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PETROLEUM ETHER SOLUBLE CONSTITUENTS OF TRICHOLEPIS GLABERRIMA AND XANTHIUM STRUMARIUM FRUITS

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Abstract.--The petroleum ether extract of Tricholepis glaberrima was found to be mainly composed of C_{27}-C_{33} n-alkanes and C_{28}-C_{32} n-alkanols. The unsaponifiable portion of the Xanthium strumarium petroleum ether solubles consisted of C_{23}-C_{35} n-alkanes, C_{22}-C_{30} n-alkanols, and a sterol mixture of sitosterol, stigmasterol, and campesterol.

During a program directed toward a study of the medicinal plants in the Chandigarh, India area, we had occasion to examine the constituents of Tricholepis glaberrima DC and Xanthium strumarium Linn. Both plants have been employed in the indigenous medicine of the area for a variety of ailments (Chopra et al., 1956, p. 247; Kirtikar and Basu, 1933, p. 1356) so it seemed of interest to do a complete examination of their chemical components. Thus far, we have reported (Chawla et al., 1976) the presence of betulin, spinasterol, stigmasterol, and stigma-7-en-3-ol in T. glaberrima. Bhakuni and coworkers (1961) had analyzed the fruit oil of X. strumarium for its fatty acid composition and also indicated the presence of sitosterol and ceryl alcohol, while Tsukamoto and coworkers (1963) and Nishioku et al. (1965) indicated the presence of stigmasterol, sitosterol, and campesterol in the fruit. Work by Khafagy et al. (1974) with X. strumarium uncovered a phytosterol, $C_{28}H_{48}O_2$, and two triterpene alcohols, $C_{30}H_{50}O_2$ and $C_{30}H_{50}O_5$. More recently, we have presented results (Kapoor et al., 1976) about the fatty acid content of the fruit and seed oils of this plant. In this paper we wish to communicate the nature of the non-nitrogenous constituents of the fruits of both T. glaberrima and X. strumarium.

METHODS AND RESULTS

General.--The plant materials used in this study were collected near Chandigarh, India, and authenicated by Dr. J. K. Bhatnagar, Panjab University. Except as noted, gas liquid chromatographs (GLC) were performed on a Varian-Aerograph Series 2700 instrument with a flame ionization detector and an Autolab System IV computing integrator. A 5 ft. by 1/8 inch column of 1.5% OV-101 on 100/120 HP Chrom G was employed at

the temperatures indicated. Infrared spectra were recorded with a Perkin-Elmer 137 spectrophotometer on solids incorporated in KBr discs. The petroleum ether used for extractions and chromatography had bp 60-80°.

Tricholepis glaberrima.--Dried powdered fruits (800 g) were extracted in a Soxhlet apparatus to yield 18 g of crude plant material, which was chromatographed on alumina (400 g, S. Merck, India). The first fractions (3 x 150 ml) eluted with pet. ether gave a waxy substance (0.6 g) which could be crystallized from acetone to mp 68-70°; ν_{max} 728 and 717 cm^{-1} $[-(CH_2)_x-]$. GLC of the substance from 90-240° at 4°/min. exhibited signals corresponding to the following n-alkanes (% in mixture): C_{21}-C_{26} (traces), C_{27}(1.9%), C_{28}(1.5), C_{29}(23.1), C_{30}(5.2), C_{31}(60.3), C_{32}(2.8), C_{33}(5.2), C_{34}-C_{35}(traces). The next two fractions collected (150 ml each) afforded 0.2 g of residue with mp 65-68° which also proved to be an n-alkane mixture. It consisted of C_{23}-C_{26}(traces), C_{27}(3.3%), C_{28}(1.4), C_{29}(26.9), C_{30}(5.0), C_{31}(56.8), C_{32}(1.6), C_{33}(4.2), C_{34}-C_{35}(traces).

Further elution of the column with pet. ether-benzene (4:1; 4 x 150 ml) gave 0.4 g, mp 88-90° (from acetone); ν_{max} 3226 (O-H), 1059(C-O), 727, and 717 cm^{-1} $[-(CH_2)_x-]$. GLC of the material at 235° revealed it to be the n-alkanols: C_{26}(trace), C_{28}(11.1%), C_{29}(4.7), C_{30}(50.3), C_{31}(3.5), and C_{32}(26.3).

Xanthium strumarium.--The powdered fruits (1 kg) were extracted with pet. ether which gave an oil (131 g). The unsaponifiable matter (2.4 g) separated from the oil was chromatographed on alumina (120 g). Elution of the column with pet. ether (3 x 100 ml) produced a n-alkane wax (0.2 g) which crystallized from ethyl acetate with mp 62-65°; ν_{max} 728 and 717 cm^{-1}. GLC resolution of the material from 90-240° at 4°/min indicated an n-alkane composition of C_{23}(trace), C_{24}(1.2%), C_{25}(4.8), C_{26}(6.6), C_{27}(19.2), C_{28}(10.0), C_{29}(27.7), C_{30}(6.4), C_{31}(12,3), C_{32}(4.1), C_{33}(4.7), C_{34}(1.6), and C_{35}(1.4).

Fractions obtained with pet. ether-benzene (1:3; 3 x 100 ml) afforded 0.17 g of n-alkanols; mp 77-80° (from MeOH); ν_{max} 3279(O-H), 1055(C-O), 728 and 718 cm^{-1} $[-(CH_2)_x-]$. GLC analysis at 235° indicated the following straight chain alkanols: C_{22}(6.2%), C_{23}(1.8), C_{24}(29.4), C_{25}(3.6), C_{26}(18.8), C_{27}(trace), C_{28}(14.5), C_{29}(7.9), and C_{30}(13.4).

Subsequent elution of the column with benzene (7 x 100 ml) resulted in 0.4 g of sterols which were recrystallized from MeOH to mp 133-135°; ν_{max} 3268(O-H), 1053(C-O), and 962 cm^{-1} (trans C=C). GLC of the silyl derivative on a 6 ft by 1/8 inch column of 3% SE-30 on Chrom Q at 240° exhibited signals corresponding to sitosterol (65%), stigmasterol (28%), and campesterol (17%).

DISCUSSION

This report represents the first study and characterization of the petroleum ether solubles obtained from the fruits of Tricholepis glaberrima DC and Xanthium strumarium Linn. Although none of the compounds identified are unknown or unusual, several observations can be made from the % content of the various homologs in the n-alkane and n-alkanol fractions. For example, it can be noted that both the n-alkanes and n-alkanols from T. glaberrima are definitely concentrated in two compounds-nonacosane and hentriacotane

in the alkane series and triacontanol and dotriacontanol for the alkanols-because their percentages are considerably higher than the others. If the biosynthetic pathway whereby a fatty acid can give rise to an alkanol with the same number of carbons or an alkane with one less carbon (by decarboxylation) is assumed, it is clear that T. glaberrima fruits produce and use mainly the C_{30} and C_{32} fatty acids for the formation of its alkanes and alkanols.

Results from Xanthium strumarium fruits are not as clear. The percent composition of both the alkanes and alkanols are more diverse with the four largest components not differing markedly from each other and these as a group differing less than 10% from the next highest percentage group. Also, there is no correlation between one or two particular fatty acids and definite high content alkanes or alkanols. For example, 29.4% of tetracasanol is present in the alkanol mixture while no tricosane (C_{23}) which would result from the same fatty acid is found. Similarly, 12.3% of the C_{32} n-alkane occurs while the C_{32} n-alkanol is absent.

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