2. Mukherjee, K. S., Bhattacharya, M. K. and Ghosh, P. K. (1982) *Phytochemistry* **21**, 2416
3. Edwards, O. E., Femak, G. and Los, M. (1962) *Can. J. Chem.* **40**, 1540
4. Brieskorn, C. H. and Buchberger, L. (1971) *Planta Med.* **24**, 190
5. Yoshizaki, F., Ruedi, P. and Engster, C. H. (1979) *Helv. Chim Acta* **62**, 2754

Phytochemistry, Vol 22, No 5, pp 1297–1299, 1983
Printed in Great Britain

0031-9422/83/051297-03$03.00/0

LIMONOID EXTRACTIVES FROM *XYLOCARPUS MOLUCCENSIS*

DAVID A. H. TAYLOR

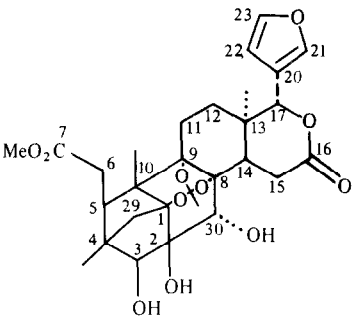
Department of Chemistry, University of Natal, Durban, Republic of South Africa

(*Revised received* 11 *October* 1982)

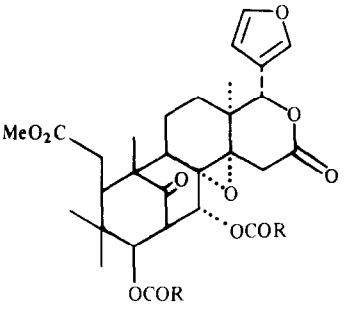
Key Word Index—*Xylocarpus moluccensis*, Meliaceae; limonoids; phragmalin, xyloccensin G, xyloccensin H

Abstract—Further examination of the timber of *Xylocarpus moluccensis* has given three new compounds, xyloccensins G, H and I. Structures are deduced for G and H. A structure is also deduced for xyloccensin C and proposals are made concerning the biosynthesis of phragmalin

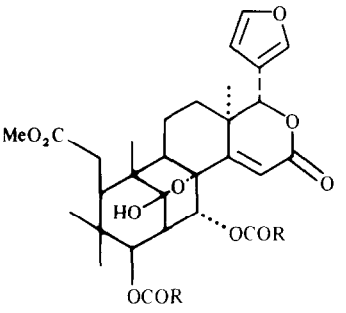
The outstanding problem in the phytochemistry of the limonoids is how the ring A bridge is formed in the 1,29-cycloswietenan group of compounds, of which phragmalin (**1**) is the simplest known example. So far the only plant investigated containing cycloswietenans and simpler limonoids which appear possible as biosynthetic intermediates is *Xylocarpus moluccensis* [1], which has given phragmalin triacetate (xyloccensin E), a group of 1,8-



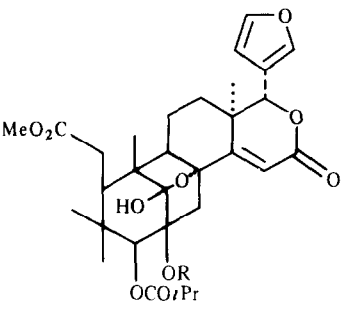
1



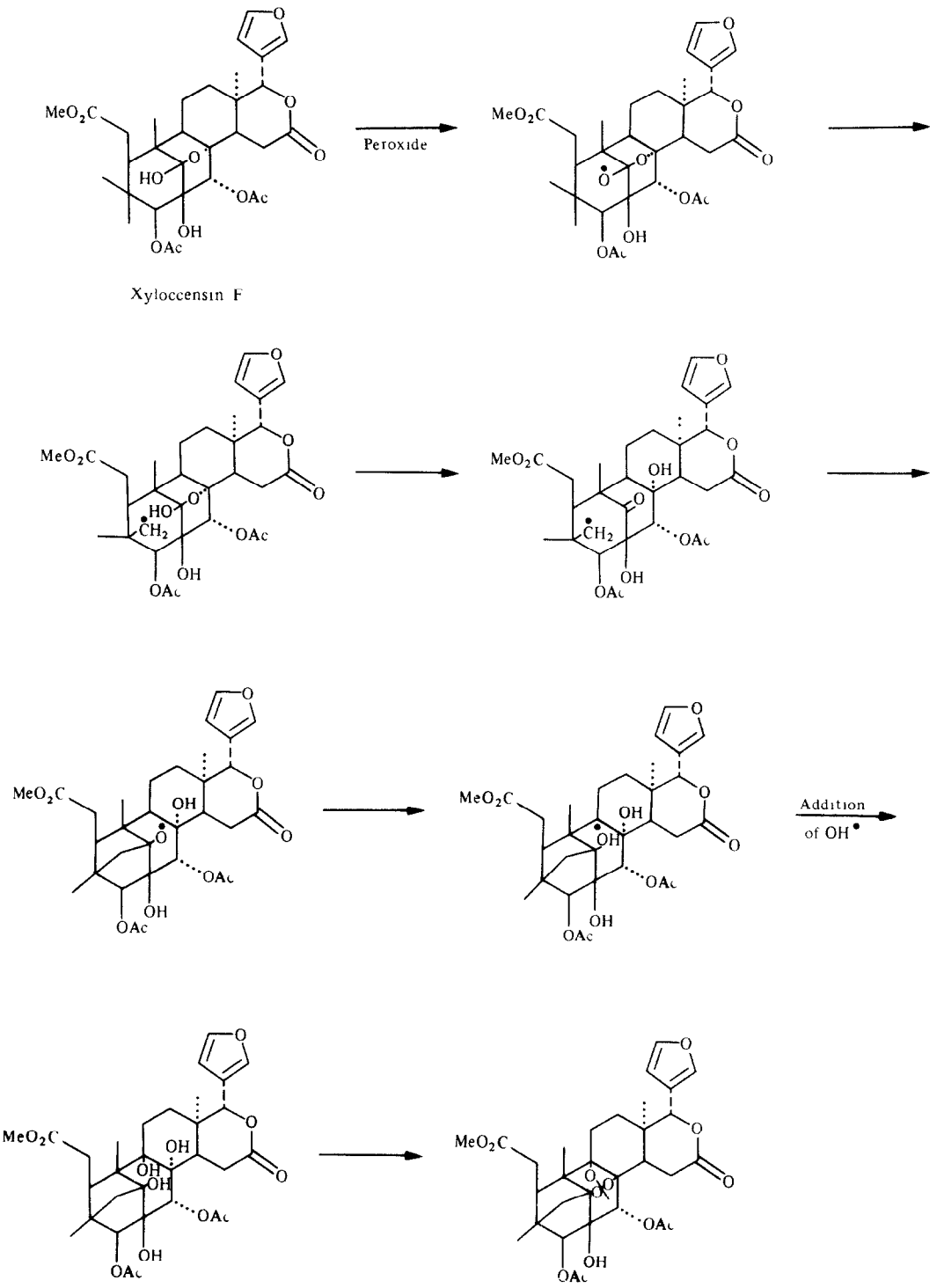
2



3



4



Scheme 1 Proposed route for the biosynthesis of phragmalin

hemiacetals, the xyloccensins A, B, D and F, and xyloccensin C, of unknown structure In a search for further possible intermediates, a re-investigation has been made of the timber of this species. This gave mainly xyloccensin A, with B, E and F in smaller amounts, C and D were not obtained. In addition to these compounds previously isolated, the present sample gave 7-oxodeacetoxy gedunin, mexicanolide and three new compounds, xyloccensins G, H and I.

Xyloccensin G was, as usual in this group, a mixture of isobutyrate and α-methyl butyrate esters, the major one was $C_{36}H_{48}O_{11}$ (63%) accompanied by the higher (17%) and lower (20%) homologues. A doublet in the ^{1}H NMR spectrum (δ 5.20, J = 10 Hz) can be identified by the characteristic coupling constant as due to H-3. Double radiation located H-2, and irradiation of this collapsed a resonance (δ 5.35), which at high field was shown to be an AMX multiplet. This must be due to H-30, the second coupling (3.3 Hz) is not large enough for the usual H-30–H-8 coupling, and we assign it to a long range coupling to H-9, which is related to H-30 in the favourable *W* conformation The absence of a normal H-30–H-8 coupling shows that C-8 is either substituted or in some abnormal conformation; the presence of a pair of doublets (δ 3.73, 2 87, J = 16.6 Hz), which can be ascribed to 2H-15, shows that C-14 is also substituted The ^{13}C NMR spectrum shows that the ketone at C-1 is present, there are also two singlets (δ 67.7, 62.9) characteristic of a di-tertiary oxide. It was, therefore, deduced that G had the structure shown by **2** and this was confirmed by treatment with methanolic sulphuric acid which gave a quantitative yield of xyloccensin A (**3**). At high resolution, the H-3 resonance is seen to consist of a pair of doublets, consistent with a mixture of esters of both the acids found H-30 was not seen to be similarly split which probably indicates a different conformational relationship with the acyl group.

Xyloccensin H was very similar, but lacked the C-30 ester group, H-2 new being a complex multiplet. It is, therefore, 30-deacyloxyxyloccensin G.

Xyloccensin C contained *ca* 60% of an isobutyrate and 40% of an α-methyl butyrate. In the ^{1}H NMR spectrum there are three singlets (δ_H 4.80, 5.28 and 5.75), there are also two hydroxyl peaks removed by D_2O. There is no ketonic carbonyl absorption in the IR spectrum This evidence is consistent with xyloccensin C being 30-deacyloxyxyloccensin D, with the structure **4**. In the absence of more material this cannot be confirmed.

Although the spectra of xyloccensin I were studied in some detail, it has not been possible to propose a structure for it, and recourse is being made to X-ray analysis.

The isolation of these compounds provides the intermediates required to rationalize the synthesis of the *Xylocarpus* hemiacetals from xylocarpin [2] through xyloccensin G to xyloccensin A. The corresponding 2-hydroxy compounds are also known [3]. Attempts to carry out this synthesis in the laboratory have not so far been successful, since double bonds in methyl meliacate are extremely resistant to chemical oxidation.

The crucial stage in the formation of phragmalin is the attack on the unactivated C-4 methyl group. So far, such reactions are only known to occur by attack by a suitably placed radical.

The C-1 oxygen in the *Xylocarpus* hemiacetals can provide such a radical, and we suggest the route starting from xyloccensin F shown in Scheme 1. The only unusual stage in this sequence is the addition of the carbon radical from C-29 to the C-1 carbonyl group. Although unusual, this is a known reaction [4], and in the present case would be highly favoured sterically. The scheme has the advantage of requiring oxidation at C-8 initially and oxidizing C-9 in the course of the reaction. This would explain why all known 1,29-cycloswietenan derivatives are hydroxylated at C-8 and C-9.

EXPERIMENTAL

Extraction of X. moluccensis A timber sample of *X moluccensis* (2 kg) collected at Kilifi, Kenya (herbarium specimen DAHT 312 at Oxford) was ground and extracted with refluxing *iso*-hexane, giving a powdery solid (42 g) This was separated by chromatography on Si gel columns, using EtOAc–CH_2Cl_2 mixtures for elution The first crystalline fraction was a mixture which, on re-chromatography, gave xyloccensins G and H

Xyloccensin G Mp 225–230° (MeOH–CH_2Cl_2) (Found M^+ 670 3349, $C_{37}H_{50}O_{11}$ requires M^+, 670 33528.) ^{1}H NMR. δ_H 7 60, 7 39 (H-21, H-23), 6 51 (H-22), 5 90 (H-17), 5 35 (*m*, $W_{1/2}$ 5 4, H-30), 5 20 (*d*, J = 10 Hz, H-3), 3 75 (CO_2Me), 3 73 (*d*, J = 16.6 Hz, H-15A), 3 41 (*dd*, J = 9.5, 4 Hz, H-5), 3.08 (*dd*, J = 2 2, 10 Hz, H-2), 2 87 (*d*, H-15B), 2.46 (*m*, 2H-6), 1 19, 1 05, 0 87, 0.77 (CMe) 1 21, 1.04 (*d*, J = 6 4 Hz, CHMe), ^{13}C NMR δ_C 213 5*s*, 175 9*s*, 174 0 (2*s*), 169 4*s*, 142 6*d*, 142.1*d*, 119 8*s*, 110 3*d*, 78 0*d*, 76 7*d*, 70.9*d*, 67.6*s*, 62 8*s*, 52.35*q*, 52 2*d*, 51 5*s*, 47 5*d*, 41.8*d*, 41 6*d*, 39 3*s*, 37 9*s*, 35.5*t*, 33 8*d*, 33 3*t*, 26 7*t*, 26 5*t*, 26 0*t*, 23 6*q*, 20 9*q*, 18 8*q*, 17.6*q*, 17 5*q*, 16 8*q*, 14 4*q*, 11 7*q*

Xyloccensin H Mp 200–205° (MeOH–$MeCl_2$) (Found M^+ 570.2850, $C_{32}H_{42}O_9$ requires M^+, 570.28285.) ^{1}H NMR δ_H 7 57, 7 39 (H-21, H-23), 6 48 (H-22), 5 89 (H-17), 4 96 (*d*, J = 10 Hz, H-3), 3 75 (CO_2Me), 3 52 (*d*, J = 16.6 Hz, H-15A), 3 37 (*m*, H-5), 2 61 (*d*, J = 16 6 Hz, H-15B), 2 46 (*d*, J = 6 2 Hz, 2H-6), 1 15, 1 06, 0 85, 0.81 (CMe) 1 21, (*d*, J = 6 4 Hz, CHMe), ^{13}C NMR δ_C 217 5*s*, 176.1*s*, 174 3*s*, 169 8*s*, 142.8*d*, 142 1*d*, 120 0*s*, 110.2*d*, 78 0*d*, 76 7*d*, 66 4*s*, 62.4*s*, 52.4*q*, 52 4*d*, 50 8*s*, 45 8*d*, 41.6*d*, 41 6*d*, 39 0*s*, 38.0*s*, 35.6*t*, 33 5*t*, 32 9*t*, 27.1*t*, 26.6*t*, 26 2*t*, 23.4*q*, 21 3*q*, 17 8*q*, 17.3*q*, 17 3*q*, 14 8*q*, 11 8*q*.

Xyloccensin I Much more strongly absorbed on the Si gel column, xyloccensin I eluted together with 7-oxodeacetoxy gedunin. After purification by HPLC, it had mp 268–270°, ^{13}C NMR· δ_C 173 9*s*, 170 1*s*, 164 5*s*, 145 9*s*, 142 8*d*, 140.9*d*, 122 4*d*, 120.9*s*, 111 5*s*, 110 0*d*, 80.3*s*, 79 7*d*, 77 3*d*, 52 1*q*, 50 0*d*, 48 1*s*, 44 1*s*, 43 0*d*, 41 5*s*, 39 5*t*, 36 2*d*, 33 9*t*, 32 7*t*, 29 4*t*, 26.0*q*, 23.8*t*, 21 7*q*, 21 5*q*, 13 8*q*; ^{1}H NMR· δ_H 7.47 (2H), 6 43 (1H), 5 71 (*s*, 1H), 5 19 (*s*, 1H), 4 94 (*s*, 1H), 3 76 (CO_2Me), 1 23, 1 09, 0 99, 0 91 (CMe)

Isomerisation of xyloccensin G Xyloccensin G (110 mg) was dissolved in MeOH (25 ml molar in H_2SO_4) and refluxed for 1 hr The crude product which crystallized was used directly for determination of ^{13}C NMR and ^{1}H NMR spectra, which were identical with those of authentic xyloccensin A.

Acknowledgement—Mass spectra were determined by Dr P Bladon, of Strathclyde University

REFERENCES

1 Connolly, J. D, MacLellan, M, Okorie, D A and Taylor, D. A. H. (1976) *J Chem. Soc Perkin Trans.* 1, 1993.
2 Okorie, D. A and Taylor, D A H. (1970) *J Chem Soc C* 211.
3. Okorie, D A. and Taylor, D. A H (1971) *Phytochemistry* **10**, 469.
4. Rust, F F, Seubold, F H and Vaughan, W. E (1948) *J Am Chem Soc* **70**, 4253.