Chemical Examination of the Seeds of Cassia spectablis

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Z. Naturforsch. 39b, 1425–1426 (1984); received March 13/June 18, 1984

Cassia spectablis, Leguminosae, 2'-O-Glycoside, 6-C-Glucosyl Chromone

Tetratriacontanyl palmitate, tetratriacontanyl nonadecanoate and 2'-O-glycoside of 5-acetonyl-7-hydroxy-6-glucoyl-2-methyl chromone have been isolated from the seeds of Cassia spectablis.

Introduction

From the seeds of Cassia spectablis two higher fatty acid esters and a chromone glycoside have been isolated and their structures elucidated. Two esters and a glycoside have not been isolated earlier from any plant sources.

Results and Discussion

From the seeds of C. spectablis two long chain esters I C₃₀H₆₀O₂ m.p. 69 °C and II C₃₅H₇₆O₂ m.p. 65 °C and a chromone glycoside III C₂₅H₂₇O₁₄ m.p. 290 °C have been isolated and Homogeneity and purity of these compounds were established by chromatography.

NMR spectrum of I (M⁺ 732) has signals at δ 4.02 ppm (2H, t, -CH₂-O-C-); 2.40 ppm (2H, t, -CH₃-C-); 1.11 ppm (s, 92H, -CH₃) and 0.84 ppm (s, 6H, -CH₃) which showed that it is ester in nature. I on hydrolysis gave tetratriacontanol and palmitic acid. On the basis of the above facts I may be assigned as

\[ \text{CH}_3-(\text{CH}_2)_{32}-\text{CH}_2-O-C-(\text{CH}_2)_{14}-\text{CH}_3 \] (I)

I was synthesised by condensing tetratriacontanol and palmitic acid in presence of DCC. Synthetic ester was found to be identical in all respect with the natural product.

The chemical behaviour and spectral data of II (M⁺ 774) showed that it has similarity with I, II on acid hydrolysis gave tetratriacontanol and nonadecanoic acid. The ester II must therefore be

\[ \text{CH}_3-(\text{CH}_2)_{32}-\text{CH}_2-O-C-(\text{CH}_2)_{14}-\text{CH}_3 \] (II)

The above structure was also confirmed by its synthesis. This compound is also new not isolated from any source.

The odd carbon fatty acids are not known to occur in fats and with exception of one or two cases [1, 2]. The isolation of ester having nonadecanoic acid as its constituents, therefore appears to be an interesting observation.

III: C₂₅H₂₇O₁₄ m.p. 290 °C showed characteristic colour reactions of chromone and its UV spectrum was typical of 7-hydroxy chromone. IR of III suggested it to be a glycoside.

1H NMR of III has two doublets of one proton each at δ 4.24 ppm (J = 7 Hz, H-1”) and 4.74 ppm (J = 9 Hz, H-1”) suggested the presence of two sugar moieties. Hydrolysis of III yielded glucose and an aglycone 5-acetonyl-6-glucoyl-7-hydroxy-2-methyl chromone. This aglycone was identical with the glycoside isolated from the leaves of Cassia multifluga [3].

Attachment of second glucose units to the C-6 glucose units and not directly to the 7-hydroxy was established by UV shifts. This established that III was a α’-O-glucoisde of 6-glucosyl-5-acetonyl-7-hydroxy-2-methyl chromone.

Treatment of III with acetone in presence of CuSO₄ afforded mono and disopropylidine derivatives indicating that second glucose unit was not linked to 4’-º or 6’-º positions [4]. Examination of the 1H NMR spectrum of acetyl derivative of III revealed no acetyl signals in the range δ 1.70–1.85 ppm. Since a C-2º acetoxyl would be expected to give rise to a signal in this region [5–7], it is...
concluded that glucose is instead attached at position-2". The absence of M-15 and M-31 peaks in the mass spectrum of the permethylated compound [9] of III is also indicative of α-2"-O-glucosylated compound [8]. Thus III is

Experimental

The seeds were extracted with pt ether, pt ether extract was concentrated and chromatographed over alumina and eluated with pt ether: benzene: chloroform (1:1 V/V). Pt ether: benzene fraction yielded compound I whereas benzene: chloroform yielded compound II.

Compound I: C_{50}H_{100}O_{2}; crystallised from benzene, m.p. 69 °C, IR ν_{max} KBr 2918, 2848, 1732 (−OH), 1462 (−CH_{2}−), 730, 720, NMR [CDCl_{3}; 200 MHz] δ 4.02 (t, 2H, −CH_{2}−O−C−), 2.24 (t, 2H, −CH_{2}−C−), 1.22 (s, 92H, −CH_{2}−) and 0.84 (s, 6H, −CH_{3}) MS, m/e 732, 704, 676, 648, 620, 508, 480, 452, 424, 409, 392, 364, 342, 313, 295, 111, 97, 85, 71, 57, 29.

Compound II: C_{53}H_{106}O_{2} crystallised from benzene m.p. 65 °C, IR ν_{max} KBr 2918, 2848, 1732, 732, and 720 cm\(^{-1}\). NMR [CDCl_{3}, 200 MHz] δ 4.02 (t, 2H, −CH_{2}−O−C−), 2.24 (t, 2H, −CH_{2}−C−), 1.22 (s, 92H, −CH_{2}−) and 0.84 (s, 6H, −CH_{3}) MS, m/e 732, 704, 676, 648, 620, 508, 480, 452, 424, 409, 392, 364, 342, 313, 295, 111, 97, 85, 71, 57, 29.

Hydrolysis: 100 mg of I and II were hydrolysed with 7% KOH and the hydrolysate were poured in distilled water when ppt were obtained. The ppt of I and II were crystallised from benzene. Filtrate were neutralised with HCl, extracted with ether. Ether fractions of I and II yielded acids which were crystallised from ether.

Synthesis: To a solution of 52 mg of palmitic acid and 100 mg of tetratriacontanol in 50 ml dry ether, 42 mg DCC was added and the solution stirred 12 hrs at room temp. After leaving overnight, the solvent evaporated and marcerated with acetone and the acetone soluble portion was ppt with pt ether and crystallised with benzene m.p. 69 °C. Compound II was also synthesised in the same way using tetratriacontanol and nonadecanoic acid.

Compound III: The defatted seeds were extracted with ethanol and poured in water giving an aqueous solution (fraction I) and coloured residue (fraction II), the aqueous fraction was concentrated and extracted with Et_{2}O and ethyl acetate. Et_{2}O fraction was chromatographed over silica gel and eluted with benzene: Et_{2}OAC (4:6). This eluate gave III m.p. 90 °C. IR ν_{max} KBr 3300, 1740, 1640, 1595, 1490, 1033, 1010 cm\(^{-1}\). UV A_{max} EtOH 220, 245, 255, 295 nm. NMR [DMSO-d_{6}, 100 MHz] δ 6.55 (1H, s, C-8), 5.93 (1H, br, C-3), 2.27 (3H, br, C−CH_{3}), 4.10 (2H, s, CO CH_{2}−), 2.18 (2H, s, COCH_{3}), 3.40−3.80 (11H, m, glucosyl); 4.24 (1H, d, J = 7 Hz, H-l′′); and 4.74 (1H, d, J = 9 Hz, H-l″). Hydrolysis: A solution of III was hydrolysed with 7% HCl by usual methods. The aglycone was crystallised from Et_{2}OAC: Pt ether m.p. 190 °C (d.). Glycoside-octaacetate: 100 mg of III was acetylated. The product after the usual work up was separated m.p. 200 °C. NMR (DMSO-d_{6}) δ 1.95, 2.00, 2.02, 2.06, and 2.12 (s, 21 sugar acetyl), 2.46 (s, 3H, 7-O-acetyl).

Permethylation: 100 mg of III was permethylated [9]. The product after the usual work up separated m.p. 150 °C. MS (m/e) 556, 509, 476, 462, 446, 433, 395, 385, 381, 367, 337, 321, 281, 231, 190.

One of us (M. Singh) is grateful to the CSIR, New Delhi, India for the award of Senior Research fellowship.