

233. *The Volatile Oil Glycosides of Thesium virgatum.*

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A glycosidic extract from *Thesium virgatum* gives on hydrolysis a volatile oil containing at least three components. An alcohol $C_{10}H_{18}O$ (or less probably $C_{10}H_{20}O$) and an alcohol $C_8H_{14}O$ (or less probably $C_8H_{16}O$) are the major constituents: both contain one double bond and give acetone on oxidation with potassium permanganate. Difficulties in obtaining supplies of plant materials have precluded the investigation being carried beyond this point.

DE KOCK and RAPSON (*Nature*, 1938, **142**, 1078) have reported that in various species of the genus *Thesium* (order *Santalaceae*) the presence or absence of the easily identifiable constituents phlobatannin and/or volatile oil glycoside corresponds to the grouping of the species according to the structures of the flowers and other morphological characters. There are very few cases recorded of the isolation of terpenoid essential oil glycosides from plant materials, although such substances have been postulated as intermediates in the production of essential oils. An examination of the glycosidic material of the most abundant species, *T. virgatum*, has therefore been carried out.

The material was isolated by extraction and proved to be an inseparable mixture of several glycosides. It was stable to prolonged incubation with emulsin or yeast and was unaffected by treatment with freshly crushed plant tissues. These facts have probably some connection with its survival in the plant. It was readily hydrolysed, however, by mineral acid to yield glucose and a steam-volatile oil identical with that derived by steam-distillation of the plant tissues in the presence of mineral acid. The oil used in the experiments here described was obtained in the latter way.

The oil is a mixture of at least three substances, but owing to the small amount available these have not been accurately characterised, and the presence of others is possible. From elementary analyses and determinations of bromine values and of molecular refractions, one compound is regarded as an alcohol $C_8H_{14}O$ (or $C_8H_{16}O$) containing one double bond and another as an alcohol $C_{10}H_{18}O$ (or $C_{10}H_{20}O$) also containing a double bond. Solid derivatives have not been obtained: with reagents such as *p*-nitrobenzoyl chloride and phenyl isocyanate, dehydration occurred and esters were not isolated. Hydrogen chloride gave no crystalline hydrochloride. Both alcohols, however, gave acetone as a neutral product of the action of potassium permanganate, indicating the presence of an isopropylidene group; the acidic products behaved like mixtures and characterisation was not possible. Oxidation by the Kuhn-Roth micro-method gave 1 mol. of acetic acid, so but the one CMe group is present. A trace of a third substance has been isolated from the high-boiling fractions of the oil; it is a crystalline unsaturated hydrocarbon C_nH_{2n} ($n = \text{approx. } 18$) and is apparently formed by dehydration of a further alcoholic component during hydrolysis or distillation.

EXPERIMENTAL.

Isolation of the Glycosidic Fraction by Extraction.—The dried and crushed plant material was extracted with ether, until the extract was colourless, and then with alcohol. The alcoholic extract was evaporated in a vacuum, the residue diluted with water, and the phlobatannin precipitated by addition of lead subacetate solution. The liquid was filtered before and after treatment with hydrogen sulphide, rendered neutral with calcium carbonate, and evaporated in a vacuum. The concentrate did not reduce Fehling's solution and left an amorphous residue when evaporated to dryness.

Hydrolysis. The glycosidic material in solution in 2% sulphuric acid was rapidly hydrolysed on heating. The oil liberated was extracted in ether, dried, and fractionally distilled; its behaviour was identical with that described below for the oil obtained from the acidified plant material by direct steam-distillation. The aqueous portion of the hydrolysis mixture was treated with barium carbonate, and the filtered solution evaporated in a vacuum. The residue gave *d*-phenylglucosazone, identified, after several crystallisations from aqueous pyridine, by mixed m. p. and crystal examination.

Steam-distillation of the Oil from the Plant.—The dry plant material (all the above-ground

portions of the plant) was moistened with 2% sulphuric acid and submitted to the action of steam. The tissues rapidly turned red and an oil distilled. The bulky distillate was extracted several times with ether and the extract was washed with dilute alkali solution to remove traces of phenolic substances, dried, and evaporated. The yield of oil was 0.1—0.2% of the dry weight of the tissues. It was found advantageous to carry out the operation with small batches of material (1—2 kg.), as with larger batches the sodden mass did not allow of proper circulation of the steam. The oil was distilled at 20 mm. pressure through a micro-fractionating column (Cooper and Fasce, *Ind. Eng. Chem.*, 1928, 20, 420), and the following fractions obtained (from a total of 25 g. of oil) :

Fraction.	Weight, g.	B. p.	$n_D^{18^\circ}$.	$d_{18^\circ}^{18^\circ}$.	$[R_L]_D$.	$[R_L]_D$, calc.
I	3	69—74°	1.4614	0.883	—	—
II	2	74—90	1.4625	0.894	—	—
III	5	90—93	1.4619 (1.4622)	0.906 (0.906)	38.2 38.8	37.7 (for $C_8H_{14}O$) 40.0 (for $C_8H_{16}O$)
IV	3	93—107	1.4716	0.921	—	—
V	5	107—109	1.4812 (1.4808)	0.933 (0.933)	47.0 47.6	47.2 (for $C_{10}H_{18}O$) 49.3 (for $C_{10}H_{20}O$)
VI	5	Residue				

Fractions III and V were well defined. Fractions I, II, and IV, which distilled without any marked break in the distillation curve, were combined and refractionated, giving further small amounts of fractions III and V, the physical properties of which are recorded in parentheses. The residue from the fractional distillation distilled at 109—*ca.* 145°/20 mm. From the fraction boiling above 130°, traces of crystals separated on addition of methyl alcohol. They were recrystallised four times from this solvent, yielding 6 mg. of colourless plate-like crystals, m. p. 50—52°. This substance was also obtained from the oil formed by hydrolysis of the glycosides.

Analyses. Fraction III. Found : C, 75.9; H, 11.5; side-chain Me, 9.5; *M* (by bromine addition, the presence of one double bond being assumed), 133. $C_8H_{16}O$ requires C, 75.0; H, 12.5; side-chain Me, 11.7%; *M*, 128. $C_8H_{14}O$ requires C, 76.2; H, 11.1; side-chain Me, 11.9%; *M*, 126.

Fraction V. Found : C, 77.1, 77.3; H, 11.8, 11.6 (different samples); side-chain Me, 9.6; *M* (by bromine addition), 155, 158; *M* (Rast), 156. $C_{10}H_{18}O$ requires C, 77.9; H, 11.7; side-chain Me, 9.7%; *M*, 154. $C_{10}H_{20}O$ requires C, 76.9; H, 12.8; side-chain Me, 9.6%; *M*, 156.

Crystals. Found : C, 85.2; H, 14.8; *M* (Rast), 257. $C_{18}H_{36}$ requires C, 85.7; H, 14.3%; *M*, 252.

Bromine additions were carried out by cooling a solution of the oil in carbon tetrachloride in ice and adding an excess of bromine in carbon tetrachloride. After 2 minutes the residual bromine and the hydrogen bromide formed were determined iodometrically. From a knowledge of the latter quantity, a correction for bromine used in substitution was made.

Permanganate oxidations. The same results were obtained with fractions III and V. The oil (2 g.) was shaken with water (100 c.c.), potassium permanganate solution (1.5%) added gradually at room temperature, and the mixture warmed; 400 c.c. of the solution were required to produce a moderately permanent pink colour. The excess of permanganate was destroyed with sulphur dioxide, and the filtered solution distilled, 100 c.c. of distillate being collected. With Brady's reagent this gave a copious precipitate of acetone-2 : 4-dinitrophenylhydrazone, identified by mixed m. p. The liquid in the flask was evaporated in a vacuum, and the residue acidified and extracted with ether. The extract left an oily acidic residue on evaporation, from which a crystalline *p*-bromophenacyl ester could not be prepared.