of Washington Arboretum in Seattle, Washington, and the U.S. National Arboretum in Washington, D.C. Ripe fruits were obtained from the U.S. National Arboretum.

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THE STRUCTURE OF AN EXTRACTIVE FROM *KHAYA IVORENSIS*

DAVID A. H. TAYLOR

Department of Chemistry, University of Natal, Durban 4001, Republic of South Africa

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Key Word Index—*Khaya ivorensis*; Meliaceae; limonoid; Baeyer–Villiger oxidation.

INTRODUCTION

The timber of *Khaya ivorensis*, the most important West African mahogany, on extraction with petrol gives a solid fraction (up to 0.1%), 90% of which is khivorin (**1**).

In an exhaustive investigation of the mother-liquors from recrystallisation of a large amount of khivorin, we found that the second most plentiful limonoid was methyl angolensate (**2**), the remainder of the material consisted of 7-deacetylkhivorin and other deacetylated khivorin derivatives, derivatives of swietenolide (**3**) acylated at the 3-hydroxyl with a range of aliphatic acids, fissinolide (**4**), and methyl ivorensate (**5**), which we partially synthesised by the Baeyer–Villiger oxidation of methyl angolensate [1].

Extraction of one sample of rootbark gave a similar mixture containing only small amounts of khivorin, from which we isolated methyl angolensate, 2-hydroxyfissinolide (**6**), 7-deacetoxy-7-oxogedunin (**7**),3-deacetyl khivorin and methyl 6-hydroxy angolensate. This result was repeated with other samples of rootbark. Extraction of a second sample of rootbark gave 2-acetoxyfissinolide, mexicanolide (**8**), the Baeyer–Villiger oxidation product of mexicanolide (**9**), and a substance which we named compound E (300 mg) of which the structure was undetermined. In spite of many efforts we have been unable to repeat this extraction, and no further supplies of compound E have been obtained. The present paper records the structural elucidation of compound E.

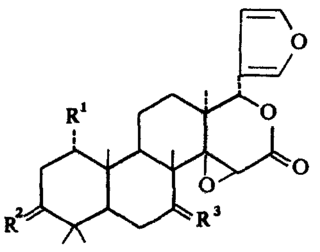
RESULTS AND DISCUSSION

Compound E, mp 172° $[\alpha]_D - 22°$, had the formula $C_{29}H_{36}O_{11}$[1]. The PMR spectrum was similar to that of the mexicanolide group of limonoids, showing four tertiary methyl groups, a carbomethoxy group, and a furan ring. The IR spectrum showed a carbonyl band at 1780 cm^{-1}, which we initially interpreted [1] as being due to a five-membered lactone ring. Chemically, compound E proved to be rather intractable. Oxidation with Jones' reagent gave a crystalline ketone, but this was the only crystalline derivative obtained. Compound E was very sensitive to alkali, refluxing with 2N NaOH destroyed it entirely, while mild hydrolysis with cold alkali gave a mixture which appeared not to be very complex, although we were unable to obtain any pure products from it. Acetylation with acetic anhydride in pyridine, or refluxing with methanolic sulphuric acid, produced no change. Since we were unable to construct any formula related to mexicanolide which would fit the spectral data, and had exhausted the material available, we gave up the problem at that time.

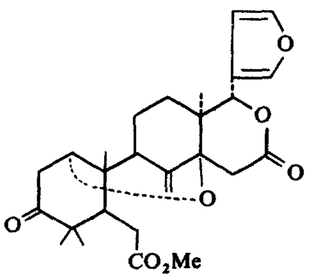
Very recently [2], we have discovered other limonoids with a carbonyl absorption at 1787 cm^{-1}, which we were able to show was due to a strained 6-membered lactone ring. With this in mind, we have reconsidered the data relating to compound E, which is now found to admit a rather simple solution.

The PMR spectrum (100 MHz in $CDCl_3$, TMS standard) shows that compound E contains an acetoxy group, a furan ring, a carbomethoxy group, a secondary hydroxyl and a tertiary hydroxyl group. This accounts for seven of the eleven oxygen atoms. It is highly probable that two more are present in the usual ring D lactone, with a double bond present in the C-8, C-14 position as in swietenolide and mexicanolide. This follows from the normal appearance of a singlet at δ 5.63, which we attribute to H-17, and the presence of an isolated pair of doublets (J = 18.5 Hz) at δ 3.10, 2.75, which are characteristic of 2H-15 in fissinolide and related compounds. The large coupling constant is particularly characteristic. The remaining two oxygen atoms can be located in the second lactone, responsible for the IR absorption at 1780 cm^{-1}. The proton adjacent to the secondary hydroxyl appears as a quartet at δ 4.23, collapsing to a doublet (J = 10 Hz) in the presence of D_2O. This residual doublet is coupled to another at δ 2.49, which is not further coupled. This can be tentatively ascribed to a hydroxyl at C-6, as in swietenolide, although the coupling is much higher than normal. The assignment is supported by the chemical shift of the carbomethoxy group (δ 3.82), which may be compared with that in swietenolide (δ 3.85) and fissinolide (δ 3.76). This downfield shift due to 6-hydroxylation, although small, has been found to be consistent. The assignment is confirmed by chromic acid oxidation of compound E to the corresponding ketone, which has a very similar PMR spectrum, except that the secondary hydroxyl resonances are missing, while the carbomethoxy resonance is shifted to δ3.91. This is in agreement with the production of a 6-ketocompound; cf. the 6-ketone from destigloyl swietenine, δ (COOMe) 3.91 [3].

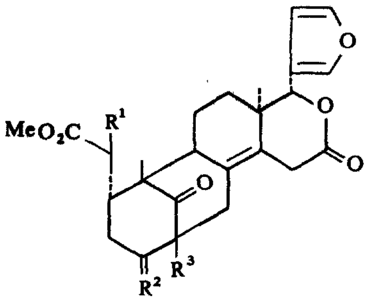
The acetoxy group in compound E may be supposed to be present at C-3, as in fissinolide and many other compounds. In such compounds, H-3 gives rise to a doublet (J = 10 Hz) at about δ 5. This is not found in the spectrum of compound E, in its place is a sharp singlet at δ 5.38. The presence of this singlet, together



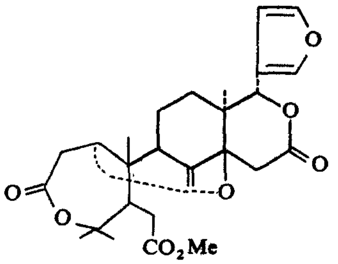
(1) R^1, R^2, R^3 = αOAc
(7) $\Delta^{1,2}, R^1$ = H, R^2, R^3 = O.



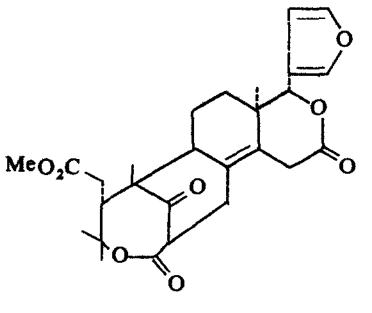
(2)



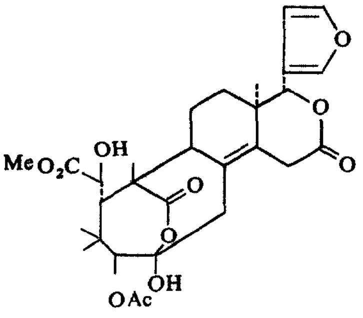
(3) R^1, R^2 = OH, R^3 = H
(4) R^1, R^3 = H, R^2 = OAc
(6) R^1 = H, R^2 = OAc, R^3 = OH
(8) R^1, R^3 = H, R^2 = O



(5)



(9)



(10)

with a tertiary hydroxyl group, suggests that the tertiary hydroxyl group is at C-2, causing H-3 to resonate as a singlet, as in 2-hydroxy fissinolide, which occurs in the same plant. The chemical shift ascribed to H-3 is unusual; in 2-hydroxy fissinolide it is at δ 5.1, whereas in 2-acetoxy fissinolide it is at δ 5.51; the extra deshielding by the acetate accounts for the extra shift in the latter case.

To summarise, the evidence so far quoted above is in agreement with the structure of 2-hydroxyswietenolide 3-acetate, with the exception that the 5–6 coupling is unusually high, the resonance of H-3 is unusually far downfield, and that there is an extra oxygen atom. The IR spectrum of compound E in $CHCl_3$ shows no ketonic carbonyl near 1710 cm^{-1}, as found in swietenolide, but two lactone, or ester, absorptions near 1740 cm^{-1}, which can be attributed to the methyl ester and the ring D lactone, and the 1780 cm^{-1} absorption. It seems therefore that the C-1 carbonyl is missing, and is replaced by a lactone.

The conclusion therefore is that compound E is the Baeyer–Villiger oxidation product of 2-hydroxy swietenolide 3-acetate. Since two ring A lactones have already been isolated from this plant, methyl ivorensate and the Baeyer–Villiger product of mexicanolide, this conclusion is not surprising.

There remain two possible structures, that in which the oxygen is inserted between C-1 and C-2, and that in which the oxygen is inserted between C-1 and C-10. Two lines of evidence show that the former is correct. Firstly, the attachement of a lactone oxygen to C-2 explains the downfield position of H-3; secondly if the lactone oxygen were attached at C-10, the resonance of the 10-Me group would be shifted downfield by some 20 Hz (cf. methyl ivorensate and mexicanolide Baeyer–Villiger product in ref. [1]). In swietenolide diacetate, the 10-Me group resonates at 70 Hz [4], whereas those in compound E resonate at 52, 61, 75 and 76 Hz. Whichever of these is to be assigned to Me-10, it is not shifted downfield by any significant amount.

Compound E is thus represented by the formula (**10**), with a lactone between C-1 and C-2. The unusual coupling constant of 10 Hz between H-5 and H-6 can be explained by the expansion of ring A from a 6- to a 7-membered ring. The consequent ring buckling alters the position of C-4 considerably and reduces the steric crowding of C-6 and C-7, allowing much greater mobility to the side chain. The IR absorption of the ring A lactone at 1780 cm^{-1} is presumably due to the bridged nature of the 7-membered lactone ring, with some consequent steric strain, as in the other cases we have reported [2].

The structure **10** explains the instability of compound E to alkali, the 7-membered lactone ring would be expected to open easily, giving an α-acetoxy ketone which may then hydrolyse and undergo isomerisation to give a mixture of the four possible isomeric ketols. The inactivity to pyridine and acetic anhydride is also explained, since a 6-hydroxy group is known to be sterically hindered to acetylation.

Compound E was isolated with di-isopropyl ether, and the possibility occurred to us that it might be an artefact produced by oxidation of the natural 2-hydroxy fissinolide with peroxide accidentally present in the ether; in this case the accompanying Baeyer–Villiger product of mexicanolide would also be an artefact. This still remains possible, although it does not explain the presence of the 6-hydroxy group in compound E. Attempts to oxidise 2-hydroxy fissinolide with peroxides in di-isopropyl ether, or in other ways, have proved unavailing, while if compound E is an artefact, it must be produced by a high-yield reaction in order to give the amount obtained from the probable amount of precursor present.

Although the matter is not settled, we favour the view that compound E is not an artefact and this would not be the first case in which rare natural products have been found difficult to obtain again.

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3-KETOSTEROIDE IN SOJA-SUSPENSIONSKULTUREN

NIKOLAUS WEBER

Bundesanstalt für Fettforschung, D-4400 Münster (Westf.), Germany

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Key Word Index—*Glycine max*; Leguminosae; suspension culture; 3-ketosteroids.

Abstract—The following steroids were found in soybean suspension cultures: ergost-4-en-3-one, stigmast-4-en-3-one, stigmasta-4, 22-dien-3-one, ergost-4-en-3, 6-dione, stigmast-4-en-3, 6-dione and stigmasta-4, 22-dien-3, 6-dione.

EINLEITUNG

Typische und wohlbekannte Produkte des Sterolstoffwechsels höherer Pflanzen und deren Zellkulturen sind Sterole, Sterylester, Sterylglykoside und acylierte Sterylglykoside [1, 2]. Über Ketosteroide mit Δ^4-3-on- und Δ-3,6-dion-Struktur sowie intakter Seitenkette in Geweben höherer Pflanzen und in pflanzlichen Zellkulturen ist dagegen nur wenig bekannt [3–15]. So