## EXPERIMENTAL

*Isolation.* The extraction scheme described by Powell [5] which fractionates indoles was used. Air-dried leaves of Dutch grown *Cannabis sativa* L. var. Fibrimon-21 (19·5 kg) were extracted with in total 160 l. of cold EtOH. After concentration of the extract under red. pres, the remaining residue (2380 g) was extracted with 6 l. $CH_2Cl_2$. This extract was concentrated and the residue was partitioned between acetonitrile and *n*-hexane. The acetonitrile soluble part was worked up to give an acidic, a basic and a neutral fraction, 2·7, 1·1 and 3·8 g resp. The last two fractions contained the main part of the Ehrlich-positive components and they were combined for further purification. Repeated column chromatography on silica, using $CHCl_3$ containing 1–4% MeOH as the eluent, successively yielded 25 mg of dihydrovomifoliol and 65 mg of vomifoliol (the stems contained 3·2 mg of vomifoliol per kg plant material).

*Vomifoliol* $R_f$ 0·18 (precoated silica plates "Merck", eluent $CHCl_3$–MeOH (93:7). Gives with Ehrlich's reagent a brownish–red colour, that turns to green. 100 MHz NMR spectrum (in $CDCl_3$): $\delta$1·01(*s*, 3H) 1·08(*s*, 3H), 1·29(*d*, *J* 6·2 Hz, 3H), 1·88(*d*, *J* 1·4 Hz, 3H), 2·00 (broad, 2H), 2·34($H_{AB}$, *J* 17 Hz, 2H), 4·39(*m*, *J* 3·5 and 6·2 Hz, 1H), 5·80(*s*, 1H), 5·82(*d*, *J* 3·0 Hz, 1H) and 5·89(*q*, *J* 1·4 Hz, 1H) ppm. IR spectrum: 3400 $cm^{-1}$ (OH) and 1650 $cm^{-1}$ (C = C − C = O). MS spectrum: *m/e* 224(0·5%), 206(3·5%), 168(9·3%),151(3·5%), 150(5·9%), 135(4·5%), 125(10·4%), 124(100%), 123(4·2%), 122(7·1%), 111(6·8%), 107(2·8%), 79(6·3%), 77(4·4%), 69(4·7%).

*Dihydrovomifoliol* $R_f$ 0·20 (precoated silica plates "Merck", eluent $CHCl_3$–MeOH (93:7). Gives with Ehrlich's reagent a violet colour. 100 MHz NMR spectrum (in $CDCl_3$): $\delta$1·05(*s*, 3H), 1·09(*s*, 3H), 1·21(*d*, *J* 6·0 Hz, 3H), 1·4–2·0(4H), 2·04(*d*, *J* 1·5 Hz, 3H), 2·3(broad, 2H), 2·36($H_{AB}$, *J* 18Hz, 2H), 3·75(*m*, *J* 2·0 and 6·0 Hz, 1H) and 5·82(*q*, *J* 1·5 Hz, 1H) ppm. IR spectrum: 3400 $cm^{-1}$ (OH) and 1650 $cm^{-1}$ (C = C − C = O) MS spectrum: *m/e* 226(1·6%), 193(2·4%), 183(4·0%), 171(7·2%), 170(72·6%), 166(6·4%), 154(4·0%), 153(59·7%), 152(77·4%), 151(3·2%), 137(4·0%), 135(3·2%), 127(3·2%), 126(3·2%), 125(25·0%), 124(12·9%), 123(12·0%), 111(63·5%), 110(100%), 109(16·9%), 107(18·5%), 96(33·9%), 95(14·5%), 93(5·6%), 91(8·9%), 83(7·2%), 82(12·9%), 81(6·4%), 79(8·0%), 77(4·0%), 69(20·1%).

*Synthetic compounds.* Spectroscopic data of the synthetic products were in full agreement with those of the natural products.

*Acknowledgements*—This research was supported (H.M.S.) by the Dutch Ministry of Public Health and Environmental Hygienics. Thanks are due to Dr. W. Heerma and Dr. J. K. Terlouw for recording the mass spectra and to Dr. J. Marsman for recording the NMR spectra.

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*Phytochemistry*, 1976, Vol. 15, pp. 831–832. Pergamon Press. Printed in England

# A NEW TRITERPENE GLYCOSIDE FROM *MOLLUGO HIRTA*

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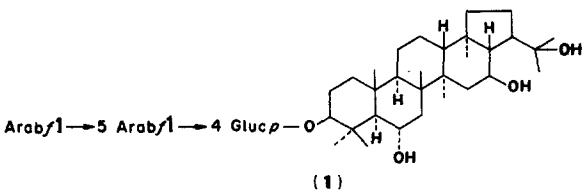
(*Received* 3 *July* 1975)

**Key Word Index**—*Mollugo hirta*; Aizoaceae; triterpene glycoside; mollugocin A.

The isolation of a number of new triterpenoid sapogenins called mollugogenol A, B, C and E[1–5] and oleanolic acid and a mixture of glucosides of sitosterol and stigmasterol[6] from *Mollugo hirta* was reported from this laboratory earlier. The present communication reports the isolation from the leaves of the same plant of a new triterpene glycoside, called mollugocin A, whose structure has been established as mollugogenol *A*-3-[α-L-arabinofuranosyl-(1→5)-α-L-arabinofuranosyl-(1→4)-β-D-glucopyranoside (**1**).

The ethanolic extract of the defatted plant material (*M. hirta*) on concentration and keeping overnight at room temperature yielded a colourless crystalline material. This on repeated crystallization from EtOH (95%) gave a saponin, $C_{46}H_{78}O_{17}$, mp 276–80° (dec), $[\alpha]_D^{27}$ −12·2° (Py) which was homogeneous by TLC, mollugocin A (**1**).

Acid hydrolysis of (**1**) with ethanolic HCl yielded mainly mollugogenol A [1,2] and traces of 22-dehydro-




(**1**)

mollugogenol A [1,2] and mollugogenol B [3] which were artefacts formed during the acid hydrolysis. Enzymatic hydrolysis of mollugocin A with β-glucosidase gave only mollugogenol A. Controlled acid hydrolysis with ethanolic sulphuric acid gave L-arabinose and D-glucose, in the ratio of 1:2 as shown by GLC.

The methylated aglycone $C_{32}H_{56}O_4$, mp 201–3°, obtained after hydrolysis of the permethylated product [7] with methanolic HCl did not show the molecular ion peak in the MS, but showed peaks at *m/e* 486 $(M\text{-}H_2O)^+$ and *m/e* 446 $(M\text{-}58)^+$ and an intense peak

at *m/e* 59 due to the ion $(CH_3)_2C{=}OH^+$. There was no peak at *m/e* 223 as has been observed in the MS of mollugogenol A.

The methylated aglycone on Jones oxidation yielded a product which gave positive Zimmerman's colour test for a 3-keto group [8] and showing that the saccharide side chain in the mollugocin A must be linked through the C-3 hydroxyl. Acid hydrolysis of the permethylated product gave 2,3,6-tri-*O*-methyl-D-glucose, 2,3,5-tri-*O*-methyl-L-arabinose and 2,3-di-*O*-methyl-L-arabinose respectively (PC and *p*-nitrobenzoates [9–12].

Identification of the methylated sugars not only suggested the pyranose ring form for D-glucose and furanose ring form for the end L-arabinose respectively, but also the straight chain nature of the saccharide unit. Enzymatic hydrolysis with β-glucosidase confirmed the β-linkage of D-glucose with the aglycone. The central can be either in the pyranose or furanose form but the ease of acid hydrolysis strongly suggests [13] the furanose ring form and α-L-glycosidic linkage between the two arabinose units and between arabinose and glucose units. It is a general observation that D-sugars occur with β-glycosidic and L-sugars with α-glycosidic linkage [14].

On the basis of the data discussed above, the structure of mollugocin A can be represented as (**1**).

*Acknowledgements*—The authors are indebted to Dr. S. M. Sircar, Director, Bose Institute, for his interest in the work. Thanks are due to Dr. K. G. Das of the National Chemical Laboratory, Poona, India, for the mass spectrum of the compound reported in this paper. One of the authors (A. Basak) is indebted to the Council of Scientific and Industrial Research for a research fellowship.

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*Phytochemistry*, 1976, Vol. 15, pp. 832–833 Pergamon Press Printed in England.

# PRENYLATED FLAVANONES FROM *MILLETIA OVALIFOLIA* SEEDS

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(*Received* 26 *September* 1975)

**Key Word Index**—*Milletia ovalifolia*; Leguminosae; Lanceolatin-B; karanjin; kanjone; pongaglabrone; β-sitosterol and two new prenylated flavanones.

*Plant. Milletia ovalifolia* (Leguminosae). *Past work*—on leaves and bark [1], on related species [2,3]. Present work on seeds obtained from L.R. Brothers, Saharanpur, India. Air-dried seeds were powdered and Soxhlet extracted with light petrol (bp 60–80°). Solvent was removed and the residue extracted with EtOH. The extract was concentrated and partitioned between *n*-hexane and acetonitrile. The acetonitrile fraction was column chromatographed on silica gel using petrol with increasing amounts of benzene as the eluent. Besides the already known compounds lanceolatin-B [4], karanjin [5], kanjone [5], pongaglabrone [6] and sitosterol, two new prenylated flavanones (A and B) were isolated.

Flavanone *A* crystallised from EtOAc–petrol as white needles mp 135–136°, mol. formula $C_{25}H_{28}O_3$ ($M^+$ 376). It was soluble in aq. alkali and gave no colour with $FeCl_3$. $\lambda_{max}^{MeOH}$ 280 nm. $\nu_{max}^{KBr}$ 3350, 1660, 1450, 1070, 765 $cm^{-1}$. NMR (δ values; solvent $CDCl_3$): showed one –OH group at 6.29 (*s*, 1H) (+ $D_2O$ exchanged); two isolated aromatic proton peaks at 7.69 (*s*, 1H) (H-5) and 7.50 (*s*, 5H) ($C_6H_5$); three aliphatic protons at 5.45 (*m*, H-2 proton overlapping two =C<u>H</u>–$CH_2$–protons); Four protons at 3.40 (*m*, two $(Me)_2C{=}CH{-}C\underline{H}_2$–units) two protons at 2.97 (*m*, H-3 proton) and a sharp doublet at 1.8 (*Jδ*, = 2Hz, 12H) δ, two $(\underline{Me})_2C{=}CH$– units). δ, These data are in agreement with the structure of 7-hydroxy-6,8-di-*C*-prenylflavanone for *A*. This was confirmed by the fact that the IR spectrum of *A* (in $CHCl_3$) was identical with that of a synthetic sample prepared from 3,5-di-*C*-prenyl resacetophenone [7] by treatment with benzaldehyde under basic conditions. The mixture of chalkone [8] and the corresponding 7-hydroxy-6,8-di-*C*-prenylflavanone was separated by TLC on silica gel.

Flavanone *B*, mp 144–45°, mol. formula $C_{20}H_{20}O_3$ ($M^+$ 308). It was soluble in aq. alkali and gave no colour with $FeCl_3$. $\lambda_{max}^{MeOH}$ 285 nm. $\nu_{max}^{KBr}$ 3125, 1650, 1570, 1430, 1040, 815 $cm^{-1}$. NMR (δ values; solvent $CDCl_3$): showed one –OH group at 7.15 (*s*, 1H) (+$D_2O$ exchanged); two isolated aromatic protons at 7.75 (*d*, *J* = 10 Hz, 1H) (H-5) and 6.55 (*d*, *J* = 9 Hz, 1H) (H-6); sharp peak at 7.45 (*s*, 5H) ($C_6H_5$); aliphatic proton peak at 5.34 (*m*, 2H) (H-2 proton overlapping $(Me)_2C{=}C\underline{H}{-}CH_2$–proton); doublet at 3.18 (2H, *J* = 8 Hz) $(Me)_2C{=}CH{-}C\underline{H}_2$–protons); peak at 2.65 (2H, *m*) (two H-3 protons) and one sharp singlet at 1.35(6H) $(C\underline{H}_3)_2$ C=CH–$CH_2$–protons). It is concluded that *B* is 7-hydroxy-8-*C*-prenyl flavanone This was confirmed by comparing the IR spectrum of *B* (in $CHCl_3$) which was