# *Afzelia cuanzensis* Seed Oil: A Source of Crepenynic and 14,15-Dehydrocrepenynic Acid

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WE (F. D. G. and G. M. T.) are presently screening a large number of less common seed oils, mainly by chromatographic and spectroscopic examination. The methyl esters derived from the seed oil of the timber tree *Afzelia cuanzensis* Welw. (Caesalpiniaceæ), when examined by gas–liquid chromatography, showed two peaks which could not be immediately identified from carbon number alone.

One component (44%) was shown to be octadec-*cis*-9-en-12-ynoic acid, identical with the previously reported crepenynic acid.[1] The methyl ester had a carbon number of 21·4 on a diethylene glycol succinate (DEGS) column and 18·0 on an Apiezon L (ApL) column. It ran midway between oleate and linoleate on thin layers of silica impregnated with silver nitrate and was readily isolated by this means. Ultraviolet and infrared spectra showed the absence of conjugated unsaturation and of *trans*-olefinic groups; its n.m.r. spectrum was identical with that of methyl crepenynate[1] thereby confirming the presence of a 1,4-*cis*-enyne group. Von Rudloff oxidation[2] gave hexanoic and azelaic acids showing the unsaturation to lie between C-9 and C-13. When treated with hydrazine (1·5 hr., 45°) the olefinic group was reduced more quickly than the acetylenic group and a concentrate of an octadecynoic ester (75%) was isolated by silver-ion chromatography. This furnished dodecanedioic acid as the major dibasic acid (74%) when oxidised, thus proving the acid to be crepenynic.

The second ester (14%, carbon number 22·4 on DEGS and 18·0 on ApL) was also isolated by silver-

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ion chromatography, running immediately after methyl oleate. We consider this to be octadeca-*cis*-9,*cis*-14-dien-12-ynoic acid (or, less likely, the 9*c*,12*c*,14*a*-isomer) for the following reasons. (i) The ultraviolet spectrum shows the presence of an enyne ($\lambda_{max}$ at 227 m$\mu$, log $\epsilon$ 4·16, and inflexion at 235 m$\mu$ in methanol solution). (ii) The infrared spectrum shows no *trans*-olefinic group. (iii) The n.m.r. spectrum is consistent with the presence of the group $\cdot CH{:}CH\cdot CH_2\cdot C{\equiv}C\cdot CH{:}CH\cdot$ or $\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot C{\equiv}C\cdot$ with unsaturation extending to the 14,15 position.[3] (iv) This ester is only observed when the glycerides are transesterified under mild alkaline conditions (boiling 0·2% methanolic sodium methoxide for 3 min.), under more vigorous conditions (boiling 1·0% methanolic sodium methoxide for 60 min.) it disappears and is replaced by an equivalent amount of conjugated tetraenoic ester. (v) Partial reduction with hydrazine (45°, 2 hr.) gives a complex mixture of products from which a fraction, rich in conjugated enynoate (55%) and monoacetylenic ester (20%), was isolated. On oxidation this furnished dodecanedioic acid (63%) as the major dibasic acid. We are continuing our investigation of this acetylenic acid.

Bu'Lock[4] considers crepenynic acid as a key intermediate in the biosynthesis of many long- and short-chain polyenynes and this view is supported by Bohlmann[5] and by Jones.[6] 14,15-Dehydrocrepenynic acid was present in trace amount in the fungus *Tricholoma grammopodium* examined by Bu'Lock and Smith[7] but *Afzelia cuanzensis* seed oil is a more useful source of this acid.

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