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MOLUCCANIN, A COUMARINOLIGNOID FROM *ALEURITES MOLUCCANA*

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Key Word Index—*Aleurites moluccana*; Euphorbiaceae; moluccanin; linear coumarinolignoid.

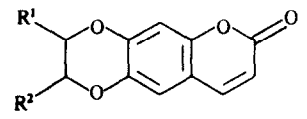
Abstract—A new coumarinolignoid has been isolated from stem chips of *Aleurrites moluccana* and its structure dctermined on the basis of chemical and spectroscopic evidence.

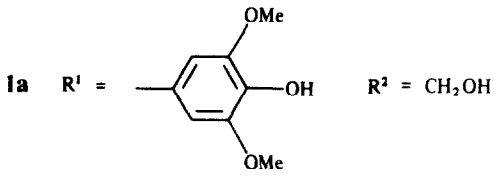
Aleurites moluccana, a member of the family Euphorbiaceae has been attributed with several medicinal properties [1]. Previous work on this plant is confined to the analysis of the drying oil derived from its seed kernels [2].

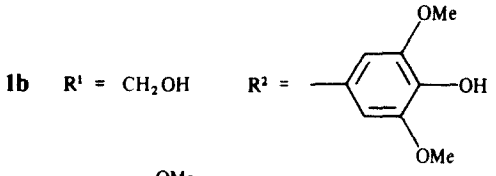
Materials used in this investigation was collected from the campus of the Forest Research Institute, Dehradun,. Chromatography of the ethanol extract yielded several components. Of these, moluccanin was isolated as pale yellow crystals, mp 220°.

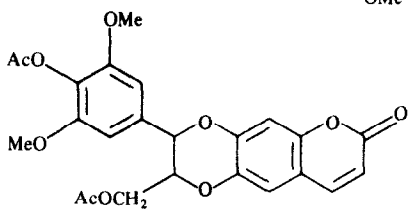
Moluccanin fluoresced blue in UV light and dissolved in aq. KOH from which it would be regenerated. The alkaline solution was yellow and fluorescent. Its ^{1}H NMR spectrum showed two pairs of doublets at δ6.36 and 7.99 (1H each *d*, $J=9$ Hz). The IR spectrum had a prominent band at 1710 cm^{-1}. Moluccanin, therefore, was a coumarin derivative. The $[M]^+$ ion appeared in the mass spectrum at *m/z* 386.0997 defining its composition as $C_{20}H_{18}O_8$. Its ^{1}H NMR spectrum revealed the presence of two methoxyl functions. Three signals appearing at δ3.60(2H, *m*), 4.35(1H, *m*) and 5.11(1H, *d*, $J=8$ Hz) resembled closely those reported for daphneticin [3] and are characteristic of coumarinolignoids. However, the substitution pattern in moluccanin differed from that in daphneticin was revealed by the presence of two 1H singlets appearing at δ7.04 and 7.36 and attributable to H-8 and H-5, respectively. The C_6–C_3 unit was thus attached through oxygens to C-6 and C-7 of the coumarin moiety, which was further demonstrated by the close resemblance of the UV spectrum of moluccanin with that of 6,7-dimethoxy coumarin (λ_{max} 255, 292 and 340 nm) [4]. Identity of the C_6-C_3 unit as sinapyl alcohol was confirmed by the formation of diacetate 2 and the close correspondence in the ^{1}H NMR spectrum of the 2H singlet appearing at δ6.83 with that appearing at 6.81 in the spectrum of daphneticin [3]. Moluccanin was, therefore, formulated as a coumarinolignoid of structure **1a**/**1b**. The mass spectral data was compatible with the postulated structure in that the genesis of all the fragment ions can be rationalized on the basis of the fragmentation pattern proposed for coumarinolignoids [3, 5]. In particular a fragment ion was present at *m/z* 178.0267 ($C_9H_6O_4$), which can be formulated as **3**. The ^{13}C NMR data assignments, which were based on 2D-$^1J_{CH}$ corre lation, also substantiated this formulation.

The $^3J_{CH}$-2D correlation spectrum was determined to enable a choice to be made between structures **1a** and **1b** for moluccanin, but no long distance coupling could be









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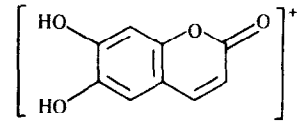

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detected between H-7′ and H-8′ and the ring carbons C-6 and C-7. Coupling constants in such cases have been reported to the order of 1Hz [6], whereas the ^3J effects are detectable only if they are of the order of 5 Hz. However, the structure **1a** could be assigned to moluccanin on the basis of a low power hetero decoupling experiment in which considerable sharpening of the signal at 139.90(C-6) could be observed on irradiation of the H-7′ (4.98) signal.

Moluccanin is an addition to the recently discovered tribe of coumarinolignoids [5], seven of which have been reported so far. Moluccanin is the first member of this series in which the mode of fusion of the nine carbon unit to the coumarin is linear.

Of seven coumarinolignoids reported sor far, three have been isolated from Capparidaceae [5, 7, 8], two from Thymelaceae [3, 9] and one each from Bursaraceae [10] and Euphorbiaceae [11]. Cleomiscosin B has been isolated from two sources in the Simaroubaceae and one in the Sapindaceae [12].

EXPERIMENTAL

Stem chips (4 kg) of *Aleurites moluccana* (Euphorbiaceae) were dried in the shade, cut into small pieces and defatted by refluxing repeatedly with petrol (bp 60–80°). The defatted material was then extracted with hot EtOH and the concd extract chromatographed on a column of silica gel. The column was eluted with C_6H_6 containing increasing proportions of EtOAc. Fractions eluted with C_6H_6–EtOAc (80:20) were combined, solvent dist. off and the residue cryst. from Me_2CO–MeOH to yield **1a**, 220°, (TLC; silica gel; MeOH–$CHCl_3$, 5:95; visualized by fluorescence in UV light). UV λ_{max}^{MeOH} nm; 260, 295 and 340. IR ν_{max}^{Nujol} cm^{-1}; 3520 and 1710. ^1H NMR (DMSO-d_6; 100 MHz); δ 3.60 (2H, *m*, H-9′), 3.85 (6H, *s*, 2 × OMe), 4.35 (1H, *m*, H-8′), 5.11 (1H*d*, J = 8 Hz, H-7′), 6.36 (1H, *d*, J = 9 Hz, H-3), 6.83 (2H, *s*, H-2′ and H-8′), 7.04 (1H, *s*, H-8), 7.36 (1H, *s*, H-5) and 7.99 (1H, *d*, J = 9 Hz, H-4). MS *m/z* (rel. int.); 386.0997 $[M]^+$ (100%), 355.0839 (4.02), 354.0742 (6.23) 353.0633 (6.28), 327.0867 (11.23), 210.0893 (53.31), 192.0784 (85.87), 191.0788 (55.20), 180.0784 (20.13), 178.0267 (16.51), 177.0551 (18.50), 167.0710 (68.05), 154.0632 (16.98), 149.0630 (18.38), 149.0229 (21.06).

Acetylation of compound **1a**. Compound **1a** was acetylated with Ac_2O-pyridine to give **2** and cryst. from MeOH mp 210°. ^1H NMR ($CDCl_3$; 400 MHz); δ 2.08 (3H, *s*, OAc), 2.35 (3H, *s*, OAc), 3.84 (6H, *s*, 2 × OMe), 4.05 (1H, *dd*, J = 4.48, and 12.32 Hz, H-9′), 4.29 (1H, *m*, H-8′), 4.40 (1H, *dd*, J = 3.28, and 12.32 Hz, H-9′), 4.98 (1H, *d*, J = 8 *Hz*, *H*-7′), 6.63 (2*H*, *s*, H-2′ and H-5′), 6.30 (1H, *d*, J = 9.56 Hz, H-3), 6.96 (1H, *s*, H-8), 7.07 (1H, *s*, H-5), 7.60 (1H, *d*, J = 9.56 Hz, H-4). ^{13}C NMR ($CDCl_3$; 100.8 MHz); δ 170.1 (*s*, Me CO O–C–9′), 168.2 (*s*, Me–CO–OC-4′), 160.92 (*dd*, C-2), 152.1 (*br s*, C-3′ and C-5′) 149.3 (*m*, C-9), 146,7 (*m* C-7), 142.70 (*dd*, C-4), 139.90 (*s*, C-6), 132.90 (*s*, C-1′), 129.50 (*s*, C-4′), 114.45 (*d*, C-3), 114.30 (*d*, C-5), 113.20 (*m*, C-10), 105.04 (*d*, C-8), 103.70 (*dq*, C-2′ and C-6′), 77.20 (*br. d*, C-8′), 62.30 (*t*, C-9′), 56.10 (*q* 2 × OMe), 20.50 (*q*, Me–CO–O–C–9), 20.30 (*q*, Me–CO–O–C-4′).

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