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HEUDEBOLIN: A NEW LIMONOID FROM *TRICHILIA HEUDELOTII*

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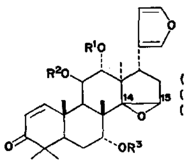
Key Word Index—*Trichilia heudelotii:* Meliaceae; limonoids; heudebolin.

Trichilia heudelotii Planchex Oliv. (Meliaceae) is a small tree which occurs in the West African rain forest area. We have reported the isolation of dregeanin[1] and three other limonoids which we named heudelottins[2,3] -*C* (Ia), -*E* (Ib) and -*F* (Ic) from the timber. We now report the isolation of a new limonoid, heudebolin, for which we suggest the structure (IIb), from the bark.

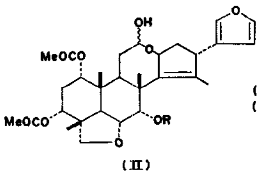
Light petrol. (b.p. 60–80°) extraction of the bark gave a precipitate and some gum. Recrystallization of the precipitate from MeOH gave a compound m.p. 148–150°, M^+ 586 and formula $C_{32}H_{42}O_{10}$. The IR spectrum showed bands indicative of the presence of a hydroxy group (ν_{max} 3450 cm^{-1}) and a β-substituted furan ring (ν_{max} 1500, 873 cm^{-1}). The NMR spectrum, unlike that of the heudelottins, had only four tertiary methyl groups, one of which was a vinyl methyl at δ 1·75. Also, instead of the characteristic 15-H, one proton broad singlet at δ 3·50 (W_H = 2·5 cps) present in the heudelottins, there was a 2H singlet. This meant that heudebolin lacks the 14,15-epoxy group. The NMR further showed the usual β-substituted furan protons as well as signals attributable to three acetates (3H, *s* δ 2·08, 6H, *s* δ 2·00). Apart from the absence of the protons of the cinnamate group and the presence of one more acetate group, the NMR of heudebolin was very similar to that of nimbolin-*B*[4] (IIa), a limonoid isolated from the trunk wood of *Azadirachta indica* L.

On complete alkaline hydrolysis, heudebolin gave an oil which could not be made to crystallize, but was homogeneous on TLC. The IR and NMR of this oil were found to be identical with those of the complete alkaline hydrolysis product of an authentic sample of nimbolin-*B* provided by Dr. C. O. Fakunle of this Department. Heudebolin is thus nimbolin-*B* (IIa) with an acetate group in the 7-position instead of cinnamate and therefore has the structure (IIb).



(I)

(Ia) $R^1 = H$; $R^2 = Bu^sCH(OAc).CO$; $R^3 = Pr^iCH(OH).CO$
(Ib) $R^1 = CHO$; $R^2 = Bu^sCH(OH).CO$; $R^3 = Pr^iCH(OH).CO$
(Ic) $R^1 = CHO$; $R^2 = Bu^sCH(OAc).CO$; $R^3 = Pr^iCH(OH).CO$



(II)

(IIa) R = CO.CH:CHPh
(IIb) R = COMe

EXPERIMENTAL

The bark of *Trichilia heudelotii* from Akure (3 kg) was powdered and extracted with refluxing light petrol. (b.p. 60–80°) giving a gum and some precipitate. The precipitate was recrystallized from MeOH to give

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heudebolin (500 mg) m.p. 148–150°, (Found: C, 65·40; H, 7·19%); M^+ 586. $C_{32}H_{42}O_{10}$ requires: C, 65·51; H, 7·22%).

Hydrolysis of heudebolin. Heudebolin (100 mg) dissolved in 30 ml MeOH and 25 ml 1M NaOH was refluxed for 7 hr, cooled, diluted with H_2O and extracted with Et_2O. Evaporation afforded an oil (55 mg) which could not be crystallized but was homogenous (TLC) and identical with the complete hydrolysis product of an authentic sample of nimbolin-*B* provided by Dr. C. O. Fakunle.

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ALKALOIDS FROM *CORYDALIS AMBIGUA*[*]

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Plant. Corydalis ambigua Cham. et Schlecht. (Japanese name: Ezo-engosaku, Voucher specimen No. 18C on deposit in these laboratories) was collected in May 1967 at Sapporo, Japan. *Previous work.* On tubers.[1,2]

Present work. From the MeOH extract of the tubers (air-dried, 820 g), tertiary non-phenolic base fraction (*Fr. A*, 0·32% yield), tertiary phenolic base fraction (*Fr. B*, 0·07%) and quaternary base fraction (*Fr. C*, 0·16%) were obtained by the method described earlier.[3] The following tertiary alkaloids, including one new alkaloid, were isolated by means of preparative chromatography (column and TLC) from Fr. *A* and *B*; (+)-*corybulbine* (0·035%, m.m.p.), (+)-*corydaline* (0·019%, m.m.p.), (+)-*base II* (0·011%, m.p., IR,[2] NMR[2]), *cavidine*[4] ((±)-base II, 0·001%, m.m.p.), (±)-*tetrahydropalmatine* (0·001%, m.m.p.), *protopine* (0·003%, m.m.p.), α-*allocryptopine* (0·001%, m.m.p.) and (+)-1-*methylcorypalline* (0·001%, new alkaloid, m.p. 156–158°, $[\alpha]_D$ 33·5° (*c* 0·23, $CHCl_3$), 1·0° (*c* 0·23, EtOH). Although (±)-1-methylcorypalline was obtained as a synthetic product,[5] this is the first record of the occurrence of (+)-form as a natural product. Its structure was deduced from the spectral data and confirmed by an alternative synthesis.[6] *Fr. C* was purified by column

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[*] Part XI in the series "Constituents of *Corydalis* Species". For Part X see NARUTO, S. and KANEKO, H. (1972) *Phytochemistry* **11**, 2644.

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