistent with this structure (II) for 1,2-dihydrocedrelone.

The third minor compound has the molecular formula $C_{12}H_8O_4$, (M^+ 216), m.p. 188-190” (yield -0.0016 per cent). Its UV spectral data (λ_{max}^{EtOH} 256, 288 and 308 nm) agreed well with that of an authentic sample of bergapten. The identity of this coumarin was finally established by direct comparison (m.p., mixed m.ps, TLC and superimposable IR spectra) with an authentic specimen.

CHEMOTAXONOMIC IMPLICATIONS

The co-occurrence of cedrelone and 1,2-dihydrocedrelone along with bergapten, in the seeds of one variety of *Cedrela toona* is of phytochemical significance. Meliaceous plants are morphologically related to rutaceous species and they are usually put in the same order Rutales. Each of the Rutaceae subfamilies *(Flindersioideae, Rutoideae* and *Aurantioideae*) which is rich in coumarins, also produces the biosynthetically important group of tetranortriterpenoids. There is not yet any record of alkaloid being identified in Meliaceae as has been found in Rutaceae; but the isolation of a coumarin from *Cedrela toona* as well as from the other two species[6,7] belonging to Meliaceae which are known to produce the modified group of tetranortriterpenoids, provides further support of phyllogenetic relation between the two families suggested by Gunderson.[8] The wide disparity between the chemical constituents of the seeds of the two varieties of a single species may be related to

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[6] C. W. L. BEVAN and D. E. U. EKONG, *Chem. Ind. 383 (1965).*

[7] S. P. BASAK and D. P. CHAKRAVARTY, *J. Ind. Chem. Soc. 47, 722 (1970).*

[8] A. GUNDERSON, ***Families of Dicotyledon,*** Waltham, Mass, 150 (1950).

difference in enzymatic reactions controlled by chromosomes which are expected to differ as observed in the different forms of *Ambrosia dumsa* Gray (Compositae)[9] showing difference in chemical constituents.

EXPERIMENTAL

General. All m.ps are uncorrected. The UV spectra were measured in 95 % ethanol (aldehyde-free), the IR spectra in Nujol mull or KBr disc. The analytical samples were dried at 80° over P_2O_5 for 24 hr *in vacuo*. Brockmann alumina was used for column chromatography. Petrol refers to light petroleum (b.p. 60–80°).

Isolation. 1·5 kg of the crushed seeds of C. *toona* (macro variety) were extracted with petrol for 30 hr. The thick extract was chromatographed. The petrol-benzene mixture (1: 1) washings of the column yielded β-sitosterol (50 mg), m.p. 137°, β-sitosteryl acetate, m.p. 122”.

The earlier fractions of benzene–$CHCl_3$ (1: 1) mixture afforded bergapten (25 mg). It crystallized from MeOH, m.p. 188°, (M^+ 216). (Found C, 66.5; H, 3.65. $C_{12}H_8O_4$ requires C, 66.6; H, 3·7%.)

Further washings of the chromatogram with benzene–$CHCl_3$ (1: 3) mixture gave a thick oily mass which upon repeated crystallization from Et_2O–EtOAc (1: 3) afforded cedrelone (I, 100 mg) in prisms; m.p. 208–10°, $[\alpha]_D^{30}$ −65° ($CHCl_3$), ν_{max} (Nujol) 1680 (cyclohexenone), 3300, 1684, 1610 (diosphenol), 1510, 875 (furan) cm^{-1}; NMR signals ($CDCl_3$) at δ 7·36, 7·18 and 6.28 (2α and 1β furano proton), 6·9, 6·1 (1H, quartet each, C-l and C-2 protons), 3.78 (2H, m, C-15 and C-17 protons). (Found: C, 73.0; H, 7·5; 0, 18·5. $C_{26}H_{30}O_5$ requires C, 73·93; H, 7·1; O, 8·97%.) (M^+ 422; peaks at m/e 407, 404, 389, 379, 361, 316, 285, 246, 241, 231, 215, 189, 159, 149, 107 and 81.)

The final elution of the column with $CHCl_3$ furnished 1,2-dihydrocedrelone (II, 40 mg), m.p. 216°, $[\alpha]_D^{30}$ −55·5° ($CHCl_3$), ν_{max} (Nujol) 1720 (cyclohexanone), 1684, 3300 (diosphenol), 1507, 874 (furan) cm-‘, NMR signals ($CDCl_3$) at δ 7.46, 7·42 and 6.35 (2a and 1β furano proton), 3.63 (2H, m, C-15 and C-17 protons). (Found: C, 73.15; H, 7.48; 0, 18.6. $C_{26}H_{32}O_5$ requires C, 73.5; H, 7.5, 0, 19·0%.) (M^+ 424; peaks at *m/e* 409,406, 391, 381, 318,287, 248, 243, 189, 161, 151, 107 and 81.)

1 kg of the finely ground seeds of C. *toona* (small size) were similarly extracted with petrol (b.p. 60–80°) and the extract upon chromatography yielded only β-sitosterol, m.p. 137°, from benzene eluents.

Conversion of cedrelone to ***dihydro cedrelone with $NaBH_4$***. To cedrelone (25 mg) in dry MeOH (3 ml) was added $NaBH_4$ (25 mg) at room temp. and kept overnight. The product after usual work up afforded dihydrocedrelone (II, 20 mg), m.p. (EtOAC) 212-214”. (Found: C, 73.0; H, 7.4; 0, 18·5. $C_{26}H_{32}O_5$ requires C, 73·5; H, 7·5; 0, 19·0%.) (M^+ 424, peaks at *m/e* 409, 406, 381, 318, 287, 248, 243, 189, 161, 151, 107 and 81.) The reaction product was found to be identical with the natural product (m.p., mixed m.ps, TLC and superimposable IR spectra).

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[9] T. A. Geissmann and T. Matsueda, *Phytochem. 7, 1613 (1968).*