

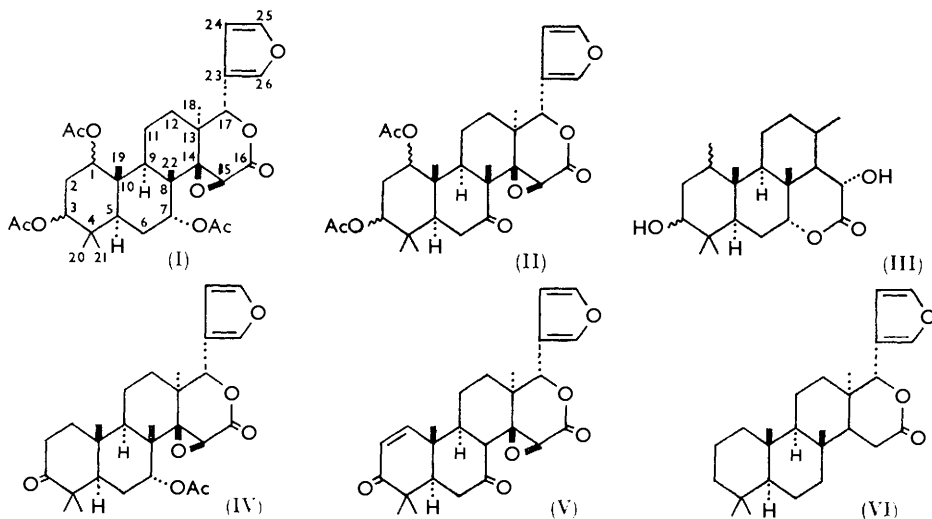
180. *West African Timbers. Part VI.*¹ *Petroleum Extracts from Species of the Genera Khaya, Guarea, Carapa, and Cedrela.*

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Heartwood timbers of the four West African species of the genus *Khaya*, two of the genus *Guarea*, and one each from the genera *Carapa* and *Cedrela* have been examined. Six new substances have been isolated, which are related to those previously isolated from other members of the same family.

THE genus *Khaya* is a main source of West African mahogany. We have examined authentic samples of the heartwood timber of all four species, obtained by courtesy of the Federal and Regional departments of forestry. *K. anthotheca* has given a substance $C_{28}H_{32}O_7$, which we name anthothecol, recognised as a diosphenol by its spectral properties. Structural diagnosis of this will be reported separately.² Extraction of *K. grandifoliola* gave khivorin (I), previously obtained from *K. ivorensis* and already described.¹

The fourth species, *K. senegalensis*, has proved to be variable. Extraction of specimens obtained from Jos, in Northern Nigeria, gave a substance melting indefinitely at about 100°, of which the analysis agrees best with the formula $C_{34}H_{50}O_9$. Spectral investigation shows the presence of a furan ring, and probably a saturated ketone and lactone or ester groups. Further investigation of this substance is being made. *K. senegalensis* obtained from a plantation of the Western Nigeria Department of Forest Research, in a wetter area out of its normal range, gave a different substance, $C_{30}H_{38}O_9$, m. p. 226—228°. It is not known whether this variation is due to genetic differences or to climatic or other changes between the two areas of growth. The spectral properties and analysis of this material together with the fact that it was not profoundly altered by alkaline hydrolysis and therefore did not contain a 7 α -hydroxyl group, suggested that it might be 7-deacetoxy-7-oxokhivorin (II), and this was confirmed by a partial synthesis.



Treatment of khivorin (I) with methanolic sodium methoxide solvolysed the acetate groups. It is remarkable that this treatment does not bring about the merolimonol type of transformation³ to give khivol¹ (III), which has now been found to be specifically

¹ Part V, Bevan, Halsall, Nwaji, and Taylor, *J.*, 1962, 768.

² Bevan, Rees, and Taylor, following paper.

³ Melera, Schaffner, Arigoni, and Jeger, *Helv. Chim. Acta*, 1957, **40**, 1420

catylsed by hydroxide ion. It was known from our earlier work⁴ that the 7-hydroxyl group is resistant to acetic anhydride and pyridine, consequently it was expected that re-acetylation of deacetykhivorin and oxidation of the product by chromic acid would give the required compound. This proved to be the case.

Two species of the large genus *Guarea* are of commercial importance in Nigeria, and we have examined both. *G. cedrata* (two specimens, Forest Herbarium Ibadan numbers 51349 and 51350) gave much oil, but the only solid isolated was β -sitosterol. *G. thompsonii* gave dihydrogedunin (IV), identical with a sample obtained by hydrogenating gedunin from *Entandrophragma angolense*.

The genus *Cedrela* does not occur naturally in West Africa but one species, *C. odorata*, the West Indian Cedar, is cultivated. This also proved to be variable. All specimens examined gave two substances A and B, but the relative amounts varied widely. Substance B is very easily hydrolysed by alkali, which leaves A unchanged; the latter was recognised as deacetoxy-7-oxogedunin (V), prepared earlier from gedunin by Mr. A. Akisanya in this laboratory. The isolation of compound B was based on its failure to react with hydroxylamine [substance (V) reacts readily to give a non-crystalline product]. Compound B had m. p. 228—232° and the formula $C_{27}H_{32}O_7$ and is under investigation.

Carapa procera, the only West African species of this genus, is a smaller tree, not commercially useful. Extraction of the timber gave crystals, m. p. 180—210°, which on chromatography gave the last-mentioned substance B as major constituent.

As we have now isolated^{1,4} a number of compounds containing the same nucleus from various species of the Meliaceae, we propose that the hypothetical parent substance (VI) should be known as meliacin. Khivorin (I) would then have the systematic name 1 ξ ,3 ξ ,7 α -triacetoxy-14 β ,15 β -epoxymeliacin, and the new substance (II) from *Khaya senegalensis* would be 1 ξ ,3 ξ -diacetoxy-14 β ,15 β -epoxy-7-oxomeliacin.

EXPERIMENTAL

Products from Khaya anthotheca.—The finely ground heartwood (Forest Herbarium Ibadan No. 24,333) was percolated with refluxing light petroleum (b. p. 60—80°). Concentration of the extract gave a resin which crystallised from methanol to give *anthothecol* (0.03%). Recrystallisation from chloroform-methanol gave crystals, m. p. 225°, $[\alpha]_D^{20} - 63^\circ$ (in $CHCl_3$) (Found: C, 69.9, 70.0; H, 6.8, 6.8; OAc, 8.35. $C_{28}H_{32}O_7$ requires C, 70.0; H, 6.7; 1OAc, 8.95%), λ_{max} 219 (log ϵ 4.03), 281 $m\mu$ (log ϵ 3.97) in methanol, shifted in alkali to 224 (log ϵ 3.92), 326 $m\mu$ (log ϵ 3.67), ν_{max} (in Nujol) 3400, 1740, 1670, 1655, 1620, 1235, 877 cm^{-1} .

Product from Khaya grandifoliola.—Finely ground heartwood (Forest Herbarium Ibadan No. 42,782) was extracted as above. Crystallisation of the extract from methanol gave khivorin (I) (0.015%) as prisms, m. p. 257°, $[\alpha]_D^{20} - 42^\circ$ (in $CHCl_3$) (Found: C, 65.6; H, 6.9; O, 27.9. Calc. for $C_{32}H_{42}O_{10}$: C, 65.5; H, 7.2; O, 27.3%). The mixed m. p. with the previous sample showed no depression, and the infrared spectra of the two samples in Nujol were identical.

Products from Khaya senegalensis.—*Type A*. Extraction of this timber gave a gum. Chromatography on neutral alumina and elution with benzene-chloroform gave a fraction crystallising from methanol to give *compound A* (0.004%) as prisms, melting rather indefinitely at 88—100° and having $[\alpha]_D^{21} - 139^\circ$ (in $CHCl_3$). Rechromatography raised the m. p. towards the higher end of the range, but did not substantially alter the spectrum or optical rotation (Found: C, 67.9, 68.5; H, 8.4, 8.4; O, 23.8. $C_{34}H_{50}O_9$ requires C, 67.75; H, 8.4; O, 23.9%). λ_{max} were 208 (log ϵ 4.11) and 284 $m\mu$ (log ϵ 1.84) in methanol, and ν_{max} (in Nujol) 1725, 1710, 877 cm^{-1} .

Type B. Extraction of this type (Forest Herbarium Ibadan No. 51,590) gave a gum which crystallised from methanol, yielding *7-deacetoxy-7-oxokhivorin* (II) (0.04%) as prisms, m. p. 228—230°, $[\alpha]_D^{20} - 106^\circ$ (in $CHCl_3$) (Found: C, 66.4; H, 7.1; O, 26.5. $C_{30}H_{38}O_9$ requires C, 66.4; H, 7.1; O, 26.5%), λ_{max} 213 (log ϵ 3.89), 282 $m\mu$ (log ϵ 1.82) in methanol.

Triacetylkhivorin.—Khivorin (12 g.) was added to a solution from sodium (0.5 g.) in dry

⁴ Akisanya, Bevan, Halsall, Powell, and Taylor, *J.*, 1961, 3705.

methanol (250 ml.) and the suspension refluxed for 3 hr., during which it dissolved. The solution was acidified, diluted with water, and extracted with chloroform, and the extract was evaporated. The partly crystalline residue was chromatographed on alumina (type H; 300 g.). Chloroform eluted partly deacetylated material, chloroform-methanol eluted *trideacetyl-khivorin* (3.8 g.) as needles, m. p. 327—330° (Found: C, 67.6; H, 7.8. $C_{26}H_{36}O_7$ requires C, 67.8; H, 7.9%). This (0.5 g.) was treated with acetic anhydride and pyridine, and the crude crystalline product was oxidised with 8*N*-chromic acid (*ca.* 1 ml.) in acetone. The product was isolated with ether. Crystallisation from ether gave 7-deacetoxy-7-oxokhivorin (II) (400 mg.), m. p. 225—227°. The infrared spectrum in Nujol was identical with that of material isolated from *Khaya senegalensis*.

Product from Guarea thompsonii.—This timber (Forest Herbarium Ibadan No. 51,346) was extracted as usual. Crystallisation of the extract from methanol gave dihydrogedunin (IV) (0.03%) as prisms, m. p. 236°, $[\alpha]_D^{20} + 8^\circ$ (in MeOH). The material was compared with a specimen prepared by the hydrogenation of gedunin.⁴ There was no depression in mixed m. p. and the infrared spectra in Nujol were identical.

Products from Cedrela odorata.—The timber (Forest Herbarium Ibadan No. 53,127) was extracted as usual. The extract gave colourless crystals (0.1%), m. p. 199—201°, from methanol. A sample of these (5 g.) was dissolved in boiling methanol (500 ml.), and 2*N*-aqueous sodium hydroxide (50 ml.) was added. After refluxing 10 min. the solution was diluted with water (500 ml.) and acidified with dilute sulphuric acid. Extraction with chloroform and crystallisation of the product from benzene-light petroleum (b. p. 60—80°) gave *deacetoxy-7-oxogedunin* (V) (0.66 g., 13%), colourless prisms, m. p. 262—265° (Found: C, 71.0; H, 6.8. $C_{26}H_{30}O_6$ requires C, 71.2; H, 6.9%), $[\alpha]_D^{20} - 50^\circ$ (in $CHCl_3$). Some extractions gave products containing up to 80% of this substance, which was then separable directly by crystallisation.

A further sample (2 g.) was dissolved in boiling methanol (200 ml.) and treated with hydroxylamine hydrochloride (5 g.) and sodium acetate (5 g.) in water (30 ml.). After refluxing for 15 min. the solution was diluted with water (700 ml.) and filtered; the solid crystallised from methanol to give *substance B* (0.6 g. 30%) as crystals, m. p. 228—232° (Found: C, 69.4, 69.1; H, 6.9, 7.0; O, 23.7. $C_{27}H_{32}O_7$ requires C, 69.2; H, 6.9; O, 23.9%), $[\alpha]_D^{20} + 41^\circ$ (in $CHCl_3$).

Deacetyl-7-oxogedunin.—Deacetylgedunin⁴ (1 g.) in acetone (25 ml.) was treated with 8*N*-chromic acid (1.2 ml.) and set aside for a few minutes. Ethanol was added, and the solution filtered and diluted with water. The precipitate was collected and recrystallised from acetone, to give deacetoxy-7-oxogedunin (910 mg.), prisms, m. p. 262° (Found: C, 71.3; H, 7.0%), $[\alpha]_D^{20} - 53^\circ$ (in $CHCl_3$). The two specimens showed no depression in mixed m. p., and the infrared spectra in Nujol were identical.

Products from Carapa procera.—The timber (Forest Herbarium Ibadan No. 50,165) was extracted as usual. The extract crystallised from methanol, to give a substance (0.06%) of which different samples melted between 180° and 210°. The infrared spectrum was similar to that of substance B from *Cedrela odorata* and rapid chromatography of a sample (1 g.; m. p. *ca.* 200°) gave a pure specimen (800 mg.), m. p. 226—228°, which gave no depression in mixed m. p. with the substance from *Cedrela odorata* and had an identical infrared spectrum in Nujol. On longer contact with alumina, the yield was less. Extraction of the bark carried out in the same way gave a material which was chromatographed on alumina. Benzene-chloroform mixtures eluted a substance (0.02%) which crystallised from methanol in prisms, m. p. 282—284° (Found: C, 58.2; H, 6.6%), $[\alpha]_D^{23} = -40^\circ$.

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