Phytochemistry, 1968, Vol. 7, pp. 1683 to 1686. Pergamon Press. Printed in England

SHORT COMMUNICATION

EXTRACTIVES FROM THE SEED OF *CEDRELA ODORATA* L.

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(*Received* 6 *March* 1968)

Abstract—The seed of *Cedrela odorata* has been examined and found to contain the known limonoids mexicanolide, andirobin and 6-deoxy swietenolide, together with a new compound which has been identified as 6-hydroxy mexicanolide.

Cedrela odorata L. is a valuable timber tree, originating in Central America, but widely planted in tropical regions. It is botanically rather variable, and it has been shown[1,2] that the timber is chemically variable. Nigerian samples have been found to contain mexicanolide (Ia) and 7-deacetyl-7-oxogedunin (II).[1,3] West Indian samples have given methyl angolensate[2] (III). These three compounds are closely related biochemically, and all three may occur together, as in *Khaya grandifoliola*[3,4] and *K. senegalensis.*[5] Zelnik and Rosito have reported that the seed of a Brazilian sample of *C. odorata* contains mexicanolide,[6] but have not investigated the minor constituents. With the approval of Dr. Zelnik, we have now investigated the seed of a Nigerian sample.

Light petroleum extraction gave an oil with some solid material, and this was separated and chromatographed on silica gel; since mexicanolide is often difficult to elute from alumina. Four fractions containing limonoids were obtained, which crystallized from methanol.

The fourth, and major, fraction gave 6-deoxyswietenolide (Ib) m.p. 192–195°, identified by comparison with an authentic sample obtained from the seed of *K. grandifoliola.*[4] This compound is the 3β-alcohol corresponding to the ketone mexicanolide, and can be oxidized to the latter, and prepared from it by borohydride reduction.[7]

The first fraction consisted of andirobin, the second of mexicanolide, both identical with authentic samples, while the third was a new compound, $C_{27}H_{32}O_8$ m.p. 251–254° $[\alpha]_D^{20} = -117°$. The i.r. and NMR spectra of this were very similar to those of mexicanolide, except that it appeared to contain an hydroxyl group of which the base proton absorbed as a singlet at δ 4·63 in deuterochloroform, after shaking with deuterium oxide. The u.v. spectrum showed a maximum at 212 nm, which with alkali rapidly changed to a more intense maximum at 288 nm. This is a very characteristic reaction of mexicanolide, and is due to the fission of

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[1] C. W. L. Bevan, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc.* 980 (1963).

[2] W. R. Chan, K. E. Magnus and B. S. Mootoo, *J. Chem. Soc., C* 171 (1967).

[3] E. K. Adesogan, C. W. L. Bevan, J. W. Powell and D. A. H. Taylor, *J. Chem. Soc., C* 2127 (1966).

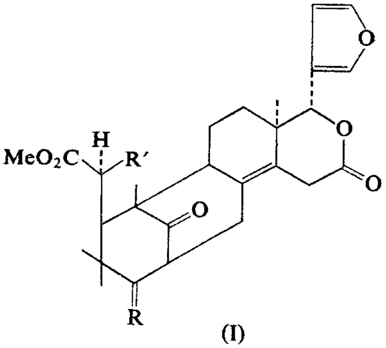
[4] E. K. Adesogan and D. A. H. Taylor, unpublished work.

[5] E. K. Adesogan and D. A. H. Taylor, *J. Chem. Soc.*, in press.

[6] R. Zelnik and C. M. Rosito, *Tetrahedron Letters* **52**, 6441 (1966).

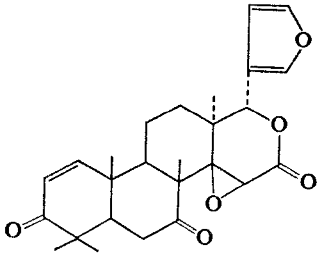
[7] J. D. Connolly, R. McCrindle and K. H. Overton, *Chem. Commun.* 162 (1965).

the ring between C_9 and C_{10}, leading to a compound which is both an enolizable β diketone, and also a diene lactone (IV). It therefore appeared that the new compound was a hydroxy derivative of mexicanolide. Since the proton at the base of the hydroxyl group absorbs as a singlet, it is highly probable that it is at C_6; as in the structure (Ic). It is known that the 6-proton in such a structure absorbs as a singlet, due to its sterically restricted rotation,[5,8,9]

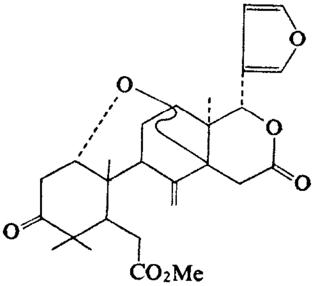


(I)

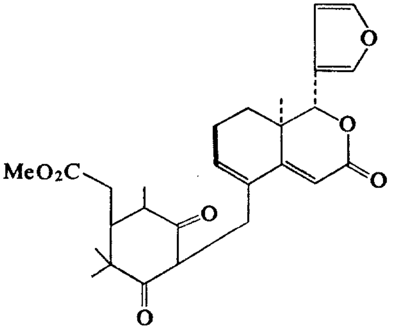
(a) $R=O$. $R^1=H$.
(b) $R=H$, βOH. $R^1=H$.
(c) $R=O$. $R^1=OH$.
(d) $R=H$, βOAc. $R^1=OAc$.



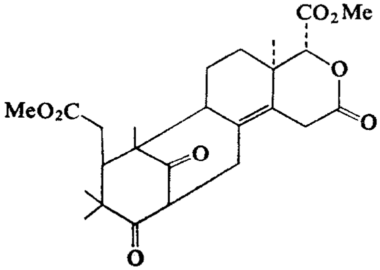
(II)



(III)



(IV)



(V)

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[8] J. D. Connolly, R. Henderson, R. McCrindle, K. H. Overton and N. S. Bhacca, *J. Chem. Soc.* 6935 (1965).

[9] G. A. Adesida, E. K. Adesogan and D. A. H. Taylor, *Chem. Commun.* 790 (1967).

and the only other position in the molecule where a singlet would be expected is H_{15}, where it would interfere with the fragmentation to give (IV). The location of the hydroxyl group at C_6 is supported by the chemical shift of the base proton, which is similar to that in methyl 6-hydroxy angolensate and swietenine, suggesting a location α to the methoxy carbonyl group; and by the characteristic small downfield shift of the methoxy carbonyl group, from δ 3·73 in mexicanolide to δ 3·85 in the present compound. Acetylation gave an amorphous acetate, in which the acetate base proton appeared as a broad singlet at δ 5·51, identical with the position in swietenolide diacetate (Id).[10] The methoxycarbonyl group in the acetate showed a small upfield shift to δ 3·76, which is characteristic of 6-acetylation.

We thus consider that our new compound is 6α-hydroxy mexicanolide (Ic) which is the 3-ketone corresponding to the 3β hydroxy compound swietenolide.[11] This structure is also supported by the positions of the tertiary methyl groups in the NMR spectrum, which show characteristic shifts on the introduction of the 6-hydroxyl group and on its acetylation.[5]

These absorptions and our assignments are shown in the table; analysis of the shifts by the same procedure as we used in the case of the similar methyl angolensate derivatives[5] suggests that they are compatible with the 6α configuration, although the analysis is more complex in the present case due to possible changes in the shape of the molecule, and correspondingly less certain. This is the same configuration as in swietenine and methyl 6-hydroxy angolensate; the convention is that proposed in our earlier paper.[5]

METHYL SHIFTS IN MEXICANOLIDE DERIVATIVES IN c/s AT 60 mc/s (IN DEUTERIOCHLOROFORM, WITH T.M.S. AS INTERNAL STANDARD)

Methyl group at	4α	4β	10	13
Mexicanolide aetio ester (V)	61	76	52	66
Mexicanolide	60	75	53	60
6α hydroxy mexicanolide	62	93	70	60
6α acetoxy mexicanolide	65	75	68	60

Since ring A is inverted in mexicanolide, the 4β methyl group is now considered to be that on the α face of the molecule.

It is interesting that we did not find the acetate of 6-deoxy swietenolide in these seeds, as it has previously appeared a more common compound, being the main limonoid of the seeds of *Khaya grandifoliola*[12] and of *Cedrela fissilis*.[6] Examination of specimens of *Cedrela odorata* seed from other areas would be of considerable interest.

EXPERIMENTAL

Extraction

The minced seeds (450 g) were extracted in a Soxhlet with boiling light petroleum (b.p. 60–80°). The extract was concentrated and the gummy solid (28 g) separated. This (7 g) was chromatographed over silica gel; eluting with mixtures of ether and light petroleum. The first fractions remained oily, 30 per cent of ether eluted andirobin (7 mg) m.p. 195–198°; identical in i.r. and mass spectra with an authentic sample provided

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[10] Dr. J. D. CONNOLLY, personal communication.

[11] J. D. CONNOLLY, R. MCCRINDLE, K. H. OVERTON and W. D. C. WARNOCK, *Tetrahedron Letters* 2937 (1965).

[12] E. K. ADESOGAN and D. A. H. TAYLOR, *Chem. Commun.* 225 (1967).

by Professor W. D. Ollis. 35 per cent of ether eluted mexicanolide (Ia) (60 mg.), m.p. 226–230°. Eluates containing 50 per cent of ether gave 6α hydroxy mexicanolide (Ic) (90 mg) m.p. 251–254°, $[\alpha]_D^{20} = -117°$. (Found C, 66·9; H, 6·9; M^+ 484; $C_{27}H_{32}O_8$ requires C, 66·9; H, 6·7 per cent). Finally, further elution with 50 per cent of ether gave 6-deoxy swietenolide (Ib), (300 mg) m.p. 192–195°. Further elution did not give more limonoids. Acetylation of 6α hydroxy mexicanolide in the usual way gave an acetate, which did not crystallize, but gave the anticipated NMR spectrum, discussed in the text.