1050. *Colouring Matters of the Aphididae. Part XXV.*[1] *A Comparison of Aphid Constituents with those of their Host Plants. A Glyceride of Sorbic Acid*

By J. H. Bowie and D. W. Cameron

The aphid *Dactynotus jaceae* (L.) contains 2-*trans,trans*-sorbo-1,3-dimyristin as its major triglyceride (65%). This compound is the first glyceride of sorbic acid to be reported. Hydrolysis of other aphid glycerides also gives sorbic acid, in quantities that vary with species, together with saturated fatty acids, chiefly myristic. The fat of four *Centaurea* species, hosts of *D. jaceae*, is quite different, however, and contains no sorbic acid. A similar difference between this aphid and its hosts is observed in flavonoid content. The latter contain substantial amounts of the flavonol jaceidin and related compounds, whilst in the former no flavonoids were found. However, the amino-acid and carbohydrate content of both plants and insect were identical, these substances being constituents of phloem sap which aphids ingest: no naphthalenic precursors of aphid pigments could be isolated from the plants, and it seems probable that such pigments are synthesised *de novo* in the insect.

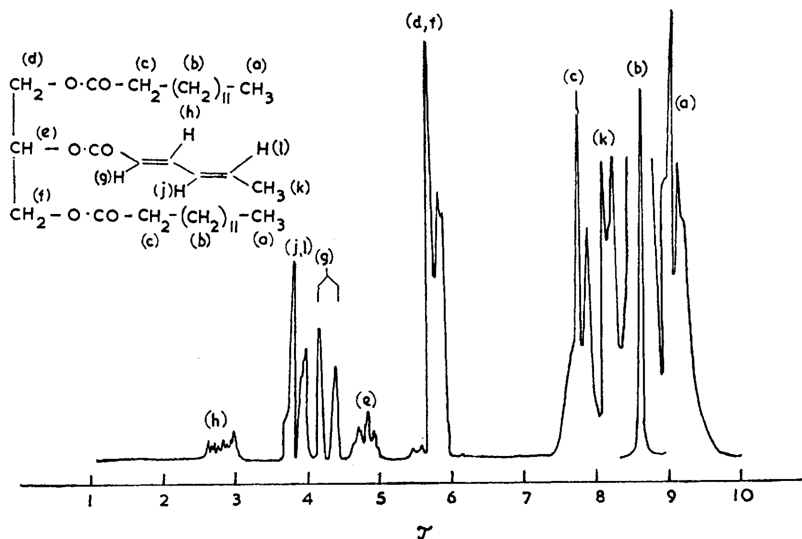
Our studies on aphid constituents have been concerned hitherto with the chemistry of their pigments. Structures for some of these substances have already been elucidated,[2] while others are currently under examination. All are polycyclic quinones. They have not been found outside the Aphididae and related families, and are certainly not present in detectable amounts in plants infested by aphids. Since the diet of any individual species of aphid is generally confined to a very few plants this shows that, whatever their detailed biogenesis, aphid pigments are synthesised, at least in part, by the insect and not simply ingested from its host. In extending this, we now discuss some other constituents of aphids and their hosts. Many of our experiments were carried out on the large bronze-coloured aphid *Dactynotus jaceae* (L.) and its hosts *Centaurea jacea*, *C. nigra*, *C. scabiosa* (knapweed), and *C. cyanus* (cornflower). These insects contain a new series of pigments, the dactynaphins, which we have not yet described but which are, in a number of respects, similar to the aphins themselves. Insect and plant materials were examined concurrently in the late summer, when infestation was most widespread.

In common with many other aphid species, *D. jaceae* yields a fat-soluble fraction, which solidifies readily and amounts to 5—6% of the live insect weight.* An extensive previous survey [3] of aphid fatty acids showed them to be mixtures of saturated compounds, with myristic acid as the chief component. However, the crude extract of *D. jaceae* absorbed strongly at 261 mμ. This is characteristic neither of unbranched conjugated dienes, αβ-unsaturated esters, nor of previously reported aphid constituents. Thin-layer chromatography on silicic acid showed the presence of two major components, one of which was identical with trimyristin. Conversion into methyl esters and vapour-phase chromatography confirmed that myristic acid (87%) was indeed the only saturated acid present to any significant extent. It could be isolated, by chromatography of the free acids on silicic acid, together with a second component (13%) having $\lambda_{max.}$ 254 mμ, readily identified as *trans,trans*-sorbic acid. This, surprisingly, appears to have been reported from only one other natural source [4] (in 1859), never as a glyceride, and never from the animal kingdom.

* From *Eriosoma lanigerum* (Hausmann), the woolly apple aphid, which surrounds itself with an extensive waxy secretion, the corresponding yield was 34%.

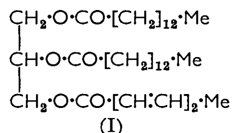
[1] Part XXIV, D. W. Cameron, H. W.-S. Chan, and D. G. I. Kingston, *J.*, 1965, 4363.
[2] A. Calderbank D. W. Cameron, R. I. T. Cromartie, Y. K. Hamied, E. Haslam, D. G. I. Kingston, Lord Todd, and J. C. Watkins, *J.*, 1964, 80.
[3] F. E. Strong, *Hilgardia*, 1963, **34**, No. 2, 43.
[4] A. W. Hofmann, *Annalen*, 1859, **110**, 129.

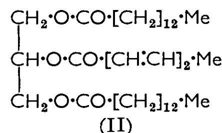
The unsaponified fat was fractionated on silicic acid and yielded the two major components trimyristin (35%) and a new triglyceride (65%) having $\lambda_{max.}$ 261 mμ. This is formulated as a *trans,trans*-sorbodimyristin since, on saponification, it yields the two acids in correct proportion and in agreement with its nuclear magnetic resonance (n.m.r.) spectrum (Figure). This was virtually a summation of the spectra of *trans,trans*-sorbic acid in the 0—10 τ region, and of trimyristin, and its peaks were of the correct relative intensities. It remains to distinguish between the two possible structures (I) and (II) for this new substance. Both were synthesised. Reaction of 1,2-*O*-isopropylideneglycerol with *trans,trans*-sorboyl chloride, followed by removal of the protecting groups [5] gave 1-sorbin as an oil. Treatment with two moles of myristoyl chloride then gave compound (I). The symmetrical analogue (II), was prepared by treatment of 1,3-dimyristin [5,6] with an excess of *trans,trans*-sorboyl chloride in pyridine under forcing conditions. Both compounds (I) and (II) had virtually the same melting point as the natural glyceride which was, however, identified as (II) by mixed melting point and infrared and n.m.r. spectra.



N.m.r. spectrum at 60 Mc./sec. of glyceride (II) in CCl_4

This structure supports the observation, made on vegetable fats, that, in mixed saturated–unsaturated triglycerides, an unsaturated residue generally esterifies the central hydroxyl of the glyceryl unit.[7a] Other short-chain acids of natural fats include butyric from milk fats [7b] and isovaleric from marine sources, *e.g.*, dolphins.[7c] Sorbic acid could of course be derived *via* the normal fatty-acid pathway from acetate–malonate units. Alternatively, as it is a six-carbon acid only two oxidation levels lower than glucose, which *D. jaceae* ingests (see below) in relatively enormous quantities, the possibility of direct conversion cannot be excluded.





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[5] H. P. Averill, J. N. Koch, and C. G. King, *J. Amer. Chem. Soc.*, 1929, **51**, 866.
[6] E. Baer and O. L. Fischer, *J. Amer. Chem. Soc.*, 1948, **70**, 609.
[7] T. P. Hilditch and P. N. Williams, "The Chemical Constituents of Natural Fats," 4th edn., Chapman and Hall, London, 1964, (*a*) p. 20; (*b*) p. 143; (*c*) p. 74.

Other species of aphids also were examined (Table 1). In only one other case, *Tuberolachnus salignus*, was a substantial quantity of sorbic acid observed. All species, however, contained material having $\lambda_{max.}$ 261 mμ, formulated, by analogy, as sorboyl glycerides. Methyl sorbate was, in such cases, detected by vapour-phase chromatography. Most of these aphid species were not examined in Strong's more extensive survey,[3] but the general trend of his results and ours is the same. Myristic acid is the most commonly occurring fatty acid, together with smaller amounts of palmitic and lauric acids in that order, and traces of other even-numbered saturated acids. One elution peak, assigned by Strong to an iso C_6-ester, has a relative retention time similar to methyl sorbate and, in view of our results, the possibility of this latter assignment being more correct must be considered.

TABLE 1

Aphid triglycerides (% of fatty acid in saponification mixture)

Aphid	$E^{1\%}_{1 cm}$ (261 mμ) *	Sorbic † (0·50)	C_6 (0·36)	C_8 (1·08)	C_{10} (2·07)	C_{12} (4·09)	C_{14} (7·32)	C_{16} (20·40)	C_{18} (41·40)
Dactynotus jaceae	252	13	tr.	—	—	tr.	87	—	—
Tuberolachnus salignus	311	16	tr.	tr.	—	3	81	—	—
Eriosoma lanigerum	41	2	tr.	tr.	tr.	17	70	11	tr.
Aphis sambuci	26	1	tr.	—	—	tr.	50	49	—
Aphis fabae	24	1	tr.	—	—	tr.	51	48	—
Macrosiphoniella artemisiae	26	1	2	—	—	5	63	29	—
Brevicoryne brassicae	14	tr.	1	—	—	2	57	40	—

* Pure compound (II) has $E^{1\%}_{1 cm}$ (261 mμ) 402. † Retention times (min. sec.) are given in parentheses.

The only other discrepancy is that, in contrast to Strong, we did not observe any C_9-acid in the hydrolysates. This may be due to the fact that his results were obtained on total fats whereas our experiments were carried out on solids obtained by low-temperature crystallisation which may well have largely eliminated trace or liquid components from the mixture. Finally, it is noteworthy that, in the species we examined, a high content of scorbic acid appears to be associated with a low content of palmitic acid, and *vice versa.* The reason for this, and whether any relationship exists between fat and pigment content of aphids is, at present, a matter for speculation.

A similar examination of the fats from the four *Centaurea* species mentioned earlier as hosts of *D. jaceae*, showed compositions almost identical with one another but substantially different from that of the insect. Thin-layer chromatography on silicic acid indicated at least fifteen different components. Column chromatography showed that 65% of the fat-soluble components were triglycerides. Conversion into methyl esters and vapour-phase chromatography indicated the presence of myristate (4·5%), palmitate (32·5%), stearate (63%), and no sorbate.

Centaurea species also contain flavonoid material in considerable quantity. Previous workers have reported the presence of glycosides of the following flavonols; apigenin (III; $R^1 = R^2 = R^3 = H$, $R^4 = OH$) from flowers of *C. scabiosa* and *C. cyanus*,[8] scutellarein (III; $R^1 = R^3 = H$, $R^2 = R^4 = OH$) from leaves of *C. scabiosa*,[9] and jaceidin (III; $R^1 = R^2 = R^3 = OMe$, $R^4 = OH$) from leaves and stems of *C. jacea*.[10] In the course of examining these species for precursors of aphid pigments, we observed these compounds not only as glycosides but also as the free aglycones in yields given in Table 2. The aglycone jaceidin does not appear to have been found in Nature before, although the possibility that it arose in our experiments by enzymic hydrolysis during preparation of plant material for extraction cannot be excluded. All species were extracted at the same time of year. The high yield of jaceidin in the leaves of *C. nigra* is particularly noteworthy. We had

8 H. Wagner and W. Kirmayer, *Naturwiss.*, 1957, **44**, 307.
9 C. Charaux and J. Rabaté, *J. pharm. Chim.*, 1940, [9], **1**, 155.
10 L. Farkas, L. Hörhammer, H. Wagner, H. Rösler, and R. Gurniak, *Chem. Ber.*, 1964, **97**, 610.

begun structural work on this substance before becoming aware of the recently reported studies of Farkas *et al.*,[10] which established structure (III; $R^1 = R^2 = R^3 = OMe$, $R^4 = OH$) both by degradation and synthesis. In addition to compounds described therein, jaceidin was readily converted into a triacetate, whilst spectroscopic methods gave

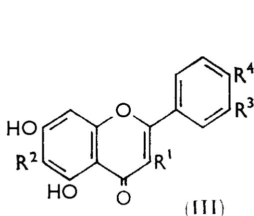
TABLE 2

Percentages of flavonoids in Centaurea species

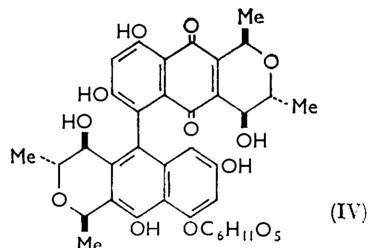
Plant	Jaceidin		Apigenin		Scutellarein	
	Aglycone	Glycoside	Aglycone	Glycoside	Aglycone	Glycoside
C. scabiosa (stems)	0·5	0·3	—	—	—	0·1
C. jacea (whole plant)	0·2	0·2	0·1	tr.	0·05	tr.
C. nigra (leaves)	6·1	0·5	—	—	0·2	—
(stems)	0·1	0·4	—	—	—	—
(flowers)	0·4	0·2	0·2	0·3	—	—
C. cyanus (whole plant) ...	—	tr.	0·12	0·29	—	—

support to its structure. For example, its ultraviolet spectrum[11] undergoes a bathochromic shift on addition of sodium acetate, indicative of a free 7-hydroxy-group, and a further bathochromic shift in sodium ethoxide, indicating a free 4′-hydroxy-group. Aluminium chloride also causes a bathochromic shift consistent with a 5-hydroxy-group, while boric acid has no effect, indicating the absence of *o*-dihydroxy-groups. The nuclear magnetic resonance spectra of a number of derivatives showed a single peak, due to the C-8 proton, which ranged from 2·71 to 3·44 τ depending on substituents, together with an ABX or ABC system due to the protons of ring C. As has been found previously with other flavonoid systems,[12] the C-5 proton is observed at higher field (2·80—2·97 τ) than either the 2′- or 6′-protons, both of which in this system are found at 2·22—2·32 τ.

A careful examination of *D. jaceae*, on the other hand, showed no detectable quantity of flavonoid material to be present. Such compounds, therefore, would seem not to be ingested by the insect. (The possibility of rapid and complete degradation following ingestion cannot be excluded but seems less likely.)



(III)



(IV)

Examination of the amino-acid content of *D. jaceae* by two-dimensional paper chromatography showed the presence of aspartic acid, glycine, serine, alanine, tyrosine, valine, phenylalanine, leucine, and several peptides which on hydrolysis produce no further amino-acids. An identical mixture was obtained from stems of the host *C. scabiosa*. Similarly, examination for free sugars has shown glucose to be the only detectable constituent of both plant and stored insect, both before and after hydrolysis. Traces of other components were also detected, but in very much smaller amount. A similar correspondence in amino-acid and sugar content has previously been observed between honeydew from the

[11] L. Jurd in " The Chemistry of Flavonoid Compounds," ed. T. A. Geissman, Pergamon, 1962, p. 107.

[12] J. Massicot and P. Marthe, *Bull. Soc. chim. France*, 1962, 1962.

aphid *Tuberolachnus salignus* and its host *Salix acutifolia*.[13] Such compounds were shown to be major constituents of phloem sap, which aphids ingest, and their presence unchanged in the insect therefore can readily be explained. Fats and flavonoids are elaborated elsewhere in the plant and are not transferred to the aphid.

These observations have an indirect bearing on the origin of aphid pigments. These, *e.g.*, protoaphin-*fb* (IV), are alike in consisting of two naphthalenic units coupled together. Our studies on the dactynaphins, from *D. jaceae*, suggest that they are no exceptions to this. We have seen that pigments must be synthesised, at least in part, by the insect, since they are not found in host plants. Our attempts to obtain direct evidence on this point by tracer experiments on the bean aphid *Aphis fabae* were unsuccessful, because of experimental difficulties in rearing this insect on synthetic media.[14] The structure of protoaphin-*fb* (IV), which *A. fabae* produces, is consistent with biogenesis by the acetate–malonate pathway. What is not obvious is whether this occurs *de novo* in the insect, or whether colourless precursors, *e.g.*, naphthalenic systems, are ingested from the plant and subsequently coupled. Indirect evidence on this comes from the results on *D. jaceae* and its hosts. Any such naphthalenic precursor of aphid pigments would be expected to occur in the phloem sap. None to date have been observed. Similarly, a careful examination of whole plants of the four *Centaurea* species and of *Sambucus nigra*, the host of *A. sambuci*, did not indicate the presence of any obvious aphin precursor. This does not, of course, exclude the possibility that such substances are present in small amounts, but we regard this as less likely, and conclude that aphid pigments are probably synthesised in their entirety within the insects. Certain compounds, *e.g.*, isoeleutherin,[15] which structurally resemble possible precursors, have indeed been isolated from the plant kingdom, but their occurrence is restricted to a few species. We would have expected any true precursor to be widespread, because of the large range of plants that act as hosts to pigment-containing aphids.

EXPERIMENTAL

Unless otherwise stated, infrared (i.r.) spectra were measured in KBr discs and ultraviolet (u.v.) spectra in 95% ethanol. Nuclear magnetic resonance (n.m.r.) spectra were measured at 60 Mc./sec. with tetramethylsilane as internal reference. Light petroleum refers to the fraction having b. p. 40—60°. Silicic acid refers to Mallinckrodt 2847.

Examination of Triglycerides.—Insects were macerated with light petroleum, the extracts evaporated to 10 ml., allowed to solidify, and filtered, and the solid was redissolved in warm methanol (1 g. in 20 ml.), and the solution refrigerated at −15° for several weeks. This method gave a 95% (or better) recovery of crystalline triglycerides, all of which had melting ranges 45—50° and $\lambda_{max.}$ 261 mμ. Each (1 g.) was refluxed for 3·5 hr. with a mixture of methanol (10 ml.) and aqueous sodium hydroxide (10 ml.; 2·5N). Methanol was then removed by evaporation, the mixture acidified with hydrochloric acid, diluted with water to 100 ml., and extracted with ether (2 × 25 ml.). The extracts were dried, and treated with an excess of diazomethane in ether. The solution of esters was then concentrated to 10 ml. and subjected to routine vapour-phase chromatography, with results shown in Table 1. Samples (1 μl.) were applied to an F and M 720 instrument having a 6-in. column of 20% silicone rubber Se 30 on 60—80P, flow rate 120 ml./min., oven temperature 175°, bridge current 150 mA.

Triglycerides from D. jaceae.—(*a*) Crude triglycerides (3·41 g.) were isolated and saponified as above. The resulting acids were dissolved in hexane (20 ml.) and chromatographed on a column of silicic acid (40 × 5 cm.). Elution with hexane–ether (4 : 1) gave myristic acid (2·52 g.), which after crystallisation from methanol formed colourless needles, m. p. 63—64°, undepressed in admixture with authentic material, having identical i.r. spectrum and, after methylation, identical behaviour on vapour-phase chromatography. Elution with hexane–ether (1 : 1) gave *trans,trans*-sorbic acid (405 mg.), which was recrystallised from the same solvent,

[13] T. E. Mittler, *J. Exp. Biol.*, 1958, **35**, 74.
[14] D. W. Cameron and E. M. Hildyard, unpublished observations.
[15] H. Schmid and A. Ebnöther, *Helv. Chim. Acta*, 1951, **34**, 1041.

as colourless blades, m. p. 133—134°, and identified by comparison with authentic material as for myristic acid above; $\lambda_{max.}$ 254 mμ (log ε 4·45).

(*b*) Crude triglyceride (0·75 g.) was chromatographed on silicic acid (40 × 5 cm.) in hexane–ether (15 : 1), collecting fractions of 25 ml. Fractions 22—30 were recrystallised from methanol (5 ml.), crystallisation being allowed to proceed at −15° for several weeks. This yielded trimyristin (232 mg.), m. p. 33—34° (lit. γ-form, 33°), and had i.r. and n.m.r. spectra identical with authentic material. Conversion into its methyl ester gave a product identical on vapour-phase chromatography with methyl myristate.

Fractions 34—51 on recrystallisation from methanol (5 ml.) gave colourless rosettes of 2-trans,trans-*sorbo*-1,3-*dimyristin* (II), m. p. 54—54·5° [Found: C, 73·5; H, 10·8%; *M* (thermistor drop method), 596. $C_{37}H_{66}O_6$ requires C, 73·3; H, 11·0%; *M*, 607]; $\lambda_{max.}$ 261 mμ (log ε 4·38); $\nu_{max.}$ 1736 (saturated ester C=O), 1719 (αβ-unsaturated ester C=O), 1648, 1620 cm.$^{-1}$ (C=C); n.m.r. in CCl_4 (Figure 2·77 (1H, multiplet, =CHCO), 3·77, 3·90, 4·14, 4·40 (3H, multiplets, =CH), 4·77 (1H, multiplet, R_2CH–O), 5·75, 5·84 (4H, multiplet, RCH_2–O), 7·70 (4H, multiplet, –CH_2CO–), 8·12 (3H, doublet *J* = 4·5 c/sec., MeCH:), 8·72 (44H, composite peak, –CH_2–), 9·12 τ (6H, muliplet, MeCH_2–). This substance was identified by m. p. and mixed m. p. with synthetic material (below). U.v., i.r., and n.m.r. spectra for the two compounds were identical.

1-*Sorbo*-2,3-*dimyristin* (I).—To a mixture of 1,2-*O*-isopropylideneglycerol (8 g.) and pyridine (5 ml.) was added *trans,trans*-sorboyl chloride (8 g.), the temperature being maintained at 0° during the addition. The mixture was stirred at room temperature for 2 hr., then treated with ice-cold dilute sulphuric acid (60 ml. of 0·5N) and ether (100 ml.). The ethereal extract was further washed with ice-cold sulphuric acid (2 × 60 ml.), saturated aqueous sodium hydrogen carbonate (3 × 50 ml.), and water (50 ml.), then dried and evaporated. The resulting oil was dissolved in ether (70 ml.) and concentrated hydrochloric acid was slowly added, the temperature being kept below 5°. After 30 min. the mixture was diluted with water (300 ml.) and extracted with ether (3 × 200 ml.). The extract was washed with water, dried, and evaporated to yield 1-sorbin (11·0 g., 95%) as a colourless liquid. Without purification this was mixed with quinoline (15 g.), and myristoyl chloride (30 g.) was added at 0° with stirring. After 1 hr. at room temperature the mixture was worked up as above to yield 1-trans,trans-*sorbo*-2,3-*dimyristin* (I) (33·8 g., 94%), which after recrystallisation from methanol formed colourless rosettes, m. p. 55·5—56°, mixed m. p. with the glyceride from *D. jaceae* 48—51° (Found: C, 73·6; H, 10·9. $C_{37}H_{66}O_6$ requires C, 73·3; H, 11·0%); $\lambda_{max.}$ 261 mμ (log ε 4·44); $\nu_{max.}$ 1732, 1708, 1645, 1619 cm.$^{-1}$; n.m.r. in CCl_4 virtually identical with that of compound (II) except for reproducible differences of a " fingerprint " kind.

2-trans,trans-*Sorbo*-1,3-*dimyristin*.—1,3-Dimyristin was synthesised by literature methods.[5,6] It had m. p. 64—65° (lit., 63·8—64·4°). To a solution of 1,3-dimyristin (2 g.) in pyridine (10 ml.) was added *trans,trans*-sorboyl chloride (3 g.) at room temperature, the mixture stirred for 24 hr., and then heated at 50° for 30 min. It was then worked up in the usual way and chromatographed in hexane on silicic acid (40 × 5 cm.), fractions of 50 ml. being collected. Concentration of fractions 19—32 gave 2-*trans,trans*-sorbo-1,3-dimyristin (1·2 g., 45%), which crystallised from methanol as colourless rosettes, m. p. 54—54·5°, identified with the natural glyceride as described previously.

Identification of Amino-acids and Sugars.—A sample of *D. jaceae* was extracted with acetone and then with water. The aqueous extract was examined for amino-acids by two-dimensional chromatography on Whatman 3 MM paper. Systems used were n-butanol–acetic acid–water (4 : 1 : 5, top layer); phenol–water–ammonia (77·5 : 21·5 : 1). Spots were developed with ninhydrin. The extract was also examined for sugars by chromatography in the first system above, spraying with aniline hydrogen phthalate.

Examination of the four *Centaurea* species for amino-acids and sugars was carried out as above, on aqueous extracts obtained as indicated below.

Extraction of Centaurea *species*.—Air-dried plants were extracted (Soxhlet) successively with light petroleum, acetone, and water with the exception of *C. scabiosa*, which was extracted in the reverse order. The petroleum extract of all species was shown to contain the same components by thin-layer chromatography on silicic acid, developing with hexane–ether–acetic acid (95 : 4 : 1), spraying the dried chromatogram with sulphuric acid (50%), and heating at 250° for 15 min.

Stems of *C. scabiosa* (2 kg.) gave a petroleum-soluble fraction (25 g.), which after chromato-

graphy on silicic acid (18 × 0·75 cm.) gave a triglyceride fraction (16·2 g.). Alkaline hydrolysis and methylation as before gave a mixture which was shown by vapour-phase chromatography to contain myristate (4·5%), palmitate (32·5%), and stearate (63%) esters.

A similar examination of the complete petroleum-solubles from *C. nigra* leaves showed the presence of myristate (19%), palmitate (21%), and stearate (53%) esters.

Solutions of the acetone-soluble components from the plants were evaporated and extracted with benzene, and the resulting extract was chromatographed on silicic acid, eluting with chloroform–methanol mixtures. Flavonols were eluted in the order jaceidin, apigenin, scutellarein. The last two were identified and determined by their absorption spectra. The benzene-insoluble material from the acetone extract was combined with the aqueous extract and refluxed with hydrochloric acid (2·5N) for 30 min. The aglycones so formed were extracted into chloroform and analysed by chromatography as above.

Jaceidin.—Crude jaceidin from chromatography above, was crystallised from acetone–water (1 : 1) as yellow needles, m. p. 99—100°. From benzene it formed rosettes of needles, m. p. 111—112°, and after drying at 125°/10^{-6} mm. had m. p. 165—166°; on standing, it absorbed water, giving m. p. 99—100°. It was identical in i.r. and u.v. spectra with an authentic specimen (lit., m. p. 127—135°) [10] (Found: C, 57·3; H, 4·7. Calc. for $C_{18}H_{16}O_8,H_2O$: C, 57·1; H, 4·8%); $\lambda_{max.}$ (*a*) in ethanol 255, 270, 354 mμ (log ε 4·25, 4·19, 4·35) (*b*) in ethanol containing sodium ethoxide (0·1N) 275, 330, 400 mμ (log ε 4·11, 4·17, 4·34), (*c*) in ethanol containing aluminium chloride (5%) 245, 265, 385 mμ (log ε 4·00, 4·21, 4·31), (*d*) in ethanol saturated with sodium acetate 273, 316, 374 mμ (log ε 4·33, 4·09, 4·22), (*e*) in ethanol saturated with sodium acetate and boric acid 273, 316, 374 mμ (log ε 4·33, 4·08, 4·22); $\nu_{max.}$ 3582, 3280 (OH), 1655, 1610, 1600, 1578, 1558, 1516 cm.$^{-1}$ (C=O, C=C); n.m.r. in $CDCl_3$, −2·86 (C_5–OH), 2·30 ($C_{2'}$–H), 2·32 ($C_{6'}$–H), 2·95 ($C_{5'}$–H), 3·41 (C_8–H), 5·96, 6·03, 6·14 τ (OMe), (J_{ortho} = 9·0 c/sec., J_{meta} = 2·0 c./sec., J_{para} = 0).

Jaceidin dimethyl ether, m. p. 158—159°, identified by comparison with an authentic specimen,[10] had n.m.r. in $CDCl_3$, −3·05 (C_5–OH), 2·22 ($C_{6'}$–H), 2·27 ($C_{2'}$–H), 2·97 ($C_{5'}$–H), 3·44 (C_8–H), 6·00, 6·05, 6·14 τ (OMe, 3 : 1 : 1), *J* as above.

Jaceidin trimethyl ether, m. p. 142—143°, identified by comparison with an authentic specimen,[10] had n.m.r. in $CDCl_3$ 2·24 ($C_{6'}$–H), 2·25 ($C_{2'}$–H), 2·96 ($C_{5'}$–H), 3·21 (C_8–H), 5·98, 6·04, 6·08. 6·12 τ (OMe, 1 : 3 : 1 : 1), *J* as above.

Jaceidin Triacetate.—Jaceidin (504 mg.) was acetylated with acetic anhydride (5 ml.) and pyridine (1 ml.) at room temperature for 4 hr. The resulting *triacetate* (650 mg.) was crystallised from ethanol as pale yellow needles, m. p. 159—160° (Found: C, 59·5; H, 4·8. $C_{24}H_{22}O_{11}$ requires C, 59·3; H, 4·5%); $\lambda_{max.}$ 248, 325 mμ (log ε 4·29, 4·17); $\nu_{max.}$ 1769, 1645 cm.$^{-1}$; n.m.r. in $CDCl_3$ *ca.* 2·30 ($C_{2'}$–H, $C_{6'}$–H), *ca.* 2·80 ($C_{5'}$–H), 2·71 (C_8–H), 6·08, 6·11, 6·17 (OMe), 7·56, 7·61, 7·63 τ (OAc).

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