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COUMARINS AND ALKALOIDS OF THE GENUS *PTELEA**

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Abstract—A study of the extractives of the three species of the genus *Ptelea* (Rutaceae) has yielded typically rutaceous coumarins and furoquinoline alkaloids. The fruit of *P. aptera* contains small amounts of a new furoquinoline alkaloid shown to be 7-isopentenyloxy-γ-fagarine (III). A further new alkaloid, identified as 3-isopentenyl-4-methoxy-7,8-methylenedioxy-2-quinolone (II), has been obtained from the extracts of one sample of *P. trifoliata* L.

INTRODUCTION

THERE have been frequent reports[1] in the nineteenth century on the medical uses of the hop tree, *Ptelea trifoliata* L. (Rutaceae). The fruit of *Ptelea* has also been used from time to time as a substitute for hops in brewing.[1] The genus *Ptelea*, which is native only to North America, is believed to have had a center of origin in Southern Mexico and migrated northward in later geological ages. This has resulted in the formation of many isolated colonies in the temperate zone undergoing divergent evolution.

Ptelea has recently been revised by Bailey[2] who recognized three species. However, the many varieties and the extreme variation within the three species makes classification on morphological grounds sometimes difficult. Bailey and Bailey[3] have recently employed the profiles of leaf extracts on TLC as a tool for population studies of *Ptelea*. The positive identification of the extractives in *Ptelea* would provide a sound basis for such a chemotaxonomic study. Accordingly, a qualitative examination on the constituents of the three main *Ptelea* species was undertaken by classical chemical methods.

RESULTS

The extractives isolated from *Ptelea* species in this study are summarized in Table 1. The extractives obtained from *P. crenulata* Greene are typically rutaceous and need no comment,

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* Part V in the series "Chemotaxonomy of the Rutaceae"; for Part IV, see D. L. DREYER, *J. Org. Chem.* **33**, 3574 (1968).

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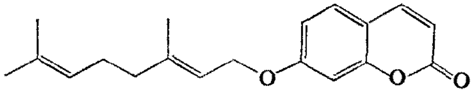
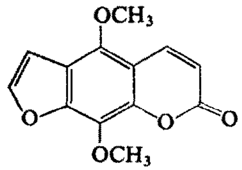
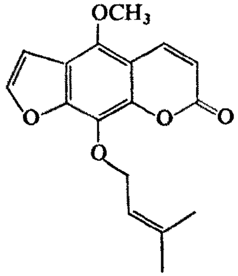
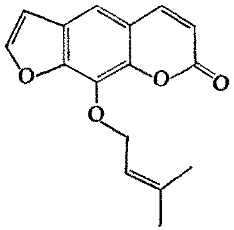
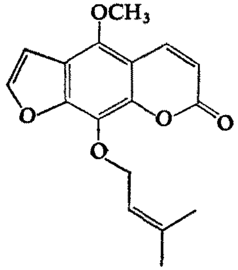
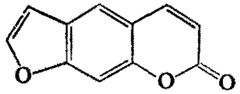
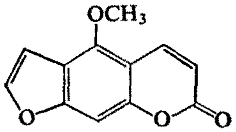
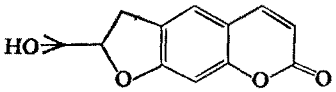
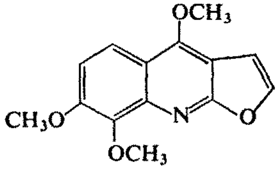
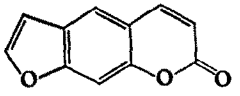
[1] For a review, see V. L. BAILEY, *Econ. Botany* **14**, 180 (1960).

[2] V. L. BAILEY, *Brittonia* **14**, 1 (1962).

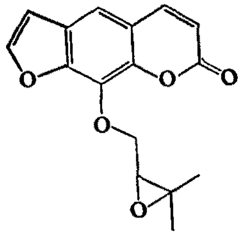
[3] H. E. BAILEY and V. L. BAILEY, *Lloydia* **28**, 27 (1965).

TABLE 1. EXTRACTIVES FROM *Ptelea* SPECIES

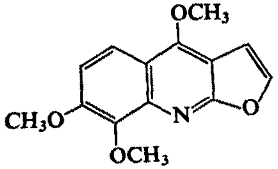
P. crenulata	*P. trifoliata*	*P. aptera*
 7-Geranyloxycoumarin	 Isopimpinellin	 Phellopterin
 Imperatorin	 Phellopterin	 Psoralen
 Bergapten	 (−) Marmesin	 Skimmianine



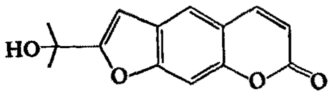
Psoralen



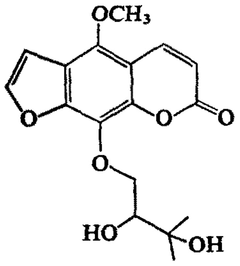
(−)-Imperatorin oxide



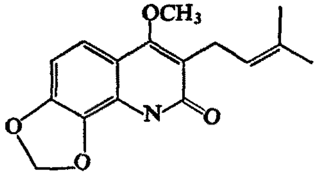
Skimmianine



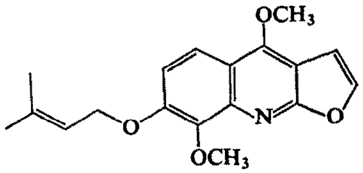
(+)-Marmesin



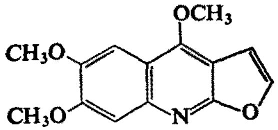
Byakangellicin



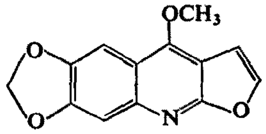
3-Isopentenyl-4-methoxy-7,8-methylenedioxy-2-quinolone



7-Isopentenyloxy-γ-fagarine



Kokusaginine



Maculine

except for the imperatorin oxide. (+)-Imperatorin oxide (heraclenin) isolated from *Heracleum candican*[4] and *Prangos pabularia*[5] (Umbelliferae), has $[\alpha]_D +22^\circ$ (pyridine). On the other hand, Chow, Duffield and Jefferies[6] found that imperatorin oxide isolated from *Phebalium drummondii* Benth. (Rutaceae) growing in one location was racemic, while that growing in another location gave the (−) antipode, $[\alpha]_D -24{\cdot}0^\circ$ (pyridine). The imperatorin oxide isolated in this study had $[\alpha]_D -1{\cdot}4$ (pyridine), indicating that, although it was the same optical antipode as imperatorin oxide previously isolated from rutaceous plants,[6] it was partly racemic. The plant material used in this study was collected from about twelve plants growing close together in a small canyon and certainly represents a homogenous population. It is not known if some of the plants produce racemic imperatorin oxide and some optically pure (−)-imperatorin oxide, or if each plant produces partly racemic (−)-imperatorin oxide. The partial optical activity of imperatorin oxide offers a potential quantitative tool for population studies on *P. crenulata* in which it may be possible to rate populations according to their degree of racemization of imperatorin oxide.

The alkaloids of *P. trifoliata* L. have been the subject of several previous investigations[7] in which skimmianine, kokusaginine, dictamnine, 6-methoxydictamnine (pteleine)[8] and probably maculosidine have been reported. Leaf extracts from *P. trifoliata* collected in Oak Creek Canyon in Central Arizona yielded only three components, isopimpinellin, phellopterin and (−)-marmesin (Table 1). The most striking feature of the extractives from *P. trifoliata* is the isolation of (−)-marmesin (nodakenetin). Thus, *P. crenulata* yields (+)-marmesin while *P. trifoliata* yields the optical antipode, (−)-marmesin. Heretofore, only (+)-marmesin has been isolated from rutaceous plants[9] while both (+)- and (−)-marmesin have been reported to occur in plants of the Umbelliferae.[10] Quinolone alkaloids of opposite absolute configuration have been previously found in two different genera of the Rutaceae, *Lunasia* and *Balfourodendron*[11] while two closely related coumarins, containing one asymmetric center, of apparently opposite absolute configuration co-occur in *Thamnosma montana* Torr. and Frem. (Rutaceae).[12]

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[4] Y. N. SHARMA, A. ZAMAN and A. R. KIDWAI, *Tetrahedron* **20**, 87 (1964).

[5] G. A. KUZNETSOVA and G. V. PIGLEVSKII, *Zh. Obshch. Khim.* **31**, 323 (1961); *Chem. Abstr.* **55**, 22281 (1961); G. A. KUZNETSOVA, *Zh. Obshch. Khim.* **35**, 403 (1965); *Chem. Abstr.* **62**, 15071 (1965). Several further reports of the isolation of imperatorin oxide (prangenin) occur in the Russian literature; from *Prangos seravschanica* (G. A. KUZNETSOVA and A. D. ZORINA, *Zh. Prikl. Khim.* **39**, 482 (1966); *Chem. Abstr.* **65**, 1043 (1966)); from *Cnidium dubium* (N. F. KOMISSARENKO and V. T. CHERNOBAI, *Khim. Prir. Soedin.* **2**, 375 (1966); *Chem. Abstr.* **67**, 11395 (1967)).

[6] P. W. CHOW, A. M. DUFFIELD and P. R. JEFFERIES, *Australian J. Chem.* **19**, 483 (1966).

[7] V. I. FROLOVAM, A. D. KUZOVKOV and P. N. KIBAL'CHICH, *Zh. Obshch. Khim.* **34**, 3499 (1964); *Chem. Abstr.* **62**, 2800 (1965); M. KOWALSKA, *Acta Polon. Pharm.* **20**, 458 (1963); *Chem. Abstr.* **62**, 6797 (1965); M. KOWALSKA and B. BORKOWSKI, *Acta Polon. Pharm.* **23**, 295 (1966); *Chem. Abstr.* **66**, 17029 (1967).

[8] F. WERNY and P. J. SCHEUER, *Tetrahedron* **19**, 1293 (1963).

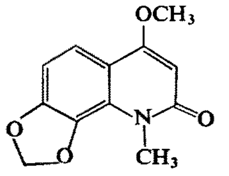
[9] A. CHATTERJEE and S. S. MITRA, *J. Am. Chem. Soc.* **71**, 606 (1949).

[10] E. A. ABU-MUSTAFA and M. B. E. FAYEZ, *J. Org. Chem.* **26**, 161 (1961); G. A. KUZNETSOVA and L. M. BELENOVSKAYA, *Rast. Resursy.* **2**, 57 (1966); *Chem. Abstr.* **65**, 5875 (1966); J. ARIMA, *J. Chem. Soc. Japan* **48**, 88 (1927); *Chem. Abstr.* **21**, 1817 (1927). Numerous reports are available on the occurrence of marmesin and its esters in umbellifers. For example, marmesin and deltoin in *Prangos fedtschenkoi* (G. A. KUZNETSOVA and L. M. BELENOVSKAYA, *Zh. Prakl. Khim.* **38**, 2368 (1965); *Chem. Abstr.* **64**, 3964 (1966)); marmesin in *Prangos isphatramica* (G. A. KUZNETSOVA and L. M. BELENOVSKAYA, *Rast. Resursy.* **2**, 57 (1966); *Chem. Abstr.* **65**, 5875 (1966)); senecioyl ester of marmesin in *Prangos tschimaganica* B. Fedtsch (G. A. KUZNETSOVA and L. M. BELENOVSKAYA, *Khim. Prir. Soed.* **2**, 235 (1966); *Chem. Abstr.* **66**, 2438 (1967)); Deltoin in *Prangos ornata* (G. A. KUZNETSOVA and L. M. BELENOVSKAYA, *Khim. Prir. Soed.* **1**, 430 (1965); *Chem. Abstr.* **64**, 13088 (1966)); Felamedin in *Ferulago meoides* (L.) Boiss. (I. OGNYANOV and D. BOTCHEVA, *Z. Naturforsch.* **22B**, 1231 (1967)).

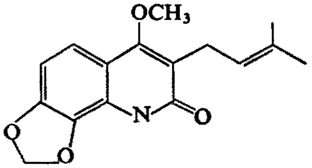
[11] H. RAPAPORT and K. G. HOLDEN, *J. Am. Chem. Soc.* **81**, 3738 (1959) and references cited therein.

[12] D. L. DREYER, *Tetrahedron* **22**, 2923 (1966).

A further sample of *P. trifoliata*, collected in the Dragoon Mountains of south-eastern Arizona, gave completely different results; it yielded byakangelicin and a new alkaloid, m.p. 159–162°. The i.r. spectrum of the alkaloid showed a broad carbonyl band at 1645 cm^{-1}. The u.v. spectrum was similar to that of numerous other 4-methoxy-2-quinolones.[13] The NMR spectrum showed resonances for an aromatic AB doublet, one *N*-methyl or *O*-methyl group and an isopentenyl side-chain. The upfield position of the isopentenyl methylene indicated it was attached to carbon and not to an ether oxygen or the nitrogen. The chemical shift of the aromatic protons compared well with the values for the H-5 and H-6 resonances in casimiroin (I). The H-5 resonance in 4-quinolones occur much further downfield than the H-5 resonance in 4-methoxy-2-quinolones,[14] providing further evidence for the 2-quinolone system in the alkaloid. A broad, featureless, one-proton resonance, well downfield, was assignable to an N—H group indicating that the methyl resonance at δ 4·00 was due to a methoxy group. These data are best accommodated by structure II which is also in accord with biogenetic considerations.



Casimiroin (I)



(II)

The constituents isolated from the leaves and stems of *P. aptera* Parry (phellopterin, psoralen and skimmianine) were unexceptional (Table 1). Sufficient fruits of *P. aptera* were available for a separate study of their constituents. They appeared (by TLC) to lack phellopterin, but contained relatively large amounts of skimmianine, kokusaginine and maculine (the latter two appear to be absent in the leaves) and a new non-polar furoquinoline alkaloid, m.p. 101–103°. The new alkaloid had a u.v. spectrum identical with that of skimmianine.[15] The NMR spectrum had resonances for an isopentenyl group and two methoxy groups as well as the skimmianine aromatic protons.[14] Since one of the methoxy resonances occurred relatively far downfield, one of the methoxy groups must be located at the 4-position.[14] Two possible structures, III and IV, follow for the alkaloid.

Furoquinoline alkaloids of type III, in which the isopentenyl side-chain has been epoxidized (VI) and hydroxylated (V), have been found naturally occurring in *Evodia zanthoxyloides* F. Muell. [15–17] Initial attempts to chemically relate the alkaloid with VI and evoxine (V) by epoxidation proved to be too demanding of material so that it was necessary to distinguish between structures III and IV by spectroscopic means. The method employed depends on

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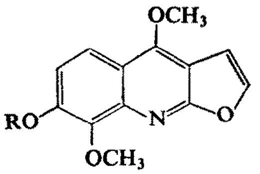
[13] For example, 3-isopentenyl-4-methoxy-2-quinolone, I. T. Eshiett and D. A. H. Taylor, *J. Chem. Soc.* (C) 481 (1968); 4,8-dimethoxy-2-quinolone (edulitin, rubustinine), T. Kappe and E. Ziegler, *Tetrahedron Letters* 1947 (1968); I. M. Saitbaeva, G. P. Sidyakin and S. Yu. Yunosov, *Khim. Prir. Soed.* **2**, 443 (1966); *Chem. Abstr.* **67**, 22062 (1967); 3-isopentenyl-4,8-dimethoxy-2-quinolone, E. A. Clark and M. F. Grundon, *J. Chem. Soc.* 438 (1964).

[14] A. V. Robertson, *Australian J. Chem.* **16**, 451 (1963).

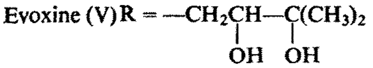
[15] F. W. Eastwood, G. K. Hughes and E. Ritchie, *Australian J. Chem.* **7**, 87 (1954).

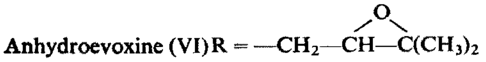
[16] J. R. Cannon, C. K. Hughes, K. G. Neill and E. Ritchie, *Australian J. Sci. Res.* **A5**, 406 (1952); *Chem Abstr.* **47**, 3857 (1953).

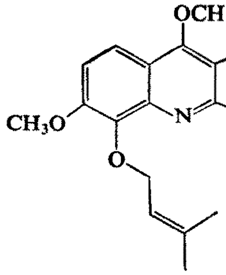
[17] D. L. Dreyer, unpublished results.



7-Isopentenyloxy-γ-fagarine (III)R = $—CH_2CH{=}C(CH_3)_3$


Evoxine (V)R = $—CH_2\underset{OH}{CH}—\underset{OH}{C}(CH_3)_2$


Anhydroevoxine (VI)R = $—CH_2—\overset{O}{CH—C}(CH_3)_2$



(IV)

the fact that methoxy groups are especially solvated by benzene and resonances for such groups occur 20–30 cps upfield in benzene relative to their position in chloroform. On the other hand, hindered methoxy groups flanked on each side by other groups are not solvated by benzene and their resonances are not shifted upfield in benzene relative to chloroform.[18] The data displayed in Table 2 show that the 8-methoxy group does not shift upfield in benzene when there is a group in the 7-position. These data indicate that the new alkaloid should be formulated as 7-isopentenyloxy-γ-fagarine (III).

TABLE 2. METHOXY RESONANCES OF SOME FUROQUINOLINE ALKALOIDS

	$CDCl_3$	Benzene
γ-Fagarine	4·43	3·72
	4·17	3·73
Skimmianine	4·35	4·32
	4·10	3·68
	4·00	3·65
Anhydroevoxine (VI)	4·28	4·22
	4·17	3·87
7-Isopentenyloxy-γ-fagarine (III)	4·47	4·37
	4·02	3·68

The results obtained in this study show clear differences in composition between the major *Ptelea* species.[19] *P. aptera* appears to contain the most diverse number of different furoquinoline alkaloids. However, since no studies on the fruit of the other two species could be carried out and three of these alkaloids in *P. aptera* came from the fruit alone, firm conclusions are difficult to draw. As a result of the limited number of samples studied and their homogenous nature, little is known of the variation of these extractives in different populations or the possible effect of climatic and seasonal factors on the metabolite composition. Until these questions can be answered the possible utility of the data presented here for detailed chemotaxonomic purposes must remain uncertain. These questions are accented by the completely different results obtained on the two different *P. trifoliata* samples. In any event the homogenous nature of the extractives obtained, consisting entirely of furoquinoline alkaloids and coumarins, would certainly not support the placement of *P. aptera* in a separate

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[18] R. G. WILSON, J. H. BOWIE and D. H. WILLIAMS, *Tetrahedron* **24**, 1407 (1968); H. M. FALES and K. S. WARREN, *J. Org. Chem.* **32**, 501 (1967); D. L. DREYER, *J. Org. Chem.* **33**, 3577 (1968).

[19] No evidence was found by TLC and spraying with Ehrlich's reagent for the presence of limonoids in any of the *Ptelea* species; see D. L. DREYER, *J. Org. Chem.* **30**, 749 (1965).

genus (*Taravalia*) as some authorities[20] have considered in the past. Reports of dermatitis (assuming that the dermatitis is of a photodynamic type)[21] caused by *Ptelea* can now be rationalized by the presence in the plant of furocoumarins, especially psoralen.

EXPERIMENTAL

In general, the content of the fractions from chromatography of the plant extracts was monitored by TLC on silica acid as described previously.[12] The spots were detected by examination under u.v. light. NMR spectra were taken at 60 MHz. The relative area of the peaks were consistent with their assignments.

Isolation of Constituents from Ptelea crenulata *Greene*

Plant material was collected under the oaks in a small canyon south of State Highway 128 between Monticello Dam and junction with State Highway 37. This is about 3 miles S.W. of Monticello Dam and is in the Coast Range West of Davis, California. Whole ends of branches, including leaves and some fruit, collected in June, were dried, ground and extracted with acetone. Solvent was removed from the acetone extracts and the residue chromatographed on alumina. The first fractions, eluted with hexane, gave 7-geranyloxycoumarin, m.p. 64–65°, from hexane. The next fractions, eluted with 10% benzene in hexane, gave imperatorin, m.p. 95–99°; from ethyl acetate–hexane. Fractions containing mostly psoralen were eluted with increasing amounts of benzene, m.p. 163–164·5°, from methanol;[22] ν 1726, 1604, 1577 cm^{-1} (Nujol); λ_{max}^{EtOH} 247, 290 333 nm; NMR spectrum 7·77(d) $J=10$ H-4, 7·69(d) $J=2$ H-7, 7·75(s) H-5, 7·49(s) H-8, 6·81(q) $J=2$, $J=1$ H-6, 6·34(d) $J=10$ H-3 ($CDCl_3$). The 1 cps splitting of H-6, due to long-range coupling with H-8, was not apparent in the latter. The H-8 resonance was a slightly broadened singlet. The splitting pattern of H-8 was presumably blurred due to *para*-coupling with H-5.[23] Further fractions were primarily mixtures of psoralen and bergapten. These were followed by fractions containing mostly bergapten, m.p. 175–181°, after repeated recrystallization from ethyl acetate–hexane and methanol. Further workup of the mother liquors of the benzene eluents gave, after removal of several crops of impure bergapten, imperatorin oxide,[4] m.p. 107–111°, from methanol; ν 1727, 1590 cm^{-1} (Nujol); $[\alpha]_D^{25^\circ} - 5·3$ ($CHCl_3$); $[\alpha]_D^{25^\circ} - 1·4$ (pyridine); NMR spectrum δ 7·77(d) $J=10$ H-4, 7·69(d) $J=2$ H-7, 7·41(s) H-5, 6·84(d) $J=2$ H-6, 6·35(d) $J=10$ H-3, 4·60(d) $J=6$ methylene, 3·37 (multiplet) epoxy, 1·35, 1·28 C-methyls ($CDCl_3$). Elution of the column with $CHCl_3$ gave fractions from which skimmianine was isolated, m.p. 178–181°, from ethyl acetate. The column was then washed with 10% acetone in $CHCl_3$. Rechromatography of the combined chloroform mother liquors and the $CHCl_3$–acetone fractions, combination and removal of solvent from those fractions containing a polar blue fluorescing spot on TLC gave (+)-marmesin, m.p. 172–176°, from benzene and benzene–hexane; ν 1719, 1639, 1579 cm^{-1} (Nujol); NMR spectrum δ 7·56(d) $J=10$ H-4, 7·27 (broad singlet) H-5, 6·66(s) H-8 6·12(d) $J=10$ H-3, 4·72(t) $J=8$ H-7, 3·22(d) $J=8$ H-6, 1·37, 1·42 C-methyls ($CDCl_3$). Marmesin showed a plain positive ORD curve down to 372 mμ; ORD in 95% ethanol (*c* 0·102) at 25°: $[\alpha]_{600} + 39°$, $[\alpha]_{372} + 880°$ (last reading).

Imperatorin Oxide

Synthetic imperatorin oxide was prepared from imperatorin and *m*-chloroperbenzoic acid in $CHCl_3$ similar to published procedures.[4,24] The product, m.p. 112–114°, from methanol, was identical with the natural material by spectroscopic criteria.

Isolation of Constituents from P. trifoliata *L.*

Plant material was collected in Oak Creek Canyon, South of Flagstaff, Arizona about the middle of August. Dried and ground branch-ends were extracted with acetone. Solvent was removed from the acetone extracts and the residue chromatographed on alumina. Elution with 20–30% benzene in hexane gave isopimpinellin, m.p. 144–147°; recrystallized from methanol, m.p. 147–149°. Fractions which followed, eluted with about 40% benzene in hexane, gave phellopterin, m.p. 100–102°; ν 1739, 1598 cm^{-1} (Nujol); NMR spectrum δ 8·11(d) $J=10$ H-4, 7·61(d) $J=2$ H-7, 6·97(d) $J=2$ H-6, 6·22(d) $J=10$ H-3, 5·60(t) $J=7$ vinyl, 4·82(d) $J=7$ allylic methylene, 4·16(s) methoxy, 1·72 C-methyls ($CDCl_3$). Fractions eluted with $CHCl_3$ and $CHCl_3$–acetone contained mostly (−)-marmesin (nodakenetin), m.p. 188–191° from ethyl acetate–

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hexane. (−)-Marmesin showed a plain negative ORD curve down to 370 nm; $[\alpha]_D^{25°}$ −45° ($CHCl_3$); ORD in 95% ethanol (c 0·152) at 25°: $[\alpha]_{600}$ −13°, $[\alpha]_{370}$ −260° (last reading).

A further sample of *P. trifoliata*, collected about 1 mile to the west of the summit of Middlemarch Pass on the slopes of Black Diamond Peak in the Dragoon Mountains, N.E. of Tombstone, Arizona, was also studied. The acetone extracts were chromatographed as described for the above sample. Benzene eluted fractions which yielded 3-isopentenyl-4-methoxy-7,8-methylenedioxy-2-quinolone, m.p. 159–161°, from ethyl acetate–hexane; ν 1645 cm^{-1} (Nujol); λ_{max}^{EtOH} ~234, 258, ~308, 319, ~330 nm; NMR δ 7·40(d) $J=9$ H-5, 6·86(d) $J=9$ H-6, 6·21(s) methylenedioxy, 5·37(t) $J=6$ vinyl, 4·00 methoxy, 3·45(d) $J=6$ α-methylene, 1·87, 1·75 C-methyls ($CDCl_3$). Fractions eluted with $CHCl_3$ gave byakangelicin, identical with a sample isolated from *Thamnosma montana*.[12]

Casimiroin: λ_{max}^{EtOH} 226, 235, 251, 259, 302, ~315 nm; NMR δ 7·60(d) $J=9$ H-5, 6 82(d) $J=9$ H-6, 6·10 methylenedioxy, 5·93(s) H-3, 3·87 methoxy, 3 75 N-methyl ($CDCl_3$).

Isolation of Constituents from P. aptera *Parry*

Plant material was collected at the foot of the grade just south of Santo Thomas, Baja, California, Mexico. It was dried, ground and extracted with acetone. Solvent was removed from the extracts and the residue chromatographed on alumina. Phellopterin was eluted by 15% benzene in hexane. A solution of 30–50% benzene in hexane eluted psoralen, m.p. 163–166°; from ethyl acetate–hexane, while benzene alone eluted skimmianine. Solvent was removed from the mother liquors and the residue rechromatographed. Further amounts of the above three compounds were obtained from the eluents. The mother liquors were combined and extracted with 30% HCl. Neutralization of the base extracts gave maculine, m.p. 190–194°, from methanol; λ_{max}^{EtOH} 244, 251, ~298, 308, 321, 334 nm. Workup of acetone extracts of the fruit in the same manner gave 7-isopentenyloxy-γ-fagarine (III) eluted from the column with 20% benzene in hexane. The non-polar alkaloid (III) showed m.p. 100–101° from ethyl acetate–hexane; recrystallized from methanol, m.p. 101–103°; λ_{max}^{EtOH} 250 (82,000), ~309, 320 (8000), 333 (7300), ~344 nm. The u.v. spectrum was superimposable on that of skimmianine; NMR spectrum δ 8·07(d) $J=9$ H-5, 7·83(d) $J=2$ H-2, 6·95(d) $J=9$ H-6, 6·75(d) $J=2$ H-3, 5·57(t) vinyl, 4·80(d) $J=6$ allyl methylene, 4·47, 4-methoxy, 4·01 8-methoxy, 1·98 C-methyls ($CDCl_3$). (Found: C, 69·0°; H, 6·02; N, 4·39. Calc. for $C_{18}H_{19}NO_4$: C, 68 98; H, 6·11; N, 4·47 per cent.) Skimmianine was recovered from the benzene–$CHCl_3$ eluents. The mother liquors from these operations were combined, solvent removed and the residue crystallized from ethanol to give kokusaginine, m.p. 170–173°; λ_{max}^{EtOH} 245 (70,000), 252 (74,000), ~297, 309 (12,000), 322 (12,000), 335 (8900) nm. The u.v. spectrum compared well with that previously reported[25] NMR spectrum δ 7·30(d) $J=2$ H-2, 7·15(s), 709(s) aromatic, 6·75(d) $J=2$ H-3, 4·22 4-methoxy, 3·74, 3·72 methoxys ($CDCl_3$). Rechromatography of the combined mother liquors gave further amounts of III.

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