$[\alpha]_D$ + 56°), and methyl maslinate (from C_6H_6–petrol., m.p. and m.m.p. 203°, $[\alpha]_D$ + 61°), respectively.

Further elution of the original column with C_6H_6–petrol. afforded the monobenzoate methy ester mixture, fractional crystallization of which (as before) gave colourless needles of methyl 2α-benzoyloxy-3β-hydroxy-urs-12-en-28-oate (m.p. and m.m.p. 225°, $[\alpha]_D$ + 3°) and methyl 2α-benzoyloxy-3β-hydroxyolean-12-en-28-oate (m.p. and m.m.p. 182°, $[\alpha]_D$ + 7·7°) as needles. Hydrolysis of both monobenzoate methyl esters, with ethanolic potassium hydroxide, yielded the corresponding diol methyl esters obtained above.

Thus from the above results we can conclude that "guaijavolic acid" is in reality 2α–hydroxyursolic acid.

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ISOLATION OF COCLAURINE FROM *ZIZYPHUS JUJUBA* BY DROPLET COUNTER-CURRENT CHROMATOGRAPHY

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Key Word Index—*Zizyphus jujuba* Mill. var. *inermis* Rehd; Rhamnaceae; frangulanine; adouétine X; coclaurine; peptide alkaloids; droplet counter-current chromatography.

From the basic fraction of methanolic extracts of the root bark of *Zizyphus jujuba* Mill. var. *inermis* Rehd., three new peptide alkaloids, *F*, *G* and *H* have been isolated besides two known peptide alkaloids, frangulanine[1] and adouétine X,[2] by the preparative TLC, while a benzylisoquinoline alkaloid, coclaurine, has been separated by the droplet counter-current chromatography (DCCC), which has been developed by Tanimura *et al.*[3] The structures of the peptides, *F*, *G* and *H* are now under investigation.

DCCC has been shown to be a very efficient method for the separation of water-soluble natural products. Coclaurine was obtained in a crystalline form, m.p. 217–218·5°, by this method.

EXPERIMENTAL

Isolation of peptide alkaloids. The alkaloid fraction was obtained by a usual method.[4] It was separated on preparative TLC (Kieselgel GF_{254}) to yield adouétine X, frangulanine substances, *F*, *G* and *H*.

Identification of adouétine X. Adouétine X, colourless needles, m.p. 278–280° from MeOH, IR_{max}^{KBr} cm^{-1}: 3250 (NH), 2790 (NCH_3), 1630 (CONH), 1238 (C–O–C); NMR ($CDCl_3$) δ 0·69 (3H, *d*, *J* 7 Hz), 0·86 (3H, *t*, *J* 7 Hz) 0·87 (3H, *d*, *J* 7 Hz), 0·94 (3H, *d*, *J* 7 Hz), 0·98 (3H, *d*, *J* 6 Hz), 1·27 (3H, *d*, *J* 6 Hz), 2·20 (6H, *s*, $N(CH_3)_2$); MS, *m/e* 500 (M^+), 114 (100%), 72 (11·3%). Amino acid analysis: Isoleucine, glycine, *erythro* and *threo*-β-hydroxyleucine.

Conditions of DCCC. The alkaloid fraction (970 mg) was developed on DCCC with the solvent system, benzene:$CHCl_3$:MeOH:H_2O = 5:5:7:2. Moving phase: upper layer; Stationary phase:lower layer; Number of glass tubes:500; Theoretical plates:1000. In one fraction 300 drops of eluated moving phase (*ca* 5 ml) were collected, and from the 69–75th fraction tubes fine needle shaped crystals of coclaurine were obtained.

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