• *Short Communication*

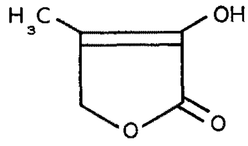
β-Methyl *α*-Tetronic Acid From Twitchell Hydrolysis of Kusum Oil *(Schleichera trijuga)*

Kusum oil is unique among vegetable oils. On saponification the oil yields 91.6% of fatty acids (mainly palmitic, oleic and arachidic acids) and a C_{20} monoene acid (1–3), and 3.6% to 4% of glycerine (2). The oil also contains 1.15% of nitrogen (2,4). On saponification 0.8% to 1.1% of CN^- expressed as hydrocyanic acid is obtained (2). Thin layer chromatography (Silica gel G; petroleum ether-ether, 95:5) shows that the oil is composed of approximately 37% of glyceride, the rest being non-glycerol esters of fatty acids (2).

The preferential hydrolysis of non-glycerol esters of kusum oil has been achieved by heating the oil with zinc oxide (1.25%), water (80% by volume) and sodium hydrosulfite (2.5%) at 120 C (2,5) or by water alone at 170 C.

The non-glycerol alcohols are quite unstable and decompose to intractable products on saponification or even on zinc oxide treatment. With a view to isolating and characterizing the non-glycerol alcohols, Twitchell hydrolysis of kusum oil was carried out by passing steam for 20 hr through a vigorously stirred mixture of oil (2 kg 16% FFA) and sulfuric acid (2 kg) containing 20 g dodecylbenzene sulfonic acid. The top fatty layer (90% FFA) was removed and the dark brown aqueous layer was concentrated in vacuo to a small volume and repeatedly extracted with ether. Removal of the ether gave a syrup 92 g (4.6% yield) which rapidly set to a thick mass of colorless crystals.

Based on chemical and spectral data, the compound was identified as β-methyl α-tetronic acid (I).



(I)

This compound was described by Schinz and Hinder (6); much of its chemistry and other properties have been discussed (6–8). Abraham and Newton (9) also have isolated this compound by treating cephalosporin C with Raney nickel followed by acid hydrolysis.

The substance isolated from kusum oil is highly hygroscopic and tends to decompose on storage. It crystallizes from benzene in large colorless prisms at mp 83 C. (Schinz and Hinder reported mp 90–92 C after purification) MW 114 (mass spectrum). The UV spectrum of the crude substance in water shows an absorption maxima at 232 mμ log ε 3.97. In alkaline solution the absorption maxima is shifted to 265 mμ, log ε 3.88. Abraham and Newton (9) reported λ max 232 mμ, log ε 3.9 in water and λ max 265 mμ, log ε 3.8 in 0.05 N·NaOH. According to Schinz and Hinder the compound has λ max 232.5 mμ, log ε 4.1.

NMR (100 MC) of the substance in CD_3SO CD_3 shows a peak at δ 1.87 (integral 3) split by long range coupling (J ~1.2 c/s) into a triplet indicating CH_3 on a double bond. A quartet (integral 2) J ~ 1.2 c/s at δ 4.62 indicates $-OCH_2$. Two protons at δ 7.17 can be explained as due to water and a hydroxyl group.

The enol ether prepared by reaction with diazomethane is also hygroscopic and has mp 35–36 C: bp 80 C/2 mm. The reported values are mp 42–43 C after several recrystallizations and bp 110–112 C/11 mm (6). MW 128 (mass spectrum). IR in $CHCl_3$: 1790 cm^{-1} shoulder, intramolecular vibrational effect; 1762 cm^{-1} (S) α, β unsaturated γ-lactone; 1690 cm^{-1} (S) C = C stretching. NMR (60 MC) $CDCl_3$; 3 proton sharp singlet at δ 3.92–OCH_3; a three proton distorted triplet at δ 2.04. CH_3 on a double bond; a two proton singlet at δ 4.7 O–CH_2.

Because of the instability and hygroscopic nature of the enol as well as the enol ether, a direct comparison with the synthetic material (7) was not attempted. Therefore, the more stable enol tosylate was prepared by treating the enol with pyridine and *p*-toluene sulfonyl chloride. The tosylate crystallized in colorless prisms; mp 102–103 C (Analysis: Calculated for $C_{12}H_{12}O_5S$, requires C, 53.73; H, 4.48. Found C, 54.01; H, 4.76). The enol tosylate from kusum oil had the same melting point, mixed melting point and infrared as the synthetic enol tosylate.

Further confirmation of the structure was obtained through the preparation of DL valine from the enol by reductive hydrogenolysis of the enamine (10). The genesis of α-tetronic acid and its relation to non-glycerol alcohols are under investigation.

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