4. Lian-niang, L. and Hung, X. (1985) *Planta Med.* **47**, 217. *Phytochemistry* **26**, 1509.
5. Urzúa, A., Freyer, A. J. and Shamma, M. (1987) 6. Pelter, A. (1968) *J. Chem. Soc.* (*C*), 74.

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A CHROMONE FROM THE ROOT-BARK OF *HARRISONIA ABYSSINICA*

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Key Word Index—*Harrisonia abyssinica*; Simaroubaceae; chromone; 2-methylalloptaeroxylin; 2-hydroxymethylalloptaeroxylin.

Abstract—In addition to the known 2-methylalloptaeroxylin, a new chromone has been isolated from a diethyl ether extract of the root-bark of *Harrisonia abyssinica*; its structure was elucidated as 2-hydroxymethylalloptaeroxylin.

INTRODUCTION

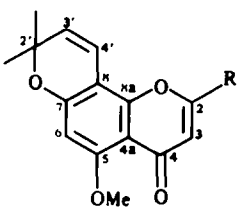
Owing to the antibacterial and antifeedant properties of *Harrisonia abyssinica* Oliv. against the African armyworm *Spodoptera exempta* and the Southern species *S. eridania*, several investigations into its chemical constituents have been reported [1–4]. Since phytochemical differences between samples of *H. abyssinica* collected from different regions have been found [4], a chemical investigation of Guinean samples was undertaken.

RESULTS AND DISCUSSION

A diethyl ether extract of the air dried root-bark of *H. abyssinica* was subjected to column chromatography and preperative thin-layer chromatography (TLC) on silica gel. Two chromones were isolated among the less polar fractions; they gave unusual positive reactions on TLC after being sprayed successively with Dragendorff and iodoplatinate reagents. Compound **1** gave a molecular ion at 272 corresponding to the molecular formula $C_{16}H_{16}O_4$ and had UV, IR and ^{1}H NMR spectral data in close agreement with the data reported for methylalloptaeroxylin [4, 5]. The assignments of the ^{1}H NMR and ^{13}C NMR signals were based on previously published data [6–8] and on the ^{1}H–^{13}C-2D chemical shift correlation spectrum. Therefore, **1** was identified as 2-methylalloptaeroxylin. Compound **1** was recently isolated from a Nigerian sample of *H. abyssinica* [4] but was not reported in East African specimens [2, 4]. Compound **2** gave a molecular ion at 288 corresponding to the molecular formula $C_{16}H_{16}O_5$. Its IR spectrum showed hydroxy absorption at 3360 cm^{-1} in addition to bands which can be assigned to a chromone structure as further confirmed by the electronic spectrum. The ^{1}H NMR spectra of **1** and **2** were similar but the 2-methyl signal at 2.28 ppm showed by **1** was replaced by a two proton singlet at 4.51 ppm suggesting a CH_2OH group; this was confirmed by a fragment at *m/z* 270 $[M - H_2O]^+$ and the ^{13}C NMR-Dept spectrum, which exhibited a negative signal at 61.16 ppm. Furthermore, acetylation of **2** resulted in the downfield shifts of the methylene signal from 4.51 to 4.96 ppm and in an additional three protons singlet at 2.18 ppm (OAc). The ^{1}H–^{13}C chemical shift correlation spectrum confirmed the assignments made for both ^{1}H NMR and ^{13}C NMR spectra. Thus, the structure of **2** can be formulated as 2-hydroxymethylalloptaeroxylin. The presence of this new chromone in Guinean samples of *H. abyssinica* confirmed the probable existence of chemical races of this plant.

EXPERIMENTAL

UV spectra were recorded in EtOH and IR in KBr discs. ^{1}H MNR (250 MHz) and ^{13}C NMR (62 MHz) were recorded in $CDCl_3$; chemical shifts are reported as δ values downfield from internal TMS. MS: direct inlet, 70 eV.



1 R = Me
2 R = CH_2OH

Plant material. Root-barks were collected around Seredou (Guinea-Conakry) in August 1985 and identified by the Department of Botany of the Research Center on Medicinal Plants of Seredou; a voucher specimen has been deposited at this Centre.

Extraction. An aq. methanolic extract of the powdered root-bark of *H. abyssinica* (500 g) was exhaustively extracted with Et_2O; the Et_2O extract was concd under vacuum, homogeneised with cellulose MN2100FF (Macherey Nagel and Co) and chromatographed on a silica gel column eluting with CCl_4 and a CCl_4–MeOH gradient; the different fractions were purified by CC and by prep. TLC on silica gel with CH_2Cl_2–Me_2CO (13:2) (detection by Dragendorff and iodoplatinate reagents).

2-Methylalloptaeroxylin **1** (576 mg). UV λ_{max}^{EtOH} nm: 239 sh, 255 sh, 263, 300 sh, 340 sh; IR γ_{max}^{KBr} cm^{-1}: 1655, 1600, 1570; ^1H NMR ($CDCl_3$): δ1.47 (6H, *s*, *gem*-Me), 2.28 (3H, *s*, Me-2), 3.91 (3H, *s*, OMe), 5.55 (1H, *d*, J = 10Hz, H-3'), 5.96 (1H, *s*, H-3), 6.28 (1H, *s*, H-6), 6.69 (1H, *d*, J = 10Hz, H-4'); ^{13}C NMR ($CDCl_3$): δ19.67 (Me-2), 28.23 (*gem*-Me), 56.40 (OMe), 77.93 (C-2'), 96.48 (C-6), 102.41, 108.62 (C-4a and C-8), 111.92 (C-3), 115.32 (C-4'), 127.32 (C-3'), 154.35, 157.65, 160.71 (C-4a, C-8, C-8a: uncertain attribution), 162.53 (C-2), 177.55 (C-4); EIMS *m/z*: 272 $[M]^+$, 257 (base peak), 243, 228, 227, 217, 202.

2-Hydroxymethylalloptaeroxylin **2** (248 mg). UV λ_{max}^{EtOH} nm: 222 sh, 239 sh, 263, 300 sh, 335 sh; IR ν_{max}^{KBr} cm^{-1}: 3360, 1655, 1600, 1568; ^1H NMR ($CDCl_3$): δ1.45 (6H, *s*, *gem*-Me), 3.89 (3H, *s*, OMe), 4.51 (2H, *s*, CH_2OH), 5.52 (1H, *d*, J = 10Hz, H-3'), 6.24 (1H, *s*, H-3), 6.27 (1H, *s*, H-6), 6.44 (1H, *d*, J = 10Hz, H-4'); ^{13}C NMR ($CDCl_3$): δ28.26 (*gem*-Me), 56.31 (OMe), 61.16 ($\underline{C}H_2OH$), 78.10 (C-2'), 96.60 (C-6), 102.48 and 108.74 (C-4a and C-8), 109.91 (C-3), 115.10 (C-4'), 127.36 (C-3'), 154.00, 157.98, 160.61 (C-4a, 8, 8a: uncertain attribution), 164.97 (C-2), 178.03 (C-4); EIMS *m/z*: 288 $[M]^+$, 273 $[M-CH_3]^+$, 270 $[M-H_2O]^+$, 259, 243, 228, 227, 217, 213, 202.

2-Hydroxymethylalloptaeroxylin acetate (38 mg) was obtained by treatment of **1** (50 mg) with Ac_2O and pyridine at room temp. overnight and purified by prep. TLC with CH_2Cl_2–Me_2CO (13:2); ^1H NMR ($CDCl_3$): δ1.44 (6H, *s*, *gem*-Me), 2.18 (3H, *s*, OAc), 3.94 (3H, *s*, OMe), 4.96 (2H, *s*, $C\underline{H}_2OAc$), 5.55 (1H, *d*, J = 10Hz, H-3'), 6.26 (1H, *s*, H-6), 6.31 (1H, *s*, H-3), 6.64 (1H, *d*, J = 10Hz, H-4').

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REFERENCES

1. Kubo, I., Tanis, S. P., Lee, Y., Miura, I., Nakanishi, K. and Chapya, A. (1976) *Heterocycles* **5**, 485.
2. Liu, H. W., Kusumi, T. and Nakanishi, K. (1981) *J. Chem. Soc., Chem. Commun.*, 1271.
3. Liu, H. W., Kubo, I. and Nakanishi, K. (1982) *Heterocycles* **17**, 67.
4. Okorie, D. A. (1982) *Phytochemistry* **21**, 2424.
5. David, R. T., John, M. W. and John, A. W. (1977) *J. Chem. Soc. Perkin I*, 397.
6. González, A. G., Bretón, J. L., López, D. H., Martinez, I. M. A. and Rodríguez, L. F. (1973) *Quimica* **69**, 1013.
7. Mourad, K., Morand, J. and Gilly, C. (1986) *J. Nat. Prod.* **49**, 508.
8. Robert, D. H. M. and David, A. H. (1985) *Phytochemistry* **24**, 2465.