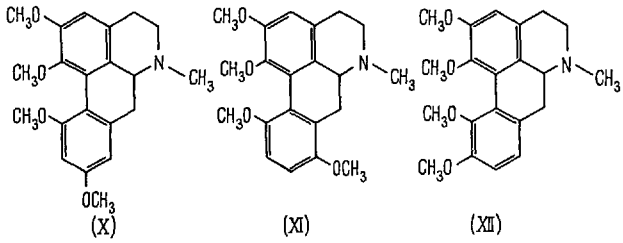
be expected to be dextrorotatory. Furthermore, the high rotation of this base indicates that it must be substituted both at positions 1 and 11[3]. If argemonine is in reality an aporphine alkaloid as SOINE with good reasons believes a perhaps more logical structure for it would be represented by either expressions (X) or (XI).



(X) (XI) (XII)

Both of the above two structures fit a basic fact about the chemistry of argemonine, namely that on oxidation with manganese dioxide in sulfuric acid argemonine yields 4,5-dimethoxy-N-methylphthalimide[13]. Furthermore, (X) and (XI), being substituted at both C-1 and C-11 would be expected to have a high specific rotation and a relatively low intensity ultraviolet absorption[3]. Argemonine has indeed been found to exhibit a relatively low absorption, $\log \varepsilon = 4.01$, at 287 mμ, and as has been mentioned previously, it is strongly levorotatory[13]. Finally, structures (X) and (XI) would not violate the biogenetic rule[6] that all natural aporphines are substituted at both C-1 and C-2.

Structure (XII) is eliminated as a possibility for argemonine since: (a) The present correlation would predict that such an aporphine would be strongly dextrorotatory. (b) Argemonine has been found not to correspond to dimethylcorytuberine which is represented by structure (XII)[13].

Résumé. L'auteur démontre qu'il existe, d'une manière générale, un rapport entre les substituants du cycle D des aporphines et la configuration absolue de ces alkaloïdes. De nouvelles structures ont été proposées pour la thalicmidine et l'argémonine.

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Department of Chemistry, The Pennsylvania State University, University Park (Penn., USA), September 25, 1961.

Triterpenoid XIII. The Constitution of Barringtogenol D

The isolation of barringtogenol D, a new triterpenoid sapogenol (m.p. 305–310°, $[\alpha]_D$ + 57° (dioxane)) from the fruits of *Barringtonia acutangula* Gaertn. was reported earlier[1]. This communication deals with its complete structural elucidation.

Barringtogenol D ($C_{30}H_{48}O_4$) formed a triacetate ($C_{36}H_{54}O_7$, m.p. 233–234°, $[\alpha]_D$ + 74° ($CHCl_3$)) which accounts for three oxygen atoms in the original alcohol. The presence of an oxide linkage, indicated by a band at 1150 cm^{-1} in the IR-spectrum of barringtogenol D and its triacetate was confirmed by opening the oxide linkage of the latter with *p*-toluene sulphonic acid and acetic anhydride[2] when a crystalline tetraacetate ($C_{38}H_{58}O_8$, m.p. 284–285° $[\alpha]_D$ – 12.5°, ($CHCl_3$)) was obtained, in which the IR-band at 1150 cm^{-1} was absent (Anal. calc. for $C_{38}H_{58}O_8$: C, 71.02; H, 9.04; found: C, 70.91; H, 8.99). The same tetraacetate was also obtained by treatment of the triacetate in acetic anhydride with dry hydrogen chloride. The tetraacetate on hydrolysis gave a tetrol ($C_{30}H_{50}O_4$, m.p. 293–295°, $[\alpha]_D$ + 48° ($CHCl_3$); Anal. calc. for $C_{30}H_{50}O_4$: C, 75.90; H. 10.62; found: C, 75.80; H, 10.55).

The ethylenic linkage in barringtogenol D, indicated by tetranitromethane colour, is hindered. The triacetate could neither be hydrogenated over Adams' catalyst nor did it react with selenium dioxide[3], but it consumed nearly 1 mole of perbenzoic acid extremely slowly. Evidence for the typical 12:13 double bond was obtained by oxidation of the triacetate with CrO_3 to yield an $\alpha\beta$-unsaturated ketone (m. p. 256–258°, λ max 241 mμ ($\log \varepsilon$ 4.1)) which is at a slightly lower wave length than is usually observed for 11-keto Δ^{12}-triterpenes[4] of the β-amyrin series. The tetraacetate consumed 1 mole of perbenzoic acid at a rate typical of the triterpenes of the β-amyrin group. The unusually hindered nature of the ethylenic linkage in barringtogenol D is probably due to the shielding effect of the oxide bridge[5,6].

The ready formation of the triacetate (at room temperature) indicated the hydroxyl groups to be primary and/or equatorially oriented secondary hydroxyl functions[7]. Barringtogenol D did not react with periodic acid but readily formed a monoacetonide ($C_{33}H_{52}O_4$, m.p. 233–236°, $[\alpha]$. + 33° ($CHCl_3$); Anal. calc. for $C_{33}H_{52}O_4$: C, 77.29; H, 10.22; found: C, 77.25; H, 10.21). The acetonide formation showed the presence of a 1:3 glycol system. Oxidation of the acetonide by SARETT's method[8] furnished a colourless crystalline product ($C_{33}H_{50}O_4$, m.p. 212–213°, $[\alpha]_D$ + 57° ($CHCl_3$); Anal. calc. for $C_{33}H_{50}O_4$: C, 77.60; H, 9.86; found: C, 77.59; H, 9.42). It has been characterized as a 3-keto derivative by Zimmerman's test and optical rotatory dispersion curve (through the courtesy of Prof. C. DJERASSI of Stanford University, USA). Further, we have evidence for believing that barringtogenol D contains no other substituents except the 3β-hydroxyl group in ring A. The 3β-configuration was confirmed by the molecular rotational data[9]. The secondary hydroxyl group of the 1:3 glycol, which of necessity should be in D/E ring, was unusually hindered toward chromic acid oxidation under varied conditions. The sapogenol, when treated with chromium trioxide-sulphuric acid in acetone[10], gave neutral and acid products. The ester of the acid on chromatographic resolution furnished two colourless crystalline compounds, characterized as methyl di-

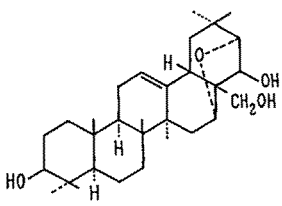
[1] A. K. BARUA, P. C. MAITI, and S. K. CHAKRABORTI, J. Amer. pharm. Assoc., *50*, 937 (1961).
[2] L. RUZICKA, W. BAUMGARTNER, and V. PRELOG, Helv. chim. Acta *32*, 2069 (1949).
[3] L. RUZICKA, G. MULLER, and H. SCHELLENBERG, Helv. chim. Acta *22*, 767 (1939); D. H. R. BARTON and C. J. W. BROOKS, J. chem. Soc. *1951*, 257.
[4] C. R. NOLLER, J. Amer. chem. Soc. *66*, 1269 (1944).
[5] C. DJERASSI, C. H. ROBINSON, and D. B. THOMAS, J. Amer. chem. Soc. *78*, 5685 (1956).
[6] G. CAINELLI, A. MELERA, D. ARIGONI, and O. JEGER, Helv. chim. Acta *40*, 2390 (1957).
[7] A. SANDOVAL, A. MANJARREZ, P. R. LEEMING, G. H. THOMAS, and C. DJERASSI, J. Amer. chem. Soc. *79*, 4468 (1957).
[8] G. I. POOS, G. E. ARTH, R. E. BEYLER, and L. H. SARETT, J. Amer. chem. Soc. *75*, 422 (1953).
[9] D. H. R. BARTON and E. R. H. JONES, J. chem. Soc. *1944*, 659; W. KLYNE and W. M. STOKES, J. chem. Soc. *1954*, 1979.
[10] R. G. CURTIS, I. HEILBRON, E. R. H. JONES, and G. F. WOODS, J. chem. Soc. *1953*, 461.

keto ester ($C_{31}H_{44}O_5$, m.p. 217–218°, Anal. calc. for $C_{31}H_{44}O_5$: C, 74.96; H, 8.93; found: C, 74.46; H, 9.12) and methyl hydroxy keto ester ($C_{31}H_{46}O_5$, m.p. 274–277°, $[\alpha]_D$ + 77.5° ($CHCl_3$); Anal. calc. for $3_{31}H_{46}O_5$: C, 74.65; H, 9.29; found: C, 74.06; H, 9.33). The formation of the above two esters indicated the presence of one primary hydroxyl group in barringtogenol D. The second ester formed an orange-red mono-2:4-dinitrophenyl hydrazone ($C_{37}H_{50}O_8N_4$, m.p. 258°; Anal. calc. for $C_{37}H_{50}O_8N_4$: C, 65.49; H, 7.37; N, 8.26; found: C, 65.34; H, 7.46; N, 8.28). A band at 1765 cm^{-1} in the infra-red spectrum of the methyl diketo ester suggested the presence of a five-membered ring ketone involving the oxide function[6]. This behaviour of barringtogenol D toward chromium trioxide oxidation finds a remarkable parallel in the case of aescigenin[6] and offers considerable support for similar disposition of the groups in barringtogenol D.

After considering all of the available positions for the site of the 1:3 glycol in a β-amyrin nucleus, and by the process of elimination in the light of various reactions, it is suggested that barringtogenol D has this group at 28:22β-position.

Regarding the oxide linkage, no evidence could be obtained for its location in barringtogenol D. Because of the similarity in some behaviour of aescigenin[6] and the formation of the methyl diketo ester, involving the oxide linkage and C_{22}-ketone, it is considered likely that barringtogenol D also has its oxide bridge linked between 16α- and 21α-position. Thus, a 3β:22β:28-trihydroxy-16α:21α-oxido-olean-12-ene structure (I) is tentatively suggested for barringtogenol D. The confirmation of this structure was accomplished as follows:

Barringtogenol D was oxidized with chromium trioxide-acetic acid in benzene and the neutral oxidation product, on HUANG-MINLON variation of Wolff-Kishner reduction[11], gave a desoxy compound ($C_{30}H_{48}O_2$, m.p. 198–200°, $[\alpha]_D$ + 61° ($CHCl_3$); IR-band at 3400 cm^{-1} and 1100 cm^{-1}; Anal. calc. for $C_{30}H_{48}O_2$; C. 81.77; H, 10.92; found: C, 81.67; H, 10.71). The above compound furnished an acetate ($C_{32}H_{50}O_3$, m.p. 201–203°, $[\alpha]_D$ + 76° ($CHCl_3$); Anal. calc. for $C_{32}H_{50}O_3$: C, 79.61; H, 10.44; found: C, 79.45; H, 10.41). The identity of the desoxy compound and its acetate with 22β-hydroxy-16α:21α-oxido-olean-12-ene (IIa) and its acetate (IIb) respectively, prepared from aescigenin[6], was established by comparison of their physical constants and also by mixed melting point determinations with corresponding authentic samples kindly supplied by Dr. ARIGONI of Zürich (Switzerland). The structure and stereochemistry of barringtogenol D may be represented as (I)[12].



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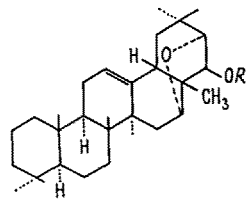

IIa, R=H; b, R=OCCH$_3$

Zusammenfassung. Die Struktur des aus der Frucht von *Barringtonia acutangula* Gaertn. isolierten neuen Triterpenoiden, Barringtogenol D, ist als 3β:22βoxy-16α:22α-Oxido-olean-12-en ermittelt worden.

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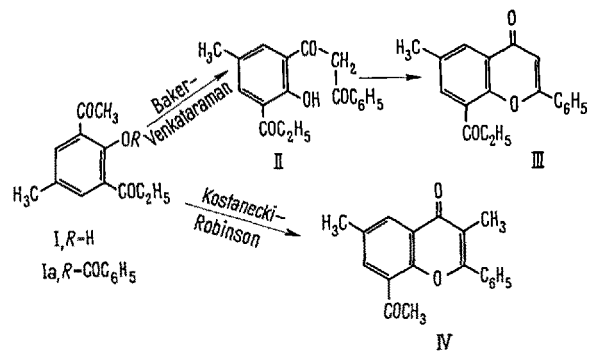
Department of Chemistry, Bose Institute, Calcutta (India), November 10, 1961.

[11] HUANG-MINLON, J. Amer. chem. Soc. *68*, 2487 (1946).

[12] *Acknowledgment*: We sincerely thank Dr. D. M. BOSE, Director, and Dr. P. K. BOSE, Head of the Department of Chemistry of this Institute, for their keen interest and encouragement during the work.

Different Behaviour of 2-Propionyl-4-methyl-6-acetyl-phenol in the Kostanecki-Robinson Acylation and in the Baker-Venkataraman Rearrangement

An identical mechanism seems to be operating in the Kostanecki-Robinson acylation of *o*-hydroxyarylalkylketones and in the Baker-Venkataraman rearrangement of the 0-benzoyloxy derivatives[1,2]. JERZMANOWSKA and MICHALSKA[3] have verified this identity by isolating the corresponding β-diketones from the acylation mixture of 6-methoxy-2-hydroxyacetophenone and benzoic or anisic anhydride. In the course of a research program, diacyl phenols have been investigated and this offered the opportunity to use these intermediates in the above-mentioned procedures. 2-Propionyl-4-methyl-6-acetyl-phenol (I), a compound with two different acyl groups in *ortho* position with respect to the phenolic hydroxyl, was selected in order to detect a hypothetical difference of behaviour. The Kostanecki-Robinson acylation of this product, with benzoyl chloride and sodium benzoate, may be predicted on the basis of a greater tendency of *o*-hydroxypropiophenones as compared to *o*-hydroxyacetophenones to form chromones[4]. In the case of the Baker-Venkataraman rearrangement prediction was doubtful, indeed this transposition occurs equally well either with 0-benzoyloxy-aceto or -propiophenone[5].



[1] W. BAKER, J. chem. Soc. *1933*, 1381.

[2] T. S. WHEELER et al., J. chem. Soc. *1950*, 1252.

[3] Z. I. JERZMANOWSKA and M. J. MICHALSKA, Chem. and Ind. *1958*, 132.

[4] D. CHAKRAVARTI and B. MAJUMDAR, J. Indian chem. Soc. *16*, 151 (1939).

[5] W. D. OLLIS and D. WEIGHT, J. chem. Soc. *1952*, 3826.