prepared from the compound (**1a**) by reduction with $LiAlH_4$ followed by acetylation was identical (mmp, co-TLC and MS) with the authentic sample [5], provided by Dr. (Miss) W.H. Hui.

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SAPONINS AND TRITERPENES FROM *ILEX OPACA*

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Key Word Index—*Ilex opaca*; Aquifoliaceae; holly; saponins; triterpenes; oleanolic acid; ursolic acid; nonacosane.

INTRODUCTION

The presence of tannins and a possible glucoside in the leaves of *Ilex opaca* has been documented [1]. The dried and powdered emulsion layer resulting after shaking a leaf and berry infusion with $CHCl_3$ was reported to have the pharmacological properties of digitalis [2]. Several sugars have been identified in leaf extracts and inositol has been isolated from the unripened fruit [3, 4]. Phytochemical classes isolated or detected in other members of the genus *Ilex* include: polyphenols, saponins, triterpenes, sterols, and alkaloids [5].

RESULTS AND DISCUSSION

An examination of *I. opaca* for toxic principles revealed the presence of saponins in both leaf and fruit extracts. An EtOH leaf extract, prepared from material previously extracted with hexane and $CHCl_3$, was consistently lethal (death within 24 hr) to mice when injected intraperitoneally in doses of 500 mg/kg and hemolytic to human erythrocytes. Similar extracts from the ripe fruits were not toxic upon injection using doses of 1000 mg/kg, but EtOH extracts were hemolytic to red blood cells. Hemolytic indices [6] of both EtOH extracts were comparable to those obtained from identical concentrations of digitonin. Acidic hydrolysis of a portion of the toxic EtOH leaf extract after subsequent purification procedures [7] resulted in the isolation of 380 mg (0.072% yield) of oleanolic acid which was characterized as its acetate derivative (mp 263–264°, mmp 263–266°, ref. mp 264–266°, IR, NMR, MS). PLC (SGPF 254: $CHCl_3$–MeOH–H_2O, 13:6:2, lower phase) of another portion of the toxic EtOH leaf extract resulted in the isolation of a crude saponin (mp 126–133°) which was not toxic upon intraperitoneal injection at doses of 1000 mg/kg, but which was hemolytic to erythrocytes. TLC after acidic hydrolysis of this amorphous saponin demonstrated it to be a glucosidic mixture containing three unidentified aglycones.

A nontoxic (1000 mg/kg) and amorphous hexane extract of leaf material yielded 40 mg (0.12% yield) of mostly nonacosane (mp 63–64°, lit. mp 64°, IR, MS, 77.9% nonacosane as demonstrated with GLC) after column chromatography on Si gel and elution with $CHCl_3$–C_6H_6(1:1).

A purification [7] of a portion of a nontoxic (1000 mg/kg) Et_2O extract from ripe holly fruits resulted in the isolation of 185 mg (0.009% yield) of ursolic acid (mp 283–285°, mmp 282–284°, ref. mp 282–284°, IR, MS).

I. opaca has a long, confused, and, perhaps, unjustified reputation as a dangerous plant [8, 9]. However, teas prepared from holly leaves are reported to be beneficial and pleasant to the taste [10]. As examined by us, successive hexane, $CHCl_3$, EtOH, and H_2O extracts of the ripe fruits did not exhibit signs of acute toxicity when injected into mice and observed for 24 hr. A leaf toxin is present in EtOH extracts, but its characterization was not accomplished. However, the presence of saponins was demonstrated, and this could explain at least part of the toxicity of the leaf extracts. Potential harm from these compounds in humans is questionable [11]. The hemolysis of erythrocytes by EtOH extracts of holly leaves and fruits may be attributable to the saponin content; however, this activity is not usually associated with oral ingestion [12].

EXPERIMENTAL

Plants. Leaves and ripe fruits of American holly, *Ilex opaca* Ait. Authentic leaf material was obtained from the University

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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*

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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