

CONVOLVULACEAE

CONSTITUENTS OF THE LEAVES OF *ARGYREIA SPECIOSA*

N. P. SAHU and R. N. CHAKRAVARTI

Indian Institute of Experimental Medicine, Jadavpur, Calcutta-32, India

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Plant. *Argyreia speciosa* (Sweet), (Syn. *Stryptocardia tiliifolia*).*Uses.* Medicinal.¹*Previous work.* On seed,² on sister species.^{3,4}

Leaves. The leaf does not appear to contain any appreciable amount of alkaloid. The light petroleum (60–80°) extract on chromatography over neutral Brockmann alumina yielded 1-triacontanol, C₃₀H₆₂O, m.p. 87–88°, (0.1%, IR, MS; acetate, m.p. 73–74°, IR), epifriedelinol acetate, C₃₂H₅₄O₂, m.p. 288–289° (mixed m.p., $[\alpha]_D^{25} + 33.9^\circ$, CHCl₃; IR), epifriedelinol, C₃₀H₅₂O, m.p. 279–281° (mixed m.p., $[\alpha]_D^{25} + 23.7^\circ$, CHCl₃; IR; acetate, m.p. and mixed m.p.), and β -sitosterol, C₂₉H₅₀O, m.p. 138° (mixed m.p., $[\alpha]_D^{25} - 39.7^\circ$, CHCl₃; acetate, m.p. and mixed m.p. 129°).

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² R. N. CHAKRAVARTI, D. CHAKRAVARTI and R. BANERJEE, *Bull. Calcutta School Trop. Med.* **15**, 139 (1967).

³ R. N. CHAKRAVARTI, D. CHAKRAVARTI and R. BANERJEE, *Bull. Calcutta School Trop. Med.* **10**, 170 (1962).

⁴ JOHN W. HYLIN and DONALD P. WATSEN; *Science* **148**, 499 (1965).

CUCURBITACEAE

STEROLS FROM FRUITS OF *TRICHOSANTHES CUCUMEROIDES*
AND *T. JAPONICA*

TAKAO MATSUNO and SEIICHI NAGATA

Kyoto College of Pharmacy, Department of Natural Products Research, Kyoto, Japan

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Abstract—Stigmast-7-en-3 β -ol and stigmasta-7,22-diene-3 β -ol (α -spinasterol) have been isolated as main sterols from the fruits of the cucurbits *Trichosanthes cucumeroides* Maxim and *T. japonica* Regel.

INTRODUCTION

IN A PREVIOUS paper¹ one of the authors had reported the presence of β -carotene, γ -carotene and lycopene from the fruits of *Trichosanthes cucumeroides* Maxim. The present communication reports the isolation and identification of the sterols from this and a second species.

RESULTS AND DISCUSSION

The sterol fraction was chromatographed on alumina and rechromatographed on silica gel column to give main sterols. Acetylation, followed by column chromatography on AgNO₃ impregnated silica gel column, resulted in the separation of sterol acetate mixture into two components. These were proved to be stigmast-7-en-3 β -ol and α -spinasterol.

The presence of α -spinasterol has been reported from five cucurbitaceous species by Sucrow *et al.*,^{2,3} and stigmast-7-en-3 β -ol and α -spinasterol from two species by Ueno *et al.*⁴ Considered together with the data described above, it seems probable that cucurbitaceous plants may all contain unsaturated C₂₉ sterols (stigmastane series) possessing at least one double bond at C₇ as their major sterols.

EXPERIMENTAL

3.4 kg of the fruits of *Trichosanthes cucumeroides* Maxim. collected in autumn were extracted 3 \times hot 80% EtOH. The EtOH was concentrated under reduced pressure and resulting aqueous solution was extracted 3 \times Et₂O. The Et₂O solubles were chromatographed on columns of neutral alumina (Woelm Grade I) with light petroleum acetone mixtures, and on silica gel with toluene-ethyl acetate (5:1) mixtures. The main sterol fractions were analyzed by using GLC on 1% XE-60 column and TLC on 20% AgNO₃-impregnated silica gel plates, and found to be mixtures of two sterols in a ratio of 4:1. 305 mg of the mixture was acetylated with acetic anhydride in pyridine and followed by chromatography on a 25% AgNO₃-impregnated silica gel column. The sterol acetate were eluted with light petrol containing Et₂O (0.3%).

The first fraction eluted was recrystallized from MeOH to give colorless needles, m.p. 152–154°, [α]_D +6.8°. Analysis by mass spectrometry showed a molecular ion peak at m/e 456 and other peaks at m/e 441 ($M^+ - CH_3$), 381 [$M^+ - (CH_3 + AcOH)$], 315 ($M^+ - \text{side chain}$), 273 [$M^+ - (\text{side chain} + 42)$], 255 [$M^+ - (\text{side chain} + AcOH)$]. The NMR spectrum of the acetate (in CDCl₃) had signals at 0.53 δ (s) for H₃C-18, 0.8 δ (s) for H₃C-19, 2.1 δ (s) for —OAc, 4.43–4.83 δ (m) for =CHOAc, 5.01–5.20 δ (m) for =C=CH—. After saponification of the acetate with 10% EtOH-KOH solution, the resulting free sterol was recrystallized from MeOH to give colorless needles, m.p. 146°, [α]_D +11°. Furthermore, the acetate was hydrogenated with Pt₂O in HOAc to afford an isomeric steryl acetate, 114–115°, [α]_D +13°, which was identical with an authentic sample of stigmast-8(14)-en-3 β -OAc. The above data indicated that the first fraction was stigmast-7-en-3 β -OAc.

The second acetate fraction was recrystallized from 95% EtOH to give colorless needles, m.p. 180–182°, [α]_D +1.8°. Analysis by mass spectrometry showed a molecular ion peak at m/e 454 and other peaks at m/e 411 ($M^+ - 43$), 313 [$M^+ - (\text{side chain} + 2)$]. The IR spectrum (in KBr) showed significant bands at 973 cm⁻¹ (*trans* —CH=CH—) and 1730 cm⁻¹. The NMR spectrum (in CDCl₃) had signals at 0.55 δ (s) for H₃C-18, 0.81 δ (s) for H₃C-19, 2.1 δ (s) for —OAc, 4.5–4.98 δ (m) for =CHOAc, 5.0–5.29 δ (m) for —CH=CH—, =C=CH—. This acetate was saponified and recrystallized from 95% EtOH to afford free sterol. The free sterol, m.p. 166°, [α]_D -1°, was completely identified by direct comparison of an authentic α -spinasterol.

The sterol fraction of the fruits of *Trichosanthes japonica* Regel, showed again stigmast-7-en-3 β -ol and stigmast-7,22-diene-3 β -ol as the main free sterols by TLC (20% AgNO₃ impregnated silica gel plate) and GLC (1% XE-60 column).

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