720. *West African Timbers. Part IV.*[1] *Some Reactions of Gedunin.*

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Some reactions of gedunin are described, and it is shown that they are explained by a structure (II) similar to that recently proved for limonin.

Recently we described[1] the isolation of gedunin from the timber of *Entandrophragma angolense*. The formula $C_{28}H_{34(36)}O_7$ was assigned to this compound, and it was shown that on hydrogenation over palladised charcoal it gave a dihydro-derivative, which we have also obtained as a natural product from several timbers.[2] It was also shown that on steam-distillation from alkali gedunin gave furan-3-aldehyde which was isolated as its dinitrophenylhydrazone. The reactions now described indicate that the formula is $C_{28}H_{34}O_7$.

Gedunin shows absorption maxima in the ultraviolet ($\lambda_{max.}$ 215 and 335 mμ, log ε 4·12 and 1·8) and in the infrared region (1668 cm.$^{-1}$) consistent with the presence of an αβ-unsaturated ketone group, and gives a red dinitrophenylhydrazone. The spectrum of dihydrogedunin does not show these characteristics, but has a new band at 1709 cm.$^{-1}$, suggesting that it is the corresponding saturated ketone. The maximum at 215 mμ is due to absorption by both the αβ-unsaturated ketone group and the furan ring. When the spectrum of dihydrogedunin, which still has the furan ring ($\nu_{max.}$ 1502 and 875 cm.$^{-1}$), is subtracted from that of gedunin, the maximum for the unsaturated ketone appears at 227 mμ (log ε 4·0). The maximum of cholest-1-en-3-one is at 230 mμ (log ε 4·0).

The molecular-rotation difference between gedunin and dihydrogedunin is −173°, in agreement with the change of −162° between 1,2-dehydrohinokione and hinokione, a 3-oxo-diterpene.[3] (In ref. 1 the rotation of gedunin and of dihydrogedunin is given with the wrong sign, as − instead of +). Reduction of gedunin with sodium borohydride gave an alcohol which on re-oxidation with chromic acid in acetone[4] gave dihydrogedunin. The molecular-rotation difference between dihydrogedunin and the borohydride reduction product was −110°, in agreement with the change of −85° between β-amyrone and β-amyrin. This unusual reduction of an unsaturated ketone to the corresponding saturated alcohol has been reported by Albrecht and Tamm[5] in the case of cholest-1-en-3-one, and we consider that the evidence suggests that gedunin is a 3-oxo-Δ^1-triterpene derivative. Further evidence on this is described below.

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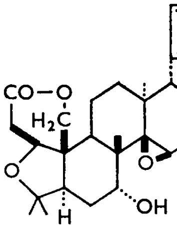
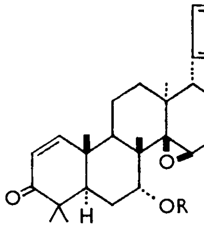
[1] Part III, Akisanya, Bevan, Hirst, Halsall, and Taylor, *J.*, 1960, 3827.
[2] Unpublished work.
[3] Personal communication from Dr. Yuan-Lang Chow.
[4] Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548.
[5] Albrecht and Tamm, *Helv. Chim. Acta*, 1957, **40**, 2217.

Hydrolysis of gedunin under mild conditions gives an alcohol, deacetylgedunin, unaffected by acetic anhydride and pyridine, but giving gedunin on treatment with acetic anhydride and toluenesulphonic acid. This suggests that gedunin is the acetate of a tertiary or sterically hindered secondary alcohol. The molecular-rotation change of —118° between deacetylgedunin and gedunin is similar to the increment of —84° accepted for acetylation of the hindered axial 7α-hydroxy-group in a steroid.

The most remarkable feature of the chemistry of gedunin is the alkaline hydrolysis leading to the production of furan-3-aldehyde. This is reminiscent of the chemistry of limonol,[6] and it seems a reasonable hypothesis that the same structural element is responsible for this change in both cases. For limonol (I) it has been shown [7] that the 7α-hydroxy-group, the ethylene oxide ring, and the lactone are all involved in the reaction. If we suppose that this element is present in gedunin, and add an unsaturated ketone group in ring A of a triterpene nucleus, we arrive at the structure (II; R = H) for deacetylgedunin, gedunin itself being the 7-acetate (II; R = Ac), in agreement with the results of mild hydrolysis. The molecular-rotation change between limonol and its acetate is —72°. Gedunin is therefore of the limonin group, being at a lower oxidation level than limonin (III) itself.[7]



(I)



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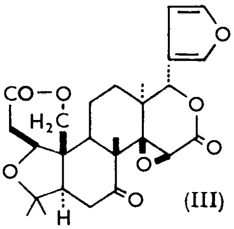
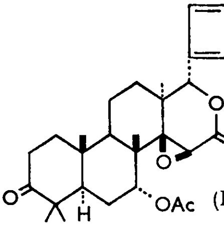
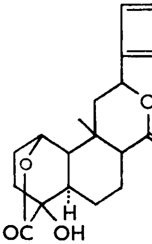


(III)

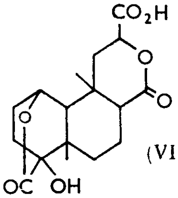
Ozonolysis of a substance having the structure (IV) suggested for dihydrogedunin would be expected to break the furan ring, giving the acid (VIII) ($C_{25}H_{34}O_8$), by analogy with the ozonolysis of dihydrocolumbin (V) to the acid[8] (VI) and of limonin (III) to ætiolimoninic acid[6] (VII). In fact, ozonolysis of dihydrogedunin gave a crystalline acid of this molecular formula. On saponification of the acid just over three mol. of alkali



(IV)



(V)



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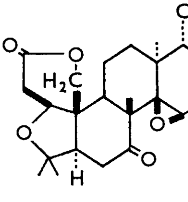
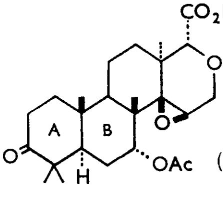
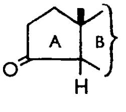


(VII)



(VIII)



(IX)

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[6] Melera, Schaffner, Arigoni, and Jeger, *Helv. Chim. Acta*, 1957, **40**, 1420.

[7] Arigoni, Barton, Corey, Jeger, and others, *Experientia*, 1960, **16**, 41; Arnott, Davie, Robertson, Sim, and Watson, *ibid.*, p. 49; Barton, Pradhan, Sternbill, and Templeton, *J.*, 1961, 255.

[8] Barton and Elad, *J.*, 1956, 2085, 2090.

were consumed, and its methyl ester was reduced with sodium borohydride to an amorphous alcohol, which on treatment with phosphorus pentachloride and then ozonolysis gave acetone. This reaction sequence is characteristic of 4,4-dimethyl-3-oxo-di- and -tri-terpenes, with rings A and B *trans*-fused. The other product of the ozonolysis, which remained amorphous, should be the cyclopentanone (IX), and in agreement with this it showed an absorption band at 1736 cm.$^{-1}$ in chloroform; the allocation of this to a cyclopentanone is, however, confused by the methoxycarbonyl absorption, which was not clearly resolved.

EXPERIMENTAL

Ultraviolet spectra were determined for ethanol solutions. Light petroleum refers to the fraction with b. p. 60—80°.

Gedunin Dinitrophenylhydrazone.—This *derivative* formed red plates, m. p. 255—256°, from methanol–chloroform (Found: C, 61·25; H, 5·65; N, 8·8. $C_{34}H_{38}O_{10}N_4$ requires C, 61·6; H, 5·8; N, 8·45%), $\lambda_{max.}$ 375 mμ (log ε 4·45).

Dihydrogedunin Dinitrophenylhydrazone.—This formed yellow plates, m. p. 195—198°.

Dihydrogedunol.—A solution of gedunin (3·09 g.) in hot methanol (100 ml.) and chloroform (50 ml.) was cooled to 10°. Sodium borohydride (0·2 g.) in methanol (5 ml.) was added, and after 45 min. acetic acid (2·5 ml.) and water (250 ml.). *Dihydrogedunol* was extracted with chloroform and crystallised from light petroleum–benzene as needles, m. p. 209—211° (Found: C, 69·0, 69·3; H, 7·8, 7·9. $C_{28}H_{38}O_7$ requires C, 69·1; H, 7·9%), ν 3580 cm.$^{-1}$ (OH), $[\alpha]_D^{20}$ $-15° \pm 3°$ (in $CHCl_3$). Reduction of dihydrogedunin in the same way gave the same alcohol.

Dihydrogedunin.—To the above alcohol (128 mg.) in acetone (10 ml.) at 0° chromium trioxide in sulphuric acid was added in slight excess. After 5 min. dilute sodium carbonate (50 ml.) and ethanol (1 ml.) were added, and the product was isolated with chloroform. Crystallisation from light petroleum–benzene gave dihydrogedunin (60 mg.), identical in infrared spectrum and m. p. with an authentic specimen.

Deacetylgedunin (II; R = H).—Gedunin (10 g.) was refluxed in methanol (750 ml.) and aqueous 2N-sodium hydroxide (175 ml.) for 10 min. The cold solution was acidified with sulphuric acid and extracted with chloroform. Chromatography of the product on alumina and crystallisation from light petroleum–benzene gave *deacetylgedunin* (4·34 g.) as prisms, m. p. 250—272° (decomp.) (Found: C, 70·7; H, 7·3. $C_{26}H_{32}O_6$ requires C, 70·9; H, 7·3%), $[\alpha]_D^{20}$ +75° (in $CHCl_3$), ν 3450 cm.$^{-1}$ (OH).

Gedunin (II; R = Ac).—Deacetylgedunin (185 mg.) and toluene-*p*-sulphonic acid (260 mg.) were dissolved in acetic acid (10 ml.) and acetic anhydride (2 ml.) and stored overnight. Water (50 ml.) was then added, and the product filtered off and recrystallised. It was identical with gedunin in m. p. and infrared spectrum.

Ozonolysis of Dihydrogedunin.—Dihydrogedunin (2·0 g.) in acetic acid (50 ml.) was ozonised at 20°. The solution was then steam-distilled, yielding no volatile carbonyl compounds, and the residual solution was stored overnight. The precipitate was collected and crystallisation from acetic acid, gave the *acid* (1·0 g.) (VIII) as needles, m. p. 224—226° [Found: C, 64·55; H, 7·25%; sap. val., 139, 140. $C_{25}H_{34}O_8$ requires C, 64·9; H, 7·4%; sap. val. (3 acid functions), 154], $[\alpha]_D^{20}$ −18° (in $CHCl_3$), $\lambda_{max.}$ 280 mμ (log ε 2·07). With ethereal diazomethane it gave the *methyl ester*, plates (from light petroleum), m. p. 188—190° (Found: C, 65·75; H, 7·3%; sap. val., 146, 147. $C_{26}H_{36}O_8$ requires C, 65·5; H, 7·6%; sap. val., 159), $[\alpha]_D^{20}$ −23° (in $CHCl_3$), $\nu_{max.}$ 1750, 1740, and 1707 cm.$^{-1}$.

Degradation of the Ozonolysis Product.—The above methyl ester (3·0 g.) in dioxan (20 ml.) and methanol (10 ml.) was treated with sodium borohydride (1 g.) in dioxan, and the solution refluxed 1 hr. The solution was kept for 3 hr. at 50°, then acidified with dilute sulphuric acid. Chloroform removed an amorphous solid, which was chromatographed on alumina. Ether–chloroform eluted a fraction (980 mg.) which partly crystallised. This showed ν 3400 cm.$^{-1}$ (OH), and no band at 1707 cm.$^{-1}$. This fraction (2 g.) in light petroleum (150 ml.) was treated with phosphorus pentachloride (2 g.). After 30 min. water was added, giving a precipitate. This was taken up in methanol and added to the petroleum layer, which was combined with an ether extract of the aqueous layer. The residue obtained on evaporation of the solvents was dissolved in acetic acid (100 ml.) and ozonised at 25° for 30 min. Water (100 ml.) and ferrous sulphate (1·0 g.) were added, and the solution was distilled into dinitrophenylhydrazine reagent.

Extraction of the distillate with benzene and chromatography on alumina gave acetone dinitrophenylhydrazone, m. p. and mixed m. p. 125—126° (correct infrared spectrum). Extraction of the distillation residue with chloroform gave an amorphous solid, which showed no absorption at 1707 cm.$^{-1}$, but had an absorption band at 1736 cm.$^{-1}$ (in $CHCl_3$).

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